UNIVERSITAT ROVIRA I VIRGILI

SOLVING THE MECHANISTIC PUZZLE OF GOLD-CATALYZED CYCLIZATION OF 1,6-ENYNES AND BEYOND

Patricia Pérez Galán

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Solving the Mechanistic Puzzle of Gold-Catalyzed Cyclization of 1,6-Enynes and Beyond

MEMORIA que para optar al grado de

DOCTORA EN QUÍMICA

Presenta

PATRICIA PÉREZ GALÁN

Tarragona

Marzo 2009

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El Prof. Dr. ANTONIO M. ECHAVARREN, Catedràtic de la Universidad Autónoma de Madrid, en comissió de serveis en la Universitat Rovira I Virgili i Group Leader de l'Institut Català d'Investigació Química,

CERTIFICA:

Que la memòria que porta per títol "Solving the Mechanistic Puzzle of Gold-Catalyzed Cyclization of 1,6-Enynes and Beyond", que presenta Patricia Pérez Galán per obtenir el Grau de Doctora en Química, ha estat realitzada sota la meva direcció en el corresponent grup de recerca de l'Institut Català d'Investigació Química.

Tarragona, Març 2010

Prof. Dr. Antonio M. Echavarren

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A mis padres

A mi yayo

A mis familia

A mis amigos

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"On ne voit bien qu'avec le cœur.
L'essentiel est invisible pour les yeux"

Antoine de Saint-Exupéry

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Este trabajo de Tesis Doctoral se ha realizado en el Institut Català d'Investigació Química bajo la dirección del Profesor Antonio M. Echavarren, a quien quiero agradecer todo el tiempo que ha dedicado durante estos años a mi formación, su entusiasmo por la química y por hacer que esa ilusión se contagie, su paciencia y disponibilidad, y la confianza que en mi trabajo ha mostrado en todo momento.

El trabajo recogido en esta memoria se ha llevado a cabo gracias a una beca predoctoral de Formación de Profesorado Investigador del Ministerio de Educación y Ciencia desde agosto del 2005. Durante este periodo he realizado una estancia breve de tres meses en el laboratorio del Profesor Mark Launtens (University of Toronto, Canadá, Mayo-Agosto 2008) a quien agradezco su acogida.

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También quisiera agradecer el trabajo y la colaboración prestada por la Dra. Noemí Cabello (espectrometría de masas), al Dr. Gabriel González (resonancia magnética nuclear) y al Dr. Jordi Benet-Buchholz y a sus colaboradores Alba Arandilla, Kerman Gómez y Eduardo Escudero.

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A todos mis amigos: Anna, por ser una de las mejores personas que he conocido, a Eli, porque eres una de las personas más especiales que tengo en mi vida, a Kerman, porque me llevo millones de buenos momentos contigo, a Vero, por ser mi pequeña hoy y siempre, a Clau, porque eres un encanto, a Simo y Serena, a Enrique, por su humor ininteligible, a Margot, por tu fortaleza y a Noemí, por ser como eres y espero no cambies nunca. Asimismo quisiera agradecer a todos aquellos que me quisieron en un momento o otro.

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Hasta el momento de redactar esta memoria, los resultados aquí descritos han dado lugar a las siguientes publicaciones:

***Gold(I)-Catalyzed Intermolecular Cyclopropanation of Enynes with Alkenes: Trapping of Two Different Gold Carbene*s**

Salomé López, Elena Herrero-Gómez, Patricia Pérez-Galán, Cristina Nieto-Oberhuber, and Antonio M. Echavarren.

Angew. Chem. In. Ed. **2006**, *45*, 6029-6032. (Hot Paper)

2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl

Patricia Pérez-Galán, and Antonio M. Echavarren.

Encyclopedia of Reagents in Organic Synthesis, Wiley, **2007**.

Gold(I)-Catalyzed Intramolecular [4+2] Cycloadditions of Arylalkynes or 1,3-Enynes with Alkenes: Scope and Mechanism

Cristina Nieto-Oberhuber, Patricia Pérez-Galán, Elena Herrero-Gómez, Thorsten Lauterbach, Cristina Rodríguez, Salomé López, Christophe Bour, Antonio Rosellón, Diego J. Cárdenas, and Antonio M. Echavarren.

J. Am. Chem. Soc. **2008**, *130*, 269-279.

Gold(I)-Catalyzed Intermolecular Addition of Carbon Nucleophiles to 1,5- and 1,6-Enynes

Catelijne H. M. Amijs, Verónia López-Carrillo, Mihai Raducan, Patricia Pérez-Galán, Catalina Ferrer, and Antonio M. Echavarren.

J. Org. Chem. **2008**, *73*, 7721-7730.

Gold(I) Complexes with Hydrogen-Bond-Heterocyclic Carbenes as Active Catalysts in Reactions of 1,6-Enynes

Camino Bartolomé, Patricia Pérez-Galán, Christophe Bour, Mihai Raducan, Antonio M. Echavarren, and Pablo Espinet.

Inorg. Chem. **2008**, *47*, 11391-11397.

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Gold(I)-Catalyzed Olefin Cyclopropanation

Auxiliadora Prieto, M. Mar Díaz-Requejo, Pedro J. Pérez, Patricia Pérez-Galán, Nicolas Delpont and Antonio M. Echavarren

Tetrahedron **2009**, *65*, 1790-1793.

Nitrogen Acyclic Gold(I) Carbenes: Excellent and Easily Accessible Catalysts in reactions of 1,6-Enynes

Camino Bartolomé, Zoraida Ramiro, Domingo García-Cuadrado, Patricia Pérez-Galán, Mihai Raducan, Christophe Bour, Antonio M. Echavarren, and Pablo Espinet.

Organometallics **2010**, *29*, 951-956.

Metal-Arene Interactions in Dialkylbiarylphosphine Complexes of Copper, Silver, and Gold

Patricia Pérez-Galán, Nicolas Delpont, Elena Herrero-Gómez, Feliu Maseras, and Antonio M. Echavarren.

Che.m Eur. J. **2010**, chem20093507.

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Esta memoria del trabajo de Tesis Doctoral se ha dividido en tres partes, una introducción general, un apartado de resultados y discusión y finalmente la parte experimental.

En la *introducción* general, se recogen los principios básicos de la catálisis homogénea de oro en las activaciones de alquinos, centrada exclusivamente en las reacciones de 1,6-eninos y en los aspectos mecanísticos de las mismas.

El apartado de *Resultados y Discusión* se divide en cinco secciones en las que se recogen los resultados más relevantes del trabajo de la Tesis Doctoral. Cada una de las secciones se compone de una introducción, unos objetivos, un apartado de resultados y discusión y, finalmente las conclusiones.

Parte del trabajo relacionado con la sección *Gold(I)-catalyzed [4+2] cycloaddition reaction of 1,6-enynes* se ha realizado en colaboración con el Dr. Christophe Bour, en la versión enantioselectiva de la reacción, y con el Dr. Thorsten Lauterbach, en el apartado de *Synthesis of the Pycnanthuquinone*. Algunos de los resultados de ambos han sido incluidos en esta memoria para asegurar la coherencia en el desarrollo de la discusión. La parte del trabajo relacionado con la sección *New silver(I) and copper(I) complexes: synthesis and applications* se ha realizado en colaboración con Nicolas Delpont.

El estudio computacional de las reacciones de cicloadición [4+2] que se incluye en la sección *Gold(I)-catalyzed [4+2] cycloaddition reaction of 1,6-enynes* ha sido realizado por el Prof. Diego J. Cárdenas y Cristina Nieto Oberhuber en el Departamento de Química Orgánica de la Universidad Autónoma de Madrid. El estudio computacional del apartado *New silver(I) and copper(I) complexes: synthesis and applications*, ha sido realizado por Elena Herrero-Gómez y el Prof. Feliu Maseras (ICIQ).

Por tener menos relación con el tema principal del trabajo aquí recogido, no se incluyen en este manuscrito los resultados aportados a las siguientes publicaciones:

Gold(I) Complexes with Hydrogen-Bond-Heterocyclic Carbenes as Active Catalysts in Reactions of 1,6-Enynes. Camino Bartolomé, Patricia Pérez-Galán, Christophe Bour, Mihai Raducan, Antonio M. Echavarren, and Pablo Espinet. *Inorg. Chem*. **2008**, *47*, 11391-11397.

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Nitrogen Acyclic Gold(I) Carbenes: Excellent and Easily Accessible Catalysts in reactions of 1,6-Enynes. Camino Bartolomé, Zoraida Ramiro, Domingo García-Cuadrado, Patricia Pérez-Galán, Mihai Raducan, Christophe Bour, Antonio M. Echavarren, and Pablo Espinet. *Organometallics* **2010**, *29*, 951-956.

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Resumen

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El oro es uno de los metales más conocidos por el ser humano, pero el uso de complejos de oro en catálisis homogénea ha surgido en los últimos 10 años, demostrándose su eficacia como catalizador en a la activación de alquinos.

Nuestro grupo de investigación se ha centrado en el estudio de la reacción de ciclación de α,ω-eninos catalizada por diferentes catalizadores de oro(I), dando lugar al desarrollo de nuevas metodologías sintéticas. En el caso particular de los 1,6-eninos, una gran variedad de productos carbo- y heterocíclicos, se obtienen usando los complejos de oro(I) como catalizadores.[1] Estudios computacionales permiten proponer un mecanismo de reacción que transcurre a través de intermedios de tipo carbeno de oro **III** y **V**, para dar lugar a los dienos **VI** y **VII**, mediante transposición simple o doble, dependiendo del enlace que se rompe en el intermedio **III** (Esquema 1).

1 Reviews on metal catalyzed cyclization of enynes: (a) Trost, B. M. *Acc. Chem. Res.* **1990**, *23*, 34-42. (b) Negishi, E. In *Comprehensive Organic Synthesis*; Trost, B. M.; Pergamon: Oxford, 1991; Vol. 5, pp. 1163-1184. (c) Tamao, K.; Kobayashi, K.; Ito, Y. *Synlett* **1992**, 539-546. (d) Schore, N. E. *Chem. Rev.* **1998**, *98*, 1081-1119. (e) Trost, B. M.; Krische, M. J. *Synlett* **1998**, 1-16. (f) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067-2096. (g) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813-834. (h) Lloyd-Jones, G. C. *Org. Biomol. Chem.* **2003**, *1*, 215-236. (i) Méndez, M.; Mamane, V.; Fürstner, A. *Chemtracts Org. Chem.* **2003**, *16*, 397-425. (j) Echavarren, A. M.; Nevado, C. *Chem. Soc. Rev.* **2004**, *33*, 431-436. (k) Añorbe, L.; Domínguez, G.; Pérez-Castells, J. *Chem. Eur. J.* **2004**, *10*, 4938-4943. (l) Diver, S. T.; Giessert, A. J. *Chem. Rev.* **2004**, *104*, 1317-1382.

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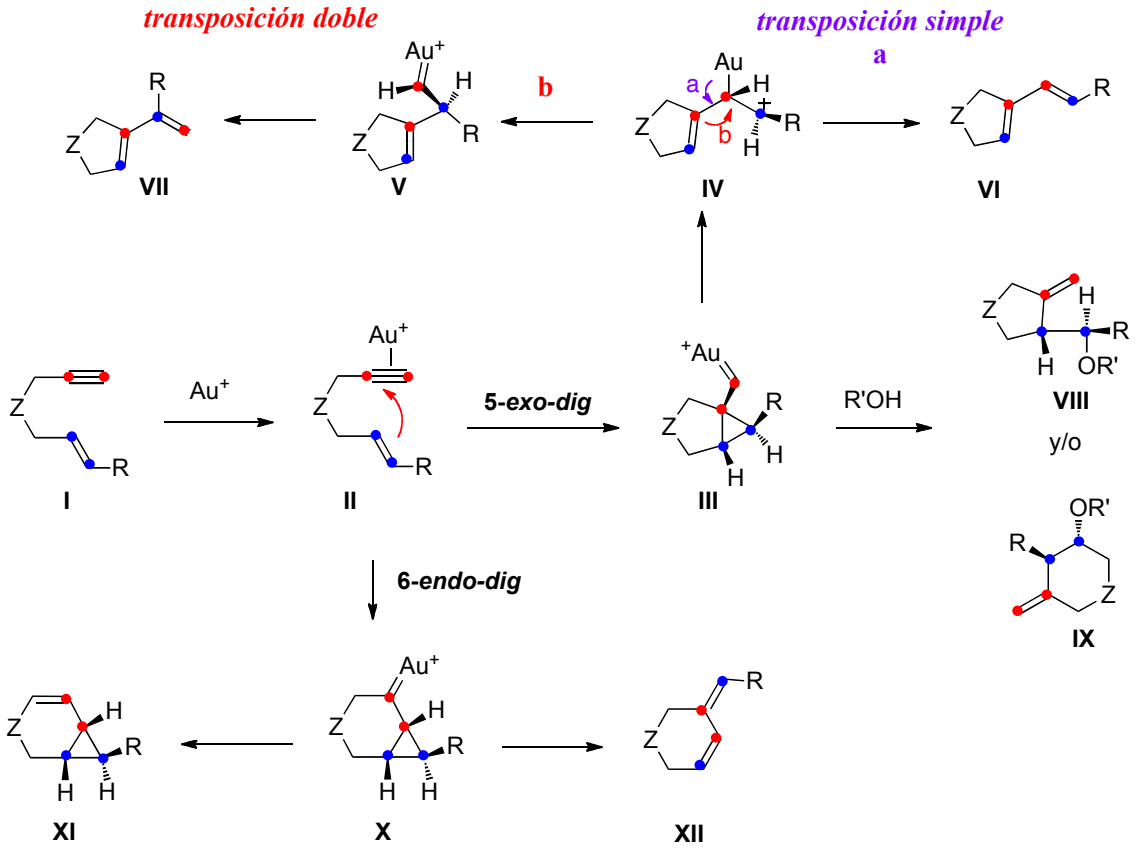
Esquema 1



De acuerdo con nuestros resultados teóricos y experimentales en nuestro grupo, la formación de estos productos se puede justificar mediante la coordinación del Au^+ al alquino para formar complejos (η^2-alquino)metal **II**, que evoluciona para formar ciclopropil-carbenos metálicos **III** (ciclación 5-*exo-dig*), **V** (ciclación 5-*exo-dig*, transposición doble) o **X** (ciclación 6-*endo-dig*).[2] Cuando en el medio de reacción hay nucleófilos, tales como alcoholes o agua, se produce un ataque de R'OH sobre **III** que genera productos de alcohoxi- o hidroxiciclación **VIII-IX**.[3] Esta reacción es estereoespecífica,[2,3,4] siendo la regioselectividad dependiente de la

2 (a) Méndez, M; Muñoz, M. P.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc*., **2001**, *123*, 10511-10520. (b) Méndez, M.; Muñoz, M. P.; Echavarren, A. M. *J. Am. Chem. Soc*., **2000**, *122*, 11549-11550. (c) Reacción catalizada por Pd(II): Nevado, C.; Charruault, L.; Michelet, C.; Nieto-Oberhuber, C.; Muñoz, M. P.; Méndez, M.; Pager, M. N.; Genêt, J. P.; Echavarren, A. M. *Eur. J. Org. Chem*., **2003**, 706-713.

3 Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Chem. Eur. J*., **2003**, *9*, 2627-2635.

4 Nishizawa, M.; Yadav, V. K.; Skwarczynski, M.; Takao, H.; Imagawa, H.; Sugihara, T. *Org. Lett*., **2003**, *5*, 1609-1611.

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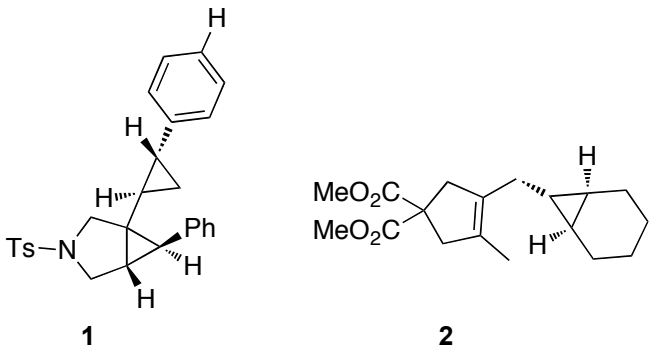
sustitución del alqueno y de los sustituyentes en la posición Z. Variaciones en la estructura de estos 1,6-eninos permiten obtener otro tipo de productos, entre las que destacan, interesantes esqueletos policíclicos.

El trabajo de esta tesis doctoral se ha centrado, en el estudio experimental de las reacciones de los intermedios **III**, en el desarrollo de nuevas reacciones usando complejos de oro como catalizadores, y en la preparación de nuevos catalizadores.

El primer capítulo de esta memoria recoge el estudio experimental para confirmar la existencia de los intermedios carbeno-oro propuestos. En este estudio se atraparon estos intermedios **III** y **V** con alquenos obteniéndose productos de bisciclopropanación. En la Figura 1 se muestran dos ejemplos seleccionados, cuya configuración se determinó mediante experimentos de NMR, difracción de rayos-X para **1**, y mediante experimentos de deuteración en el caso de **2**.

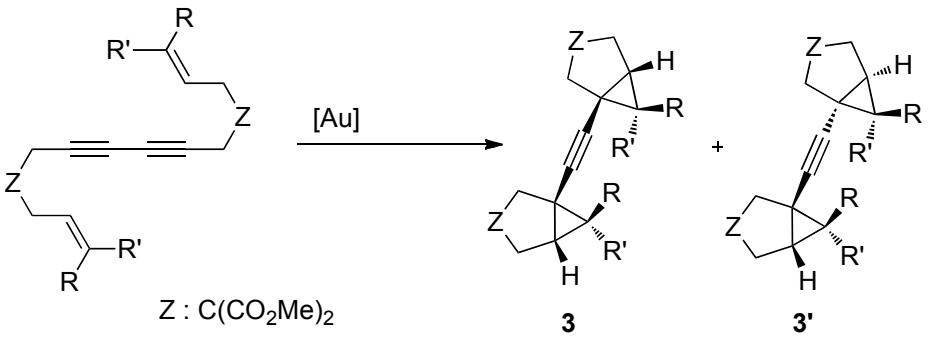


1 **2**

Figura 1

Por otra parte, un estudio sobre la reacción de biseninos, produjo los productos **3** y **3'**, cuya formación se explica a través del intermedio ciclopropilo-oro-carbeno, seguida por una transposición metalotrópica 1,3 para formar el segundo carbeno de oro (Esquema 2).

Esquema 2



3 **3'**

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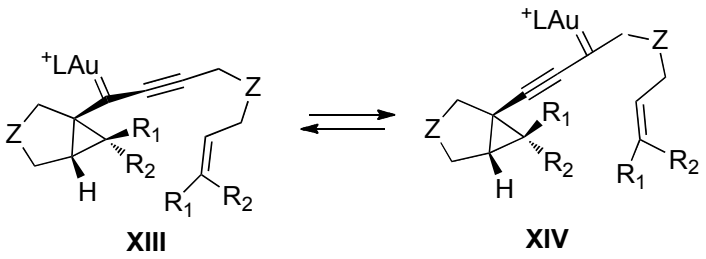

Un estudio competitivo con diferentes estirenos substituidos en la posición *para* (grupos OMe-, Cl-, H-, CF_3-, OCOMe-) y usando diferentes complejos de oro como catalizadores, nos desveló información sobre las propiedades electrónicas de los catalizadores, mediante representaciones de Hammet-Brown (Figura 2). Por otro lado, los estudios cinéticos realizados también confirmaron las distintas características de los diferentes catalizadores de oro.

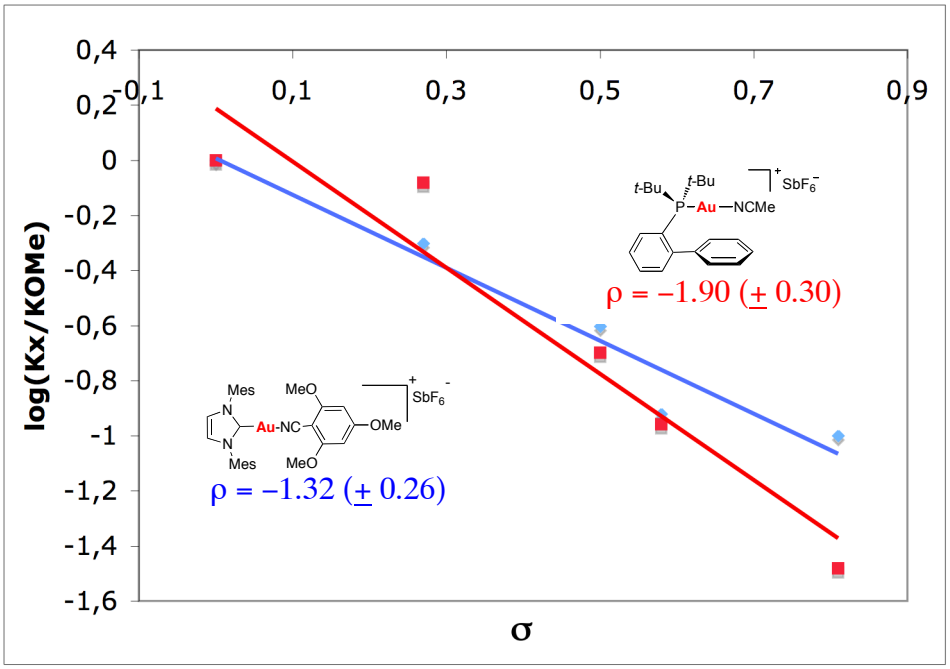

Figura 2: Representación de Hammett-Brown entre σ y $\log(K_x/K_{OMe})$

El segundo capítulo, recoge un estudio sobre la adición de nucleofilos a los intermedios **III** (camino de reacción 5-*exo-dig*) y **X** (camino de reacción 6-*endo-dig*) (Esquema 3) en reacciones de eninos catalizadas por complejos de oro(I).

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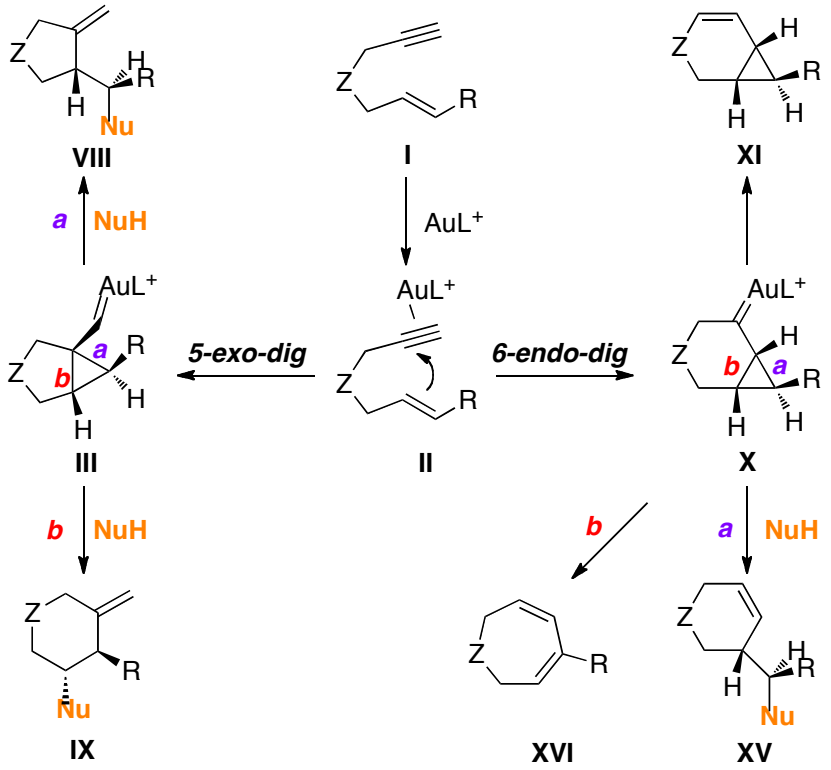
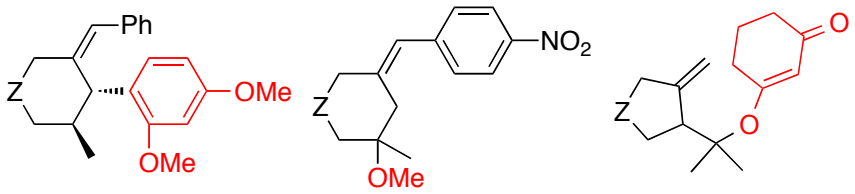
Esquema 3



En la Figura 3 se muestran tres ejemplos seleccionados del ataque de reactivos núcleofilos. El producto **4** proviene del ataque del indol al carbono *a*, del intermedio **X**. Los productos **5** y **6** provienen del ataque del nucleófilo en el carbono *b* del intermedio **III**. En el caso del producto **5**, debido a impedimentos estéricos, hay una trasposición de hidrógeno previa al ataque del 1,3-dimetoxibenceno. Por último, el producto **7** se obtiene por ataque del núcleofilo al carbono *a* en el intermedio **III**.



5, 30% **6**, 83% **7**, 87%

Figura 3: ejemplos seleccionados de los productos obtenidos en la reacción de adición de núcleofilos a 1,6-eninos catalizada por complejos de oro(I)

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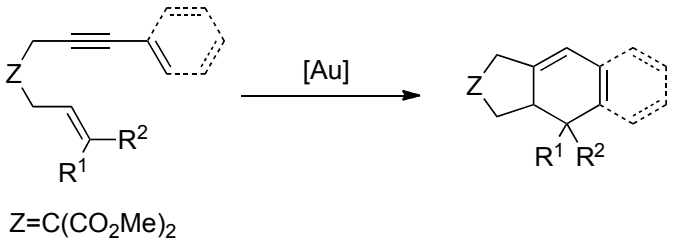
El tercer capítulo de los resultados se centra en el estudio detallado de la reacción de cicloadición [4+2] catalizada por oro(I). Esta reacción tiene lugar en presencia de complejos de oro(I), y se obtienen bi- o triciclos, como productos de la cicloadición [2+2] y [4+2], respectivamente (Esquema 4).

Esquema 4



Los mejores resultados de esta reacción se obtienen cuando se usa el catalizador de oro con ligando fosfito, permitiendo obtener mayores rendimientos y menores tiempos de reacción (Figura 4).

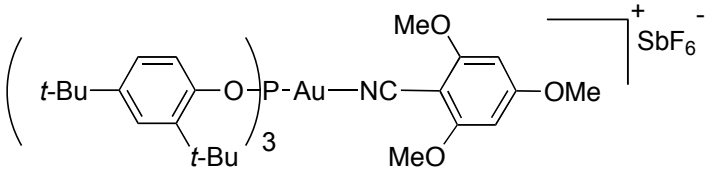


Figura 4

Algunos de los resultados se muestran en la siguiente Figura 5.

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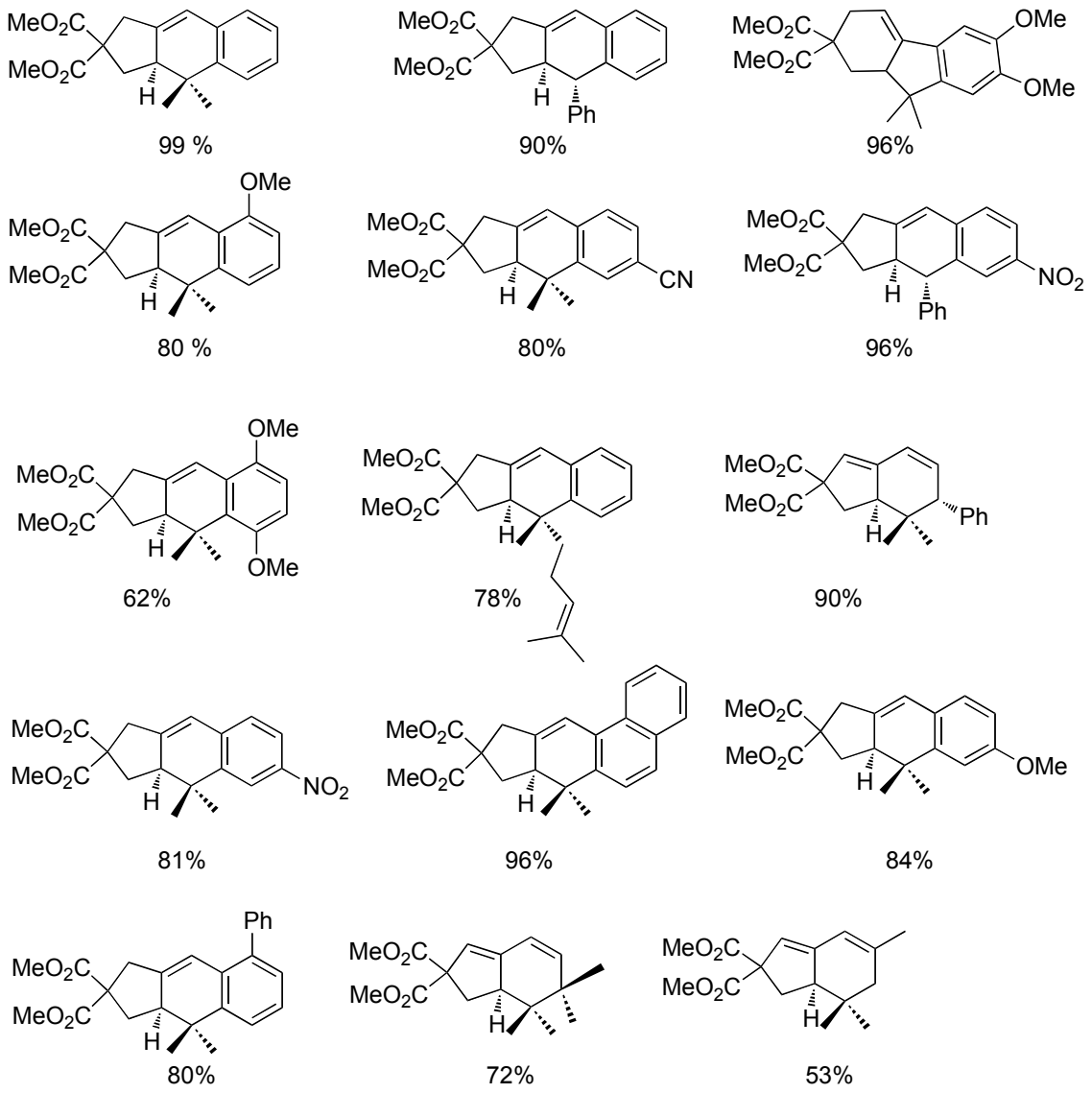

Figura 5

En este tercer capítulo de la memoria se recoge también el estudio de la reacción enantioselectiva de cicloadición [4+2] usando diferentes catalizadores.

Otra parte importante de este estudio, se ha centrado en la aplicación de esta reacción en la síntesis total de productos naturales. El esqueleto carbonado de los triciclos derivados de la reacción de cicloadición [4+2] catalizada por Au(I) corresponden al esqueleto carbonado de las *pycnanthuquinonas A-C,* una familia de productos naturales. Parte del trabajo se orientó hacia la síntesis de la *pycnanthuquinona C*.

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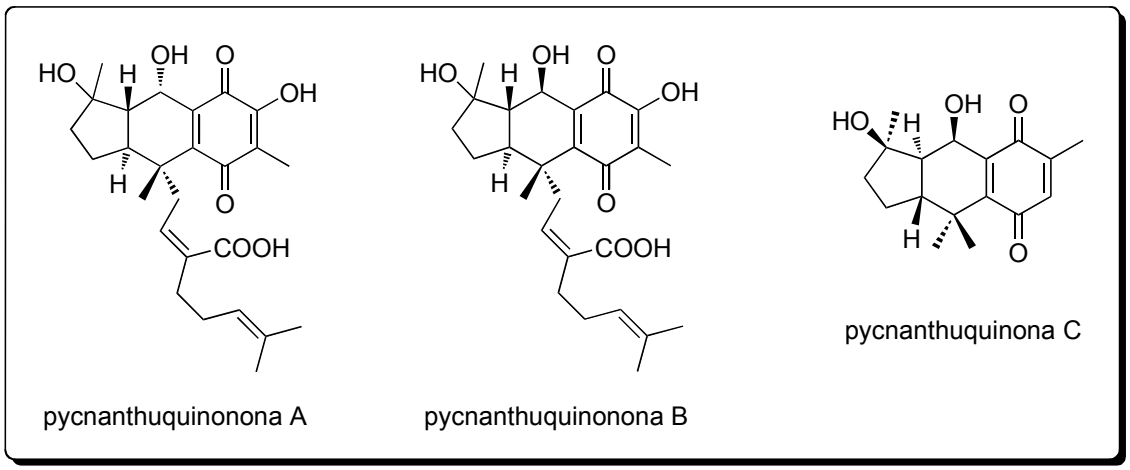
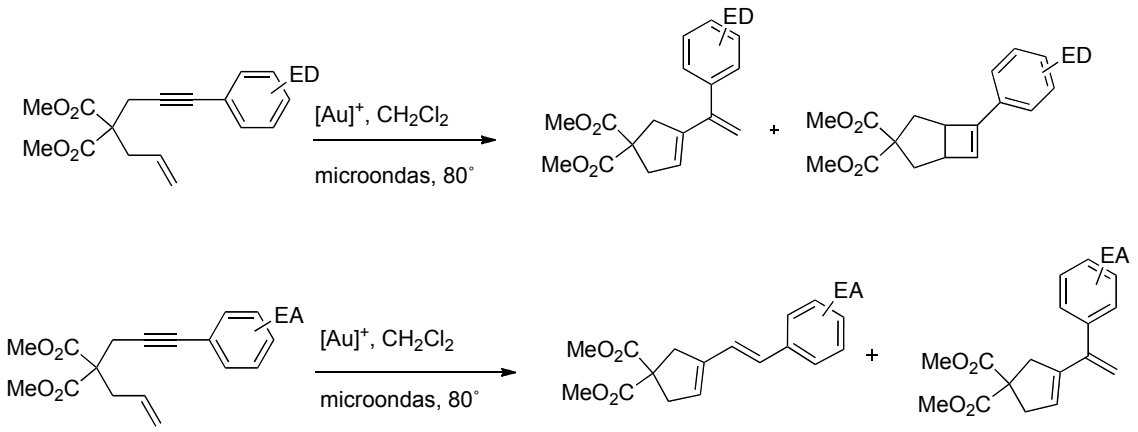


Figura 6

El cuarto capítulo de esta memoria recoge un estudio detallado del mecanismo de las trasposiciones simples y dobles de 1,6-eninos substituidos en el alquino por un anillo aromático catalizadas por complejos de oro(I). Los productos obtenidos son productos de simple y doble transposición dependiendo de si el grupo en el anillo es electro-donador o electro-atractor, respectivamente. La cestructura de los productos se ha determinado por experimentos de NMR, y mediante marcaje isotópico con ^{13}C. En este estudio se pudo comprobar que la formación de estos dienos no transcurre a través de una apertura del ciclobuteno.

Esquema 5



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El quinto capítulo resume el trabajo sobre síntesis de nuevos complejos de oro, plata y cobre con fosfinas voluminosas. Estudios computacionales y estudio de las propiedades catalíticas de estos nuevos complejos frente a las reacciones de 1,6- y 1,7-eninos ya estudiadas previamente. Las estructuras de rayos-X de estos complejos mostraban una evidente distorsión en el ángulo formado entre el metal, el fósforo y el nitrógeno, siendo prácticamente lineal para el complejo de oro(I) (173.03º), menos lineal para el complejo de plata(I) (168.01º) y claramente angular para el cobre(I) (148.79º) (Figura 7). Este estudio concluye que esta diferencia de ángulo se debe a la interacción π con el anillo aromático situado sobre el metal, siguiendo el orden decreciente Cu>Ag>Au.

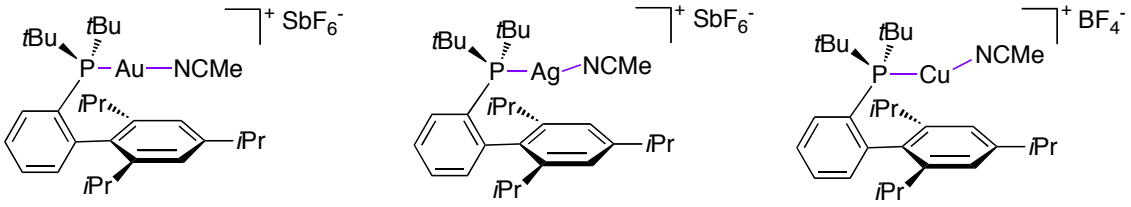

Figura 7

En este trabajo también se han preparado los primeros complejos de Ag(I) con arenos. En la Figura 8 se recoge un ejemplo representativo.[3].

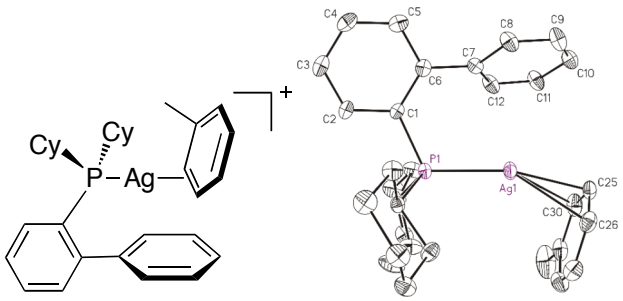

Figura 8

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Abbreviations and acronyms

In this manuscript, the abbreviations and acronyms most commonly used in organic and organometallic chemistry have been used following the recommendations of "*Guidelines for authors*" from the American Chemical Society (ACS, *J. Org. Chem.*).
Additionally, I have also used the following ones:

All	allyl
Cy	cyclohexyl
dppe	1,1'-bis(diphenylphosphino)ethane
dppm	1,1'-bis(diphenylphosphino)methane
NMO	*N*-methylmorpholine-*N*-oxide
SEM	2-(trimethylsilyl)ethoxymethyl
TES	triethylsilyl
Tol	tolyl

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Introduction

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One of the main objectives in chemistry is the development of new strategies for the synthesis highly functionalized polycyclic molecules under catalytic conditions. Catalysis with electrophilic transition metal complexes provides new opportunities to obtain these products with high levels of atom-economy[5] and selectivity. Particularly attractive transformations are those based on the activation of alkynes, for which the most commonly used metals in these reactions are Pd, Pt, Ru, Ni, Rh, Cu[1,6] and Au, which has come out as the best transition metal catalyst for this purpose.[7]

5 (a) Trost, B. M. *Science* **1991**, *254*, 1471-1477. (b) Trost, B. M. *Acc. Chem. Res.* **2002**, *35*, 695- 705.

6 Reviews: (a) Tamao, K.; Kobayashi, K.; Ito, Y. *Synlett* **1992**, 539-546. (b) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49-92. (c) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635-662. (d) Nakamura, I.; Yamamoto, Y. *Chem. Rev.* **2004**, *104*, 2127-2198. (e) Schore, N. E. *Chem. Rev.* **1998**, *88*, 1081-1119. (f) Frühauf, H.-W. *Chem. Rev.* **1997**, *97*, 523-596.

7 Recent reviews on gold catalyzed reactions: (a) Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Commun.* **2007**, 333-346. (b) Gorin, D. J.; Toste, F. D. *Nature* **2007**, *446*, 395-403. (c) Fürstner, A.; Davies, P. W. *Angew. Chem. Int. Ed.* **2007**, *46*, 3410-3449. (d) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180-3211. (e) Zhang, L.; Sun, J.; Kozmin, S. A. *Adv. Synth. Catal.* **2006**, *348*, 2271- 2296.

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1. Gold

Gold is certainly a rare element, but it is more abundant than palladium, platinum, rhodium and many other precious metals. It is probably the only chemical element that every adult has heard about. In nature it is encountered in elemental form because it has low reactivity due to its highly positive normal potential for oxidation. Metallic gold is highly biocompatible, and it is used in dental medicine, in the treatment of arthritis, and no allergic reactions are associated with gold.

Gold(I) is a "soft" cation and shows high electrophilic affinity for π–bonds as in alkynes, arenes and allenes, and activates these groups towards nucleophilic attack. The relativistic effects of gold explain this unique π-acidity, which reaches a maximum in the periodic table with gold.[7b,8] Reactions catalyzed by gold usually take place under mild conditions. In the presence of organic substrates the possible oxidation status of gold are gold(0), gold(I) and gold(III).

2. Alkyne activation

2.1. *Reactivity of gold complexes with alkynes*

The bonding of an alkyne (acetylene) to gold complex is similar to that in an alkene complex. Alkynes tend to be more electropositive and therefore bind more tightly to gold than alkenes. In fact, alkynes will often displace alkenes. This

8 (a) Pyykkö, P. *Angew. Chem. Int. Ed*. **2002**, *41*, 3573-3578. (b) Pyykkö, P. *Angew. Chem. Int. Ed.* **2004**, *43*, 4412-4456. (c) Pyykkö, P. *Inorg. Chim. Acta* **2005**, *358*, 4113-4130. (d) Schwartz, H. *Angew. Chem. Int. Ed.* **2003**, *42*, 4442-4454.

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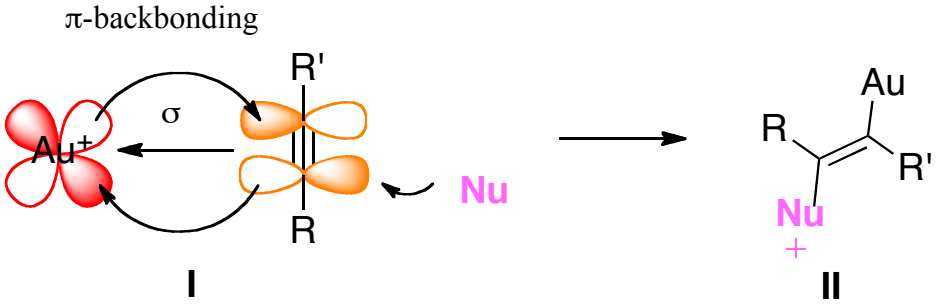
bonding can be explained in terms of the Dewar-Chatt-Duncanson[9] model as a combination of a σ interaction between the π orbital of the acetylene and the empty *dsp* orbital of the metal, and a π interaction between *d* orbital of the metal and the π* orbital of the alkyne, known as backbonding (**I**, Scheme 1).[10]

Scheme 1



The coordination of an alkyne to a metal significantly modifies the geometry of the alkyne. The Dewar-Chatt-Duncanson model predicts an elongation of the C-C triple bond and bending as a consequence of the resultant rehybridization. And depending on the substituents on the alkyne, the ligands on the gold, and the nucleophile, the π-complex is susceptible to nucleophilic attack on the unsaturated C atoms to give trans-alkenyl-gold complexes of type **II** as reactive intermediates (Scheme 1).

3. Enyne Cycloisomerization

Particularly attractive transformations are those known as cycloisomerization reactions, in which a tethered alkene acts as the nucleophile (Scheme 1, **II**).

A cycloisomerization reaction is defined as a reaction in which a section of a carbon or carbon–heteroatom chain, which is unsaturated at two positions, is isomerized, with concomitant loss of one or more units of unsaturation, no (formal)

9 (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C51-79. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939-2947.

10 Schmidbaur, H.; Schier, A. *Organometallics* **2010**, *29*, 2-23.

loss or gain of any atoms, and the generation of one or more ring systems.[11] These cyclizations are usually performed with unsaturated substrates bearing π-electrons such as alkynes, alkenes, and allenes. Stoichiometric cyclizations of enynes promoted by a number of transition metal complexes have been extensively studied.

The $[AuL]^+$ fragment, which is isolobal to H^+ and HgL^{2+},[12] is prone to linear coordination. The mechanistic studies about this reaction have been reported with enynes as substrates, and reveal that the gold activates selectively the alkyne function of the enyne. This fact can be explained by the higher reactivity of the alkyne-gold complexes and also by the higher nucleophilicity of the double bonds, compared, on the contrary, with alkene-gold complexes and alkynes as nucleophiles. However, complexes of gold(I) with the alkene moiety of the enyne are most probably formed in solution, in equilibrium with complexes of gold(I) and the alkyne moiety.[13] In addition, gold(I)-alkene complexes have been reported and structurally characterized.[14,15,16,17,18]

---

11 Lloyd-Jones, G. C. *Org. Biomol. Chem*. **2003**, *1*, 215-236.

12 (a) Hoffmann, R. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 711-724. (b) Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1984**, *32*, 237-325. (c) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, 391-400.

13 A gold-alkene complex is formed in CD_2Cl_2 solution from a 1:1 mixture of the 1,7-enyne (dimethyl 2-(but-3-enyl)-2-(prop-2-ynyl)propanedioate) and a cationic Au(I) complex: García-Mota, M.; Cabello, N.; Maseras, F.; Echavarren, A. M.; Pérez-Ramírez, J.; López, N. *Chem. Phys. Chem.* **2008**, *9*, 1624-1629.

14 Ethylene-gold(I) complexes: (a) Rasika Dias, H. V.; Wu, J. *Angew. Chem. Int. Ed.* **2007**, *46*, 7814-7816. (b) Rasika Dias, H. V.; Fianchini, M.; Cundari, T. R.; Campana, C. F. *Angew. Chem. Int. Ed.* **2008**, *47*, 556-559.

15 Styrene-gold(I) complex: (a) Cinellu, M. A.; Minghetti, G.; Stoccoro, S.; Zucca, A.; Manassero, M. *Chem. Commun.* **2004**, 1618-1619. (b) Cinellu, M. A.; Minghetti, G.; Cocco, F.; Stoccoro, S.; Zucca, A.; Manassero, M.; Arca, M. *Dalton Trans.* **2006**, 5703-5716.

16 [Au(*trans*-cyclooctene)$_3$]OTf: Komiya, S.; Kochi, J. K. *J. Organomet. Chem.* **1977**, *135*, 65-72.

17 Diene-Au(I) complexes: (a) Bis(1,5-cyclooctadiene)-Au(I) complex: Roulet, R.; Favez, R. *Chimia* **1975**, *29*, 346-348. (b) (1,5-Cyclooctadiene)-Au(I) complex: Usón, R.; Laguna, A.; Sanjoaquin, J. L. *J. Organomet. Chem.* **1974**, *80*, 147-154. (c) Cyclooctatetraene-AuCl complex: Tauchner, P.; Huettel, R. *Chem. Ber.* **1974**, *107*, 3761-3770.

3.2. 1,6-Enyne cycloisomerizations.

In particular, the cyclization of 1,6-enynes affords highly functionalized carbo- and heterocycles[19] in which C-C bonds are formed regio- and stereoselectively, a feature that could not be achieved by conventional organic methods.[20]

Various cyclic products have been synthesized starting from enynes by transition metal catalysis with a variety of metals. These cyclic products can be organized according to reaction mechanisms, which depend on the coordination mode of the metal. It should be noted that the same metal could give different coordination patterns due to the absence or presence of various ligands, including coordinating solvents. Reactions of 1,6-enynes catalyzed by electrophilic transition metal complexes or salts proceed through two general pathways depending on whether the metal coordinates both the alkyne and the alkene bonds (**IV**) (see Scheme 2) or only the alkyne moiety (**X**) (Scheme 3).[1,2,19,21]

In the first pathway, the Alder-ene cycloisomerization of enynes,[11,12,22,23,24,25,26,27] occurs when the metal coordinates both the alkyne and the

18 Diene-Au(III) complexes: (a) Bis(1,5-cyclooctadiene)-AuCl3 complex: Leedham, T. J.; Powell, D. B.; Scott, J. G. V. *Spectrochimica Acta, A* **1973**, *29*, 559-565 (b) Hexamethyl Dewar benzene complex with AuCl3: Huettel, R.; Tauchner, P.; Forkl, H. *Chem. Ber.* **1972**, *105*, 1-7.

19 Reviews on metal catalyzed cyclization of enynes: (a) Tamao, K.; Kobayashi, K.; Ito, Y. *Synlett* **1992**, 539-546. (b) Schore, N. E. *Chem. Rev.* **1998**, *98*, 1081-1119. (c) Trost, B. M.; Krische, M. J. *Synlett* **1998**, 1-16. (d) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067-2096. (e) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813-834. (f) Lloyd-Jones, G. C. *Org. Biomol. Chem.* **2003**, *1*, 215-236. (g) Méndez, M.; Mamane, V.; Fürstner, A. *Chemtracts Org. Chem.* **2003**, *16*, 397-425. (h) Echavarren, A. M.; Nevado, C. *Chem. Soc. Rev.* **2004**, *33*, 431-436. (i) Añorbe, L.; Domínguez, G.; Pérez-Castells, J. *Chem. Eur. J.* **2004**, *10*, 4938-4943. (j) Diver, S. T.; Giessert, A. J. *Chem. Rev.* **2004**, *104*, 1317-1382.

20 (a) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49-92. (b) Ojima, I.; Tzamarioudaki, M.; Zhaoyang, L.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635-662.

21 (a) Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Chem. Eur. J.* **2003**, *9*, 2627-2635. (b) Nevado, C.; Ferrer, C.; Echavarren, A. M. *Org. Lett.* **2004**, *6*, 3191-3194.

22 Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev*. **2002**, *102*, 813-834.

alkene bonds (**IV**) (see Scheme 2). Intermediate **V** is formed via an oxidative cyclometalation, which usually evolves via β-hydrogen elimination from one of the alkyl chains to give **VI**, which undergoes reductive elimination to give Alder-ene type products **VII** and regenerates catalytically active M^n[28,29] In addition, intermediate **V** could also evolve via double electrophilic cleavage to form **VIII**.[30]

23 Hoffmann-Röder, A.; Krause, N. *Org. Biomol. Chem.* **2005**, *3*, 387-391.

24 Ma, S.;Yu, S.; Gu, Z. *Angew. Chem. Int. Ed.* **2006**, *45*, 200-203.

25 Bruneau, C. *Angew. Chem. Int. Ed.* **2005**, *44*, 2328-2334.

26 (a) Trost, B. M.; Tanoury, G. J. *J. Am. Chem. Soc*. **1988**, *110*, 1636-1638. (b) Trost, B. M.; Trost, M. K. *Tetrahedron Lett.* **1991**, *32,* 3647-3650. (c) Trost, B. M.; Doherty, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 3801-3810. (d) Trost, B. M.; Yanai, M.; Hoogsteed, K. *J. Am. Chem. Soc.* **1993**, *115*, 5294-5295.

27 Bajracharya, G. B.; Nakamura, I.; Yamamoto, Y. *J. Org. Chem.* **2005**, *70*, 892-897.

28 Pd: (a) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1985**, *107*, 1781-1783. (b) Trost, B. M.; Lautens, M. *Tetrahedron Lett.* **1985**, *26*, 4887-4890. (c) Trost, B. M.; Chen, S.-F. *J. Am. Chem. Soc.* **1986**, *108*, 6053-6054. (d) Trost, B. M.; Tour, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5268-5270. (e) Trost, B. M.; Lautens, M.; Chan, C.; Jebaratnam, D. S.; Mueller, T. *J. Am. Chem. Soc.* **1991**, *113*, 636-644. (f) Trost, B. M.; Gelling, O. J. *Tetrahedron Lett.* **1993**, *34*, 8233-8236. (g) Wartenberg, F.-H.; Hellendahl, B.; Blechert, S. *Synlett* **1993**, 539-540. (h) Trost, B. M.; Czeskis, B. A. *Tetrahedron Lett*. **1994**, *35*, 211-214. (i) Trost, B. M.; Tanoury, G. J.; Lautens, M.; Chan, C.; MacPherson, D. T. *J. Am. Chem. Soc*. **1994**, *116*, 4255-4267.

29 Cycloisomerization with other metals: Co: (a) Kraft, M. E.; Wilson, A. M.; Dasse, O. A.; Bonaga, L. V. R.; Cheung, Y. Y.; Fu, Z.; Shao, B.; Scott, I. L. *Tetrahedron Lett.* **1998**, *39*, 5911-5914. (b) Cruciani, P.; Stammler, R.; Aubert, C.; Malacria, M. *J. Org. Chem*. **1996**, *61*, 2699-2708 and references therein. (c) Buisine, O.; Aubert, C.; Malacria, M. *Chem. Eur. J*. **2001**, *7*, 3517-3525. Ti: (d) Sturla, S. J.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 1976-1977. Ru: (e) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2000**, *122*, 714-715. Rh: (f) Cao, P.; Zhang, X. *Angew. Chem. Int. Ed.* **2000**, *39,* 4104-4106. Fe: (g) Fürstner, A.; Martín, R.; Majima, K. *J. Am. Chem. Soc.* **2005**, *127*, ja0532739.

30 Montchamp, J.-L.; Negishi, E. *J. Am. Chem. Soc.* **1998**, *120*, 5345-5346.

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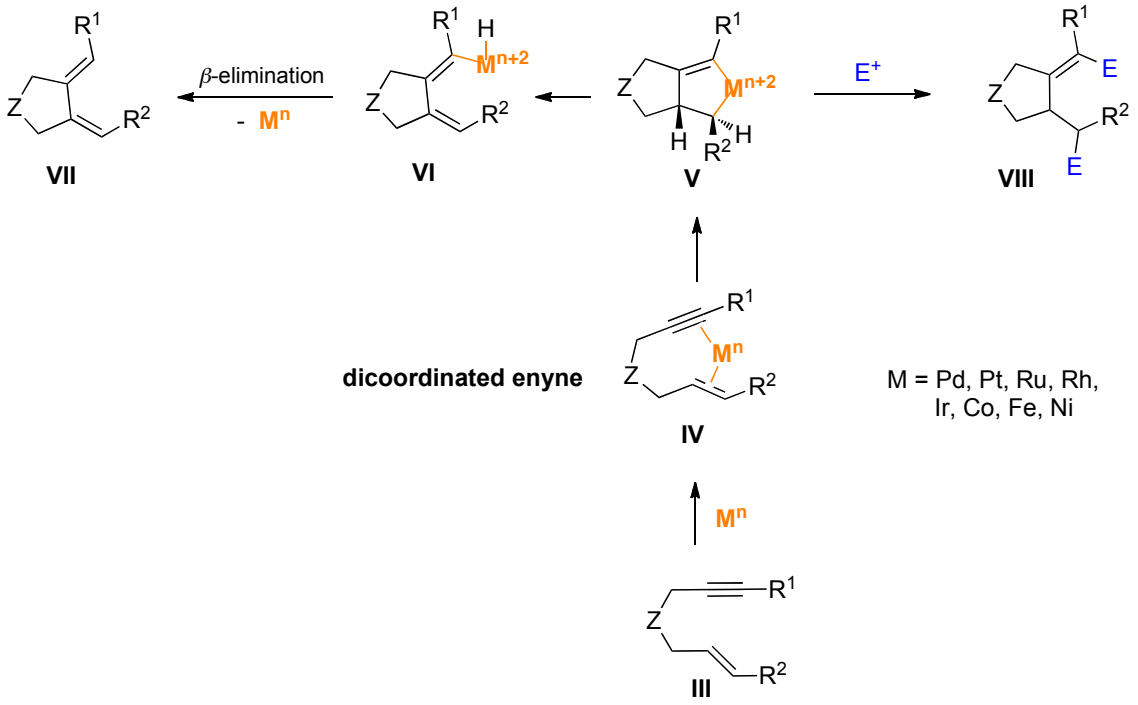
Scheme 2



In the second pathway, which is most favorable for Au(I), Pd(II),[31] and Pt(II) catalysis,[6,7,32] the metal center only coordinates with the alkyne moiety of the 1,6-enyne (**X**) and the alkene acts as nucleophile (Scheme 3). Cyclopropyl metal carbenes **XVI** and **XI** can be formed from **X** by *endo-dig* or *exo-dig* processes respectively (depending if the olefin attacks to the alkyne occurs in an endo or an exo fashion).[19j,26,33] The two types of cyclopropyl metal carbenes can be generated

31 (a) Liu, H.; Yu, J.; Wang, L.; Tong, X. *Tetrahedron Lett.* **2008**, *49*, 6924-6928. (b) Yang, S.-R.; Jiang, H.-F.; Li, Y.-Q.; Chen, H.-J.; Luo, W.; Xu, Y.-B. *Tetrahedron* **2008**, *64*, 2930-2937. (c) Corkey, B. K.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 2764-2765. (d) Rubina, M.; Conley, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2006**, *128*, 5818-5827. (e) Yamamoto, Y.; Kuwabara, S.; Ando, Y.; Nagata, H.; Nishiyama, H.; Itoh, K. *J. Org. Chem.* **2004**, 69, 6697-6705. (f) Zhu, G.; Zhang, Z. *Org. Lett.* **2003**, *5*, 3645-3648. (g) Hatano, M.; Yamanaka, M.; Mikami, K. *Eur. J. Org. Chem.* **2003**, *14*, 2552-2555. (h) Trost, B. M.; Hashmi, A. S. K.; Ball, R. G. *Adv. Synthesis & Catalysis* **2001**, *343*, 490-494.

32 (a) Ye, L.; Chen, Q.; Zhang, J.; Michelet, V. *J. Org. Chem.* **2009**, *74*, 9550-9553. (b) Brissy, D.; Skander, M.; Jullien, H.; Retailleau, P.; Marinetti, A. *Org. Lett.* **2009**, *11*, 2137-2139.

33 (a) Chatani, N.; Kataoka, K.; Murai, S. *J. Am. Chem. Soc.* **1998**, *120*, 9104-9105. (b) Fürstner, A.; Stelzer, F.; Szillat, H. *J. Am. Chem. Soc.* **2001**, *123*, 11863-11869. (c)

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depending on the nature of the tether (Z), the substitution on the alkene and the steric hindrance. Both intermediates can be attacked by *O*-nucleophiles (H_2O/ROH) in similar ways to give different alkoxycyclization products **VIII**,[2,19,34,35,36] **IX**[2,33b,33c,37] or **XIX**. In the absence of nucleophiles, after the 5-*exo*-*dig* cyclization, *anti*-cyclopropyl gold carbenes **XI** are formed. Intermediates **XI** evolve to give carbocations **XII**, which then undergo metal-elimination to provide single cleavage dienes (only the alkene is cleaved) **XIII**[19,33b,30b,35a,38,39] and/or bicyclic cyclobutenes **XXI**.[38,40] For the double cleavage rearrangement (alkene and alkyne are cleaved) intermediates **XIV** can be formed by a carbocationic 1,2-shift of the cyclic alkenyl group in **XII**. Subsequent 1,2–migration and proto-demetalation forms double

Mainetti, E.; Mouries, V.; Fensterbank, L.; Malacria, M.; Marco-Contelles, J. *Angew. Chem. Int. Ed.* **2002**, *41*, 2132-2135.

34 (a) Muñoz, M. P.; Méndez, M.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Synthesis* **2003**, 2898-2902. (b) Nevado, C.; Charruault, L.; Michelet, V.; Nieto-Oberhuber, C.; Muñoz, M. P.; Méndez, M.; Pager, M.-N.; Genêt, J.-P.; Echavarren, A. M. *Eur. J. Org. Chem.* **2003**, 706-713. (c) Charruault, L.; Michelet, V.; Taras, R.; Gladiali, S.; Genêt, J.-P. *Chem. Commun.* **2004**, 850-851.

35 (a) Nieto-Oberhuber, C.; Muñoz, M. P.; Buñuel, E.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2004**, *43*, 2402-2408. (b) Muñoz, M. P.; Adrio, J.; Carretero, J. C.; Echavarren, A. M. *Organometallics*, **2005**, *24*, 1293-1300.

36 (a) Galland, J.-C; Savignac, M.; Genêt, J.-P. *Tetrahedron Lett.* **1997**, *38*, 8695-8698. (b) Galland, J.-C; Savignac, M.; Genêt, J.-P. *Tetrahedron Lett.* **2001**, *57*, 5137-5148. (c) Nishizawa, M.; Yadav, V. K; Skwarczynski, M.; Takao, H.; Imagawa, H.; Sugihara, T. *Org. Lett.* **2003**, *5*, 1609-1611.

37 (a) Blum, J.; Beer-Kraft, H.; Badrieh, Y. *J. Org. Chem.* **1995**, *60*, 5567-5569. (b) Borodkin, V. S.; Shapiro, N. A.; Azov, V. A.; Kochetkov, N. K. *Tetrahedron Lett*. **1996**, *37*, 1489-1492. (c) Fürstner, A.; Szillat, H.; Stelzer, F. *J. Am. Chem. Soc*. **2000**, *122*, 6785-6786. (d) Bruneau, C. *Angew. Chem. Int. Ed.* **2005**, *44*, 2328-2334.

38 (a) N. Chatani, H. Inoue, T. Kotsuma, S. Murai, *J. Am. Chem. Soc*. **2002**, *124*, 10294-10295. (b) Marion, F.; Coulomb, J.; Courillon, C.; Fernsternbank, L.; Malacria, M. *Org. Lett.* **2004**, *6*, 1509-1511. (c) Bajracharya, G. B.; Nakamura, I.; Yamamoto, Y. *J. Org. Chem.* **2005**, *70*, 892-897.

39 Chowdhury, S. K.; Amarasinghe, K. K. D.; Heeg, M. J.; Montgomery, J. *J. Am. Chem. Soc.* **2000**, *122*, 6775-6776.

40 (a) Nieto-Oberhuber, C.; López, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178-6179. (b) Fürstner, A.; Davies, P. W.; Gress, T. *J. Am. Chem. Soc.* **2005**, *127*, 8244-8245.

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cleavage dienes **XV**. A few unsubstituted 1,6-enynes, as well as those bearing alkyl or aryl substituents at the alkyne can cyclize by endo pathways via intermediates **XVI** to form bicyclic compounds as **XVII** by 1,2-migration loss and protodemetalation,[2,21,33b,34,37,41,42,43] or **XVIII** by cleavage of bond labeled *b*.[44] The formation of dienes **XX** from **XI** will be discussed later. Those intermediates were trapped intramolecularly in presence of palladium-,[31h, 45] ruthenium-,[33a] platinum-,[33c,46,47,48] and gold-complexes. [111c,112]

41 Nieto-Oberhuber, C.; Muñoz, M. P.; López, S.; Jiménez-Núñez, E.; Nevado, C.; Herrero-Gómez, E.; Raducan, M.; Echavarren, A. M. *Chem. Eur. J.* **2006**, *12*, 1677–1693.

42 (a) Shibata, T.; Kobayashi, Y.; Maekawa, S.; Toshida, N.; Takagi, K. *Tetrahedron* **2005**, *61*, 9018-9024. (b) Lee, S. I.; Kim, S. N.; Kim, S. Y.; Cheng, Y. K. *Synlett* **2006**, 2256-2260.

43 Chao, C.-M.; Beltrami, D.; Toullec, P. Y.; Michelet, V. *Chem. Comm*. **2009**, 6988-6990.

44 Ferrer, C.; Raducan, M.; Nevado, C.; Claverie, C. K.; Echavarren, A. M. *Tetrahedron* **2007**, *63*, 6306-6316.

45 (a) Trost, B. M.; Hashmi, A. S. K. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1085-1087. (b) Trost, B. M.; Hashmi, A. S. K. *J. Am. Chem. Soc.* **1994**, *116*, 2183-2184.

46 Harrak, Y.; Blaszykowski, C.; Bernard, M.; Cariou, K.; Mainetti, E.; MouriMs, V.; Dhimane, A.-L.; Fensterbank, L.; Malacria, M. *J. Am. Chem. Soc*. **2004**, *126*, 8656-8657.

47 Peppers, B. P.; Diver, S. T. *J. Am. Chem. Soc*. **2004**, *126*, 9524-9525.

48 Diver, S. T.; Giessert, A. *J. Chem. Rev*. **2004**, *104*, 1317-1382.

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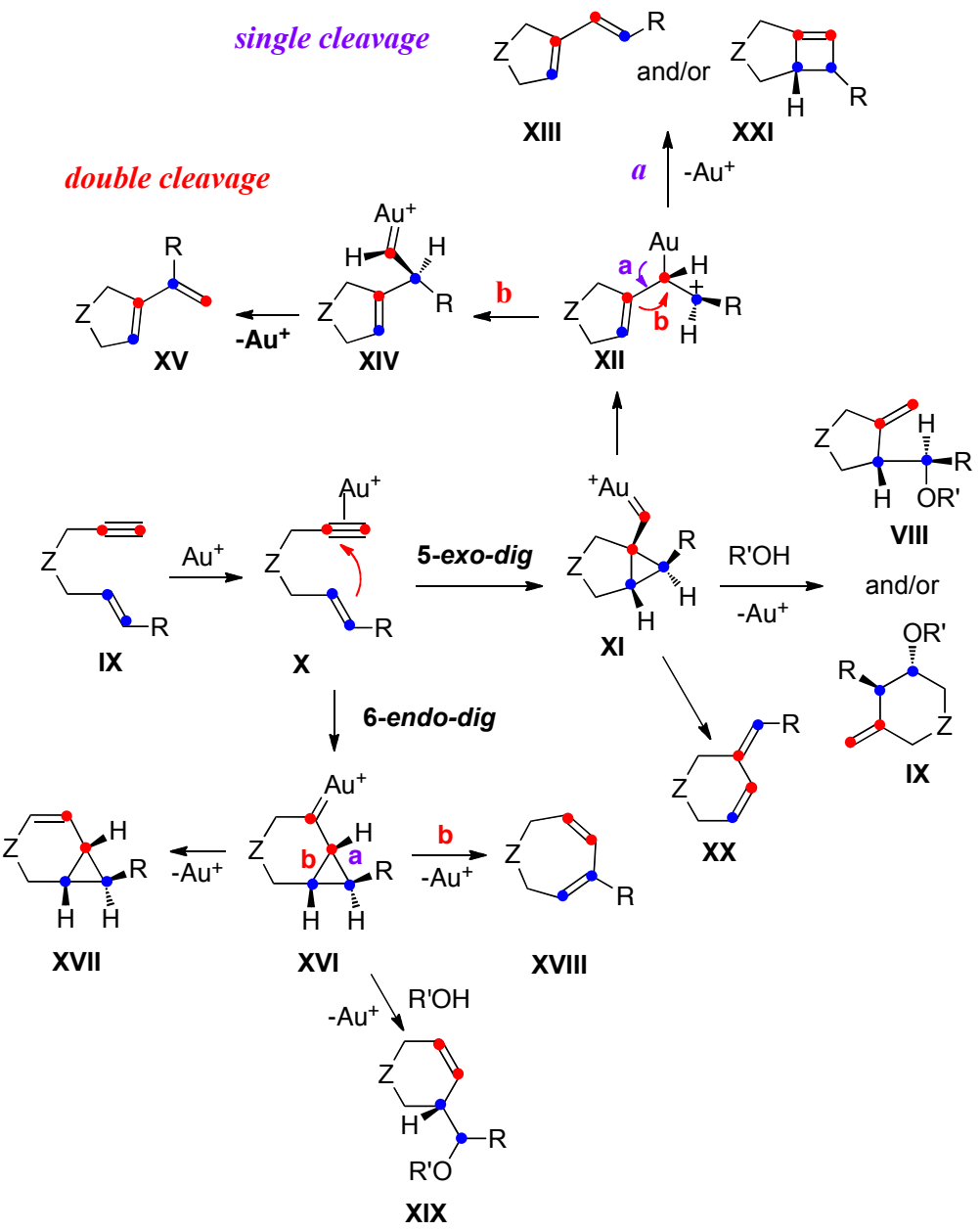
Scheme 3



Some examples of single cleavage rearrangement, in which only the alkene is cleaved, are depicted in Scheme 4. It should be noted that the configuration geometry of the starting alkene is retained in the final product. Thus, the Au-catalyzed enyne cycloisomerization is a stereospecific rearrangement process.[49,50,51,52]

49 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.

50 Mézailles, N.; Ricard, L.; Gagosz, F. *Org. Lett.* **2005**, *7*, 4133-4136.

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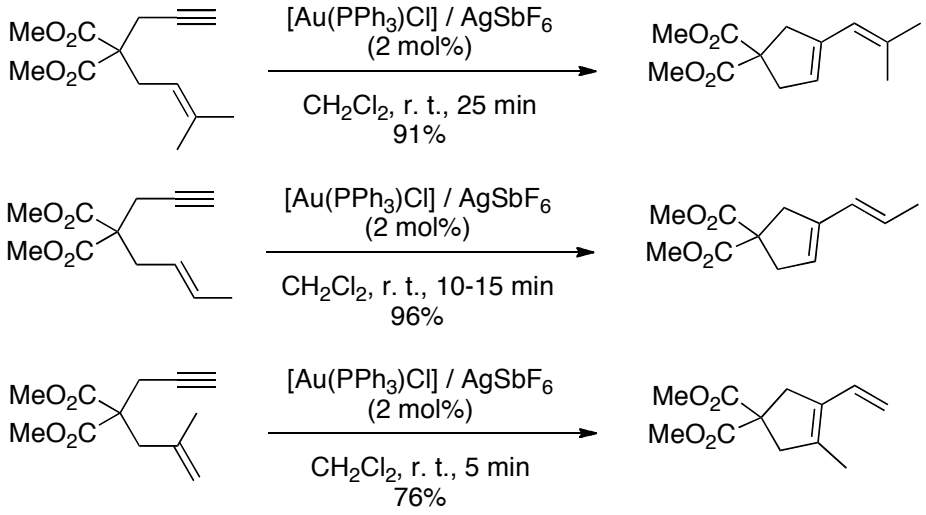
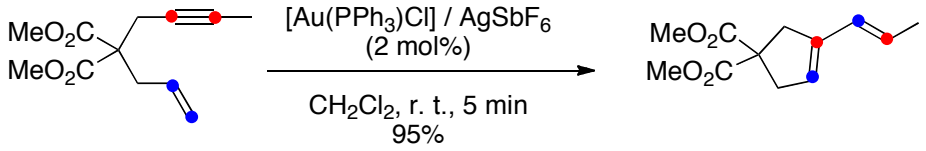
Scheme 4



On the other hand, an example of double cleavage rearrangement is shown in Scheme 5. This enyne with a methyl group at the alkyne, yields only a diene in which both the alkyne and the alkene have been cleaved.[26,33a-b,38c,53,54,55]

Scheme 5



With gold(I) as catalyst, the Alder-ene cycloisomerization does not occur because the cation $[AuL]^+$, being isolobal to H^+,[12] cannot coordinate to both the alkene and the alkyne.[7b] Moreover, the resulting gold(I) species are unlikely to

51 Ricard, L.; Gagosz, F. *Organometallics* **2007**, *26*, 4704-4707.

52 Freytag, M.; Ito, S.; Yoshifuji, M. *Chem. Asian J.* **2006**, *1*, 693-700.

53 (a) Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6049-6050. (b) Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996**, *15*, 901-903. (c) Chatani, N.; Inoue, H.; Morimoto, T.; Muto, T.; Murai, S. *J. Org. Chem.* **2001**, *66*, 4433-4436. (d) Miyanohana, Y.; Inoue, H.; Chatani, N. *J. Org. Chem.* **2004**, *69*, 8541-8543. (f) Miyanohana, Y.; Chatani, N. *Org. Lett.* **2006**, *8*, 2155-2158

54 (a) Fürstner, A.; Szillat H.; Stelzer, F. *J. Am. Chem. Soc.* **2000**, *122*, 6785-6786. (b) Fürstner, A.; Szillat, H. F.; Gabor, B.; Mynott, R. *J. Am. Chem. Soc.* **1998**, *120*, 8305-8314.

55 Oi, S.; Tsukamoto, I.; Miyano, S.; Inoue, Y. *Organometallics* **2001**, *20*, 3704-3709.

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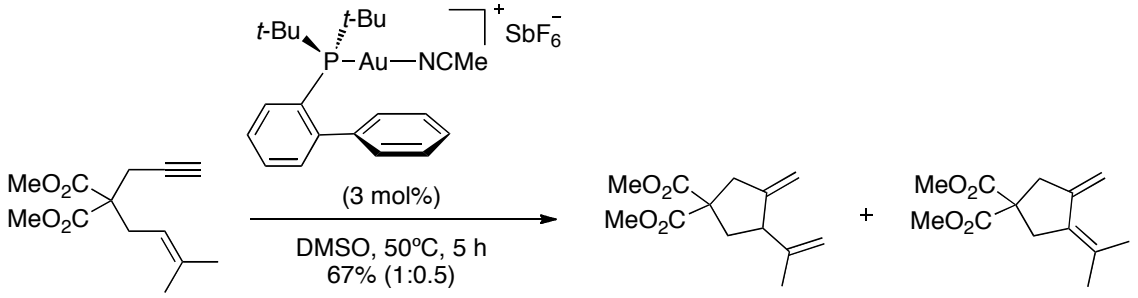
undergo oxidative addition processes.[35a,41,56] However there are known examples of products of formal Alder-ene type cycloisomerization with gold(I) as catalysts (Scheme 6).

Scheme 6



A deuterium labeling experiment (Scheme 7) reveals that the reaction of Scheme 6 does not proceed by Alder-ene type cycloisomerization, but by a formation of the exo cyclopropyl gold carbene **XXII**, followed by a ring opening to form the carbocation **XXIII**. Similar products have been observed in reactions with allylstannanes and allylsilanes with alkynes.[57]

56 Nieto-Oberhuber, C.; López, S.; Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Eur. J.* **2006**, *12*, 5916-5923.

57 (a) Fernández-Rivas, C.; Méndez, M.; Echavarren, A. M. *J. Am. Chem. Soc.* **2000**, *122*, 1221-1222. (b) Fernández-Rivas, C.; Méndez, M.; Nieto-Oberhuber, C.; Echavarren, A. M. *J. Org. Chem.* **2002**, *67*, 5197-5201.

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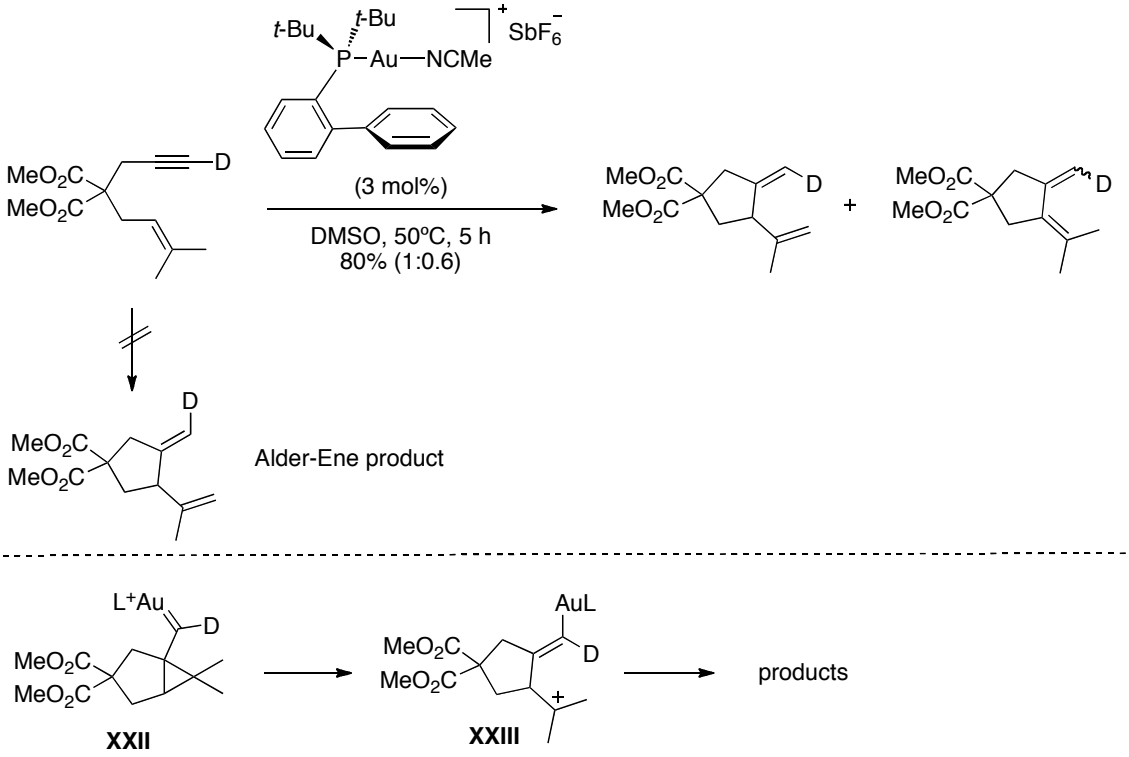
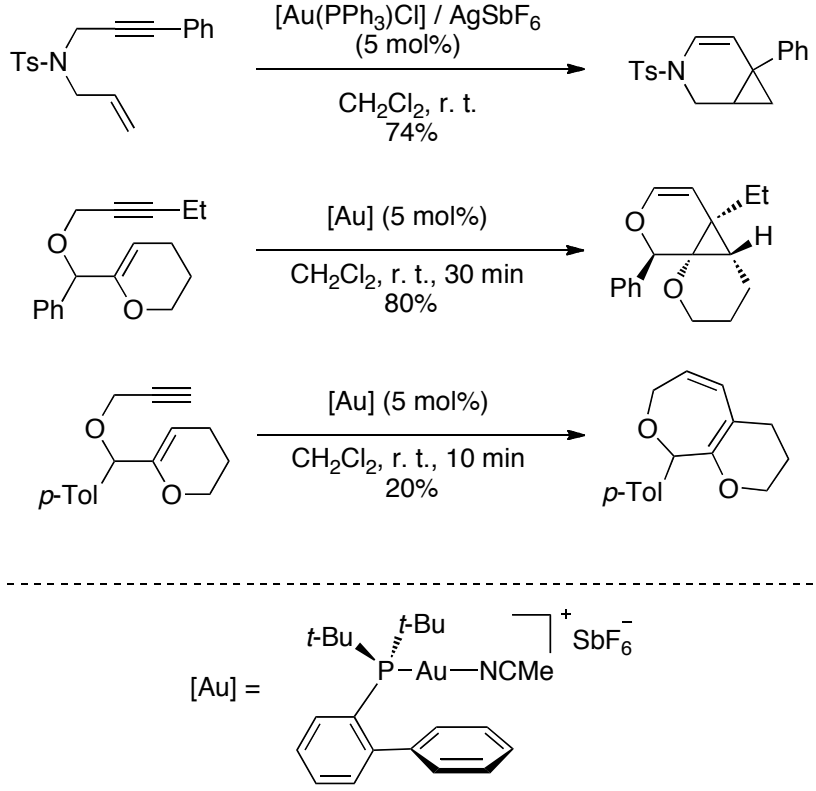
Scheme 7



Some examples of *endo*-cyclizations are depicted in Scheme 8.[1]

Scheme 8



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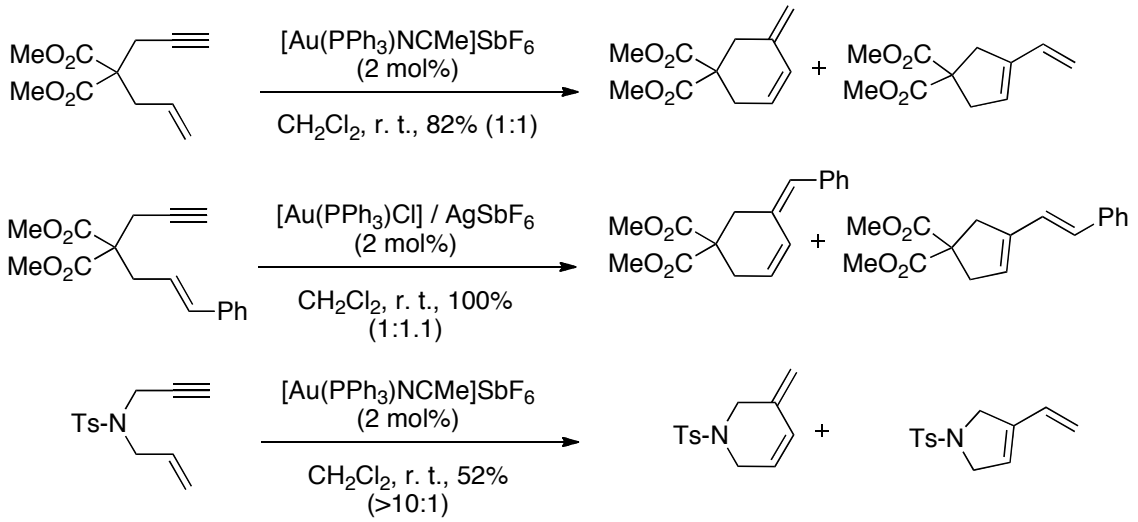
A new rearrangement using gold(I) as catalyst that affords dienes **XX** (see Scheme 3) has been described as an apparent endocyclic skeletal rearrangement.[35,41,56] Only a few additional examples of this type of transformation have been reported from simple 1,6-enynes, using $InCl_3$[53f] and Ru(II).[58,59] In Scheme 9 some examples of this new rearrangement are shown.

Scheme 9



Labeling experiments are consistent with an intramolecular process in which the terminal C atom of the alkene is finally attached to the C-2 of the alkyne (Scheme 10).[60] The mechanism for the "*endo*"-skeletal rearrangement is just a variation of the *exo*-single-cleavage rearrangement, in which cyclopropyl gold carbenes **XXIV** rearrange with ring expansion to give cations **XXV**, followed by metal loss from **XXV**.

58 Faller, J. W.; Fontaine, P. P. *J. Organomet. Chem.* **2006**, *691*, 1912-1918.

59 Kim, H.; Lee, C. *J. Am. Chem. Soc.* **2005**, *127*, 10180-10181

60 Cabello, N.; Jiménez-Núñez, E.; Buñuel, E.; Cárdenas, D.; Echavarren, A. M. *Eur. J. Org. Chem*. **2007**, 4217-4223.

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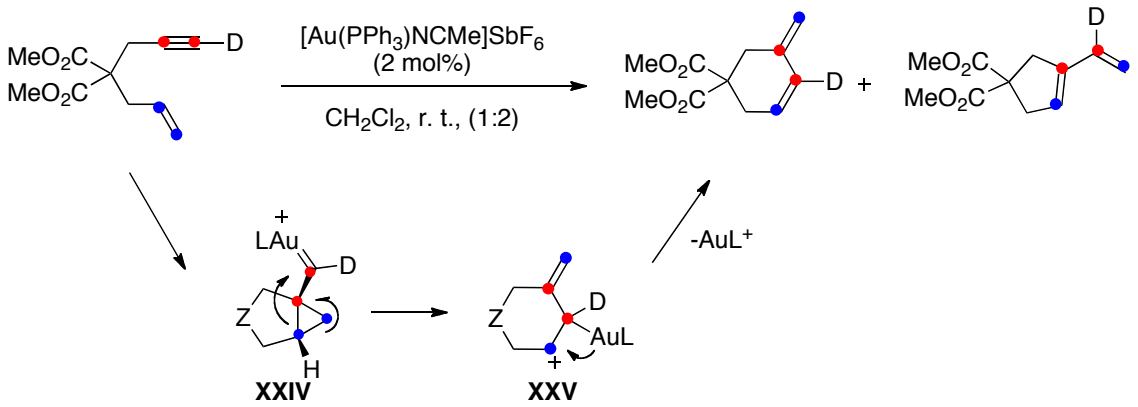
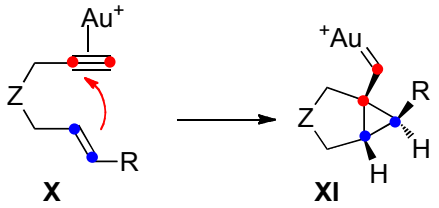
Scheme 10



3.2.2. On the nature of the cyclopropyl gold carbenes intermediates

There are a few publications that discuss about the nature of the intermediates in the cycloisomerization reaction of 1,6-enynes catalyzed by gold(I) as gold-stabilized carbocations[62,63] or gold carbenes.[7b,61,62,63,64]

Scheme 11



61 Jiménez-Núñez, E.; Claverie, C. K.; Bour, C.; Cárdenas, D. J.; Echavarren, A. M. *Angew. Chem. Int. Ed*. **2008**, *47*, 7892-7895.

62 Fürstner, A.; Morency, L. *Angew. Chem. Int. Ed*. **2008**, *47*, 5030-5033.

63 Seidel, G.; Mynott, R.; Fürstner, A. *Angew. Chem. Int. Ed*. **2009**, *48*, 2510-2513.

64 Selected reviews: (a) Fürstner, A.; Davies, P. W. *Angew. Chem. Int. Ed*. **2007**, *46*, 3410-3449. (b) Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Commun*. **2007**, 333-346. (c) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem. Int. Ed*. **2006**, *45*, 7896-7936. (d) Bongers, N.; Krause, N. Angew. Chem. **2008**, 120, 2208-2211; *Angew. Chem. Int. Ed*. **2008**, *47*, 2178-2181. (e) Michelet, V.; Toullec, P. Y.; Genèt, J.-P. *Angew. Chem*. **2008**, *120*, 4338-4386; *Angew. Chem. Int. Ed*. **2008**, *47*, 4268-4315. (f) Jiménez-Núñez, E.: Echavarren, A. M. *Chem. Rev*. **2008**, *108*, 3326-3350.

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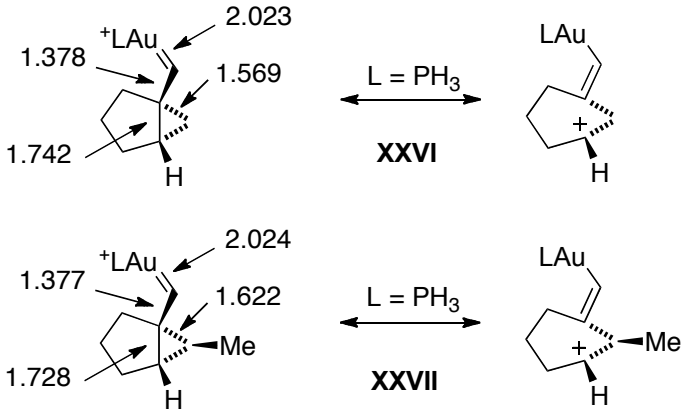
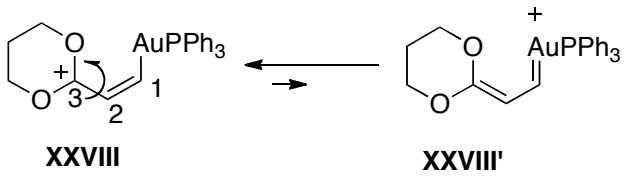
Initial theoretical studies, using DFT calculations, show that these intermediates have distorted structures with a short C-C bond connecting the carbene and the cyclopropane C atoms.[49,60] Structures **XXVI** and **XXVII** agree with a delocalized cyclopropylmethyl/ cyclobutyl/ homoallyl carbocation stabilized by gold.

Scheme 12: Calculated bond distances (Å) for **XXVI-XXVIII**. DFT calculations B3LYP/6-31G(d) (C,H,P), LANL2DZ (Au) level



Recently, it was reported that intermediates **XXVIII** show a highly cationic character. [62] The results are based on ^{1}H- and ^{13}C-NMR studies at low temperatures, which found rotational barriers around C^2-C^3 that are more consistent with an open carbocationic structure (Scheme 13).

Scheme 13



Analysis of allylic system **XXXIII**,[65] without strongly carbocation-stabilizing oxygen atoms, shows that the Au-PMe_3 fragment has a donating effect that is comparable to a methoxy group.[65] The stabilization provided by gold grows when

65 Benitez, D.; Shapiro, N. D.; Tkatchouk, E.; Wang, Y.; Goddard III, W. A.; Toste, D. Nature Chem. 2009, 1, 482-486

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the electrophilicity of the allyl cation increases. Regarding the charges (Figure 1, blue parameters), **XXXII** is unaffected by the gold comparing with the free **XXIX**, whereas for **XXXIII** and **XXXIV** the charge on C^3 decreases in comparison of the free **XXX** and **XXXI** respectively. In addition, it should be noted that **XXXII** reacts as a gold-stabilized carbocation, whereas **XXXIII** reacts more as gold-stabilized carbene.

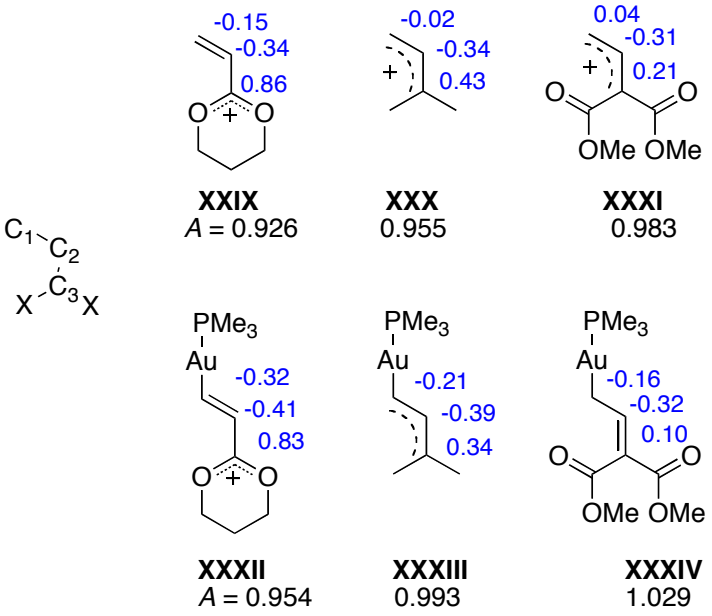

Figure 1

Moreover, an experiment with a non-vinylic gold(I) intermediate, reveals that in the absence of a delocalized neighboring vinyl group, the gold moiety stabilizes carbenes of varying electrophilicity by modulating the nature of the gold-carbon bond.

To evaluate the impact of the ligand calculations were carried out with computed structures $\mathbf{XXXIII_X}$ with the same vinylic gold intermediates but with different ligands on the gold moiety. The results are consistent with the fact that on increasing trans ligand σ-donation (trans influence), the Au-C^1 bond order decreases, and, in consequence, the bond length increases. In the absence of ligands, $\mathbf{XXXIII_0}$ the Au-C^1 bond is shorter, whereas $\mathbf{XXXIII_{Me}}$ (strong trans influence) has a higher Au-C^1 bond distance (2.053 Å). Furthermore, strongly π-acidic ligands decrease back-donation from the gold moiety, giving longer Au-C^1 bonds (for

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instance $\mathbf{XXXIII_{OMe}}$ with 2.057 Å). In contrast, the π-donating chloride ligand in $\mathbf{XXXIII_{Cl}}$ increases back-donation to C^1 resulting in a shorter Au-C^1 bond (1.969 Å). In conclusion, the strength of the back-donation to C^1 depends on ligand and the electrophilicity of the π-acceptor on C^1. Furthermore, π-acidic ligands are expected to increase carbocation-like character by decreasing gold-to-C^1 π-donation, whereas on the contrary, ligands that are σ-donating should increase carbene-like reactivity (for instance $\mathbf{XXXIII_{NHC}}$, which a strong σ-donating and weakly π-acceptor ligand) because of a decrease in C^1-to-gold σ-donation.

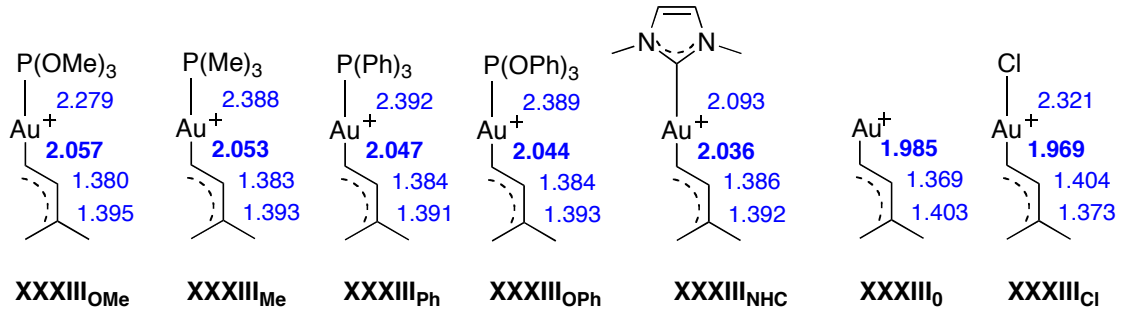

Figure 2

Moreover, these theoretical results were confirmed experimentally using the cyclopropanation reaction. Substrate **A** provides an intermediate similar to **XXXII** that should have carbocation-like reactivity, and then cyclopropanation reaction does not occur under these conditions. On the other hand, substrate **B** reacts through intermediates as $\mathbf{XXXIII_X}$ with carbene-like reactivity depend on the ligand at gold moiety. As expected, the best yield and stereoselectivity have been achieved with the 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene ligand (IPr), which yielded the more carbene-like intermediate.

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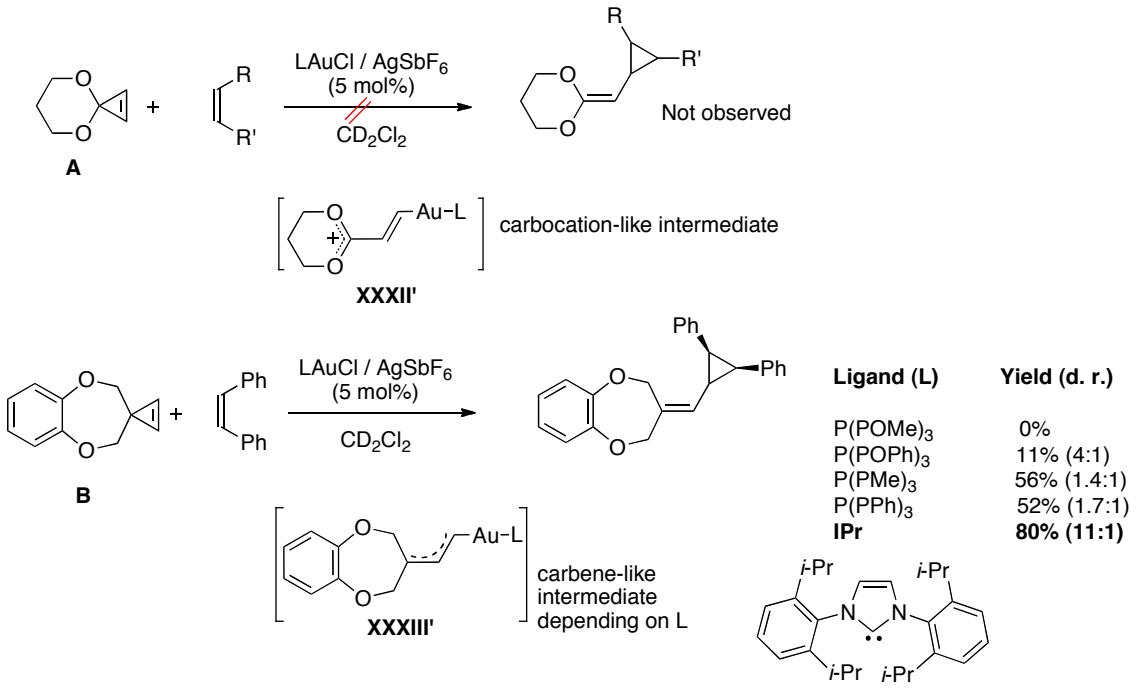
Scheme 14



In conclusion, the nature of the intermediates in their reactions is determined by the carbene substituents and the ancillary ligand.

It was demonstrated that *Z* dienes are obtained with substrates (*E*)-**5**-**7** bearing electron-rich substituents at the alkene group.[61,41] Similarly, enynes **6** and **7**, bearing more electron-donating groups at the alkene function, afforded mixtures of diastereoisomers *E* and *Z* in the single cleavage products. In the case of **7**, the *Z* isomer was observed exclusively, whereas with **6** (less electron-donating than **7**), a 4:17 (*Z*/*E*) mixture was achieved.

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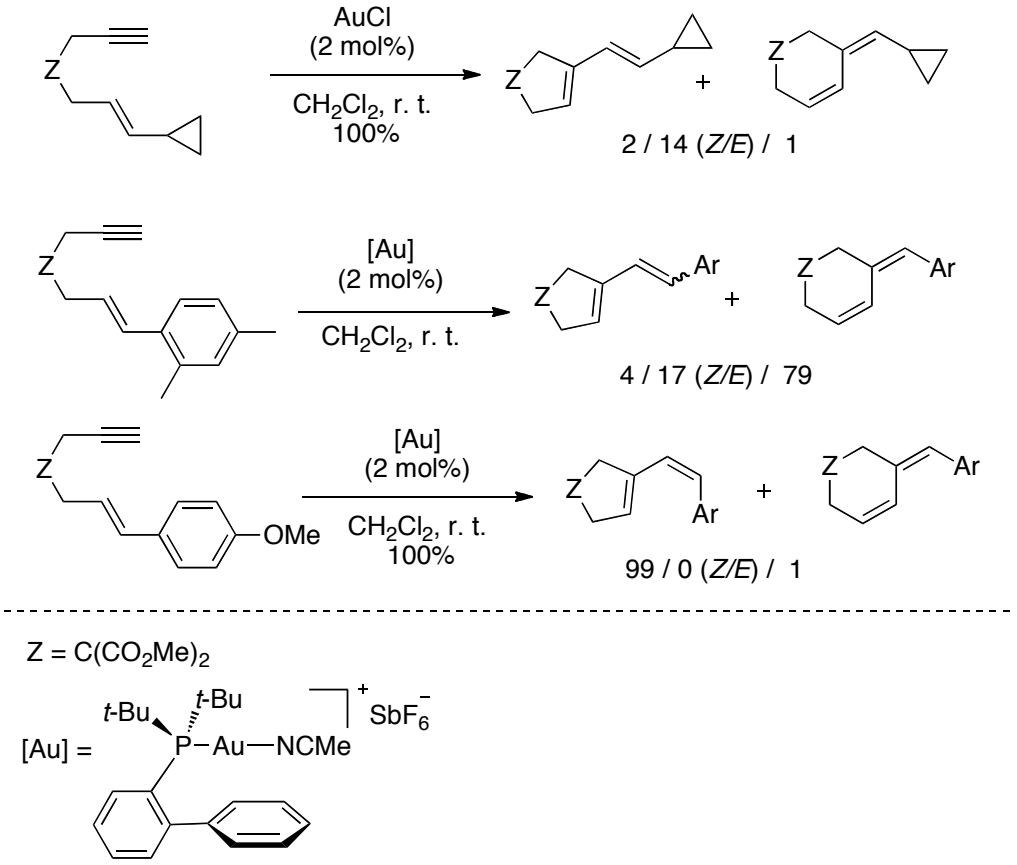
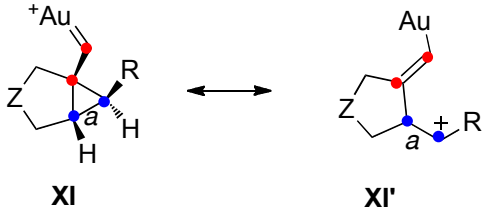
Scheme 15



These differences in reactivity are explained by the formation of intermediate **XI**, which can be expressed by two canonical forms, **XI** (carbene-like) or **XI'** (carbocation-like) (Scheme 16). In the case of enynes **5**-**7** the more relevant canonical structure is **XI'**, in which rotation around the *a* bond is possible leading to the observed non-stereospecific rearrangement due to the presence of a electron-donating group R (Scheme 16).

Scheme 16



XI **XI'**

In summary, when the cycloisomerization of 1,6-enynes is carried out with electrophilic gold catalysts it can be interpreted as a stereospecific addition of

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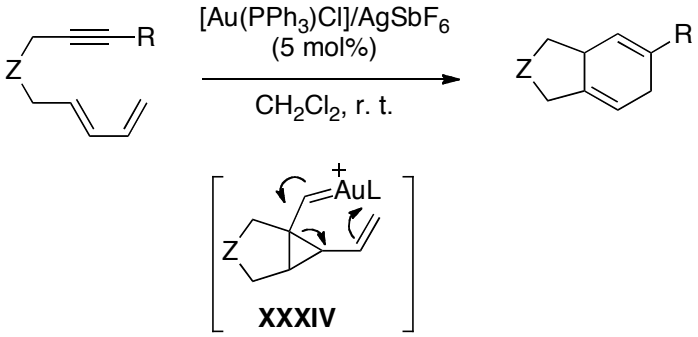
alkenes, to the η^2-alkyne-gold-complex (**XI**). However, for enynes containing alkenes bearing strongly electron-donating substituents, the reaction proceeds through open carbocations **XI'**.

3.3. *Other cyclizations reactions of 1,6-enynes catalyzed by gold(I)*

Gold(I) catalyzes the formal intramolecular Diels-Alder reactions of 1,3-dien-8-ynes.[66] The mechanism of this transformation was explained as formation of the vinylcyclopropyl gold carbene intermediate by a 5-*exo-dig* pathway, followed by a metalla-Cope rearrangement or by formation of a six-membered ring cation.

Scheme 17



Certain acetoxylated 1,6-enynes in presence of gold catalysts undergo the Ohloff-Rautenstrauch rearrangement to form bicyclic enol acetates.[67,68,69,70] This reaction has been used as a key step in the total synthesis of cubebene and cubebol (Scheme 18).[68] The mechanism of this transformation corresponds by the formation of cyclopropyl gold carbene intermediate **XXXV** by an *endo*-cyclization process.

66 Fürstner, A.; Stimson, C. C. *Angew. Chem. Int. Ed*. **2007**, *46*, 8845-8849.

67 Fürstner, A.; Hannen, P. *Chem. Eur. J*. **2006**, *12*, 3006-3019.

68 Fehr, C.; Galindo, J. *Angew. Chem. Int. Ed*. **2006**, *45*, 2901-2904.

69 Fürstner, A.; Hannen, P. *Chem. Commun*. **2004**, 2546-2547.

70 Marion, N.; de Frémont, P.; Lamière, G.; Stevens, E. D.; Fensterbank, L.; Malacria, M.; Nolan, S. P. *Chem. Commun*. **2006**, 2048-2050.

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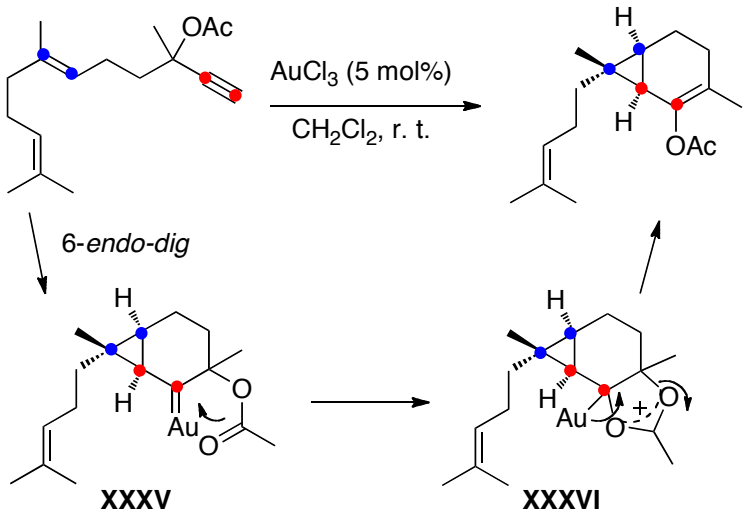
Subsequent attack of the adjacent acetyl group onto the electrophilic carbene affords the bicyclic enol acetate product via oxatricycle **XXXVI**.

Scheme 18



Cyclization of *ortho*-alkynylated biphenyl derivatives with gold as catalysts proceeds through an endo pathway to afford phenanthrenes.[71] In contrast, when haloalkynes react with gold, the corresponding phenanthrenes suffer a 1,2-shift of the halide. This migration of the halide has been described in a similar cyclization promoted by $W(CO)_5$.[72] On the contrary, when this reaction is performed with $InCl_3$ retention of the halide is observed. It was proposed that this electrocyclization process proceeds through vinylidene **XXXVII** as intermediates. DFT calculations have also supported the involvement of this type of intermediates.[73] Gold-vinylidene species have also been described as intermediates in some reactions of 1-alkynyl-2-alkenylbenzenes catalyzed by gold to form naphthalenes.[74]

71 (a) Fürstner, A.; Mamane, V. *J. Org. Chem.* **2002**, *67*, 6264-6267. (b) Fürstner, A.; Mamane, V. *Chem. Commun.* **2003**, 2112-2113. (c) Mamane, V.; Hannen, P.; Fürstner, A. *Chem. Eur. J.* **2004**, *10*, 4556-4575.

72 Miura, T.; Iwasawa, N. *J. Am. Chem. Soc.* **2002**, *124*, 518-519.

73 Soriano, E.; Marco-Contelles, J. *Organometallics* **2006**, *25*, 4542-4553.

74 Dankwardt, J. W. *Tetrahedron Lett.* **2001**, *42*, 5809-5812.

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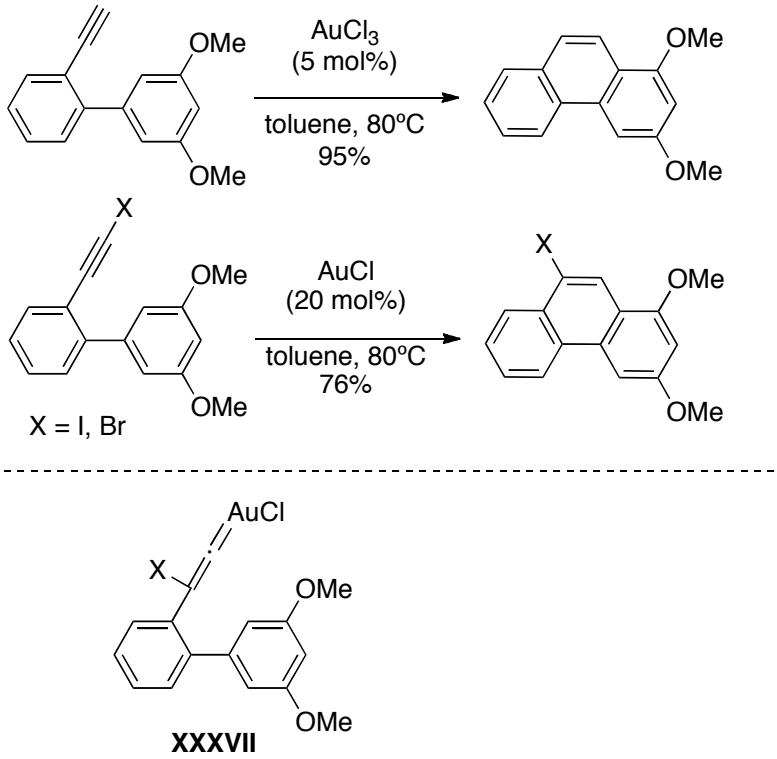
Scheme 19



XXXVII

The reaction of furans with alkynes affords phenols in good to excellent yields, using $AuCl_3$,[75] Au(I),[76] heterogeneous gold,[77] and Pt(II)[78] as catalysts.

75 (a) Hashmi, A. S. K.; Frost, T. M.; Bats, J. W. *J. Am. Chem. Soc.* **2000**, *122*, 11553-11554. (b) Hashmi, A. S. K.; Frost, T. M.; Bats, J. W. *Org. Lett.* **2001**, *3*, 3769-3771. (c) Hashmi, A. S. K.; Frost, T. M.; Bats, J. W. *Catal. Today* **2001**, *72*, 19-27. (d) Hashmi, A. S. K.; Ding, L.; Bats, J. W.; Fischer, P.; Frey, W. *Chem. Eur. J.* **2003**, *9*, 4339-4345. (e) Hashmi, A. S. K.; Weyrauch, J. P.; Rudolph, M.; Kurpejovic, E. *Angew. Chem. Int. Ed.* **2004**, *43*, 6545-6547. (f) Hashmi, A. S. K.; Rudolph, M.; Weyrauch, J. P.; Wölfle, M.; Frey, W.; Bats, J. W. *Angew. Chem. Int. Ed.* **2005**, *44*, 2798-2801. (g) Hashmi, A. S. K.; Weyrauch, J. P.; Kurpejovic, E.; Frost, T. M.; Miehlich, B.; Frey, W. Bats, J. W. *Chem. Eur. J.* **2006**, *12*, 5806-5814. (h) Hashmi, A. S. K.; Kurpejovic, E.; Frey, W.; Bats, J. W. *Tetrahedron* **2007**, *63*, 5879-5885.

76 Hashmi, A. S. K.; Haufe, P.; Schmid, C.; Rivas Nass, A.; Frey, W. *Chem. Eur. J.* **2006**, *12*, 5376-5382.

77 Carrettin, S.; Blanco, M. C.; Corma, A.; Hashmi, A. S. K. *Adv. Synth. Catal.* **2006**, *348*, 1283-1288.

78 (a) Martín-Matute, B.; Cárdenas, D. J.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2001**, *40*, 4754-4757. (b) Martín-Matute, B.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2003**, *125*, 5757-5766.

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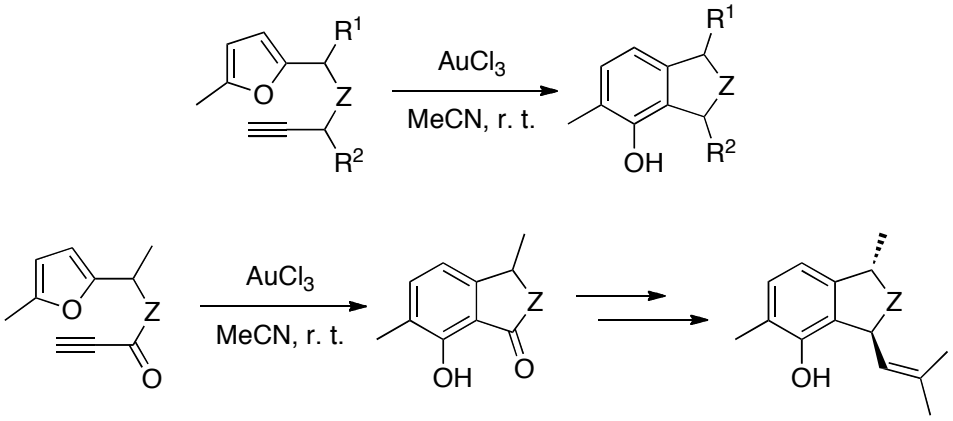
Moreover, the Michael addition of furans to ethynyl vinyl ketones catalyzed by gold[79,80,81] affords hydroxyindanones in a domino process.[80,82] This reaction has been used as a key step towards the synthesis of sesquiterpene jungianol (Scheme 20).[75d]

Scheme 20



The proposed mechanism was consistent with the experimental and theoretical studies.[75b,e,f,78] Selective activation of the alkyne by the gold affords the (η^2-alkyne)-gold complex **XXXVIII**, which suffers a nucleophilic attack of the furan to form carbene **XXXIX** by a 5-*exo*-dig pathway. Cleavage of a C-C and C-O bond of the tricyclic intermediate gives a new carbene intermediate **XL**, which cyclizes to form **XLI**. Elimination of the metal affords oxepine **XLII**, which is in equilibrium with the arene oxide **XLIII** and opens to form phenols **XLIV**, as a major product. Oxepines **XLII** and arene oxides **XLIII** (Scheme 18) have been observed in the reaction catalyzed by the Au(III) complex.[75f,83]

79 Dyker, G.; Muth, E.; Hashmi, A. S. K.; Ding, L. *Adv. Synth. Catal.* **2003**, *345*, 1247-1252.

80 Hashmi A. S. K.; Grundl, L. *Tetrahedron* **2005**, *61*, 6231-6236.

81 Aguilar, D.; Contel, M.; Navarro, R.; Urriolabeitia, E. P. *Organometallics* **2007**, *26*, 4604-4611.

82 Hashmi, A. S. K.; Hamzic, M.; Rudolph, M.; Ackermann, M.; Rominger, F. *Adv. Synth. Catal*. **2009**, *351*, 2469-2481.

83 Hashmi, A. S. K.; Kurpejovic, E.; Wölfle, M.; Frey, W.; Bats, J. W. *Adv. Synth. Catal.* **2007**, *349*, 1743-1750.

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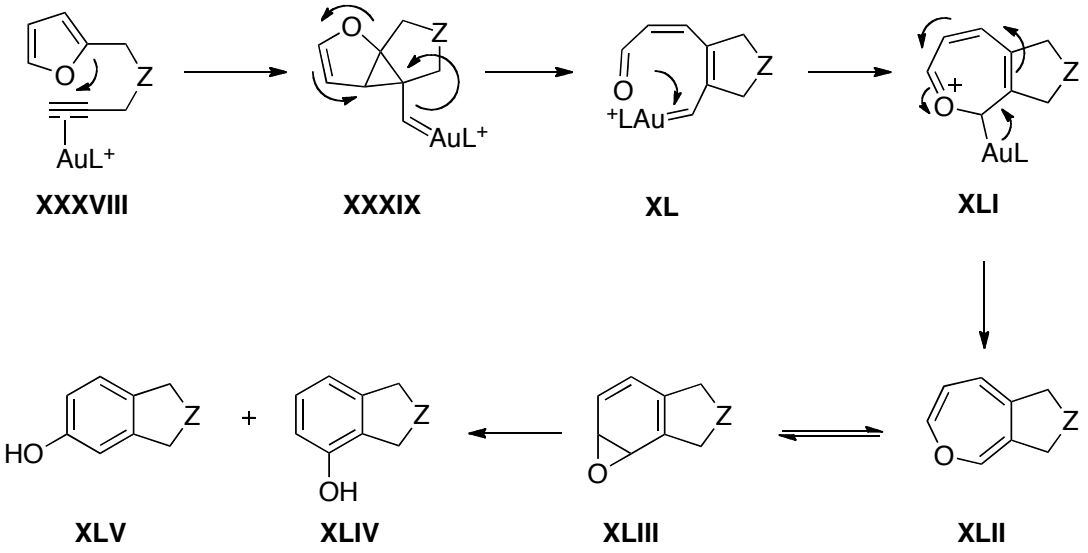
Scheme 21



The stereoselective gold-catalyzed [2+2+2] cycloaddition of functionalized ketoenynes was recently described.[84] In this reaction, the alkenyl-gold intermediate can be trapped in a Prins cyclization to form oxatricyclic derivatives (Scheme 22). This reaction was applied as a key step in the total synthesis of a natural product, the (+)-orientalol F.[84b] Moreover cyclopropylenynes lead to tricycles with an octahydrocyclobuta[*a*]pentalene skeleton by a Prins cyclization catalyzed by gold(I) (Scheme 22).[85,86,87]

84 (a) Jiménez-Núñez, E.; Claverie, C. K.; Nieto-Oberhuber, C.; Echavarren, A. M. *Angew. Chem. Int. Ed*. **2006**, *45*, 5452-5455. (b) Jiménez-Núñez, E.; Molawi, K.; Echavarren, A. M. *Chem. Commun*. **2009**, 7327-7329.

85 Rh(I)-catalyzed reaction of cyclopropylenynes: (a) Wender, P. A.; Takahashi, H.; Witulski, B. *J. Am. Chem. Soc*. **1995**, *117*, 4720-4721. (b) Yu, Z.-X.; Wender, P. A.; Houk, K. N. *J. Am. Chem. Soc*. **2004**, *126*, 9154-9155, and references therein.

86 Ru(II)-catalyzed reaction of cyclopropylenynes: (a) Trost, B. M.; Toste, F. D.; Shen, H. *J. Am. Chem. Soc*. **2000**, *122*, 2379-2380. (b) Trost, B. M.; Shen, H. C.; Horne, D. B.; Toste, F. D.; Steinmetz, B. G.; Korandin, C. *Chem. Eur. J*. **2005**, *11*, 2577-2590.

87 Ni(I)-catalyzed cyclization of cyclopropylenynes: Zuo, G.; Louie, J. *J. Am. Chem. Soc*. **2005**, *127*, 5798-5799.

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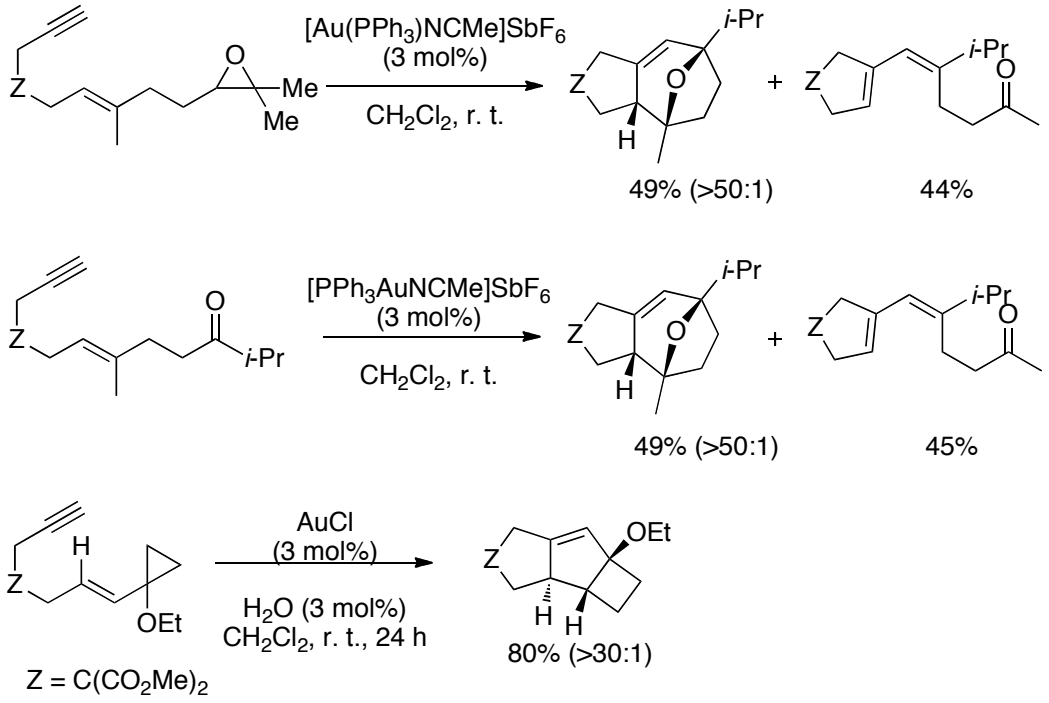
Scheme 22



The mechanism in Scheme 23 for the formation of oxatricyclic compounds starts by the formation of cyclopropyl gold carbene **XLVI** by a 5-*exo*-dig pathway, followed by nucleophilic attack of the carbonyl group to the cyclopropyl gold intermediate **XLVI** to form an oxonium cation intermediate **XLVII**. Subsequent Prins cyclization[88] affords the substituted 4-tetrahydropyranyl cation **XLVIII**.[89] Finally elimination of the metal gives the tricyclic product. Alternatively, an elimination with fragmentation of the seven-member ring via **XLIX** leads to rearranged carbonyl compounds. A similar mechanism was proposed, when the epoxide acts as nucleophiles.

88 (a) Overman, L. E.; Pennington, L. D. *J. Org. Chem.* **2003**, *68*, 7143-7157. (b) Jasti, R.; Anderson, C. D.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **2005**, *127*, 9939-9945.

89 Alder, R. W.; Harvey, J. N.; Oakley, M. T. *J. Am. Chem. Soc.* **2002**, *124*, 4960-4961.

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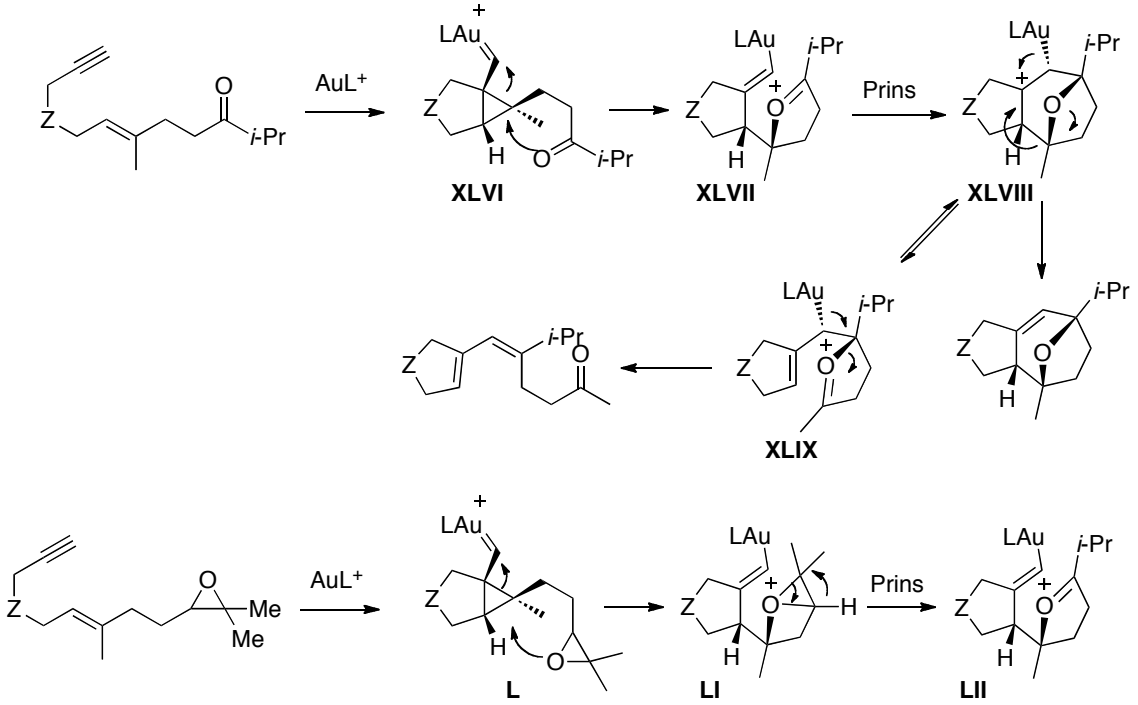
Scheme 23



Cycloisomerizations of 3-methoxy and 3-silyloxy 1,6-enynes catalyzed by gold(I) catalysts give product **A** as a result of a nucleophilic attack of the olefin to the η^2-alkenyl gold to form a cationic intermediate **LV** by 6-*exo*-dig pathway.[90] This intermediate undergoes a pinacol-type 1,2-shift to afford products such as **A**. On the other hand, formation of **B** corresponds to a nucleophilic attack of the oxygen atom that competes with the alkene, to form the oxonium cation **LIV** by a 5-*exo*-dig pathway. Intermediate **LIV** can undergo a [3,3]-sigmatropic rearrangement, which generates the 1-alcoxy-1,4-cycloheptadiene **9** in the presence of alcohols (Scheme 24).

90 (a) Baskar, B.; Bae, H. J.; An, S. E.; Cheong, J. Y.; Rhee, Y. H.; Duschek, A.; Kirsch, S. F. *Org. Lett*. **2008**, *10*, 2605-2607. (b) Bae, H. J.; Baskar, B.; An, S. E.; Cheong, J. Y.; Thangadurai, D. T.; Hwang, I.-C.; Rhee, Y. H. *Angew. Chem. Int. Ed*. **2008**, *47*, 2263-2266.

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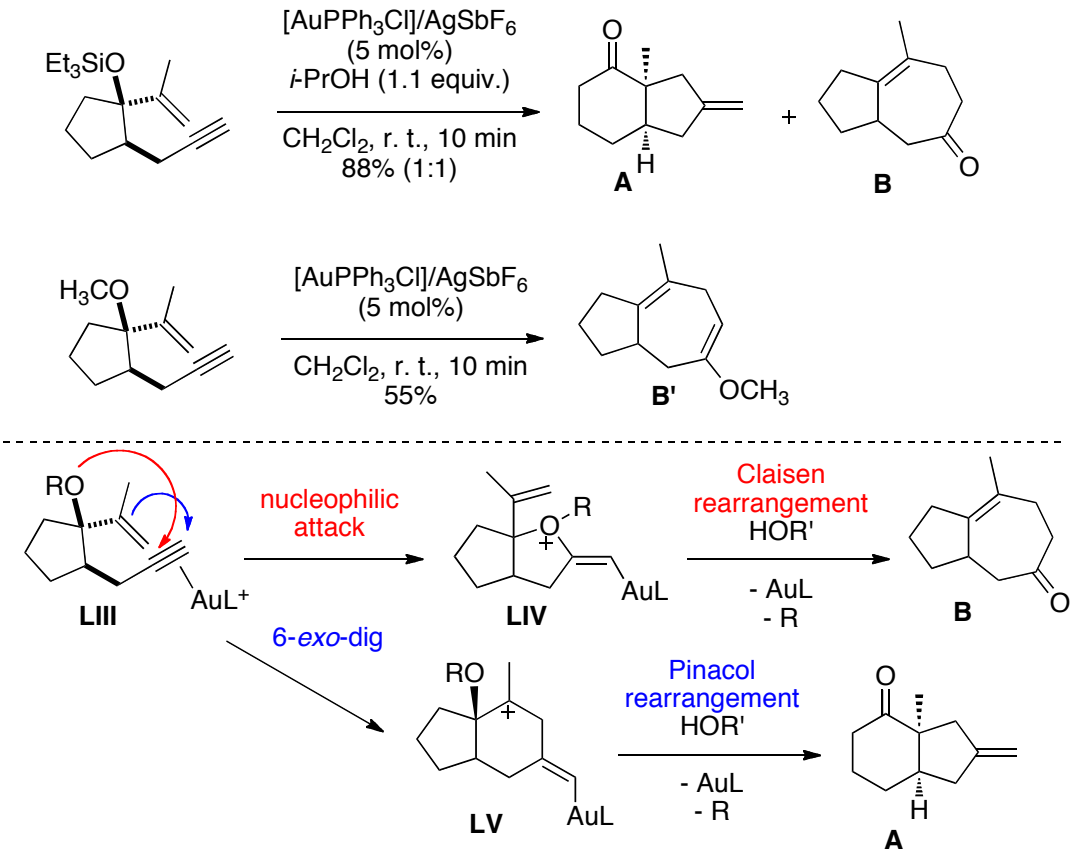
Scheme 24



Propargyl alcohols, ethers and silyl ethers can react with gold(I) catalysts by a 1,5-migration of OR groups.[91] This reaction gives rise to tricyclic compounds, with a similar carbon skeleton to the globulols. The mechanism that explain this transformation begins with the formation of the cyclopropyl gold intermediate **LVI**, which suffers a migration of the OR group to form **LVII**. This intermediate evolves to give allyl cation **LVIII**. An intramolecular cyclopropanation reaction of the alkene of the side chain affords the tricyclic products (Scheme 25).

91 Jiménez-Núñez, E.; Raducan, M.; Lauterbach, T.; Molawi, K.; Solorio, C. R.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2009**, *48*, 6152-6155

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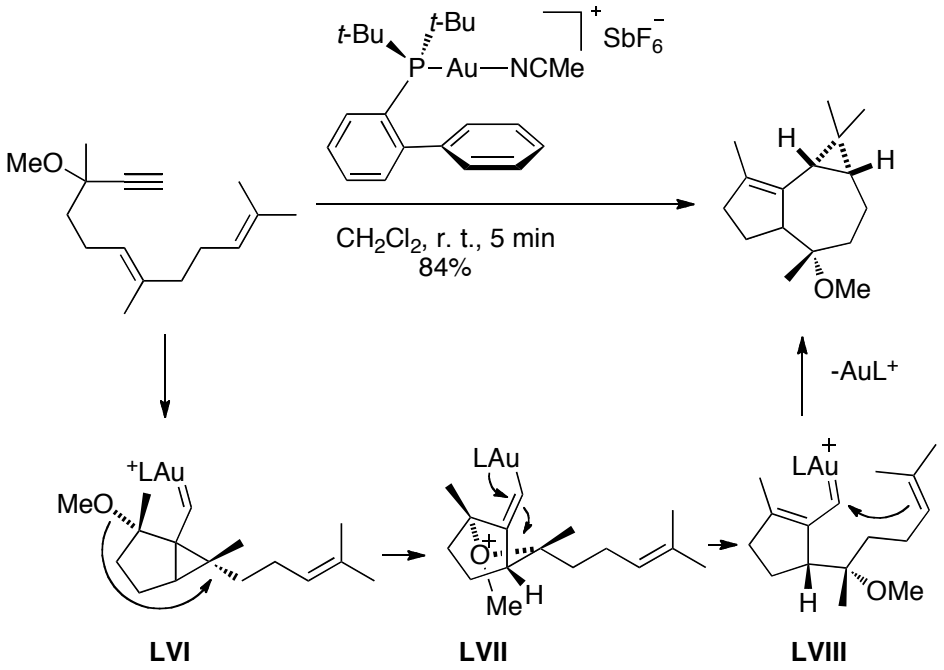
Scheme 25



Recently, stable vinylgold compounds from acceptor-substituted allenes and alkynes have been characterized. [92,93,94,95]

It should be noted that all this reactions are also performed with 1,n-enynes,[6,7] but this introduction is only focus on the 1,6-enynes.

92 Liu, L.-P.; Xu, B.; Mashuta, M. S.; Hammond, G. B. *J. Am. Chem. Soc*. **2008**, *130*, 17642.

93 Weber, D.; Tarselli, M. A.; Gagné, M. R. *Angew. Chem. Int. Ed*. **2009**, *48*, 5733.

94 (a) Hashmi, A. S. K.; Weyrauch, J. P.; Frey, W.; Bats, J. W. *Org. Lett*. **2004**, *6*, 4391. (b) Weyrauch, J. W.; Hashmi, A. S. K.; Schuster, A.; Hengst, T.; Schetter, S.; Littmann, A.; Rudolph, M.; Hamzic, M.; Visus, J.; Rominger, F.; Frey, W.; Bats, J. W. *Chem. Eur. J*. **2009**, *15*, 956-963. (c) Hashmi, A. S. K.; Schuster, A.; Rominger, F. *Angew. Chem. Int. Ed*. **2009**, *48*, 8247.

95 Hashmi, A. S. K. *Gold Bull*. **2009**, *42*, 275-279.

4. Au(I) Complexes.

Gold catalysis has flourished as one of the most active areas of research in organic synthesis.[64,96] Tuning the neutral donating ligand L in cationic complexes $[AuL]^+$ plays a very significant role in the activation of alkynes, allenes, and alkenes.[7d,64,97,98,99] Gold complexes with sterically hindered ligands have been shown to be particularly useful catalysts. Electron-donating ligands such as N-heterocyclic carbenes,[40a,98,100,101,102,103] open carbenes,[104] and bulky cyclic amino carbenes[105] moderate the high electrophilicity of gold(I) leading to increased selectivity with the most reactive substrates and stabilize the gold(I) oxidation state. On the other hand, less electron-donating phosphines give rise to very reactive gold catalysts. Simple AuCl or $AuCl_3$ are alkynophilic enough to catalyze many reactions, however for many gold-catalyzed transformations other gold(I) complexes have to be used.

---

96 Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351-3378.

97 Benitez, D.; Shapiro, N. D.; Tkatchouk, E.; Wang, Y.; Goddard III, W. A.; Toste, F. D. *Nature Chem.* **2009**, *1*, 482-486.

98 Amijs, C. H. M.; López-Carrillo, V.; Raducan, M.; Pérez-Galán, P.; Ferrer, C.; Echavarren, A. M. *J. Org. Chem*. **2008**, *73*, 7721-7730.

99 Mauleón, P.; Zeldin, R. M.; Gonzalez, A. Z.; Toste, F. D. *J. Am. Chem. Soc*. **2009**, *131*, 6348-6349.

100 Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612-3676.

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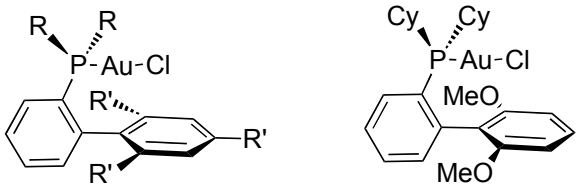
In this group different types of gold(I) complexes (Figure 3) have been developed using bulky phosphines, the Buchwald biphenyl-based phosphines,[106] which were introduced as ligands for palladium in cross coupling and carbon-heteroatom bond forming reactions.[107,108,109,110]



1a: R= Cy, R'= H
1b: R= *t*-Bu, R'= H
1c: R= Cy, R'= *i*-Pr
1d: R= *t*-Bu, R'= *i*-Pr

1e

Figure 3

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The cationic derivatives of these neutral complexes are very active catalysts for the alkoxycyclization, skeletal rearrangement[35a,41,56,111] and intramolecular cyclopropanation[112] of a variety of enynes. The cationic complexes were prepared in situ by chloride abstraction with Ag(I) salts. Instead of preparing the active catalysts in situ, stable and crystallines $[Au(PR_3)(L)]^+X^-$ complexes, **1f** and **1g** have been prepared as stable compounds with a weakly coordinating solvent molecule that could easily be replaced by the alkyne of the reacting enyne[113] (Figure 4). These cationic complexes allow performing catalytic transformations under silver-free conditions, which is important as Ag(I) can lead to unwanted side reactions.[114] Complexes **1f** and **1g** are amongst the most reactive in gold-catalyzed transformation. Closely related complexes **1i** and **1j** with a weakly coordinated bis(trifluoromethanesulfonyl)amide NTf_2 (Tf = CF_3SO_2) ligand have also been reported.[115,116]

111 (a) Nieto-Oberhuber, C.; Muñoz, M. P.; Buñuel, E.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Angew. Chem. Int. Ed*. **2004**, *43*, 2402-2406. (b) Nieto-Oberhuber, C.; López, S.; Muñoz, M. P.; Cárdenas, D. J.; Buñuel, E.; Nevado, C.; Echavarren, A. M. *Angew. Chem. Int. Ed*. **2005**, *117*, 6302-6304.

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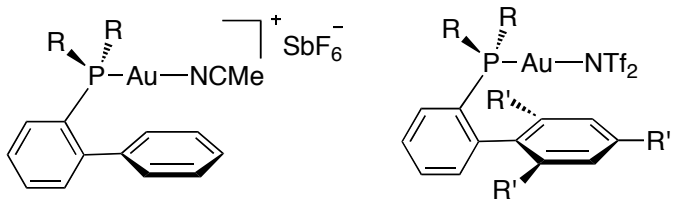


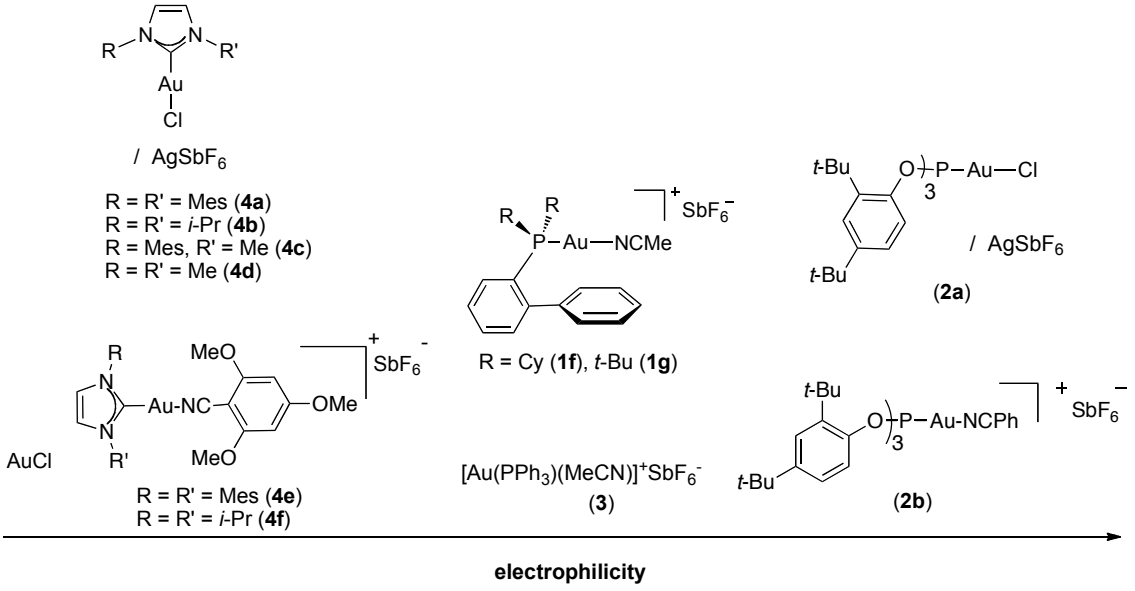
1f: R = *t*-Bu
1g: R = Cy

1i: R = *t*-Bu, R' = H
1j: R = Cy, R' = *i*-Pr

Figure 4

The geometry of the ligands is important but also the electrophilicity of the ligands has a large effect on the catalysis. In this context, the phosphite-gold complex **2a** has recently been developed,. This complex is the most electrophilic gold catalyst reported to date (Table 1).

Table 1: Electrophilicity of the gold complexes



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Objectives

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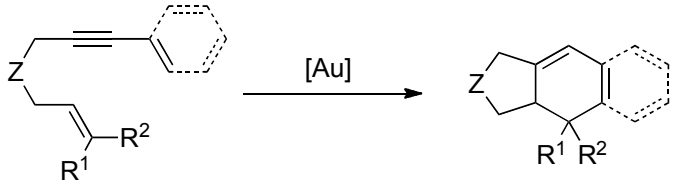
Objectives

The proposed mechanism for the cycloisomerization of 1,6-enynes involves the formation of cyclopropyl-gold carbenes as intermediates. One of the main objectives of this work was the study of this mechanism by trapping the key intermediates with simple alkenes [117] and other nucleophiles.

As a second objective we decided to study in detail the [4+2] cycloaddition reaction of allyl or aryl substituted 1,6-enynes,[118] which leads to hydrindanes or linearly fused tricyclic systems, respectively. Furthermore, we planned to apply this reaction towards the total synthesis of the pycnanthuquinones.

Scheme 26



Finally, we decided to develop new gold(I)-, silver(I)-, and copper(I)-catalysts and evaluate their catalytic properties in cycloisomerization reactions of enynes.

117 (a) López, S.; Herrero-Gómez, E.; Pérez-Galán, P.; Nieto-Oberhuber, C.; Echavarren, A. M. *Angew. Chem. Int. Ed*. **2006**, *45*, 6029.

118 Nieto-Oberhuber, C., Pérez-Galán, P., Herrero-Gómez, E., Lauterbach, T., Rodríguez, C., López, S., Bour, C., Rosellón, A., Cárdenas, D.J. and Echavarren, A.M.. J. *Am. Chem. Soc.* **2008**, *130*, 269-279.

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Results and Discussion

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Results 1.

Gold(I)-Catalyzed Intermolecular Cyclopropanation Reaction of 1,6-Enynes with Alkenes

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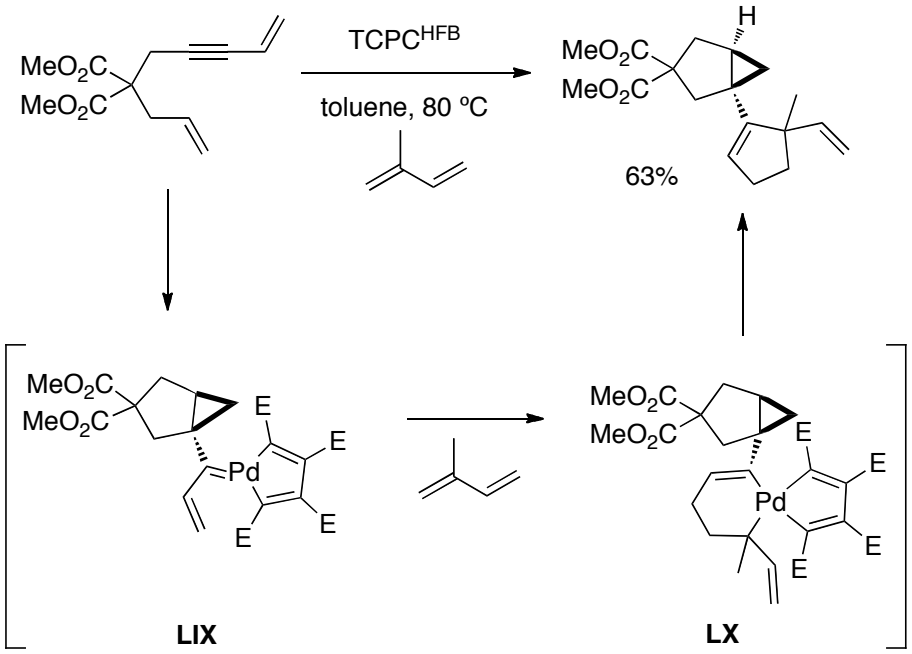
Introduction.

The first example of intermolecular trapping of the key intermediate in the cycloisomerization of 1,6-enynes was reported using a Pd(II) catalyst and isoprene as the trapping agent,[45] via [4+2] cycloaddition reaction giving **LX**, followed by reductive elimination (Scheme 27).

Scheme 27



The proposal for the involvement of cyclopropyl metal carbenes in these reactions was supported by the intramolecular cyclopropanation reaction, in which carbene-intermediates **LXI** were trapped using ruthenium as catalyst.[33a]

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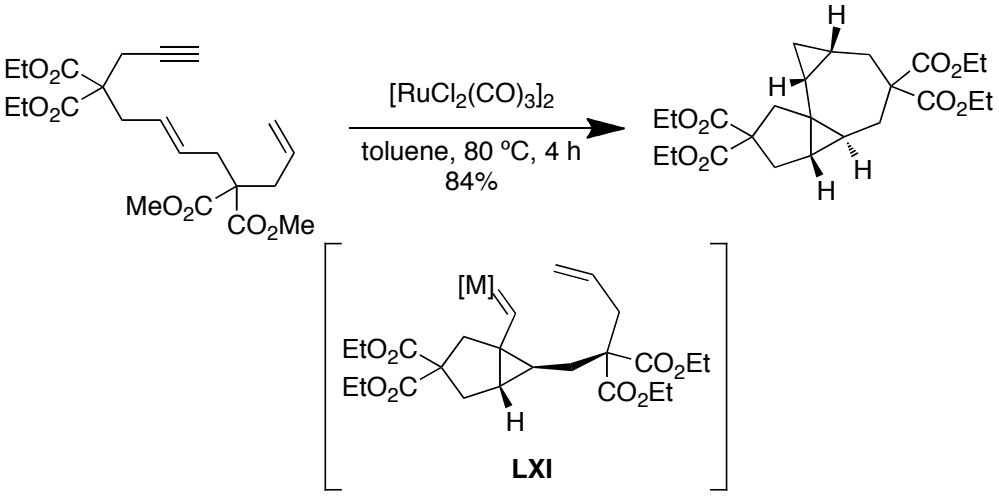
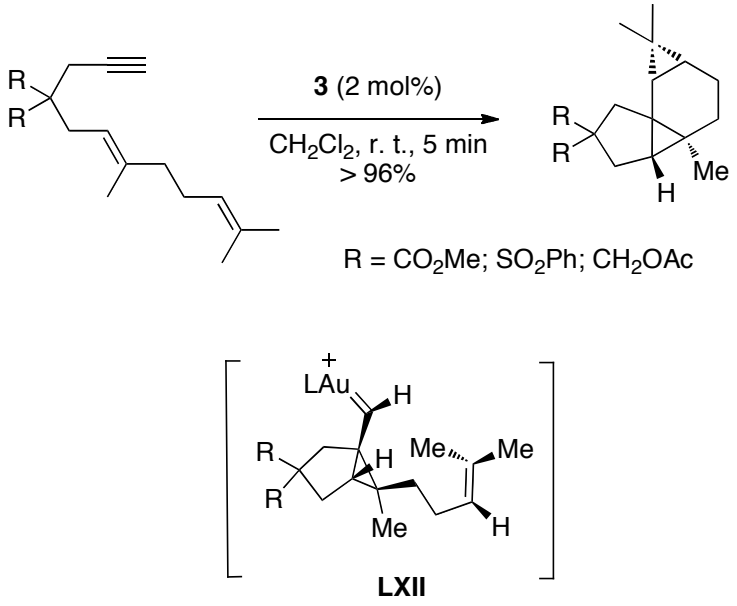
Scheme 28



Examples of intramolecular trapping of the intermediates using gold(I)-catalysts were also reported,[96a,112,119] in which tetracyclic compounds were formed under very mild conditions. The reaction proceeded through intermediate **LXII**, the *anti*- cyclopropyl gold carbene. The formation of this intermediate was confirmed by DFT calculations.2[a,,120]

Scheme 29



119 (a) Soriano, E.; Ballesteros, P.; Marco-Contelles, J. *Organometallics* **2005**, *24*, 3172-3181. (b) Soriano, E.; Ballesteros, P.; Marco-Contelles, J. *Organometallics* **2005**, *24*, 3182-3191.

120 Nevado, C.; Cardenas, D.; Echavarren, A. M. *Chem. Eur. J.* **2003**, *9*, 2627-2635.

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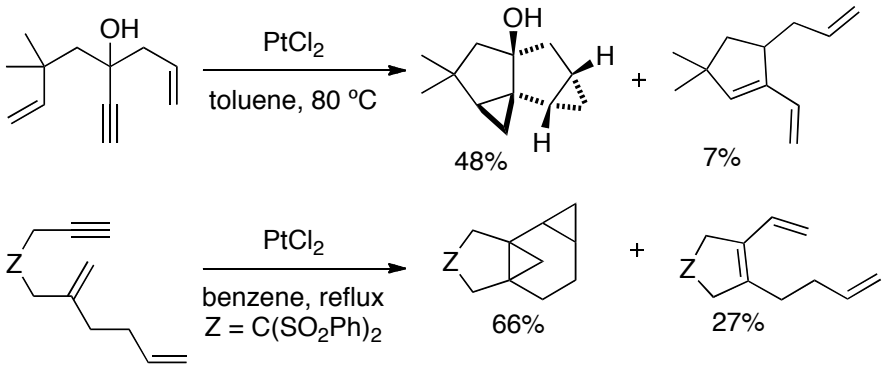
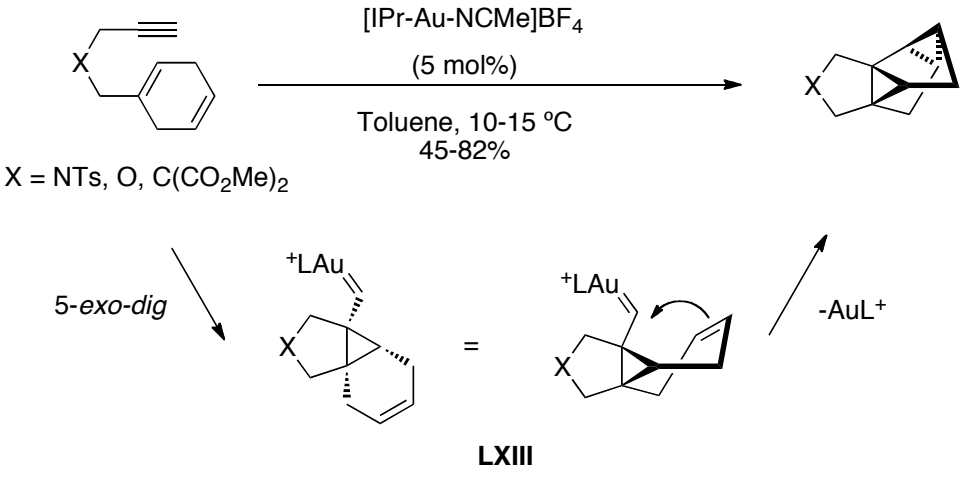
Similar results were reported using $PtCl_2$ as catalyst (Scheme 30).[112,33c,119,121]

Scheme 30



Additional examples of the intramolecular biscyclopropanation reaction using gold(I) as catalyst have been more recently reported (Scheme 31).[122]

Scheme 31



LXIII

121 (a) Peppers, B. P.; Diver, S. T. *J. Am. Chem. Soc.* **2004**, *126*, 9524-9525. (b) Diver, S. T.; Giessert, A. J. *Chem. Rev.* **2004**, *104*, 1317-1382.

122 Kim, S. M.; Park, J. H.; Choi, S. Y.; Chung, Y. K. *Angew. Chem. Int. Ed*. **2007**, *46*, 6172-6175.

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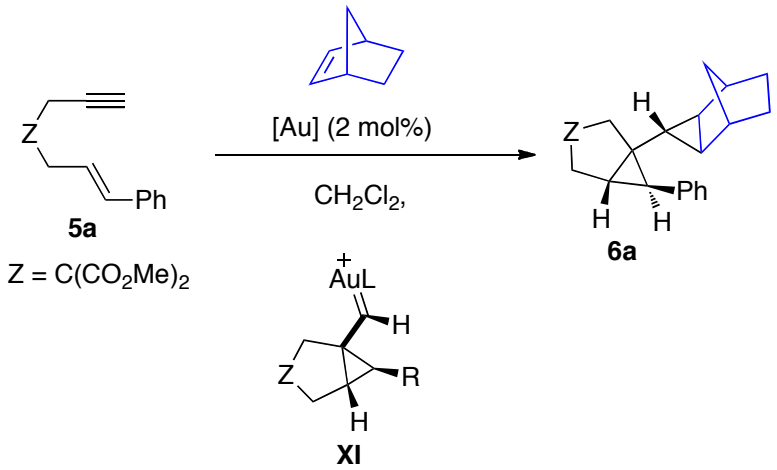
Results.

Previous work[123] showed that carbene **XI** could be intermolecularly trapped with norbornene in the reaction of 1,6-enyne **5a** to give **6a** intermolecularly as a single isomer (Scheme 32).[124,125,126]

Scheme 32: First results about intermolecular biscyclopropanation[126]



The best catalysts in this case were **4a** and AuCl.[126] More electrophilic catalysts favour the skeletal rearrangement of 1,6-enyne, which is an intramolecular process (Table 2).

123 In collaboration with E. Herrero-Gómez, Doctoral Thesis, 2009.

124 Intermolecular trapping of carbenes formed by the Rautenstrauch rearrangement of propargyl carboxylates have been reported: (a) Johansson, M. J.; Gorin, D. J.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 18002-18003. (b) Miki, K.; Ohe, K.; Uemura, S. *Tetrahedron Lett.* **2003**, *44*, 2019-2022. (c) Miki, K.; Ohe, K.; Uemura, S. *J. Org. Chem.* **2003**, *68*, 8505-8513; See also: (d) Miki, K.; Yokoi, T.; Nishino, F.; Kato, Y.; Washitake, Y.; Ohe, K.; Uemura, S. *J. Org. Chem.* **2004**, *69*, 1557-1564. (e) Miki, K.; Nishino, F.; Ohe, K.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 5260-5261.

125 Fructos, M. R.; Belderrain, T. R.; Frémont, P. N.; Scott, M.; Nolan, S. P.; Díaz-Requejo, M. M.; Pérez, P. J. *Angew. Chem.* **2005**, *117*, 5418-5422; *Angew. Chem. Int. Ed.* **2005**, *44*, 5284-5288.

126 López, S.; Herrero-Gómez, E.; Pérez-Galán, P.; Nieto-Oberhuber, C.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2006**, *45,* 6028-6032.

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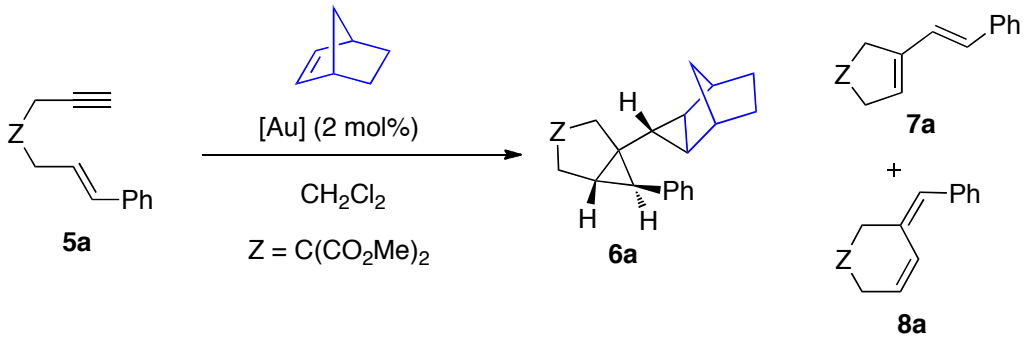
Table 2: Gold(I)-catalyzed reaction of enyne **5a** with norbornene [a]

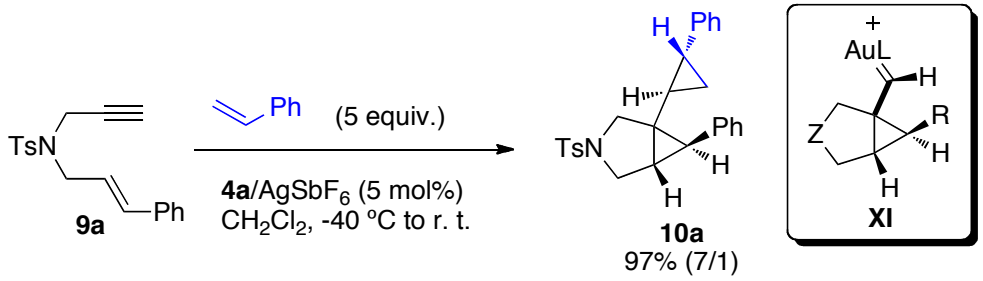


Entry	[Au]	Norbornene (equiv)	Yield of 6a (%)	7a + 8a yield (%)	7a+8a ratio[b]
1	**3**	-	-	99	1 : 1.4
2	**3**	5	66	29	1 : 1.2
3	**1g**	5	34	62	1 : 1.1
4[d]	**2a**	5	40	52	1 : 1.6
5[d]	**4a**	5	93	3	>10 : 1
6	AuCl	5	94	0[c]	-
7	**4e**	5	95	0[c]	-

[a] Reactions carried by show warming from -50 to 23 ºC over 15 h. [b] Yields and ratios determined by GC for reactions with 100% conversion. [c] Approximately 2% of **7a** + **8a**. [d] $AgSbF_6$ (2 mol%) was added to the mixture.

The reaction of 1,6-enyne **9a** with styrene led to adduct **10a**, as a result of the intermolecular trapping of intermediate **XI**.[126] The configuration of **10a**, was assigned by NMR experiments and by X-ray diffraction (Scheme 33, Figure 5).

Scheme 33



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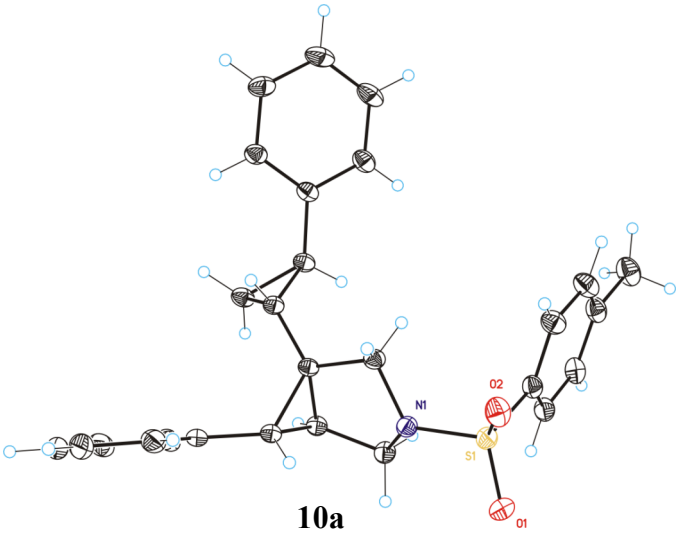
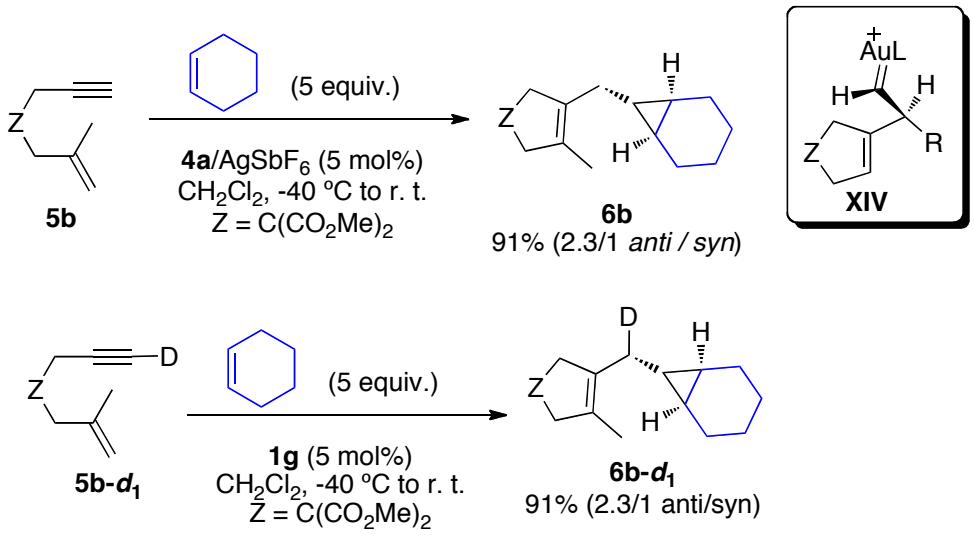


10a

Figure 5

On the other hand, reaction of 1,6-enyne **5b** with cyclohexene led exclusively to cyclopropane **6b**, as a result of the trapping of intermediate **XIV**, which corresponds to the intermediate proposed for the double-cleavage rearrangement (see Scheme 3). This was the first experimental support for the involvement of such intermediate in the cycloisomerization of 1,6-enynes. Reaction of **5b-*d*$_1$** led to **6b-*d*$_1$**, which assignment of the configuration was done and by NMR experiments was assigned (Scheme 34).

Scheme 34



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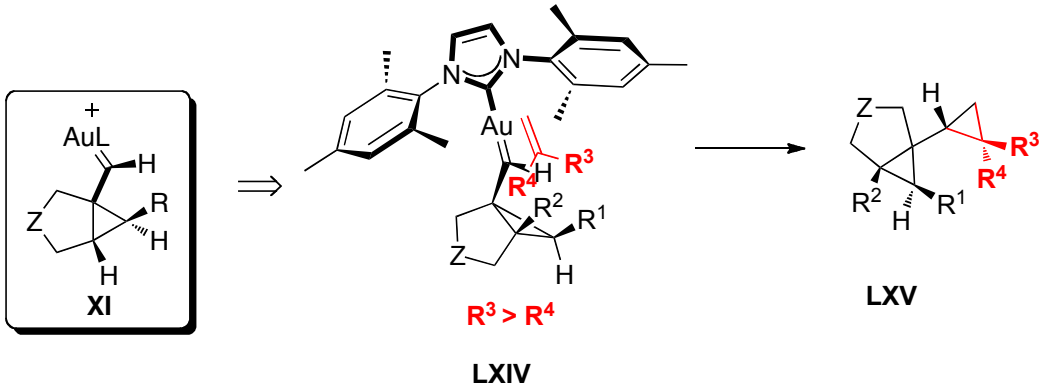
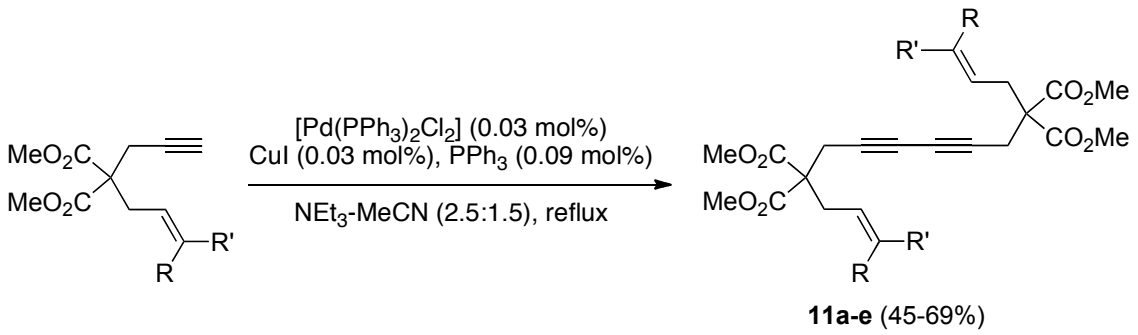
The regiochemistry and the stereoselectivity of the reaction were explained using the model for the approach of the alkene to cyclopropyl gold-carbene **XI** (see **XIV** in Scheme 35) in which the bulky ligand of the gold center directs the cyclopropanation towards the less sterically hindered alkene.

Scheme 35



To obtain additional evidence of the existence of gold-carbenes, enynes **11a-e** were synthesized.[126] These dimeric enynes were prepared by homocoupling of the corresponding 1,6-enyne (Scheme 36).

Scheme 36



Different gold complexes were assayed with **11b** (Table 3). The best catalyst for this reaction was the bulky-phosphine gold complex **1g** (Table 3, entry 2).

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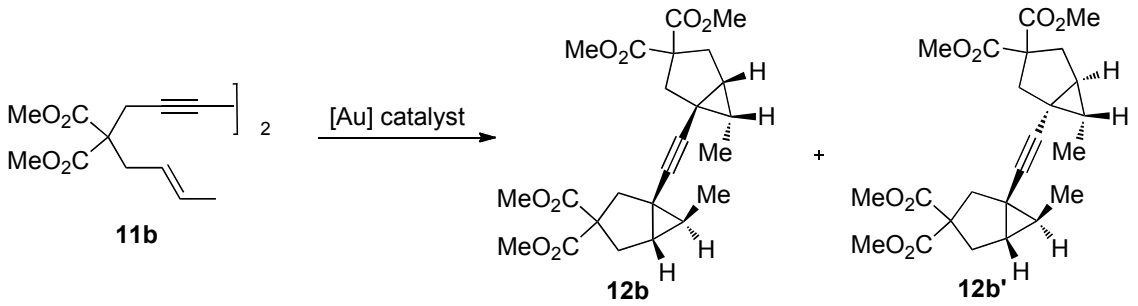
Table 3: Cyclization of the bisenyne **11b**[a]



Entry	Catalyst	Yield (%) Ratio of isomers
1	**3**	80
2	**1g**	90 (1.5:1)
3	**2a**	70 (1.5:1)
4	AuCl	[b]
5	$AuCl_3$	10
6	AuCl + $AgSbF_6$	complex mixture of products

[a] Reaction conditions: (0.15 mol% of $Au^{I, III}$, 2 mL of dry CH_2Cl_2; 24 h at r. t.. [b] Starting material was recovered.

The reaction with other bisenynes was carried out using **1g** and the phosphite-Au complex **2a**. The results are shown in Table 4. The ratio of isomers was determined by NMR but the particular configurations (meso or racemic) could not be assigned.

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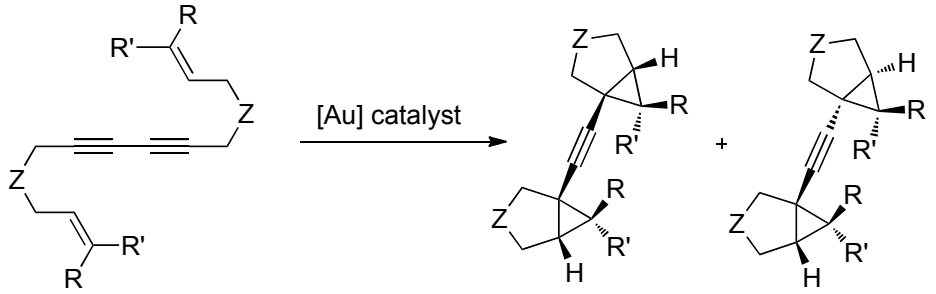
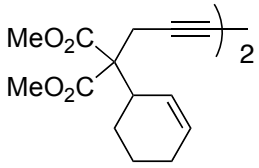
Table 4: Cyclization of different bisenynes **11a-e** [a]



Z : $C(CO_2Me)_2$

Entry	Bisenyne	Catalyst (% mol)	Time (h)	Yield (%)	Isomers relation
1	R = R' = H (**11a**)	**1g** (5)	5	91 (**12a**/**12a'**)	1:1
		2a (5)	9	[b]	-
2	R = H; R' = Me (**11b**)	**1g** (15)	24	90 (**12b**/**12b'**)	1.5:1
		2a (5)	7	70 (**12b**/**12b'**)	1.5:1
3	R = R' = Me (**11c**)	**1g** (10)	24	87 (**12c**/**12c'**)	3:1
		2a (5)	9	[b]	-
4	R = H; R' = Ph (**11d**)	**1g** (5)	144	[b]	-
		2a (5)	9	[b]	-
5	 **11e**	**1g** (5)		[b]	-
		2a (5)		[b]	-

[a] Reaction conditions: (0.15 mol% of Au^I, 2 mL of dry CH_2Cl_2; 24 h at r. t.. [b] Decomposition was observed.

The mechanism of these reactions can be explained by isomerization of the initially formed cyclopropyl gold carbene **LXVI** to form **LXVII** by a [1,3]-metallotropic shift, followed by intramolecular trapping of the gold carbene by the alkene (Scheme 37). This type of [1,3]-metallotropic shifts has been observed before

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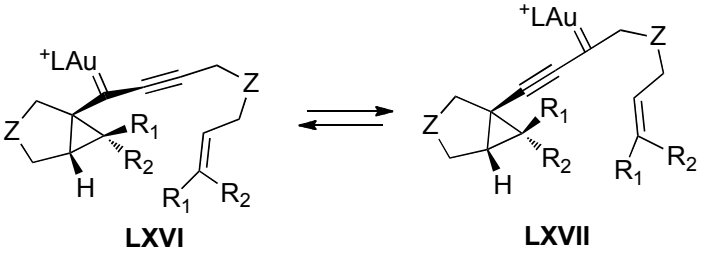
for Rh,[127] Cr, Mo, W,[128] and Ru[129,130] carbene complexes. Very recently two additional examples in gold chemistry have been reported.[131]

Scheme 37: 1,3-metallotropic shift



On the other hand, the reaction with differently substituted styrenes was studied using several Au(I) catalysts (Table 5). The configuration of the major isomer obtained using catalyst **4e** was assigned by analogy to that of **10a** (Scheme 33). Interestingly when catalyst **4f** was used, lower stereoselectivities were observed (Table 5, entry 6).

127 Padwa, A.; Austin, D. J.; Gareau, Y.; Kassir, J. M.; Xu, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 2637-2647

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129 (a) Kim, M.; Miller, R. L.; Lee, D. *J. Am. Chem. Soc.* **2005**, *127*, 12818-12819. (b) Kim, M.; Lee, D. *J. Am. Chem. Soc.* **2005**, *127*, 18024-18025. (c) van Otterlo, W. A. L.; Ngidi, E. L.; de Koning, C. B.; Fernandes, M. A. *Tetrahedron Lett.* **2004**, *45*, 659-662.

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131 (a) Ohe, K.; Fujita, M.; Matsumoto, H.; Tai, Y.; Miki, K. *J. Am. Chem. Soc*., **2006**, *128*, 9270-9271. (b) Cho, E. J.; Kim, M.; Lee, D. *Eur. J. Org. Chem*. **2006**, 3074-3078

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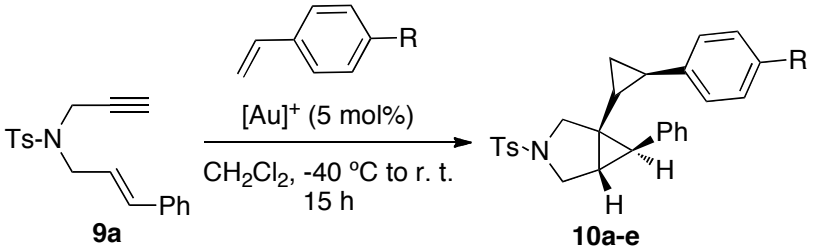
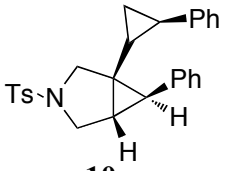
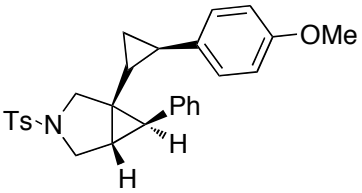
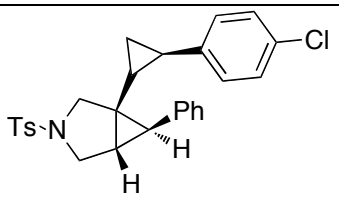
Table 5: intermolecular cyclopropanation reaction with styrenes[a]



Entry	R	[Au]	Yield (%)	Product
1	H	**4e**	97	 **10a** **87**/12/2/0
2	H	**1g**	95	**10a** **87**/12/4/0
3	H	**4f**	83	**10a** **61**/36/3/0
4	OMe	**4e**	80	 **10b** **75**/23/2/0
5	OMe	**1g**	70	**10b** **73**/23/4/0
6	OMe	**4f**	84	**10b** **22**/6015/3
7	Cl	**4e**	85	 **10c** **92**/8/0/0

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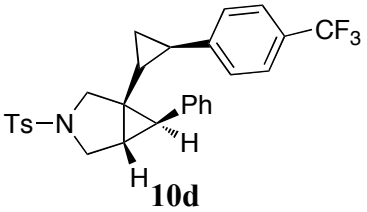
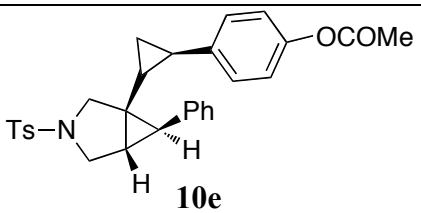
8	Cl	**1g**	90	**10c** **89**/10/1/0
9	CF_3	**4e**	98	 **10d** **93**/7/0/0
10	CF_3	**1g**	82	**10d** **92**/7/1/0
11	OCOMe	**4e**	86	 **10e** **89**/11/0/0
12	OCOMe	**1g**	93	**10e** **84**/14/2/0

[a] Reaction at -40 ºC and slowly warmed to r. t. (15 h), using 5 equiv of the styrene and 5 mol% of catalyst.

To obtain additional mechanistic information, a competitive study was carried out with a variety of substituted styrenes and enyne **9a** in the presence of gold(I)-catalysts **1g** and **4e** (Table 6). The relative reactivities were determined by ^{1}H-NMR on the isolated reaction mixtures.

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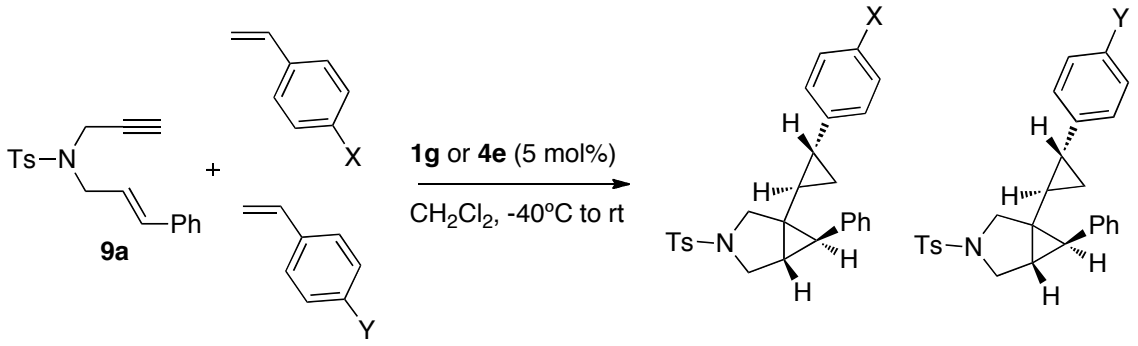
Table 6: Competitive intermolecular cyclopropanation reaction between different styrenes[a]



Entry	Styrenes X/Y	[Au]	Product	Ratio
1	OMe /H	**4e**	**10b/10a**	2 / 1
2	Cl / H	**4e**	**10c/10a**	1 / 1.4
3	CF_3 / H	**4e**	**10d/10a**	1 / 6.7
4	OMe / Cl	**4e**	**10b/10c**	4 /1
5	OMe / CF_3	**4e**	**10b/10d**	10 /1
6	Cl / CF_3	**4e**	**10c/10d**	3.3 / 1
7	OCOMe/ CF_3	**4e**	**10e/10d**	5/1
8	OCOMe/ OMe	**4e**	**10e/10b**	1/ 8.3
9	OMe /H	**1g**	**10b/10a**	1.2 / 1
10	Cl / H	**1g**	**10c/10a**	0.13 / 1
11	CF_3 / H	**1g**	**10d/10a**	1 / 10
12	OMe / Cl	**1g**	**10b/10c**	1 / 0.2
13	OMe / CF_3	**1g**	**10b/10d**	30 / 1
14	Cl / CF_3	**1g**	**10c/10d**	3.3 / 1
15	OCOMe/ CF_3	**1g**	**10e/10d**	7/1
16	OCOMe/ OMe	**1g**	**10e/10b**	1/ 9

[a] Reaction at -40 ºC and slowly and warmed to r. t. (15 h), using 5 equiv of the substituted styrene and 5 mol% of catalyst.

These experiments show that electron-rich styrenes (4-vinyl anisole) are cyclopropanated more efficiently than styrenes bearing electron-withdrawing groups (4-CF_3-styrene).

The ratios obtained in this competitive study were correlated with Hammett's constants[132] of the substituent on the styrene (Table 7).

Table 7: Hammett constants[132]

R	σ
- OMe	-0.27
- H	0
- Cl	0.23
- OCOMe	0.31
- CF_3	0.54

The Hammett correlations using 4-vinyl anisole adduct **10b** as the reference for the reactions using catalysts **4e** and **1g** are shown in Figure 6.

132 Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev*. **1991**, *91*, 165-195.

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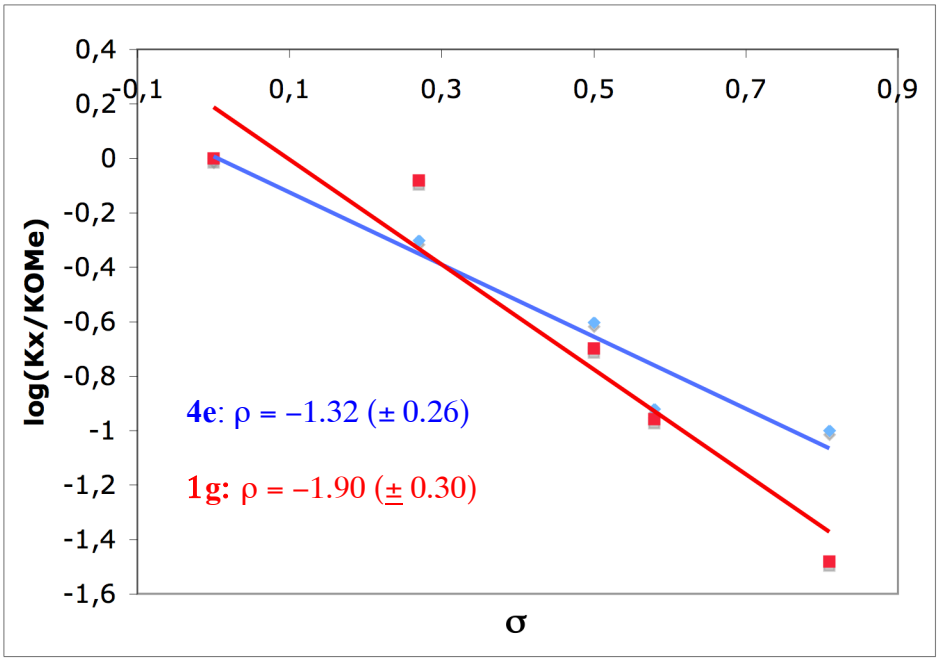
Figure 6: Hammett-Brown plots of relative rates with catalysts **1g** and **4e**

$\log[K_x/K_{OMe}]$ vs σ



The value of the slope showed that this cyclopropanation reaction is an electrophilic process. These results are consistent with than obtained in the cyclopropanation reaction catalyzed with others transition metals.[141,133,134,135,136,137,138] Selected examples of that are shown in Table 8. The Simmons-Smith cyclopropanation shows a more negative value (-2.4)[139] than with the Furukawa modification[139] (-1.6) or with the copper-catalyzed cyclopropanation with ethyl diazoacetate (-0.9 to -1.23).[138] Accordingly, the carbenoid generated in the Simmons-Smith reaction is more electrophilic than the intermediate involved in the gold(I)-catalyzed cyclopropanation reactions.

133 Doyle, M. P. *Acc. Chem. Res.*, **1986**, 19, 348-356

134 Bellucci, G.; Bianchini, R.; Chiappe, C.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.*, **1991**, *113*, 8012-8016.

135 Yueh, W.; and Bauld, N. L. *J. Am. Chem. Soc.*, **1995**, *117*, 5671-5676.

136 Doyle, M. P.; Griffin, J. H.; Bagheri, V.; and Dorow, R. L. *Organometallics*, **1984**, *3*, 53-61.

137 Charette, A.; Molinaro, C.; Brochu, C. *J. Am. Chem. Soc.* **2001**, 12168.

138 Díaz-Requejo, M. M.; Nicasio, M. C.; Pérez, P. J. *Organometallics* **1998**, *17*, 3051-3057.

139 Davies, H. M. L.; Antoulinakis, E. G. *Org. Reac.* **2001**, *57*, Chapter I.

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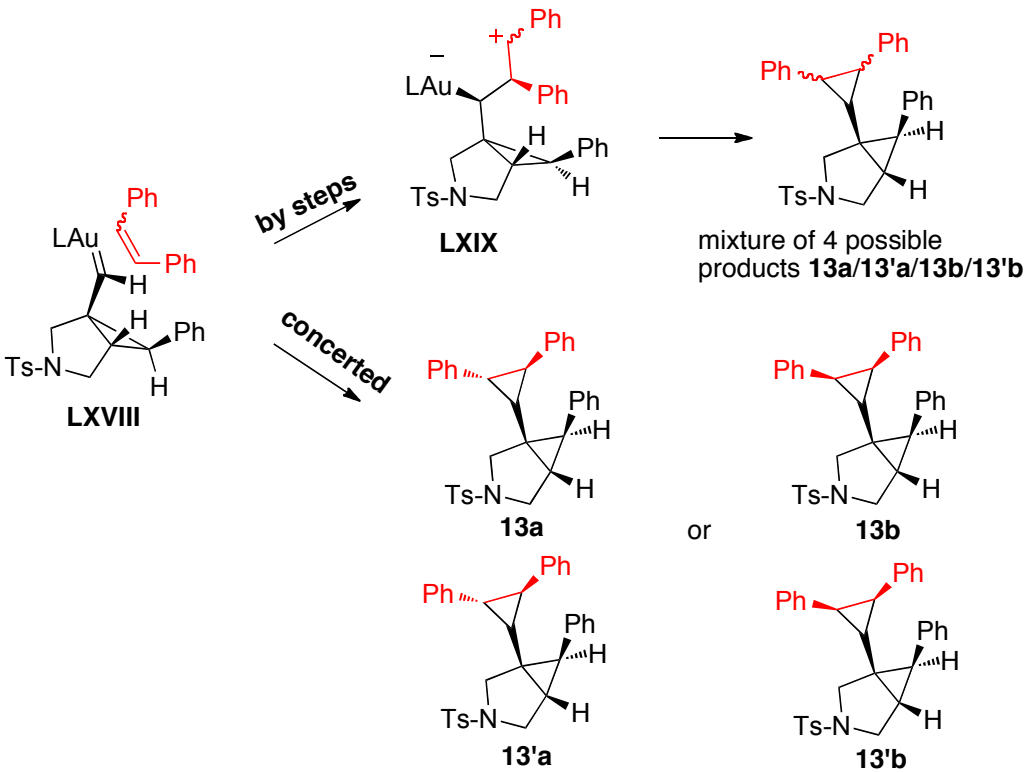
Table 8: Slope values (ρ) from Hammett-Brown plots of selected cyclopropanation reactions

Reaction	Reactives	ρ
Simmons-Smith	CH_2I_2 / Zn(Cu)	-2.4
Furukawa	$ZnEt_2$ / CH_2I_2	-1.6
	TpCuL and N_2CHCO_2Et	-0.9 to -1.23

Therefore, the intermediate formed with catalyst **1g** is more electrophilic than **4e**, with a more carbene-like character.

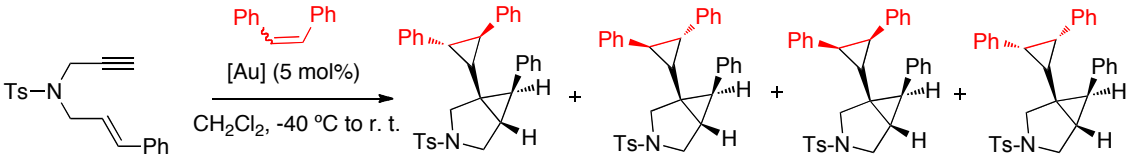
Reactions with *cis*- and *trans*-stilbene were carried out to determine if the cyclopropanation reaction is a concerted process. If the reaction occurs stepwise, cationic intermediate **LXIX** should to be formed and a mixture of products would be obtained using *trans*- or *cis*-stilbene. On the other hand, if the reaction occurs by a concerted pathway a maximum of two diastereoisomers have to be observed for each substrate (Scheme 38).

Scheme 38: Mechanism by steps or concerted



The reaction of 1,6-enyne **9a** with *trans*-stilbene and gold(I)-catalyst **4e**, led to a single product of cyclopropanation almost quantitatively (98% yield) (Table 9, entry 1). However in the case of the *cis*-stilbene no reaction was observed with all the catalysts (Table 9, entries 2-7).[140]

Table 9: Gold(I)-catalyzed intermolecular cyclopropanation-mechanistic study[a]



9a **13a** **13'a** **13b** **13'b**

Entry	Alkene (equiv)	[Au]	Yield (%) Ratio (13a/13'a/13b/13'b)
1	*Trans*-stilbene (5)	**4e**	98 (1/0/0/0)
2	*Cis*-stilbene (5)	**4e**	-
3	*Cis*-stilbene (5)	**1f**	-
4	*Cis*-stilbene (5)	**2b**	-
5	*Cis*-stilbene (5)	AuCl	-
6[b]	*Cis*-stilbene (5)	**4a**	-
7	*Cis*-stilbene (5)	**1g**	-

[a] Reaction done under inert atmosphere, at -40 ºC and slowly was warmed to r. t. (15 h). [b] 5 Mol% of $AgSbF_6$ was added.

The configuration of **13a** was confirmed by X-ray diffraction (Figure 7), which shows the expected trans-relative configuration of the phenyl substituents.

140 Unpublished results

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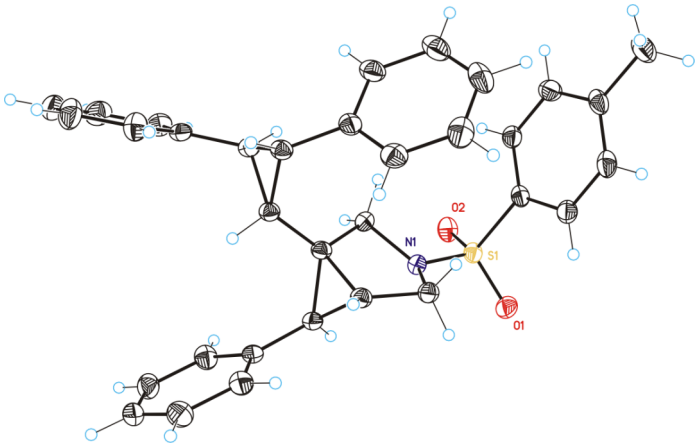
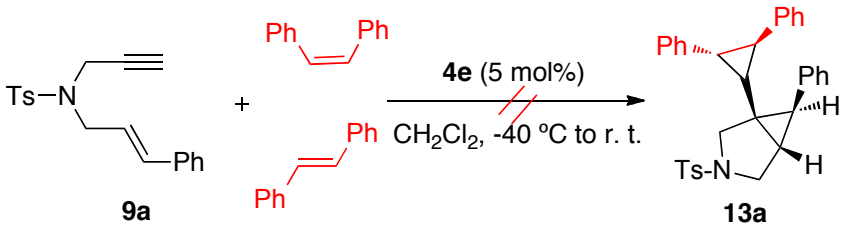


Figure 7: X-ray of **13a**

Then the results revealed that *cis*-stilbene inhibits the reactivity of the gold(I)-catalysts, probably by a tight coordination with gold(I). To confirm this aspect, different reactions were carried out. Thus, whereas the reaction of **9a** with *trans*-stilbene gave **13a** in nearly quantitative yield after 15 h (Table 9, entry 1), when the same reaction was carried out with a 1:1 mixture of *trans*- and *cis*-stilbenes, no reaction was observed after 24 h.

Scheme 39



The skeletal rearrangement of **5b**[96a] was reported to proceed in 1 min with 100% conversion, whereas in the presence of *cis*-stilbene 3 h were necessary to complete the reaction. Similarly, enyne **5c**[96a] was reported to react in 5 min (100% conversion), but in presence of *cis*-stilbene after 3 h, the conversion was 80%. Finally in the case of the cyclopropanation of propargyl pivaloate **14** with *cis*-stilbene,[141] which was reported to proceed in 81% yield, no reaction was observed after 48 h in the presence of *cis*-stilbene.

141 Johansson, M. J.; Gorin, D. J.; Staben, S. T.; Toste. E. D. *J. Am. Chem. Soc.* **2005**, *127*, 18002-18003.

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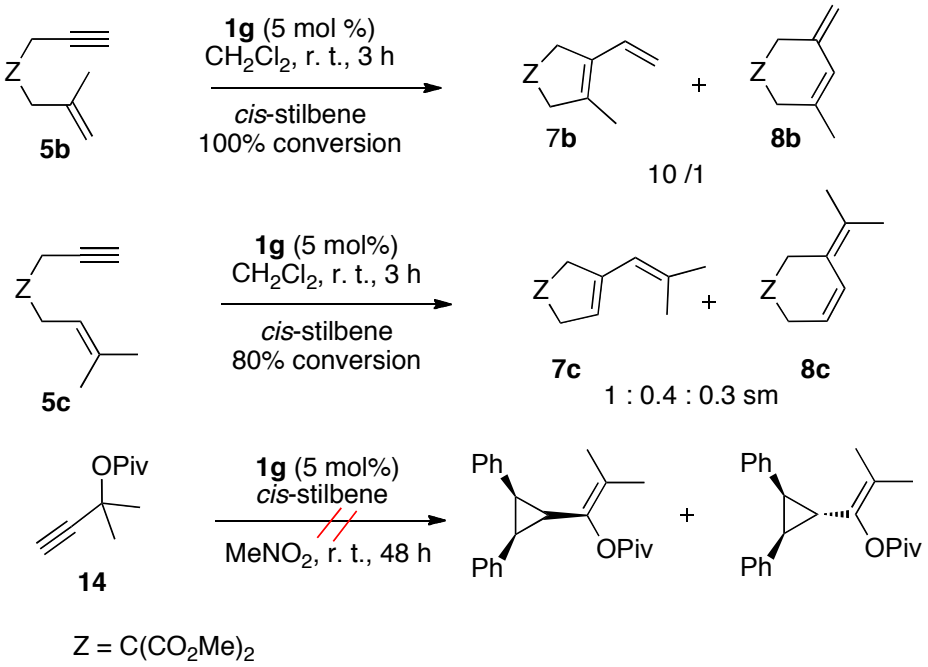
Scheme 40



In conclusion, these results demonstrated that *cis*-stilbene inhibits the activity of the gold(I)-catalysts.

For the mechanistic study we also prepared *cis*-deuterated 4-vinyl anisole following the procedure described in the literature.[142]

The reaction of **9a** with *cis*-deuterated vinyl anisole in the presence of catalyst **4f** led to the formation of a mixture of inseparable products. Unfurtunately, this result did not allow determining if the cyclopropanation reaction is a concerted or a stepwise process. The configuration of the major diastereoisomer **10b-*d*$_1$** was assigned by analogy with **10b**. This reaction was carried out to identify if the process is concerted or stepwise, but no information was obtained.

142 (a) M. Brookhart, S.E. Kegley, *Organometallics,* **1984**, *3*, 650-652. (b) Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc*. **1966**, *88*, 2213.

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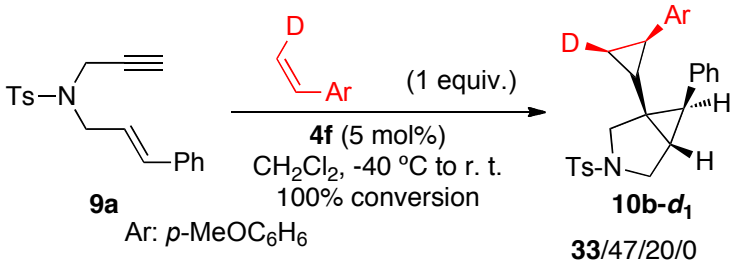
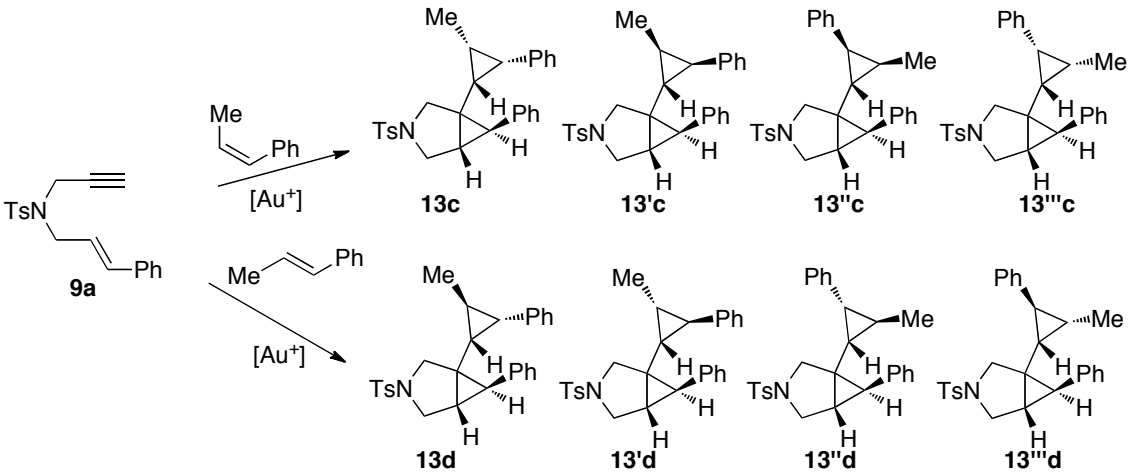
Scheme 41



The reaction of **9a** with *cis*-β-methylstyrene and *trans*-β-methylstyrene should lead to eight diastereoisomers is the reaction is stepwise. The reaction of enyne **9a** with *cis*-β-methylstyrene using catalyst **4e** led to **13c** as a major diastereoisomer, which is confirmed by X-ray diffraction. On the other hand, reaction with *trans*-β-methylstyrene led to three diastereoisomers. Importantly, the products are different to those obtained with *cis*-β-methylstyrene. Therefore, the intermolecular cyclopropanation reaction is a concerted process. Similar results than with styrenes were achieved, in which catalyst **4e** resulted more selective for that reaction than **4f** (Table 10).[143]

Table 10



Entry	Cat.	Alkene	Yield (%)	Ratio 13/13'/13''/13'''
1	**4e**	trans	83	53/39/8

143 In collaboration with Dr. Nolwenn Martin.

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2	**4e**	cis	68	85/13/2
3	**4f**	trans	78	70/29/23
4	**4f**	cis	62	46/33/21

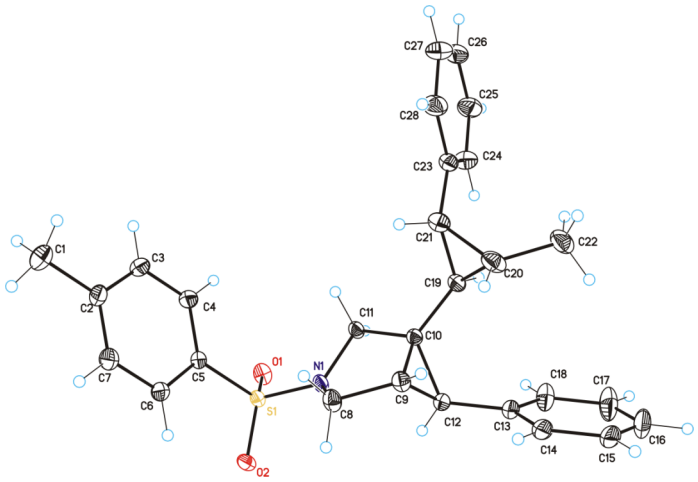

Figure 8: X-ray structure of **13c**

Kinetics Studies.

Following preliminary studies carried out with complexes **1f** and **1g**,[144] kinetics studies under the same conditions were performed on the skeletal rearrangement of 1,6-enyne **5c**.

The activation parameters are shown in Table 11, along with the previously obtained with phosphine catalysts **1f** and **1g**.[49] Interestingly, although the reaction rates of the skeletal rearrangement of 1,6-enye 5c are similar with the four catalysts, there are important differences between the phosphine- and NHC-Au(I) complexes. Thus, $\Delta H^{\neq}$ are considerably higher for **4e** and **4f**, whereas the opposite occurs with the $\Delta S^{\neq}$. The effect of the ligands on the activation enthalpies can be easily explained since more donating NHC ligands should lead to less-electrophilic intermediates. On the other hand, steric hindrance appears to play a major role in complexes **1f** and **1g** leading to very high and negative $\Delta S^{\neq}$.

144 Results obtained from PhD-thesis Cristina Nieto-Oberhüber, **2006**. Unpublished results.

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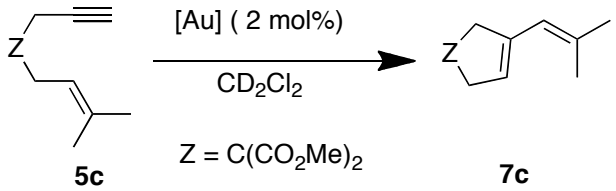
Table 11: Activation parameters for the skeletal rearrangement with complexes **1f**, **1g**,[49] and **4e**, **4f**.



5c **7c**

Catalyst	$\Delta G^{\ddagger}_{298}$ (Kcal/mol)	$\Delta H^{\ddagger}$ (Kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol·K)
1f	21.7 ± 1.1	3.7 ± 0.3	-60.6 ± 1.2
1g	21.2 ± 2.1	6.2 ± 0.5	-50.3 ± 2.0
4e	19.9 ± 2.1	13.1 ± 0.5	-22.8 ± 2.1
4f	19.3 ± 1.5	11.1 ± 0.3	-27.5 ± 1.4

A kinetic study[145] on the reaction of 1,8-enynes with complexes **1g** and **4f** was also carried out. The conditions used were the same, and the range of temperatures was 215.0 to 245.0 K for complex **1g** and 225.0 to 245.0 K for complex **4f**. The results obtained are in the same range of those obtained in the skeletal rearrangement of enyne **5c** for the same complexes.

145 In collaboration with Dr. D. Jansen.

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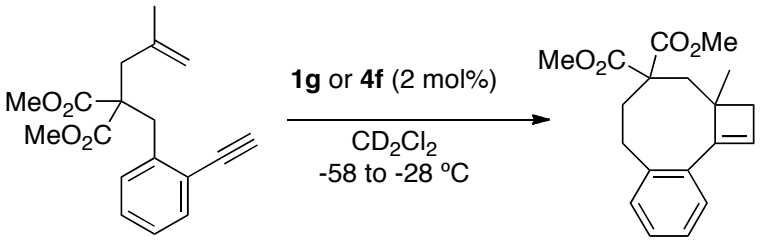
Table 12: Activation parameters for [2+2] cycloaddition with complexes **1g** and **4f**.



16 **17**

Catalyst	$\Delta G^{\ddagger}_{298}$ (Kcal/mol)	$\Delta H^{\ddagger}$ (Kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol·K)
1g	21.2 ± 4.4	6.3 ± 0.4	-46.4 ± 4.0
4f	19.2 ± 4.8	11.3 ± 0.3	-26.5 ± 4.5

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Conclusions.

- Gold-catalyzed reactions of 1,6-enynes with alkenes confirms the involvement of cyclopropyl gold(I) carbenes in processes. This was further supported by the metallotropic 1,3-shift observed with dienynes as substrates.
- A Hammett study revealed that the intermolecular cyclopropanation reaction is an electrophilic process. Gold(I) complexes with highly donating NHC ligands are less electrophilic than with phosphine ligands, and, accordingly, the resulting gold(I) intermediates show a more pronounced carbene-like character.
- The different character of gold(I) complexes with NHC and phosphine ligands was also demonstrated in a kinetic study on the skeletal rearrangement of 1,6-enynes and on the [2+2] cycloaddition of a 1,8-enyne.

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Results 2.
Gold(I)-Catalyzed Intermolecular Addition of Nucleophiles to 1,6-Enynes

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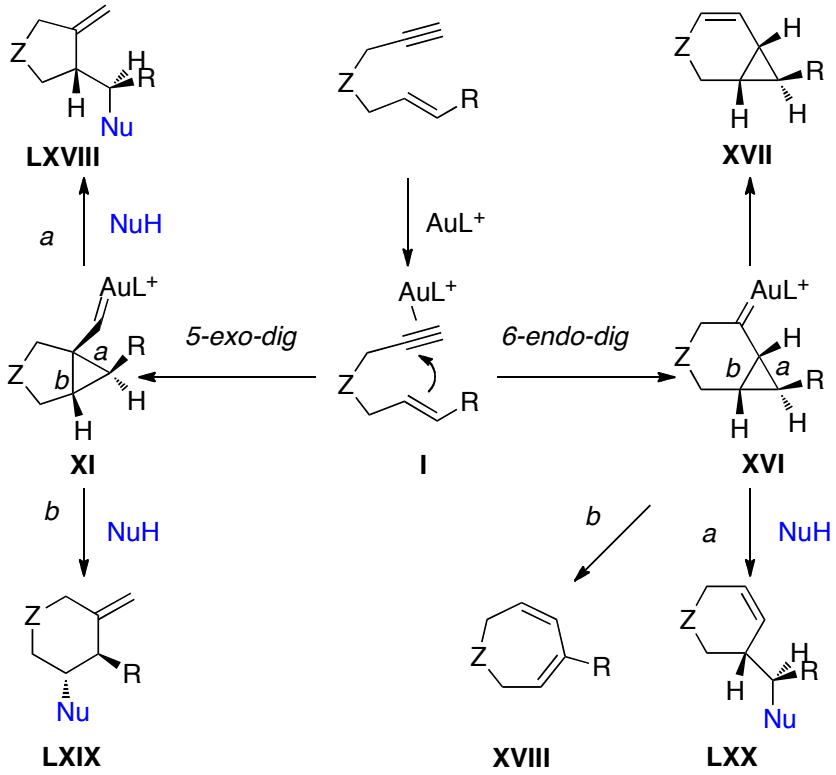
Introduction.

We also studied the addition of certain nucleophiles to 1,6-enynes. In the proposed mechanism two main pathways can be possible, the 5-*exo-dig* and the less common 6-*endo-dig* pathway (Scheme 42).[7a] In the case of the 5-*exo-dig* pathway, the cyclopropyl gold(I)-intermediate (**XI**) can be attacked by nucleophiles at carbon *a* to form a five member ring **LXVIII** or at carbon *b* to form a six member ring **LXIX**. In the 6-*endo-dig* pathway attack of the nucleophiles to carbon *a* leads to six-member ring compounds **LXX**. Cleavage of carbon *b* of intermediate **XVI** can lead to seven member ring compounds **XVIII**.

Scheme 42



The addition of hetero-nucleophiles such as water or ROH to 1,6-enynes have been reported using gold(I)-complexes,[111,112,146,147] chiral gold(I)-complexes[148,149] or

146 Genin, E.; Leseurre, L.; Toullec, P. Y.; Genêt, J. P.; Michelet, V. *Synlett* **2007**, 1780-1784.

147 Matsumoto, Y.; Selim, K. B.; Nakanishi, H.; Yamada, K.; Yamamoto, Y. *Tetrahedron Lett.* **2010**, *51*, 404-406.

other electrophilic metal complexes as catalysts.[34b,35b,150,151,152] Moreover some examples of intermolecular addition of carbamates RO_2CNH_2 or anilines $ArNH_2$ to 1,6-enynes have known.[153] Addition of electron-rich arenes and heteroarenes to enynes using gold(I)-complexes have also been reported.[154,155,156,157]

Selected examples of nucleophilic addition at carbon *a* in the 5-*exo*-*dig* pathway with different carbon nucleophiles,[158] such as electron-rich arenes, heteroarenes, allylsilanes and 1,3-dicarbonyl compounds, are shown in next Scheme 43.

148 Matsumoto, Y.; Selim, K. B.; Nakanishi, H.; Yamada, K.; Yamamoto, Y. *Tetrahedron Lett*. **2010**, *51*, 404-406.

149 Chao, C.-M.; Genin, E.; Toullec, P. Y.; Genêt, J.-P.; Michelet, V. *J. Organomet. Chem*. **2009**, *694*, 538-545.

150 Michelet, V.; Charruault, L.; Gladiali, S.; Genêt, J. P. *Pure Appl. Chem. Comm*. **2006**, *78*, 397-407.

151 Charruault, L.; Michelet, V.; Taras, R.; Gladiali, S.; Genêt, J. P. *Chem. Comm*. **2004**, 850-851.

152 (a) Galland, J.-C.; Savignac, M.; Genêt, J. P. *Tetrahedron Lett.* **1997**, *38*, 8695-8698. (b) Galland, J.-C.; Dias, S.; Savignac, M.; Genêt, J. P. *Tetrahedron* **2001**, *57*, 5137-5148. (c) Charruault, L.; Michelet, V.; Genêt, J. P. *Tetrahedron Lett.* **2002**, *43*, 4757-4760.

153 Leseurre, L.; Toullec, P. Y.; Genêt, J.-P.; Michelet, V. *Org. Lett.* **2007**, *9*, 4049-4052.

154 Toullec, P. Y.; Genin, E.; Leseurre, L.; Genêt, J.-P.; Michelet, V. *Angew. Chem., Int. Ed.* **2006**, *45*, 7427-7430.

155 Amijs, C. H. M.; Ferrer, C.; Echavarren, A. M. *Chem. Commun.* **2007**, 698-700.

156 Electron-rich arenes and heteroarenes also react with propargyl propiolates with gold catalysts to give substituted *δ*-yrones: (a) Luo, T.; Schreiber, S. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 8250-8253.

157 Chao, C.-M.; Vitale, M. R.; Toullec, P. Y.; Genêt, J.-P.; Michelet, V. *Chem. Eur. J*. **2009**, *15*, 1319-1323.

158 Amijs, C. H. M.; López-Carrillo, V.; Raducan, M.; Pérez-Galán, P.; Ferrer, C.; Echavarren, A. M. *J. Org. Chem*. **2008**, *73*, 7721-7730.

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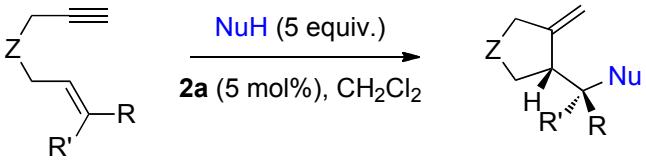
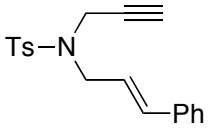
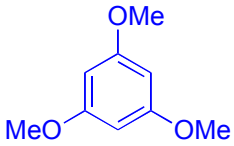
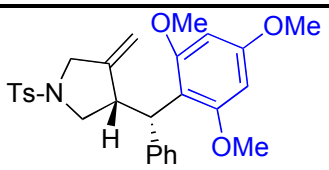
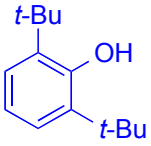
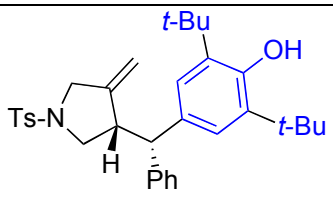
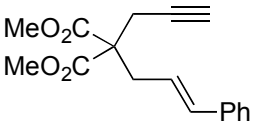
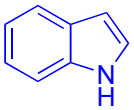
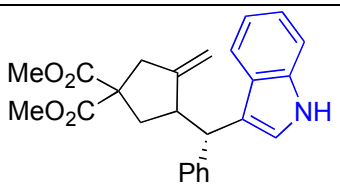
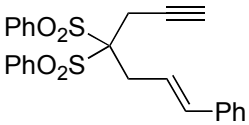
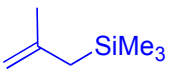
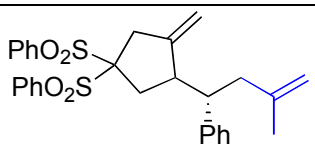
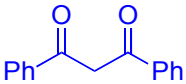
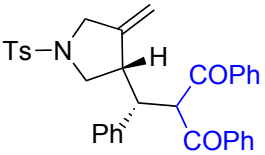
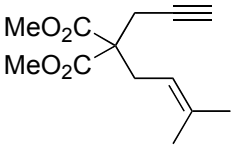
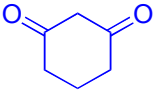
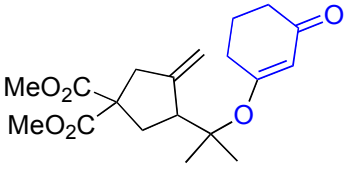
Scheme 43: Selected examples of nucleophilic addition to 1,6-enynes



Enyne	NuH	T (ºC) T (h)	Yield (%)	Product
 **9a**		23 48	66	 **18a**
9a		-40 4	76	 **18b**
 **5a**		23 1	71	 **19**
 **15a**		23 16	57	 **20**
9a		-50 0,5	75	 **18c**
 **5c**		23 2	87	 **21**

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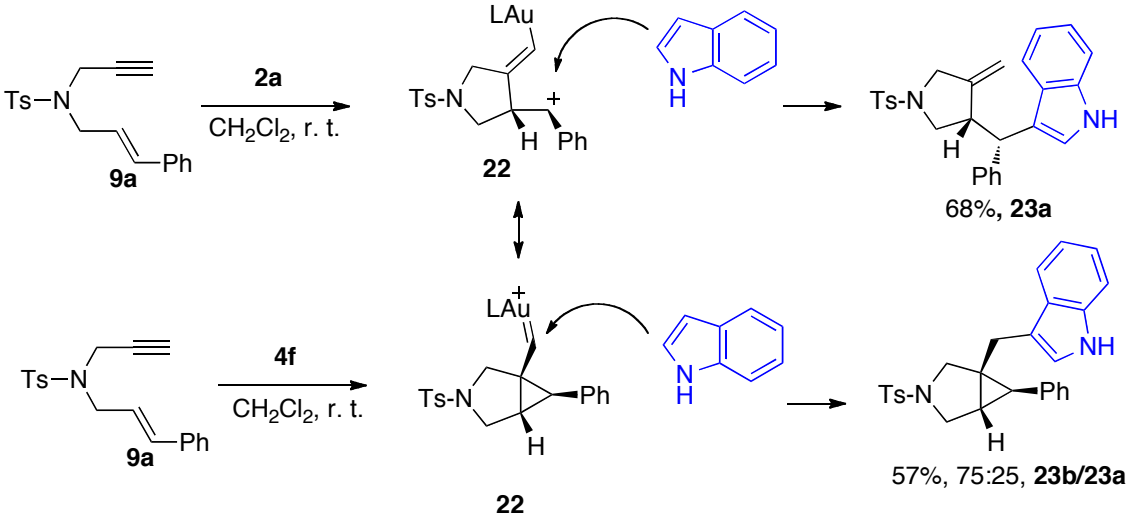
Interestingly reaction of enyne **9a** with indole led to adducts **23a** and **23b**. Using catalyst **2a** the major product was the nucleophilic attack of the indole to the carbon *a* of the intermediate **22** (Scheme 44). When the catalyst was **4f** the major product was the derivative of the direct attack of indole at the carbene carbon of intermediate **22** (Scheme 44).

Scheme 44



Results.

This reaction provides compelling evidence of the existence of the intermediate **XI** (Scheme 45). Products of direct attack of the nucleophile to the alkyne were not observed in the reaction with the 1,6-enynes.[159,160,161,162,163,164]

159 Gold-catalyzed intra- and intermolecular reactions of indoles with alkynes: (a) Ferrer, C.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1105-1109. (b) Ferrer, C.; Amijs, C. H. M.; Echavarren, A. M. *Chem. Eur. J.* **2007**, *13*, 1358-1373.

160 Reetz, M. T.; Sommer, K. *Eur. J. Org. Chem.* **2003**, 3485-3496.

161 Li, Z. G.; Shi, Z. J.; He, C. *J. Organomet. Chem.* **2005**, *690*, 5049-5054.

162 Nevado, C.; Echavarren, A. M. *Synthesis* **2005**, 167-182.

163 Nevado, C.; Echavarren, A. M. *Chem. Eur. J.* **2005**, *11*, 3155-3164.

164 (a) Hashmi, A. S. K.; Blanco, M. C.; Kurpejovic, E.; Frey, W.; Bats, J. W. *Adv. Synth. Catal.* **2006**, *348*, 709-713. (b) Hashmi, A. S. K.; Blanco, M. C. *Eur. J. Org. Chem.* **2006**, 4340-4342.

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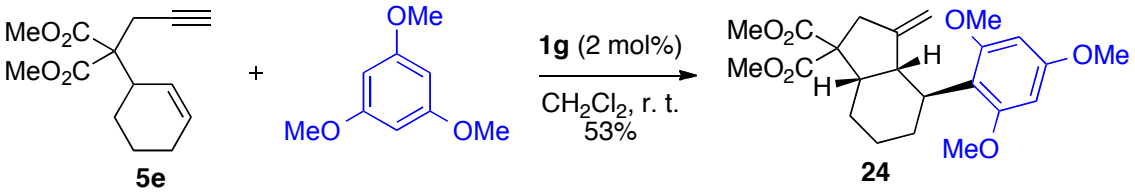
To further confirm the stereoselectivity of this reaction, addition of 1,3,5-trimethoxybenzene to 1,6-enyne **5e** was studied (Scheme 45).

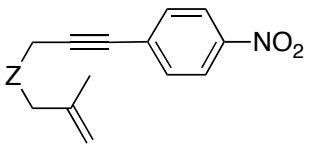
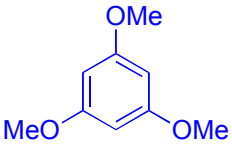
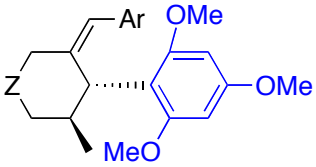
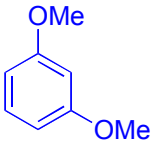
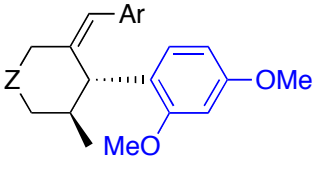
Scheme 45



This reaction gave a single stereoisomer, which has the same relative configuration such as the product of the Pt(II)-catalyzed reaction of **5e** with methanol.[2]

Examples of products obtained by addition of nucleophiles to cleavage of the bond labeled *b* in the intermediate **XI** (Scheme 42) were obtained with enyne **38p** and **38l** in the reaction with 1,3-dimethoxybenzene, 1,3,5-trimethoxybenzene and methanol in the presence of cationic catalyst **1g** (see Table 13, entries 1-4). In all the cases the yields were good to excellent.

Table 13: Examples of addition of nucleophiles to the bond labeled *b*[a]

Entry	Enyne	NuH	Yield (%)	Product
1[b]	 **38p**		81 (7:1 *trans/cis*)	 **25**
2[b]	**38p**		63 (13:1 *trans/cis*)	 **26**

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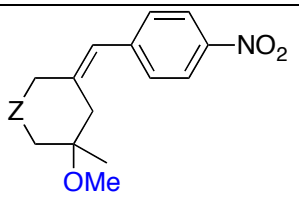
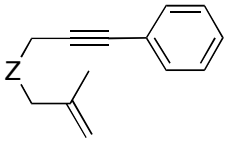
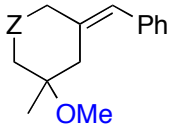
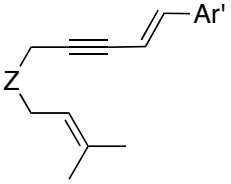
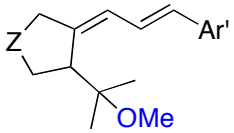
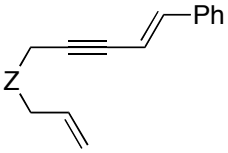
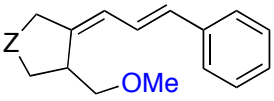
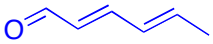
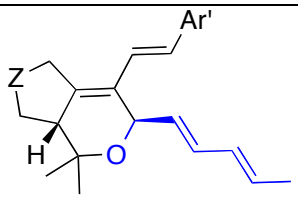
3	**38p**	MeOH	83	 **27**
4	 **38l**	MeOH	99	 **28**
5[c]	 **40c**	MeOH	90	 **29**
6[d]	 **40j**	MeOH	60[e]	 **30**
7[c]	**40c**		99	 **31**

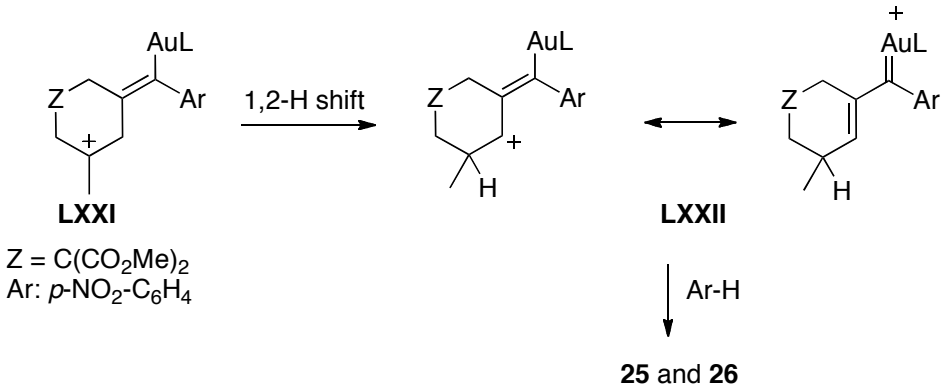
Z : $C(CO_2Me)_2$; Ar: *p*-$NO_2C_6H_4$; Ar': *p*-$CF_3C_6H_4$

[a] Reactions carried out with 2% of gold complex **1g**, in CH_2Cl_2 and 5 equiv of the nucleophile at r. t.. [b] Reactions done at 15 ºC for 3 h. [c] Reactions carried out with 5% of catalyst **1g**. [d] Reaction carried out under microwave heating at 80 ºC for 20 min. [e] An impurity appeared in the NMR spectra (ca. 10%).

Reaction of enyne **38p** with 1,3,5-trimethoxybenzene and 1,3-dimethoxybenzene in the presence of catalyst **1g** afforded adducts **25** and **26** with good trans selectivity. These compounds are the result of an exo cyclization via intermediates of type **XI** (see Scheme 3), although the site of the nucleophile

attachment in the final product was unexpected. Thus, the mechanism for that reaction is explained as a 1,2-H shift of the homoallylic cation **LXXI** to form gold-stabilized allyl cation **LXXII** prior to the attack by the nucleophile. Also it can be viewed as 1,4-addition to α,β-unsaturated gold carbene **LXXII** (Scheme 46).[165]

Scheme 46



In the case of methanol as nucleophile less sterically hindered nucleophile attacks to the initial intermediate **XI** (Scheme 42) before the 1,2-H shift takes place (see Table 13, entries 3-6). On the other hand, in the case of addition of an aldehyde the product formed proceeds by formal [2+2+2] cycloaddition reaction (Table 13, entry 5),[168,169] where the aldehyde attacks to **LXXIII** (Scheme 47) to form the oxonium cation **LXXIV** which could undergo a Prins cyclization to form tetrahydropyranyl cation **LXXV** (Scheme 47).[166,167] Elimination of the metal leads to the final compound.[168,169,169,168]

165 Amijs, C. H. M.; López-carrillo, V.; Echavarren, A. M. *Org. Lett*. **2007***, 9*, 4021-4024.

166 Jiménez-Núñez, E.; Claverie, C. K.; Nieto-Oberhuber, C.; Echavarren, A. M. Angew. Chem. Int. Ed. **2006**, 45, 5452-5455.

167 4-Tetrahydropyranyl cation is a delocalized species with aromatic stabilization: Alder, R. W.; Harvey, J. N.; Oakley, M. T. *J. Am. Chem. Soc*. **2002**, *124*, 4960-4961.

168 Escribano-Cuesta, A.; López-Carrillo, V.; Jansen, D.; Echavarren, A. M. *Chem. Eur. J*. **2009**, *15*, 5646.

169 Schelwies, M.; Moser, R.; Dempwoff, A. L.; Rominger, F.; Helmchem, G. *Eur. J. Chem*. **2009**, *15*, 10888-10900.

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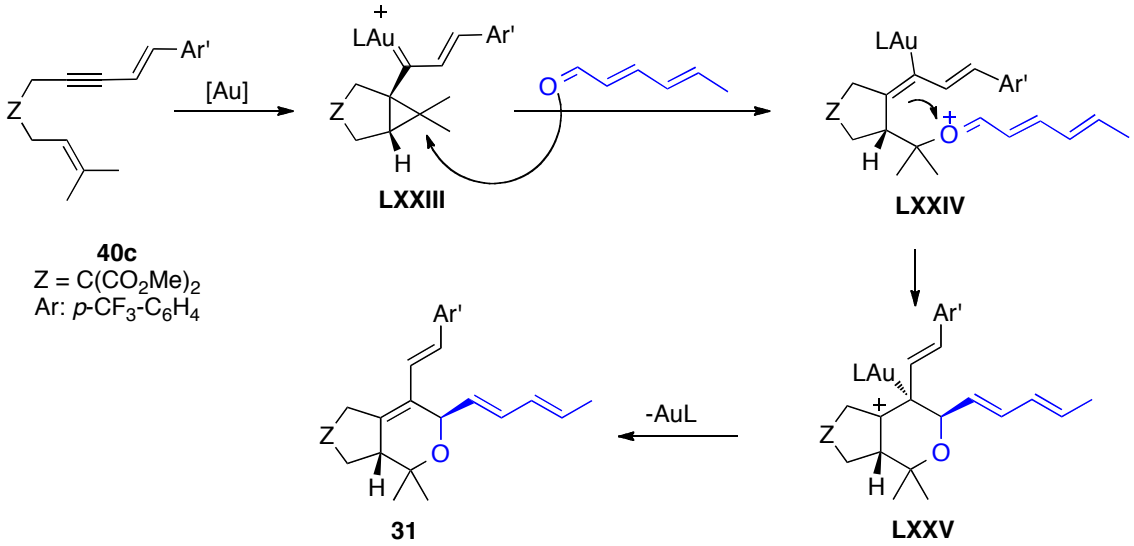
Scheme 47: Mechanism for the formation of **31**



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Conclusions.

- The existence of the proposed intermediates in the skeletal rearrangement of 1,6-enynes catalyzed by gold(I) catalysts were supported by the addition of nucleophiles to obtain the products by exo and endo cyclization.

- In the case of the endo cyclization, a 1,2-H shift leads to formally α,β-unsaturated gold(I) carbenes that are trapped by electron-rich arenes.

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Results 3.

Gold(I)-Catalyzed [4+2]-Cycloaddition Reaction

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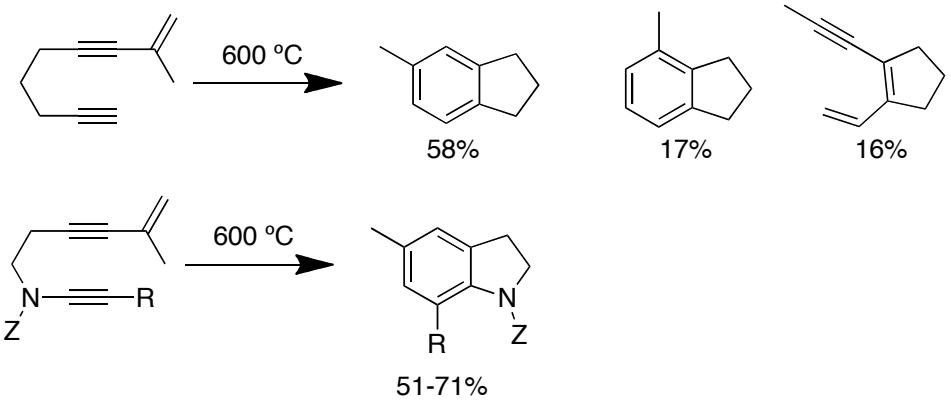
Introduction.

Metal-catalyzed cycloadditions are powerful tools in organic synthesis to access complex molecular frameworks.[179] For this reason, it is important to develop new cycloaddition reactions using new metal complexes.

Precedents in the literature of the [4+2] cycloaddition reaction of enediynes and dienynes have been described in a thermal transformation that required high temperatures[170] (Scheme 48).

Scheme 48



The first examples of intermolecular [2+2+2] cycloaddition reaction between an enyne and an alkyne were reported using Pd(II) as catalyst (Scheme 49).[171,172] More recently, other metals such as Rh(I),[173,174,175] Pd(II)[176] or Ir(I)[177] were used as catalysts for this type of reaction.

---

170 (a) Burrell, R. C.; Daoust, K. J.; Bradley, A. Z.; DiRico, K. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1996**, *118*, 4218-4219. (b) Coudanne, I.; Balme, G. *Synlett* **1998**, 998-1000. (c) Danheiser, R. L.; Gould, A. E.; Fernández de la Pradilla, R.; Helgason, A. L *J. Org. Chem.* **1994**, *59*, 5514-5515. (d) Dunetz, J. R.; Danheiser, R. L. *J. Am. Chem. Soc.* **2005**, *127*, 5776-5777.

171 Trost, B. M.; Krische, M. J. *J. Am. Chem. Soc*. **1996**, *118*, 233-234.

172 For a review on [2+2+2] cycloadditions: Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984,** *96*, 865.

173 (a) Grigg, R.; Scott, R.; Stevenson, P. *J. Chem. Soc., Perkin Trans 1*, **1988**, 1357. (b) Grigg, R.; Scott, R.; Stevenson, P. *J. Chem. Soc., Perkin Trans 1*, **1988**, 1365.

174 Evans, P. A.; Sawyer, J. R.; Lai, K. W.; Huffman, J. C. *Chem. Commun.* **2005**, 3971.

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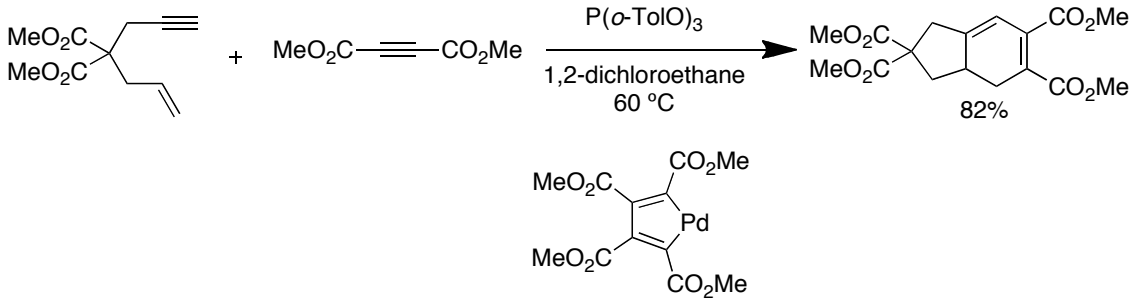
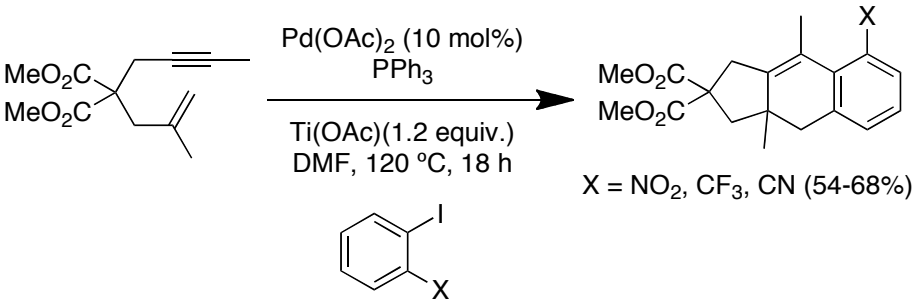
Scheme 49



The intermolecular [2+2+2] cycloaddition reaction of enynes with aryl or vinyl halides, under mild conditions was developed using Pd(0) as catalyst (Scheme 50).[178,179]

Scheme 50



The mechanism of this reaction consists in a oxidative addition of the aryl or arkenyl halides to Pd(0), giving an aryl-palladium(II) complex **LXXVI** (ligands are omitted for clarity). Then a carbopalladation of the alkyne takes place to form the alkenyl-palladium(II) complex **LXXVII**, which gives an intramolecular insertion of

175 For an asymmetric version: Evans, P. A.; Wah, K.; Sawyer, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 12466-12467. (b) Dalton, D. M.; Oberg, K. M.; Yu, R. T.; Lee, E. E.; Perreault, S. *J. Am. Chem. Soc*. **2009**, *131*, 15717-15728. (c) Oinen, M. E.; Yu R. T.; Rovis, T. *Org. Lett.*, **2009**, *11*, 4934-4937.

176 Yamomoto, Y.; Kuwabara, S.; Ando, Y.; Nagata, H.; Nishiyama, H.; Itoh, K. *J. Org. Chem.* **2004**, *69,* 6697-6705.

177 Kezuka, S.; Okado, T.; Niou, E.; Takeuchi, R. *Org. Lett.* **2005**, *7*, 1711-1714.

178 Brown, S.; Clarkson, S.; Grigg, R.; Sridharan, V. *Tetrahedron Lett.* **1993**, *34*, 157-160.

179 Lee, S. I.; Park, S. Y.; Cheng, Y. K. *Adv. Synth. Catal*. **2006**, *348*, 2531-2539.

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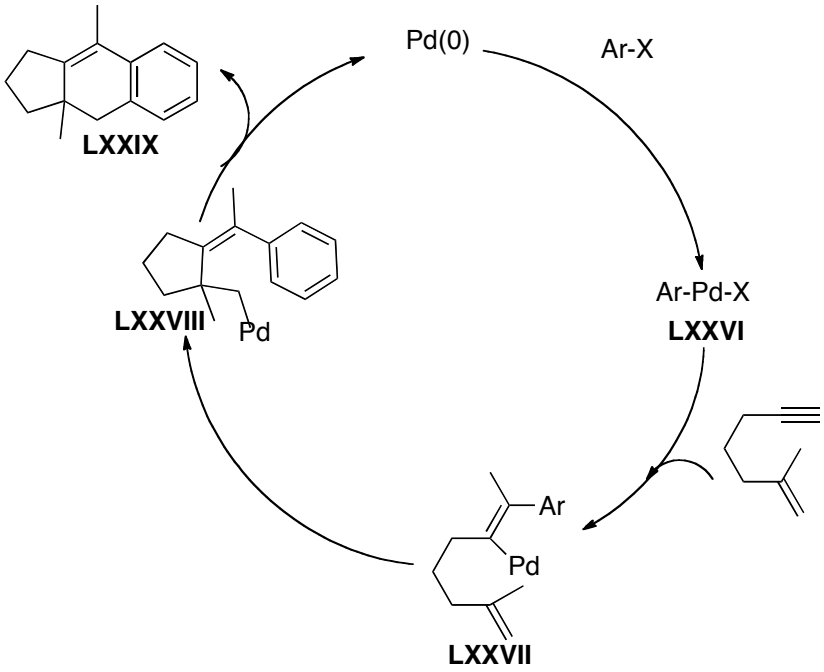
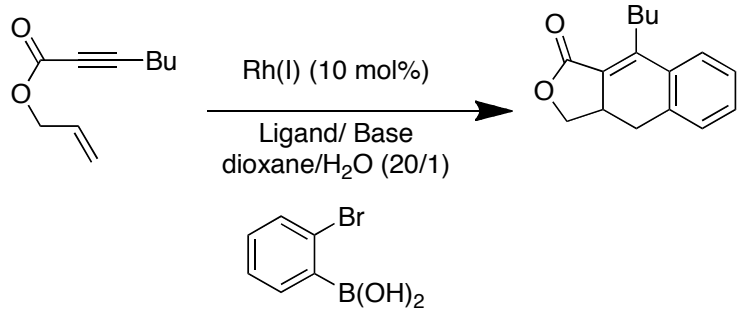
the alkene. Subsequent cyclization onto the aryl ring gives **LXXVIII**, which suffers a β-Hydride elimination to form the corresponding tricycle **LXXIX** (Scheme 51).

Scheme 51



A formal [2+2+2] cycloaddition reaction of 1,6-enyne with 2-bromophenylboronic acid to form fused tricycles catalyzed by Rh(I)-complexes has also been reported (Scheme 52).[180]

Scheme 52



180 Fang, X.; Li, C.; Tong, X. *Chem. Commun*. **2009**, 5311-5313.

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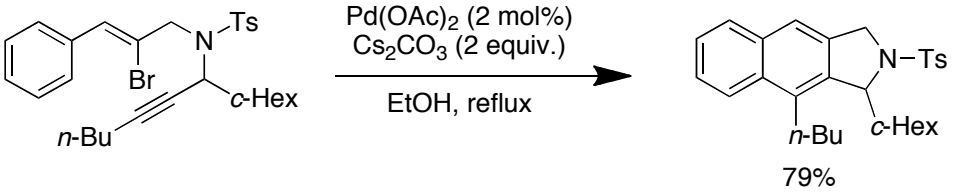
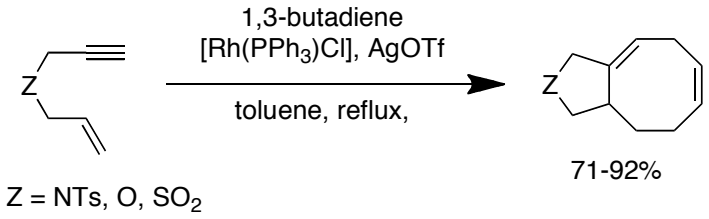
The intramolecular Pd-catalyzed tandem cyclization of bromoenynes[181] involves an oxidative addition of the bromoenyne to Pd(0), carbopalladation into the alkyne, and finally an aromatic C-H bond aromatization (Scheme 53).

Scheme 53



The first formal [4+2+2] cycloaddition reaction of a 1,6-enyne and a diene was described using Rh(I)-complexes as catalysts (Scheme 54).[182]

Scheme 54



The formal [4+2] benzoannulation between enynal or enynone unit and 2π-systems such as alkynes,[183,184,185,186] enol ethers, and carbonyl compounds, to

181 (a) Ohno, H.; Yamamoto, M.; Iuchi, M.; Tanaka, T. *Angew. Chem. Int. Ed.* **2005**, *44*, 5103-5106. (b) See also for cyclization of allenenes with aryl halides: Ohno, H.; Miyaura, K.; Takeoka, Y.; Tanaka, T. *Angew. Chem. Int. Ed.* **2003**, *42*, 2647-2650.

182 Evans, P. A.; Robinson, J. E.; Baum, E. W.; Fazal, A. N. *J. Am. Chem. Soc.* **2002**, *124*, 8782-8783.

183 Asao, N. *Synlett*, **2006**, *11*, 1645-1656.

184 (a) Asao, N.; Sato, K.; Menggenbateer, Yamamoto, Y. *J. Org. Chem*., **2005**, *70*, 3682-3685. (b) Hsu, Y.-C.; Ting, C.-M.; Liu, R.-S. J. *Am. Chem. Soc*. **2009**, *131*, 2090-2091. (c) Asao, N.; Nogami, T.; Lee, S.; Yamamoto, Y. *J. Am. Chem. Soc*. **2006**, *125*, 10921-10925.

185 Gevorgyan, V.; Yamamoto, Y. *J. Organomet. Chem*. **1999**, *576*, 232-247.

186 Asao, N.; Takahashi, K.; Lee, S.; Kasahara, T.; Yamamoto, Y. *J. Am. Chem. Soc*. **2002**, *124*, 12650.

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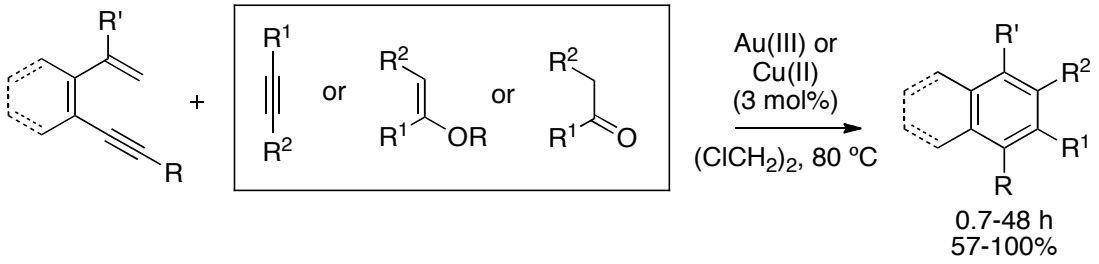
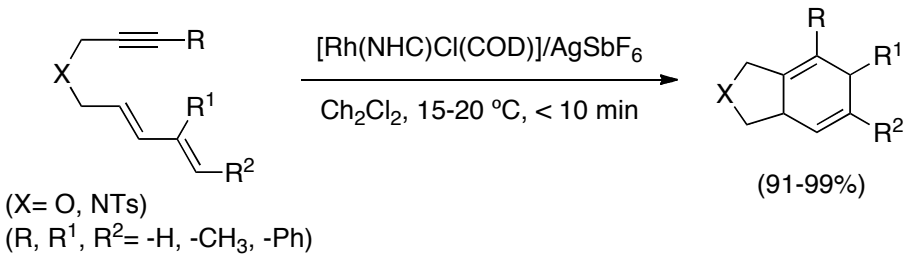
produce aromatic ketones in good yields, and Lewis acids such as Au(III) or Cu(II) as catalysts (Scheme 55).

Scheme 55



Intramolecular formal [4+2] cycloaddition reaction is achieved when the alkene, alkyne or diene are part of the molecule. The first examples were reported using Ni(II)[187] and Rh[188] complexes as catalysts. Complexes as Rh-NHC catalyzed the intra- and intermolecular [4+2] cycloaddition reaction of dienynes, under mild conditions with high yields[189] (Scheme 56).

Scheme 56



(X= O, NTs)
(R, R^1, R^2= -H, $-CH_3$, -Ph)

Related products have been observed when the alkene has a pendant cyclopropane. The reactions take place by formal [4+2] cycloaddition reaction using different metal-complexes as catalysts (Scheme 57).[190,191]

187 (a) Wender, P. A.; Jenkins, T. E. *J. Am. Chem. Soc.* **1989**, *111*, 6432-6434. (b) Wender, P. A.; Smith, T. E. *J. Org. Chem.* **1995**, *60*, 2962-2963. (c) Wender, P. A.; Smith, T. E. *J. Org. Chem.* **1996**, *60*, 824-825. (d) Wender, P. A.; Smith, T. E. *Tetrahedron* **1998**, *54*, 1255.

188 Jolly, R. S.; Luedtke, G.; Sheehan, D.; Livinghouse, T. *J. Am. Chem. Soc.* **1990**, *112*, 4965.

189 Lee, S. I.; Park, J. H.; Jung, I. G.; Choi, S. Y.; Cheng, Y. K. *J. Org. Chem.* **2006**, *71*, 91-96.

190 Rh-catalyzed reaction: (a) Wender, P. A.; Dyckman, A. J.; Husfeld, C. O.; Kadereit, D.; Love, J. A.; Rieck, H. *J. Am. Chem. Soc.* **1999**, *121*, 10442-10443. (b) Wender, P. A.; Bi, F. C.; Brodney, M. A.; Gosselin, F. *Org. Lett.* **2001**, *3*, 2105-2108. (c) Wender, P. A.; Barzilay,

Scheme 57

R = Me [Rh(PPh$_3$)Cl] / AgOTf (0.5 mol%), toluene, 110 ºC 77%

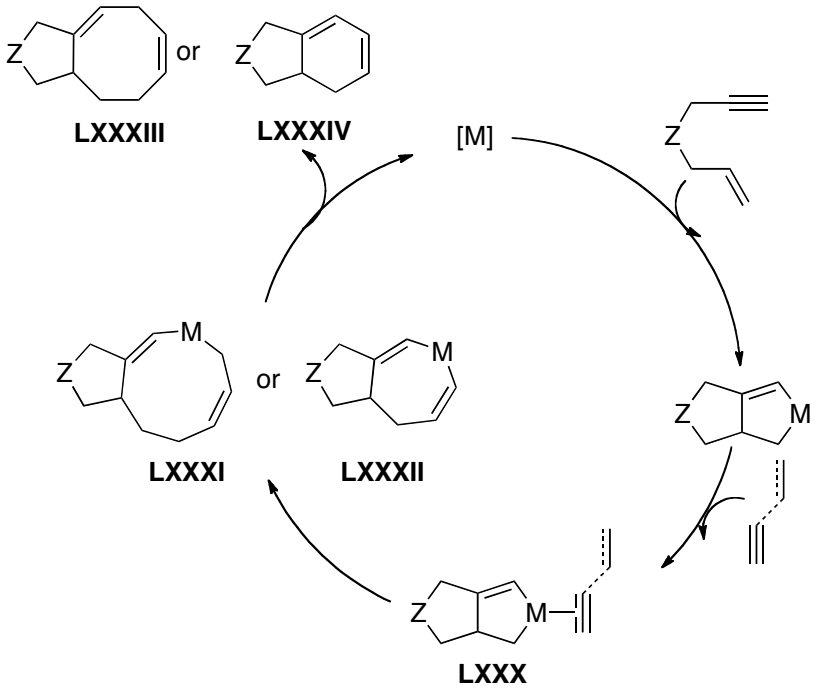
R = H [CpRu(CH$_3$CN)$_3$]PF$_6$ (10 mol%), acetone, r. t. 77%

A general mechanism for the [2+2+2] cycloaddition is shown in Scheme 58. First, the formation of the metallacyclopentene takes place, followed by the coordination of unsaturated molecule to form the complex **LXXX**. In the reaction with dienes, migratory insertion leads to metallacyclononene **LXXXI**, which after reductive elimination affords **LXXXIII**. On the contrary, in the reaction with alkynes, the migratory insertion affords **LXXXII**, which after reductive elimination gives **LXXXIV**.

C. M.; Dyckman, A. J. *J. Am. Chem. Soc.* **2001**, *123*, 179-180. Ru: (d) Trost, B. M.; Shen, H. C. *Org. Lett.* **2000**, *2*, 2523-2525. (e) Trost, B. M.; Toste, F. D.; Shen, H. *J. Am. Chem. Soc.* **2000**, *122*, 2379-2380.

191 Similar seven-membered carbocycles have been obtained in a related Ni-catalyzed [4+2+1] cycloaddition of diazoalkane, diene, and alkyne: Ni, Y.; Montgomery, J. *J. Am. Chem. Soc.* **2004**, *126*, 11162-11163.

Scheme 58



Examples of gold(I)-catalyzed ring expansion cycloisomerizations have been described.[192] For instance, cycloisomerization of an alkylidenecyclopropane would lead to a spirocyclic cyclopropylmethyl cation **LXXXV**. σ-Bond migration leads intermediate **LXXXVI**, followed by a Nazarov-type electrocyclization assisted by the double bond of the aryl group leads intermediate **LXXXVII** by subsequent loss of a proton. Finally proto-demetallation gives the tetracycles (Scheme 59).

192 Sethofer, S. G.; Staben, S. T.; Hung, O. Y.; Toste, F. D. *Org. Lett*. **2008**, *10*, 4315-4318.

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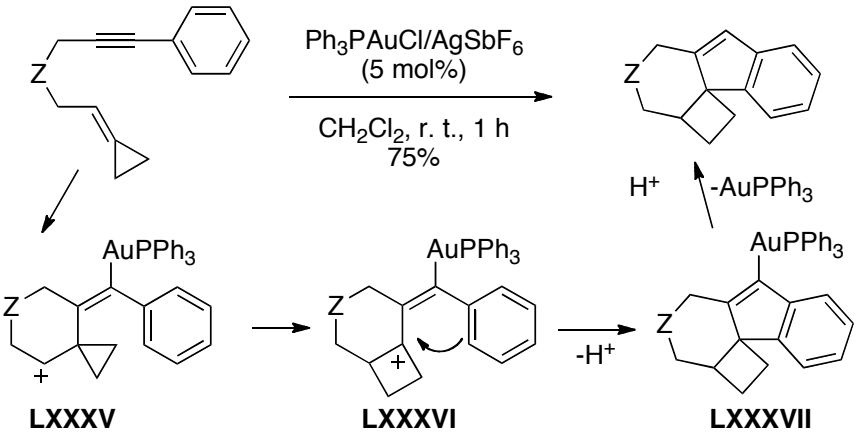
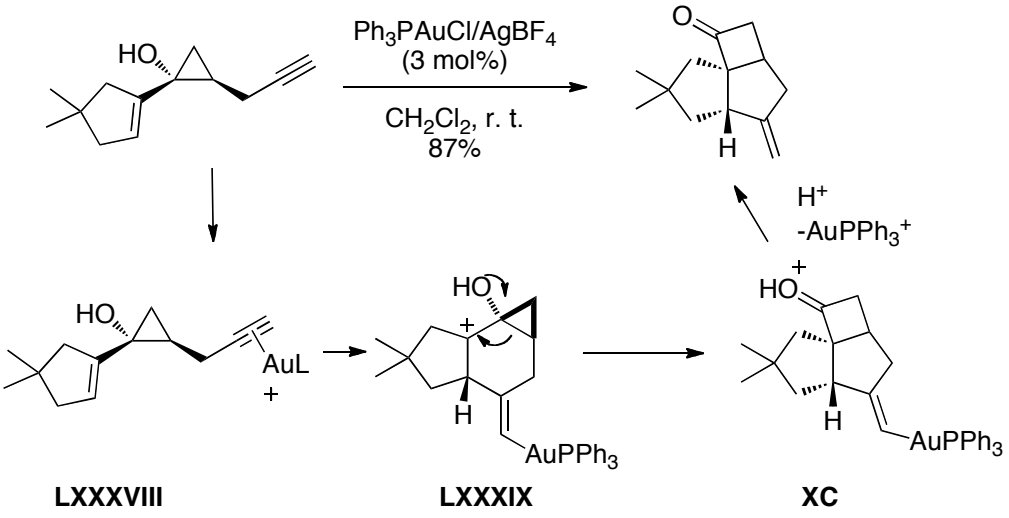
Scheme 59



Other example of ring expansion has been described,[192] in which the cyclization of a vinylcyclopropanol onto a gold(I)-alkyne complex **LXXXVIII** affords a carbocation intermediate **LXXXIX**. This intermediate suffers a semipinacol rearrangement leading to cyclobutanone products **XC** (Scheme 60).

Scheme 60



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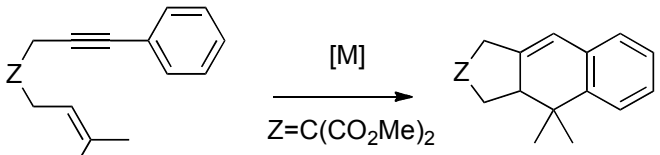
Results

3.1. *Cycloaddition of arylenynes.*

Enynes with substituted alkynes, in particular those bearing an aryl group, are quite reluctant to undergo cycloisomerization, and alkoxycyclization reactions.[111a] As has been reported before, higher reactivity of Au(I) complexes can be achieved by using bulky, biphenyl-based phosphines.[40a] The enynes with alkenyl or aryl groups at the alkyne react to give hydrindanes or linearly fused tricyclic systems, respectively, in a formal [4+2] cycloaddition reaction. This reaction is catalyzed by the highly active biphenyl-based Au(I) complexes at room temperature.[118] In this work, we decided to study in more detail this reaction with a variety of gold(I) complexes to fully stablish its scope and limitations. First, the reaction of **33a** was studied under different conditions (Table 14).[40a]

Table 14: Cyclization of arylenyne **33a**



33a **34a**

Entry	[M] (mol %)	Solvent	Conditions[a]	Time	Yield (%)
1	$[AuCl(PPh_3)]/ AgSbF_6$ (2)	CH_2Cl_2	A	12 h	83
2	**1a**(2)	CH_2Cl_2	A	2 h	85
3	**1g** (2)	CH_2Cl_2	A	2 h	83
4	**1g** (2)	acetone	A	6 h	81
5	**1g** (2)	toluene	A	20 h	27
6	**1g** (2)	DMF	A	20 h	25
7	**1g** (2)	$MeNO_2$	A	5 h	77
8	**1g** (2)	Et_2O	A	20 h	78

9	**1g** (2)	MeCN	A	20 h	< 2
10	**2a**/ $AgSbF_6$ (2)	CH_2Cl_2	A	2 h	99
11	$PtCl_2$ (5)	CH_2Cl_2	A	24 h	< 2
12	**1g** (2)	CH_2Cl_2	B	1 min	93[b]
13	**1g** (2)	CH_2ClCH_2Cl	B	1 min	92[b]
14	**1g** (2)	acetone	B	1 min	74[b]
15	**1g** (2)	toluene	B	1 min	16[b]
16	**2a**/ $AgSbF_6$ (2)	CH_2Cl_2	B	0.5 min	95[b]

[a] A = r. t.. B = microwave heating, 50 ºC. [b] Yield determined by GC.

The faster reactions were then carried out with the gold complexes with bulky phosphine/phosphite ligands **1g-2a** (Table 14, entries 2, 3 and 10). Among the assayed solvents, the best results were obtained when CH_2Cl_2 was used (Table 14, entry 3). Other solvents such as acetone, toluene, dimehtylformamide or acetonitrile (Table 14, entries 4-6, 9) lead to slower reactions. In the case of the catalyst generated *in situ* by abstraction of the chlorine from complex **2a** provided quantitatively the tricyclic product (Table 14, entry 10). Moreover when the reactions were carried out under microwave heating (Table 14, entries 12-14,16) the times decreased considerably and the yields were excellent, whereas in the same conditions but using toluene as solvent the reaction was not completed (Table 14, entry 15). When the reaction was carried out with $PtCl_2$ (Table 14, entry 11) no conversion was observed.

Substituted arylenynes **33b**-**33f** reacted with gold(I)-catalysts to give 2,3,9,9a-tetrahydro-1*H*-cyclopenta[*b*]naphthalenes **34b**-**34c** stereospecifically. Retention of the configuration was observed when the enyne **33c** cyclized to form only the *trans*-cinnamyl derivative (Table 15, entry 3). Using precatalyst **2a** or microwave irradation the reactions were accelerated considerably and the yields increased, whereas in the case of phenylenyne **33d**, the ether **33f**, and the tosylamide **33e** the reaction failed to give the product of *endo*-cyclization (Table 15, entries 5-7). The lack of reactivity of these enynes can be explained by the electron-withdrawing effect of the groups at the tether position, disfavoring the coordination of the gold to the alkyne.

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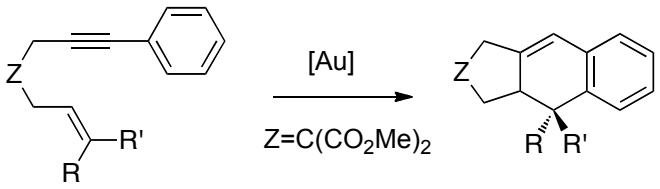
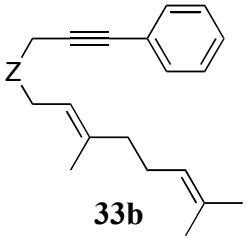
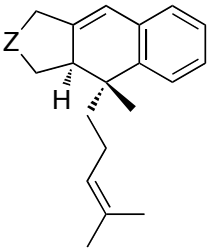
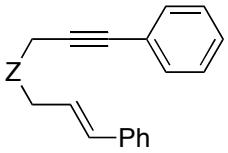
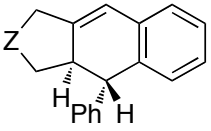
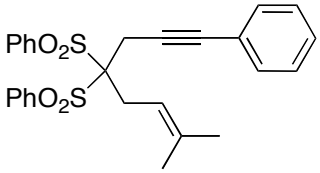
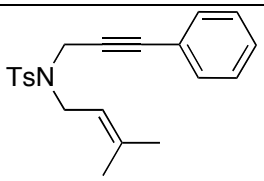
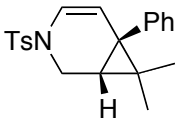
Table 15: Gold(I)-catalyzed cyclization of phenyl-enynes **33b-33f**[a]



entry	enyne	[Au(I)]	time	product (yield, %)
1[d]	 **33b**	**1g**	18 h	 **34b** (78)
2	**33b**	**2a** / $AgSbF_6$	30 min	**34b** (60)
3[c]	 **33c**	**1g**	20 min	 **34c** (85)
4	**33c**	**2a** / $AgSbF_6$	30 min	**34c** (90)
5[d]	 **33d**	**1g**	40 h	-
6[d]	 **33e**	**1g**	12 h	 **34e** (70)

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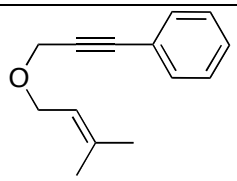
7[d]	 **33f**	**1g**	40 h	-

[a] Reaction run with 2 mol% catalyst in CH_2Cl_2 at r. t.. [b] Reaction in acetone at r. t. with 5 mol% catalyst. [c] Reaction under microwave heating at 80 ºC with 2 mol% catalyst in CH_2Cl_2.[d] Results from ref. 40,118

This study was extended to *para*-substituted arylenynes. The reaction tolerates a variety of *para*-substituted groups at the aryl ring with different electronic properties, providing good to excellent yields. In the case of the enyne **33h**, with a methoxy group a product of a 6-*endo*-cyclization was obtained as a minor product (Table 16, entry 1). Best results were obtained using pre-catalyst **2a** or microwave heating. In the case of enyne **33l**, tetracyclic compound **34l** was obtained as a single diastereoisomer, whose configuration was determined by 2D ^{1}H NMR experiments.

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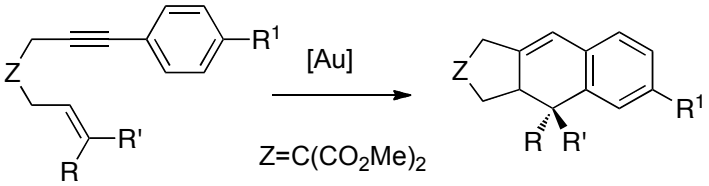
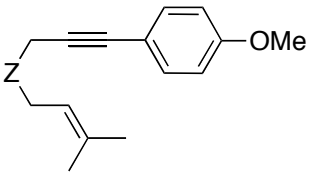
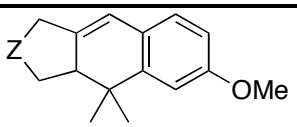
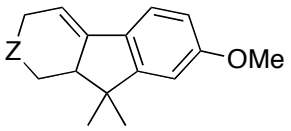
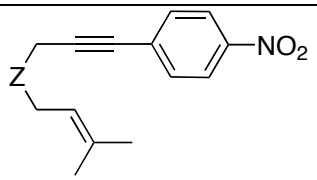
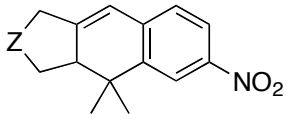
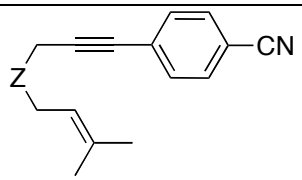
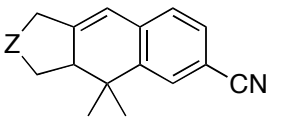
Table 16: Au(I)-catalyzed cyclization of arylenynes **33h-33l**[a]



Entry	Enyne	[Au(I)]	Time	Product(s) (yield, %)
1[c]	 **33g**	**1g**	3 h	 **34g** +  **35g** (75, 4:1)
2[b]	**33g**	**1g**	12 min	**34g** + **35g** (84, 4:1)
3[c]	 **33h**	**1g**	3 h	 **34h** (74)
4[b]	**33h**	**1g**	12 min	**34h** (84, 4:1)
5	**33h**	**2a** / $AgSbF_6$	20 min	**34h** (65)
6[c]	 **33i**	**1g**	96 h	 **34i** (68)
7	**33i**	**2a** / $AgSbF_6$	3 h	**34i** (80)

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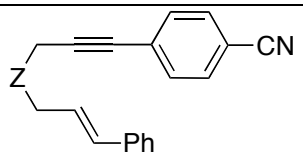
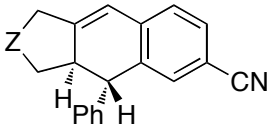
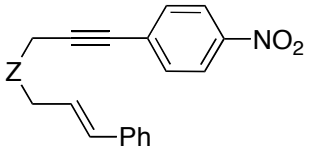
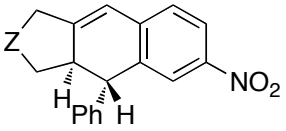
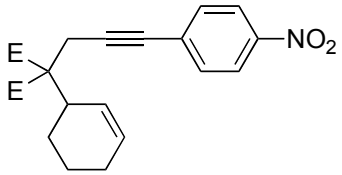
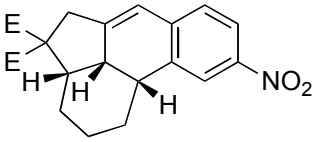
8[c]	 **33j**	**1g**	58 h	 **34j** (54)
9	**33j**	**2a** / $AgSbF_6$	20 min	**34j** (65)
10[c]	 **33k**	**1g**	54 h	 **34k** (58)
11[b]	**33k**	**1g**	50 min	**34k** (75)
12	**33k**	**2a** / $AgSbF_6$	2 h	**34k** (96)
13	 **33l**	**1g**	40 min	 **34l** (95)

[a] Reactions run with 2 mol% catalyst in CH_2Cl_2 at r. t. [b] Reaction under microwave heating at 50°C with 2 mol% catalyst in CH_2Cl_2.[c] Results carried out by C. Nieto-Oberhuber

Substrates bearing *meta* substituents at the aryl ring were also assayed. The cyclization products obtained with these substrates were a mixture of regioisomeric cycloadducts (Table 17). Enyne **33m** was cyclized by **1g** or **2a**/$AgSbF_6$ to form four products, two from 5-*exo*-cyclization and the other two from 6-*endo*-cyclization, whereas under microwave heating only the products from the 5-*exo*-cyclization were obtained (Table 17, entries 1-3). Also the same succeed with enyne **33o**. Enyne **33n** needed more time to complete the reaction, although the quantity of the catalyst was increased to 5 mol% (Table 17, entry 4). Finally with enyne **33p** different results were achieved depending of the reaction conditions. Thus, using catalyst **1g** at room temperature, a mixture of the four products derived from 5-*exo*- and 6-*endo*-cyclization were formed, whereas when the reaction was performed using catalyst **2a**/$AgSbF_6$ or microwave heating only one compound **35''p** was formed almost

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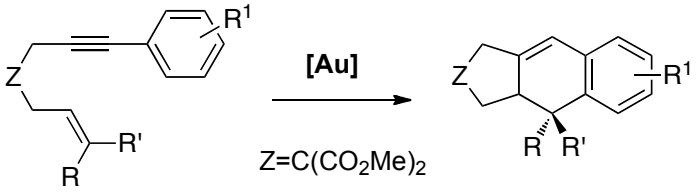
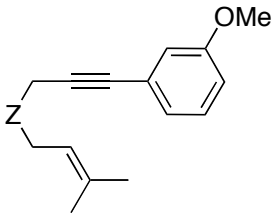
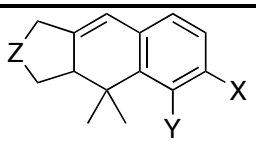
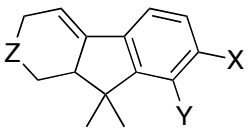
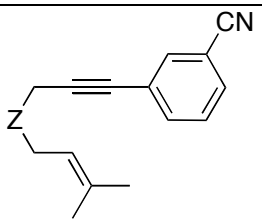
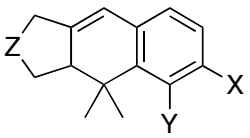
quantitatively (Table 17, entries 9 snd 10). This product is the result of an initial *endo*-dig cyclization followed by the isomerization of the alkene to the internal position.

Table 17: Au(I)-catalyzed cyclization of arylenynes **33m-33p**[a]



Entry	Enyne	[Au(I)]	Time	Product(s) (yield, %)
1[e]	 **33m**	**1g**	1 h	 **34m**: X = OMe, Y = H (54) **34'm**: X = H, Y = OMe (35) +  **35m**: X = OMe, Y = H (6) **35'm**: X = H, Y = OMe (5)
2[b]	**33m**	**1g**	20 min	**34m** + **34'm** (92, 2:1)
3	**33m**	**2a** / $AgSbF_6$	30 min	**34m** + **35m** (59, 16:1) **34'm** + **35'm** (37, 11:1)
4[c,e]	 **33n**	**1g**	54 h	 **34n**: X = CN, Y = H (26) **34'n**: X = H, Y = CN (26)

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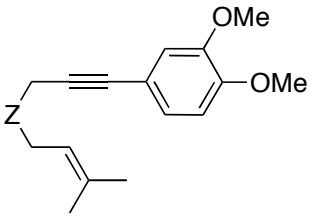
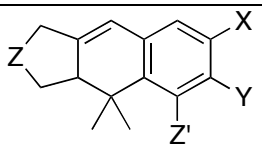
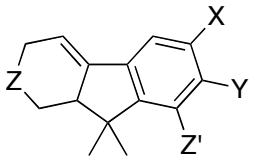
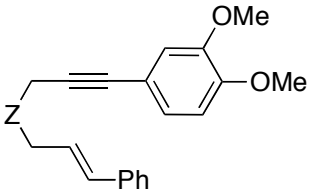
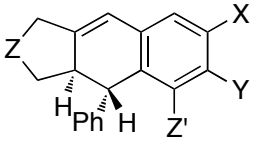
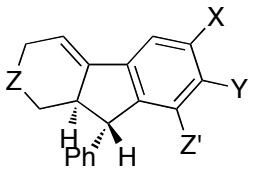
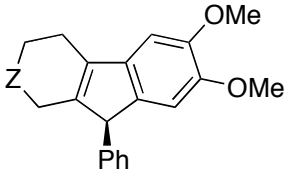
6[b]	 **33o**	**1g**	30 min	 **34o**: X = Y = OMe, Z' = H **34'o**: X = H, Y = Z' =OMe **34o** + **34'o** (92, 2:1)
7	**33o**	**1g**	3 h	**34o** + **34'o** (70, 6:1) +  **35o**: X = Y = OMe, Z' = H **35'o**: X = H, Y = Z' = OMe **35o** (8) + **35'o** (2)
8[c,d,e]	 **33p**	**1g**	15 h	 **34p**: X = Y = OMe, Z' = H **34'p**: X = H, Y = Z' =OMe **34p** (40) + **34'p** (51) +  **35o**: X = Y = OMe, Z' = H **35'o**: X = H, Y = Z' = OMe **35p** (5) + **35'p** (2)
9	**33p**	**2a** / $AgSbF_6$	8 h	 **35''p** (96)

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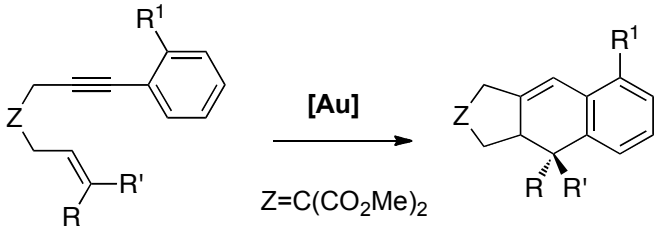
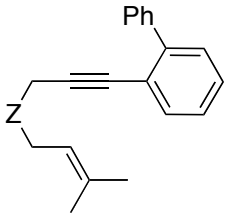
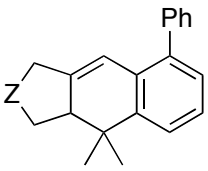
10[b]	**33p**	**1g**	20 min	**35''p** (93)

[a] Reactions run with 2 mol% catalyst in CH_2Cl_2 at r. t.. [b] Reaction under microwave heating at 80°C with 2 mol% catalyst in CH_2Cl_2. [c] 5 mol% catalyst. [d] Reaction in the presence of 4 Å molecular sieves. [e] Results carried out by C. Nieto-Oberhuber

Enynes **33q-s**, bearing *ortho*-substituted groups at the aryl ring, were cyclized to form the expected products **34q-s** (Table 18). In the case of the enynes **33q** and **33s** (Table 18, entries 2 and 5) cyclohexadienes **36q** and **36s** were obtained as minor products. These cyclohexadienes presumably were formed by a 6-*endo* cyclization followed by cyclopropane opening followed by 1,2-H migration.

Table 18: Au(I)-catalyzed cyclization of arylenynes **33q-33s**[a]



entry	enyne	[Au(I)]	time	Product(s) (yield, %)
1[c]	 **33r**	**1g**	20 h	 **34r** (80)

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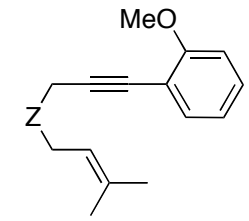
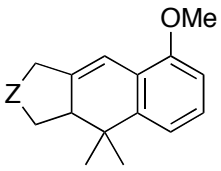
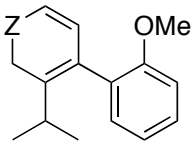
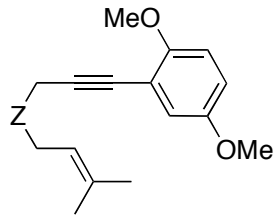
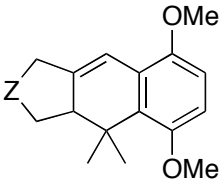
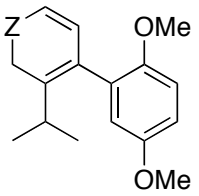
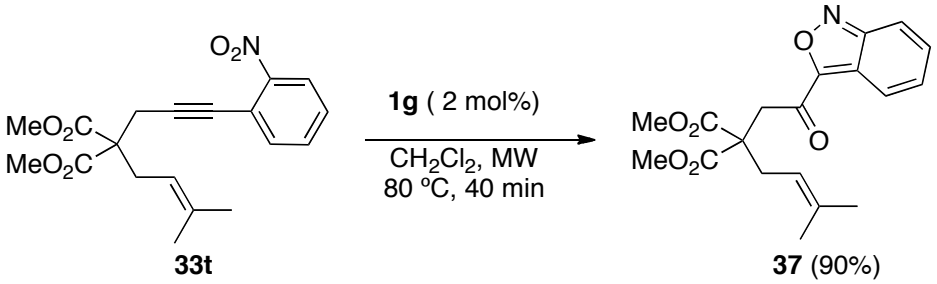
2[c]	 **33q**	**1g**	3 h	 **34q** (83) +  **36q** (16)
3[b]	**33q**	**1g**	18 min	**34q** +**36q** (87, 2:1)
4	**33q**	**2a**/ $AgSbF_6$	1 h	**34q** +**36q** (99, 5:1)
5[c]	 **33s**	**1g**	3 h	 **34s** (62) +  **36s** (28)

[a] Reactions run with 2 mol% catalyst in CH_2Cl_2 at r. t.. [b] Reaction under microwave heating at 50°C with 2 mol% catalyst in CH_2Cl_2. [c] results csrried out by C. Nieto-Oberhuber

The enyne **33t** bearing an *ortho*-nitro group at the aryl ring did not react using catalyst **1g** or **2a**/$AgSbF_6$ at room temperature. However when the reaction

was carried out under microwave heating, the benzo[*c*]isoxazole (anthranyl) derivative **37** was obtained in 90% of yield, instead of the expected cycloadduct. The formation of that product was explained as an attack of the nitro group to the alkyne (Scheme 61). This type of reactivity had precedent in the cyclization of *o*-(alkynyl)nitrobenzenes catalyzed by $AuBr_3$ to form anthranils.[193]

Scheme 61



33t **37** (90%)

The [4+2] cycloaddition reaction tolerates a large variety of substrates with different electronic properties. The phosphite-gold complex **2a**, which is highly electrophilic, gives higher yields in shorter reaction times than the biphenyl-based phosphines gold complex **1g**. For instance, the reaction time with substrate **33k** decreased from 54 h to 30 min and the yield increased from 56 to 96% (Table 16, entry 8).

Mechanistic Discussion.

Mechanistic studies based on DFT calculations[194] revealed that the reaction proceeds by an initial formation of *anti* cyclopropyl gold(I)-carbene **XCIIa**, in a thermoneutral process (Scheme 62). Interestingly, **XCIIa** opens to form **XCII'a**, an aryl-stabilized π-cation complex (Scheme 62-b). The transition state connecting intermediates **XCIIa** and **XCII'a** was not located. Particularly important is the fact that these intermediates are stationary points in the reaction, with different bond

193 Asao, N.; Sato, K.; Yamamoto, Y. *Tetrahedron Lett*. **2003**, *44*, 5675-5677.

194 DFT calculations were carried out by Prof. Diego J. Cárdenas (Universidad Autónoma de Madrid).

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lengths and angles, and not canonical forms. The difference in energy between **XCIIa** and **XCII'a** is small. Thus, at the B3LYP/6-31G(d) (C, H, P), LANL2DZ (Au) level, ΔG was found to be 3.6 kcal·mol^{-1}, whereas at a higher level (B3LYP / 6-311+G(d,p) (C,H,P) LANL2DZ (Au)) the energies are more similar (ΔG = 2.0 kcal·mol). Next, the Wheland intermediate **XCIII** is formed via $\mathbf{TS_{XCII'a\text{-}XCIIIa}}$ in a exothermic process and with low activation energy. The skeletal rearrangement via $\mathbf{TS_{XCIIa\text{-}XCIVa}}$ and **XCIVa** requires relatively high activation energy. DFT calculations show that the skeletal rearrangement for the dimethyl substituted 1,6-enyne would proceed by a single cleavage mechanism. [26, 33b,38a,c,44,47,111c,111d,195]

195 (a) Fürstner, A.; Szillat, H. F.; Gabor, B.; Mynott, R. *J. Am. Chem. Soc.* **1998**, *120*, 8305-8314. (b) Trost, G. A. Doherty, *J. Am. Chem. Soc.* **2000**, *122*, 3801-3810. (c) Fürstner, A.; Szillat H.; Stelzer, F. *J. Am. Chem. Soc.* **2000**, *122*, 6785-6786. (d) Oh, C. H.; Bang, S. Y.; Rhim, C. Y. *Bull. Korean Chem. Soc*. **2003**, *24*, 887-888.

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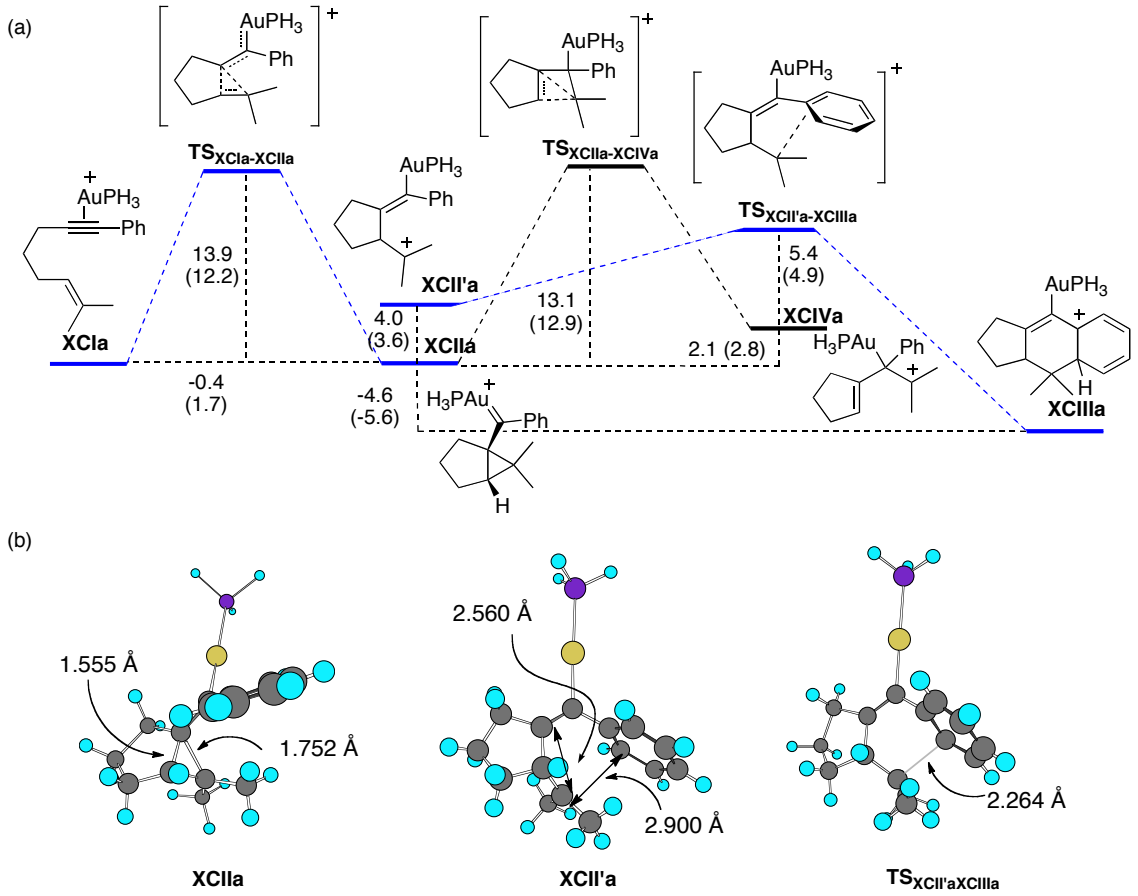
Scheme 62: Reaction pathway and energies for the *exo*-cycloaddition of **XCIa** to Wheland intermediate **XCIIIa** [a]



[a] Calculations at the B3LYP/6-31G(d) (C, H, P), LANL2DZ (Au) level (+ ZPE-corrected electronic energies are given in kcal·mol^{-1}; ΔG in brackets), including solvent effect for CH_2Cl_2.

The mechanistic studies of the endocyclic pathway revealed that the reaction proceeds by an initial formation of the intermediate **XCV'a**, which closes to form the cyclopropyl gold(I)-carbene intermediate **XCVa**.[194] The transition state that connects both intermediates could not determined (Scheme 63). Intermediate **XCVa** via **TS$_{XCVa-XCVIa}$** evolves by a Friedel-Crafts-type process to form **XCVIa**. On the other hand, the formation of the carbocation **XCVIIa** via **Ts$_{XCVa-XCVIIa}$** proceeds with much higher activation energy.

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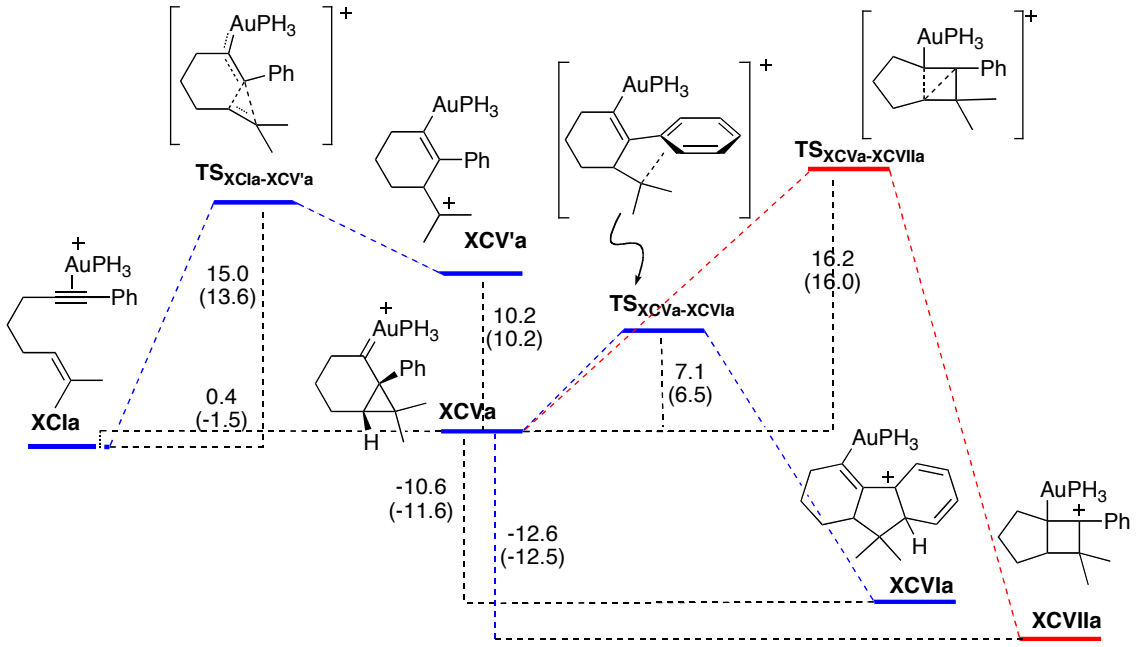
Scheme 63: Reaction pathway and energies for the *endo*-cycloaddition of **XCIa** to Wheland intermediate **XCVIa** or cyclobutene precursor **XCVIIa**.[a]



[a] Calculations at the B3LYP/6-31G(d) (C, H, P), LANL2DZ (Au) level (+ ZPE-corrected electronic energies are given in kcal·mol^{-1}; ΔG in brackets), including solvent effect for CH_2Cl_2.

Therefore, the proposed mechanism of the [4+2] cycloaddition reaction of arylenynes proceeds via **XCIa-XCIIIa**, followed by aromatization to form alkenyl gold intermediate **XCVIII**. Proto-demetallation of **XCVIII** forms **XCIX** (Scheme 64). Furthermore for substrates such as **XCIa**, the rate determining step is the attack of the alkene to the alkyne coordinated to Au(I) and not the electrophilic aromatic substitution. This fact explains the results obtained previously, since the presence of electro-withdrawing groups at the para position did not slow the overall reaction rate (see Table 16).

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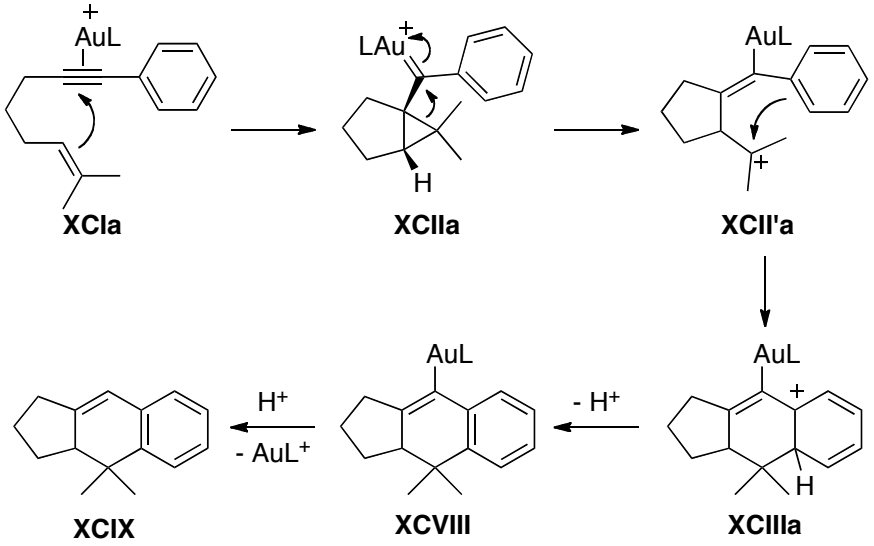
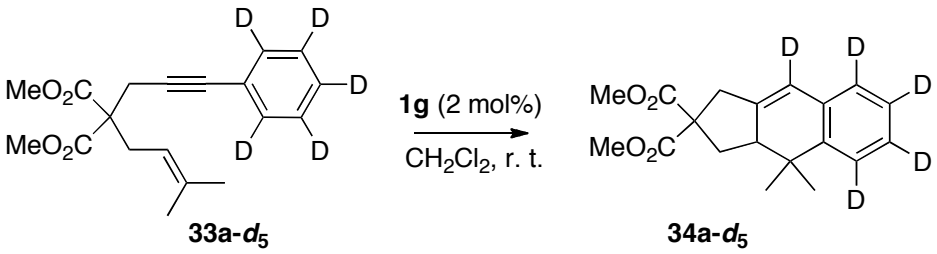
Scheme 64



Besides the DFT calculations, an experiment with **33a-*d*$_5$** to confirm that the deuterium that is lost from the aryl group ends up at the position that was activated by gold(I) (see **XCIIIa** in Scheme 62) to give selectively **34a-*d*$_5$** (Scheme 65).

Scheme 65 [a]



[a] 66% deuterium content at the alkene

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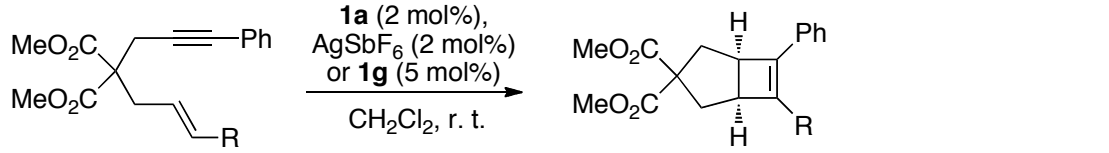
ISBN:978-84-693-7664-5/DL:T-1746-2010

3.2. *Cycloaddition of arylenynes with less substituted alkenes.*

The reaction of enynes **38a** and **38b** were also studied. In these cases cyclobutenes **39a** and **39b** were obtained, which suggests that [4+2] cycloaddition reaction only proceeds with substrates with substituents at the alkene capable to stabilize a carbocation intermediate. The best results obtained were when **1a** was used as catalyst (Scheme 66). This type of cyclobutenes had been reported before [26a,b] using palladacylopentadienes and Pt(II) as catalyst under a CO atmosphere.[40b]

Scheme 66



38b: R = H
38j: R = Me

39b'': R = H (3 h, 57% with **1a**; 33% with **1g**)
39j'': R = Me (12 h, 77% with **1a**; 64% with **1g**)

Mechanistic Discussion.

Mechanistic studies by DFT calculations[194] on formation of the cyclobutenes reveals that *syn*-cyclopropyl gold(I) carbene **XCIIc** is not formed from **XCIb** due to the high activation energy. The formation of the *anti*-cyclopropyl gold(I) carbene **XCIIb** is more likely, which can undergo bond-rotation to form the *syn*-**XCIIc** ($\Delta G^{\ddagger}$ = 8.6 kcal·mol^{-1}) (Scheme 67).

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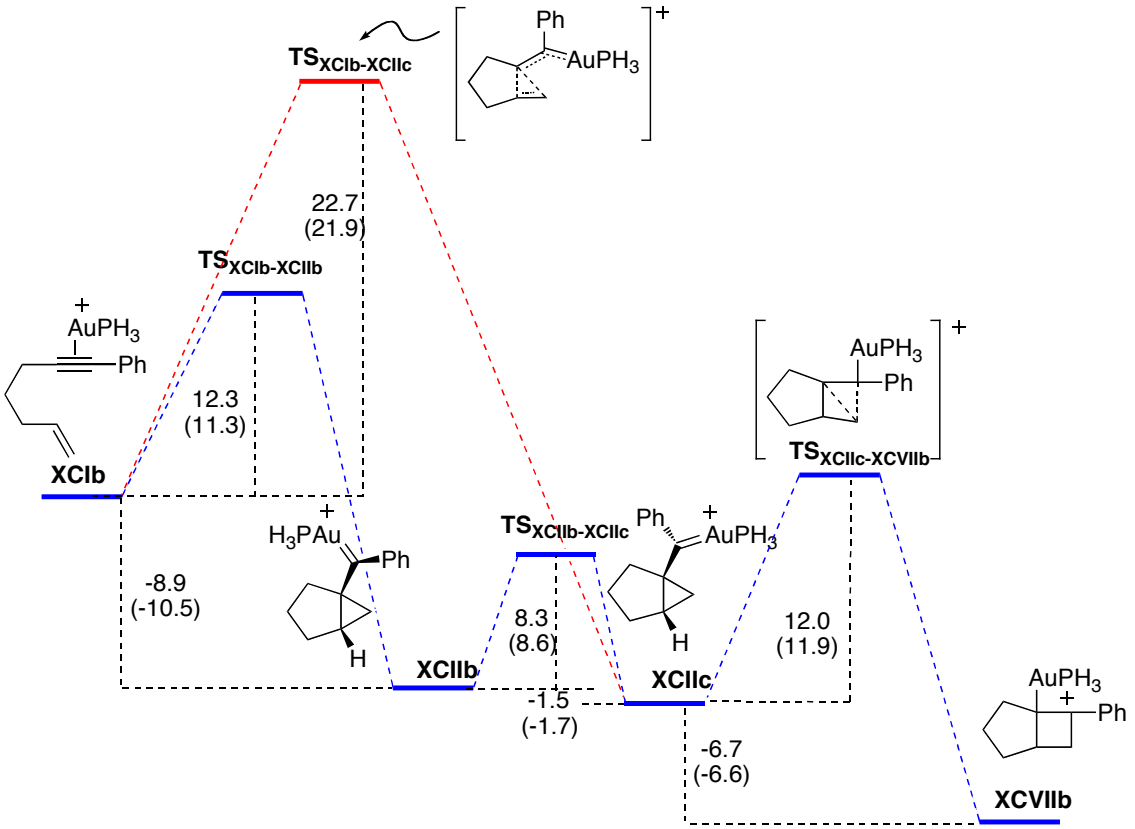
Scheme 67: Reaction Pathway and Energies for the Reaction of **XCIb** to Cyclobutene Precursor **XCVIIb** via **XCIIc**



[a] Calculations at the B3LYP/6-31G(d) (C, H, P), LANL2DZ (Au) level (+ ZPE-corrected electronic energies are given in kcal·mol^{-1}; ΔG in brackets), including solvent effect for CH_2Cl_2.

Overall, according to the calculations, *syn*-cyclopropyl carbene **XCIIc** opens to form **XCVIIb** with activation energy of 11.9 kcal·mol^{-1}. The isomerization of the syn cyclopropyl carbene to anti competes with the opening of **XCVb** to form **XCVIIb** (formation of **XCVb** by endocyclic pathway) (Scheme 68). Presumably carbocation **XCVIIb** gives **Cb** by a proton-elimination, followed by the protonolisys of the C-Au bond. These two mechanisms compete to obtain the cyclobutenes.

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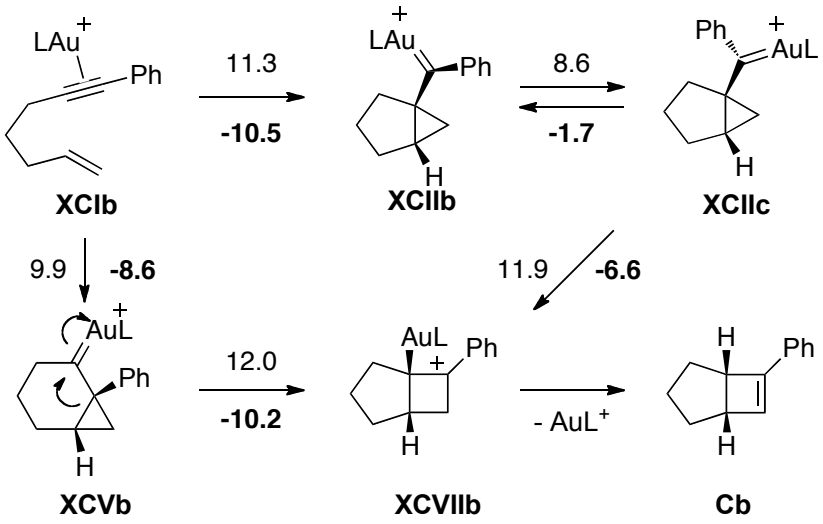
Scheme 68: Two pathways for the formation of **Cb** from **XCIb**[a]



[a] Energies correspond to $\Delta G^{\ddagger}$ and ΔG (bold face) in kcal·mol^{-1}.

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3.3. *Cycloaddition of Dienynes.*

We also studied the scope and limitations of the reaction of 1,8-dien-3-ynes with gold(I)-catalysts by a 5-*exo*-dig pathway to form hydrindanes. Enyne **40a** led to **41a** in moderate yield when catalyst **1g** was employed (Table 19, entry 1). When the same catalyst was assayed under microwave heating the yield increase considerably and the reaction time decrease to 10 minutes (Table 19, entry 2). Enyne **40b** reacted under different conditions and different catalysts and the best results were obtained when the reaction was carried out with catalyst **1g** under microwave heating (Table 19, entry 4-7) to give hydrindane **41b** in excellent yield. Enyne **40c** gave **41c** in almost quantitative yield using catalyst **1g** (Table 19, entry 8). However when $PtCl_2$ was used only decomposition products were observed (Table 19, entry 9). In contrast, enynes **40d**, **40e**, and **40j** suffered decomposition under these conditions (Table 19, entries 10-11, 18). Enynes **40f**, **40g**, **40k**, and **40i** led to complex mixture of products (Table 19, entries 12-13, 16, 19). In the case of enyne **40h** with catalyst **1g**, **42** was obtained as a major product, which corresponds to the attack of the malonate to the activated alkyne-gold(I) complex (Table 19, entry 15). The configuration of the products was determined by NMR studies.

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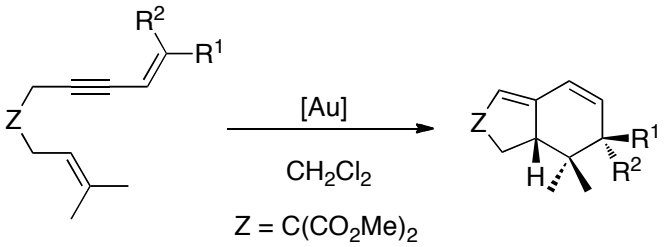
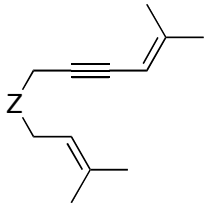
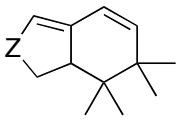
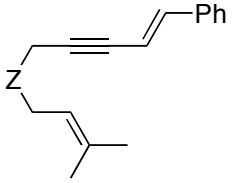
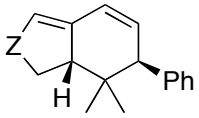
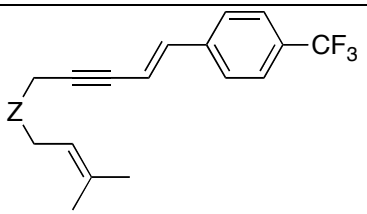
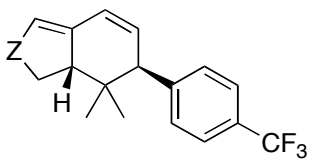
Table 19: Au(I)-catalyzed cyclization of 1,8-dien-3-ynes **40a**-**40k** [Z = $C(CO_2Me)_2$][a]



Entry	Substrate	Catalyst	Time (min)	Product(s) (yield, %)
1	 **40a**	**1g**	120	 **41a** (52)
2[b]	**40a**	**1g**	10	**41a** (72)
3	**40a**	**2a** / $AgSbF_6$	30	**41a** (70)
4	 **40b**	**1g**	120	 **41b** (77)
5[b]	**40b**	**1g**	12	**41b** (90)
6	**40b**	**2a** / $AgSbF_6$	15	**41b** (71)
7[b]	**40b**	**2a** / $AgSbF_6$	10	**41b** (75)
8	 **40c**	**1g**	50	 **41c** (94)

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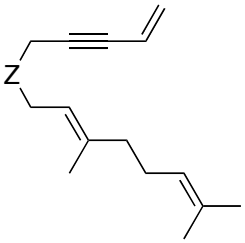
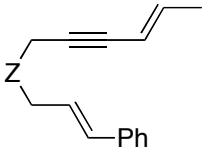
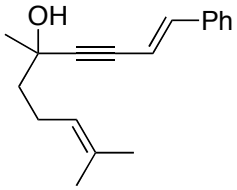
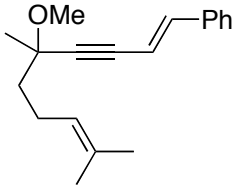
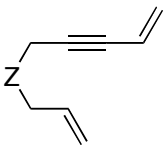
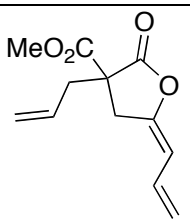
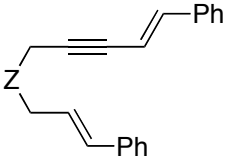
9[c]	**40c**	$PtCl_2$	180	decomposed
10	 **40d**	**1g**	180	decomposed
11	 **40e**	**1g**	180	decomposed
12	 **40f**	**1g**	180	Complex mixture of products
13	 **40g**	**1g**		Complex mixture of products
14	 **40h**	**1g**	48h	 **42** (80)
16	 **40i**	**1g**	3h	Complex mixture of products
17[b]	**40i**	**1g**	10	Complex mixture of products

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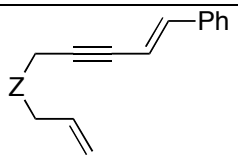
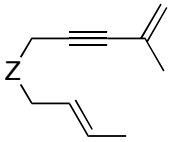
18[b]	 **40j**	**1g**	10	Decomposition + traces hydroxycyclization
19[b]	 **40k**	**1g**	10	Complex mixture of products

[a] Reactions carried out at r. t. in CH_2Cl_2 with 2 mol% catalyst. [b] Reaction under microwave heating in CH_2Cl_2 at 80°C with 2 mol% catalyst. [c] Reaction carried out with dioxane as a solvent and 70ºC. [d] CD_2Cl_2 as a solvent

Mechanism Discussion.

Mechanistic studies based on DFT calculations[196] on the formation of the hydrindanes revealed that the reaction proceeds by an initial formation of **CIa**, which is attacked by the alkene to afford **CIIIa**, via intermediate **CIIa**. This mechanism accounts for the configuration observed in **41b** and **41c**. Formation of **CIVa**, with the opposite configuration, requires a higher activation energy (Scheme 69).

196 DFT calculations were done by Prof. Diego J. Cárdenas and Dr. Araceli Campaña (UAM).

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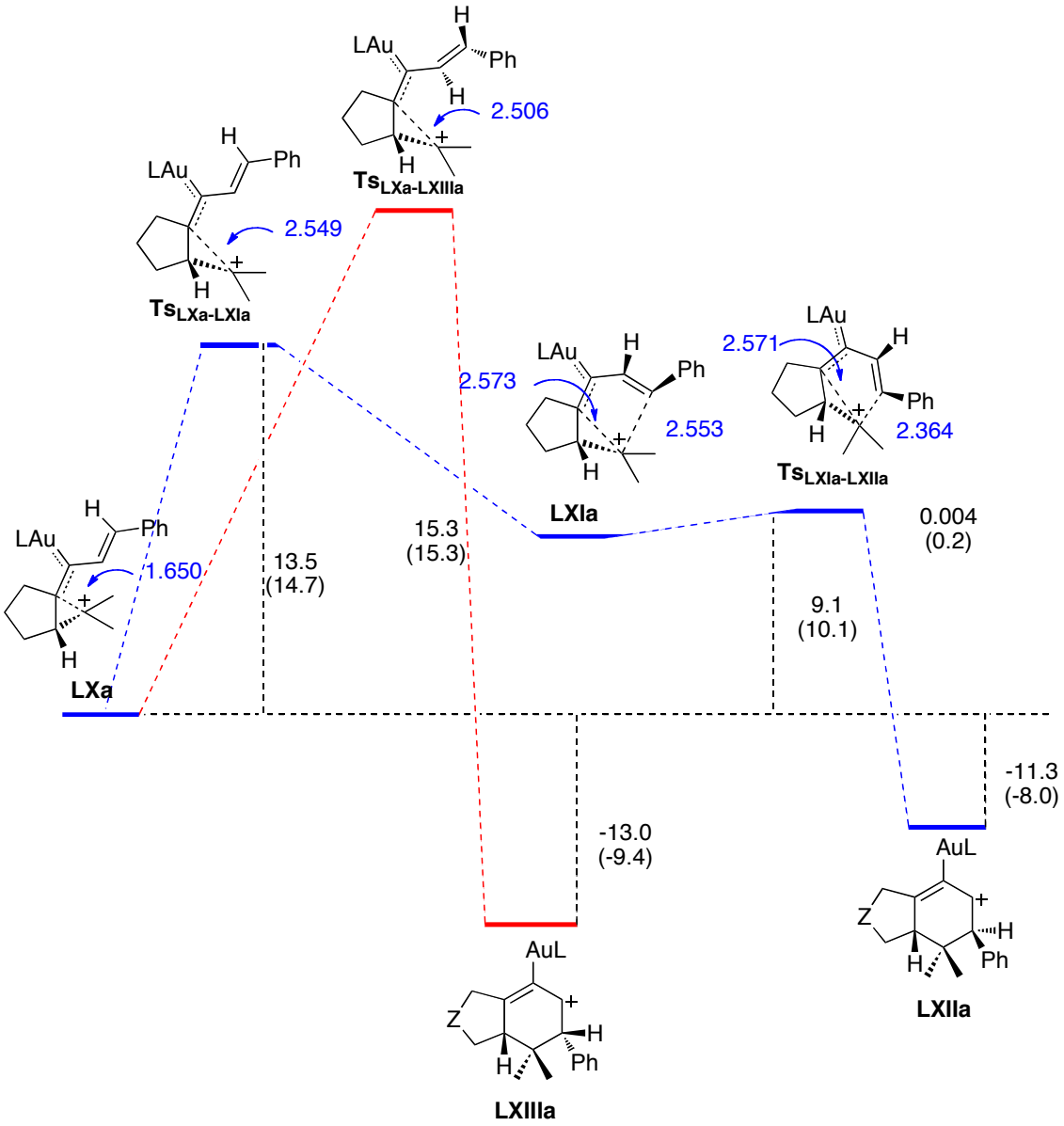
Scheme 69: Reaction Pathway and Energies for the Reaction of **CIa** to Hydrindane Precursor **CIIIa** via **CIIa**



Overall, the formation of hydrindanes **41a-41c** takes place by a 5-*exo*-dig pathway to form an intermediate such as **CI**, followed by attack of the alkene to form intermediate **CIII** (Scheme 70).

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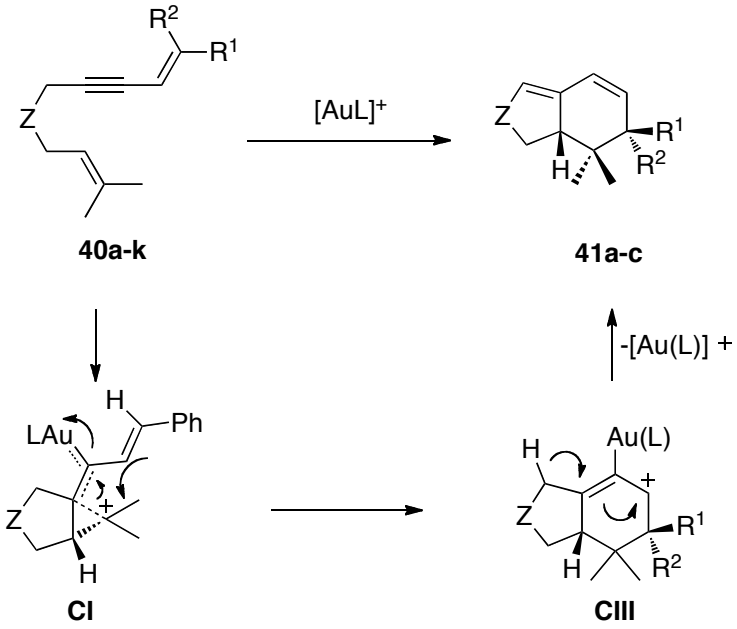
Scheme 70



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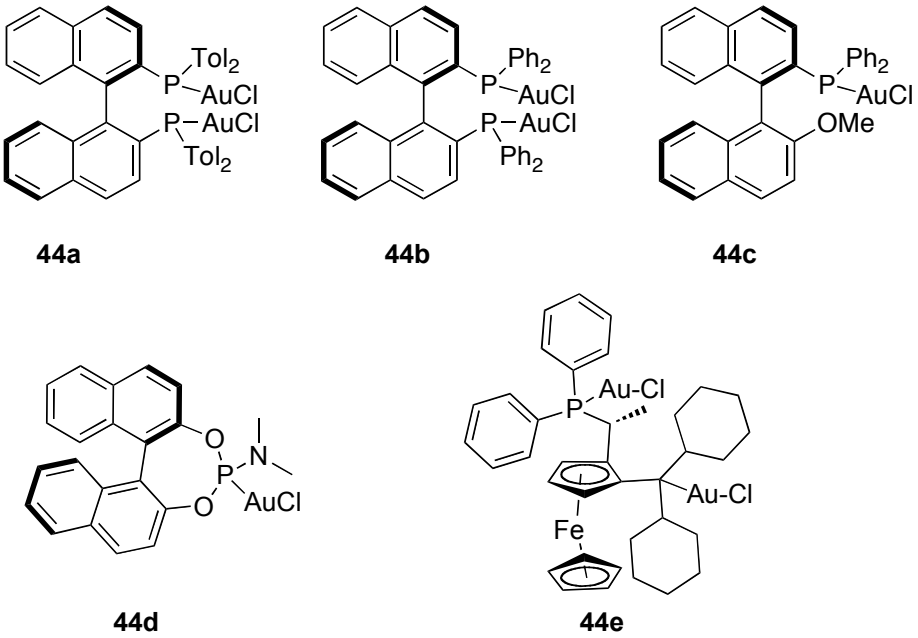
3.4. *Enantioselective [4+2] cycloaddition reaction.*

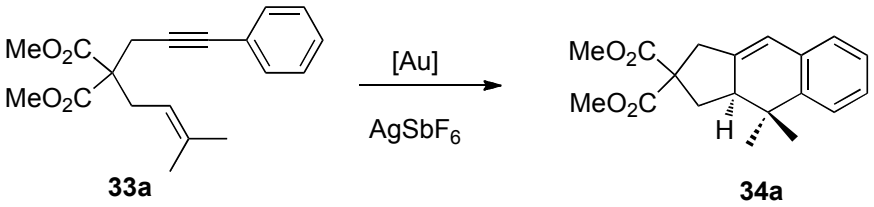
Different chiral ligands were tested in the [4+2] cycloaddition reactions to develop the enantioselective version of this reaction. Previous work on gold(I)-catalyzed methoxycyclizations showed that bidentate ligand TolBINAP gave the best results.[111b,147] Related bulky ligands, including TolBINAP were tested (Figure 9). Results with these catalysts are shown in the Table 20.



44a **44b** **44c** **44d** **44e**

Figure 9

Table 20: Results of asymmetric [4+2] cycloaddition [a]



33a **34a**

Entry	Catalyst	Time (h)	Yield (%)	ee (%)
1	**44a**	48	94	26
2	**44b**	48	94	24
3	**44c**	78	50	18

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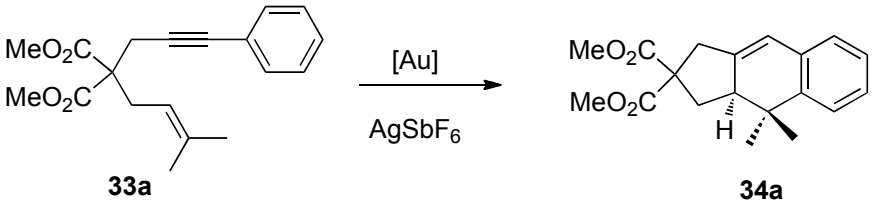
4	**44d**	50	93	16
5	**44e**	78	76	0

[a] Reaction conditions: 10 mol% of catalyst, 10 mol% of $AgSbF_6$, 2 mL dry CH_2Cl_2 at r. t..

Low enantioselectivities were obtained using complexes **44a**-**44e**. The effect of different solvents in the enantiomeric excesses was studied (Table 21).

Table 21: Solvent effect in the enantiomeric excesses [a]



33a **34a**

Entry	Catalyst	Solvent	Yield	ee (%)
1	**44a**	$ClCH_2CH_2Cl$	85	14
2	**44a**	$CHCl_3$	91	38
3	**44a**	toluene	-	[b]
4	**44a**	CH_2Cl_2	94	26
5	**44d**	$ClCH_2CH_2Cl$	97	16
6	**44d**	$CHCl_3$	86	26
7	**44d**	toluene	-	[b]
8	**44d**	CH_2Cl_2	93	16

[a] reaction conditions: 10 mol% of the catalysts, 10 mol% of $AgSbF_6$, 2 mL dry solvent at r. t.. [b] no reaction is observed

From these results, it can be concluded that the solvent plays a role in the enantiomeric excess, and that the best results were obtained in $CHCl_3$ (Table 21, entry 2).

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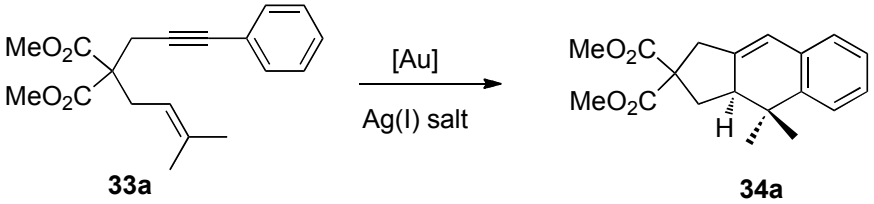
The effect of the counter anion was also studied since it is know that the anions affect the reaction rates and enantiomeric excesses [197] (Table 22).[198]

Table 22: Effect of counter anions [a]



33a **34a**

Entry	Catalyst	Silver salt	Time (h)	Yield (%)	ee (%)
1[b]	**44a**	Ag_2CO_3	120	-	[b]
2	**44a**	$AgSbF_6$	24	94	38
3	**44a**	$AgPF_6$	24	89	56
4[c]	**44a**	$AgPF_6$	0.2	89	56
5[b]	**44a**	$AgNO_3$	120	-	-
6[b]	**44a**	$AgBF_4$	24	86	42
7	**44a**	AgTFA	120	-	-
8	**44a**	$AgCF_3SO_3$	24	96	10
9[d]	**44b**	Ag_2CO_3	24	-	[b]
10[e]	**44b**	Ag_2CO_3	0.2	-	[b]
11[d]	**44b**	$AgSbF_6$	24	94	24
12[e]	**44b**	$AgSbF_6$	0.2	92	6.5
13[d]	**44b**	$AgPF_6$	24	81	31
14[e]	**44b**	$AgPF_6$	0.2	90	39
15[d]	**44b**	$AgNO_3$	120	-	-
16[e]	**44b**	$AgNO_3$	0.2	-	-
17[d]	**44b**	$AgBF_4$	24	85	20
18[e]	**44b**	$AgBF_4$	0.2	90	21

197 (a) Kündig, P.; Saudan, C.M.; Bernardinelli, G. *Angew. Chem. Int. Ed*. **1999**, *38*, 1219-1223. (b) Källström, K.; Munslow, I.; Andersen, P.G. *Chem. Eur. J*. **2006**, *12*, 3196-3200. (c) Huang, Y.; Iwama, T.; Rawal, V. H. *J. Am. Chem. Soc.* **2000**, *122*, 7843-7844.

198 This part of the work was carried out in collaboration with Dr. Christophe Bour.

19[d]	**44b**	AgTFA	120	-	-
20[e]	**44b**	AgTFA	0.2	-	-
21[d]	**44b**	$AgCF_3SO_3$	24	90	26
22[e]	**44b**	$AgCF_3SO_3$	0.2	87	29
23[d]	**44c**	Ag_2CO_3	78	-	[b]
24[e]	**44c**	Ag_2CO_3	0.2	-	[b]
25[d]	**44c**	$AgSbF_6$	78	50	18
26[e]	**44c**	$AgSbF_6$	0.2	78	20
27[d]	**44c**	$AgPF_6$	78	67	23
28[e]	**44c**	$AgPF_6$	0.2	84	25
29[d]	**44c**	$AgNO_3$	78	-	-
30[e]	**44c**	$AgNO_3$	0.2	-	-
31[d]	**44c**	$AgBF_4$	24	70	10
32[e]	**44c**	$AgBF_4$	0.2	88	18
33[d]	**44c**	AgTFA	78	-	-
34[e]	**44c**	AgTFA	0.2	-	-
35[d]	**44c**	$AgCF_3SO_3$	78	67	16
36[e]	**44c**	$AgCF_3SO_3$	0.2	68	20
37[d]	**44d**	Ag_2CO_3	24	-	[b]
38[e]	**44d**	Ag_2CO_3	0.2	-	[b]
39[d]	**44d**	$AgSbF_6$	24	93	16
40[e]	**44d**	$AgSbF_6$	0.2	95	12
41[d]	**44d**	$AgPF_6$	24	88	9
42[e]	**44d**	$AgPF_6$	0.2	94	14
43[d]	**44d**	$AgNO_3$	120	-	-
44[e]	**44d**	$AgNO_3$	0.2	-	-
45[d]	**44d**	$AgBF_4$	24	82	8
46[e]	**44d**	$AgBF_4$	0.2	88	8
47[d]	**44d**	AgTFA	78	-	-
48[e]	**44d**	AgTFA	0.2	-	-
49[d]	**44d**	$AgCF_3SO_3$	78	89	11

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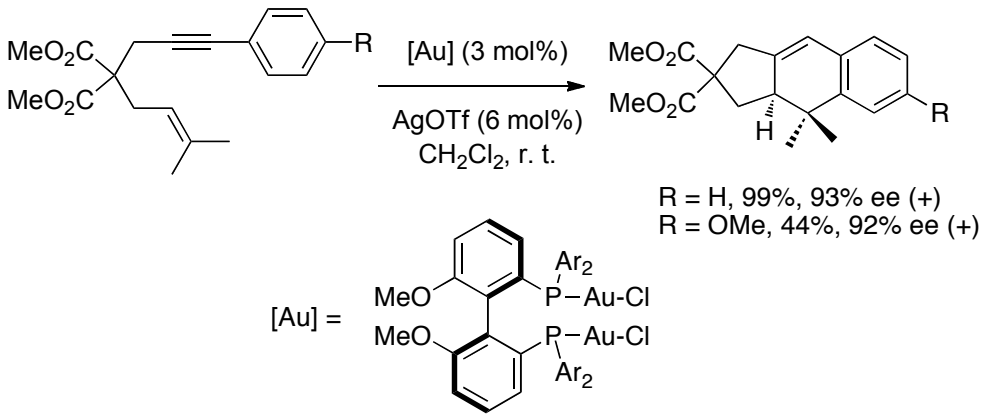
50[e]	**44d**	$AgCF_3SO_3$	0.2	78	11

[a] reaction conditions : 5 mol% of **44a**, 2.5 mol% of silver salt, 2mL of $CHCl_3$, at r. t.. [b] no reaction is observed. [c] Reaction carried out under microwave heating. [d] At r. t. and using CH_2Cl_2 as solvent. [e] Reaction carried out under microwave heating using CH_2Cl_2.

The enantiomeric excesses varied considerably with different counter anions and also when the reaction was carried out under microwave heating versus room temperature. Overall the best results were obtained using $AgPF_6$ and microwave irradiation (Table 22, entry 3, 13-14, 27-28, 41-42). Therefore, the best results (56% ee) were obtained with **44a** (Tol-BINAP as a ligand), using $CHCl_3$ as a solvent, under microwave heating (80 ºC, 20 min), and $AgPF_6$ as a counterion.

More recently, the enantioselective [4+2] cycloaddition reaction of 1,6-enynes using (*R*)-4-OMe-3,5-(*t*-Bu)$_2$MeOBIPHEP(AuCl)$_2$ as catalyst was reported (Scheme 71).[157]

Scheme 71



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3.5. *Application of the [4+2] cycloaddition reaction towards the total synthesis of the pycnanthuquinones.*

The carbon skeleton of the products obtained in the [4+2] cycloaddition reaction catalyzed by gold(I)-catalysts (Figure 10) is the same than that of the pycnanthuquinones A, B and C.

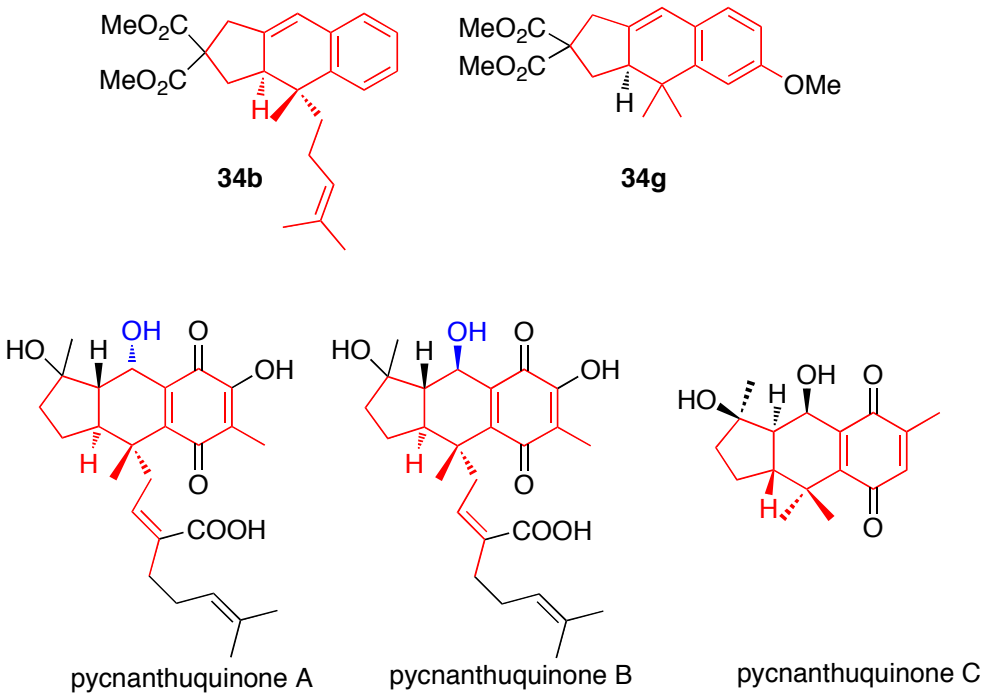
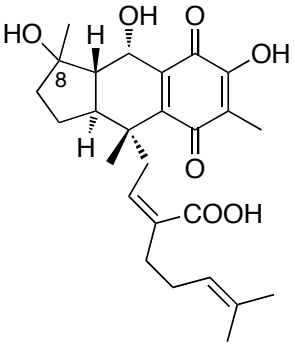


Figure 10

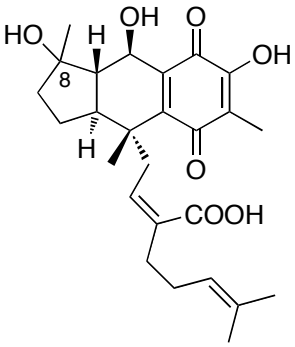
Pycnanthuquinone A and B were extracted from the extracts of leaves and stems of an African tree *Pycnanthus angolensis*,[199] or the common "African nutmeg", which grows in West and Central Africa (Figure 11). This tree was chosen because traditional healers used this plant for the treatment of oral thrush, fungal skin infections, headache, body aches, and chest pain. All those symptoms can occur when a person have Type 2 diabetes mellitus (disorder that is characterized by high blood glucose in the context of insulin resistance and relative insulin deficiency). Hot water extract of the bark is used as a purgative, to treat leprosy, and to treat

199 Fort, D. M.; Ubillas, R. P.; Mendez, C. D.; Jolad, S. D.; Inman, W. D.; Carney, J. R.; Chen, J. L.; Ianiro, T. T.; Hasbun, C.; Bruening, R. C.; Luo, J.; Reed, M. J.; Iwu, M.; Carlson, T. J.; King, S. R.; Bierer, D. E.; Cooper, R. *J. Org. Chem*. **2000**, *65*, 6534-6539..

sterility in women in Guinea.[200] Other extracts were used against rheumatism, hemorrhoids,[201] anthelmintic,[202] for the treatment of toothache, and various skin diseases.[203] The only compounds reported in the literature from this tree were allantoin,[204] flavanoids,[205] kombic acid,[206] dihydroguaiaretic acid,[207] and pycnanthuquinones A and B.[199]



Pycnanthuquinone A



Pycnanthuquinone B

Figure 11

Pycnanthuquinone A and B are novel terpenoid-type quinone structures

200 Viera, A. *Subsidio para o Estudo da Flora Medicinal da Guinea Portuaguesa*; Agencia General do Ultramar: Lisboa, Portugal, 1959.

201 Akendengué, B. *J. Ethnopharmacol*. **1992**, *37*, 165-173.

202 Ayensu, E. S. *Medicinal Plants of West Africa*; Reference Publications: Algonac, Michigan, 1978.

203 Keay, R. W.; Onochie, C. F. A.; Stanfield, D. P. *Nigerian Trees*; Federal Department of Forest Research Publication: Ibadan, Nigeria, 1964.

204 Noguiera, P. L.; Correia Alves, A.; Fátima C.; De Araújo, M. *Garcia Orta* **1960**, 8, 327-331.

205 Omobuwajo, O. R.; Adesanya, S. A.; Babalola, G. O. *Phytochemistry* **1992**, *31*, 1013-1014.

206 Lok, C. M.; Groenewegen, A.; Stroink, J. B. A.; Ward, J. P. *Phytochemistry* **1983**, *22*, 1973-1976.

207 Njoku, C. J.; Hopp, D. C.; Alali, F.; Asuzu, I. U.; McLaughlin, J. L. *Planta Med.* **1997**, *63*, 580-581.

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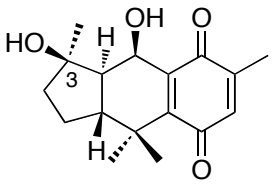
containing a fused 6,6,5-ring skeleton. A test using a db/db mouse model for Type 2 diabetes revealed that pycnanthuquinone A and B are potentially new drugs for the treatment of this disease. The configuration of both compounds was determined by NMR experiments, allowing the assignment of the ring junction as trans and also the relative configuration of C-1 and C-2. However the relative configuration at C-8 (Figure 11) could not be determined due to the lack of NOE crosspeaks from the methyl group at that carbon to any other protons.

Pycnanthuquinone C was isolated from *Cystophora harveyi* Womersley (Figure 12), which is a brown alga that lives in Western Australia waters, near Cape Leeuwin.[208]

Cystophora harveyi Womersley



Pycnanthuquinone C

Figure 12: Image of the alga and pycnanthuquinone C

The isolation of this novel geranyltoluquinone received the name of pycnanthuquinone C because contained a linearly fused 6,6,5-ring system with a similar backbond of pycnanthuquinone A and B (Figure 12). Some of the compounds found in this alga are being used as Asian medicinal herbs.[209,210]

The configuration of pycnanthuquinone C was assigned by NMR experiments that reveals the relative configuration of that compound to be partially assigned as 1*R**, 2*R**, 6*R**. The configuration at C-3 could not determined by NMR experiments, although molecular modeling (MMFF) experiments suggested a 3*R** configuration at C-3.

208 Laird, D.W.; Poole, R.; Wikström, M.; van Altena, I. A. *J. Nat. Prod*. **2007**, *70*, 671-674.

209 Resh, M.; Steigel, A.; Chen, Z.; Bauer, R. *J. Nat. Prod*. **1998**, *61*, 347-350.

210 Pachaly, P.; Lansing, A.; Sin, K. S. *Planta Med*. **1989**, *55*, 59-6.

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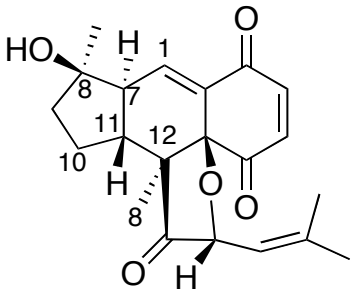
Recently, the structure of a novel meroterpenoid metabolite rossinone B[211] (Figure 13) was isolated from an Antarctic collection of an *Aplidium* ascidian. This molecule is also a terpenoid-type quinone structure containing a fused 6,6,5-ring skeleton such as pycnanthuquinones A, B and C. The rossinone B exhibited antileukemic, antiviral, and anti-inflammatory activity. This linear fused 6,6,5-ring core is extremely rare, being the skeleton of only the pycnanthuquinones and rossinone B.



Rossinone B

Figure 13: Structure and relative configuration of Rossinone B

We tried to apply the [4+2] cycloaddition reaction towards the synthesis of the pycnanthuquinones. First we carried out the reaction of enyne **33u** with catalyst **1g**, which led to tricycle **34u** with the same carbon skeleton that the pycnanthuquinones A and B (Scheme 72). On the other hand, reaction of **33v** gave **34v**, but only in 35% yield.

211 Appleton, D. R.; Chuen, C. S.; Berridge, M. V.; Webb, V. L.; Copp, B. R. *J. Org. Chem.* **2009**, *74*, 9195-9198.

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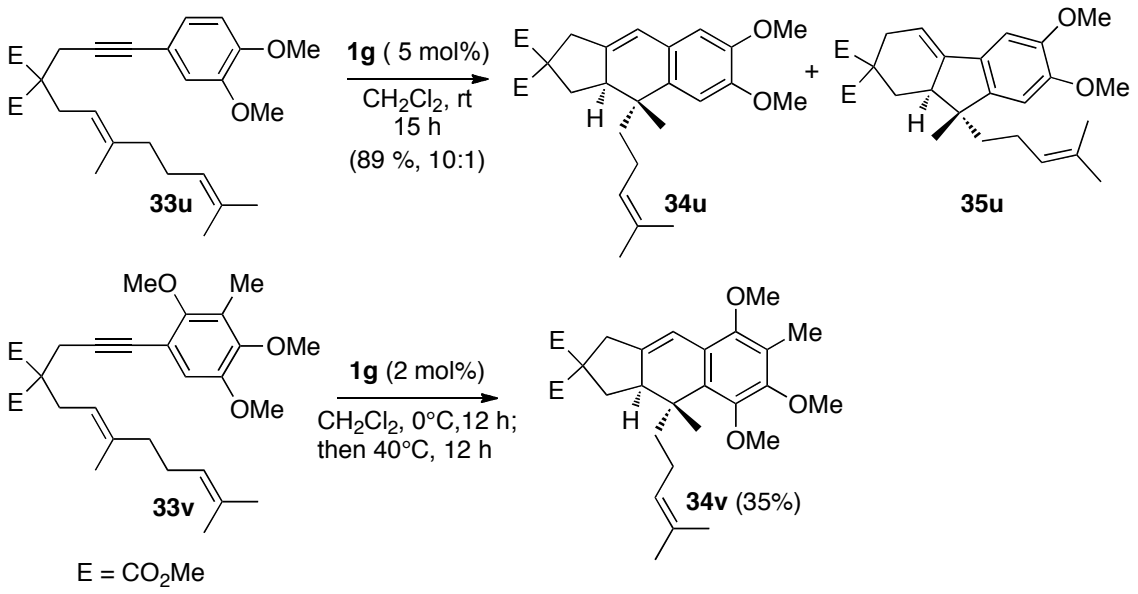
Scheme 72



Enynes **46a-q** were also synthesized as model compounds for the synthesis of pycnanthuquinones A, B and C. However, all the attempted cyclization failed using a variety of gold(I) complexes as catalysts (Scheme 73). [212]

212 Results obtained from Dr. Thorsten Lauterbach, ICIQ, Tarragona, 2007-2008

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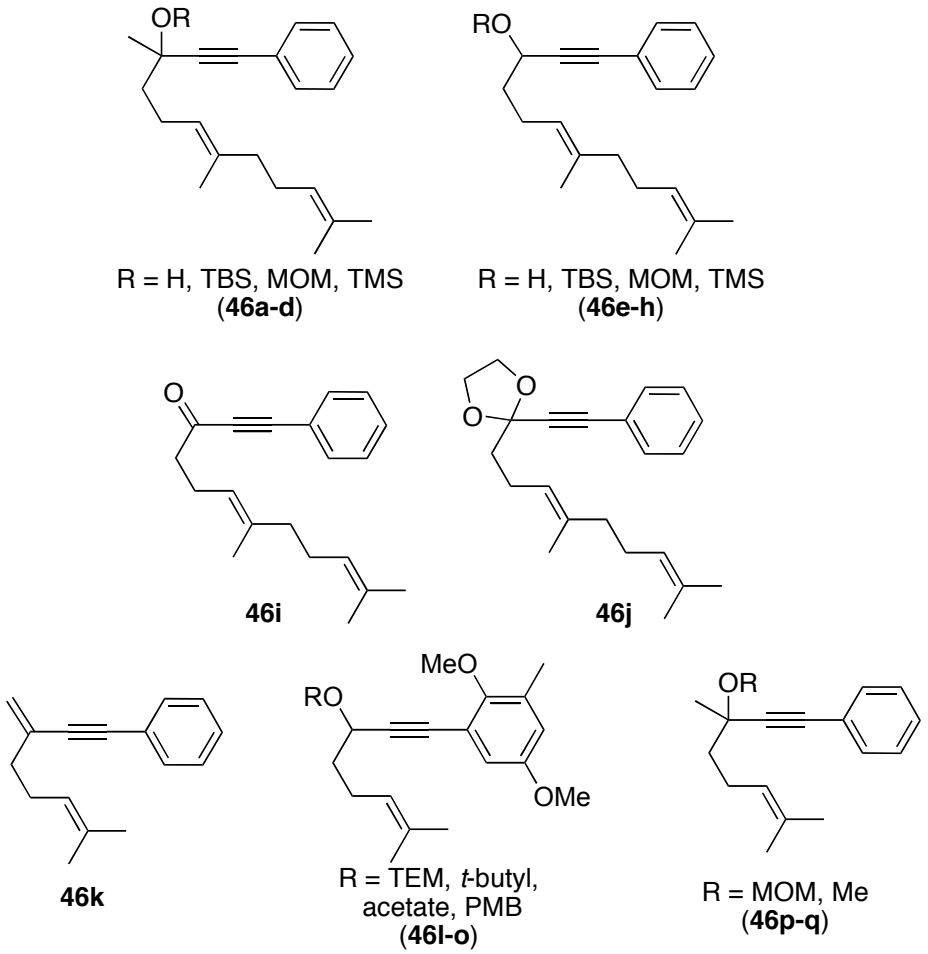
Scheme 73



On the other hand, more simple substrates **46r-s** reacted with gold(I) catalysts to give products **47-48** (Scheme 74). These results are consistents with the mechanism shown in Scheme 74.[91]

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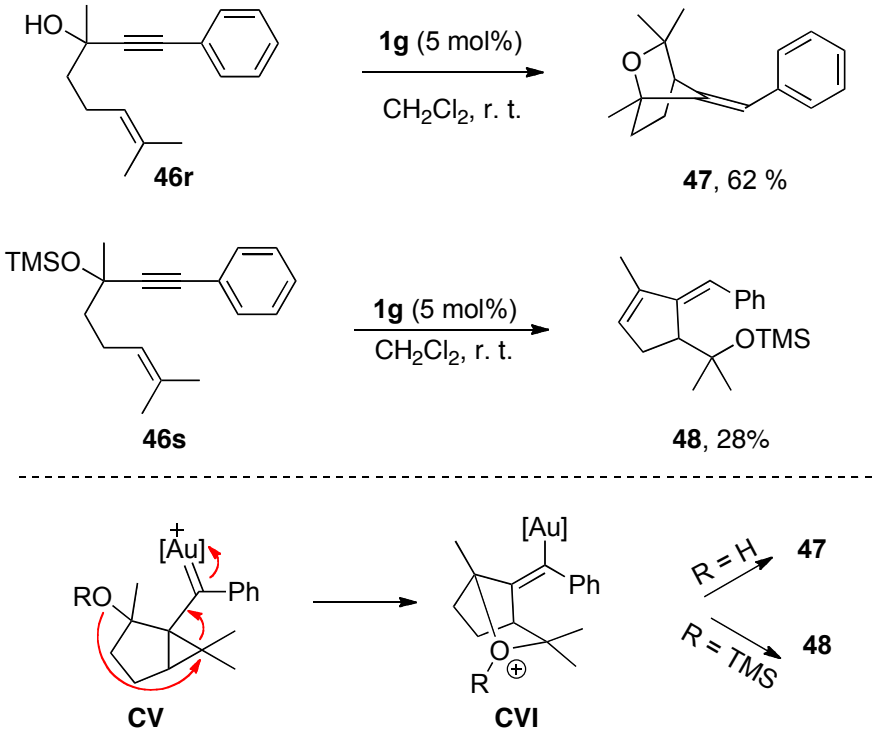
Scheme 74



Substrates **46t** and **46u** with secondary alcohols reacted with gold(I) differently to afford compounds **49** and **50**, respectively (Scheme 75). The mechanism corresponds a first formation of intermediate **CVII** via 6-*endo*-dig pathway.

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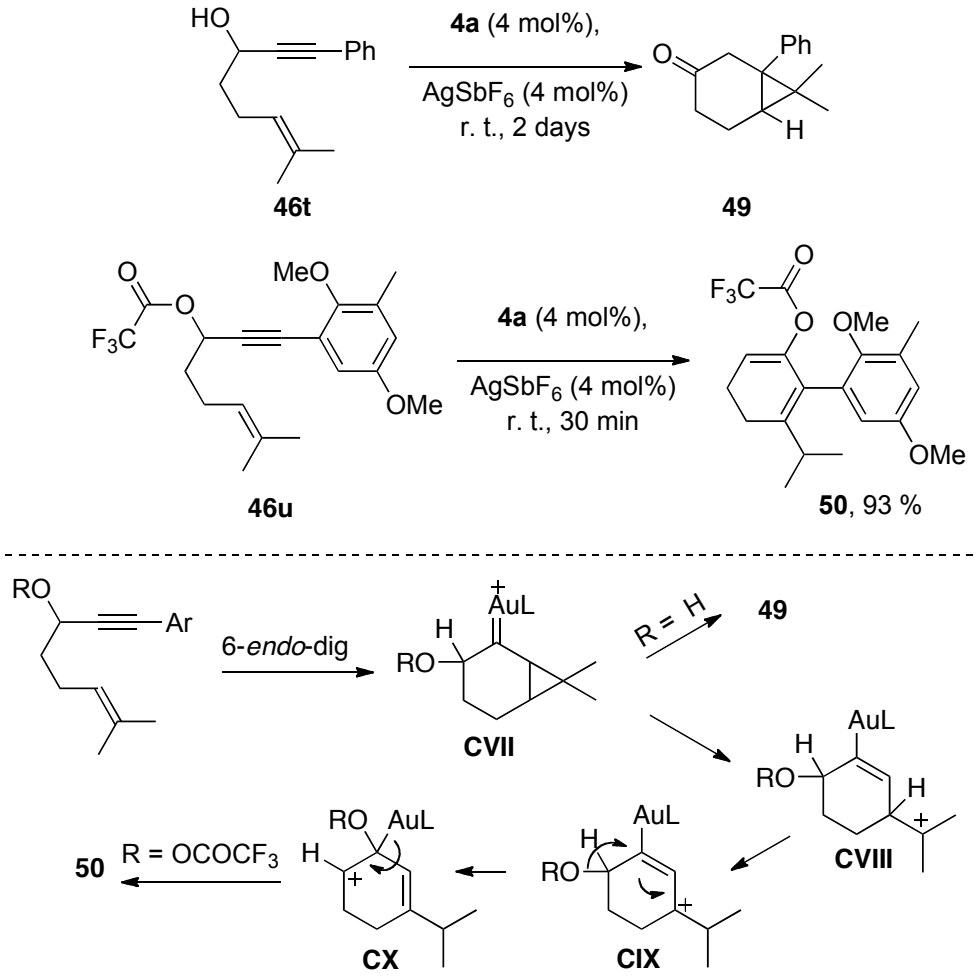
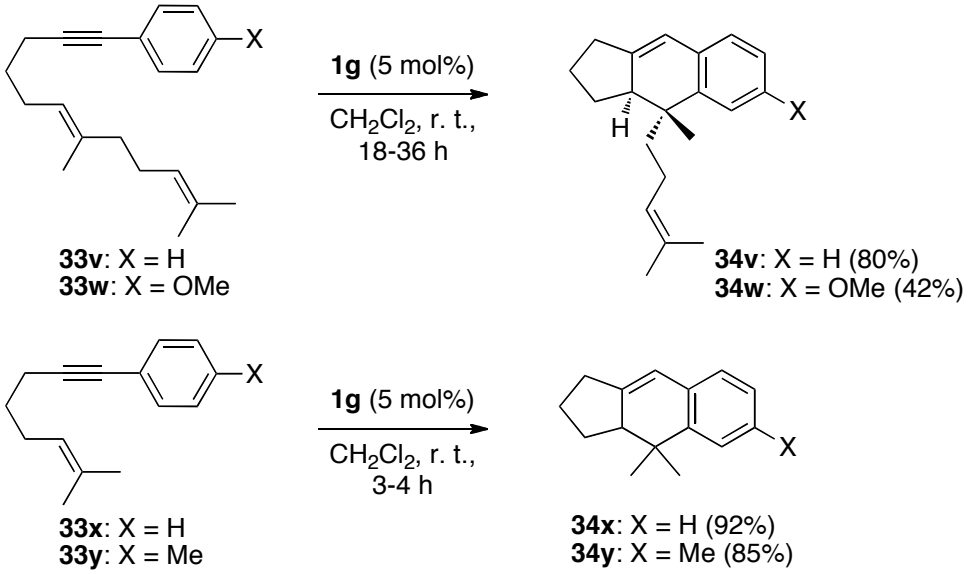
Scheme 75



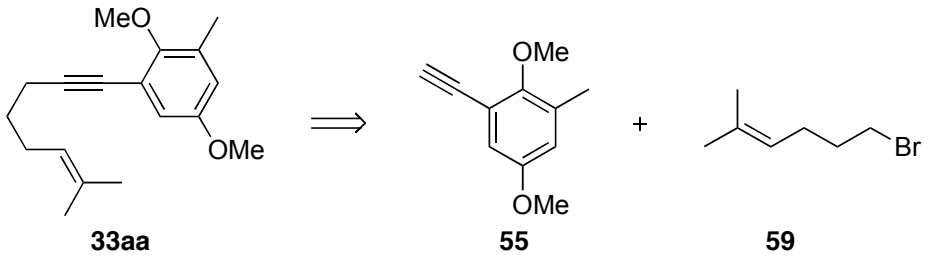
Finally, substrates **33w-z**, lacking any propargylic substituents, were allowed to react with catalyst **1g** (Scheme 76). The cyclization of these compounds proceeded uneventfully to give **34w-z** in moderate to good yields. It is, however important to note that in these cases the enynes are not substituted at the tether and, therefore do not benefit from any Thorpe in-gold effect.

Scheme 76



Therefore, for the synthesis of pycnanthuquinone C, we decided to prepare enyne **33aa** by alkylation of the lithium acetylide derived from **55** with known bromide **59**.

Scheme 77



The synthesis of the arylalkyne **55** started from commercial available *o*-cresol (Scheme 78).[213] Bromination of **51** led to **52** in 97% yield. Oxidation of 52 with CrO_3 gave 1,4-benzoquinone **53** (98% yield), which was followed by reduction with $Na_2S_2O_4$ and methiation to give dimehtyl ether **54** (73% yield). Stille coupling with tri-n-butylstanyl acetylene gave **55** in 82% yield. [214]

213 D. J. Maloney, S. M. Hecht, *Org. Lett.* **2005**, *7*, 4297-4300

214 Results obtained in collaboration with Dr. Thorsten Lauterbach.

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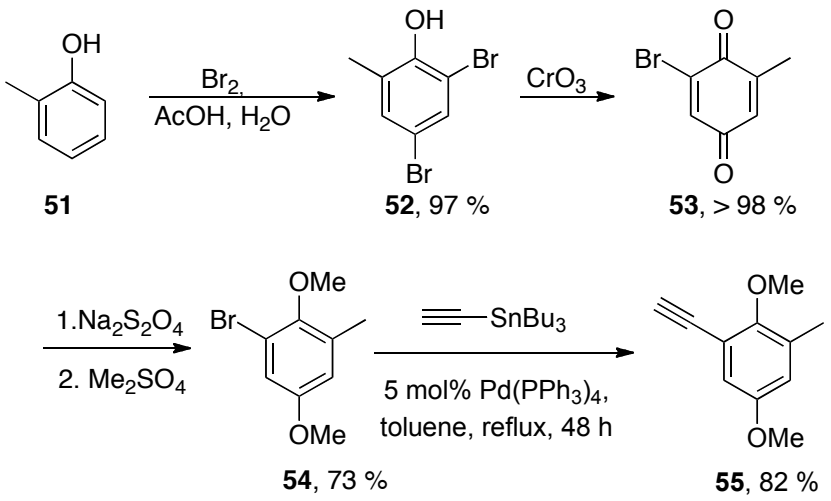
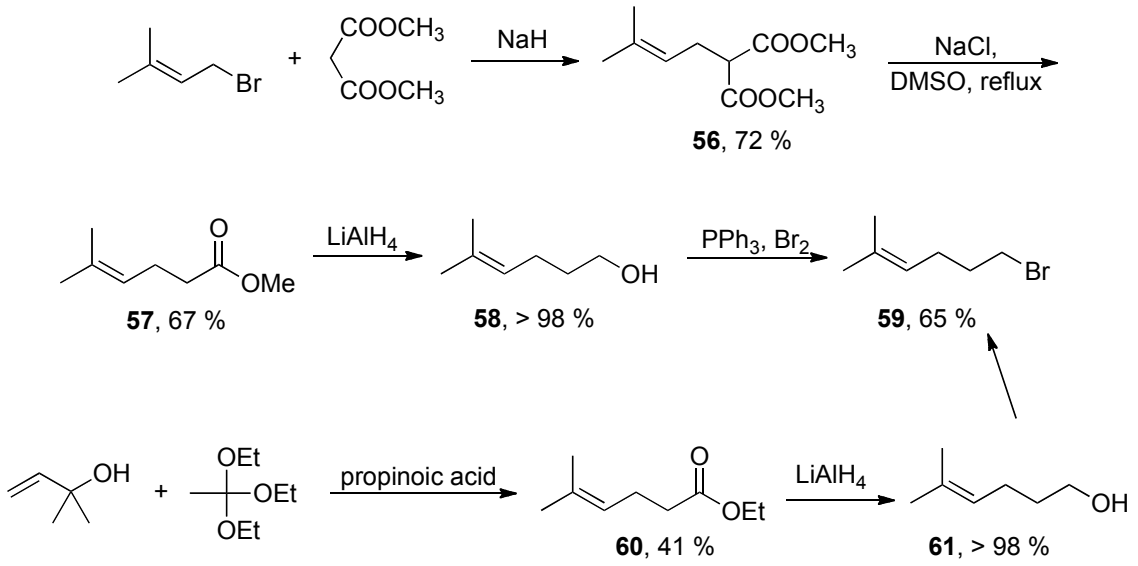
Scheme 78



For the synthesis of 6-bromo-2-methylhex-2-ene **59** was carried out by two parallel routes (Scheme 79). The first one was a homologation. This methodology allowed the desired product in four steps. But finally the reaction was optimized in meaning of steps to be substituted by a Johnson-Claisen rearrangement (Scheme 79).

Scheme 79



Finally the 1,6-enyne **33aa** was prepared by alkylation reaction of the lithium salt of **55** with bromide **59** in 55% yield (Scheme 80).

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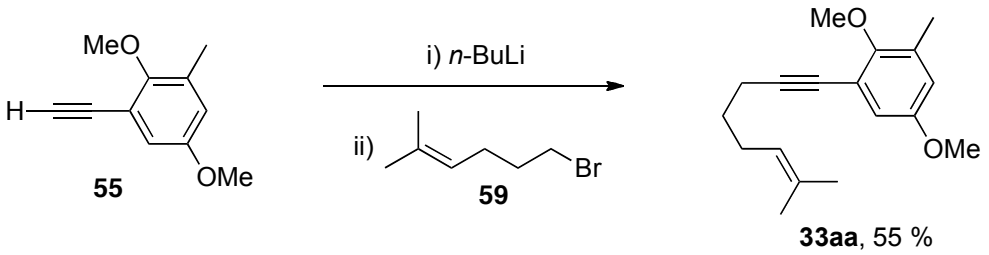
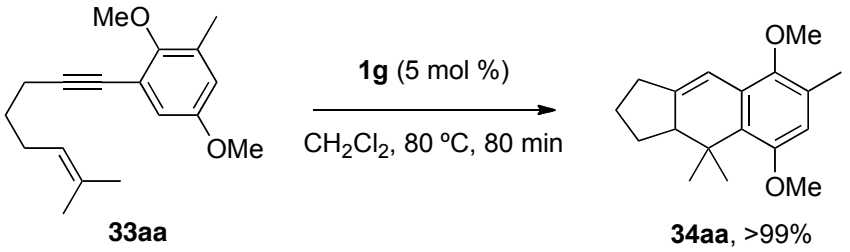
Scheme 80



Cyclization of enyne **33aa** was carried out with catalyst **1g** under microwave heating (80 ºC, 80 min) to give the desired tricycle **34aa** in quantitative yield (Scheme 81). This reaction could be performed reproducibly in up to 2.0 g scale under these conditions.

Scheme 81



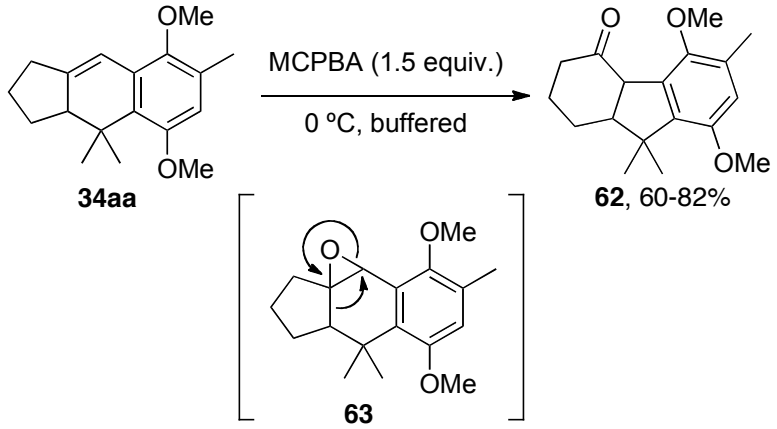
Functionalization of **34z** towards the synthesis of the pycnanthuquinone C was attempted under a variety of conditions. First we tried the allylic oxidation under a variety of conditions. Thus, the following reactions failed to give the desired compound: reaction with selenium oxide or chromium trioxide[215] in the presence of *tert*-butylhydroperoxide (TBHP) as a cooxidant; treatment with manganese (III)

215 Examples for metal-based allylic oxidation. Cr-based: (a) Muzart, J. *Chem. Rev*. **1992**, *92*, 113. Cu-based: (b) Salvador, J. A. R.; Sá e Melo, M. L.; Campos Neves, A. S. *Tetrahedron Lett.* **1997**, *38*, 119. Co-based: (c) Salvador, J. A. R.; Clark, J. H. *Chem. Commun.* **2001**, *6*, 33. (d) Jurado-Gonzalez, M.; Sullivan, A. C.; Wilson, J. R. H. *Tetrahedron Lett.* **2003**, *44*, 4283. Fe-based: (e) Barton, D. R. H.; Le Gloahec, V. N. *Tetrahedron* **1998**, *54*, 15457. Pd-based: (f) Yu, J. Q.; Corey, E. J. *J. Am. Chem. Soc.* **2003**, *125*, 3232. (g) Yu, J. Q.; Wu, H. C.; Corey, E. J. *Org. Lett.* **2005**, *7*, 1415. Rh-based: (h) Catino, A. J.; Forslund, R. E.; Doyle, M. P. *J. Am. Chem. Soc.* **2004**, *126*, 13622.

acetate using TBHP as cooxidant[216]; copper iodide (1 mol%) and TBHP[215b]; rhodium caprolactam/TBHP as cooxidant[217]; or magnesium monoperoxyphthalate. Unfortunately, decomposition was observed under all the assayed conditions.[218]

On the other hand, epoxidation of the double bond was assayed under several conditions (Scheme 82). Thus, no reaction was observed with oxone or sodium chlorite[219]. Reaction with m-chloroperbenzoic acid (MCPBA) led to rearranged ketone under all the reaction conditions. Other epoxidation methods failed to give the desired epoxide or led to decomposition products. Hydroxylation with OsO_4 also failed. Ketone **62** is probably formed by opening of the intermediate epoxide in an acid-catalyzed reaction.

Scheme 82



Oxidation of the aromatic ring with AgO led to quinone **64** in 70% yield. Oxidation with CAN[220] or DDQ failed. The desired quinone was obtained as orange product in a 70% yield (Scheme 83).

216 Shing, T. K. M.; Yeung, Y.- Y.; Su, P. L. *Org. Lett*. **2006**, *8*, 3149.

217 Doyle, M. P.; Westrum, L. J.; Wolthuis, W. N. E.; See, M. M.; Boone, W. P.; Bagueri, V.; Pearson, M. M. J. Am. Chem. Soc. 1993, 115, 958.

218 Results obtained in collaboration with Dr. Thorsten Lauterbach.

219 Geng, X.- L.; Wang, Z.; Li, X.- Q.; Zhang, C. *J. Org. Chem*. **2005**, *70*, 9610.

220 Harrowven, S. C.; Tyte, M. J, *Tetrahedron Lett.*, **2001**, *42*, 8709-8711.

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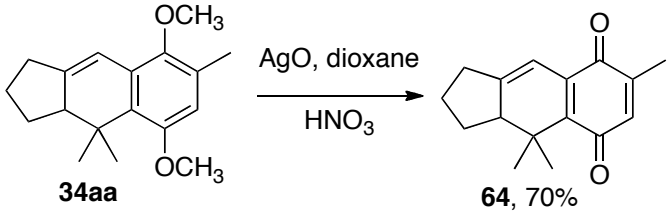
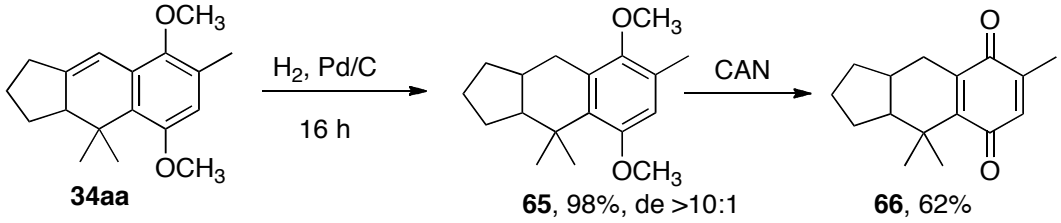
Scheme 83



Hydrogenation of **34aa** gave **66**, which could be oxidized with CAN to afford the quinone **66** in 62% yield (Scheme 84).

Scheme 84



This work demonstrates that formation of compound **66**, a model for the synthesis of the pycnanthuquinone C, is possible using a [4+2] cycloaddition reaction. However, problems found in the functionalization of the olefin in **34aa** led to development of an alternative approach based on the reaction of benzyl-substituted 1,5-enynes.[221]

221 Núria Huguet, PhD Thesis in development.

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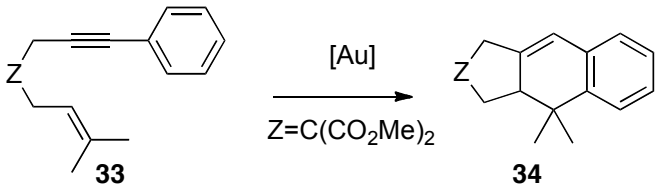
Conclusions.

- The [4+2] cycloaddition reaction of aryl substituted enynes. The reaction takes place with excellent yields by using cationic Au(I) complexes as catalysts. The phosphite-gold complex **2a** is an excellent catalyst for these [4+2] cycloadditions. Yields are better and reaction times shorter than those obtained with other gold catalysts. A mechanism for this reaction has been proposed based on DFT calculations.

Scheme 85



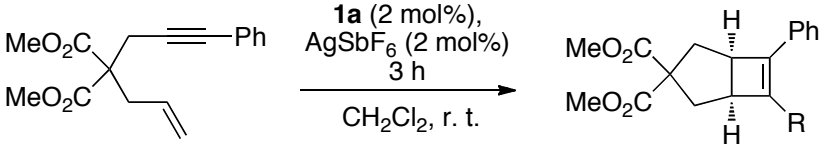
33 **34**

- The enantioselective [4+2] cycloaddition could be carried out with chiral gold complexes. The best enantiomeric excess was obtained using TolBINAP as the chiral ligand and $AgPF_6$, which gave **34a** in 56% ee.

- The cycloaddition reaction of dienynes catalyzed by gold(I) complexes affords hydrindanes. The mechanism for this transformation has also been proposed based on DFT calculations.

- Arylenynes with terminally mono- or unsubstituted alkenes give bicyclo[3.2.0]heptenes, whose formation has been rationalized by DFT calculations.

Scheme 86



38a **39a,** 57%

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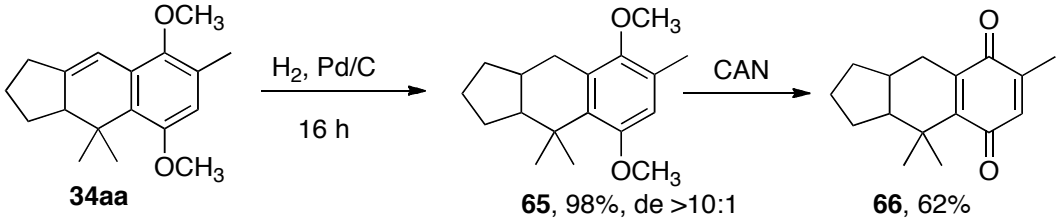
- The [4+2] cycloaddition reaction has been applied for the synthesis of a model of pycnanthuquinone C.

Scheme 87



34aa

65, 98%, de >10:1

66, 62%

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Results 4.

Mechanistic Study of Single/ Double

Cleavage Rearrangement of 1,6- and 1,7-Enynes

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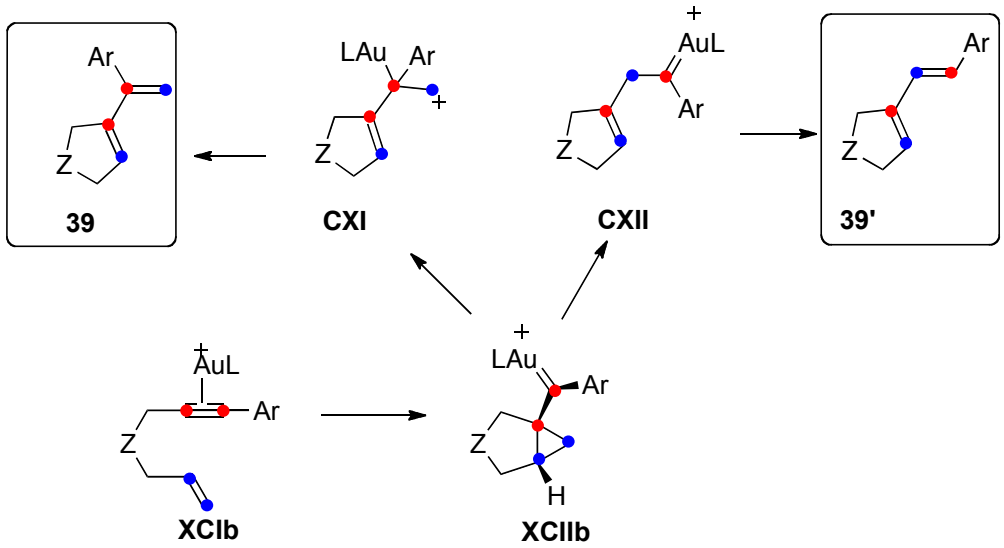
Introduction.

We decided to study the skeletal rearrangement of 1,6-enynes substituted at the alkyne with aryl groups but unsubstituted at the terminal alkene carbon (Scheme 88). These are challenging substrates that combine an unreactive alkene with a disubstituted alkyne, which has been shown to react only with highly electrophilic gold(I) catalysts. Furthermore, in this case, the single cleavage rearrangement appears to be unlikely since the corresponding intermediate **CXI**, with a primary carbocationic center, would be of higer energy than intermediate **CXII**, which leads to the product of double-cleavage rearrangement 39'.

Scheme 88



Results

Reactions of **39a** and **39j** were carried out by heating at 80 ºC (microwave irradiation) to get consistent reaction rates (Table 23). Enyne **38a** failed to give products **39a**, **39'a** and **39''a** with catalysts $AuCl_3$, $PtCl_4$, AuCl, **3** and **2b** were unreactive for that reaction (Table 23 entry 1-3, 7-8). Surprisingly, both gold(I) and Pt(II) catalysts **1g** and **67** gave the product of single cleavage rearrangement 39

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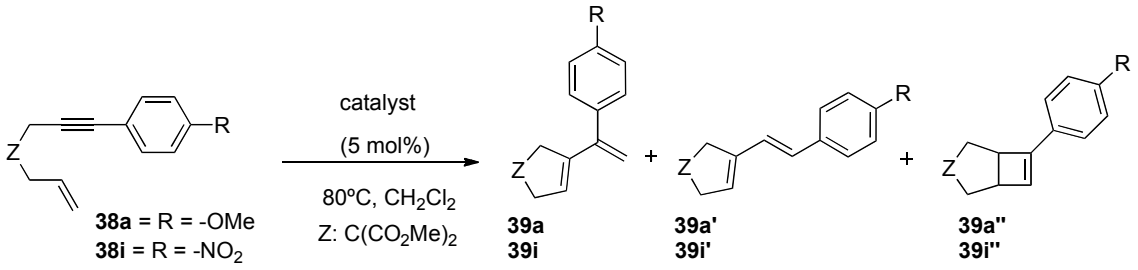
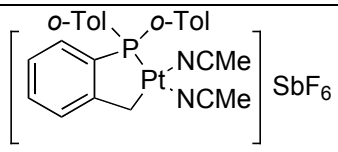
allowing starting material or decomposed products. In the case of catalyst **63**[44] the catalyst was very good and selective for the reaction of the enyne **38a**, whereas with enyne **38j** was unreactive. For enyne **38j**, similar results comparing with **38a** were found (Table 23 entries 9, 11, 13-14). One exception was showed when $PtCl_4$ was used, because the product that was formed in 60% yield was the product from single cleavage **39j**. Overall, best conditions were obtained using **1g** as catalyst, the yields were good to excellent and the time reaction were shorter that with the others.

Table 23 [a]



Entry	Enyne	Cat.	Time (min)	Yield (%) 39	Yield (%) 39'	Yield (%) 39''
1	**38a**	$AuCl_3$	10	dec.	dec.	dec.
2	**38a**	$PtCl_4$	10	dec.	dec.	dec.
3	**38a**	AuCl	60	sm	sm	sm
4	**38a**	**1g**	10	78	2	10
5	**38a**	 **67**	60	96	0	0
6	**38a**	**4e**	60	sm	sm	sm
7	**38a**	**2b**	60	sm	sm	sm
8	**38i**	$AuCl_3$	10	dec.	dec.	dec.
9	**38i**	$PtCl_4$	20	60	10	0
10	**38i**	AuCl	60	sm	sm	sm
11	**38i**	**1g**	10	0	93	0
12	**38i**	**67**	60	dec.	dec.	dec.

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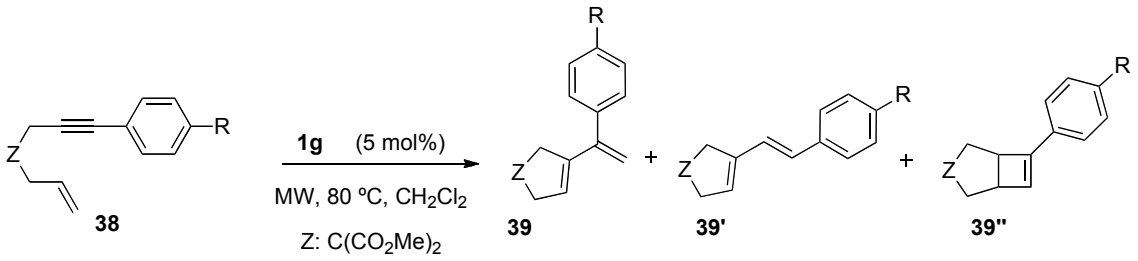
13	**38i**	**4e**	60	sm	10	sm
14	**38i**	**2b**	15	0	90	0

[a] Z = $C(CO_2Me)_2$. Reaction carried out under microwave heating, with dried CH_2Cl_2, 5% of catalyst **1g**. Yields referred by isolated product by flash chromatography

The effect of the R grups was studied using 1g as catalyst (Table 24). Enynes bearing *para*-electron-donating groups at the aryl substituted at the alkyne position (R = OMe, Cl, OAc, OBz), led to products of single cleavage or cyclobutenes (Table 24, entries 1, 4, 5, 6). In the case of electron-withdrawing groups (R = COMe, CF_3, CN, NO_2), the major compounds were the products of double-cleavage rearrangement (Table 24, entries 8, 9, 10). The double against single cleavage rearranged products is more favored with electron-withdrawing groups.

Table 24[a]



Entry	Enyne	Time (min)	Yield (%) 39	Yield (%) 39'	Yield (%) 39''
1	R = OMe (**38a**)	10	78	2	10
2[c]	R = H (**38b**)	10	73	3	23
3	R = Cl (**38c**)	25	55	0	40
4	R = OCOMe (**38d**)	40	63	0	25
5	R = OCOPh (**38e**)	60	30	15	38

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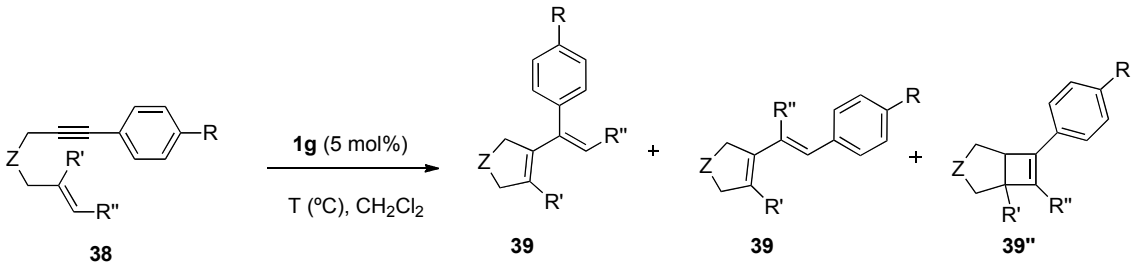
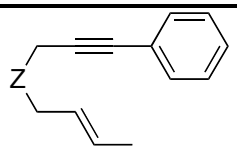
6	R = COMe (**38f**)	20	30	40	0
7	R = CF_3 (**38g**)	20	20	65	0
8	R = CN (**38h**)	55	11	70	0
9	R = NO_2 (**38i**)	10	0	93	0

[a] Z = $C(CO_2Me)_2$. Reactions were done under microwave heating, with dried CH_2Cl_2, 5% of catalyst **1g**. Yields referred by isolated product by flash chromatography. [b] complex mixture of products. [c] **39** and **39'** products are not separated

Enynes **39j-o** led to single/double cleavage rearranged products and cyclobutenes (Table 25).

Table 25: Reaction with enyne **38j-38o**[a]



Entry	Enyne	Time (min)	T (ºC)	Yield % 39	Yield % 39'	Yield % 39''
1	 **38j**	30	80	98 (15:1 *E/Z*)	0	0
2	**38j**	90	25	0	0	65

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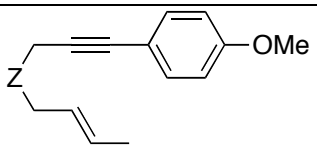
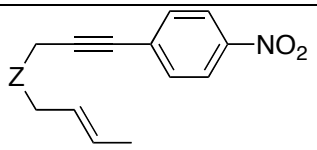
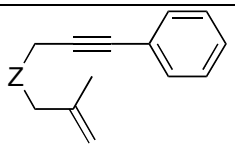
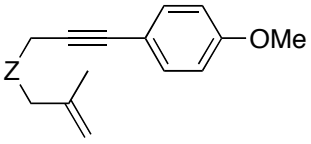
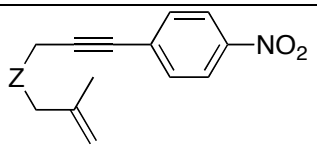
5[b]	 **38k**	20	80	36	0	43
6	**38k**	120	25	31	0	59
9	 **38l**	60	80	75 (10:1 *E/Z*)	25	0
10	**38l**	120	25	60 (6:1 *E/Z*)	26	0
3	 **38m**	30	80	[e]	[e]	[e]
4	**38m**	90	25	50	50	0
7	 **38n**	40	80	nd	nd	Complex mixture[f]
8	**38n**	150	25	nd	nd	0
11[c]	 **38o**	15	25	50	0	0
12[d]	**38o**	60	80	60	0	0

[a] Z = $C(CO_2Me)_2$. Reaction carried out under microwave heating, with dried CH_2Cl_2, 5% of catalyst **1g**. Yields referred by isolated product by flash chromatography. [e] Mixture of **39**, **39'** and **39''** in proportions 1:1:2 [f] With some impurities after flash chromatography.

[b] Compound **68** was obtained (16%)

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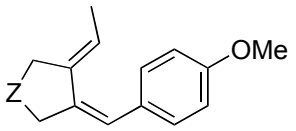
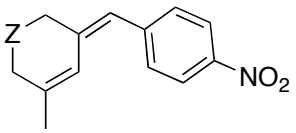


68

[c] Compound **69** was obtained in 50%.

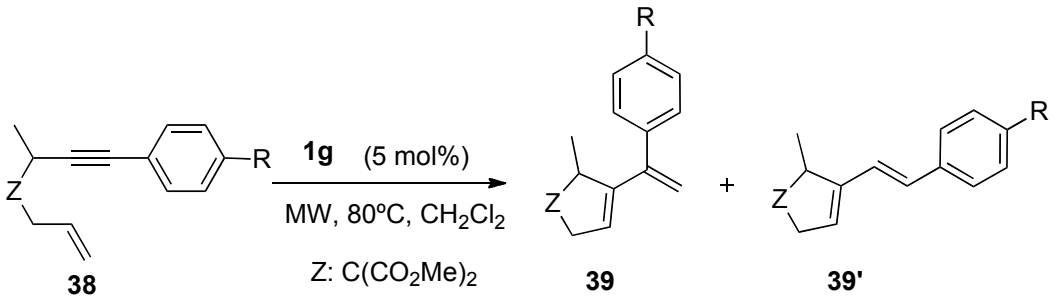


69

[d] Compound **69** was obtained in 38%.

Enynes substituted with a methyl at the propargylic position were assayed. Only enyne **38p** reacted to give a mixture of single and double cleavage products **39p** and **39'p** in 1:9 ratio (Scheme 89).

Scheme 89



R = NO_2 (**38p**)
R = H (**38q**)

R = NO_2; 9% **39p**; 88% **39'p** after 60 min.

The reaction was also studied with *ortho*- and *meta*-substituted derivatives **38r** and **38s** (Scheme 90). In the reaction of substrate **38r**, cyclobutenes **39''r** was the major product, whereas **38s** with a *m*-OMe substituted led to diene **39s** as the major compound.

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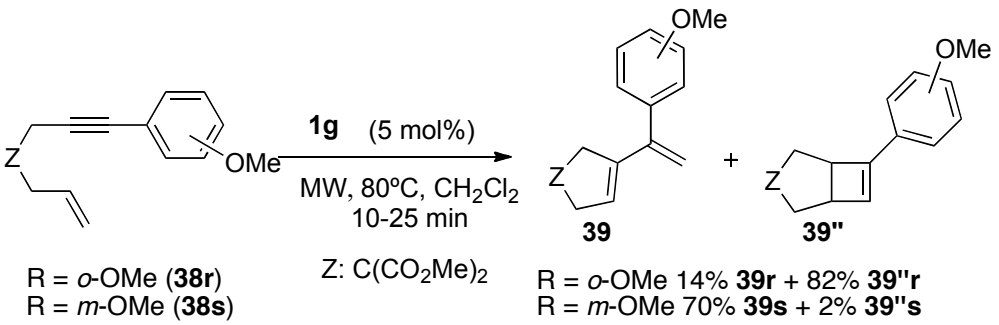
Scheme 90



To confirm that the products formed with these types of enynes correspond to single and double cleavage rearrangement, we prepared **38c-*^{13}C*** and **38f-*^{13}C*** labeled with ^{13}C at the terminal alkene carbon (Figure 14).[222]

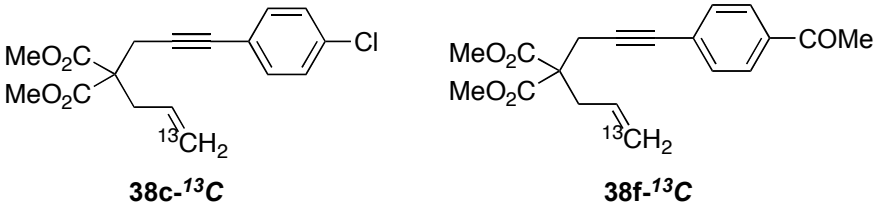


Figure 14

Cyclization of these enynes allowed us to confirm that dienes **39** are the products of single cleavage rearrangement, and that dienes **39'** correspond to products of double cleavage rearrangement (Scheme 91).

222 Miyanohana, Y.; Chatani, N. *Org. Lett*. **2006**, *8*, 2155-2158.

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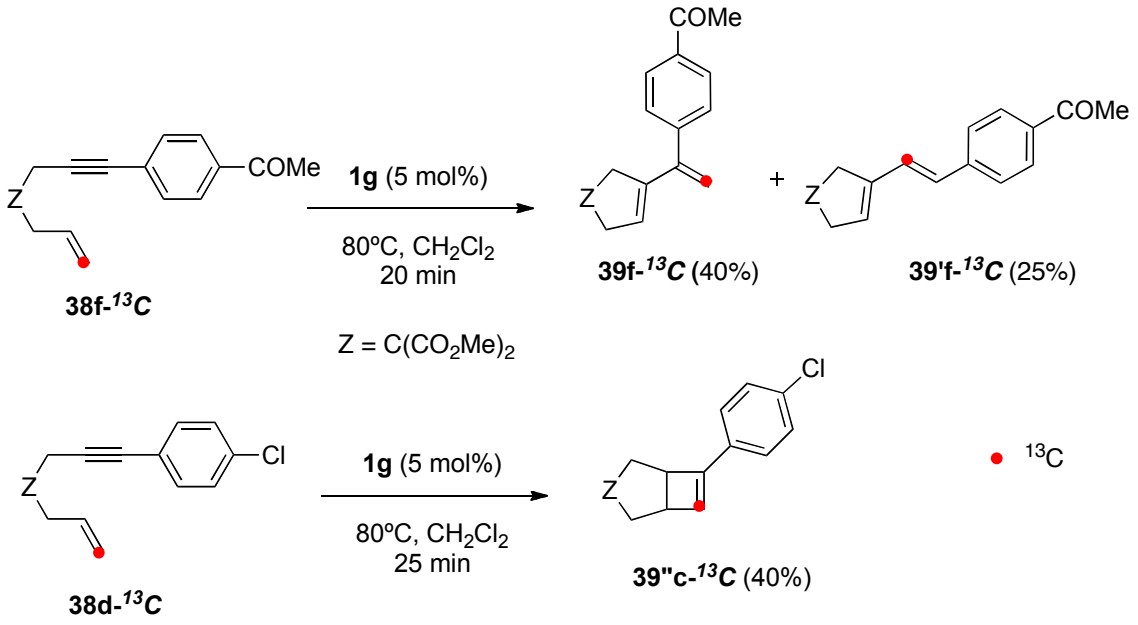
Scheme 91



DFT calculations show that *anti*-cyclopropyl gold carbene **XCIIb** is formed in an exothermic transformation (ΔG = -10.5 kcal·mol^{-1}). The second step corresponds to the skeletal rearrangement to give **CXIIIa**, which is the intermediate in the double cleavage rearrangement (Scheme 92).

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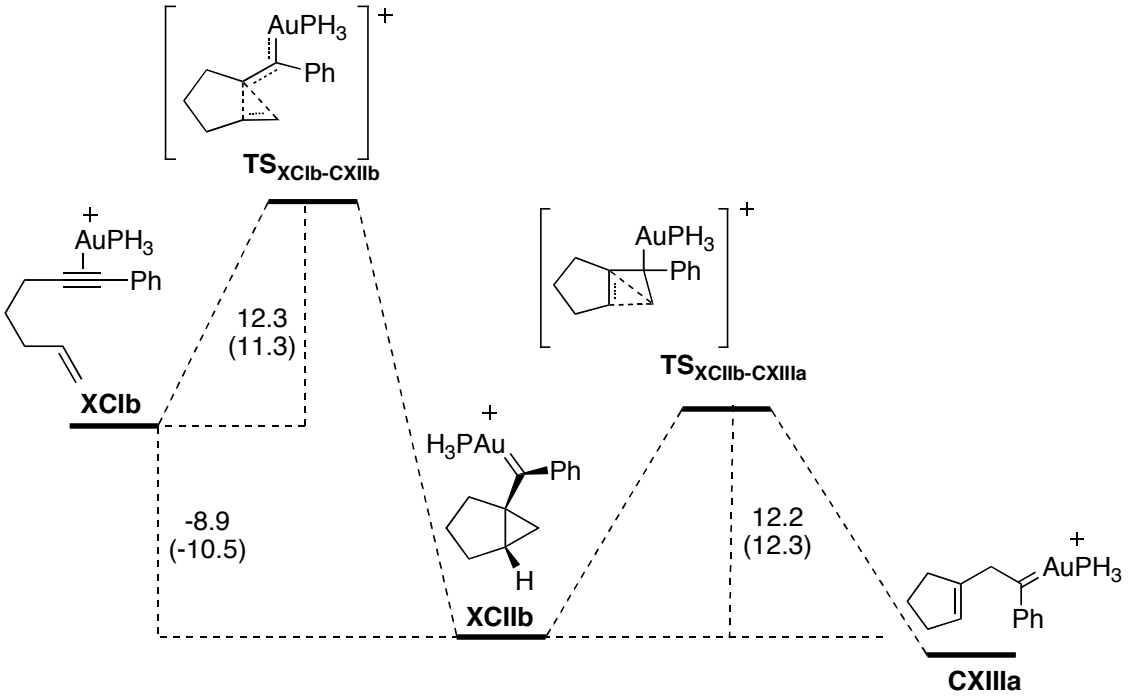
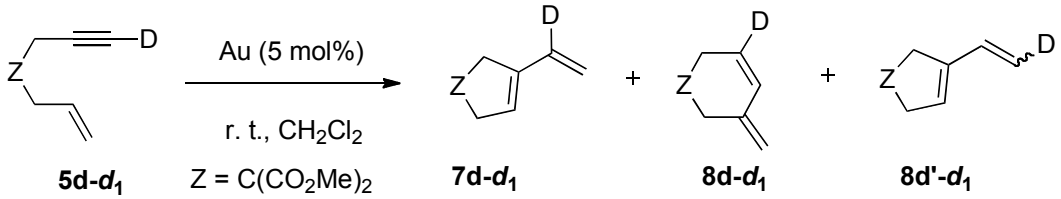
Scheme 92: Reaction pathway to form **CXIIIa**.



Calculations at the B3LYP/6-31G(d) (C, H, P), LANL2DZ (Au) level (+ ZPE-corrected electronic energies are given in kcal·mol^{-1}; ΔG in brackets), including solvent effect for CH_2Cl_2.

A deuterated derivative **5d-*d*$_1$** was also studied. In this case only mixtures of *endo*- and *exo*-single-cleavage cyclization products were observed. Interestingly, in contrast to gold(I), the reaction with $PtCl_4$ led exclusively to the product of double-cleavage rearrangement **8d-*d*$_1$** as a 4:1 *Z/E* mixture (Table 26). [111b]

Table 26[a]



Entry	Catalyst	Time (h)	Conversion	Ratio 7d/8d/8d'-*d*$_1$
1	**1g**	0.5	100	58 / 42 / 0
2	**4e**	24	60	33 / 67 / 0

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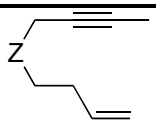
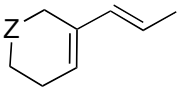
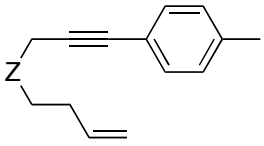
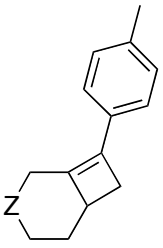
3	**2b**	0.5	100	29 / 71 / 0
4[60]	**3**	0.5	100	67 / 33 / 0
5[60]	$PtCl_4$	36	100	65% **8d'-*d*$_1$** (Z/ E 4:1)

[a] Z = $C(CO_2Me)_2$. Reaction done under microwave heating, with dried CH_2Cl_2, 5 mol% of the catalyst. Yields measured by NMR and using 1,3,5-trimethoxybenzene as standard.

Finally, the reaction of 1,7-enynes was also studied. Enyne **70a** led to the **71a**, the product from double cleavage. Enynes **70b** and **70c** (Table 27, entry 2 and 3) reacted with catalyst **1g** to give cyclobutenes **71b** and **71c** respectively. Finally, the enyne **70d** (Table 27, entry 4) allowed to the formation of three compounds. The ratio observed in ^{1}H NMR was 2:1:1, being the major product the double cleavage adduct **71d**, whereas the other two were the single cleavage adduct and other new compound **72**.

Table 27

Entry	Enyne	T (ºC)	Time	Products (yield %)
1	 **70a**	25	14h	 **71a** (99)
2	 **70b**	80	15h	 **71b** (99)

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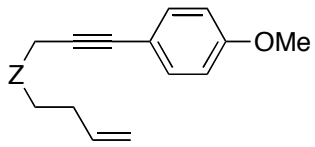
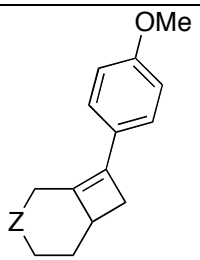
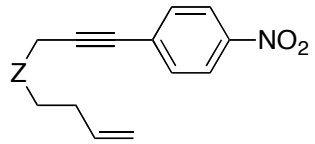
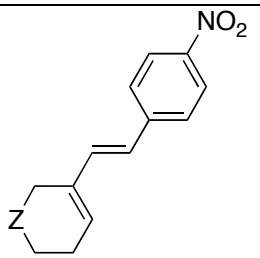
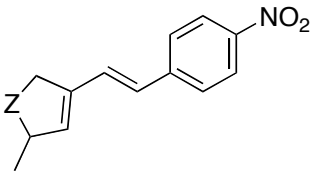
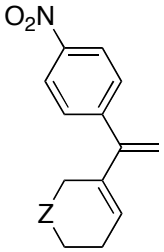
3	 **70c**	80	15h	 **71c** (80)
4	 **70d**	80	15h	 **71d** (45)  **72** (20)  **71'd** (10)

[a] Z = $C(CO_2Me)_2$. Reaction carried out under microwave heating, with dried CH_2Cl_2, 5% of catalyst **1g**. Isolated yields by flash chromatography

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Conclusions.

- The reaction with 1,6-enynes substituted at the alkyne with an aryl group lead to single or double cleavage rearrangement depending of the electronic effect at the substituents on the aryl. Cyclobutenes were also obtained with the enynes bearing electron-donating groups at the aryl.
- 1,7-Enynes substituted at the alkyne with electron-rich aryl groups give cyclobutenes, which do not undergo electrocyclic ring opening at 80 ºC.
- Further theoretical studies are required to fully explain this substitution-effects.

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Results 5.

New Silver(I) and Copper(I) Complexes

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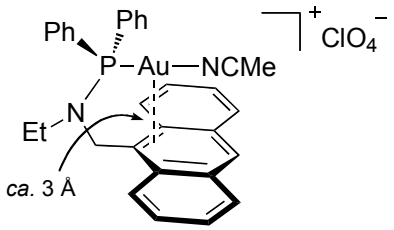
Introduction.

Au(I) complexes bearing arenes have been investigated by different groups,[223] but in the literature only three examples of Au(I) complexes in which the Au center interacts with an arene have been reported.[224] They described the complexes as η^2-arene with an intramolecular interaction with the phosphine ligand and the anthracene unit that is covalently attached (Figure 15). In cationic gold complex **73**, the Au-C distances are 2.958 and 3.097 Å (Figure 15),[224b] being the strongest η^2-arene interaction, while other anthracene complexes show Au-C contacts in the 3.0-3.2 Å range.[224]



73

Figure 15

We have reported previously the X-ray structures of the first gold complexes **74a-d** with arenes as ligands, which showed separation between Au and the mean

115 Herrero-Gómez, E.; Nieto-Oberhuber, C.; López, S.; Benet-Buchholz, J.; Echavarren, A. M. *Angew. Chem. Int. Ed*. **2006**, *45*, 5455-5459

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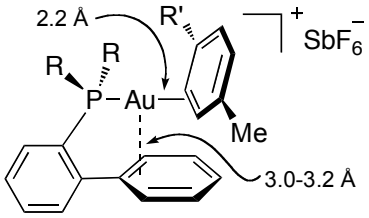
aromatic plane at 2.20-2.24 Å (Figure 16).[113] Similar bond distances were observed in a cationic toluene-gold complex bearing a cyclic amino carbene.[113] The metal center in complexes **1a-b**, **1e**, **1f-g**, and **74a-d** also interacts more weakly with the covering phenyl group (3.0-3.3 Å).[113]



74a R = *t*Bu, R' = H
74b R = Cy, R' = H
74c R = *t*Bu, R' = Me
74d R = Cy, R' = Me

Figure 16

Cationic gold(I)-complexes with strong (2.20-2.24 Å) and weak (3.0-3.3 Å) Au(I)-arene interactions

The P-Au-L angles for complexes **1a-b**, **1e**, **1f-g**, **74a-d** [113] and similar complexes[225] are in the 172-176º range, which is similar to those found in complexes with triphenylphosphine as ligands, such as cationic $[Au(PPh_3)(NCMe)]SbF_6$ (**3**) (177.1°)[113] and neutral $[Au(PPh_3)(NTf_2)]$ (174.2°).[115] Complex $[AuPPh_2(o\text{-anisyl})Cl]$, in which a weak interaction between the ortho OMe group an the Au^I center could distort the linear arrangement, shows a similar P-Au-Cl angle of 175.96º.[226] This is consistent with that observed in the vast majority of gold complexes that are linear 14-electron species, although a small number of complexes with higher coordination numbers have also been reported.[227,228,229] Interestingly,

115 Herrero-Gómez, E.; Nieto-Oberhuber, C.; López, S.; Benet-Buchholz, J.; Echavarren, A. M. *Angew. Chem. Int. Ed*. **2006**, *45*, 5455-5459.

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226 Nishina, N.; Yamamoto, Y. *Tetrahedron* **2008**, *49*, 4908-4911.

227 Gimeno, M. P.; Laguna, A. *Chem. Rev.* **1997**, *97*, 511-522.

whereas for $[Au(NCMe)_2]SbF_6$ linear coordination had been found in the solid state,[230] in solution $[Au(NCMe)_4]^+$ is formed.[231] In contrast to Au^I, for Ag^I and Cu^I tetracoordination is the rule.[231, 232, 233]

Gold(I)-arene bonds in **74a-d** are much shorter than those of related silver(I)-arene bonds.[223a,234,235] For these cases, Kochi found that the distance parameter *d* (the separation of Ag from the mean aromatic plane) was invariant at $d = 2.41 \pm 0.05$ Å, independently of the hapticity (η^1 or η^2), hybridization, or multiple coordination.[223a]

Ag^I- and Cu^I-arene bonding play an important role in the metal transport by the periplasmatic copper/silver-binding protein (CusF),[236, 237, 238] where a tryptophan

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236 (a) Loftin, I. R.; Franke, S.; Balckburn, N. J.; Mcevoy, M. M. *Protein Sci.* **2007**, *16*, 2287-2293. (b) Xue, I.; Davis, A. V.; Balakrishnan, G.; Stasser, J. P.; Staehlin, B. M.; Focia, P.; Spiro, T. J.; Penner-Hahn, J. E.; O'Halloran, T. V. *Nature Chem. Biol.* **2008**, *4*, 107-109.

237 Kühl, O.; Hinrichs, W. *ChemBioChem.* **2008**, *9*, 1697-1699.

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amino acid binds to Ag^I or Cu^I by a η^2-coordination with the C4-C5 bond of the indole ring (2.67/2.86 Å for Cu^I and 2.99/3.29 Å for Ag^I). A tighter coordination of Cu^I with the C2-C3 indole bond (2.23 and 2.27 Å) has been shown in *N*-(3-indolylethyl)-*N,N*-bis(6-methyl-2-pyridylmethyl)amine-Cu^I.[239] A few other Cu^I-arene complexes have been structurally characterized. Unsymmetrical η^2-coordination (2.13-2.66 Å) has been observed in Cu^I-arene complexes.[240, 241]

It has been argued that the largest meaningful silver-arene interaction should be less than 2.85 Å.[234] This value was based on an effective thickness of 3.4 Å for the aromatic plane (1.7 Å in each side) and an ionic radius of 1.15 Å for Ag^I. Considering the more accurate values of the radii for Cu^I (1.13 Å), Ag^I (1.33 Å), and Au^I (1.25 Å),[242,243,244] significant interactions with arenes should show distances less than 2.83 Å for Cu^I, 3.03 for Ag^I, and 2.95 Å for Au^I. This is consistent to that reported for Ag^I-arene complexes, which with the exception of that found in the copper/silver-binding protein,[236,237,238] show a maximum $Ag^I\cdots C$ distance of 2.46 Å.[245] In the case of Au^I, complexes **74a-d** show a strong Au-arene bond with toluene or *p*-xylene ligands, whereas the interaction with the covering phenyl or anthracenyl groups in complexes **74a-d** and **73** is much weaker (distance > 2.95 Å).

Close contacts (distance of Hg(II) to the centroid of an anthracene of 3.129 Å) have been also invoked for an arene-mercury(II) N-heterocyclic carbene

238 (a) Ma, Z.; Jacobsen, F. E.; Giedroc, D. P. *Chem. Rev.* **2009**, *109*, 4644-4681. (b) Boal, A. K.; Rosenzweig, A. C. *Chem. Rev.* **2009**, *109*, 4760-4779.

239 Shimazaki, Y.; Yokoyama, H.; Yamauchi, O. *Angew. Chem.* **1999**, *111*, 2561-2563; *Angew. Chem. Int. Ed.* **1999**, *38*, 2401-2403.

240 (a) Osako, T.; Tachi, Y.; Taki, M.; Fukuzumi, S.; Itoh, S. *Inorg. Chem.* **2001**, *40*, 6604-6609. (b) Osako, T.; Tachi, Y.; Doe, M.; Shiro, M.; Ohkubo, K.; Fukuzumi, S.; Itoh, S. *Chem. Eur. J.* **2004**, *10*, 237-246.

241 Conry, R. R.; Striejewske, W. S.; Tipton, A. A. *Inorg. Chem.* **1999**, *38*, 2833-2843.

242 Bayler, A.; Schier, A.; Bowmaker G. H.; Schmidbaur, H. *J. Am. Chem. Soc.* **1996**, *118*, 7006-7007.

243 Radii for tetracoordinated complexes of MI complexes of group 11 metals: Tripathi, U. M.; Bauer, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **1997**, 2865-2868

244 Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; S. Alvarez, *Dalton Trans.* **2008**, 2832-2838.

245 Lindeman, S. V.; Rathore, R.; Kochi, J. K. *Inorg. Chem.* **2000**, *39*, 5705-5716.

complex.[246] However, since the covalent radii for Hg(II) is 1.32 Å,[244] a significant interaction should had shown $d \leq 3.02$ Å, and in consequence this metal-arene interaction corresponds to a weak bond.[247]

Although gold-arene bonds are considered to be weaker than gold-alkyne or gold-alkene bonds,[248] this interaction could nevertheless play some role in catalytic transformations. In addition, weak interactions with the π-system might provide additional stabilization to the transitions states or intermediates in reactions of dialkylbiarylphosphines gold complexes with alkynes, allenes, or alkenes.[249] Gold-aryl intermolecular interactions also play an important role in the crystal structures of Au^{I} and Au^{III} complexes.[250] In order to better understand the importance of these interactions we decided to study in detail the structural differences of a series of complexes between group 11 metals in oxidation state +1 with bulky dialkylbiarylphosphines as ligands.

246 Liu, Y.; Wan, X.; Xu, F. *Organometallics*, **2009**, *28*, 5590-5592.

247 A closer intermolecular Hg-C contact (3.05 Å) was found in a 1:1 complex between bowl-shaped polyarene C26H12 and perfluoro-ortho-penylenemercury: Filatov, A. S.; Jackson, E. A.; Scott, L. T.; Petrukhina, M. A. *Angew. Chem. Int. Ed.* **2009**, *48*, 8473-8476.

248 (a) Review on η^2-coordination of alkenes, alkynes, and aromatic compounds to gold(I): Schmidbaur, H.; Schier, A. *Organometallics* DOI: 10.1021/om900900u. (b) Review on ethylene-gold(I) complexes: Rasika Dias, H. W.; Wu, J. *Eur. J. Inorg. Chem.* **2008**, 509-522.

249 Brown, T. J.; Dickens, M. G.; Widenhoefer, R. A. *Chem. Commun.* **2009**, 6451-6453.

250 Tiekink, E. R. T.; Zukerman-Schpector, J. *CrystEngComm.* **2009**, 11, 1176-1186.

Results.

Synthesis of the complexes.

Different complexes of Au, Ag, and Cu were prepared and studied their properties. Gold complexes were prepared following our described procedure,[113] whereas the complexes of silver(I) requires other strategy.[251]

Silver complexes **75c-d** were prepared by addition of silver(I) hexafluoroantimonate (1 equivalent) to a suspension of the required phosphine (1 equivalent) in dry acetonitrile (Figure 17).

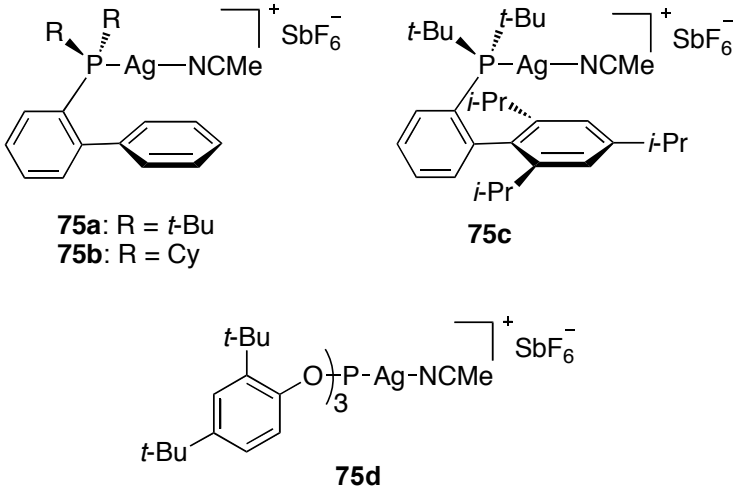

Figure 17

Copper complexes bearing NHC ligands **76e-h** were prepared according to the literature,[252] whereas copper(I) complexes **76a-d** were prepared by the addition of the required phosphine ligand to a $[Cu(NCMe)_4]BF_4$ in acetonitrile. This new methodology allowed us a new series of cationic copper(I) complexes (Figure 18).

251 Porcel, S.; Echavarren, A. M. *Angew. Chem.* **2007**, *119*, 2726-2730; *Angew. Chem. Int. Ed.* **2007**, *46*, 2672-2676.

252 Fructos, M. R.; Belderrain, T. R.; de Frémont, P.; Scott, N. M.; Nolan, S. P.; Requejo, M. M.; Pérez, P. J. *Angew. Chem. Int. Ed*. **2005**, *44*, 5284-5288.

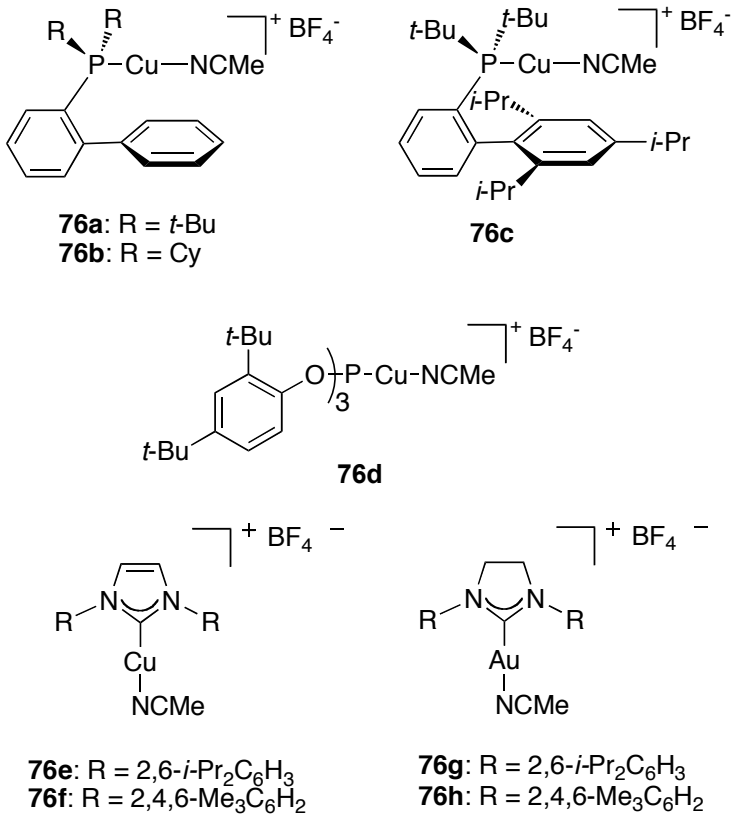

Figure 18

The first family of complexes that was studied was a family of Au, Ag and Cu[253] complexes **1d**, **75c** and **76c** with 2-di-*tert*-butylphosphino-2',4',6'-triisopropylbiphenyl (*t*-BuXPhos).[254]

The structures of complexes **1d** and **75c** are isomorphous crystals (monoclinic, space group *P*2(1)/c, Z = 4) (Figure 19, and Table 28), which are very closely related to complex **1f** (Table 28).[113] Complex **76c**, have also crystals, which are also monoclinic, and the same space group than **1d** and **75c**, but has a different counterion (tetrafluoroborate).

253 Work on Cu complexes in collaboration with Nicolas Delpont, PhD.Thesis in progress, ICIQ.

254 Ikawa, T.; Barder, T. E.; Biscoe, M. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 13001-13007.

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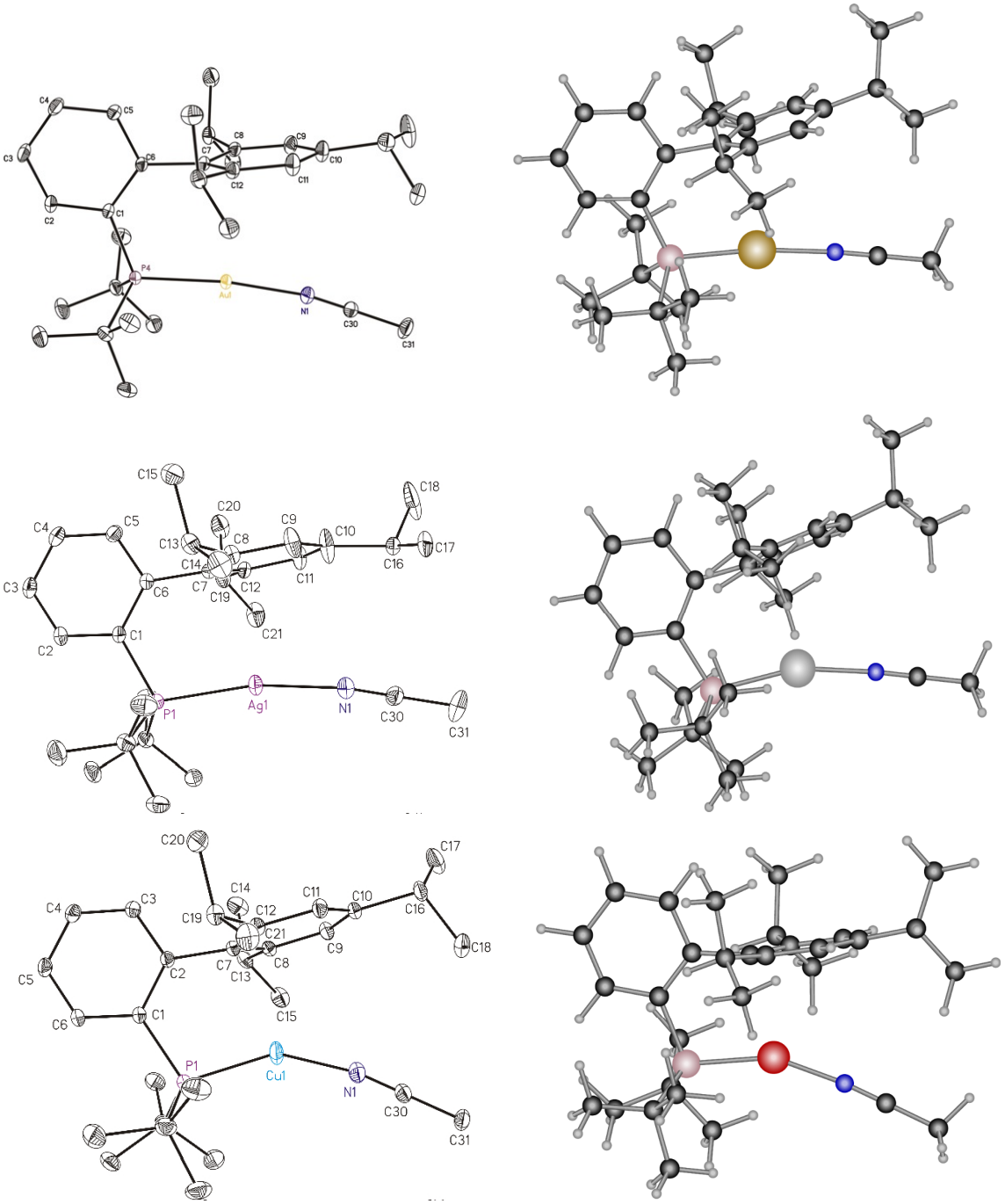

Figure 19:

X-ray crystal structures of cationic gold(I), silver(I), and copper(I) complexes **1d, 75c, 76c** with *tert*-butyl-X-Phos and acetonitrile ligands and their computed structures **1d', 75c', 76c'**. The anions have been omitted in the experimental structures for clarity.

The most remarkable difference in this family of complexes is the angle between the phosphorus, metal, and acetonitrile ligand, which is close to linearity in

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gold complex **1d** (173.1º), slightly bent for silver complex **75c** (168.0)º, and highly bent for copper complex **76c** (148.8º) (Table 28). In these complexes, the acetonitrile C_{sp} carbon is shifted downfield relative to free CH_3CN ($CDCl_3$ solution), following the trend (*d* values) **1d** < **75c** < **76c**.

Table 28: Selected experimental (X-ray diffraction) and calculated[a] distances (Å) and angles (º) for complexes **1d, 75c, 76c**.

Complex	[M]-P	[M]-N	[M]-Ar[b]	P-[M]-N	Dihedral angle[c]
1d (Au)	2.2541(8)	2.046(3)	3.04 (3.04)	173.06(9)	87.98
1d' (Au)	2.321	2.094	3.19	172.7	86.1
75c (Ag)	2.3583(5)	2.1100(18)	2.91 (2.89)	168.01(5)	86.91
75c' (Ag)	2.413	2.161	3.01	163.8	87.8
76c (Cu)	2.1961(3)	1.8853(10)	2.58 (2.48)	148.79(3)	88.81
76c' (Cu)	2.233	1.912	2.70	155.9	86.8

[a] DFT, B3LYP 6-31G(d) (C, P, N, H) and SDD (Au, Ag, Cu). [b] M]-C_{ipso} bond distance. In parenthesis, shortest distance between Au and the plane of the complexed arene. [c] Dihedral angle between aryl groups.

As expected[231,242,255,256,257,258] the metal-ligand distances in **1d, 75c, 76c** increase in the order Cu < Au < Ag. Thus, for the cations $[MPH_3]^+$, the following M-P bond distances were calculated (MP2 calculations): 2.291 Å (Au), 2.475 Å (Ag), and

255 Rasika Dias, H. V.; Flores, J. A.; Wu, J.; Kroll, P. *J. Am. Chem. Soc.* **2009**, *131*, 11249-11255.

256 Fianchini, M.; Dai, H.; Rasika Dias, H. V. *Chem. Commun.* **2009**, 6373-6375.

257 Reisinger, A.; Trapp, N.; Knapp, C.; Himmel, D.; Breher, F.; Rüegger, H.; Krossing, I. *Chem. Eur. J.* **2009**, *15*, 9505-9520.

258 Schwerdtfeger, P.; Hermann, H. L.; Schmidbaur, H. *Inorg. Chem.* **2003**, *42*, 1334-1342.

2.206 Å (Cu).[258] This trend has been also observed for the M-C bond distances in two series of η^2-2-butyne[255] and η^2-norbornene[256] metal complexes. In complexes **1d, 75c, 76c** the closest metal arene distances are 3.04, 2.89, and 2.84 Å, respectively. Thus, whereas for gold complex **1d** this distance is higher that the limit predicted for significant metal-arene bonding (2.95 Å), for silver and copper complexes **75c** and **76c** this interaction is more significant. Compounds **75c** and **76c** are the first dicoordinated Ag(I) and Cu(I) complexes with phosphine and acetonitrile as ligands. Thus, no Ag(I) complex of formula $[Ag(PPh_3)(MeCN)]^+A^-$ has been synthesized, although the nitrate was found to be the predominant species by electrospray mass spectrometry (ESMS) in a 1:1 mixture of $AgNO_3$ with PPh_3 in acetonitrile.[259] $[Cu(PPh_3)(MeCN)]^+$ was also the predominant species detected by ESMS from a 1:1 ratio of $[Cu(MeCN)_4]BF_4$ and PPh_3.[259] Cu(I) usually forms tetrahedral complexes with phosphine and halide ligands.[260] [(*S*)-BINAP$Cu(MeCN)_2]ClO_4$ also shows a tetrahedral coordination.[261] In the case of $[Cu(Ph_3P)_n(CH_3CN)_{4-n}]^+$, complexes with n = 0-4 are known.[262] Isomorphous complexes $[Cu(PPh_3)_3(CH_3CN)]X$ (X = BF_4, ClO_4) show P–Cu–P, P–Cu–N angles, and Cu–P bond lengths of 115(4)º, 103(4)º, and 2.32(1) Å.[262c] The Cu-N bond lengths for these complexes are around 2.05 Å, whereas the related complexes with SiF_5 and PF_6 anions, which crystallize as the acetonitrile solvates, show longer Cu-N bonds (2.080(2) and 2.097(1) Å, respectively). In Cu(I) complex **76c**, the lower coordination number is reflected in shorter Cu–P (2.1961(3) Å) and Cu-N (1.8853(10) Å) bonds.

259 Bonnington, L. S.; Coll, R. K.; Gray, E. J.; Flett, J. I.; Henderson, W. *Inorg. Chim. Acta* **1999**, *290*, 213-221.

260 Fife, D. J.; Moore, W. M.; Morse, K. W. *Inorg. Chem.* **1984**, *23*, 1684-1691.

261 Ferraris, D.; Young, B.; Cox, C.; Drury III, W. J.; Dudding, T.; Lectka, T. *J. Org. Chem.* **1998**, *63*, 6090-6091.

262 (a) Barron, P. F.; Dyason, J. C.; Engelhardt, L. M.; Healy, P. C.; White, A. H.; Allan H. *Aust. J. Chem.* **1985**, *38*, 261-271. (b) Leiva, A. M.; Rivera, L.; Loeb, B. *Polyhedron* **1991**, *10*, 347-350. (c) Green, J.; Sinn, E.; Woodward, S.; Butcher, R. *Polyhedron* **1993**, *12*, 991-1001. (d) Hanna, J. V.; Boyd, S. E.; Healy, P. C.; Bowmaker, G. A.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2005**, 2547-2556.

These results indicate that there is a significant interaction between the Ag^{I} and Cu^{I} and the aromatic ring of the dialkylbiarylphosphine ligands. In contrast, the corresponding Au^{I}-arene interaction is not significant.

Aquo Ag^{I} complexes **77a** and **77b** related to **75a'**, but with H_2O instead of acetonitrile, were prepared and structurally characterized (Figure 20). Two independent molecules were observed for **77a**, which correspond to almost identical conformers. The P-Ag-O angles (162.5-165.8º) are similar to those found for **75c** (168.0º) and computed for **75c'** (163.8) and **75a'** (165.6º). In these cases the closest contact is established with the ortho carbon (2.72-2.76 Å).

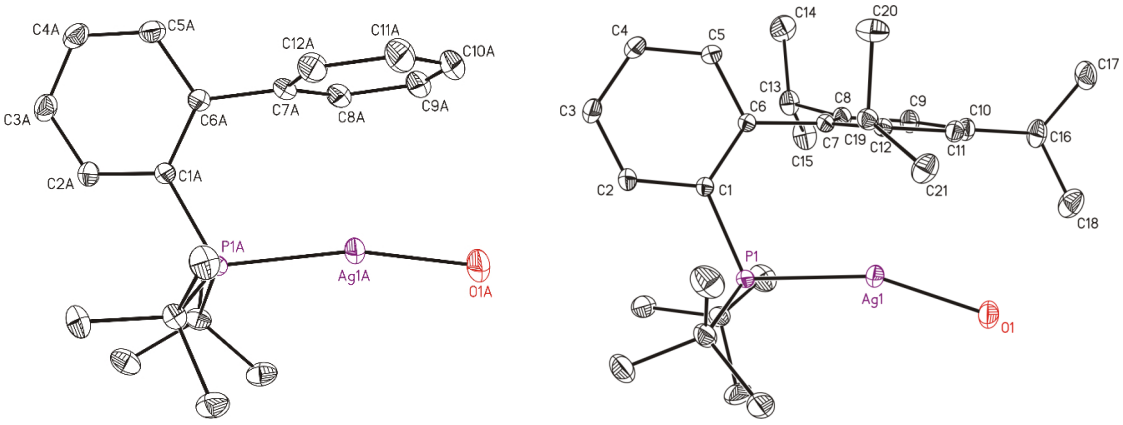


Figure 20: X-ray crystal structure of complexes **77a** (only one of the two independent conformers shown) and **77b**.

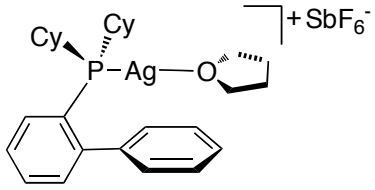
Selected bond distances (Å) and angles (º): **77a**: Ag-P 2.3532(3) [2.3615(3)], Ag-O 2.1533(9) [2.1664(9)], Ag-C7 3.02 [3.04], Ag-C8 2.76 [2.76], P-Ag-O 165.80 (3) [162.47(3)] (values in brackets correspond to the second conformer of **77**). **77b**: Ag-P 2.3656(3), Ag-O 2.1766(9), Ag-C7 3.04, Ag-C12 2.72, 3, P-Ag-O 159.74(3).

Complexes **77a** and **77b** are the first dicoordinated silver aquo complexes. Indeed, only two aquo complexes of Ag^{I} have been characterized before.[263,264,265]

263 Bachechi, F.; Burini, A.; Galassi, R.; Pietroni, B. R.; Tesei, D. *Eur. J. Inorg. Chem.* **2002**, 2086-2093.

264 Effendy, M.; Marchetti, F.; Pettinari, C.; Pettinari, R.; Skelton, B. W.; White, A. H.; Allan H. *Inorg. Chim. Acta* **2007**, *360*, 1451-1465.

Significantly, complexes **77a** and **77b** display a relatively short Ag-O bond with distances of 2.1533(9) and 2.1766(9) Å, respectively, whereas in $[Ag(TFP)_2(OH_2)]BF_4$ (TFP = trifurylphosphine)[263] and $[Ag(PPh_3)(bpy)(OH_2)]TFA$[264] the Ag-O bonds were found to be 2.36(1) and 2.340(3) Å, respectively. It is interesting to compare structures **77a** and **77b** with that of silver complex **87**, which was an excellent catalyst for the intramolecular carbostannylation of alkynes.[251] Whereas the Ag-P and Ag-O bond distances are similar (2.3405(3) and 2.1445(10) Å, respectively), in contrast with **77a** and **77b**, complex **78** displays an almost linear arrangement of ligands around Ag^I with a P-Ag-O angle of 174.50(4) (Figure 21).



78

Figure 21: Structure of Ag^I complex **78** with an almost linear arrangement of phosphine and THF ligands around Ag^I.[251]

Silver(I)-arene complexes **79a-c**, related to gold(I) complexes **74a-d**,[113] were prepared by crystallization of complex **75a** in toluene or *p*-xylene (Figure 11). It is noteworthy that, whereas complexes **79a** and **79b** have a η^2-arene ligand, in complex **79c** the coordination of toluene to Ag^I is intermediate between η^1 and η^3. This is similar to that we found for Au^I complexes **74a-d**,[113] for which **74a**,**c-d** display a η^2 coordination, whereas **74b** was better described as a η^1 or η^3 complex.

265 A complex in which the $Ag[OH_2]$ fragment bridges a Ru-CF_2 bond has also been prepared, but it was not structurally characterized: Clark, G. R.; Hoskins, S. V.; Jones, T. C.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1983**, 719-721.

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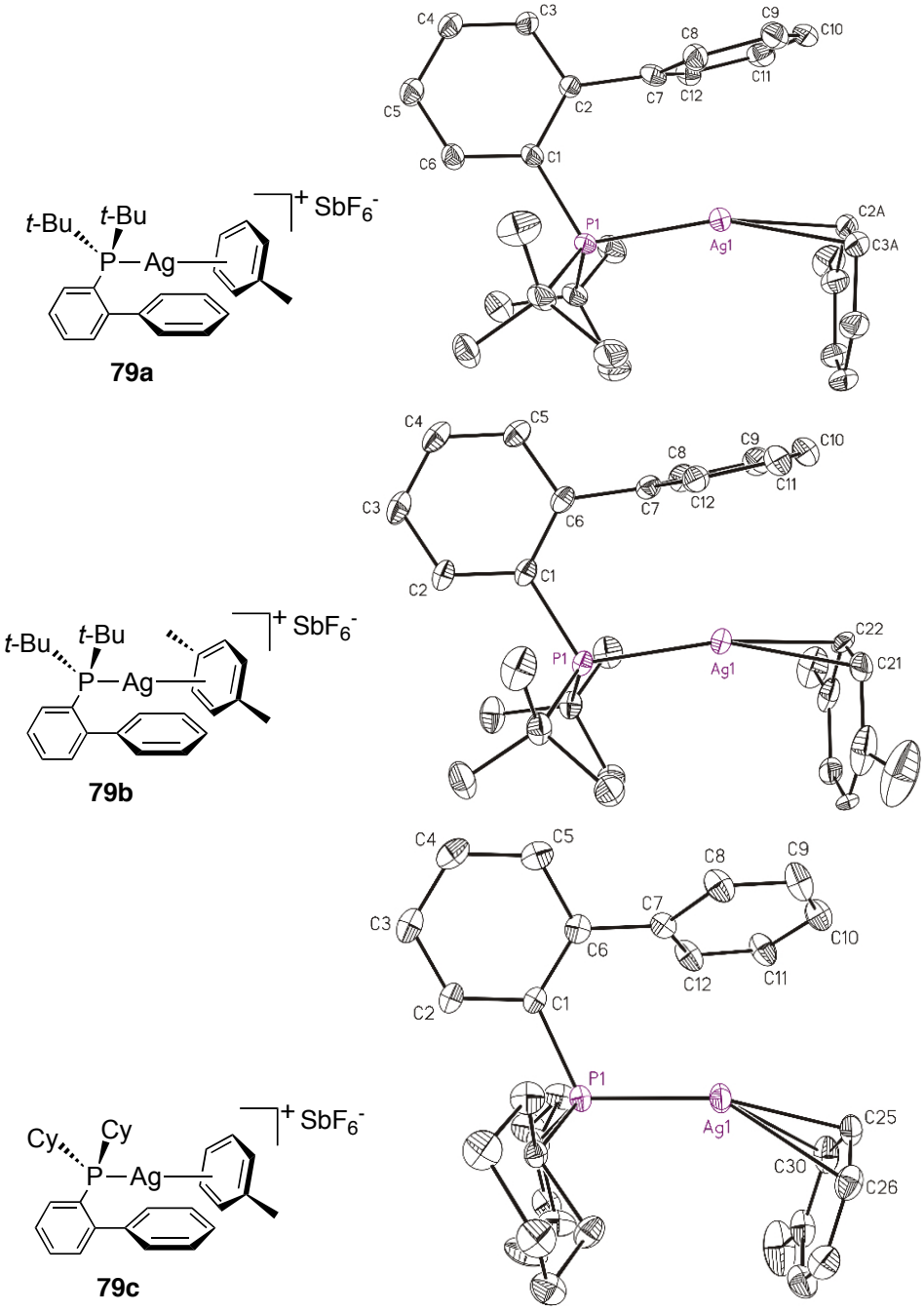


Figure 22: X-ray crystal structures of Ag^{I}-arene complexes **79a-c.** Selected bond distances (Å) and angles (º): **79a**: Ag-P 2.3864(13), Ag-C2A 2.474(5), Ag-C3A 2.366(6), Ag-C7 2.89, P1-Ag-C3A 158.82(13), P1-Ag-C2A 150.24(16). **79b**: Ag-P 2.4023(4), Ag-C21 2.367(8), Ag-C22 2.387(7), Ag-C7 2.98, P1-Ag-C21 160.72(12), P1-Ag-C22 146.68(13). **79c**: Ag-P 2.371(14), Ag-C25 2.322(6), Ag-C26 2.626(6), Ag-C30 2.696(8), Ag-C7 3.08, Ag-C12 2.91, P-Ag-C25 165.49(18), C1-C6-C7-C12 59.5(8).

According to the geometrical criteria of Kochi,[266] the hapticities of complexes **79a** and **79b** are η = 1.76 and 1.97, respectively. The separation between Ag and the mean aromatic plane of complexes **79a-c** is 2.3Å, slightly higher than that found for the analogous Au^I complexes **74a** and **74c** (*ca.* 2.2 Å). Similarly, the closest distance between Ag^I and toluene in **79c** (2.322(6) Å) is slightly larger that that found in gold complex **74b** (2.263(5) Å). Complex **79c** shows a P-M-C angle 165.49 (18) that is more bent than that found in **74b** (174.64 Å).

The distances between Ag^I and the main aromatic plane (*d*) (2.30-2.32 Å) and the D parameters in **79a-c** are significantly shorter than those observed in all previously known silver(I)-arene complexes that show consistently *d* = 2.41 ± 0.05 Å)[223a] (Table 29). This is in line with the short bonds observed before the analogous gold(I)-arene complexes **74a-d**.[113] The closest Ag^I···C distances *d* found in silver(I)-arene complexes **79a-c** actually fall in the range observed for silver(I)-alkene complexes (2.20-2.41 Å).[267] The same holds true for gold analogues **74a-d**, which show Au^I···C distances *d* very similar to those found in gold(I)-alkene complexes.[248, 249, 268, 269]

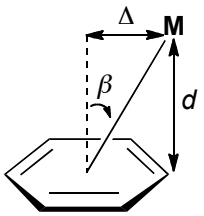
266 (a) Vasilyev, A. V.; Lindeman, S. V.; Kochi, J. K. *Chem. Commun.* **2001**, 909-910. (b) Ogawa, K.; Kitagawa, T.; Ishida, S.; Komatsu, K. *Organometallics* **2005**, *24*, 4842-4844.

267 Reisinger, A.; Trapp, N.; Knapp, C.; Himmel, D.; Breher, F.; Rüegger, H.; Krossing, I. *Chem. Eur. J.* **2009**, *15*, 9505-9520, and references therein.

268 Brown, T. J.; Dickens, M. G.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2009**, *131*, 6350-6351.

269 Hooper, T. N.; Green, M.; McGrady, J. E.; Patel, J. R.; Russell, C. A. *Chem. Commun.* **2009**, 3877-3879.

Table 29: Comparison of structural features of complexes **79a-c** with known silver(I)-[223] and gold(I)-arene complexes.[113]



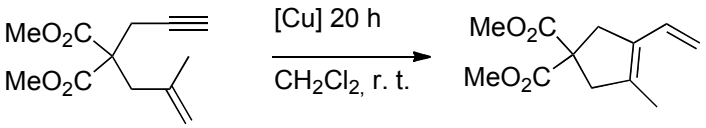
M = Ag, Au

complex	d (Å)	b (º)	D (Å)
Ag^{I}-arene[245]	2.41 ± 0.05	32 ± 3	1.53 ± 0.2
79a (Ag)	2.30	31.0	1.38
79b (Ag)	2.32	31.3	1.41
79c (Ag)	2.30	29.7	1.31
74a (Au)	2.23	31.9	1.39
74b (Au)	2.24	29.5	1.27
74c (Au)[a]	2.22, 2.20	30.8, 33.1	1.33, 1.43
74d (Au)	2.23	29.4	1.26

[a] Values for the two independent molecules of **74c** observed in the crystal parking.[113]

The complexes were assayed as catalysts for different cycloisomerization reaction of 1,6- and 1,7-enynes. Enyne **5b** reacted with copper(I) complexes. Best catalyst resulted **76g** (Table 30, entry 3).[270,96a]

Table 30



5b **7b**

Entry	Catalyst	Yield
1	**76e**	75% 10% s. m.

270 Non-published results

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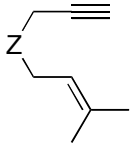
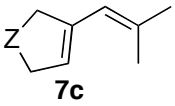
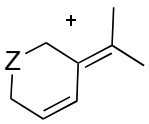
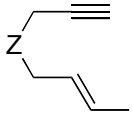
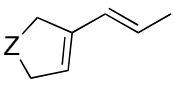
2	**76f**	62% 38% sm
3	**76g**	89%
4	**76h**	63.5% 7.5% sm

Copper(I) complex **76g** was assayed with different enynes (Table 31). Especially interesting resulted the cyclization of enyne **5c** (Table 31, entry 2), which the major product was the product from the *endo*-cyclization, whereas in gold chemistry the major product resulted the product from *exo*-cyclization.[96a]

Table 31: Cyclization of different 1,6-enynes using **76g** as catalyst

Entry	Enyne	Time (h)	T (ºC)	Products	Yield (%) (Ratio)
1	 **5c**	20	r. t.	sm	-
2	**5c**	70	50	 **7c** +  **8c**	90 (1: 4.5)
3	 **5f**	20	r. t.	 **7f**	22
4	**5f**	70	50	**7f**	70

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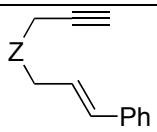
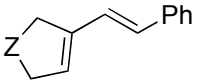
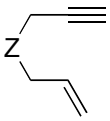
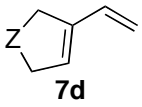
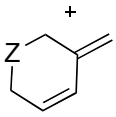
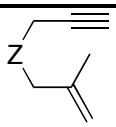
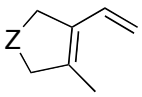
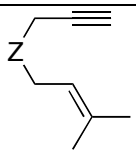
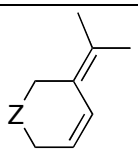
5	 **5a**	30	r. t.	 **7a**	90
6	**5a**	10	50	**7a**	89
7	 **5d**	40	r. t.	 **7d** +  **8d**	40 (2:1)
8	**5d**	40	50	**7d** + **8d**	71 (2:1)

Z = $C(CO_2Me)_2$

Silver(I) complexes were assayed in the cycloisomerization reaction of enynes (Table 32).

Table 32: Cyclization of different 1,6-enynes using **751a-d** as catalyst

Entry	Enyne	Catalyst	Time	Yield (%)	Products
1	 **5b**	**75a**	30 min	90	 **7b**
2	**5b**	**75c**	30 min	93	**7b**
3	 **5c**	**75b**	10 h	96	 **7c**
4	**5c**	**75c**	13 h	95	**7c**

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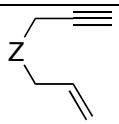
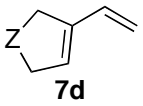
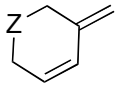
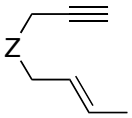
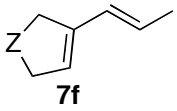
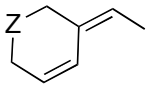
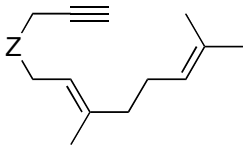
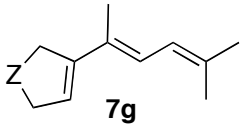
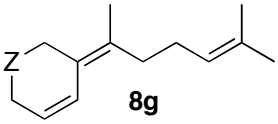
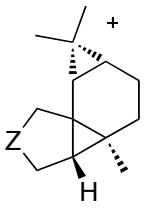
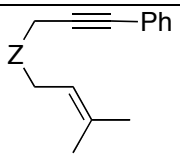
5	 **5d**	**75d**	48 h	-	**-**
6	**5d**	**75b**	22 h	48:6	 **7d** +  **8d**
7	**5d**	**75c**	96 h	33	**7d**
8	 **5f**	**75b**	5 h	48:50	 **7f** +  **8f**
9	**5f**	**75c**	5 h	36:36	**7f + 8f**
10	 **5g**	**75a**	48 h	3:11:86	 **7g**  **8g** +  **7g'**
11	**5g**	**75c**	48 h	78	**7g'**
12		**75b**	1 h MW 100 ºC	sm	**-**

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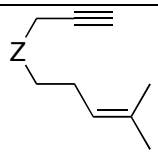
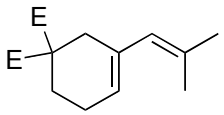
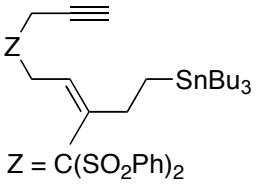
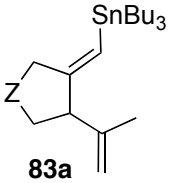
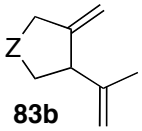
13	 **80**	**75a**	2 h	50	 **81**
14	**80**	**75c**	2 h	60	**81**
15	 **82**	**75b**	30 min	100 (1.5:1)	 **83a** +  **83b**
16	**82**	**75c**	30 min	100 (1.5:1)	**83a + 83b**

Gold(I)-, silver(I)-, and copper(I)-complexes show different reactivities and selectivities in the skeletal rearrangement of 1,6- and 1,7-enynes, being the reactivity Au > Ag > Cu for the skeletal rearrangement of enynes.

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Conclusions.

- Gold(I) interacts weakly with the covering arene ring in complexes with diakylbiphenylphosphine ligands. Thus, in complex **75a** the gold-arene distance of 3.04 Å was larger than the maximum estimated for a meaningful metal-arene interaction (2.95 Å). In contrast, isoleptic Ag^I and Cu^I complexes **75b** and **75c** show close contacts of 2.89 Å (**75b**) and 2.48 Å (**75c**), shorter than the limiting values of 3.03 Å (Ag^I) and 2.83 Å (Cu^I). Strong metal-arene interactions were also found in aquo Ag^I complexes **77a-b**.

- Three cationic diakylbiphenylphosphine Ag^I-arene complexes **79a-c**, which are structurally related to Au^I complexes **74a-d**,[113] show the shortest silver-arene distances that have been reported. This leads to the following reformulation of the structural criteria (see figure in Table 4) established by Kochi[223a] for silver(I)-arene complexes:

  - Silver(I)-arene complexes show structures that fall within a narrow range with the separation of silver(I) from the mean plane of the coordinated arene $d = 2.38 \pm 0.08$ Å, the angular parameter $b = 31° \pm 2°$ and the linear D = 1.43 ± 0.1 Å.

Although only a few structures of gold(I)-arene complexes are known,[105a,113] in these cases:

- Gold(I)arene complexes show $d = 2.23 \pm 0.01$ Å, $b = 32° \pm 3°$ and D = 1.33 ± 0.1 Å.

Other aspects of these diakylbiphenylphosphine metal complexes are also noteworthy.

- Thus, very bulky 2-di-*tert*-butylphosphino-2',4',6'-triisopropylbiphenyl (*t*-BuXPhos) ligand leads to the first dicoordinated Ag^I (**75b**) complex with phosphine and acetonitrile as ligands. We have also characterized the first dicoordinated silver aquo complexes **77a** and **77b**.

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Experimental Section

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Experimental Section: Index

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EXPERIMENTAL PART

Methods:

All reactions were carried out under Ar on N_2 in dry freshly distilled solvents under anhydrous conditions. Solvents were used from a Solvent Purification System (SPS-400-6).

Thin layer chromatography was carried out using TLC-aluminium sheets with 0.2 mm of silica gel (Merk GF234). Chromatography purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 μm) with distilled solvents.

NMR spectra were recorded at 23 ºC on the following spectrometers: Bruker Avance 400 Ultrashield (400 MHz in ^{1}H, 100 MHz in ^{13}C, and 161.32 MHz in ^{31}P) and Bruker Avance 500 Ultrashield (500 MHz in ^{1}H, 100 MHz in ^{13}C, and 202.5 MHz in ^{31}P).

Melting points were determined using a Büchi-B450 apparatus. Elemental analyses were carried out in Universidad Complutense de Madrid.

Mass Spectrometry was performed on a Waters LCT Premier (ESI) or Waters GCT (EI, CI) spectrometers.

X-ray: Crystal structure determination was carried out using a Bruker-Nonius diffractometer equipped with a APPEX 2 4K CCD area detector, a FR591 rotating anode with $Mo_{K\alpha}$ radiation, Montel mirrors as monochromator and a Kryoflex low temperature device (T = 100 K). Fullsphere data collection omega and phi scans. Programs used: Data collection Apex2 V. 1.0-22 (Bruker-Nonius 2004), data reduction Saint + Version 6.22 (Bruker-Nonius 2001) and absorption correction SADABS V. 2.10 (2003). Crystal structure solution was achieved using direct methods as implemented in SHELXTL Version 6.10 (Sheldrick, Universtität Göttingen (Germany), 2000) and visualized using XP program. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F2 using all measured intensities was carried out using the program SHELXTL Version 6.10 (Sheldrick, Universtität Göttingen (Germany),

2000). All non-hydrogen atoms were refined including anisotropic displacement parameters.

The enynes **5a-g**, **9a, 80, 82** and the corresponded products tested in catalysis have been reported before.[271] The 2-phenyldiazoacetate was prepared according to the literature.[272]

Catalysts

The following complexes were prepared according to the described procedures: $[Pd(PPh_3)_2Cl_2]$,[273] $[Pd(MeCN)_2Cl_2]$, $PdCl_2$, $PtCl_4$ (Johnson Matthey PLC), $AuCl_3$, AuCl, $[AuMe_2SCl]$, [AuIPrCl] (Aldrich), and $[Au(PPh_3)Cl]$ (Stream). The silver salts: AgSbF6, AgBF4, and AgOTf (Aldrich), were used as received. CuI was purified by refluxing in a saturated solution of NaI followed by crystallization.

Synthesis of [Au(L)Cl] complexes:[274]

Sodium tetrachloroaurate(III) dihydrate[275] (1 mmol) was dissolved in water, and the orange solution is cooled in ice. To this solution 2,2'-thiodiethanol (3 mmol) was added undiluted, with stirring, slowly (ca. 45 min) and may be stopped when the color of the solution was discharged. A solution of the phosphine ligand (1 mmol) in EtOH was added dropwise with stirring. Immediately a white solid appear. The solid was filtered off and washed with MeOH. The solid was dried in vacuo.

271 (a) Nieto-Oberhuber, C.; Muñoz, M. P.; Buñuel, E.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Angew. Chem. Int. Ed*. **2004**, *43*, 2402–2406. (b) 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. (c) Nieto-Oberhuber, C.; Muñoz, M. P.; López, S.; Jiménez-Núnez, E.; Nevado, C.; Herrero-Gómez, E.; Raducan, M.; Echavarren, A. M. *Chem.; Eur. J*. **2006**, *12*, 1677–1693. (d) Nieto-Oberhuber, C.; López, S.; Jiménez-Núñez, E.; Echavarren, A. M. *Chem.; Eur. J*. **2006**, *12*, 5916–5923.

272 Maier, C.; Fu, G. C. *J. Am. Chem. Soc*. **2006**, 128, *4594*.

273 Cotton, F. A. *Inorg. Synth*. **1972**, *13*, 121.

274 Al-Sa'Ady, A. K.; McAuliffe, C. A.; Parish, R. V.; Sandeank, J. A. *Inor. Synt*. **1985**, 191-194.

275 Tetrachloroauric acid can also be used instead of sodium tetrachloroaurate(III) dihydrate.

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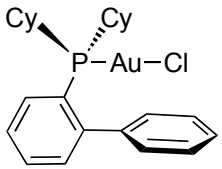
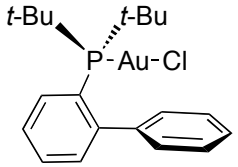
Complex 1a



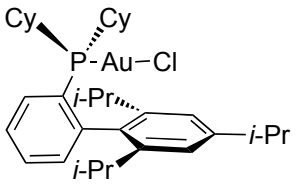
Yield 69%: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.71 (m, 1H), 7.57-7.44 (m, 5H), 7.33-7.28 (m, 1H), 7.18 (d, J = Hz, 3H), 2.08-1.94 (m, 4H) 1.83-1.74 (m, 4H), 1.68-1.43 (m, 6H) 1.33-1.18 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 134.3, 132.5 (d, $^{3}J(^{13}C-^{31}P)$ = 7.4 Hz), 130.7, 129.2, 128.6, 128.3, 127.4 (d, $^{3}J(^{13}C-^{31}P)$ = 8.4 Hz), 124.4, 36.6 (d, $^{1}J(^{13}C-^{31}P)$ = 33.3 Hz), 31.2 (d, $^{3}J(^{13}C-^{31}P)$ = 4.5 Hz), 29.4, 26.5 (d, $^{2}J(^{13}C-^{31}P)$ = 10 Hz), 24.4 (d, $^{2}J(^{13}C-^{31}P)$ = 14 Hz), 25.6; ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 47.1; HRMS-ESI calcd. for $C_{26}H_{34}AuNP$ [M^++MeCN-Cl]: 588.2094. Found: 588.2075.

Complex 1b



Yield 67%: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (td, J = 7.7, 1.7 Hz, 1H), 7.51 (m, 5H), 7.31 (m, 1H), 7.13 (dd, J = 8.0. 1.0 Hz, 2H), 1.43 (s, 9H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2 (d, $^{2}J(^{13}C-^{31}P)$ = 13.5 Hz), 142.1 (d, $^{3}J(^{13}C-^{31}P)$ = 6.3 Hz), 133.5 (d, $^{4}J(^{13}C-^{31}P)$ = 3.0 Hz), 133.2 (d, $^{3}J(^{13}C-^{31}P)$ = 7.5 Hz), 129.2, 128.7, 128.2, 126.7 (d, $^{3}J(^{13}C-^{31}P)$ = 6.8), 126.1 (d, $^{1}J(^{13}C-^{31}P)$ = 45.3 Hz), 37.7 (d, $^{1}J(^{13}C-^{31}P)$ = 25.7 Hz), 30.8 (d,$^{2}J(^{13}C-^{31}P)$ = 6.7 Hz); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 63.1; HRMS-ESI calcd. for $C_{22}H_{30}AuNP$ [M^++MeCN-Cl]: 536.1781. Found: 536.1779.

Complex 1c



Yield 62%: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 1H), 7.47-7.45 (m, 2H),

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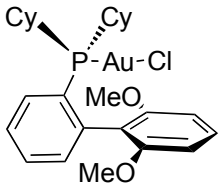
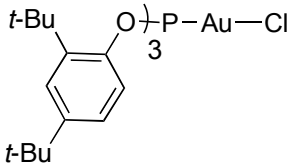
7.23 (m, 1H), 7.05 (s, 2H), 2.95 (hept, J = 7.0 Hz, 1H), 2.21 (hept, J = 6.7 Hz, 2H) 2.05-2.01 (m, 4H), 1.83-1.71 (m, 6H), 1.67-1.61 (m, 2H), 1.53-1.42 (m, 3H), 1.35 (s, 3H), 1.34 (s, 3H), 1.28 (s, 3H), 1.26 (s, 3H), 1.23-1.13 (m, 7H), 0.92 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 145.5, 133.8 (d, $^3J(^{13}C\text{-}^{31}P)$ = 8.1 Hz), 132.0 (d, $^1J(^{13}C\text{-}^{31}P)$ = 3.2 Hz), 130.3 (d, $^1J(^{13}C\text{-}^{31}P)$ = 1.8 Hz), 127.1 (d, $^1J(^{13}C\text{-}^{31}P)$ = 7.1 Hz), 121.7, 37.2 (d, $^1J(^{13}C\text{-}^{31}P)$ = 33.5 Hz), 34.3, 30.9, 30.8, 27.0 (d, $^1J(^{13}C\text{-}^{31}P)$ = 13.5 Hz), 26.7 (d, $^1J(^{13}C\text{-}^{31}P)$ = 12.9 Hz), 24.4, 23.2; ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 38.5; HRMS-ESI calcd. for $C_{33}H_{49}AuPNa$ $[M+Na]^+$: 731.2823. Found: 731.2789.

Complex 1e



Yield 73%: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.42 (m, 4H), 7.23-7.20 (m, 1H), 6.66 (d, J = 8.4 Hz, 2H), 3.70 (s, 6H), 2.18-2.13 (m, 2H), 1.98-1.93 (m, 2H) 1.83-1.64 (m, 8H), 1.48- 1.36 (m, 4H), 1.33-1.15 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 152.4 (d, $^1J(^{13}C\text{-}^{31}P)$ = 7.9 Hz), 151.1 (d, $^1J(^{13}C\text{-}^{31}P)$ = 3.9 Hz), 150.2 (d, $^1J(^{13}C\text{-}^{31}P)$ = 2.4 Hz), 149.2, 146.3 (d, $^1J(^{13}C\text{-}^{31}P)$ = 3.3 Hz), 146.2 (d, $^1J(^{13}C\text{-}^{31}P)$ = 2.9 Hz), 123.6, 74.5, 55.6 (d, $^1J(^{13}C\text{-}^{31}P)$ = 34.20 Hz), 49.5 (d, $^1J(^{13}C\text{-}^{31}P)$ = 3.8 Hz), 48.4, 45.9 (d, $^1J(^{13}C\text{-}^{31}P)$ = 12.8 Hz), 45.8 (d, $^1J(^{13}C\text{-}^{31}P)$ = 14.3 Hz), 44.9 (d, $^1J(^{13}C\text{-}^{31}P)$ = 1.6 Hz); ^{31}P NMR (MHz, $CDCl_3$) δ 41.8; HRMS-ESI calcd. for $C_{28}H_{38}AuPNO_2$ $[M^+$+MeCN-Cl]: 648.2306. Found: 648.2286.

Complex 2a



Yield 94%: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.40 (m, 6H), 7.13 (dd, J = 8.6, 2.5 Hz, 3H), 1.44 (s, 27 H), 1.29 (s, 27 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3 (C), 147.4 ($^2J(^{13}C\text{-}^{31}P)$ = 5.9 Hz, C), 139.3 ($^3J(^{13}C\text{-}^{31}P)$ = 6.9 Hz, C), 125.5 (CH), 124.3

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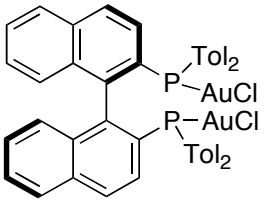
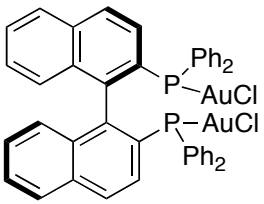
(CH), 119.3 (^3J(^{13}C-^{31}P) = 8.8 Hz, CH), 35.3 (C), 34.8 (C), 31.6 (CH_3), 30.7 (CH_3); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 103.8.

Complex 44a



White solid (84%): mp > 200 °C (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.9 Hz, 2H), 7.96 (d, J = 8.1 Hz, 2H), 7.51-7.39 (m, 8H), 7.10-6.96 (m, 14H), 6.74 (d, J = 8.5 Hz, 2H), 2.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 141.70 (m, C), 134.6 (d, J (^{13}C-^{31}P) = 14.1 Hz, CH), 134.0 (C), 133.8 (d, J (^{13}C-^{31}P) = 14.5 Hz, CH), 129.8 (CH), 129.7 (CH), 129.6 (CH), 129.4 (d, J (^{13}C-^{31}P) = 1.8 Hz, CH), 128.7 (CH), 128.3 (CH), 128.1 (C), 127.2 (C), 126.8 (d, J (^{13}C-^{31}P) = 4.2 Hz, CH), 126.6 (C), 124.4 (C), 123.5 (C), 21.3 (CH_3); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 22.2 (s); $[\alpha]^{25}$ = -53.5 (c = 0.40, $CHCl_3$); Anal. calcd. for $C_{48}H_{40}Au_2Cl_2P_2$: C, 50.41; H, 3.53. Found: C, 50.55; H, 3.69.

Complex 44b



White solid (86%): mp > 200 °C (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.7 Hz, 2H), 7,96 (d, J = 8.1 Hz, 2H), 7.26-7.32 (m, 17H), 7.31-7.28 (m, 7H), 6.87 (t, J = 7.9 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.7 (d, J (^{13}C-^{31}P) = 13.7 Hz), 134.2 (d, J (^{13}C-^{31}P) = 14.7 Hz), 133.9 (d, J (^{13}C-^{31}P) = 10.5 Hz), 133.0, 131.4 (d, J (^{13}C-^{31}P) = 6.3 Hz), 131.4 (d, J (^{13}C-^{31}P) = 5.2 Hz), 130.9, 129.9 (d, J (^{13}C-^{31}P) = 13.6 Hz), 129.9 (d, J (^{13}C-^{31}P) = 11.5 Hz), 128.6 (d, J (^{13}C-^{31}P) = 21.9 Hz), 128.1, 127.3, 126.9 (d, J (^{13}C-^{31}P) = 10.5 Hz), 126.9, 126.0; $[\alpha]^{25}$ = -16 (c = 0.20, $CHCl_3$).

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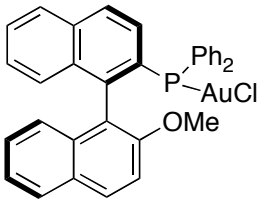
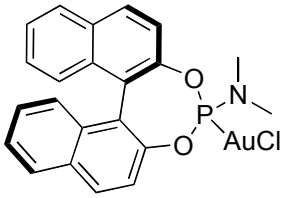
Complex 44c



White solid (92%): mp 162.0-165.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 9.1 Hz, 1H), 7.93 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 8.3 Hz, 1H), 7.57-7.19 (m, 16H), 6.95 (t, J = 8.1 Hz, 1H), 6.55 (d, J = 8.5 Hz, 1H), 3.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 143.9, 134.5 (br s), 134.2 (d, J (^{13}C-^{31}P) = 14.6 Hz), 133.7, 133.6 (d, J (^{13}C-^{31}P) = 10.4 Hz), 131.3, 131.2 (dd, J (^{13}C-^{31}P) = 6.3, 2.1 Hz), 130.3 (d, J (^{13}C-^{31}P) = 8.4 Hz), 129.5 (d, J (^{13}C-^{31}P) = 8.4 Hz), 128.9, 128.8 (d, J (^{13}C-^{31}P) = 3.1 Hz), 128.8, 128.7 (d, J (^{13}C-^{31}P) = 3.1 Hz), 128.5, 128.1 (d, J (^{13}C-^{31}P) = 23.0 Hz), 128.2 (d, J (^{13}C-^{31}P) = 8.4 Hz), 126.9 (d, J (^{13}C-^{31}P) = 37.6 Hz), 118.8 (d, J (^{13}C-^{31}P) = 8.4 Hz), 112.8, 55.2; $[\alpha]^{25}$ = + 9.4 (c = 0.80, $CHCl_3$).

Complex 44d



White solid (88%): mp = 220 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-7.93 (m, 4H), 7.58 (dd, J = 1.2, 8.8 Hz, 1H), 7.54-7.29 (m, 7H), 2.78 (d, J= 12.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 147.5, 132.4 (d, J = 2.2 Hz) 132.2 (d, J = 2.1 Hz*)*, 132.0 (d, J = 1.4 Hz), 131.8 (d, J = 1.5 Hz), 131.5 (d, J = 1.5 Hz), 131.2 (d, J = 2.2 Hz), 128.7 (d, J = 1.5 Hz), 128.4, 127.1, 127.0 (d, J = 3.6 Hz), 126.9 (d, J = 4.4 Hz), 125.9 (d, J = 5.1 Hz), 122.6 (d, J = 3.0 Hz), 120.9 (d, J = 3.0 Hz), 120.3 (d, J = 2.0 Hz), 37.39 (d, J = 11.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 131.4, 128.28; IR: ν_{max} solid/cm^{-1}= 2982, 2363, 1222, 948, 831, 753, 728, 653; HMRS-ESI+ve calcd. for $C_{22}H_{18}AuClNO_2PNa$ $[M+Na]^+$: 614.0327; Found: 614.0339.

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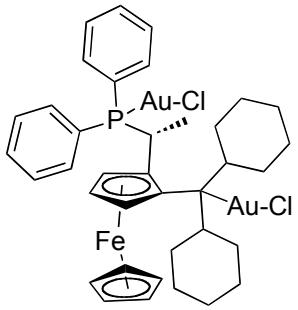
Complex 44e

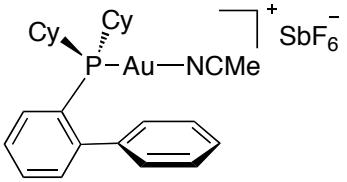


Orange solid (70%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.86 (m, 2H), 7.62-7.52 (m, 5H), 7.45-7.32 (m, 3H), 5.10 (s, 1H), 4.89 (m, 1H), 4.58 (s, 1H), 4.37 (s, 5H), 4.27 (s, 1H), 2.58 (t, *J* = 10.1 Hz, 1H), 2.39 (q, *J* = 11.0 Hz, 1H), 2.25 (d, *J* = 11.0 Hz, 1H), 2.04-0.9 (m, 19H), 088 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2 (d, *J* = 13.*1* Hz) 133.6 (d, *J* = 11.8 Hz*)*, 132.4 (d, *J* = 2.1 Hz*)*, 131.6, 129.4 (d, *J* = 11.9 Hz), 129.1 (d, *J* = 11.0 Hz), 70.8, 39.5 (d, *J* = 35.4 Hz), 37.7 (d, *J* = 34.8 Hz), 33.8 (d, *J* = 3.6 Hz), 31.6, 30.4 (d, *J* = 5.5 Hz), 29.4, 27.4 (d, *J* = 15.3 Hz), 26.9 (d, *J* = 11.8 Hz), 26.5 (d, *J* = 13.5 Hz), 25.6 (d, *J* = 25.35 Hz), 24.4 (d, *J* = 5.3 Hz), 22.65, 14.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.7, 35.95; HMRS-ESI+ve calcd. for $C_{36}H_{44}AuClP_2Au_2Fe$ [M^+-Cl^-]: 1023.1287; Found: 1023.1267.

General Procedure for cationic Au(I) complexes:

The AuLCl complex (0.5 mmol) and $AgSbF_6$ (0.5 mmol) were suspended in MeCN (4 ml). The reaction was stirred at r. t. for 12 h. The solvent was evaporated and the crude dissolved in 1 ml of $CHCl_3$ and stirred at r. t. for 30 min. Then the mixture was filtered through a pad of celite. The solvent was evaporated under reduce pressure to give a white solid.

Complex 1f



Yield 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.50 (m, 6H), 7.45 (m, 1H), 7.15 (m, 2H), 2.41 (s, 3H), 2.25-2.15 (m, 2H), 2.05-1.95 (m, 2H), 1.93-1.86 (m, 2H), 1.83-1.78 (m, 2H), 1.74-1.58 (m, 5H), 1.18-0.90 (m, 9H); ^{13}C NMR (100 MHz,

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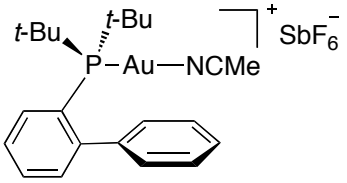
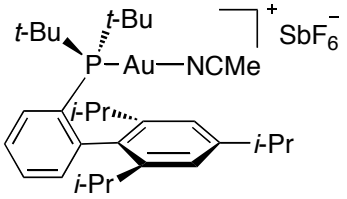
$CDCl_3$) δ 149.9 (d, $J(^{13}C\text{-}^{31}P)$ = 11.7 Hz), 141.7 (d, $J(^{13}C\text{-}^{31}P)$ = 6.7 Hz), 132.5 (d, $J(^{13}C\text{-}^{31}P)$ = 7.8 Hz), 132.1 (d, $J(^{13}C\text{-}^{31}P)$ = 4.9 Hz), 131.4 (d, $J(^{13}C\text{-}^{31}P)$ = 2.5 Hz), 129.6, 129.1, 128.2 (d, $J(^{13}C\text{-}^{31}P)$ = 8.6 Hz), 128.1, 122.2 (d, $J(^{13}C\text{-}^{31}P)$ = 57.9 Hz), 119.4, 36.1 (d, $J(^{13}C\text{-}^{31}P)$ = 35.6 Hz), 31.1 (d, $J(^{13}C\text{-}^{31}P)$ = 2.9 Hz), 29.2, 26.4 (d, $^3J(^{13}C\text{-}^{31}P)$ = 12.7 Hz), 26.2 (d, $^3J(^{13}C\text{-}^{31}P)$ = 14.7 Hz), 25.5, 15.3, 2.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.2; HRMS-ESI calcd. for $C_{26}H_{34}AuNP$ [M^+-SbF_6^-]: 588.2094.Found: 588.2103.

Complex 1g



Yield 93%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, 1H), 7.65-7.50 (m, 5H), 7.35-7.30 (m, 1H), 7.20 (m, 2H), 2.42 (s, 3H), 1.44 (s, 9H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0 (d, $J(^{13}C\text{-}^{31}P)$ = 11.7 Hz), 142.4 (d, $J(^{13}C\text{-}^{31}P)$ = 7.20 Hz), 133.2 (d, $J(^{13}C\text{-}^{31}P)$ = 7.6 Hz), 133.0 (d, $J(^{13}C\text{-}^{31}P)$ = 3.8 Hz), 131.4 (d, $J(^{13}C\text{-}^{31}P)$ = 2.4 Hz), 129.4, 129.2, 129.0, 127.6 (d, $J(^{13}C\text{-}^{31}P)$ = 7.8 Hz), 123.7 (d, $J(^{13}C\text{-}^{31}P)$ = 53.2 Hz), 119.0, 38.0 (d, $J(^{13}C\text{-}^{31}P)$ = 27.2 Hz), 30.8, 2.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 60.3; HRMS-ESI calcd. for $C_{22}H_{30}AuNP$ [M^++SbF_6^-]: 536.1781. Found: 536.1791.

Complex 1h



^1H NMR (400 MHz, $CDCl_3$) δ 7.97–7.89 (m, 1H), 7.65-7.60 (m, 2H), 7.37-7.32 (m, 1H), 7.18 (s, 2H), 3.00 (quint, J = 7.0 Hz, 1H), 2.34 (quint, J = 6.8 Hz, 2H), 2.28 (s, 3H), 1.47 (d, J = 16.2 Hz, 18H), 1.36 (d, J = 7.0 Hz, 6H), 1.31 (d, J = 6.8 Hz, 6H), 0.96 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 147.3, 147.1, 135.9, 134.7, 134.6, 134.1, 131.3, 127.5, 127.4, 121.9, 118.5, 126.1, 125.5, 38.8, 38.5, 33.9, 31.1, 26.1, 24.1, 23.0, 2.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 58.2.

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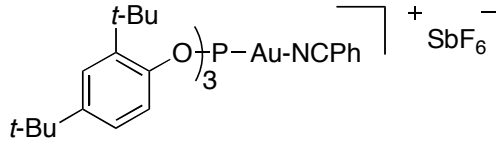
Complex 2b



Yield 88%. $^{1}H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 2H), 7.77 (t, J = 7.9 Hz, 1H), 7.57 (t, J = 8.0 Hz, 2H), 7.47 (d, J = 2.5 Hz, 3H), 7.43 (d, J = 8.5 Hz, 3H), 7.27 (dd, J = 8.4, 2.4 Hz, 3H), 1.44 (s, 27 H), 1.29 (s, 27 H); ^{13}C NMR (100 MHz, $CDCl_3$, PENDANT) δ 149.1 (C), 147.2 (d, J = 6.4 Hz, C), 139.3 (d, J = 7.2 Hz, C), 136.3 (CH), 134.5 (CH), 129.8 (CH), 125.9 (CH), 124.9 (CH), 120.8 (CN), 119.2 (d, J = 8.9 Hz, CH), 106.9 (C), 35.3 (C), 34.9 (C), 31.5 (CH_3), 30.7 (CH_3); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 90.9 (br s, 1P).

Catalyst 3

$[Au(PPh_3)(MeCN)]^{+}SbF_6^{-}$

Yield 95%: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.46 (m, 15H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 134.1 (d, $J(^{13}C\text{-}^{31}P)$ = 13.2 Hz), 132.9 (d, $J(^{13}C\text{-}^{31}P)$ = 2.9 Hz), 129.8 (d, $J(^{13}C\text{-}^{31}P)$ = 12.44 Hz), 126.4 (d, $J(^{13}C\text{-}^{31}P)$ = 66.55 Hz), 2.6 (one carbon signal was not observed); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.4; HRMS-ESI calcd. for $C_{20}H_{18}AuNP$ $[M^{+}\text{-}SbF_6^{-}]$: 500.0842. Found: 500.0829.

General Procedure for NHC Au(I) complexes:[276]

Ag_2O (0.5 mmol) was added to a solution of the imidazolium ligand (1mmol) in CH_2Cl_2. The suspension became clear after stirring 3 h at room temperature. Then a solution of Me_2SAuCl (1 mmol) in CH_2Cl_2 was added dropwise. The reaction mixture was stirred for another 4 h. Then the solution was filtered through Celite and the solvent evaporated to leave a volume of ca. 3 ml. The addition of hexane led to the precipitation of a white solid.

276 (a) Wang, H. M. J.; Lin, I. J. B. Organomet. **1998**, *17*, 972-975. (b) Wang, H. M. J.; Chen, C. Y.L.; Lin, I. J. B. Organomet. **1999**, *18*, 1216-1223.

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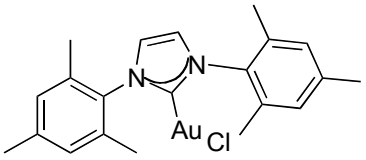
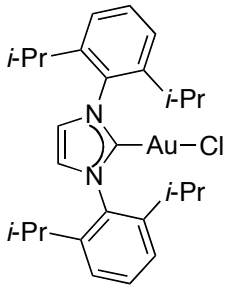
Complex 4a



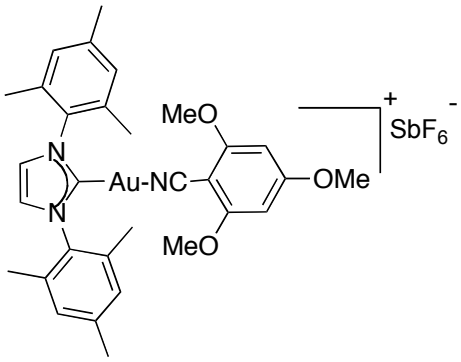
Yield 49%: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 2H), 6.97 (bs, 4H), 2.33 (s, 6H), 2.09 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 139.8, 134.7, 134.6, 129.5, 122.2, 21.1, 17.7. HRMS-FAB calcd. for $C_{21}H_{25}AuN_2Cl$ $[M+H]^+$: 537.1372. Found: 537.1361.

Complex 4b[277]



Yield 75%. ^{1}H NMR (CD_2Cl_2) δ 7.57 (t, J = 7.8 Hz, 2H), 7.35 (d, J = 7.8 Hz, 4H), 7.24 (s, 2H), 2.57 (septet, J = 6.8 Hz, 4H), 1.34 (d, J = 6.8 Hz, 12H), 1.23 (d, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 175.1 (C), 145.8 (CH), 134.0 (CH), 130.7 (CH), 124.3 (CH), 123.3 (CH), 28.8 (CH), 24.2. 23.7.

Complex 4e [278]



277 de Frémont, P.; Scott, N. M.; Stevens, E. D.; Nolan, S. P. *Organometallics*, **2005**, *24*, 2411–2418.

278 Bartolomé, C.; Ramiro, Z.; Pérez-Galán, P.; Bour, C.; Raducan, M.; Echavarren, A. M.; Espinet, P. Inorg. Chem. 2008, 47, 113911-11397.

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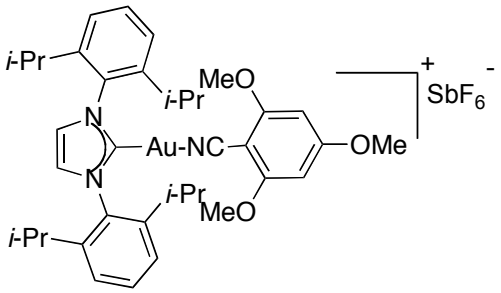
Yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 2H), 7.07 (s, 4H), 6.10 (s, 2H), 3.90 (s, 3H), 3.87 (s, 6H), 2.39 (s, 6H), 2.13 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2 (C), 165.8 (C), 165.2 (C), 140.6 (C), 134.8 (C), 134.2 (C), 129.8 (CH), 124.1 (CH), 118.4 (C), 91.3 (CH), 78.2 (C), 56.8 (CH_3), 56.6 (CH_3), 21.3 (CH_3), 17.9 (CH_3).

Complex 4f



Yield 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.77 (m, 3H), 7.60 (t, J = 7.9 Hz, 2H), 7.58 (t, J = 7.9 Hz, 2H), 7.43 (s, 2H), 7.38 (d, J = 7.8 Hz, 4H), 2.51 (septet, J = 7.0 Hz, 4H), 1.34 (d, J = 6.9 Hz, 6H), 1.27 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, PENDANT) δ 165.7 (C), 145.8 (C), 136.7 (CH), 133.9 (CH), 133.2 (C), 131.5 (CH), 130.1 (CH), 125.3 (CH), 124.8 (CH), 119.8 (C), 106.6 (C), 29.0 (CH), 24.9 (CH_3), 24.1 (CH_3).

METHODS

GENERAL PROCEDURE FOR THE SYNTHESIS OF ENYNES AND ALKYNE SUBSTITUTED ENYNES.

Procedure A: General procedure for alkylation of malonate derivates, bis(sulfonyl)methane derivates, alcohols and 4-toluenesulfonamides: To a suspension of NaH (60% in mineral oil, 10 mmol) in DMF (15 mL) at 0 ºC, was added the corresponding nucleophile (10 mmol) and the mixture was stirred at r. t. for 30 min. Then, the corresponding electrophile was added dropwise. After extractive work-up (Et_2O/HCl (3.5%)) and chromatography (EtOAc:hexane mixtures), the corresponding enyne was obtained.

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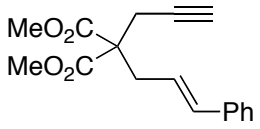
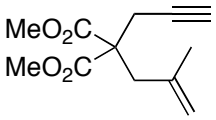
Procedure B: General procedure for Sonogashira cross-couplings:[279] CuI (0.1 mmol) and $[Pd(PPh_3)_2Cl_2]$ (0.05 mmol) were suspended in *i*-Pr_2NH, and stirred for 5 min. Then the corresponding halide (1.3 mmol) and a solution of the alkyne (1 mmol) in *i*-Pr_2NH were added sequentially. The reaction was stirred at r. t. (unless other temperature was specify in each case) until T.L.C. show total conversion. The crude was dissolved in Et_2O, filtered through Celite, and purified by chromatography to give the corresponding substituted alkynes.

Dimethyl 2-Cinnamyl-2-(prop-2-yn-1-yl)malonate (5a)[280]



Starting from dimethyl propargyl malonate and cinnamyl chloride, and following Procedure A for alkylations, **5a** was obtained in 80% yield as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.19 (m, 5H), 6.62 (d, J = 15.6 Hz, 1H), 6.01 (dt, J = 15.6, 7.5 Hz, 1H), 3.77 (s, 6H), 2.98 (d, J = 7.5 Hz, 2H), 2.83 (d, J = 2.7 Hz, 2H), 2.05 (t, J = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 136.8, 134.6, 128.2, 126.2, 122.9, 78.7, 71.6, 57.1, 52.7, 35.7, 22.8, 22.5.

Dimethyl 2-(2-Methylallyl)-2-(prop-2-yn-1-yl)malonate (5b/5b-d_1)



Starting from dimethyl propargyl malonate and the corresponding allyl bromide, and following Procedure A for alkylations, **5b** was obtained as pale yellow oil (65%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.89 (t, J = 1.6 Hz, 1H), 4.83 (s, 1H), 3.72 (s, 6H), 2.83 (s, 2H), 2.82 (s, 2H), 2.01 (dd, J = 2.9 Hz, 1H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 135.4, 112.0, 74.8, 67.3, 52.1, 48.4, 35.2, 18.8, 18.3. Deuterated enyne **5b-d_1** was obtained by deprotonation with *n*-BuLi in THF at -78 ºC and

279 Forsyth, C. J.; Clardy, J. *J. Am. Chem. Soc.* **1990**, *112*, 3497-3505.

280 Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6049-6050.

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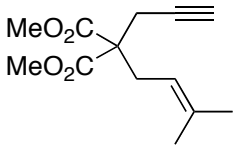
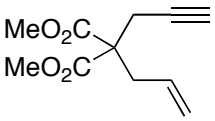
subsequent quenching with D_2O. Disappearance of the alkynyl hydrogen signal at 2.01 ppm on the ^1H NMR spectra was observed.

Dimethyl 2-(3-Methylbut-2-en-1-yl)-2-(prop-2-yn-1-yl)malonate (5c)[281]



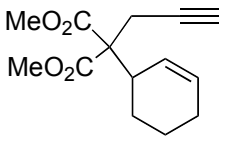
Starting from dimethyl propargyl malonate and 4-bromo-2-methyl-2-butene, and following Procedure A for alkylations, **5c** was obtained in 96% yield as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 4.91 (t, J = 7.8 Hz, 1H), 3.69 (s, 6H), 2.74 (m, 2H), 2.73 (d, J = 2.8 Hz, 2H), 1.97 (t, J = 2.8 Hz, 1H), 1.66 (d, J = 1.2 Hz, 3H), 1.60 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 136.9, 116.9, 79.2, 71.1, 57.1, 52.6, 30.7, 26.0, 22.4, 17.9.

Dimethyl 2-Allyl-2-(prop-2-yn-1-yl)malonate (5d)[282]



Starting from dimethyl propargyl malonate and the corresponding allyl bromide, and following Procedure A for alkylations, **5d** was obtained in 85% yield as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$): δ 5.55 (ddt, J = 17.4, 10.1, 7.5 Hz, 1H), 5.22-5.12 (m, 2H), 3.75 (s, 6H), 2.81-2.78 (m, 4H), 2.02 (t, J = 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9 (C), 131.5 (CH), 119.7 (CH_2), 78.5 (C), 71.4 (CH), 56.6 (C), 52.5 (CH_3), 36.3 (CH_2), 22.5 (CH_2).

Dimethyl 2-(Cyclohex-2-en-1-yl)-2-(2-propynyl) malonate (5e)



Starting from dimethyl propargyl malonate and 3-bromocyclohexene, and following Procedure A for alkylations, **5e** was obtained in 95% yield as a colorless

281 Trost, B. M.; Braslau, R. *Tetrahedron Lett.* **1988**, *29*, 1231-1234.

282 Miura, K.; Saito, H.; Fujisawa, N.; Hosomi, A. *J. Org. Chem.* **2000**, *65*, 8119.

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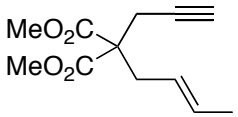
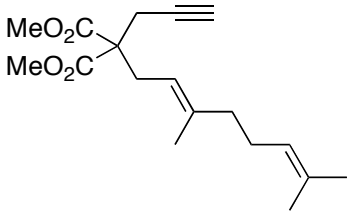
oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (m, 2H), 3.76 (s, 3H), 3.73 (s, 3H), 3.13 (m, 1H), 2.89 (dd, J = 16.9, 2.6 Hz, 1H), 2.82 (dd, J = 16.9, 2.6 Hz, 1H), 2.01 (t, J = 2.6 Hz, 1H), 1.95 (m, 1H), 1.82 (m, 2H), 1.58 (m, 1H), 1.38 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 170.1, 129.2, 127.3, 79.5, 60.4, 52.5, 52.3, 39.0, 24.9, 24.3, 22.5, 22.3; Anal. calcd. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.13; H, 7.58.

(*E*)-Dimethyl 2-(But-2-en-1-yl)-2-(prop-2-yn-1-yl)malonate (5f)[283]



Starting from dimethyl propargyl malonate and the corresponding allyl bromide, and following Procedure A for alkylations, **5f** was obtained as a colorless oil (*ca.* 4:1 *E*/*Z*; 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62-5.50 (m, 1H), 5.23-5.05 (m, 1H), 3.75 (s, 6H, *Z*), 3.74 (s, 6H, *Z*), 2.84 (d, J = 4.8 Hz, 2H, *Z*), 2.79 (d, J = 2.8 Hz, 2H, *Z*), 2.78 (d, J = 2.8 Hz, 2H, *E*), 2.73 (dt, J= 11.7, 1.2 Hz, 2H, *E*), 2.02 (t, J = 2.6 Hz, 1H, *Z*), 2.00 (t, J = 2.8 Hz, 1H, *E*), 1.65 (m, 3H, *E* and *Z*); ^{13}C NMR (100 MHz, $CDCl_3$) (*E* isomer) δ 170.2, 130.6, 123.8, 78.9, 71.3, 57.0, 52.6, 29.4, 18.0, 12.9; ^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer) δ 170.2, 129.1, 122.8, 79.0, 21.3, 56.9, 52.7, 35.2, 22.5, 12.9.

Dimethyl 2-Geranyl-2-propargylmalonate (5g)[284]



Starting from dimethyl propargyl malonate and geranyl bromide, and following Procedure A for alkylations, **5g** was obtained in 98% yield as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10-5.00 (m, 1H), 4.98-4.86 (m, 1H), 3.63 (s, 6H), 2.85-2.68 (m, 4H), 2.10-1.90 (m, 5H), 1.68 (d, J = 1.2 Hz, 3H), 1.60 (s, 3H), 1.52 (s,

283 Gibson, S. E.; Johnstone, C.; Stevenazzi, A. *Tetrahedron* **2002**, *58*, 4937-4942.

284 Trost, B. M.; Lautens, M.; Chan, C.; Jebaratnam, D. J.; Mueller, T. *J. Am. Chem. Soc.* **1991**, *113*, 636-644.

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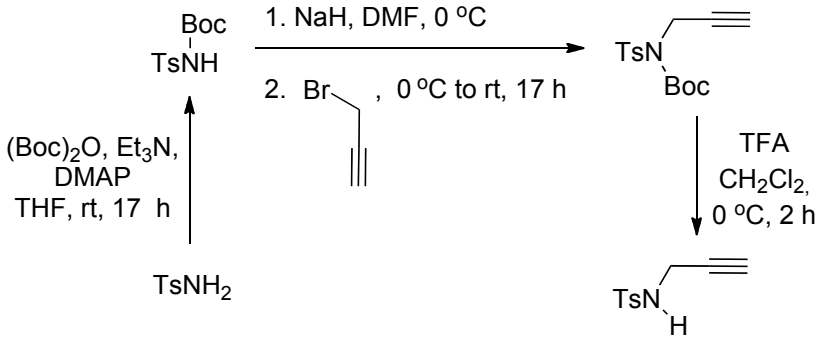
3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 140.4, 131.5, 123.9, 117.4, 79.3, 71.1, 57.1, 52.6, 39.9, 31.8, 26.4, 25.6, 22.4, 17.6, 16.1.

N-2-Propynyl-(4-Toluene)sulfonamide[285]



To a mixture of (4-toluene)-sulfonamide (15.00 g, 87.60 mmol), $(Boc)_2O$ (19.10 g, 87.60 mmol), and DMAP (10.70 g, 87.60 mmol) in THF (50 mL), was added Et_3N (14.6 mL, 105.10 mmol).The mixture was stirred at 23 °C overnight. After extractive work-up (EtOAc/ HCl (10%)), *N-tert*-butoxycarbonyl-(4-toluene)-sulfonamide[286] was obtained as a white solid and used without further purification. ^{1}H NMR (400MHz, $CDCl_3$) δ 7.89 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 2.44 (s, 3H), 1.38 (s, 9H).

To a suspension of NaH (60% in mineral oil, 3.27 g, 81.70 mmol) in DMF (20 ml) at 0 ºC was added *N-tert*-butoxycarbonyl-(4-toluene)-sulfonamide (22.18 g, 81.70 mmol). After 10 min, propargyl bromide (80% in toluene, 9.10 mL, 81.70 mmol) was added, and the resulting mixture was stirred at 23 °C overnight. After the usual work up (EtOAc/ HCl (10%)), *N-tert*-butoxycarbonyl-*N*-(2-propynyl)-(4-toluene)-sulfonamide[287] was obtained as a white solid and used without purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 4.60 (d, J = 2.4 Hz, 2H), 2.43 (s, 3H), 2.31 (t, J = 2.4 Hz, 1H), 1.33 (s, 9H).

N-tert-Butoxycarbonyl-*N*-(2-propynyl)-(4-toluene)-sulfonamide (23.70 g, 81.00 mmol) was stirred in CH_2Cl_2 (50 mL) and TFA (26.82 mL, 348.1 mmol) was added at 0 °C. The mixture was stirred at the same temperature for 2 h. After

285 Oppolzer, W.; Bedoya-Zurita, M.; Switzer, C. Y. *Tetrahedorn Lett.* **1988**, *29*, 6433-6436.

286 Henry, J. R.; Marcin, L. R.; Mcintosh, M. C.; Scola, P. M.; Harris, G. D. Jr. *Tetrahedorn Lett.* **1989**, *30*, 5709-5712.

287 Oppolzer, W.; Stammen, B. *Tetrahedron* **1997**, *53*, 3577-3586.

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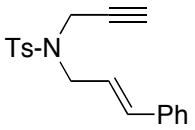
extractive work-up (EtOAc/$NaHCO_3$ (5%)), *N*-(2-propynyl)-(4-toluene)-sulfonamide was obtained as a white solid (11.41 g, 62% from (4-toluene)-sulfonamide, 3 steps): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 4.69 (s, 1H), 3.88 (dd, J = 6.1, 2.6 Hz, 2H), 2.48 (s, 3H), 2.15 (t, J = 2.6 Hz, 1H).

_N_-Cinnamyl-4-Methyl-_N_-(prop-2-yn-1-yl)benzenesulfonamide (9a)[288]



To a suspension of NaH (60% in mineral oil, 573 mg, 14.33 mmol) in DMF (10 mL) at 0 °C, was added a solution of *N*-(2-propynyl)-(4-toluene)-sulfonamide (3.00 g, 14.33 mmol) in DMF (30 mL), followed by cinnamyl chloride (1.99 mL, 14.33 mmol). The mixture was stirred 5 h at 23 °C and then quenched with H_2O After extractive work-up (Et_2O) and chromatography (4:1 Hexane-EtOAc), **9a** was obtained as a white solid (3.73 g, 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.3 Hz, 2H), 7. 32 (m, 7H), 6.58 (d, J = 15.8 Hz, 1H), 6.09 (dt, J = 15.8, 6.8 Hz, 1H), 4.14 (m, 2H), 4.00 (d, J = 6.8 Hz, 2H), 2.44 (s, 3H), 2.07 (s, 1H).

General procedure for the synthesis of bisenynes

CuI (0.03 mmol), [$Pd(Cl)_2(PPh_3)_2$] (0.03 mmol) and PPh_3 (0.09 mmol) were suspended in NEt_3-MeCN (2.5:1.5) and the 1,6-enyne (1 mmol) was added. The resulting mixture was stirred overnight at 90 °C. The crude mixture was diluted with Et_2O, filtered through Celite, and purified by chromatography (hexane-EtOAc).

288 Nevado, C.; Charruault, L.; Michelet, V.; Nieto-Oberhuber, C.; Muñoz, M. P.; Méndez, M.; Rager, M.-N.; Genêt, J.-P.; Echavarren, A. M. *Eur. J. Org. Chem.* **2003**, 706-713.

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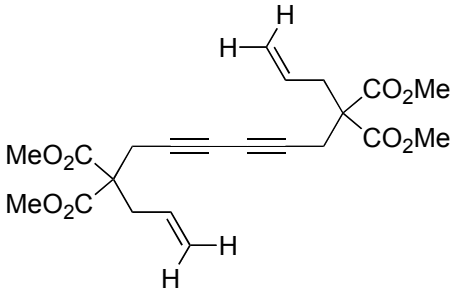
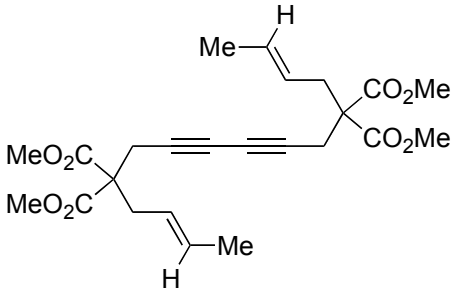
Bisenyne 11a



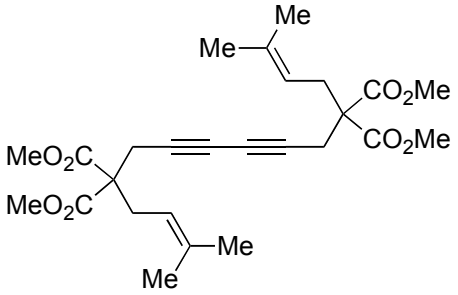
Yield 69%. Brown solid: mp 67-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67-5.57 (m, H), 5.18 (d, J = 20.1 Hz, 2H), 5.15 (d, J = 13.2 Hz, 2H), 3.76 (s, 12H), 2.88 (s, 4H), 2.80 d, J= 7.5 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 131.5, 120.1, 72.4, 67.9, 66.9, 52.9, 36.8, 23.6; HMRS-ESI calcd. for $C_{22}H_{26}O_8Na$ $[M+Na]^+$: 441.1525. Found: 441.1516.

Bisenyne 11b



Yield 45%. Brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65-5.52 (m, 2H), 5.22-5.14 (m, 2H), 3.71 (s, 12H), 2.82 (s, 4H), 2.67 (d, J = 7.4 Hz, 4H), 1.62 (d, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0 (C), 130.8 (CH), 123.7 (CH), 72.6 (C), 67.7 (C), 57.1 (C), 52.7 (CH_3), 35.6 (CH_2), 29.8 (C), 23.4 (CH_2), 18.0 (CH_3); HMRS-ESI calcd. for $C_{24}H_{30}O_8Na$ $[M+Na]^+$: 469.1819. Found: 469.1838.

Bisenyne 11c



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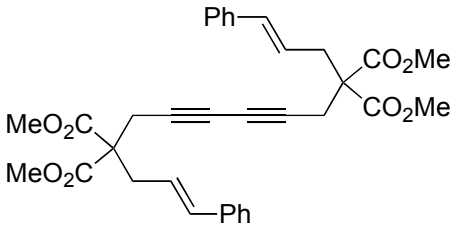
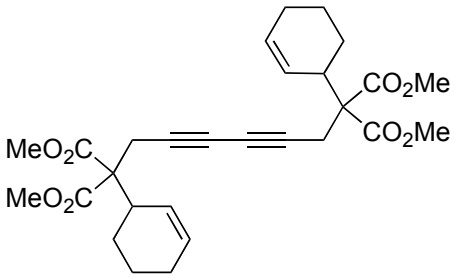
Yield 55%. Yellow solid: mp 96-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87 (t, J = 7.6 Hz, 2H), 3.74 (s, 12H), 2.84 (s, 4H), 2.75 (d, J = 7.6 Hz, 4H), 1.70 (s, 6H), 1.65 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 137.1, 116.8, 72.8, 67.7, 57.2, 52.8, 31.0, 26.1, 23.4, 17.9; HMRS-ESI calcd. for $C_{26}H_{34}O_8K$ $[M+K]^+$: 513.1891. Found: 513.1866.

Bisenyne 11d



Yield 45%. Brown solid: mp 126-128 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.24 (m, 10H), 6.55 (d, J = 15.7 Hz, 2H), 6.02 (dt, J = 7.6, 15.7 Hz, 2H), 3.79 (s, 12H), 2.98 (d, J = 7.6 Hz with s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170, 136.9, 134.9, 128.5, 127.6, 126.3, 122.9, 72.6, 68.1, 57.3, 52.9, 36.2, 23.9; HMRS-ESI calcd. for $C_{34}H_{34}O_8Na$ $[M+Na]^+$: 593.6198. Found: 593.2094.

Bisenyne 11e



Yield 45%. Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (d, J = 9.3 Hz, 2H), 5.65 (d, J = 9.3 Hz, 2H), 3.75 (d, J = 10.2 Hz, 12H), 3.18-3.09 (m, 4H), 2.79 (q, J = 17.7 Hz, 4H), 1.98-1.80 (m, 4H), 1.79 (d, J = 10.2 Hz, 4H), 1.40-1.27 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 129.5, 127.2, 73.4, 67.8, 60.5, 52.6, 39.2, 24.8, 24.3, 23.1, 22.2; HMRS-ESI calcd. for $C_{28}H_{35}O_8$ $[M+H]^+$: 499.2332. Found: 499.2346.

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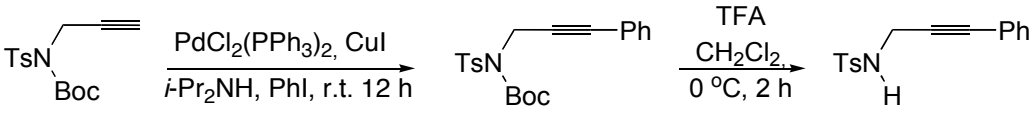
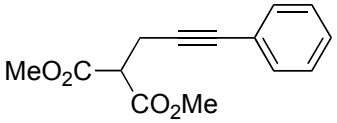
_N_-(3-Phenylprop-2-Ynyl)-(4-toluene)sulfonamide



Starting from *N-tert*-butoxycarbonyl-*N*-(2-propynyl)-(4-toluene)sulfonamide and the corresponding aryl halide, and following the general procedure for the Sonogashira coupling, the title compound was obtained in 52% yield as a pale orange solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2H), 7.73 (dd, J = 8.2, 1.1 Hz, 2H), 7.38-7.32 (m, 3H), 7.16-7.09 (m, 2H), 4.85 (s, 2H), 2.42 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 150.3 (C), 144.3 (C), 137.5 (CH), 136.7 (C), 131.7 (2CH), 130.2 (2CH), 129.2 (2CH), 128.3 (CH), 128.3 (CH), 84.8 (C), 84.5 (C), 83.8 (C), 36.7 (CH_2), 27.8 ($3CH_3$), 21.6 (CH_3).

To a solution of *N-tert*-butoxycarbonyl-N-(3-phenylprop-2-ynyl)-(4-toluene)sulfonamide in CH_2Cl_2 TFA was added. The mixture is stirred at r. t. for 3 h. Extractive work-up and chromatography (Hex: EtOAc, 5:1) affords *N*-(3-phenylprop-2-ynyl)-(4-toluene)sulfonamide in 56% as a pale brown solid, mp = 121-123 ºC: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 2H), 7.31-7.23 (m, 5H), 7.15-7.13 (m, 2H), 4.82 (t, J = 6.1 Hz, 1H), 4.08 (d, J = 6.1 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 143.7 (C), 136.8 (C), 131.5 (2CH), 129.7 (2CH), 128.5 (CH), 128.1 (2CH), 127.5 (2CH), 122.0 (C), 84.7 (C), 83.2 (C), 33.7 (CH_3), 21.4 (CH_2); HRMS-ESI calcd. for $C_{16}H_{15}O_2NSNa$ $[M+Na]^+$: 308.0721. Found: 308.0736.

Dimethyl 2-(3-Phenylprop-2-ynyl)malonate



Starting from dimethyl propargyl malonate and the corresponding aryl halide, and following Procedure B for cross-couplings, the title compound was obtained in 99% yield as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.36 (m, 2H), 7.31-7.27 (m, 3H), 3.81 (s, 6H), 3.72 (t, J = 7.7 Hz, 1H), 3.04 (d, J = 7.7 Hz, 2H); ^{13}C NMR

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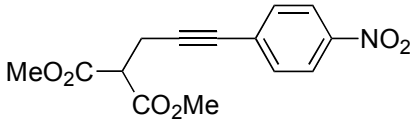
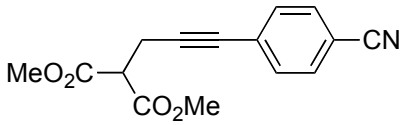
(100 MHz, $CDCl_3$, DEPT) δ 168.5 (2C), 131.6 (2CH), 128.2 (2CH), 128.0 (CH), 123.1 (C), 85.2 (C), 82.6 (C), 52.8 ($2CH_3$), 51.2 (CH), 19.5 (CH_2); HRMS-ESI calcd. for $C_{14}H_{14}O_4Na$ $[M+Na]^+$: 269.0790. Found: 269.0787.

Dimethyl 2-(3-(4-Nitrophenyl)prop-2-ynyl)malonate



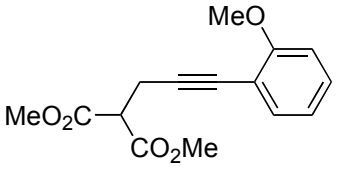
Starting from dimethyl propargyl malonate and the corresponding aryl halide, and following Procedure B for cross-couplings, the title compound was obtained in 53% yield as an orange solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.9 Hz, 2H), 7.50 (d, J = 8.9 Hz, 2H), 3.80 (s, 6H), 3.71 (t, J = 7.7 Hz, 1H), 3.06 (d, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 168.1 (2C), 147.0 (C), 132.4 (2CH), 130.0 (C), 123.5 (2CH), 91.2 (C), 81.0 (C), 53.0 ($2CH_3$), 50.8 (CH), 19.5 (CH_2); HRMS-ESI calcd. for $C_{14}H_{13}NO_6Na$ $[M+Na]^+$: 314.0641. Found: 314.0670.

Dimethyl 2-(3-(4-Cyanophenyl)prop-2-ynyl)malonate



Starting from dimethyl propargyl malonate and the corresponding aryl halide, and following Procedure B for cross-couplings, the title compound was obtained in 73% yield as a white solid, m. p. = 63-65 ºC: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 3.79 (s, 6H), 3.69 (t, J = 7.7 Hz, 1H), 3.04 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 168.2 (2C), 132.2 (2CH), 131.9 (2CH), 128.1 (C), 118.4 (C), 111.5 (C), 90.2 (C), 81.2 (C), 52.9 ($2CH_3$), 50.8 (CH), 19.5 (CH_2); HRMS-ESI calcd. for $C_{15}H_{13}NO_4Na$ $[M+Na]^+$: 294.0742. Found: 294.0753.

Dimethyl 2-(3-(2-Methoxyphenyl)prop-2-ynyl)malonate



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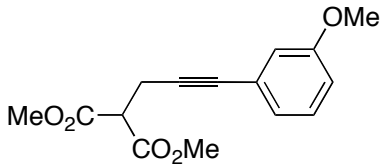
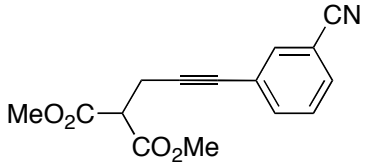
Starting from dimethyl propargyl malonate and the corresponding aryl halide, and following Procedure B for cross-couplings, the title compound was obtained in 74% yield as an orange solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 7.6, 1.7 Hz, 1H), 7.25 (ddd, J = 7.8, 7.7, 1.7 Hz, 1H), 6.88 (dd, J = 7.8, 0.8 Hz, 1H), 6.84 (d, J = 7.7 Hz, 1H), 3.86 (s, 3H), 3.79 (6H), 3.73 (t, J = 7.8 Hz, 1H), 3.07 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 168.5 (2C), 160.0 (C), 133.8 (CH), 129.4 (CH); 120.4 (CH), 112.3 (C), 110.6 (CH), 89.3 (C), 78.8 (C), 55.7 (CH_3), 52.8 ($2CH_3$), 51.3 (CH), 19.9 (CH_2); HRMS-ESI calcd. for $C_{15}H_{16}O_5Na$ $[M+Na]^+$: 299.0895. Found: 299.0891.

Dimethyl 2-(3-(3-Methoxyphenyl)prop-2-ynyl)malonate



Starting from dimethyl propargyl malonate and the corresponding aryl halide, and following the general procedure for the Sonogashira coupling, the title compound was obtained in 50% yield as an orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, J = 8.0, 7.0 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.92 (m, 1H), 6.86 (dd, J = 8.2, 2.6 Hz, 1H), 3.82 (s, 6H), 3.81 (s, 3H), 3.72 (t, J = 7.8 Hz, 1H), 3.03 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 168.4 (2C), 159.3 (C), 129.3 (CH), 124.2 (CH), 124.1 (CH), 116.6 (CH), 114.6 (CH), 85.1 (C), 82.5 (C), 55.2 ($2CH_3$), 52.8 (CH_3), 51.2 (CH), 19.6 (CH_2); HRMS-ESI calcd. for $C_{15}H_{16}O_5Na$ $[M+Na]^+$: 299.0895. Found: 299.0885.

Dimethyl 2-(3-(3-Cyanophenyl)prop-2-ynyl)malonate



Starting from dimethyl propargyl malonate and the corresponding aryl halide, and following the general procedure for the Sonogashira coupling, the title compound was obtained in 83% yield as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (t, J = 1.8 Hz, 1H), 7.57 (m, 2H), 7.40 (dd, J = 8.0, 7.8 Hz, 1H), 3.80 (s, 6H), 3.70, (dd,

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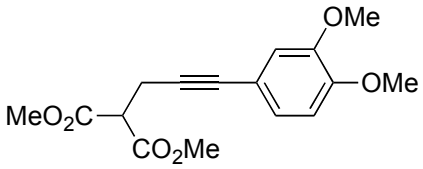
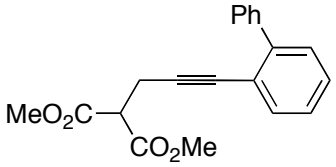
J = 8.1, 7.1, 1H), 3.02 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 168.2 (2C), 135.8 (CH), 135.0 (CH), 131.3 (CH), 129.1 (CH), 124.7 (C), 118.0 (C), 112.8 (C), 88.1 (C), 80.4 (C), 52.9 ($2CH_3$), 50.8 (CH), 19.4 (CH_2); HRMS-ESI calcd. for $C_{15}H_{13}NO_4Na$ $[M+Na]^+$: 294.0742. Found: 294.0735.

Dimethyl 2-(3-(3,4-Dimethoxyphenyl)prop-2-ynyl)malonate



Starting from dimethyl propargyl malonate and the corresponding aryl halide, and following Procedure B for cross-couplings, the title compound was obtained in 61% yield as a pale yellow solid, m. p. = 67-69 ºC: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.80 (d, *J* = 2.1 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.72 (s, 6H), 3.62 (t, *J* = 7.5 Hz, 1H), 2.93 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 168.2 (2C), 149.1 (C), 148.3 (C), 124.6 (CH), 115.0 (C), 114.2 (CH), 110.7 (CH), 83.3 (C), 82.2 (C), 55.5 ($2CH_3$), 52.5 ($2CH_3$), 52.4 (CH), 19.5 (CH_2); HRMS-ESI calcd. for $C_{16}H_{18}O_6Na$ $[M+Na]^+$: 329.1001. Found: 329.0998.

Dimethyl 2-(2-Biphenyl)prop-2-ynyl)malonate



Starting from dimethyl propargyl malonate and the corresponding aryl halide, and following the general procedure for the Sonogashira coupling, the title compound was obtained in 52% yield as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (m, 2H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.44-7.38 (m, 3H), 7.37-7.30 (m, 3H), 3.70 (s, 6H), 3.55 (t, *J* = 7.8 Hz, 1H), 2.90 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 168.4 (2C), 143.7 (C), 133.3 (CH), 133.1 (CH), 131.3 (CH), 129.5 (CH), 129.2 (CH), 128.3 (CH), 127.9 (CH), 127.3 (CH), 126.9 (CH), 122.7 (C), 121.4 (C), 88.2 (C), 82.1 (C), 52.7 ($2CH_3$), 51.0 (CH), 19.7 (CH_2).

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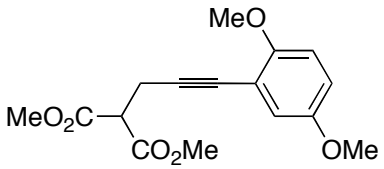
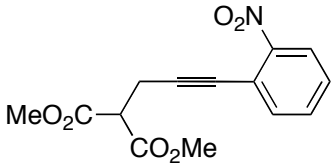
Dimethyl 2-(3-(2,5-Dimethoxyphenyl)prop-2-ynyl)malonate



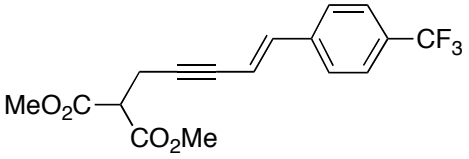
Starting from dimethyl propargyl malonate and the corresponding aryl halide, and following the general procedure for the Sonogashira coupling, the title compound was obtained in 59% yield as a pale orange solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (d7, J = 2.9 Hz, 1H), 6.79 (dd, J = 9.0, 2.9 Hz, 1H), 6.75 (d, J = 9.0 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 6H), 3.74 (s, 3H), 3.71 (t, J = 7.8 Hz, 1H), 3.05 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 168.4 (2C), 154.5 (C), 153.2 (C), 118.6 (CH), 115.2 (CH), 112.9 (C), 112.1 (CH), 89.3 (C), 78.7 (C), 56.4 (CH_3), 55.7 (CH_3), 52.7 (CH_3), 51.2 (CH), 19.8 (CH). One signal is missing due to overlapping; HRMS-CI calcd. for $C_{16}H_{19}O_6$ $[M+H]^+$: 307.1182. Found: 307.1184.

Dimethyl 2-(3-(2-Nitrophenyl)prop-2-ynyl)malonate



Starting from dimethyl propargyl malonate and the corresponding aryl halide, and following the general procedure for the Sonogashira coupling, the title compound was obtained in 84% yield as an orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, J = 8.6, 1.2 Hz, 1H), 7.56 (dd, J = 7.6, 2.0 Hz, 1H), 7.52 (dd, J = 7.9, 1.6 Hz, 1H), 7.43 (ddd, J = 8.5, 7.6, 2.0 Hz, 1H), 3.81 (s, 6H), 3.75 (t, J = 7.6 Hz, 1H), 3.09 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 168.3 (2C), 150.0 (C), 134.9 (CH), 132.7 (CH), 128.5 (CH), 124.5 (CH), 118.4 (C), 93.9 (C), 77.8 (C), 53.1 ($2CH_3$), 50.7 (CH), 19.8 (CH_2); HRMS-ESI calcd. for $C_{14}H_{13}NO_6Na$ $[M+Na]^+$: 314.0641. Found: 314.0628.

(*E*)-Dimethyl 2-(5-(4-(Trifluoromethyl)phenyl)pent-4-en-2-ynyl)malonate



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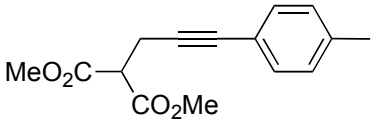
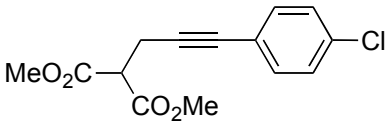
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 6.91 (d, J = 16.3 Hz, 1H), 6.23 (dt, J = 16.3, 2.1 Hz, 1H), 3.83 (s, 6H), 3.69 (dd, J = 9.7, 5.6 Hz, 1H), 3.03 (dd, J = 7.6, 2.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 139.7, 126.4, 125.8, 111.0, 89.3, 81.3, 53.0, 51.2, 19.9; HRMS-ESI calcd. for $C_{17}H_{15}O_4F_3Na$ [M+Na]$^+$: 363.0820. Found: 363.0829.

Dimethyl 2-(3-*p*-Tolylprop-2-ynyl)malonate



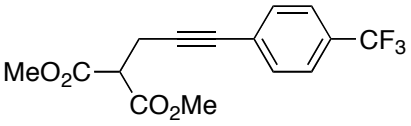
Starting from dimethyl propargyl malonate and the corresponding aryl halide, and following Procedure B for cross-couplings, the title compound was obtained in 84% yield as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 7.9 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 3.80 (s, 6H), 3.71 (t, J = 7.8 Hz, 1H), 3.02 (d, J = 7.8 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 138.1, 131.5, 129.0, 120.0, 84.4, 82.6, 52.8, 51.3, 21.4, 19.5; HMRS-ESI calcd. for $C_{15}H_{16}O_4Na$ [M+Na]$^+$: 283.0946. Found: 283.0959.

Dimethyl 2-(3-(4-Chlorophenyl)prop-2-ynyl)malonate



Starting from dimethyl propargyl malonate and the corresponding aryl halide, and following Procedure B for cross-couplings, the title compound was obtained in 99% yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.23 (m, 4H), 3.80 (s, 6H), 3.70 (t, J = 7.7 Hz, 1H), 3.01 (d, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 134.0, 132.9, 128.5, 121.6, 86.3, 81.5, 52.8, 51.0, 19.5; HRMS-ESI calcd. for $C_{14}H_{13}O_4NaCl$ [M+Na]$^+$: 303.0400. Found: 303.0402.

Dimethyl 2-(3-(4-(Trifluoromethyl)phenyl)prop-2-ynyl)malonate



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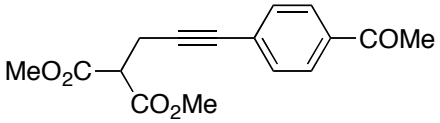
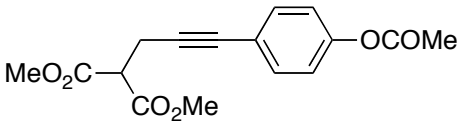
Starting from dimethyl propargyl malonate and the corresponding aryl halide, and following Procedure B for cross-couplings, the title compound was obtained in 90% brown solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 3.79 (s, 6H), 3.70 (t, J = 7.6 Hz, 1H), 3.03 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 131.9, 126.8, 125.2, 122.5, 88.0, 81.4, 52.9, 50.9, 19.5; HRMS-ESI calcd. for $C_{15}H_{13}O_4NaF_3$ $[M+Na]^+$: 337.0653. Found: 337.0664.

Dimethyl 2-(3-(4-Acetylphenyl)prop-2-ynyl)malonate



Starting from dimethyl propargyl malonate and the corresponding aryl halide, and following Procedure B for cross-couplings, the title compound was obtained in 90% brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 3.80 (s, 6H), 3.71 (t, J = 7.9 Hz, 1H), 3.04 (d, J = 7.6 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 168.3, 136.1, 131.8, 128.0, 88.9, 81.9, 53.4, 51.0, 26.6, 19.6; HRMS-ESI calcd. for $C_{16}H_{16}O_5Na$ $[M+Na]^+$: 311.0895. Found: 311.0884.

Dimethyl 2-(3-(4-Acetoxyphenyl)prop-2-ynyl)malonate



To a suspension of the 4-iodophenol (1 g, 4.54 mmol) in pyridine was added at room temperature the anhydride acid (4.3 mL, 45 mmol) and the mixture was stirred for 3 h. The reaction was quenched adding a solution of HCl (10%) and the organic layer was extracted with CH_2Cl_2 (50 mL x 3). The combined organic layers were dried using $MgSO_4$ and the solvent was removed under reduced pressure. The crude was purified by flash chromatography to obtain 4-iodophenyl acetate as brown oil (1.18 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 9.2 Hz, 2H), 6.91 (d, J = 9.2 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 150.52, 138.5, 123.8, 89.9, 21.1.

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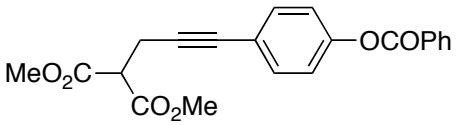
Starting from dimethyl propargyl malonate and the 4-iodophenyl acetate, and following Procedure B for cross-couplings, the title compound was obtained in 60% yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 3.77 (s, 6H), 3.67 (t, J = 7.9 Hz, 1H), 2.98 (d, J = 7.7 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 150.3, 132.7, 121.7, 120.9, 85.3, 81.7, 52.9, 51.2, 21.1, 19.5; HRMS-ESI calcd. for $C_{16}H_{16}O_6Na$ $[M+Na]^+$: 327.0845. Found: 327.0847.

Dimethyl 2-(3-(4-(Benzoyloxy)phenyl)prop-2-ynyl)malonate



To a suspension of the 4-iodophenol (1.075 g, 4.90 mmol) in dichloromethane (20 mL) were added at 0 ºC the benzoyl chloride (0.57 mL, 4.90 mmol) and the triethylamine (0.68 mL, 4.90 mmol) and the mixture was stirred for 3 h at 0º C. The reaction was diluted with more dichloromethane and washed with a solution of $NaHCO_3$ (1 M). The combined organic layers were dried using $MgSO_4$ and the solvent was removed under reduced pressure. The crude was purified by flash chromatography to obtain 4-iodophenyl benzoate as brown oil (1.50 g, 98%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 1.4, 8.2 Hz, 2H), 7.74 (dd, J = 2.0, 6.9 Hz, 2H), 7.52 (t, J = 7.6 Hz, 3H), 7.00 (dd, J = 2.6, 6.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 138.6, 133.6, 130.2, 128.7, 124.0, 89.9; HRMS-ESI calcd. for $C_{13}H_9IO_2Na$ $[M+Na]^+$: 346.9545. Found: 346.9551.

Starting from dimethyl propargyl malonate and 4-iodophenyl benzoate, and following Procedure B for cross-couplings, the title compound was obtained in 87% yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 1.7, 8.3 Hz, 2H), 7.64 (td, J = 7.3, 2.9 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.43 (dd, J = 2.1, 6.9 Hz, 2H), 7.15 (dd, J = 2.1, 6.9 Hz, 2H), 3.78 (s, 6H), 3.70 (t, J = 7.8 Hz, 1H), 3.02 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 150.3, 132.9, 130.2, 128.6, 125.5, 121.7, 85.4, 81.8, 52.9, 51.2, 20.7, 19.4; HRMS-ESI calcd. for $C_{21}H_{18}O_6Na$ $[M+Na]^+$: 389.1001. Found: 389.1009.

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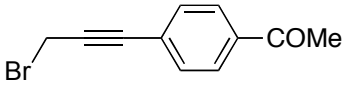
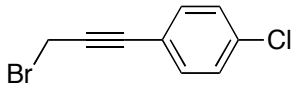
1-(4-(3-Bromoprop-1-Ynyl)phenyl)ethanone



Starting from the propargylic alcohol and 4-iodo-acetophenone, and following the Procedure B for cross-couplings, the corresponding 1-(4-(3-hydroxyprop-1-ynyl)phenyl)ethanone compound was obtained in 55%: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 2.0, 6.6 Hz, 2H), 7.50 (dd, J = 2.1, 6.9 Hz, 2H), 4.52 (s, 2H), 2.59 (s, 3H), 1.92 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 136.2, 131.8, 128.2, 127.3, 90.3, 84.6, 51.6, 26.6.

To a suspension of the 1-(4-(3-hydroxyprop-1-ynyl)phenyl)ethanone (0.64 g, 3.67 mmol) in chloroform was added dropwise the PBr_3 (0.41 mL, 4.40 mmol). The mixture was stirred 2 h and was quenched adding dropwise a saturated solution of $NaHCO_3$. The combined organic layers were washed with brine, dried using $MgSO_4$ and the solvent was removed under reduced pressure. The crude was purified by flash chromatography to obtain a 98% of light yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 2.0, 6.6 Hz, 2H), 7.51 (dd, J = 2.1, 6.9 Hz, 2H), 4.51 (s, 2H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 136.7, 132.0, 128.2, 126.9, 87.4, 85.7, 26.6, 14.6.

1-(3-Bromoprop-1-Ynyl)-4-chlorobenzene



Starting from the propargylic alcohol and 2-bromoiodobenzene, and following the Procedure B for cross-couplings, the corresponding 1-(3-hydroxyprop-1-ynyl)-4-chlorobenzene compound was obtained in 60%: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, J = 2.1, 6.6 Hz, 2H), 7.28 (dd, J = 2.1, 6.7 Hz, 2H), 4.45 (s, 2H), 1.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3, 132.6, 128.4, 120.7, 87.9, 84.3, 51.3.

To a suspension of the 1-(4-(3-hydroxyprop-1-ynyl)phenyl)ethanone (0.75 g, 4.5 mmol) in chloroform was added dropwise the PBr_3 (0.51 mL, 5.4 mmol). The mixture was stirred 2 h and was quenched adding dropwise a saturated solution of $NaHCO_3$. The combined organic layers were washed with brine, dried using $MgSO_4$ and the solvent was removed under reduced pressure. The crude was purified by

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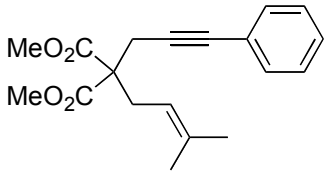
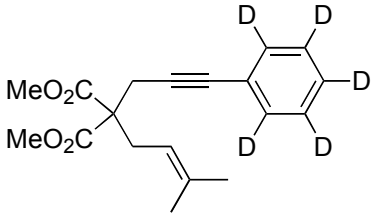
flash chromatography to obtain a 78% of light yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 4.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 133.1, 128.7, 120.6, 85.6, 85.3, 15.1.

Dimethyl 2-(3-Methylbut-2-enyl)-2-(3-phenylprop-2-ynyl)malonate (33a)



Starting from dimethyl 2-prenyl-2-propargylmalonate and the corresponding aryl halide, and following Procedure B for cross-couplings, the title compound was obtained in 58% yield as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.33 (m, 2H), 7.29-7.23 (m, 3H), 4.96 (t, J = 7.7 Hz, 1H), 3.75 (s, 6H), 2.99 (s, 2H), 2.84 (d, J = 7.7 Hz, 2H), 1.71 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 170.6, 136.8, 131.6, 128.18, 127.9, 123.3, 117.2, 84.8, 83.3, 57.5, 52.7, 30.8, 26.1, 23.5, 18.0; HRMS-CI calcd. for $C_{19}H_{22}O_4$ [M+H]: 315.1596. Found: 315.1596.

***d*^{5}-Dimethyl 2-(3-Methylbut-2-enyl)-2-(3-phenylprop-2-ynyl)malonate (33a-d_5)**



Starting from dimethyl 2-prenyl-2-propargylmalonate and the corresponding deutered-aryl halide, and following Procedure B for cross-couplings, the title compound was obtained in 65% yield as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.96 (t, J = 7.7 Hz, 1H), 3.75 (s, 6H), 2.99 (s, 2H), 2.84 (d, J = 7.7 Hz, 2H), 1.71 (s, 3H), 1.67 (s, 3H).

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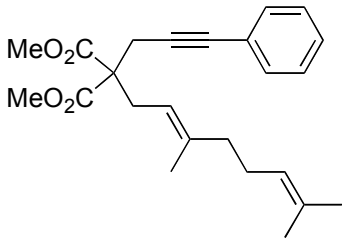
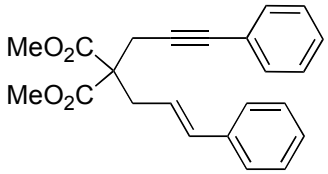
Dimethyl 2-(3,7-Dimethylocta-2*E*,6-dienyl)-2-(3-phenylprop-2-ynyl)malonate (33b)



Starting from enyne dimethyl 2-geranyl-2-propargylmalonate and iodobenzene, and following Procedure B for cross-coupling, the desired product was obtained in 79% as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.33 (m, 2H), 7.28-7.24 (m, 3H), 5.05 (m, 1H), 4.95 (m, 1H), 3.75 (s, 6H), 2.99 (s, 2H), 2.85 (d, J = 7.7 Hz, 2H), 2.11-1.98 (m, 4H), 1.68 (s, 3H), 1.66 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 170.6, 140.4, 131.6, 131.6, 128.2, 127.9, 124.0, 123.4, 117.2, 84.8, 83.3, 57.5, 52.7, 40.0, 30.9, 26.5, 25.7, 23.4, 17.7, 16.2; HRMS-CI calcd. for $C_{24}H_{31}O_4$ $[M+H]^+$: 383.2222. Found: 383.2223.

Dimethyl 2-Cinnamyl-2-(3-phenylprop-2-ynyl)malonate (33c)



Starting from Dimethyl 2-(3-phenylprop-2-ynyl)malonate and cinnamyl chloride, and following Procedure A for alkylations, the desired product was obtained in 85% yield as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.18 (m, 10H), 6.51 (d, J = 15.7 Hz, 1H), 6.02 (dt, J = 15.5, 7.6 Hz, 1H), 3.78 (s, 6H), 3.07 (s, 2H), 3.02 (dd, J = 7.6, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 137.0, 134.6, 131.7, 128.5, 128.2, 128.0, 127.5, 126.3, 123.3, 84.3, 83.8, 57.7, 52.8, 36.2, 24.0 (one signal is missing due to overlapping); HRMS-CI calcd. For $C_{23}H_{23}O_4$ $[M+H]^+$: 363.1596. Found: 363.1597.

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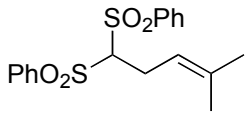
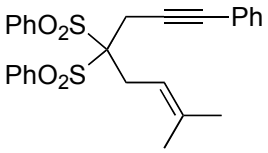
1-(4-Methyl-1-(Phenylsulfonyl)pent-3-enylsulfonyl)benzene [289]



Starting from bis(phenylsulfonyl)methane and 4-bromo-2-methyl-2-butene, and following general procedure for alkylations, 1-(4-methyl-1-(phenylsulfonyl)pent-3-enylsulfonyl)benzene was obtained in 80% yield as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.92 (m, 4H), 7.70-7.65 (m, 2H), 7.58-7.53 (m, 4H), 5.01 (bt, J = 6.9 Hz, 1H), 4.42 (t, J = 6.1 Hz, 1H), 2.86 (t, J = 6.4 Hz, 2H), 1.57 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; DEPT) δ 138.1 (C), 136.0 (C), 134.4 (CH), 129.4 (CH), 130.0 (CH), 118.0 (CH), 84.0 (CH), 25.5 (CH_3), 24.6 (CH_2), 17.6 (CH_3).

4,4-Bis(Phenylsulfonyl)-7-methyl-6-octen-1-phenyl-1-yne (33d)



Starting from 1-(4-methyl-1-(phenylsulfonyl)pent-3-enylsulfonyl)benzene and 1-(3-bromoprop-1-ynyl)benzene, and following the general procedure for alkylations, **33d** was obtained in 80% yield as a white solid; mp 100-102 ºC: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.13 (m, 4H), 7.70-7.64 (m, 2H), 7.57-7.52 (m, 4H), 7.36-7.24 (m, 5H), 5.51- 5.52 (m, 1H), 3.39 (s, 2H), 3.10 (d, J = 6.5 Hz, 2H), 1.76 (d, J = 1.2 Hz, 3H), 1.57 (d, J = 0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 136.8, 134.5, 131.5 (2C), 128.4, 128.3, 128.1, 122.7, 115.0, 89.6, 85.7, 81.8, 28.2, 26.1, 21.5, 18.2; Anal. calcd for $C_{27}H_{26}O_4S_2$: C, 67.65; H, 5.48; S, 13.40. Found: C, 67.80; H, 5.45; S, 13.66.

289 Benedetti, F.; Berti, F.; Fabrissin, S.; Gianferraro, T.; Rialiti, A. *J. Org. Chem.* **1991**, *56*, 3530-3537.

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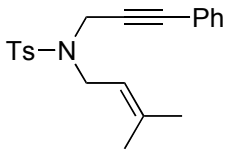
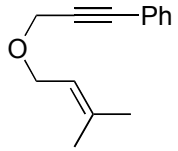
_N_-(3-Methylbut-2-Enyl)-_N_-(3-phenylprop-2-ynyl)-(4-toluene)sulfonamide (33e)



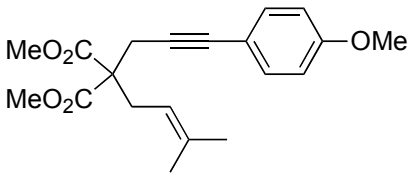
Starting from *N*-(3-phenylprop-2-ynyl)-(4-toluene)sulfonamide and 4-bromo-2-methyl-2-butene, and following Procedure A for alkylations, **33e** was obtained in 85% yield as a pale brown solid, m. p. = 75-77 ºC: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0 Hz, 2H), 7.31-7.18 (m, 5H), 7.05 (d, J = 7.8 Hz, 2H), 5.18 (dd, J = 7.5, 7.2 Hz, 1H), 4.28 (s, 3H), 3.87 (d, J = 7.3 Hz, 2H), 2.32 (s, 3H), 1.75 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8 (C), 138.5 (C), 135.6 (C), 130.9 (2CH), 128.9 (2CH), 127.8 (CH), 127.6 (2CH), 127.3 (2CH), 121.8 (C), 117.5 (CH), 84.8 (C), 81.7 (C), 43.6 (CH_2), 35.8 (CH_2), 25.4 (CH_3), 20.9 (CH_3); 17.4 (CH_3); HRMS-ESI calcd. for $C_{21}H_{23}O_2NSNa$ $[M+Na]^+$: 376.1347. Found: 376.1347.

1-(3-(3-Methylbut-2-Enyloxy)prop-1-ynyl)benzene (33f)



Starting from 3-phenyl-2-propyn-1-ol and 4-bromo-2-methyl-2-butene, and following the general procedure for alkylations, **33f** was obtained in 61% yield as an orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.42 (m, 2H), 7.32-7.27 (m, 3H), 5.38 (t, J = 7.2 Hz, 1H), 4.35 (s, 2H), 4.12 (d, J = 7.1 Hz, 2H), 1.77 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 138.2 (C), 131.7 (2CH), 128.4 (CH), 128.3 (2CH), 122.8 (C), 120.4 (CH), 86.0 (C), 85.5 (C), 66.0 (CH_2), 57.6 (CH_2), 25.8 (CH_3), 18.1 (CH_3); HRMS-ESI calcd. for $C_{14}H_{16}ONa$ $[M+Na]^+$: 223.1099. Found: 223.1104.

Dimethyl 2-(3-(4-Methoxyphenyl)prop-2-ynyl)-2-(3-methylbut-2-enyl)malonate (33g)



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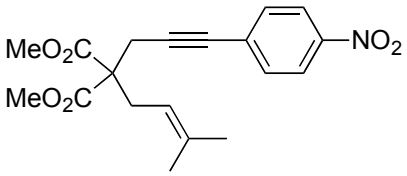
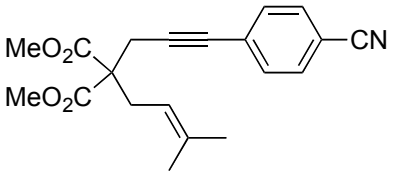
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.8Hz, 3H), 4.97 (t, J = 7.7 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 6H), 2.98 (s, 2H), 2.85 (d, J = 7.7 Hz, 2H), 1.73 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 159.3, 136.7, 133.0, 117.2, 115, 5, 113.8, 83.1, 60.4, 57.6, 55.2, 52.6, 31.0, 26.1, 23.5, 18.0; HRMS-CI calcd. for $C_{20}H_{25}O_5$ $[M+H]^+$: 345.1702. Found: 345.1697.

Dimethyl 2-(3-Methylbut-2-enyl)-2-(3-(4-nitrophenyl)prop-2-ynyl)malonate (33h)



Starting from dimethyl 2-(3-(4-nitrophenyl)prop-2-ynyl)malonate and 4-bromo-2-methyl-2-butene, and following Procedure A for alkylations, the desired product was obtained in 65% as an orange solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 9.1 Hz, 2H), 7.50 (d, J = 9.1 Hz, 2H), 4.94 (t, J = 7.7 Hz, 1H), 3.77 (s, 6H), 3.04 (s, 2H), 2.83 (d, J = 7.8 Hz, 2H), 1.72 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 170.4 (2C), 147.0 (C), 137.1 (2C), 132.3 (2CH), 123.5 (2CH), 116.8 (CH), 90.9 (C), 81.8 (C), 57.3 (C), 52.8 ($2CH_3$), 31.1 (CH_2), 26.6 (CH_3), 23.6 (CH_2), 17.9 (CH_3); HRMS-ESI calcd. For $C_{19}H_{21}NO_6Na$ $[M+Na]^+$: 382.1267. Found: 382.1279.

Dimethyl 2-(3-(4-Cyanophenyl)prop-2-ynyl)-2-(3-methylbut-2-enyl)malonate (33i)



Starting from dimethyl 2-(3-(4-cianophenyl)prop-2-ynyl)malonate and 4-bromo-2-methyl-2-butene, and following Procedure A for alkylations, the desired product was obtained in 91% as a white solid; m.p. = 41-43 ºC: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 4.96 (t, J= 7.7 Hz, 1H), 3.78 (s, 6H), 3.04 (s, 2H), 2.84 (d, J = 7.7 Hz, 2H), 1.73 (s, 3H), 1.68 (s, 3H); ^{13}C NMR

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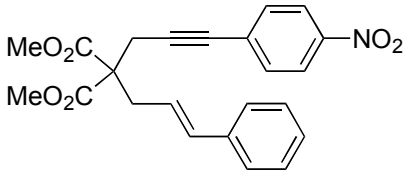
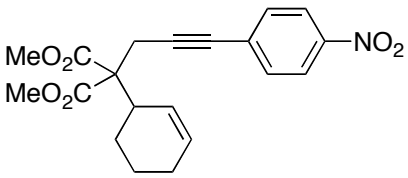
(100 MHz, $CDCl_3$) δ 170.4, 137.1, 132.2, 131.9, 128.2, 118.4, 116.9, 111.4, 89.9, 82.0, 57.3, 52.8, 31.0, 26.1, 23.5, 17.9; HRMS-ESI calcd. for $C_{20}H_{21}NO_4Na$ $[M+Na]^+$: 362.1368. Found: 362.1356.

Dimethyl 2-Cinnamyl-2-(3-(4-nitrophenyl)prop-2-ynyl)malonate (33k)



Starting from dimethyl 2-(3-(4-nitrophenyl)prop-2-ynyl)malonate and cinnamyl chloride, and following Procedure A for alkylations, the desired product was obtained in 42% as an orange solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.36-7.20 (m, 5H), 6.54 (d, J = 15.6 Hz, 1H), 6.05 (dt, J = 15.6, 7.7 Hz, 1H), 3.79 (s, 6H), 3.11 (s, 2H), 3.01 (dd, J = 7.6, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1 (2C), 147.0 (C), 136.8 (C), 134.9 (CH), 132.5 (2CH), 130.1 (C), 128.6 (2CH), 127.7 (CH), 126.3 (2CH), 123.5 (2CH), 123.0 (CH), 90.4 (C), 82.2 (C), 57.4 (C), 53.1 (CH_3), 53.0 (CH_3), 36.4 (CH_2), 24.1 (CH_2). Two signals are missing due to overlapping; HRMS-ESI calcd. for $C_{23}H_{21}O_6Na$ $[M+Na]^+$: 430.1267. Found: 430.1274.

Dimethyl 2-(Cyclohex-2-enyl)-2-(3-(4-nitrophenyl)prop-2-ynyl)malonate (33l)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.9 Hz, 2H), 7.49 (d, J = 8.9 Hz, 2H), 5.84-5.70 (m, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 3.22-3.15 (m, 1H), 3.10 (q, J = 16.1 Hz, 2H), 1.99 (bs, 2H), 1.90-1.78 (m, 2H), 1.66-1.51 (m, 1H), 1.48-1.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.1, 147.0, 132.4, 130.4, 129.5, 127.3, 123.6, 91.6, 81.9, 60.8, 52.8, 39.4, 25.0, 24.5, 23.4, 22.4; HRMS-ESI calcd. for $C_{20}H_{21}NO_6Na$ $[M+Na]^+$: 394.1267. Found: 394.1266.

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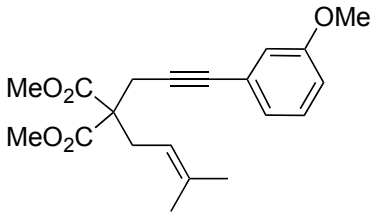
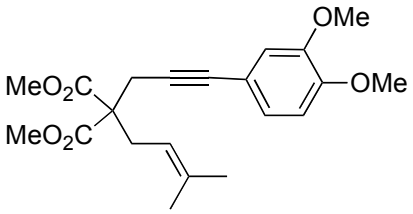
Dimethyl 2-(3-(3-Methoxyphenyl)prop-2-ynyl)-2-(3-methylbut-2-enyl)malonate (33m)



Starting from dimethyl 2-(3-(3-methoxyphenyl)prop-2-ynyl)malonate and 4-bromo-2-methyl-2-butene, and following the general procedure for alkylations, **33m** was obtained in 67% as a dark orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 7.8 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 6.89 (bs, 1H), 6.83 (dd, J = 7.8, 2.0 Hz, 1H), 4.95 (t, J = 7.6 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 6H), 2.99 (s, 2H), 2.84 (d, J = 7.6 Hz, 2H), 1.71 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6 (2C), 159.2 (C), 136.8 (C), 129.2 (CH), 124.3 (C), 124.2 (CH), 117.1 (CH), 116.6 (CH), 114.3 (CH), 84.6 (C), 83.2 (C), 57.5 (C), 55.2 (CH_3), 52.7 (2CH_3), 30.9 (CH_2), 26.1 (CH_3), 23.4 (CH_2), 17.9 (CH_3); HRMS-ESI calcd. for $C_{20}H_{24}O_5Na$ $[M+Na]^+$: 367.1521. Found: 367.1212.

Dimethyl 2-(3-(3,4-Dimethoxyphenyl)prop-2-ynyl)-2-(3-methylbut-2-enyl)malonate (33o)



Starting from dimethyl 2-(3-(3,4-dimethoxyphenyl)prop-2-ynyl)malonate and 4-bromo-2-methyl-2-butene, and following the general procedure for alkylations, **33o** was obtained in 50% as a pale yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (dt, J = 8.1, 1.6 Hz, 1H), 6.85 (t, J = 1.5 Hz, 1H), 6.75 (dd, J = 8.1, 1.4 Hz, 1H), 4.94 (m, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.74 (s, 6H), 2.94 (s, 2H), 2.83 (d, J = 8.1 Hz, 2H), 1.71 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 149.2, 136.6, 127.2, 117.1, 115.5, 114.3, 110.9, 107.9, 83.3, 83.1, 57.5, 55.9, 52.7, 31.0, 26.1, 23.5, 18.0; HRMS-ESI calcd. for $C_{21}H_{26}O_6Na$ $[M+Na]^+$: 397.1627. Found: 397.1617.

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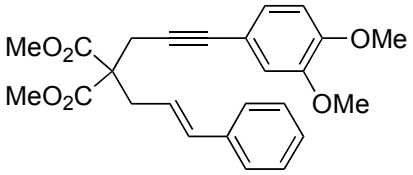
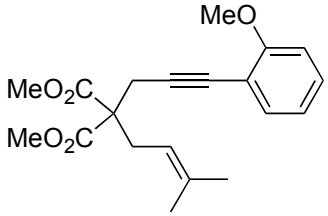
Dimethyl 2-Cinnamyl-2-(3-(3,4-dimethoxyphenyl)prop-2-ynyl)malonate (33p)



Starting from dimethyl 2-(3-(3,4-dimethoxyphenyl)prop-2-ynyl)malonate and cinnamyl chloride, and following Procedure A for alkylations, the desired product was obtained in 76% as a pale orange solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.17 (m, 5H), 6.99 (dd, J = 8.3, 1.8 Hz, 1H), 6.88 (d, J = 1.8 Hz, 1H), 6.77 (d, J = 8.3 Hz, 1H), 6.54 (d, J = 16.0 Hz, 1H), 6.08 (dt, J = 15.8, 7.6 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.76 (6H), 3.07 (s, 2H), 3.03 (d, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2 (2C), 149.2 (C), 148.5 (C), 136.9 (C), 134.4 (CH), 128.4 (2CH), 127.4 (CH), 126.2 (CH), 124.8 (2CH), 123.3 (CH), 115.3 (C), 114.3 (CH), 110.9 (CH), 83.6 (C), 82.5 (C), 57.5 (C), 55.7 ($2CH_3$), 52.6 ($2CH_3$), 36.1 (CH_2), 23.8 (CH_2). Two signals are missing due to overlapping; HRMS-ESI calcd. for $C_{25}H_{26}O_6Na$ $[M+Na]^+$: 445.1627. Found: 445.1622.

Dimethyl 2-(3-(2-Methoxyphenyl)prop-2-ynyl)-2-(3-methylbut-2-enyl)malonate (33q)



Starting from dimethyl 2-(3-(2-methoxyphenyl)prop-2-ynyl)malonate and 4-bromo-2-methyl-2-butene, and following Procedure A for alkylations, the desired product was obtained in 93% as an orange solid; m. p. = 46-48 ºC: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, J = 7.6, 1.6 Hz, 1H), 7.24 (ddd, J = 9.2, 7.6, 1.6Hz, 1H), 6.87 (dd, J = 7.6, 1.2 Hz, 1H), 6.83 (d, J = 7.5 Hz, 1H), 4.97 (t, J = 7.7 Hz, 1H), 3.84 (s, 3H), 3.74 (s, 6H), 3.04 (s, 2H), 2.87 (d, J = 7.8 Hz, 2H); 1.71 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7 (2C), 160.1 (C), 136.7 (C), 133.5 (CH), 129.3 (CH), 120.3 (CH), 117.3 (CH), 112.6 (C), 110.6 (CH), 88.8 (C), 79.5 (C), 57.6 (C), 55.7 (CH3), 52.6 ($2CH_3$), 31.0 (CH_2), 26.1 (CH_3), 23.8 (CH_2), 17.9 (CH_3); HRMS-ESI calcd. for $C_{20}H_{24}O_5Na$ $[M+Na]^+$: 367.1521. Found: 367.1211.

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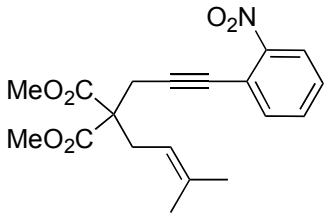
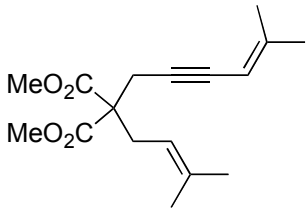
Dimethyl 2-(3-Methylbut-2-enyl)-2-(3-(2-nitrophenyl)prop-2-ynyl)malonate (33t)



Starting from dimethyl 2-(3-(2-nitrophenyl)prop-2-ynyl)malonate and 4-bromo-2-methyl-2-butene, and following the general procedure for alkylations, **33t** was obtained in 59% as a dark orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 1H), 7.58- 7.51 (m, 2H), 7.42 (dd, J = 8.2, 7.0 Hz, 1H), 4.96 (t, J = 6.8 Hz, 1H), 3.77 (s, 6H), 3.08 (s, 2H), 2.86 (d, J = 7.7 Hz, 2H), 1.72 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 170.4 (2C), 150.1 (C), 137.0 (C), 135.0 (CH), 132.6 (CH), 128.4 (CH); 124.5 (CH), 118.6 (C), 117.0 (CH), 93.7 (C), 78.5 (C), 57.4 (C), 52.8 ($2CH_3$), 31.1 (CH), 26.1 (CH3), 23.9 (CH2), 17.9 (CH); HRMS-ESI calcd. for $C_{19}H_{21}NO_6Na$ $[M+Na]^+$: 382.1267. Found: 382.1259.

Dimethyl 2-(3-Methylbut-2-enyl)-2-(5-methylhex-4-en-2-ynyl)malonate (40a)



Starting from dimethyl 2-prenyl-2-propargylmalonate and the bromo-2-propene, and following Procedure B for cross-couplings, the title compound was obtained in 98% yield as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (t, J= 1.5 Hz, 1H), 4.95 (tt, J= 1.5, 7.8 Hz, 1H), 3.75 (s, 6H), 2.94 (d, J= 1.5 Hz, 2H), 2.8 (d, J= 7.6 Hz, 2H), 1.86 (s, 3H), 1.8 (s, 3H), 1.71 (d, J= 1.0 Hz, 3H), 1.66 (d, J= 0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 136.7, 117.2, 105.0, 86.1, 57.5, 52.6, 30.8, 26.0, 24.6, 23.6, 20.8, 17.9; HMRS-ESI calcd. for $C_{17}H_{24}O_4Na$ $[M+Na]^+$: 315.1572 Found: 315.1558.

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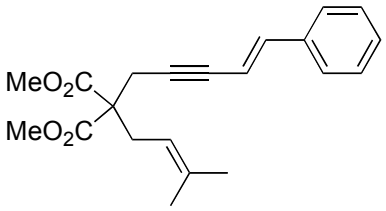
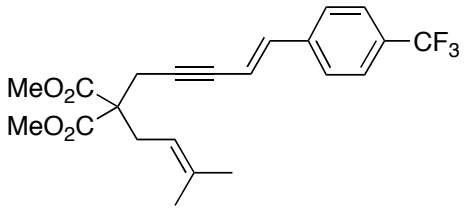
(*E*)-dimethyl 2-(3-Methylbut-2-enyl)-2-(5-phenylpent-4-en-2-ynyl)malonate (40b)



Starting from dimethyl 2-prenyl-2-propargylmalonate and the β-bromostyrene, and following Procedure B for cross-couplings, the title compound was obtained in 91% yield as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 5H), 6.87 (d, *J*= 16.1 Hz, 1H), 6.13 (dt, *J*= 16.1, 2.3 Hz, 1H), 4.96 (dquint, *J* = 7.7, 1.4 Hz, 1H), 3.77 (s, 6H), 2.98 (d, *J*= 1.9 Hz, 2H), 2.84 (d, *J*= 7.7 Hz, 2H), 1.74 (d, *J*= 1.0 Hz, 3H), 1.70 (d, *J*= 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 141.0, 136.9, 128.7, 128.5, 126.1, 117.1, 108.1, 87.0, 57.4, 52.7, 31.0, 26.1, 23.7, 18.0; HMRS-ESI calcd. for $C_{21}H_{24}O_4Na$ $[M+Na]^+$: 363.1572 Found: 363.1555.

(*E*)-dimethyl 2-(3-Methylbut-2-enyl)-2-(5-(4-(trifluoromethyl)phenyl)pent-4-en-2-ynyl)malonate (40c)



Starting from (*E*)-dimethyl 2-(5-(4-(trifluoromethyl)phenyl)pent-4-en-2-ynyl)malonate and the corresponding allyl bromide, and following Procedure A for alkylation, the title compound was obtained in 89% yield as a orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 16.3 Hz, 1H), 6.19 (dt, *J* = 16.3, 2.1 Hz, 1H), 4.94 (tt, *J* = 7.8, 1.6 Hz, 1H), 3.75 (s, 6H), 2.97 (d, *J* = 2.0, 2H), 2.81 (d, *J* = 7.7, 2H), 1.71 (d, *J* = 0.8, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 139.9, 139.5, 137.1, 126.4, 125.9, 117.2, 111.1, 88.9, 82.1, 57.6, 52.9, 31.2, 26.3, 23.9, 18.2; HRMS-ESI calcd. for $C_{22}H_{23}O_4F_3Na$ $[M+Na]^+$: 431.1446. Found: 431.1450.

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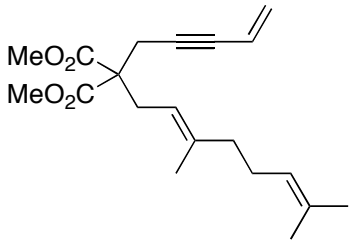
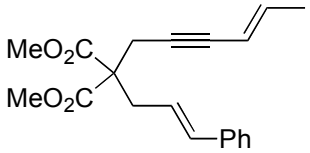
Dimethyl 2-(3,7-Dimethylocta-2*E*,6-dienyl)-2-(pent-4-en-2-ynyl)malonate (40d)



Starting from enyne **5g** and vinyl bromide, and following Procedure B for cross-coupling, **40d** was obtained in 68% as a pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (ddt, J = 17.5, 11.0, 2.1 Hz, 1H), 5.53 (dd, J = 17.5, 2.3 Hz, 1H), 5.39 (dd, J = 11.0, 2.3 Hz, 1H), 5.05 (t, J = 6.6 Hz, 1H), 4.91 (t, J = 7.7 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 2.88 (d, J = 2.1Hz, 2H), 2.78 (d, J = 7.7 Hz, 2H), 2.10-2.00 (m, 4H), 1.68 (s, 3H), 1.65 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 140.3, 131.5, 126.5, 124.0, 117.2, 117.1, 85.4, 81.9, 57.4, 52.6, 40.0, 30.8, 26.5, 25.6, 23.3, 17.7, 16.1; HRMS-CI cald. for $C_{20}H_{29}O_4$ $[M+H]^+$: 333.2066. Found: 333.2065.

Dimethyl 2-Cinnamyl-2-((*E*)-hex-4-en-2-yn-1-yl)malonate (40e)



Starting from (*E*)-dimethyl 2-(hex-4-en-2-yn-1-yl)malonate following Procedure B for cross-coupling (^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09-5.98 (m, 1H), 5.39 (dd, J = 15.7, 2.5 Hz, 1H), 3.77 (s, 6H), 3.57 (t, J = 7.7 Hz, 2H), 2.85 (d, J = 7.7 Hz, 2H), 1.72 (dd, J = 6.7, 1.8 Hz, 3H)), **40e** was obtained following the Procedure A for alkylations to obtain it in 75% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.20 (m, 5H), 6.51 (d, J = 15.4, Hz, 1H), 6.15-5.99 (m, 2H), 5.46 (dd, J = 15.4, 1.9 Hz, 1H), 3.76 (s, 6H), 2.97 (d, overlap., 2H), 2.95 (s, 2H), 1.77 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 139.0, 136.8, 134.1, 127.9, 125.9, 123.2, 110.1, 81.8, 57.3, 52.3, 35.8, 23.6, 18.2.

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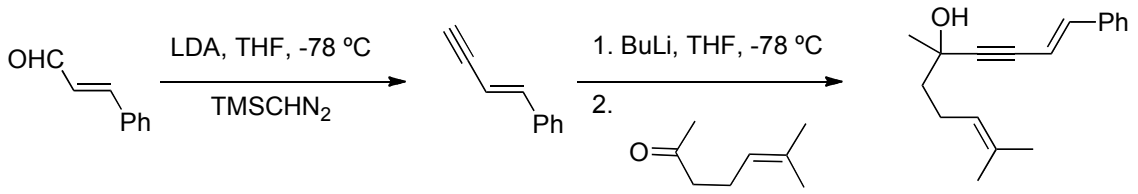
(*E*)-5,9-Dimethyl-1-Phenyldeca-1,8-dien-3-yn-5-ol (40f)



To a solution of freshly prepared LDA (1 equiv., 0.0144 mol) and dry THF was slowly added *trans*-cinnamaldehyde (2 mL, 0.016 mol) at -78 ºC. The mixture was stirred at this temperature for 30 minutes, after that the diazocompound (7.2 mL, 0.0144 mol) was added to the mixture at -78 ºC. The mixture was slowly warmed to room temperature and was quenched adding water. Extraction with of organic layer, evaporation of the solvent and purification by flash chromatography afforded the (*E*)-but-1-en-3-yn-1-ylbenzene (1.24 g, 61%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.32 (m, 5H), 7.11 (d, J = 16.3 Hz, 1H), 6.19 (dd, J = 16.3, 2.4 Hz, 1H), 3.11 (d, J = 2.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 135.7, 128.9, 128.8, 126.4, 107.0, 82.8, 79.3. To a suspensión of the alkyne (0.3 mmol) in dry THF at -78 ºC was added the BuLi (0.3 mmol). After 30 minutes stirring at that temperature was added the 6-methyl-5-hepten-2-one (0.3 mmol) and the mixture was stirred at -78 ºC 1 h more and then was warmed to room temperature. The reaction was sttired overnight and the crude was quenched adding water, extraction of the organic layer and purification by flash chromatography afforded **40f** (0.070 g, 88%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.31 (m, 5H), 6.98 (d, J = 16.3 Hz, 1H), 6.23 (d, J = 16.3 Hz, 1H), 5.25 (t, J = 7.4 Hz, 1H), 2.44-2.21 (m, 2H), 1.8 (td, J = 8.1, 2.3 Hz, 2H), 1.76 (s, 3H), 1.72 (s, 3H), 1.68 (bs, 1H), 1.59 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.0, 135.9, 128.4, 125.9, 123.6, 107.4, 94.8, 82.4, 72.6, 43.2, 41.3, 29.6, 25.4, 23.5, 17.5. HRMS-CI cald. for $C_{18}H_{22}ONa$ $[M+Na]^+$: 277.1568. Found: 277.1578.

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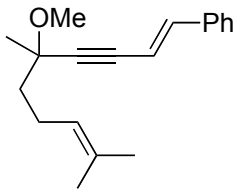
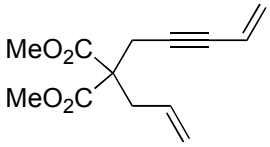
Enyne 40g



Starting from a solution of dry THF and **40f** (0.108 g, 0.04 mmol) was slowly added the sodium hydride (0.020 g, 0.051 mmol). After Hydrogen evolution had ceased, MeI (0.037 mL, 0.059 mmol) was slowly added and the mixture was warmed gently. After 30 minutes NaI precipitated from the solution. The reaction was then quenched adding water, and extracted adding a solution of 10% HCl and ether. The combined organic layers were dried using $MgSO_4$ and evaporated by reduced pressure. The crude was purified by short flash chromatography (100%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.26 (m, 5H), 6.94 (d, J = 16.3 Hz, 1H), 6.19 (d, J = 16.3 Hz, 1H), 5.15 (t, J = 7.4 Hz, 1H), 3.39 (s, 3H), 2.20-2.17 (m, 2H), 1.79-1.72 (m, 2H), 1.70 (s, 3H), 1.64 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 136.0, 128.4, 126.0, 123.7, 107.5, 92.4, 84.3, 73.7, 53.1, 51.2, 40.9, 37.0, 29.5, 25.4, 21.9, 17.4, 13.9.

Dimethyl 2-Allyl-2-(pent-4-en-2-yn-1-yl)malonate (40h)



Starting from dimethyl 2-(pent-4-en-2-yn-1-yl)malonate, which was obtained following the Procedure B for cross-coupling reactions (^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81-5.70 (m, 1H), 5.58 (dd, J = 17.3, 2.5 Hz, 1H), 5.44 (dd, J = 11.2, 2.5 Hz, 1H), 3.80 (s, 6H), 3.64 (t, J = 7.6 Hz, 1H), 2.93 (dd, J = 17.3, 7.6 Hz, 2H)), **40h** was obtained following the Procedure A for alkylations using the corresponding allyl bromide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78-5.60 (m, 2H), 5.55 (dd, J = 17.5, 2.4Hz, 1H), 5.41 (dd, J = 10.8, 2.4Hz, 1H), 5.18 (dq, J = 16.8, 3.0, 1.5Hz, 1H), 5.10 (dd, J = 10.0, 2.0 Hz, 1H), 3.74 (s, 6H), 2.9 (d, J = 2 Hz, 2H), 2.8 (d, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 132, 127, 120, 117, 85, 82, 57, 53, 37,

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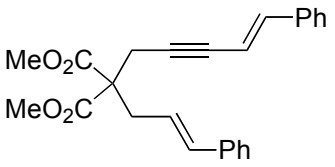
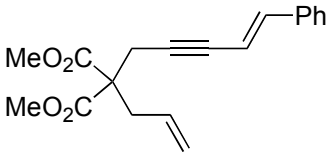
24; LMRS-ESI calcd. for $C_{24}H_{30}O_8Na$ $[M+Na]^+$: 259.1. Found: 259.2; HRMS-ESI calcd. for $C_{13}H_{15}O_4Na$ $[M+Na]^+$: 259.0946. Found: 259.0935.

Dimethyl 2-Cinnamyl-2-((*E*)-5-phenylpent-4-en-2-yn-1-yl)malonate (40i)



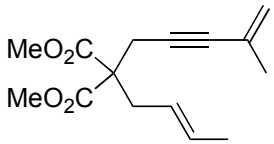
Starting from dimethyl 2-prenyl-2-propargylmalonate and the β-bromostyrene, and following Procedure B for cross-couplings, the title compound was obtained in 91% yield as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.21 (m, 10H), 6.88 (d, *J*= 16.5 Hz, 1H), 6.53 (d, *J*= 15.7 Hz, 1H), 6.13 (dt, *J* = 16.5, 2.4 Hz, 1H), 6.05 (m, *J* = 7.6 Hz, 1H), 3.77 (s, 6H), 3.03 (s, 2H), 2.99 (d, *J*= 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 140.9, 136.8, 136.0, 134.3, 128.4, 128.2, 128.0, 127.2, 126.0, 125.9, 123.1, 107.8, 86.2, 82.7, 57.4, 52.6, 36.0, 24.0; HMRS-ESI calcd. for $C_{25}H_{24}O_4Na$ $[M+Na]^+$: 411.1572 Found: 411.1560.

(*E*)-Dimethyl 2-Allyl-2-(5-phenylpent-4-en-2-yn-1-yl)malonate (40j)



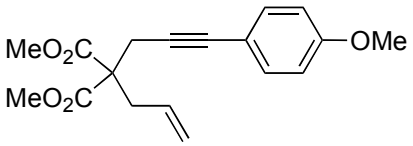
Starting from dimethyl dimethyl 2-allyl-2-(prop-2-yn-1-yl)malonate and the β-bromostyrene, and following Procedure B for cross-couplings, the title compound was obtained in 82% yield as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.25 (m, 5H), 6.86 (d, *J*= 16.5 Hz, 1H), 6.11 (dt, *J*= 16.4, 2.1 Hz, 1H), 5.73-5.61 (m, 1H), 5.29-5.14 (m, 2H), 3.75 (s, 6H), 2.99 (d, *J* = 2.1 Hz, 2H), 2.84 (d, *J*= 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 140.8, 136.0, 131.6, 128.4, 128.2, 125.7, 119.6, 107.8, 86.1, 82.5, 57.0, 52.5, 36.6, 24.0; HMRS-ESI calcd. for $C_{19}H_{20}O_4Na$ $[M+Na]^+$: 335.1259 Found: 335.1261.

(*E*)-Dimethyl 2-(But-2-en-1-yl)-2-(4-methylpent-4-en-2-yn-1-yl)malonate (40k)



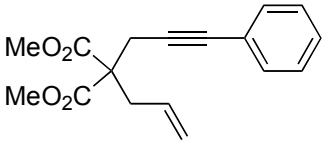
Starting from (*E*)-dimethyl 2-(but-2-en-1-yl)-2-(prop-2-yn-1-yl)malonate, which was obtained following the Procedure B for cross-coupling reactions: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66-5.53 (m, 1H), 5.29-5.21 (m, 1H), 5.18 (d, J = 17.8 Hz, 2H), 3.74 (s, 6H), 2.87 (d, J = 12.6 Hz, 2H), 2.72 (d, J = 7.5 Hz, 2H), 1.84 (s, 3H), 1.66 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 130.2, 126.4, 123.8, 123.4, 120.9, 84.4, 83.1, 57.1, 52.4, 35.3, 23.6, 17.7; HMRS-ESI calcd. for $C_{15}H_{21}O_4$ $[M+H]^+$: 265.1440 Found: 265.1448.

Dimethyl 2-Allyl-2-(3-(4-methoxyphenyl)prop-2-ynyl)malonate (38a)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 79% as a orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, J = 8.8, 4.7 Hz, 2H), 6.82 (dd, J = 8.8, 4.7 Hz, 2H), 5.76-5.64 (m, 1H), 5.25-5.14 (m, 2H), 3.81 (s, 3H), 3.77 (s, 6H), 3.02 (s, 2H), 2.88 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 159.5, 133.2, 132.2, 120.0, 115.6, 114.1, 83.6, 57.5, 55.5, 52.8, 36.9, 23.8; HRMS-ESI calcd. for $C_{18}H_{20}O_5Na$ $[M+Na]^+$: 339.1218. Found: 339.1208.

Dimethyl 2-Allyl-2-(3-phenylprop-2-ynyl)malonate (38b)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 84% as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.36 (m, 2H), 7.33-7.27 (m, 3H), 5.78-5.64 (m, 1H), 5.28-5.15 (m, 2H), 3.78 (s, 6H), 3.05 (s, 2H), 2.90 (d, J = 7.5 Hz,

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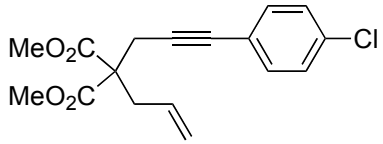
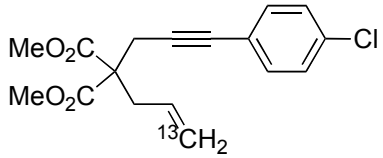
2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 131.9, 131.6, 128.2, 127.9, 123.3, 119.9, 84.3, 83.7, 57.3, 52.8, 36.9, 23.7; HRMS-CI calcd. for $C_{17}H_{19}O_4$ $[M+Na]^+$: 287.1283. Found: 287.1276.

Dimethyl 2-Allyl-2-(3-(4-chlorophenyl)prop-2-ynyl)malonate (38c)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 99% as a brown solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.25 (m, 4H), 5.75-5.63 (m, 1H), 5.26-5.15 (m, 2H), 3.78 (s, 6H), 3.03 (s, 2H), 2.88 (d, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 134.0, 132.9, 131.7, 128.5, 121.6, 119.9, 85.3, 82.6, 57.2, 52.8, 36.8, 23.7; HRMS-ESI calcd. for $C_{17}H_{17}O_4ClNa$ $[M+Na]^+$: 343.0706. Found: 343.0713.

^{13}C-Dimethyl 2-Allyl-2-(3-(4-chlorophenyl)prop-2-ynyl)malonate (38c-^{13}C)



A two necked bottom flash was connected to a trap containing a saturated solution of KI. The dimethyl allyl malonate (2 mL, 12.4 mmol) dissolved in MeOH were added at -78 ºC. The ozone stream was bubbled during 30 minutes. Then PPh_3 (4.9 g, 18.6 mmol) was added and stirred 18h at -78 ºC and warmed to room temperature. The crude was purified by flash chromatography (4:1 hexane/ethyl acetate) to obtain 1.87 g (87%) of the dimethyl 2-(2-oxoethyl)malonate as an colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 3.89 (d, J = 13.8 Hz, 1H), 3.74 (s, 6H), 3.09 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 168.8, 52.9, 45.2, 42.4.

To a mixture of $^{13}CH_3PPh_3I$ (0.61 g, 1.52 mmol) and the dimethyl 2-(2-oxoehtyl)malonate (0.20 g, 1.17 mmol) in THF (30 mL) was added 0.7 M NaHMDS in THF (3.9 mL, 2.73 mmol) at -78 ºC, and the mixture was warmed gradually to room temperature. After the mixture was stirred for 20 h the reaction was quenched

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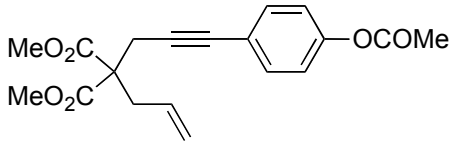
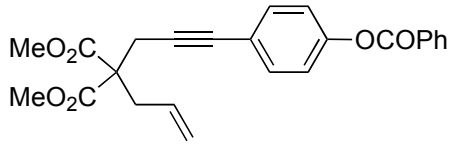
by adding saturated aqueous NH_4Cl (150 mL) and the mixture was extracted with Et_2O (50 mL x 3). The organic layer was washed with water (50 mL x 3) and dried over $MgSO_4$. After the solvent was removed, the residue was used for the next step. Starting from ^{13}C-dimethyl allyl malonate and 1-(3-bromoprop-1-ynyl)-4-chlorobenzene, and following Procedure A for the alkylation, was obtained in 30%, for all the steps, as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.23 (m, 5H), 5.74- 5.60 (m, 1H), 5.43-5.27 (m, 1H), 5.05 (m, 1H), 3.76 (s, 6H), 3.01 (s, 2H), 2.85 (t, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.1; HRMS-ESI calcd. for $^{12}C_{16}{}^{13}CH_{17}O_4Na^{35}Cl$ $[M+Na]^+$: 344.0747. Found: 344.0733.

Dimethyl 2-(3-(4-Acetoxyphenyl)prop-2-ynyl)-2-allylmalonate (38d)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.7 Hz, 1H), 7.00 (d, J = 8.7 Hz, 2H), 5.67 (ddt, J = 17.5, 10.1, 7.5 Hz, 1H), 5.19 (dd, J = 17.0, 1.9 Hz, 1H), 5.14 (dd, J = 10.1, 2.0 Hz, 1H), 3.75 (s, 6H), 3.00 (s, 2H), 2.85 (d, J = 7.5 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.3, 150.4, 132.9, 132.0, 121.7, 121.0, 120.0, 84.5, 83.0, 57.4, 52.9, 37.0, 23.8, 21.3; HRMS-ESI calcd. for $C_{19}H_{20}O_6Na$ $[M+Na]^+$: 367.1158. Found 367.1147.

Dimethyl 2-Allyl-2-(3-(4-(benzoyloxy)phenyl)prop-2-ynyl)malonate (38e)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 7.1 Hz, 2H), 7.68 (t, J = 7.6, 2.8 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H), 7.19 (d, J = 8.7 Hz, 2H), 5.80-5.66 (m, 1H), 5.25 (dd, J = 17.0, 1.9 Hz, 1H), 5.20 (dd, J = 10.1, 1.9 Hz, 1H), 3.81 (s, 6H), 3.07 (s, 2H), 2.92 (d, J = 7.4 Hz, 2H), 2.08 (s, 1H), 1.30 (t, J = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 164.9, 150.6, 133.7, 132.9, 131.75, 130.2, 129.3, 128.6, 128.4, 127.6, 125.6, 121.8, 120.9, 119.9, 84.4, 82.9, 57.3, 52.8,

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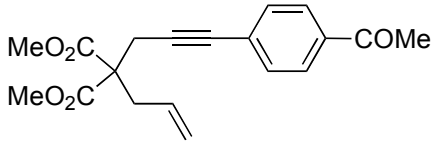
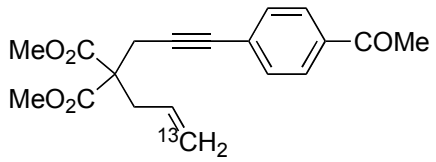
36.8, 23.7, 20.70, 19.8; HRMS-ESI calcd. for $C_{24}H_{22}O_6Na$ $[M+Na]^+$: 429.1314. Found 429.1316.

Dimethyl 2-(3-(4-Acetylphenyl)prop-2-ynyl)-2-allylmalonate (38f)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 89% as a brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 5.75-5.04 (m, 1H), 5.20 (dd, J = 23.0, 1.9 Hz, 1H), 5.17 (dd, J = 16.0, 1.9 Hz, 1H), 3.77 (s, 6H), 3.05 (s, 2H), 2.86 (d, J = 7.4 Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 159.1, 132.7, 130.2, 128.7, 123.9, 122.9, 115.1, 113.1, 82.9, 82.4, 57.3, 57.1, 55.0, 53.2, 52.4, 35.3, 29.4, 23.3, 17.8, 12.7; HRMS-ESI calcd. for $C_{19}H_{20}O_5Na$ $[M+Na]^+$: 351.1208. Found: 351.1220.

^{13}C-Dimethyl 2-(3-(4-Acetylphenyl)prop-2-ynyl)-2-allylmalonate (38f-^{13}C)



A two neecked bottom flash was connected to a trap containing a saturated solution of KI. The dimethyl allyl malonate (2 mL, 12.4 mmol) dissolved in MeOH were added at -78ºC. The ozone stream was bubbled during 30 minutes. The reaction was following by TLC. Then PPh_3 (4.9 g, 18.6 mmol) was added and stirred 18 h at -78 ºC and warmed to room temperature. The crude was purified by flash chromatography (4:1 hexane/ethyl acetate) to obtain 1.87 g (87%) of the dimethyl 2-(2-oxoehtyl)malonate as an colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 3.89 (d, J = 13.8 Hz, 1H), 3.74 (s, 6H), 3.09 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 168.8, 52.9, 45.2, 42.4.

To a mixture of $^{13}CH_3PPh_3I$ (0.61 g, 1.52 mmol) and the dimethyl 2-(2-oxoehtyl)malonate (0.20 g, 1.17 mmol) in THF (30 mL) was added 0.7 M NaHMDS in THF (3.9 mL, 2.73 mmol) at -78 ºC, and the mixture was warmed gradually to

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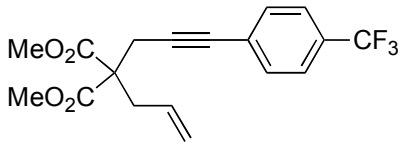
room temperature. After the mixture was stirred for 20 h the reaction was quenched by adding saturated aqueous NH_4Cl (150 mL) and the mixture was extracted with Et_2O (50 mL x 3). The organic layer was washed with water (50 mL x 3) and dried over $MgSO_4$. After the solvent was removed, the residue was used for the next step.

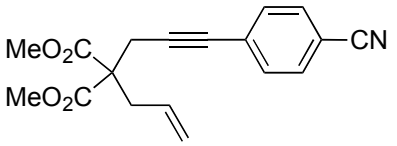
Starting from ^{13}C-dimethyl allyl malonate and 1-(4-(3-bromoprop-1-ynyl)phenyl)ethanone, and following Procedure A for the alkylation, was obtained in 22%,for all the steps, as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 5.75-5.04 (m, 1H), 5.20 (dd, J = 23.0, 1.9 Hz, 1H), 5.17 (dd, J = 16.0, 1.9 Hz, 1H), 3.77 (s, 6H), 3.05 (s, 2H), 2.86 (d, J = 7.4 Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 131.8, 128.2, 120.0, 119.8, 87.8, 82.9, 52.8, 36.9, 26.4, 23.8; HRMS-ESI calcd. for $^{12}C_{18}{}^{13}CH_{20}O_5Na$ $[M+Na]^+$: 352.1242. Found: 352.1231.

Dimethyl 2-Allyl-2-(3-(4-(trifluoromethyl)phenyl)prop-2-ynyl)malonate (38g)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 99% as a brown solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 3.79 (s, 6H), 5.75-5.63 (m, 1H), 5.20 (d, J = 20.0 Hz, 1H), 5.17 (d, J = 13.4 Hz, 1H), 3.76 (s, 6H), 3.03 (s, 2H), 2.86 (d, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 131.6, 131.4, 129.7, 129.4, 126.7, 124.9, 122.3, 119.7, 86.8, 82.2, 56.9, 52.3, 36.6, 31.3, 23.4, 13.8; HRMS-ESI calcd. for $C_{18}H_{17}O_4F_3Na$ $[M+Na]^+$: 377.0987. Found: 377.0977.

Dimethyl 2-Allyl-2-(3-(4-cyanophenyl)prop-2-ynyl)malonate (38h)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 75% as a

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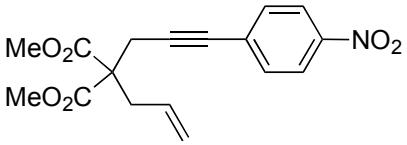
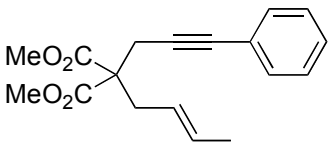
white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 5.74-5.62 (m, 1H), 5.25-5.16 (m, 2H), 3.79 (s, 6H), 3.07 (s, 2H), 2.88 (d, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 132.2, 132.0, 131.6, 128.1, 120.1, 118.5, 111.5, 89.3, 82.3, 57.1, 52.9, 36.9, 23.7; HRMS-ESI calcd. for $C_{18}H_{17}NO_4Na$ $[M+Na]^+$: 334.1067. Found: 334.1055.

Dimethyl 2-Allyl-2-(3-(4-nitrophenyl)prop-2-ynyl)malonate (38i)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 87% as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 5.75-5.63 (m, 1H), 5.26-5.17 (m, 2H), 3.80 (s, 6H), 3.08 (s, 2H), 2.90 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 146.9, 132.5, 130.1, 123.7, 120.3, 90.4, 82.2, 57.2, 52.9, 37.0, 23.9; HRMS-ESI calcd. for $C_{17}H_{17}NO_6Na$ $[M+Na]^+$: 354.0957. Found: 354.0954.

Dimethyl 2-(but-2*E*-enyl)-2-(3-phenylprop-2-ynyl)malonate (38j)



Starting from the above enyne and iodobenzene, and following Procedure B for cross-coupling, **38k** was obtained in 84% as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.34 (m, 2H), 7.28-7.24 (m, 3H), 5.66-5.56(m, 1H), 5.32-5.22 (m, 1H), 3.75 (s, 6H), 2.99 (s, 2H), 2.84 (dt, J = 7.5, 1.1 Hz, 2H), 1.65 (dd, J = 6.5, 1.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 131.6, 130.6, 128.2, 127.9, 124.1, 123.3, 84.4, 83.47, 57.5, 52.7, 35.6. 23.5, 18.0; HRMS-ESI calcd. for $C_{18}H_{21}O_4$ $[M+H]^+$: 301.1440. Found: 301.1441.

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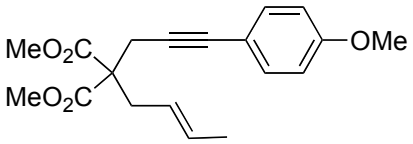
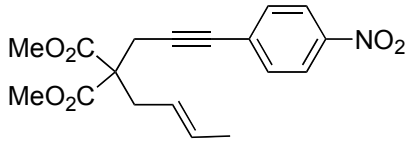
(*E*)-Dimethyl 2-(But-2-enyl)-2-(3-(4-methoxyphenyl)prop-2-ynyl)malonate (38k)



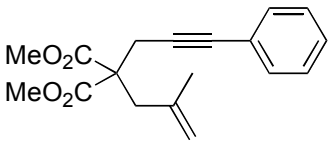
Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 70% as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.2 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 5.67-5.51 (m, 1H), 5.29-5.16 (m, 1H), 3.74 (s, 3H), 3.70 (s, 6H), 2.93 (s, 2H), 2.74 (d, J = 7.4 Hz, 2H), 1.62 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 159.5, 133.2, 130.7, 129.1, 124.3, 123.3, 115.6, 114.0, 83.4, 83.0, 57.7, 55.4, 52.9, 35.7, 29.9, 23.7, 18.2, 13.1; HRMS-ESI calcd. for $C_{19}H_{22}O_5Na$ $[M+Na]^+$: 353.1365. Found: 353.1351.

(*E*)-Dimethyl 2-(But-2-enyl)-2-(3-(4-nitrophenyl)prop-2-ynyl)malonate (38l)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 86% as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.9 Hz, 2H), 7.50 (d, J = 8.9 Hz, 2H), 5.70-5.58 (m, 1H), 5.35-5.23 (m, 1H), 3.77 (s, 6H), 3.06 (s, 2H), 2.79 (d, J = 7.5 Hz, 2H), 1.68 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 169.75, 147.1, 132.6, 131.1, 130.8, 124.1, 124.0, 90.8, 82.2, 60.8, 57.3, 52.6, 41.8, 35.7, 23.9, 18.2; HRMS-ESI calcd. for $C_{18}H_{19}NO_6Na$ $[M+Na]^+$: 368.1110. Found: 368.1098.

Dimethyl 2-(2-Methylallyl)-2-(3-phenylprop-2-ynyl)malonate (38m)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 74% as a

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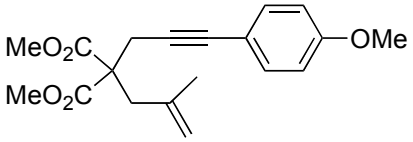
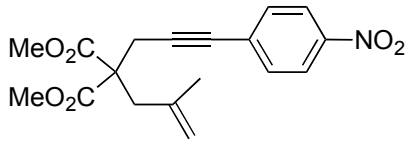
colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.28-7.24 (m, 3H), 4.94 (m, 1H), 4.88 (m, 1H), 3.76 (s, 6H), 3.05 (s, 2H), 2.91 (s, 2H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 139.9, 131.6, 128.2, 127.9, 123.3, 116.3, 84.6, 83.9, 56.9, 52.7, 39.8, 23.6; HRMS-CI calcd. for $C_{18}H_{21}O_4$ $[M+H]^+$: 301.1440. Found: 301.1450.

Dimethyl 2-(3-(4-Methoxyphenyl)prop-2-ynyl)-2-(2-methylallyl)malonate (38n)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 89% as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.9 Hz, 2H), 6.80 (d, J = 8.9 Hz, 2H), 4.93 (t, J = 1.8 Hz, 1H), 4,88 (s, 1H), 3.79 (s, 3H), 3.75 (s, 6H), 3.04 (s, 2H), 2.90 (s, 2H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 159.6, 140.2, 133.2, 116.5, 115.6, 114.0, 83.8, 83.1, 57.1, 55.5, 52.9, 39.9, 23.8, 23.4; HRMS-ESI calcd. for $C_{19}H_{22}O_5Na$ $[M+Na]^+$: 353.1365, found 353.1374.

Dimethyl 2-(2-Methylallyl)-2-(3-(4-nitrophenyl)prop-2-ynyl)malonate (38o)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 89% as a yellow solid, mp 76-77 ºC: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.9 Hz, 2H), 7.51 (d, J = 8.9 Hz, 2H), 4.97 (q, J = 1.5 Hz, 1H), 4,87 (q, J = 0.89 Hz, 1H), 3.79 (s, 6H), 3.11 (s, 2H), 3.04 (q, J = 0.89 Hz, 3H), 2.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 147.0, 139.7, 132.4, 130.1, 116.5, 90.7, 82.3, 56.6, 52.9, 40.0, 23.7, 23.1; HRMS-ESI calcd. for $C_{18}H_{19}NO_6Na$ $[M+Na]^+$: 368.1094. Found 368.1110.

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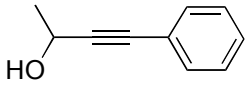
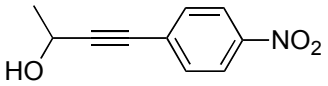
4-Phenylbut-3-Yn-2-ol



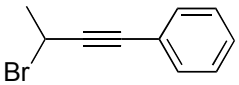
Starting from 3-butyn-1-ol and the corresponding aryl halide, and following Procedure B for cross-couplings, the title compound was obtained in 75% yield as a colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.4 Hz, 2H), 7.37-7.30 (m, 3H), 4.89 (q, J = 6.8 Hz, 1H), 2.03 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 128.8, 128.3, 122.2, 89.2, 86.1, 31.9, 27.5; HRMS-ESI calcd. for $C_{10}H_{10}ONa$ $[M+Na]^+$: 169.0629. Found: 169.0629.

4-(4-Nitrophenyl)But-3-yn-2-ol



Starting from 3-butyn-1-ol and the corresponding aryl halide, and following Procedure B for cross-couplings, the title compound was obtained in 99%, brown solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.9 Hz, 2H), 7.58 (d, J = 8.9 Hz, 2H), 4.85-4.76 (m, 1H), 2.01 (d, J = 3.9 Hz, 1H), 1.59 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 132.6, 132.4, 129.6, 123.5, 96.3, 82.2, 58.7, 24.1.

(3-Bromobut-1-Ynyl)benzene



To a solution of PPh_3 (1.1 equiv.) in CH_2Cl_2 at 0 ºC was added slowly the bromine (1 eq). When the color changed to dark yellow, the pyridine was added (2 equiv.). The mixture was stirred 5 minutes and then was added the alcohol (1 equiv.). After 3 h the reaction was finished. The solvent was removed under reduced pressure and was extracted with a solution of HCl (3.5%), pentane (4 x 20 mL) and brine (3 x 20 mL). The combined organic layers were dried using $MgSO_4$ and the solvent was removed under reduced pressure. The crude was purified by flash chromatography (hexane: ethyl acetate, 5:1) to obtain the light yellow oil in 75% of yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.3 Hz, 2H), 7.37-7.30 (m, 3H), 4.89 (q, J = 6.8 Hz, 1H), 2.03 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 128.8,

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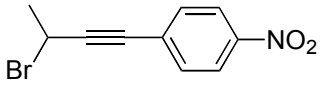
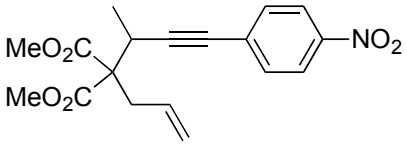
128.3, 122.2, 89.2, 86.1, 31.9, 27.5; HRMS-ESI calcd. for $C_{10}H_9BrNa$ $[M+Na]^+$: 207.9897. Found: 207.9888.

1-(3-Bromobut-1-ynyl)-4-Nitrobenzene



To a solution of PPh_3 (1.1 equiv.) in CH_2Cl_2 at 0 ºC was added slowly the bromine (1 equiv.). When the color changed to dark yellow, the pyridine was added (2 equiv.). The mixture was stirred 5 minutes and then was added the alcohol (1equiv.). After 3 h the reaction was finished. The solvent was removed under reduced pressure and was extracted with a solution of HCl (3.5%), pentane (4 x 20 mL) and brine (3 x 20 mL). The combined organic layers were dried using $MgSO_4$ and the solvent was removed under reduced pressure. The crude was purified by flash chromatography (hexane: ethyl acetate, 5:1) to obtain the light yellow oil in 83% of yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.9 Hz, 2H), 7.61 (d, J = 8.9 Hz, 2H), 4.87 (q, J = 6.9 Hz, 1H), 2.04 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6, 132.6, 129.0, 125.0, 123.6, 94.1, 83.8, 30.4, 27.0.

Dimethyl 2-Allyl-2-(4-(4-nitrophenyl)but-3-yn-2-yl)malonate (38p)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in XX % as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.9 Hz, 2H), 7.53 (d, J = 8.9 Hz, 2H), 5.86-5.76 (m, 1H), 5.21-5.11 (m, 2H), 3.79 (s, 3H), 3.77 (s, 3H), 2.93-2.82 (m, 2H), 3.45 (q, J = 7.0 Hz, 1H), 1.40 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 169.7, 146.9, 132.9, 132.3, 130.4, 123.5, 119.3, 95.9, 81.7, 61.1, 52.5, 52.5, 52.4, 38.4, 31.1, 17.1; HRMS-ESI calcd. for $C_{18}H_{19}NO_6Na$ $[M+Na]^+$: 368.1093. Found: 368.1110.

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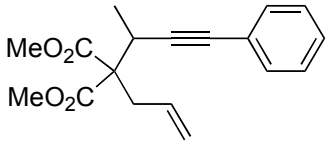
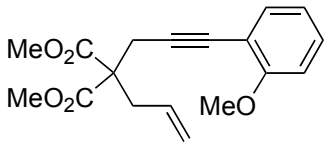
Dimethyl 2-Allyl-2-(4-phenylbut-3-yn-2-yl)malonate (38q)



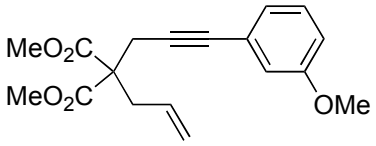
Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 99% as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.36 (m, 2H), 7.30-7.26 (m, 3H), 5.29-5.27 (m, 1H), 5.19-5.07 (m, 2H), 3.77 (s, 3H), 3.74 (s, 3H), 2.93-2.82 (m, 2H), 1.38 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 169.9, 132.9, 131.6, 128.2, 127.9, 123.4, 119.9, 89.7, 83.3, 61.4, 52.5, 52.3, 52.3, 38.6, 31.2, 17.5; HRMS-ESI calcd. for $C_{18}H_{20}O_4Na$ $[M+Na]^+$: 323.1259. Found: 323.1259.

Dimethyl 2-Allyl-2-(3-(2-methoxyphenyl)prop-2-ynyl)malonate (38r)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 81% as a orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, J = 1.7, 7.5 Hz, 2H), 7.27-7.21 (m, 1H), 6.88-6.82 (m, 2H), 5.75-5.64 (m, 1H), 5.23 (dq, J = 17.0, 1.2 Hz, 1H), 5.14 (dq, J = 17.0, 1.2 Hz, 1H), 3.84 (s, 3H), 3.75 (s, 6H), 3.06 (s, 2H), 2.90 (d, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 160.1, 133.6, 132.0, 129.4, 120.3, 119.8, 112.5, 110.6, 88.3, 79.9, 57.4, 55.7, 52.7, 36.7, 24.0; HRMS-ESI calcd. for $C_{18}H_{20}O_5Na$ $[M+Na]^+$: 339.1208. Found: 339.1208.

Dimethyl 2-Allyl-2-(3-(3-methoxyphenyl)prop-2-ynyl)malonate (38s)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 99% as a brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18(d, J = 16.4 Hz, 1H), 6.96 (d, J = 8.5

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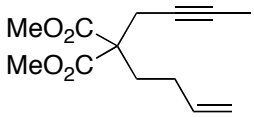
Hz, 1H), 6.89 (s, 1H), 6.84 (dd, *J* = 9.0, 2.8 Hz, 1H), 5.74-5.62 (m, 1H), 5.19 (dd, *J* = 17.1, 2.3 Hz, 1H), 5.16 (dd, *J* = 2.3, 19.7 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.01 (s, 2H), 2.87 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 159.3, 131.8, 129.3, 124.3, 119.9, 116.6, 114.5, 84.1, 83.6, 57.3, 55.3, 52.8, 36.8, 23.7; HRMS-ESI calcd. for $C_{18}H_{20}O_5Na$ $[M+Na]^+$: 339.1205. Found: 339.1208.

Dimethyl 2-(But-2-ynyl)-2-(but-3-enyl)malonate (70a)



To a dry flask containing dimethyl malonate (6.9 mmol) and THF (23 mL) was slowly added NaH (2.5 mmol) at 0 ºC. 1-Bromo-2-butyne (2.3 mmol) was then added slowly, the solution was stirred for 30 min at this temperature at which time a white precipitated formed. The mixture was warmed to r. t. and stirred for 5 h. Aqueous solution of NH_4Cl was added slowly and was extracted with ether. The crude was purified by flash chromatography (10:1 hexane/ethyl acetate) to obtain 56% of dimethyl 2-(but-2-ynyl)malonate as yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 6H), 3.55 (t, *J* = 7.8 Hz, 1H), 2.73 (dq, *J* = 7.8, 2.4 Hz, 2H), 1.75 (t, *J* = 2.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 78.0, 74.6, 52.9, 51.6, 23.1, 20.0, 3.5.

To a dry flask containing dimethyl 2-(but-2-ynyl)malonate (1.3 mmol) and diisopropylamine (23 mL) was slowly added NaH (1.5 mmol) at 0 ºC. 4-bromo-1-butene (1.5 mmol) was then added slowly. The mixture was warmed to r. t. and stirred for 5 h. Aqueous solution of NH_4Cl was added slowly and was extracted with ether. The crude was purified by flash chromatography (10:1 hexane/ethyl acetate) to obtain 80% of dimethyl 2-(but-2-ynyl)-2-(but-3-enyl)malonate as yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87-5.72 (m, 1H), 5.05 (dq, *J* = 17.0, 1.7 Hz, 1H), 4.98 (dq, *J* = 10.4, 1.7 Hz, 1H), 3.73 (s, 6H), 2.78 (q, *J* = 2.5 Hz, 2H), 2.17-2.11 (m, 2H), 1.75 (t, *J* = 2.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 137.6, 115.3, 79.0, 73.4, 57.1, 52.8, 31.5, 28.5, 23.5, 3.7; HRMS-ESI calcd. for $C_{13}H_{18}O_4Na$ $[M+Na]^+$: 261.1103. Found: 261.1103.

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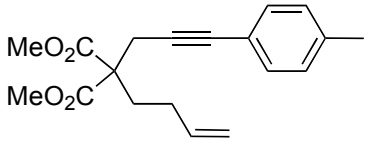
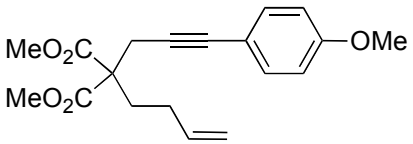
Dimethyl 2-(But-3-enyl)-2-(3-p-tolylprop-2-ynyl)malonate (70b)



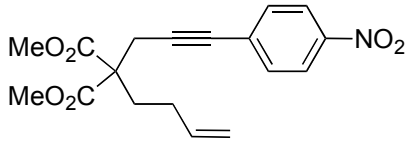
Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 70% as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 5.88-5.77 (m, 1H), 5.12-4.98 (m, 2H), 3.77 (s, 6H), 3.03 (s, 2H), 2.34 (s, 3H), 2.28-2.21 (m, 2H), 2.09-2.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 138.0, 137.3, 131.5, 128.9, 120.1, 115.3, 83.6, 83.3, 57.1, 52.7, 31.5, 28.4, 23.9, 21.4; HRMS-ESI calcd. for $C_{19}H_{22}O_4Na$ $[M+Na]^+$: 337.1420. Found: 337.1416.

Dimethyl 2-(But-3-enyl)-2-(3-(4-methoxyphenyl)prop-2-ynyl)malonate (70c)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 80% as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 5.87-5.73 (m, 1H), 5.10-4.98 (m, 2H), 3.77 (s, 6H), 3.11 (s, 2H), 2.25-2.18 (m, 2H), 2.08-1.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 159.4, 137.4, 133.0, 115.3, 113.8, 83.3, 82.5, 57.1, 55.3, 52.7, 31.5, 28.4, 23.9; HRMS-ESI calcd. for $C_{19}H_{22}O_6Na$ $[M+Na]^+$: 353.1365. Found: 353.1371.

Dimethyl 2-(but-3-enyl)-2-(3-(4-nitrophenyl)prop-2-ynyl)malonate (70d)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, and following Procedure A for the alkylation, was obtained in 72% as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.5

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Hz, 2H), 5.87-5.73 (m, 1H), 5.10-4.98 (m, 2H), 3.77 (s, 6H), 3.11 (s, 2H), 2.25-2.18 (m, 2H), 2.08-1.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 147.0, 137.1, 132.4, 123.5, 115.5, 90.3, 81.9, 56.8, 52.9, 31.6, 28.4, 24.0; HRMS-ESI calcd. for $C_{18}H_{19}NO_6Na$ $[M+Na]^+$: 368.1110. Found: 368.1102.

1. Gold(I)-Catalyzed Intermolecular Cyclopropanation reaction of 1,6-Enynes with external alkenes

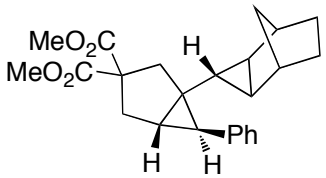
General procedure for Au(I)-catalyzed intermolecular cyclopropanation of enynes:

0.05 eq. of the cationic catalyst, were dissolved in 1.5 mL CH_2Cl_2 and cooled down to -40 ºC. A solution of 5.0 equiv. of the alkene and the enyne (1 equiv.) in 0.5 mL CH_2Cl_2 was added. The reaction mixture was stirred for 1 h at -40 ºC and was allowed to warm up to r. t. in 16 h. The reaction was quenched adding 1 mL of a 0.1 M solution of NEt_3 in hexane. The crude was purified by flash chromatography (hexane:EtOAc, V:V = 10:1).

General Procedure for the Cyclizations of Bisenynes

To a solution of Au(I) cationic complex (5-15% mol) in dry CH_2Cl_2 (0.5 mL) was added the enyne dissolved in dry CH_2Cl_2 (0.5 mL). The reaction was stirred at the stated conditions for 1-48 h. The resulting mixture was filtered through Celite and purified by chromatography (hexane-EtOAc).

(5*R**,6*S**)-Dimethyl 6-Phenyl-1-((1*S**,2*R**,3*S**,4*S**,5*R**)-tricyclo[3.2.1.0^{2,4}]octan-3-yl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (6a)



Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.19 (m, 2H), 7.17-7.09 (m, 3H), 3.73 (s, 3H), 3.71 (s, 3H), 2.72 (d, J = 14.0 Hz, 1H), 2.62-2.58 (m, 2H), 2.40 (d, J = 14.0 Hz, 1H), 2.15-2.10 (m, 1H), 1.76-1.73 (m, 1H), 1.71 (d, J = 4.1 Hz, 1H), 1.56 (dt, J = 4.1, 1.5 Hz, 1H), 1.29 (dtt, J = 26.0, 10.7, 3.5 Hz, 2H), 1.18-1.01 (m, 2H), 0.67 (d, J = 10.4 Hz, 1H), 0.59 (t, J = 2.9 Hz, 1H), 0.54 (dd, J = 7.2, 2.9 Hz, 1H),

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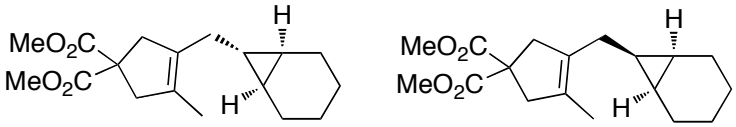
0.42 (d, J = 10.5 Hz, 1H), 0.26 (dd, J = 7.2, 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4 (C), 172.8 (C), 138.9 (C), 129.3 (CH), 127.9 (CH), 125.7 (CH), 60.5 (C), 53.1 (CH_3), 53.0 (CH_3), 42.2 (CH_2), 37.3 (CH_2), 36.1 (C), 36.0 (CH), 35.8 (CH), 32.6 (CH), 29.7 (CH_2), 29.6 (CH_2), 28.5 (CH_2), 28.1 (CH), 24.0 (CH), 21.9 (CH), 13.8 (CH); HRMS-ESI calcd for $C_{24}H_{28}NaNO_4$ $[M+Na]^+$: 403.1885. Found: 403.1877. The structure of **6a** was confirmed by COSY, HMQC, HMBC, and NOESY experiments.

Cyclopropanes 6b/6b-d_1



Colorless oil, mixture of two isomers (anti/syn = 2.3:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 6H), 3.05 (bs, 2H minor), 3.02 (bs, 2H major), 2.93 (bs, 2H), 2.02 (d, J = 7.1 Hz, 2H minor), 1.89 (d, J = 6.8 Hz, 2H major), 1.92-1.77 (m, 2H), 1.65-1.54 (m, 2H), 1.61 (s, 3H minor), 1.57 (s, 3H major), 1.43-1.33 (m, 2H minor), 1.33-1.04 (m, 4H), 0.89-0.80 (m, 2H minor), 0.64-0.54 (m, 1H minor), 0.58 (t, J = 5.0 Hz, 2H major), 0.32 (tt, J = 6.9, 4.6 Hz, 1H major); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2 (C), 132.9 (C, major), 132.9 (C, minor), 127.7 (C, major), 127.5 (C, minor), 57.6 (C, major), 57.5 (C, minor), 52.9 (CH_3), 46.0 (CH_2, minor), 45.9 (CH_2, major), 44.2 (CH_2, major), 43.9 (CH_2, minor), 32.8 (CH_2, major), 23.7 (CH_2, major), 22.9 (CH_2, minor), 22.8 (CH_2, minor), 22.7 (CH, major), 21.8 (CH_2, major), 19.1 (CH_2, minor), 17.5 (CH, minor), 17.2 (CH, major), 13.6 (CH_3, minor), 13.4 (CH_3, major), 10.4 (CH, minor); HRMS-ESI calcd for $C_{18}H_{26}NaO_4$ [M+Na]+: 329.1729. Found: 329.1743.

The structure of **6b** was confirmed by COSY, HMQC, HMBC, NOESY and by deuterium labeled experiments, in which **6b/6b'-D_1** was formed. On the ^{1}H NMR espectra was observed that the signal at 1.89 ppm integred to 1, and the proton from the cyclopropane at 0.32 ppm appeared with less multiplicity.

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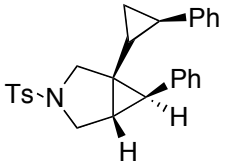
(1*R,5*S**,6*R**)-6-Phenyl-1-((1*R**,2*R**)-2-phenylcyclopropyl)-3-tosyl-3-azabicyclo[3.1.0]hexane (10a)**



White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.69 (m, 2H), 7.36 (t, *J* = 6.6 Hz, 2H), 7.25-7.19 (m, 2H), 7.18-7.12 (m, 3H), 7.12-7.07 (m, 3H), 6.76 (dd, *J* = 5.2, 3.3, 2H), 3.70 (dd, *J* = 11.5, 9.4, 2H), 3.23 (dd, *J* = 9.3, 3.9, 1H), 3.17 (d, *J* = 9.4, 1H), 2.46 (s, 3H), 2.18 (d, *J* = 4.2, 1H), 1.73 (t, *J* = 4.1, 1H), 1.49 – 1.42 (m, 1H), 1.33-1.21 (m, 3H), 1.02-0.94 (m, 1H), 0.91-0.81 (m, 3H), 0.67-0.50 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ* 143.8, 142.3, 137.1, 133.8, 129.9, 129.1, 128.3, 127.7, 126.3, 125.8, 125.8, 54.6, 50.7, 36.0, 30.6, 25.2, 22.3, 21.7, 21.3,16.0; HRMS-ESI calcd. for $C_{27}H_{27}NO_4NaS$ [M+Na]: 452.1660. Found: 452.1640; Elemental analysis (%) calcd. $C_{27}H_{27}NO_4Na$ S: C, 75.49; H, 6.34; N, 3.26; O, 7.45; S, 7.46; found: C, 74.96; H, 6.33; N, 3.17.

X-Ray Structure for compound **10a**

Table 1. Crystal data and structure refinement for **10a**.

Identification code	**10a**	
Empirical formula	C27 H27 N O2 S	
Formula weight	429.56	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 13.6368(12) Å	a= 90.00 °.
	b = 7.9693(8) Å	b = 97.724(2) °.
	c = 21.2530(17) Å	g = 90.00 °.
Volume	2288.7(4) Å^3	
Z	4	

Density (calculated)	1.247 Mg/m^3
Absorption coefficient	0.165 mm^{-1}
F(000)	912
Crystal size	0.60 x 0.60 x 0.60 mm^3
Theta range for data collection	1.51 to1.51 °.
Index ranges	-18 <=h<=20 ,-12 <=k<=11 ,-32 <=l<=16
Reflections collected	8536
Independent reflections	7333 [R(int) = 0.0234]
Completeness to theta =33.17 °	0.976 %
Absorption correction	Empirical
Max. and min. transmission	0.9075 and 0.9074
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8536 / 0 / 281
Goodness-of-fit on F^2	1.109
Final R indices [I>2sigma(I)]	R1 = 0.0483 , wR2 = 0.1327
R indices (all data)	R1 = 0.0563 , wR2 = 0.1393
Largest diff. peak and hole	0.546 and -0.362 $e.Å^{-3}$

Table 2. Bond lengths [Å] and angles [°] for **10a**.

Bond lengths----	
C1-C2	1.386(2)
C1-C6	1.389(2)
C2-C3	1.3936(18)
C3-C4	1.3966(17)
C4-C5	1.3969(17)
C4-C7	1.4861(16)
C5-C6	1.3903(17)
C7-C8	1.5107(16)
C7-C9	1.5236(16)
C8-C9	1.502(16)

C9-C10	1.4884(16)
C10-C18	1.5084(15)
C10-C20	1.5212(15)
C10-C11	1.5302(16)
C11-C12	1.4888(16)
C11-C18	1.5095(16)
C12-C17	1.3934(17)
C12-C13	1.3979(17)
C13-C14	1.39(2)
C14-C15	1.382(3)
C15-C16	1.386(3)
C16-C17	1.3984(19)
C18-C19	1.5094(16)
C19-N1	1.4829(15)
C20-N1	1.4816(15)
C21-C22	1.393(17)
C21-C27	1.3969(17)
C21-S1	1.7621(13)
C22-C23	1.3897(19)
C23-C24	1.3949(19)
C24-C26	1.3993(19)
C24-C25	1.503(2)
C26-C27	1.39(19)
N1-S1	1.6263(10)
O1-S1	1.4348(10)
O2-S1	1.4345(10)

Angles----------

C2-C1-C6	119.56(12)
C1-C2-C3	120.17(12)
C2-C3-C4	120.73(12)
C3-C4-C5	118.58(11)

C3-C4-C7	119.12(11)
C5-C4-C7	122.24(10)
C6-C5-C4	120.53(12)
C1-C6-C5	120.43(13)
C4-C7-C8	122.76(10)
C4-C7-C9	120.17(10)
C8-C7-C9	59.34(8)
C9-C8-C7	60.76(8)
C10-C9-C8	123.27(9)
C10-C9-C7	118.95(9)
C8-C9-C7	59.90(8)
C9-C10-C18	125.47(9)
C9-C10-C20	116.35(9)
C18-C10-C20	106.91(9)
C9-C10-C11	122.09(9)
C18-C10-C11	59.57(7)
C20-C10-C11	114.07(9)
C12-C11-C18	122.62(10)
C12-C11-C10	121.12(9)
C18-C11-C10	59.50(7)
C17-C12-C13	118.59(12)
C17-C12-C11	123.84(11)
C13-C12-C11	117.56(11)
C14-C13-C12	120.77(14)
C15-C14-C13	120.02(15)
C14-C15-C16	120.19(13)
C15-C16-C17	119.81(15)
C12-C17-C16	120.62(14)
C10-C18-C19	108.07(9)
C10-C18-C11	60.93(7)
C19-C18-C11	115.82(10)
N1-C19-C18	102.33(9)

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N1-C20-C10	102.85(8)
C22-C21-C27	120.41(12)
C22-C21-S1	119.41(10)
C27-C21-S1	120.15(9)
C23-C22-C21	119.28(12)
C22-C23-C24	121.41(12)
C23-C24-C26	118.40(12)
C23-C24-C25	120.44(13)
C26-C24-C25	121.16(13)
C27-C26-C24	121.04(12)
C26-C27-C21	119.44(12)
C20-N1-C19	109.40(9)
C20-N1-S1	119.22(7)
C19-N1-S1	118.29(8)
O2-S1-O1	120.32(6)
O2-S1-N1	106.94(5)
O1-S1-N1	105.93(6)
O2-S1-C21	107.72(6)
O1-S1-C21	107.98(6)
N1-S1-C21	107.31(6)

Table 3. Torsion angles [°] for **10a**.

C6-C1-C2-C3	0.1(2)
C1-C2-C3-C4	-0.2(2)
C2-C3-C4-C5	0.35(18)
C2-C3-C4-C7	-176.88(11)
C3-C4-C5-C6	-0.34(18)
C7-C4-C5-C6	176.81(11)
C2-C1-C6-C5	-0.1(2)
C4-C5-C6-C1	0.21(19)

C3-C4-C7-C8	-155.09(11)
C5-C4-C7-C8	27.78(17)
C3-C4-C7-C9	134.02(12)
C5-C4-C7-C9	-43.11(16)
C4-C7-C8-C9	-108.26(12)
C7-C8-C9-C10	-106.79(12)
C4-C7-C9-C10	-133.66(11)
C8-C7-C9-C10	113.82(11)
C4-C7-C9-C8	112.52(12)
C8-C9-C10-C18	1.65(17)
C7-C9-C10-C18	-69.53(14)
C8-C9-C10-C20	140.37(11)
C7-C9-C10-C20	69.18(13)
C8-C9-C10-C11	-71.65(15)
C7-C9-C10-C11	-142.84(10)
C9-C10-C11-C12	3.17(15)
C18-C10-C11-C12	-112.04(12)
C20-C10-C11-C12	151.82(10)
C9-C10-C11-C18	115.21(11)
C20-C10-C11-C18	-96.15(10)
C18-C11-C12-C17	5.56(17)
C10-C11-C12-C17	77.05(14)
C18-C11-C12-C13	-176.12(10)
C10-C11-C12-C13	-104.64(13)
C17-C12-C13-C14	-0.52(19)
C11-C12-C13-C14	-178.93(12)
C12-C13-C14-C15	0.1(2)
C13-C14-C15-C16	0.2(2)
C14-C15-C16-C17	-0.1(2)
C13-C12-C17-C16	0.61(18)
C11-C12-C17-C16	178.91(12)
C15-C16-C17-C12	-0.3(2)

C9-C10-C18-C19	140.19(11)
C20-C10-C18-C19	-1.63(13)
C11-C10-C18-C19	-110.05(11)
C9-C10-C18-C11	-109.76(12)
C20-C10-C18-C11	108.41(10)
C12-C11-C18-C10	109.58(11)
C12-C11-C18-C19	-153.23(10)
C10-C11-C18-C19	97.19(10)
C10-C18-C19-N1	19.95(12)
C11-C18-C19-N1	-45.85(12)
C9-C10-C20-N1	-163.25(9)
C18-C10-C20-N1	-17.43(12)
C11-C10-C20-N1	46.21(12)
C27-C21-C22-C23	-1.05(19)
S1-C21-C22-C23	-179.09(10)
C21-C22-C23-C24	1.5(2)
C22-C23-C24-C26	-0.8(2)
C22-C23-C24-C25	179.87(13)
C23-C24-C26-C27	-0.4(2)
C25-C24-C26-C27	178.97(13)
C24-C26-C27-C21	0.79(19)
C22-C21-C27-C26	-0.08(19)
S1-C21-C27-C26	177.94(10)
C10-C20-N1-C19	31.48(12)
C10-C20-N1-S1	172.08(8)
C18-C19-N1-C20	-32.36(12)
C18-C19-N1-S1	-173.37(8)
C20-N1-S1-O2	47.58(11)
C19-N1-S1-O2	-175.25(9)
C20-N1-S1-O1	177.06(9)
C19-N1-S1-O1	-45.77(11)
C20-N1-S1-C21	-67.77(10)

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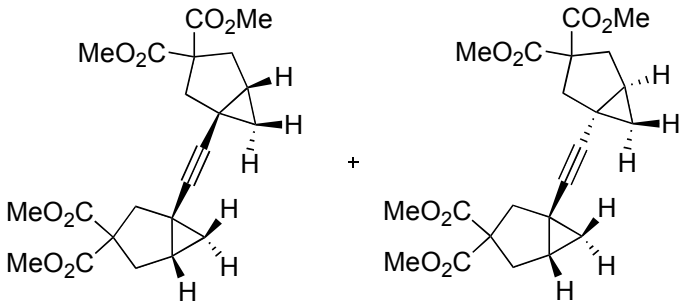
C19-N1-S1-C21	69.39(10)
C22-C21-S1-O2	-19.07(12)
C27-C21-S1-O2	162.88(10)
C22-C21-S1-O1	-150.44(10)
C27-C21-S1-O1	31.52(12)
C22-C21-S1-N1	95.77(11)
C27-C21-S1-N1	-82.28(11)

Tetramethyl 1,1'-(Ethyne-1,2-diyl)bis(bicyclo[3.1.0]hexane-3,3-dicarboxylate) (12a/12'a)



Colorless oil: 1:1 mixture of isomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (d, J = 7.4, 12H), 2.76 (d, J = 13.7 Hz, 2H), 2.53 (d, J = 19.6 Hz, 2H), 2.54 (d, J = 1.0 Hz, 4H), 1.61 (q, J = 4.1 Hz, 2H), 0.83 (t, J = 6.4 Hz, 2H), 0.47 (t, J = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 172.5 (C, both isomers), 171.2 (C, both isomers), 80.6 (C, **12a** or **12'a**), 80.6 (C, **12a** or **12'a**), 59.4 (C, both isomers), 52.3 (CH_2, **12a** or **12'a**), 52.2 (CH_2, **12a** or **12'a**), 40.9 (CH_3, both isomers), 35.8 (CH_2, both isomers), 29.8 (CH_2, both isomers), 27.4 (CH, both isomers), 18.3 (CH_2, **12a** or **12'a**), 18.3 (CH_2, **12a** or **12'a**); HMRS-ESI calcd. for $C_{22}H_{26}O_8Na$ $[M+Na]^+$: 441.1525. Found: 441.1512. The structure of **12a/12a'** was confirmed by COSY, HMQC, HMBC, and NOESY experiments.

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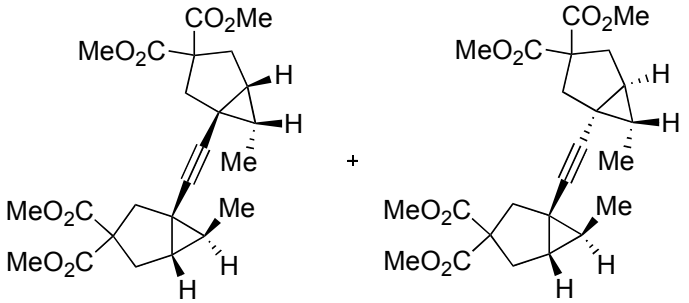
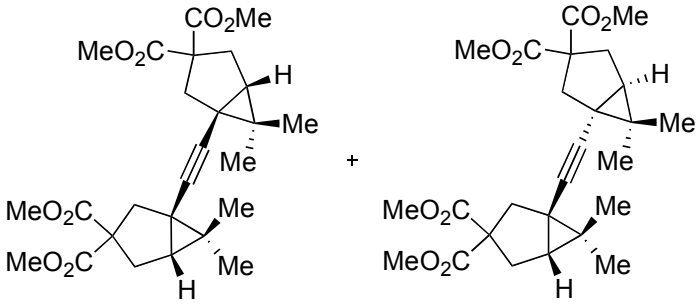
Tetramethyl 1,1'-(Ethyne-1,2-diyl)bis(6- methylbicyclo[3.1.0]hexane-3,3-dicarboxylate) (12b/12b')



Yellow oil: 1.5:1 mixture of isomers, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (d, J = 0.6 Hz, 6H), 3.68 (d, J = 0.6 Hz, 6H), 2.7 (d, J = 1.4 Hz, 2H), 2.57 (dd, J = 14.1, 2.6 Hz, 2H), 2.55-2.50 (m, 4H), 1.19 (q, J = 4.4 Hz, 2H), 1.06 (dd, J = 6.0, 2.9 Hz, 6H), 0.62 (qt, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9 (C, both isomers), 171.9 (C, both isomers), 79.9 (C, **12b** or **12'b**), 79.9 (C, **12b** or **12'b**), 60.1 (C, both isomers), 53.0 (CH_3, **12b** or **12'b**), 52.9 (CH_3, **12b** or **12'b**), 41.5 (CH_2, **12b** or **12'b**), 41.4 (CH_2, **12b** or **12'b**), 36.1 (CH_2, **12b** or **12'b**), 36.1 (CH_2, **12b** or **12'b**), 34.7 (CH, **12b** or **12'b**), 34.6 (CH, **12b** or **12'b**), 22.7 (CH, **12b** or **12'b**), 22.5 (CH, **12b** or **12'b**), 15.0 (CH_3, **12b** or **12'b**), 14.8 (CH_3, **12b** or **12'b**); LMRS-ESI calcd. for $C_{24}H_{30}O_8Na$ $[M+Na]^+$: 469.4. Found: 469.2. The structure of **12b/12'b** was confirmed by COSY, HMQC, HMBC, and NOESY experiments.

Tetramethyl 1,1'-(ethyne-1,2-diyl)bis(6,6-dimethylbicyclo[3.1.0]hexane-3,3-dicarboxylate) (12c/12c')



Colorless oil: 3:1 mixture of isomers, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 6H), 3.68 (s, 6H), 2.68 (dd, J = 7.4, 7.2 Hz, 2H), 2.6 (d, J = 14.6 Hz, 2H), 2.3 (d, J = 14.6 Hz, 2H), 1.88 (dd, J = 14.6, 3.0 Hz, 2H), 1.45 (dd, J = 7.6, 3.0 Hz, 2H), 1.17 (s, 6H), 1.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1 (C, both isomers), 81.2 (C, **12c** or **12'c**), 80.9 (C, **12c** or **12'c**), 68.6 (C, both isomers), 52.9 (CH_3, **12c** or

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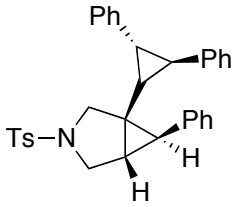
12'c), 52.6 (CH_3, **12c** or **12'c**), 40.3 (CH, both isomers), 40.1 (CH_2, both isomers), 33.6 (CH_2, both isomers), 31.1 (C, both isomers), 25.1 (CH_3, **12c** or **12'c**), 25.00 (CH_3, **12c** or **12'c**), 15.3 (CH_3, **12c** or **12'c**), 15.2 (CH_3, **12c** or **12'c**); HMRS-ESI calcd. for $C_{26}H_{34}O_8Na$ $[M+Na]^+$: 497.2151. Found: 497.2128. The structure of **12c/12'c** was confirmed by COSY, HMQC, HMBC, and NOESY experiments.

(1*R,5*S**,6*R**)-1-((2*R**,3*R**)-2,3-diphenylcyclopropyl)-6-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexane (13a)**



White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.26 (dd, J = 8.0, 6.6 Hz, 3H), 7.20 (t, J = 7.3 Hz, 3H), 7.16-7.08 (m, 4H), 6.98-6.89 (m, 6H), 3.46 (dd, J = 14.2, 9.5 Hz, 2H), 2.95 (d, J = 9.7 Hz, 1H), 2.88 (dd, J = 9.2, 3.8 Hz, 1H), 2.50 (s, 3H), 2.26 (s, 1H), 2.24 (d, J = 1.7 Hz, 1H), 1.92 (d, J = 4.6 Hz, 1H), 1.38 (t, J = 4.1 Hz, 1H), 1.32 (dd, J = 8.3, 6.9 Hz, 1H), 0.91-0.82 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.7, 141.6, 138.1, 137.1, 133.9, 130.1, 128.7, 128.2, 127.9, 126.9, 126.6, 126.2, 54.7, 50.9, 33.7, 32.1, 31.1, 28.1, 27.7; HRMS-ESI calcd. for $C_{33}H_{31}NO_2NaS$ $[M+Na]^+$: 528.1973. Found: 528.1978.

X-ray Structure for compound **13a**:

Table 1. Crystal data and structure refinement for **13a**.

Identification code	**13a**
Empirical formula	C33 H31 N O2 S
Formula weight	505.65
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c

Unit cell dimensions	a = 52.0309(19) Å	a= 90.00 °.
	b = 6.2004(2) Å	b = 98.150(2) °.
	c = 16.2321(6) Å	g = 90.00 °.
Volume	5183.8(3) $Å^3$	
Z	8	
Density (calculated)	1.296 Mg/m^3	
Absorption coefficient	0.157 mm^{-1}	
F(000)	2144	
Crystal size	0.15 x 0.10 x 0.05 mm^3	
Theta range for data collection	0.79 to0.79 °.	
Index ranges	-67 <=h<=67 ,-8 <=k<=8 ,-21 <=l<=21	
Reflections collected	5942	
Independent reflections	5272 [R(int) = 0.0453]	
Completeness to theta =27.50 °	1.000 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9922 and 0.9769	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5942 / 0 / 335	
Goodness-of-fit on F^2	1.103	
Final R indices [I>2sigma(I)]	R1 = 0.0396 , wR2 = 0.1089	
R indices (all data)	R1 = 0.0464 , wR2 = 0.1219	
Largest diff. peak and hole	0.457 and -0.440 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **13a**.

Bond lengths----	
C1-C6	1.395(2)
C1-C2	1.396(2)
C2-C3	1.378(3)
C3-C4	1.386(3)
C4-C5	1.396(2)

C5-C6	1.396(2)
C6-C7	1.4986(19)
C7-C8	1.51(2)
C7-C15	1.5209(17)
C8-C9	1.4961(19)
C8-C15	1.5267(19)
C9-C10	1.391(2)
C9-C14	1.394(2)
C10-C11	1.392(2)
C11-C12	1.385(3)
C12-C13	1.381(3)
C13-C14	1.395(2)
C15-C16	1.5006(17)
C16-C24	1.5147(19)
C16-C26	1.5301(19)
C16-C17	1.5379(18)
C17-C18	1.4972(18)
C17-C24	1.5094(19)
C18-C23	1.387(2)
C18-C19	1.4(2)
C19-C20	1.393(2)
C20-C21	1.381(3)
C21-C22	1.386(2)
C22-C23	1.398(2)
C24-C25	1.5109(18)
C25-N1	1.4784(18)
C26-N1	1.4814(16)
C27-C28	1.39(2)
C27-C33	1.396(2)
C27-S1	1.7679(14)
C28-C29	1.395(2)
C29-C30	1.394(2)

C30-C32	1.393(2)
C30-C31	1.509(2)
C32-C33	1.392(2)
N1-S1	1.6289(11)
O1-S1	1.4351(11)
O2-S1	1.4356(11)

Angles----------

C6-C1-C2	120.52(16)
C3-C2-C1	120.38(16)
C2-C3-C4	119.96(15)
C3-C4-C5	119.82(17)
C6-C5-C4	120.86(15)
C1-C6-C5	118.44(14)
C1-C6-C7	122.44(14)
C5-C6-C7	119.10(13)
C6-C7-C8	121.96(12)
C6-C7-C15	121.21(11)
C8-C7-C15	60.49(9)
C9-C8-C7	122.15(12)
C9-C8-C15	119.51(12)
C7-C8-C15	60.11(9)
C10-C9-C14	117.93(14)
C10-C9-C8	119.36(13)
C14-C9-C8	122.70(14)
C9-C10-C11	121.18(15)
C12-C11-C10	120.30(16)
C13-C12-C11	119.22(15)
C12-C13-C14	120.50(16)
C9-C14-C13	120.86(15)
C16-C15-C7	122.89(11)
C16-C15-C8	123.49(12)

C7-C15-C8	59.39(9)
C15-C16-C24	120.89(12)
C15-C16-C26	121.63(11)
C24-C16-C26	106.40(11)
C15-C16-C17	119.29(11)
C24-C16-C17	59.26(9)
C26-C16-C17	113.25(11)
C18-C17-C24	121.94(12)
C18-C17-C16	120.57(11)
C24-C17-C16	59.60(9)
C23-C18-C19	118.19(13)
C23-C18-C17	123.08(13)
C19-C18-C17	118.73(13)
C20-C19-C18	121.04(15)
C21-C20-C19	120.01(15)
C20-C21-C22	119.71(14)
C21-C22-C23	120.23(16)
C18-C23-C22	120.79(15)
C17-C24-C25	117.17(12)
C17-C24-C16	61.13(9)
C25-C24-C16	108.16(11)
N1-C25-C24	101.63(11)
N1-C26-C16	102.56(11)
C28-C27-C33	120.82(13)
C28-C27-S1	119.96(11)
C33-C27-S1	119.21(11)
C27-C28-C29	119.30(14)
C30-C29-C28	120.91(14)
C32-C30-C29	118.73(13)
C32-C30-C31	120.26(15)
C29-C30-C31	121.01(15)
C33-C32-C30	121.39(14)

C32-C33-C27	118.84(14)
C25-N1-C26	109.67(10)
C25-N1-S1	119.12(9)
C26-N1-S1	121.63(9)
O1-S1-O2	120.30(7)
O1-S1-N1	106.38(6)
O2-S1-N1	106.33(6)
O1-S1-C27	107.79(6)
O2-S1-C27	107.80(7)
N1-S1-C27	107.66(6)

Table 3. Torsion angles [°] for **13a**.

C6-C1-C2-C3	0.2(2)
C1-C2-C3-C4	-0.9(2)
C2-C3-C4-C5	0.6(2)
C3-C4-C5-C6	0.6(2)
C2-C1-C6-C5	0.9(2)
C2-C1-C6-C7	179.27(13)
C4-C5-C6-C1	-1.3(2)
C4-C5-C6-C7	-179.69(13)
C1-C6-C7-C8	34.75(19)
C5-C6-C7-C8	-146.90(13)
C1-C6-C7-C15	107.25(16)
C5-C6-C7-C15	-74.41(18)
C6-C7-C8-C9	-141.54(13)
C15-C7-C8-C9	108.05(14)
C6-C7-C8-C15	110.41(14)
C7-C8-C9-C10	173.27(13)
C15-C8-C9-C10	-115.42(15)
C7-C8-C9-C14	-8.1(2)

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C15-C8-C9-C14	63.24(19)
C14-C9-C10-C11	-0.7(2)
C8-C9-C10-C11	178.06(14)
C9-C10-C11-C12	0.8(2)
C10-C11-C12-C13	-0.3(3)
C11-C12-C13-C14	-0.3(3)
C10-C9-C14-C13	0.1(2)
C8-C9-C14-C13	-178.58(14)
C12-C13-C14-C9	0.4(3)
C6-C7-C15-C16	0.8(2)
C8-C7-C15-C16	112.39(14)
C6-C7-C15-C8	-111.61(15)
C9-C8-C15-C16	136.25(13)
C7-C8-C15-C16	-111.42(14)
C9-C8-C15-C7	-112.33(14)
C7-C15-C16-C24	79.39(17)
C8-C15-C16-C24	151.98(13)
C7-C15-C16-C26	-59.63(18)
C8-C15-C16-C26	12.96(19)
C7-C15-C16-C17	149.07(13)
C8-C15-C16-C17	-138.34(13)
C15-C16-C17-C18	0.89(19)
C24-C16-C17-C18	111.47(15)
C26-C16-C17-C18	-152.68(13)
C15-C16-C17-C24	-110.57(14)
C26-C16-C17-C24	95.85(12)
C24-C17-C18-C23	-17.8(2)
C16-C17-C18-C23	-88.91(17)
C24-C17-C18-C19	162.65(13)
C16-C17-C18-C19	91.57(16)
C23-C18-C19-C20	1.7(2)
C17-C18-C19-C20	-178.71(13)

C18-C19-C20-C21	-0.1(2)
C19-C20-C21-C22	-1.4(2)
C20-C21-C22-C23	1.1(2)
C19-C18-C23-C22	-2.0(2)
C17-C18-C23-C22	178.46(13)
C21-C22-C23-C18	0.6(2)
C18-C17-C24-C25	154.07(12)
C16-C17-C24-C25	-96.72(13)
C18-C17-C24-C16	-109.21(14)
C15-C16-C24-C17	107.90(13)
C26-C16-C24-C17	-107.68(11)
C15-C16-C24-C25	-140.51(12)
C26-C16-C24-C25	3.90(14)
C17-C16-C24-C25	111.58(12)
C17-C24-C25-N1	43.69(15)
C16-C24-C25-N1	-22.56(13)
C15-C16-C26-N1	160.52(11)
C24-C16-C26-N1	16.43(13)
C17-C16-C26-N1	-46.61(14)
C33-C27-C28-C29	0.4(2)
S1-C27-C28-C29	179.43(10)
C27-C28-C29-C30	-0.2(2)
C28-C29-C30-C32	-0.4(2)
C28-C29-C30-C31	179.68(14)
C29-C30-C32-C33	0.8(2)
C31-C30-C32-C33	-179.28(14)
C30-C32-C33-C27	-0.6(2)
C28-C27-C33-C32	0.0(2)
S1-C27-C33-C32	-179.05(11)
C24-C25-N1-C26	34.61(13)
C24-C25-N1-S1	-178.61(9)
C16-C26-N1-C25	-32.44(13)

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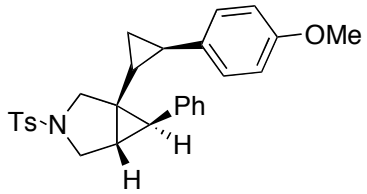
C16-C26-N1-S1	-178.24(9)
C25-N1-S1-O1	49.68(11)
C26-N1-S1-O1	-167.61(10)
C25-N1-S1-O2	179.03(10)
C26-N1-S1-O2	-38.26(12)
C25-N1-S1-C27	-65.65(11)
C26-N1-S1-C27	77.06(12)
C28-C27-S1-O1	150.36(11)
C33-C27-S1-O1	-30.60(13)
C28-C27-S1-O2	19.10(13)
C33-C27-S1-O2	-161.87(11)
C28-C27-S1-N1	-95.25(12)
C33-C27-S1-N1	83.79(12)

(1*R,5*S**,6*R**)-1-((1*R**,2*R**)-2-(4-Methoxyphenyl)Cyclopropyl)-6-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexane (10b/10b-d_1)**



White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.6 Hz, 3H), 7.36 (d, J = 8.6 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.19-7.13 (m, 3H), 7.1 (d, J = 8.0 Hz, 3H), 3.74 (s, 3H), 3.68 (d, J = 9.6 Hz , 2H), 3.23 (dd, J = 9.5, 4.2 Hz, 1H), 3.17 (d, J = 9.5 Hz, 1H), 2.46 (s, 3H), 2.17 (d, J = 4.2 Hz , 1H), 1.72 (t, J = 4.1 Hz, 1H), 1.45-1.40 (m, 1H), 0.94-0.83 (m, 2H), 0.56-0.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.9, 143.8, 137.2, 134.2, 133.9, 129.9, 129.1, 128.3, 127.7, 127.1, 126.3, 113.8, 55.5, 54.6, 50.8, 36.1, 30.6, 25.3, 21.8, 21.5, 20.6, 15.5; HRMS-ESI calcd. for $C_{28}H_{29}NO_3NaS$ [M+Na]: 482.1766. Found: 482.1765; Elemental analysis (%) calcd. $C_{28}H_{29}NO_3NaS\cdot 1/2H_2O$: C, 71.77; H, 6.45; N, 2.99; O, 11.95; S, 6.84; found: C, 71.75; H, 6.55; N, 2.88.

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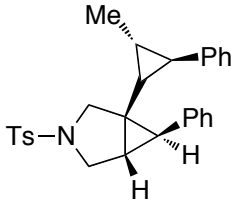
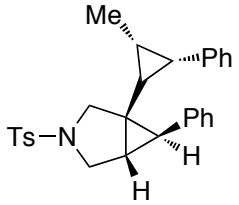
10b-d_1: Disappearance of the methylene hydrogen of the cyclopropyl function that appeared at 0.56-0.45 as multiplet and appeared at 0.51-0.45 (m, 1H) with an integral of 1.

(1R*,5S*,6R*)-1-((2R*,3R*)-2-Methyl-3-Diphenylcyclopropyl)-6-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexane (13c)



White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.31-7.20 (m, 3H), 7.08-7.02 (m, 3H), 6.96 (d, J = 8.4 Hz, 2H), 6.78 (dd, J = 7.6, 0.8 Hz, 2H), 3.39 (dd, J = 9.2, 6.0 Hz, 2H), 2.85 (d, J = 10.0 Hz, 1H), 2.73 (dd, J = 9.2, 3.6 Hz, 1H), 2.51 (s, 3H), 1.87 (d, J = 4.4 Hz, 1H), 1.64 (dd, J = 8.8, 5.6 Hz, 1H), 1.18 (t, J = 4.0 Hz, 1H), 1.14-1.10 (m, J = 5.6 Hz, 1H), 1.01 (d, J = 5.6 Hz, 3H), 0.66-0.63 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.4, 129.6, 128.1, 128.1, 127.9, 127.9, 127.6, 126.0, 125.8, 125.4, 54.4, 50.7, 31.8, 30.7, 28.0, 26.0, 21.6, 19.0, 17.5.

(1*R,5*S**,6*R**)-1-((1*R**,2*S**,3*R**)-2-methyl-3-phenylcyclopropyl)-6-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexane (13d)**



White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 7.6 Hz, 2H), 7.20-7.13 (m, 6H), 6.93 (d, J = 7.2 Hz, 2H), 3.77 (d, J = 9.2 Hz, 1H), 3.69 (d, J = 10.4 Hz, 1H), 3.20-3.14 (m, 2H), 2.42 (s, 3H), 2.25 (d, J = 4.0 Hz, 1H), 1.75-1.68 (m, 2H), 0.84 (t, J = 5.4 Hz, 1H), 0.60-0.54 (m, 1H), 0.17 (d, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.5, 138.3, 137.1, 134.0, 129.7, 129.0, 129.0, 128.2, 127.9, 127.4, 126.1, 125.8, 54.1, 50.4, 35.9, 30.1, 27.4,

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24.4, 22.8, 21.5, 21.2, 12.3; HRMS-ESI calcd. for $C_{28}H_{29}NO_2NaS$ $[M+Na]^+$: 466.1817. Found: 466.1833.

Table 1. Crystal data and structure refinement for **13d**.

Identification code	**13d**	
Empirical formula	C28 H29 N O2 S	
Formula weight	443.58	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pccn	
Unit cell dimensions	a = 34.3459(17) Å	a= 90.00 °.
	b = 11.0908(6) Å	b = 90.00 °.
	c = 12.4392(5) Å	g = 90.00 °.
Volume	4738.4(4) $Å^3$	
Z	8	
Density (calculated)	1.244 Mg/m^3	
Absorption coefficient	0.162 mm^{-1}	
F(000)	1888	
Crystal size	0.40 x 0.40 x 0.35 mm^3	
Theta range for data collection	1.19 to 36.38 °.	
Index ranges	-56 <=h<=50 ,-14 <=k<=17 ,-20 <=l<=8	
Reflections collected	10549	
Independent reflections	8021 [R(int) = 0.0434]	
Completeness to theta =36.38 °	0.913 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9456 and 0.9382	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10549 / 0 / 291	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0480 , wR2 = 0.1260	
R indices (all data)	R1 = 0.0676 , wR2 = 0.1386	
Largest diff. peak and hole	0.695 and -0.344 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **13d**.

Bond lengths----

C1-C2	1.5035(17)
C2-C7	1.3920(16)
C2-C3	1.4002(17)
C3-C4	1.3869(15)
C4-C5	1.3965(13)
C5-C6	1.3911(14)
C5-S1	1.7608(10)
C6-C7	1.3909(15)
C8-N1	1.4790(14)
C8-C9	1.5141(14)
C9-C12	1.5061(15)
C9-C10	1.5096(13)
C10-C19	1.4926(14)
C10-C11	1.5174(14)
C10-C12	1.5231(13)
C11-N1	1.4740(12)
C12-C13	1.4961(14)
C13-C14	1.3943(17)
C13-C18	1.3958(17)
C14-C15	1.3981(16)
C15-C16	1.381(2)
C16-C17	1.384(2)
C17-C18	1.3949(17)
C19-C20	1.4986(18)
C19-C21	1.5076(16)
C20-C22	1.5041(17)
C20-C21	1.5236(16)
C21-C23	1.4951(14)
C23-C24	1.3916(17)
C23-C28	1.4005(17)
C24-C25	1.3908(15)
C25-C26	1.383(2)
C26-C27	1.382(2)
C27-C28	1.3963(18)
N1-S1	1.6140(9)
O1-S1	1.4374(8)
O2-S1	1.4363(8)

Angles----------

C7-C2-C3	118.61(10)
C7-C2-C1	121.35(11)
C3-C2-C1	120.04(11)
C4-C3-C2	120.96(10)
C3-C4-C5	119.33(10)
C6-C5-C4	120.68(9)
C6-C5-S1	119.61(7)
C4-C5-S1	119.71(8)
C7-C6-C5	119.11(9)
C6-C7-C2	121.31(10)
N1-C8-C9	102.11(7)
C12-C9-C10	60.67(6)
C12-C9-C8	115.57(10)
C10-C9-C8	107.61(8)
C19-C10-C9	124.98(10)
C19-C10-C11	117.69(8)
C9-C10-C11	107.02(7)
C19-C10-C12	119.02(8)
C9-C10-C12	59.55(6)
C11-C10-C12	115.64(9)
N1-C11-C10	102.39(7)
C13-C12-C9	121.00(10)
C13-C12-C10	118.42(9)
C9-C12-C10	59.78(6)
C14-C13-C18	118.50(10)
C14-C13-C12	122.46(10)
C18-C13-C12	119.03(10)
C13-C14-C15	120.59(12)
C16-C15-C14	120.36(13)
C15-C16-C17	119.55(11)
C16-C17-C18	120.45(14)
C17-C18-C13	120.54(13)
C10-C19-C20	122.79(9)
C10-C19-C21	121.11(9)
C20-C19-C21	60.90(8)
C19-C20-C22	120.55(12)

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C19-C20-C21	59.84(7)
C22-C20-C21	122.25(9)
C23-C21-C19	122.28(10)
C23-C21-C20	123.16(9)
C19-C21-C20	59.25(8)
C24-C23-C28	117.88(10)
C24-C23-C21	123.25(10)
C28-C23-C21	118.75(11)
C25-C24-C23	121.18(12)
C26-C25-C24	120.25(13)
C27-C26-C25	119.72(11)
C26-C27-C28	120.06(13)
C27-C28-C23	120.90(13)
C11-N1-C8	109.50(8)
C11-N1-S1	122.47(7)
C8-N1-S1	120.67(6)
O2-S1-O1	119.76(5)
O2-S1-N1	107.08(5)
O1-S1-N1	106.54(4)
O2-S1-C5	106.93(4)
O1-S1-C5	108.13(5)
N1-S1-C5	107.92(5)

Table 3. Torsion angles [°] for **13d**.

C7-C2-C3-C4	0.3(2)
C1-C2-C3-C4	179.81(13)
C2-C3-C4-C5	-0.13(18)
C3-C4-C5-C6	-0.32(17)
C3-C4-C5-S1	179.65(9)
C4-C5-C6-C7	0.58(18)
S1-C5-C6-C7	-179.39(10)
C5-C6-C7-C2	-0.4(2)
C3-C2-C7-C6	0.0(2)
C1-C2-C7-C6	-179.54(14)
N1-C8-C9-C12	-46.10(11)
N1-C8-C9-C10	19.20(11)
C12-C9-C10-C19	-105.99(10)

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C8-C9-C10-C19	144.07(10)
C12-C9-C10-C11	110.18(9)
C8-C9-C10-C11	0.24(12)
C8-C9-C10-C12	-109.94(10)
C19-C10-C11-N1	-166.57(9)
C9-C10-C11-N1	-19.67(11)
C12-C10-C11-N1	44.17(11)
C10-C9-C12-C13	107.01(10)
C8-C9-C12-C13	-156.34(9)
C8-C9-C12-C10	96.65(9)
C19-C10-C12-C13	4.49(15)
C9-C10-C12-C13	-111.26(11)
C11-C10-C12-C13	153.33(9)
C19-C10-C12-C9	115.75(11)
C11-C10-C12-C9	-95.42(9)
C9-C12-C13-C14	31.70(15)
C10-C12-C13-C14	101.67(12)
C9-C12-C13-C18	-148.29(11)
C10-C12-C13-C18	-78.32(15)
C18-C13-C14-C15	-0.38(18)
C12-C13-C14-C15	179.63(11)
C13-C14-C15-C16	-0.2(2)
C14-C15-C16-C17	0.6(2)
C15-C16-C17-C18	-0.4(2)
C16-C17-C18-C13	-0.3(2)
C14-C13-C18-C17	0.6(2)
C12-C13-C18-C17	-179.36(13)
C9-C10-C19-C20	-1.13(15)
C11-C10-C19-C20	139.27(11)
C12-C10-C19-C20	-72.52(14)
C9-C10-C19-C21	-74.46(13)
C11-C10-C19-C21	65.94(13)
C12-C10-C19-C21	-145.85(10)
C10-C19-C20-C22	137.88(11)
C21-C19-C20-C22	-111.94(12)
C10-C19-C20-C21	-110.17(11)
C10-C19-C21-C23	-135.02(11)
C20-C19-C21-C23	112.15(12)

C10-C19-C21-C20	112.83(11)
C19-C20-C21-C23	-110.70(12)
C22-C20-C21-C23	-1.5(2)
C22-C20-C21-C19	109.18(15)
C19-C21-C23-C24	8.60(17)
C20-C21-C23-C24	80.57(16)
C19-C21-C23-C28	-175.35(11)
C20-C21-C23-C28	-103.39(14)
C28-C23-C24-C25	0.06(18)
C21-C23-C24-C25	176.14(11)
C23-C24-C25-C26	-0.9(2)
C24-C25-C26-C27	1.0(2)
C25-C26-C27-C28	-0.1(2)
C26-C27-C28-C23	-0.8(2)
C24-C23-C28-C27	0.78(19)
C21-C23-C28-C27	-175.48(12)
C10-C11-N1-C8	33.51(10)
C10-C11-N1-S1	-176.40(7)
C9-C8-N1-C11	-33.28(10)
C9-C8-N1-S1	176.00(7)
C11-N1-S1-O2	158.39(8)
C8-N1-S1-O2	-54.74(9)
C11-N1-S1-O1	29.12(10)
C8-N1-S1-O1	176.00(8)
C11-N1-S1-C5	-86.81(9)
C8-N1-S1-C5	60.06(9)
C6-C5-S1-O2	17.62(11)
C4-C5-S1-O2	-162.35(9)
C6-C5-S1-O1	147.82(9)
C4-C5-S1-O1	-32.14(11)
C6-C5-S1-N1	-97.29(10)
C4-C5-S1-N1	82.74(10)

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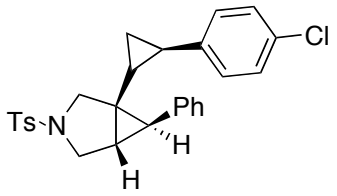
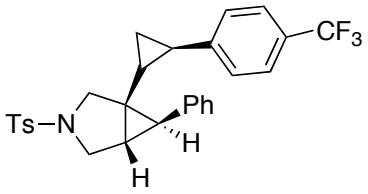
SOLVING THE MECHANISTIC PUZZLE OF GOLD-CATALYZED CYCLIZATION OF 1,6-ENYNES AND BEYOND
Patricia Pérez Galán
ISBN:978-84-693-7664-5/DL:T-1746-2010

(1*R,5*S**,6*R**)-1-((1*R**,2*R**)-2-(4-Chlorophenyl)Cyclopropyl)-6-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexane (10c)**



White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.24 – 7.15 (m, 3H), 7.09 (t, J = 7.6 Hz, 4H), 6.64 (d, J = 8.4 Hz, 2H), 3.68 (dd, J = 9.3, 4.8 Hz, 2H), 3.24 (dd, J = 9.4, 3.9 Hz, 1H), 3.13 (d, J = 9.4 Hz, 1H), 2.46 (s, 3H), 2.17 (d, J = 4.2 Hz, 1H), 1.75 (t, J = 4.0 Hz, 1H), 1.43 (q, J = 7.3 Hz, 1H), 1.00-0.77 (m, 2H), 0.58 (dt, J = 12.9, 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.8, 140.8, 137.0, 133.9, 131.4, 129.9, 128.4, 127.7, 127.2, 126.4, 54.3, 50.7, 35.8, 30.6, 25.4, 21.8, 21.5, 15.9; HRMS-ESI calcd. for $C_{27}H_{26}NO_2NaS^{35}Cl$ [M+Na]: 486.1270. Found: 486.1252; Elemental analysis (%) calcd. $C_{27}H_{26}NO_2NaS^{35}Cl \cdot 1/2H_2O$: C, 68.56; H, 5.75; Cl, 7.49; N, 2.96; O, 8.46; S, 6.78; found: C, 68.79; H, 5.52; N, 2.86.

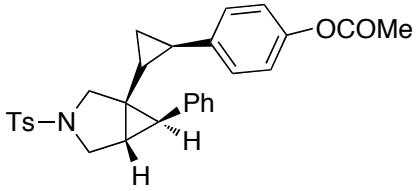
(1*R,5*S**,6*R**)-6-Phenyl-3-Tosyl-1-((1*R**,2*R**)-2-(4-(trifluoromethyl)phenyl)cyclopropyl)-3-azabicyclo[3.1.0]hexane (10d)**



White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.2 Hz, 2H), 7.43 (t, J = 7.6 Hz, 4H), 7.29-7.18 (m, 3H), 7.13 (d, J = 6.9 Hz, 2H), 6.85 (d, J = 8.1 Hz, 2H), 3.74 (dd, J = 9.4, 2.4 Hz, 2H), 3.31 (dd, J = 9.4, 3.9 Hz, 1H), 3.18 (d, J = 9.4 Hz, 1H), 2.52 (s, 3H), 2.25 (d, J = 4.2 Hz, 1H), 1.83 (t, J = 4.0 Hz, 1H), 1.59-1.51 (m, 1H), 1.37-1.28 (m, 2H), 1.07 (dd, J = 13.2, 6.3 Hz, 1H), 0.96-0.87 (m, 2H), 0.78-0.69 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.6, 143.9, 137.0, 133.9, 129.9, 129.0, 128.5, 127.8, 126.5, 125.8, 125.9, 125.3, 54.3, 50.7, 35.8, 30.6, 25.4, 22.3, 21.8,16.4; HRMS-ESI calcd. for $C_{28}H_{26}NO_2NaSF_3$ $[M+Na]^+$: 520.1534. Found:

520.1514; Elemental analysis (%) calcd. $C_{28}H_{26}NO_2NaSF_3 \cdot 1/2H_2O$: C, 66.39; H, 5.37; F, 11.25; N, 2.76; O, 7.90; S, 6.33; found: C, 66.17; H, 5.39; N, 2.71.

4-((1*R,2*R**)-2-((1*R**,5*S**,6*R**)-6-Phenyl-3-Tosyl-3-azabicyclo[3.1.0]hexan-1-yl)cyclopropyl)phenyl acetate (10e)**



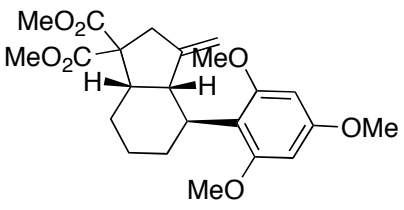
White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.36 (t, J = 8.4 Hz, 2H), 7.25 – 7.16 (m, 3H), 7.10 (d, J = 7.1 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 6.74 (d, J = 8.7 Hz, 2H), 3.69 (dd, J = 9.5, 6.4 Hz, 2H), 3.23 (dd, J = 9.5, 4.3 Hz, 1H), 3.13 (d, J = 9.5 Hz, 1H), 2.46 (s, 3H), 2.26 (s, 3H), 2.19 (d, J = 4.3 Hz, 1H), 1.74 (t, J = 4.3 Hz, 1H), 1.49-1.42 (m, 1H), 0.99-0.95 (m, 1H), 0.63-0.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.8, 148.7, 143.8, 139.8, 137.0, 133.8, 129.9, 129.1, 128.3, 127.7, 126.9, 126.4, 121.4, 54.5, 50.8, 35.9, 30.6, 25.2, 21.8, 21.3, 15.9; HRMS-ESI calcd. for $C_{29}H_{29}NO_4NaS$ [M+Na]: 510.1715. Found: 510.1714.

II. Gold(I)-Catalyzed Addition of Nucleophiles

II.1 General procedure for the nucleophillic attack of 1,6-enynes

A solution of enyne and the nucleophile in CH_2Cl_2 (2 mL) was added to a previously prepared mixture of the gold catalyst and $AgSbF_6$ in CH_2Cl_2 (1 mL). The reaction mixture was stirred at room temperature. The mixture was filtered trough silica gel with CH_2Cl_2 and the solvents evaporated. The residue was chromatographed to give the desired product.

3a*R,4*S**,7a*S**)-Dimethyl 3-Methylene-4-(2,4,6-trimethoxyphenyl)hexahydro-1*H*-indene-1,1(2*H*,3*H*)-dicarboxylate (24)**



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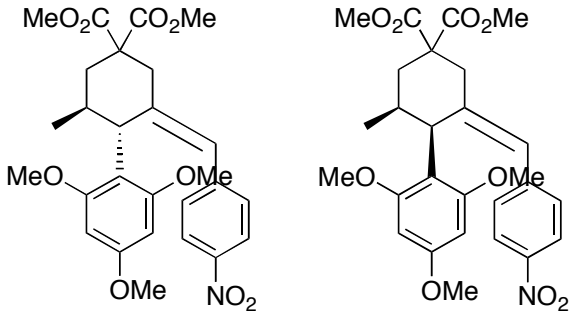
Compound **22** was synthesized following the general procedure starting from **5e** (28,9 mg, 0.11 mmol), 2,4,6-trimetoxybenzene (97.1 mg, 0.58 mmol) and gold catalyst **1g** (4.2 mg, 0.0058 mmol). The mixture was stirred 3 h at r. t.. The residue was purified by chromatography (20:1, hexane: EtOAc) to give **22** as a colorless oil (25 mg, 53%): ^{1}H NMR (400 MHz, C_6D_6) δ 6.25 (s, 2H), 4.93 (s, 1H), 4.76 (s, 1H), 4.06 (dq, J = 17.0. 2.4, 1.8 Hz, 1H), 3.89 (td, J = 10.7, 3.7 Hz, 1H), 3.80 (td, J = 7.3, 1.3 Hz, 1H), 3.75-3.68 (s, 1H), 3.51 (s, 6H), 3.50 (s, 3H), 3.49 (s, 3H), 3.43 (s, 3H), 2.99 (d, J = 17.0 Hz, 1H), 2.54-2.41 (m, 1H), 2.19-2.09 (m, 1H), 1.91-1.82 (m, 1H), 1.81-1.70 (m, 2H), 1.69-1.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 172.1, 159.5, 159.0, 151.6, 114.5, 106.3, 91.2, 61.8, 55.8, 55.2, 52.6, 46.6, 43.7, 39.9, 32.8, 26.5, 22.3, 21.5; HRMS-ESI calcd. for $C_{23}H_{30}O_7Na$ $[M+Na]^+$: 441.1870. Found: 441.1889.

(3*R,4*S**,*Z*)-Dimethyl 3-Methyl-5-(4-nitrobenzylidene)-4-(2,4,6-trimethoxyphenyl)cyclohexane-1,1-dicarboxylate (25, 25')**



Compounds **25** and **25'** were synthesized following the general procedure starting from **38p** (35.8 mg, 0.1 mmol), 2,4,6-trimetoxybenzene (92 mg, 0.54 mmol) and gold catalyst **1g** (3.9 mg, 0.005 mmol). The mixture was stirred 2h at 15 ºC. The residue was purified by chromatography (20:1, hexane: EtOAc) to give **25**/**25'** (7:1) as a yellow solid (43 mg, 81%): mp: 49-51 ºC; ^{1}H NMR (400 MHz, C_6D_6) δ 7.91 (d, J = 8.8 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H), 6.28 (s, 2H), 6.20 (s, 1H), 4.12 (d, J = 11.3 Hz, 1H), 3.87 (dd, J = 14.2, 2.3 Hz, 1H), 3.55 (s, 6H), 3.48 (s, 6H), 3.40 (s, 3H), 3.38 (s, 3H), 3.07-2.95 (m, 1H), 2.87 (dt, J = 13.3, 3.2 Hz, 1H), 2.65 (d, J = 14.2 Hz, 1H), 1.95 (t, J = 13.0 Hz, 1H), 1.06 (d, J = 6.4 Hz, 3H) for the major product, and some selected signals for the minor diastereoisomer; ^{13}C NMR (100 MHz, C_6D_6) δ 172.0, 170.6, 160.6, 159.7, 146.07, 145.7, 141.0, 129.4, 129.1, 128.2,

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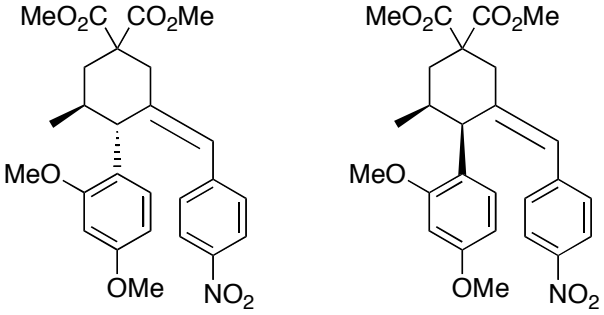
128.1, 124.8, 123.1, 122.9, 122.0, 109.8, 90.41, 56.1, 54.6, 54.5, 52.0, 51.5, 46.7, 41.3, 40.5, 40.4, 34.3, 31.4; HRMS-ESI calcd. for $C_{27}H_{32}NO_9Na$ $[M+Na]^+$: 514.2090. Found: 514.2077.

(3*R,4*S**,*Z*)-Dimethyl 4-(2,4-Dimethoxyphenyl)-3-methyl-5-(4-nitrobenzylidene)cyclohexane-1,1-dicarboxylate (26, 26')**



Compounds **26** and **26'** were synthesized following the general procedure starting from **38p** (30 mg, 0.09 mmol), 2,4-dimetoxybenzene (60.5 mg, 0.44 mmol) and gold catalyst **1g** (3.4 mg, 0.004 mmol). The mixture was stirred 5 h at 15 ºC. The residue was purified by chromatography (20:1, hexane: EtOAc) to give **26**/**26'** (13:1) as a sticky yellow solid (25 mg, 63%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.6 Hz, 1H), 6.52(dd, J = 8.6, 2.2 Hz, 1H), 6.49 (d, J = 2.4 Hz, 1H), 5.79 (s, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.70 (s, 3H), 3.54 (s, 3H), 3.46 (d, J = 11.7 Hz, 1H), 2.56-2.46 (m, 2H), 2.28-2.13 (m, 1H), 1.74 (d, J = 13.5 Hz, 1H), 0.80 (d, J = 6.4 Hz, 3H) for the major product, and some selected signals for the minor diastereoisomer; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 170.9, 159.4, 158.8, 145.7, 143.6, 143.4, 129.5, 129.3, 123.3, 122.6, 120.7, 104.6, 104.3, 98.8, 98.0, 55.6, 55.3, 52.9, 52.2, 39.9, 34.1, 33.7, 21.0; HRMS-ESI calcd. for $C_{26}H_{29}NO_8Na$ $[M+Na]^+$: 506.1776. Found: 506.1791.

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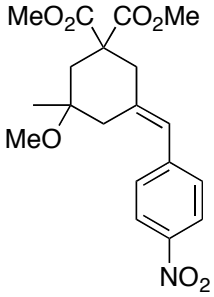
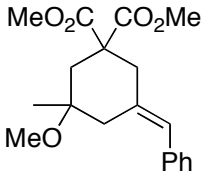
(*Z*)-Dimethyl 3-Methoxy-3-methyl-5-(4-nitrobenzylidene)cyclohexane-1,1-dicarboxylate (27)



Compound **27** was synthesized following the general procedure starting from **38p** (37 mg, 0.11 mmol), gold catalyst **1g** (3.9 mg, 0.005 mmol) and methanol as a solvent. The mixture was stirred 3 h at r. t.. The residue was purified by chromatography (10:1, hexane: EtOAc) to give **27** as a sticky yellow solid (40 mg, 98%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 9.0 Hz, 2H), 7.45 (d, J = 9.0 Hz, 2H), 6.64 (s, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.15 (dt, J = 13.5, 1.7 Hz, 1H), 2.95 (dt, J = 14.2, 1.8 Hz, 1H), 2.83 (s, 3H), 2.67 (dt, J = 14.4, 2.2 Hz, 1H), 2.40 (dt, J = 13.5, 1.5 Hz, 1H), 2.11 (d, J = 14.4 Hz, 1H), 1.95 (dt, J = 14.2, 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 170.8, 144.6, 138.3, 129.6, 126.4, 123.6, 74.6, 54.3, 52.9, 52.2, 49.2, 41.4, 40.6; HRMS-ESI calcd. for $C_{19}H_{23}NO_7Na$ $[M+Na]^+$: 400.1358. Found: 400.1372.

(*Z*)-Dimethyl 5-Benzylidene-3-methoxy-3-methylcyclohexane-1,1-dicarboxylate (28)



Compound **28** was synthesized following the general procedure starting from **38l** (29,8 mg, 0.1 mmol), gold catalyst **1g** (3.6 mg, 0.005 mmol) and methanol as a solvent. The mixture was stirred 3 h at r. t.. The residue was purified by chromatography (10:1, hexane: EtOAc) to give **28** as a colorless oil (32,5 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.25 (m, 4H), 7.22 (tt, J = 7.0, 1.7 Hz, 1H), 6.60 (s, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.10 (dt, J = 13.7, 1.3 Hz, 1H), 3.00 (dt, J = 14.4, 1.6 Hz, 1H), 2.79 (s, 3H), 2.60 (dt, J = 14.3, 2.1 Hz, 1H), 2.40 (dt, J = 13.7, 1.3 Hz,

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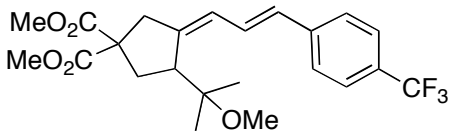
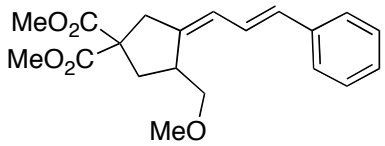
1H), 2.13 (d, *J* = 14.1 Hz, 1H), 1.94 (dt, *J* = 14.4, 1.5 Hz, 1H), 1.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 171.2, 137.6, 134.0, 128.8, 128.1, 128.0, 126.3, 74.3, 54.2, 52.8, 52.2, 49.1, 41.2, 40.4, 37.1, 24.2; HRMS-ESI calcd. for $C_{19}H_{24}O_5Na$ $[M+Na]^+$: 355.1509. Found: 355.1521.

(*Z*)-Dimethyl 3-(2-Methoxypropan-2-yl)-4-((*E*)-3-(4-(trifluoromethyl)phenyl)allylidene)cyclopentane-1,1-dicarboxylate (29)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.07 (dd, *J* = 15.6, 11.1 Hz, 1H), 6.46-6.39 (m, 1H), 6.23 (d, *J* = 11.0 Hz, 1H), 3.75 (s, 3H), 3.72 (d, *J* = 2.3 Hz, 1H), 3.69 (s, 3H), 3.18 (s, 4H), 3.13-3.08 (m, 1H), 2.80 (d, *J* = 15.0 Hz, 1H), 2.66 (ddd, *J* = 13.9, 8.8, 1.2 Hz, 1H), 2.29 (dd, *J* = 14.0, 5.9 Hz, 1H), 1.20 (s, 3H), 1.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 172.2, 172.0, 145.7, 129.6, 126.4, 125.9, 125.7, 58.6, 53.0, 53.0, 49.4, 49.2, 44.9, 35.6, 23.3, 22.5; HRMS-ESI calcd. for $C_{23}H_{27}O_5F_3Na$ $[M+Na]^+$: 463.1708. Found: 463.1724.

(*Z*)-Dimethyl 3-(Methoxymethyl)-4-((*E*)-3-phenylallylidene)cyclopentane-1,1-dicarboxylate (30)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 3H), 7.08 (dd, *J* = 15.5, 11.1 Hz, 1H), 6.50 (d, *J* = 15.5 Hz, 1H), 6.11 (d, *J* = 11.1 Hz, 1H), 3.75 (s, 3H), 3.65 (s, 3H), 3.50-3.41 (m, 1H), 3.37 (s, 3H), 2.74-2.54 (m, 4H), 2.13 (t, *J* = 11.3 Hz, 1H), 1.86 (dd, *J* = 13.2, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.9, 137.8, 134.2, 132.3, 128.8, 128.0, 127.9, 127.5, 126.4, 124.4, 76.6, 56.4, 55.6, 53.1, 52.7, 42.2, 36.4, 34.1.

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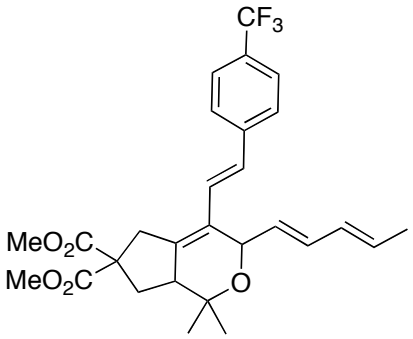
Dimethyl 1,1-Dimethyl-3-((1*E*,3*E*)-penta-1,3-dienyl)-4-(4-(trifluoromethyl)styryl)-3,5,7,7a-tetrahydrocyclopenta[*c*]pyran-6,6(1*H*)-dicarboxylate (31)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 6.80 (d, J = 16.6 Hz, 1H), 6.47 (d, J = 16.7 Hz, 1H), 6.35 (dd, J = 15.2, 10.4 Hz, 1H), 6.08-5.98 (m, 1H), 5.72 (dd, J = 15.0, 6.8 Hz, 1H), 5.51 (dd, J = 15.0, 7.8 Hz, 1H), 4.79 (d, J = 5.7 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 1H), 3.76 (d, J = 2.8 Hz, 3H), 3.44 (d, J = 18.3 Hz, 1H), 3.18-3.10 (m, 1H), 2.70 (s, 1H), 2.56 (dd, J = 11.7, 8.2 Hz, 1H), 1.73 (d, J = 5.2 Hz, 3H), 1.32 (s, 3H), 1.06 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 141.1, 139.7, 134.1, 131.0, 130.3, 129.9, 127.5, 127.1, 126.2, 125.5, 73.2, 72.0, 58.5, 35.1, 48.9, 38.4, 36.3, 31.6, 29.1, 22.6, 19.0, 18.1, 14.1.

III. Gold(I)-catalyzed [4+2] cycloaddition reaction

III.1 Arylenynes

General Procedure for the Cyclization Substituted Enynes; [4+2]-Cycloadditions:

To a mixture of [Au(L)Cl] (2 mol%)) and silver(I) salt (2 mol%) (or the corresponding cationic Au(I)complex) in CH_2Cl_2 (2 mL) was added the enyne (0.10-0.50 mmol) in CH_2Cl_2 (1 mL) and the mixture was stirred for the time and at the temperature indicated. The resulting mixture was filtered through SiO_2 and the solvent was evaporated to give the corresponding product.

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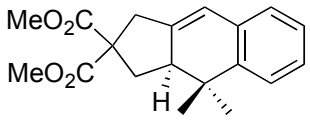
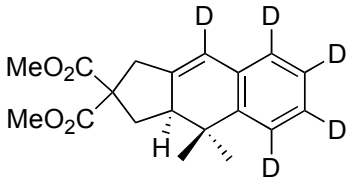
Dimethyl 4,4-Dimethyl-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)dicarboxylate (34a)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.27 (m, 1H), 7.13 (m, 2H), 7.01 (m, 1H), 6.34 (bs, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 3.27 (dd, *J* = 18.0, 1.3 Hz, 1H), 2.97 (dt, *J* = 18.0, 3.0 Hz, 1H), 2.69-2.63 (m, 1H), 2.57 (ddd, *J* = 12.3, 7.6, 1.1 Hz, 1H), 2.13 (t, *J* = 12.3 Hz, 1H), 1.42 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 171.2, 144.0, 142.8, 133.9, 126.9, 123.2, 126.2, 123.4, 119.3, 58.9, 52.8, 52.8, 48.4, 39.1, 36.6, 34.8, 25.6, 22.0; HRMS-CI calcd. for $C_{19}H_{22}O_4$ $[M+H]^+$: 314.1518. Found: 314.1511.

D^5-Dimethyl 4,4-Dimethyl-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)dicarboxylate (34a-d_5)



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (bs, 0,3H), 3.77 (s, 3H), 3.71 (s, 3H), 3.27 (d, *J* = 18.0 Hz, 1H), 2.97 (dd, *J* = 18.0, 3.0 Hz, 1H), 2.69-2.63 (m, 1H), 2.57 (ddd, *J* = 12.3, 7.6, 1.1 Hz, 1H), 2.13 (t, *J* = 12.3 Hz, 1H), 1.42 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 172.0, 143.9, 142.9, 133.7, 126.87, 123.23, 126.20, 123.42, 119.3, 58.9, 52.8, 48.4, 39.1, 36.6, 34.8, 30.4, 25.6, 22.0.

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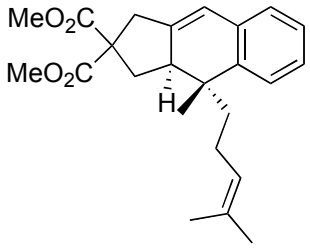
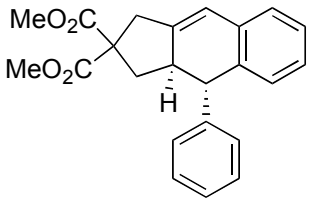
Patricia Pérez Galán
ISBN:978-84-693-7664-5/DL:T-1746-2010

(3a*R,4*S**)-Dimethyl 4-Methyl-4-(4-methylpent-3-enyl)-3a,4-dihydro-1*H*cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (34b)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.10 (m, 3H), 7.04-7.01 (m, 1H), 6.31 (bs, 1H), 5.19 (m, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.30 (dd, *J* = 17.8, 1.0 Hz, 1H), 3.02 (dt, *J* = 21.1, 2.9 Hz, 1H) 2.94 (m, 1H) 2.56 (dd, *J* = 11.4, 7.4 Hz, 1H), 2.11-1.98 (m, 5H), 1.71 (s, 3H), 1.60 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 171.9, 142.8, 141.5, 134.8, 131.5, 126.8, 126.8, 126.1, 124.6, 124.0, 118.2, 58.9, 52.8, 43.8, 40.3, 39.3, 36.9, 34.3, 25.7, 23.3, 23.0, 17.6; HRMS-CI calcd. for $C_{24}H_{31}O_4$ $[M+H]^+$: 383.2222. Found: 383.2220. The structure was confirmed by COSY, NOESY, HMQC and HMBC experiments.

(3a*R,4*S**)-Dimethyl 4-Phenyl-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (34c)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 6.9 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 3H), 7.12 (td, *J* = 7.3, 1.1 Hz, 1H), 7.06 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.97 (td, *J* = 7.5, 1.4 Hz, 1H), 6.55 (d, *J* = 7.7 Hz, 1H), 6.41(bs, 1H), 3.79 (d, *J* = 15.4 Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.33 (d, *J* = 18.5 Hz, 1H), 3.16 (dt, *J*= 17.7, 2.4 Hz, 1H), 3.14 (m, 1H), 2.34 (dd, *J* = 13.0, 7.4 Hz, 1H), 1.95 (dd, *J* = 13.1, 11.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 144.4, 141.8, 138.0, 135.2, 128.7, 128.3, 126.9, 126.9, 126.6, 126.5, 125.6, 119.4, 59.1, 52.8, 52.2, 45.1, 39.7, 38.8; HRMS-CI calcd. for $C_{23}H_{23}O_4$ $[M+H]^+$: 363.1596. Found: 363.1598. The structure was confirmed by COSY, HMQC and HMBC experiments. The configuration was assigned on the basis of the observed ^3J:

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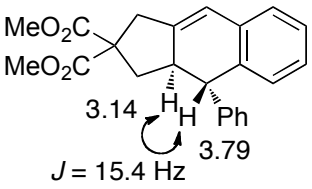
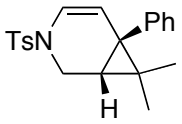
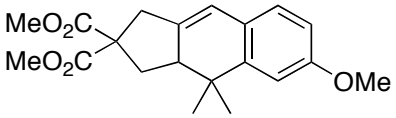


7,7-Dimethyl-6-Phenyl-3-tosyl-3-azabicyclo[4.1.0]hept-4-ene (34e)



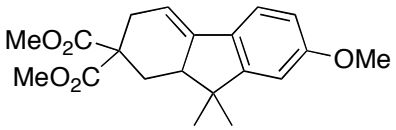
White solid; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.69 (d, J = 8.3 Hz, 2H); 7.31 (d, J = 7.9 Hz, 2H), 7.26-7.22 (m, 3H); 7.09-7.06 (m, 2H), 6.59 (d, J = 8.4 Hz, 1H), 5.08 (dd, J = 8.4, 0.9 Hz, 1H), 3.71 (dd, J = 12.2, 1.6 Hz, 1H), 3.54 (dd, J = 12.2, 5.9 Hz, 1H), 2.45 (d, 3H); 1.47 (dt, J = 5.8, 1.3 Hz 1H), 0.96 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 143.7 (C), 142.2 (C), 134.7 (C), 131.3 (CH), 129.7 (2CH), 128.7 (2CH), 128.3 (2CH), 127.1 (2CH), 126.1 (CH), 121.4 (CH), 38.7 (CH_2), 30.7 (C), 30.2 (C), 27.0 (CH_3), 24.7 (CH), 21.5 (CH_3), 15.7 (CH_3); HRMS-ESI calcd. for $C_{21}H_{23}O_2NSNa$ $[M+Na]^+$: 376.1351. Found: 376.1347. The structure was confirmed by COSY, NOESY, HMQC and HMBC experiments.

Dimethyl 6-Methoxy-4,4-dimethyl-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)dicarboxylate (34g)



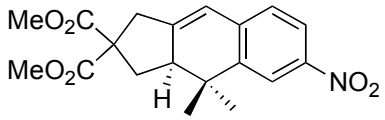
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, J = 8.3 Hz, 1H), 6.88 (d, J = 2.5 Hz, 1H), 6.67 (dd, J = 8.2, 2.6 Hz, 1H), 6.31 (bs, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.73 (s, 3H), 3.28 (dd, J = 17.9, 1.5 Hz, 1H), 2.98 (dt, J = 17.8, 3.0 Hz, 1H), 2.69-2.63 (m, 1H), 2.59 (ddd, J = 13.6, 7.5, 1.3 Hz, 1H), 2.14 (t, J = 12.3 Hz, 1H), 1.41 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 172.0, 158.7, 146.0, 140.2, 127.1, 118.7, 110.8, 110.0, 100.0, 59.0, 55.3, 52.9, 52.8, 48.2, 39.1, 37.0, 34.8, 25.6, 21.9; HMRS-CI calcd. for $C_{20}H_{25}O_5$ $[M+H]^+$: 345.1702. Found: 345.1692. The structure was confirmed by COSY, HMQC and HMBC experiments.

Dimethyl 7-Methoxy-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (35g)



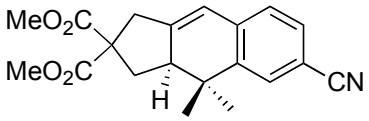
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.7 Hz, 1H), 6.73 (dd, J = 8.7, 2.7 Hz, 1H), 6.58 (d, J = 2.7 Hz, 1H), 5.85 (bs, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H), 3.07 (d, J = 18.4 Hz, 1H), 2.52- 2.43 (m, 2H), 2.42-2.33 (m, 1H), 1.90 (t, J = 12.4 Hz, 1H), 1.38 (s, 3H), 0.95 (s, 3H).

Dimethyl 4,4-Dimethyl-6-nitro-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (34h)



Orange solid, mp = 125-127 ºC: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 2.2 Hz, 1H), 8.02 (dd, J = 8.4, 2.3 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H); 6.45 (bs, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.34 (d, J = 18.7 Hz, 1H), 3.03 (dt, J = 18.6, 3.0 Hz, 1H), 2.80-2.71 (m, 1H), 2.63 (ddd, J = 12.6, 7.6, 1.3 Hz, 1H), 2.18 (t, J = 12.6 Hz, 1H), 1.49 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 171.7 (C), 171.7 (C), 149.2 (C), 146.5 (C), 145.3 (C), 140.2 (C), 126.5 (CH), 122.1 (CH), 119.3 (CH), 118.5 (CH), 48.7 (C), 53.0 ($2CH_3$), 48.3 (CH), 39.4 (CH_2), 37.0 (C), 34.4 (CH_2), 25.5 (CH_3), 21.9 (CH_3); HRMS-ESI calcd. for $C_{19}H_{22}NO_6Na$ $[M+Na]^+$: 360.1447. Found: 360.1451.

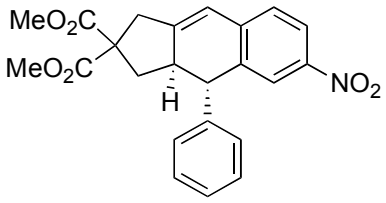
Dimethyl 6-Cyano-4,4-dimethyl-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (34i)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.41 (dd, J = 7.8, 1.4 Hz, 1H), 7.05 (d, J = 7.8 Hz, 1H), 6.37 (bs, 1H), 3.77 (s, 3H), 3.73 (s, H), 3.31 (d, J = 18.5 Hz, 1H), 3.00 (dt, J = 18.5, 2.9 Hz, 1H), 2.73-2.69 (m, 1H), 2.60 (dd, J = 12.5, 7.6 Hz, 1H), 2.15 (t, J = 12.5 Hz, 1H), 1.43 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$,

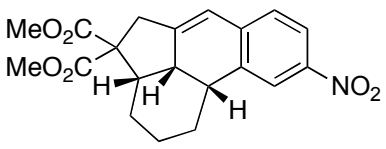
DEPT) δ 171.7 (2C), 147.9 (C), 144.9 (C), 138.3 (C), 130.4 (CH), 127.5 (CH), 126.6 (CH), 119.6 (C), 118.6 (CH), 109.8 (C), 58.7 (C), 53.0 (CH_3), 53.0 (CH_3), 48.2 (CH), 39.4 (CH_2), 36.3 (C), 34.4 (CH_2), 25.4 (CH_3), 21.9 (CH_3); HRMSES calcd. for $C_{20}H_{21}NO_4Na$ $[M+Na]^+$: 362.1368. Found: 362.1370. The structure was confirmed by COSY, NOESY, HMQC and HMBC experiments.

(3a*R,4*S**)-Dimethyl 6-Nitro-4-phenyl-3a,4-dihydro-1*H*cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (34k)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, J = 8.5, 2.3 Hz, 1H) 7.47-7.34 (m, 4H), 7.31- 7.27 (m, 2H), 7.16 (d, J = 8.5 Hz, 1H), 6.49 (bs, 1H), 3.83 (d, J = 15.0 Hz, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.38 (d, J = 18.6 Hz, 1H), 3.25-3.13 (m, 2H), 2.38 (dd, J = 13.0, 8.0 Hz, 1H), 1.98 (dd, J = 13.0, 11.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 171.7 (C), 171.6 (C), 150.4 (C), 146.3 (C), 141.4 (C), 139.8 (C), 139.4 (C), 129.2 (3CH), 127.8 (2CH), 125.8 (CH), 122.5 (CH), 122.2 (CH), 118.9 (CH), 58.9 (C), 52.9 (CH_3), 52.9 (CH_3), 51.7 (CH), 45.0 (CH), 39.5 (CH_2), 39.1 (CH_2); HRMS-CI calcd. for $C_{23}H_{22}NO_6$ $[M+H]^+$: 408.1447. Found: 408.1448. The structure was confirmed by COSY, NOESY, HMQC and HMBC experiments.

Methyl 9-Nitro-1,2,3,3a,5,10b-hexahydroacephenanthrylene-4,4(3a^1*H*)-dicarboxylate (34l)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, J = 2.6, 8.4 Hz, 1H), 7.96 (d, J = 2.6 Hz, 1H), 7.08 (d, J = 8.4 Hz, 1H), 6.41 (q, J = 3.2 Hz, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.54 (dt, J = 19.7, 2.9 Hz, 1H), 3.17 (bs, 1H), 3.10 (d, J = 19.7 Hz, 1H), 3.03-2.94 (m, 2H), 1.71 (dt, J = 13.4, 3.4 Hz, 1H), 1.51 (t, J = 14.6 Hz, 2H), 1.37-1.14 (m,

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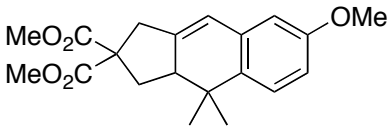
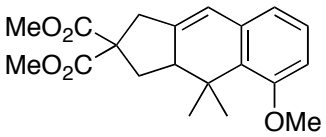
3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.9, 147.9, 140.2, 126.4, 123.1, 122.6, 118.9, 63.1, 53.2, 53.0, 43.5, 42.6, 38.5, 36.1, 29.9, 29.6, 24.3, 23.4; HRMS-ESI calcd. for $C_{20}H_{21}NO_6Na$ $[M+Na]^+$: 394.1267. Found 394.1261.

Dimethyl 7-Methoxy-4,4-dimethyl-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (34m)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.6 Hz, 1H), 6.69 (dd, J = 8.5, 2.9 Hz, 1H), 6.58 (d, J = 2.9 Hz, 1H), 6.31 (bs, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.71 (s, 3H), 3.29 (d, J = 18.2 Hz, 1H), 2.97 (dt, J = 18.2, 2.8 Hz, 1H), 2.71-2.63 (m, 1H), 2.58 (ddd, J = 12.4, 7.5, 1.4 Hz, 1H), 2.12 (t, J = 12.4 Hz, 1H), 1.40 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1 (C), 171.9 (C), 157.9 (C), 143.8 (C), 136.5 (C), 135.2 (C), 124.5 (CH), 119.3 (CH), 111.8 (CH), 111.7 (CH), 58.9 (C), 55.2 (CH_3), 52.9 (CH_3), 52.9 (CH_3), 48.8 (CH), 39.2 (CH_2), 36.1 (C), 34.8 (CH_2), 25.9 (CH_3), 22.2 (CH_3); HRMS-CI calcd. for $C_{20}H_{25}O_5$ $[M+H]^+$: 345.1702. Found: 345.1701. The structure was confirmed by COSY, NOESY, HMQC, and HMBC experiments.

Dimethyl 5-Methoxy-4,4-dimethyl-3a,4-dihydro-1*H*-cyclopenta[b]naphthalene-2,2(3*H*)-dicarboxylate (34'm)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (dd, J = 7.9, 7.6 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 6.64 (dd, J = 7.4, 0.9 Hz, 1H), 6.25 (bs, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.72 (s, 3H), 3.28 (d, J = 18.0 Hz, 1H), 2.97 (dt, J = 18.0, 3.1 Hz, 1H), 2.78-2.69 (m, 1H), 2.60 (ddd, J = 12.6, 7.6, 1.4 Hz, 1H), 2.15 (t, J = 12.5 Hz, 1H), 1.60 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2 (C), 172.1 (C), 158.3 (C), 141.9 (C), 136.2 (C), 131.2 (C), 127.1 (CH), 119.9 (CH), 119.6 (CH), 111.2 (CH), 58.7 (C), 55.4 (CH_3), 52.9 (CH_3), 52.8 (CH_3), 49.9 (CH), 39.2 (CH_2), 37.6 (C), 35.03 (CH_2), 27.6 (CH_3), 19.5 (CH_3); HRMS-CI calcd. for $C_{20}H_{25}O_5$ $[M+H]^+$: 345.1702. Found:

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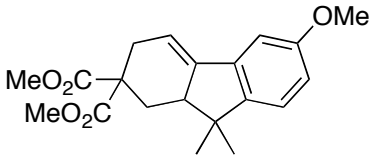
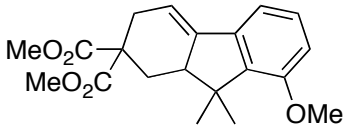
345.1700. The structure was confirmed by COSY, NOESY, HMQC, and HMBC experiments.

Dimethyl 6-Methoxy-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (35m)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 8.2 Hz, 1H), 6.89 (d, J = 2.3 Hz, 1H), 6.78 (dd, J = 8.3, 2.4 Hz, 1H), 5.98 (dt, J = 4.6, 2.7 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 3.09 (d, J = 18.4 Hz, 1H), 2.53-2.45 (m, 2H), 2.43-2.34 (m, 1H), 1.89 (t, J = 12.3 Hz, 1H), 1.37 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1 (C), 172.0 (C), 158.9 (C), 146.5 (C), 141.1 (C), 139.5 (C), 123.0 (CH), 114.9 (CH), 114.3 (CH), 104.7 (CH), 55.4 (CH_3), 54.0 (C), 52.8 (CH_3), 52.8 (CH_3), 48.8 (CH), 43.9 (C), 31.3 (CH_2), 28.6 (CH_2); 26.3 (CH_3), 26.1 (CH_3); HRMS-CI calcd. for $C_{20}H_{25}O_5$ $[M+H]^+$: 345.1702. Found: 345.1702. The structure was confirmed by COSY, NOESY, HMQC, and HMBC experiments.

Dimethyl 8-Methoxy-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (35'm)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, J = 7.6, Hz, 1H), 6.99 (d, J = 7.6 Hz, 1H), 6.71 (d, J = 7.6 Hz, 1H), 5.94 (dt, J = 4.4, 2.9 Hz, 1H), 3.81 (s, 3H), 3, 79 (s, 3H), 3.76 (s, 3H), 3.07 (d, J = 18.5 Hz, 1H), 2.52-2.42 (m, 2H), 2.39-2.31 (m, 1H), 1.88 (t, J = 12.5 Hz, 1H), 1.50 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2 (C), 172.1 (C), 156.9 (C), 141.6 (C), 140.4 (C), 139.9 (C), 128.1 (CH), 114.0 (CH), 112.8 (CH), 110.2 (CH), 55.1 (CH_3), 54.1 (C), 52.8 (CH_3), 52.7 (CH_3), 48.5 (CH), 45.2 (C), 31.3 (CH_2), 28.2 (CH_2), 26.2 (CH_3), 22.6 (CH_2); HRMS-CI calcd. for $C_{20}H_{25}O_5$ $[M+H]^+$: 345.1702. Found: 345.1709. The structure was confirmed by COSY, NOESY, HMQC, and HMBC experiments.

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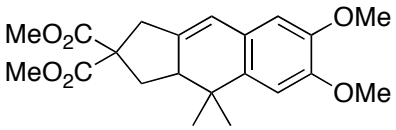
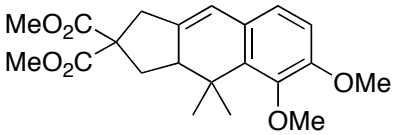
Dimethyl 6,7-Dimethoxy-4,4-dimethyl-3a,4-dihydro-1*H*cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (34o)



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (s, 1H), 6.51 (s, 1H), 6.19 (bs, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.70 (s, 3H), 3.65 (s, 3H), 3.21 (d, J = 17.8 Hz, 1H), 2.90 (dt, J = 17.8, 2.8 Hz, 1H), 2.63-2.46 (m, 2H), 2.05 (t, J = 12.0 Hz, 1H), 1.34 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 171.9, 147.6, 147.1, 141.0, 136.7, 127.2, 118.7, 109.9, 107.9, 58.9, 56.2, 55.9, 52.8, 48.6, 39.1, 36.4, 38.8, 25.9, 21.9; HRMS-CI calcd. for $C_{21}H_{27}O_6$ $[M+H]^+$: 375.1808. Found: 375.1796. The structure was confirmed by COSY, NOESY, HMQC, and HMBC experiments.

Dimethyl 5,6-Dimethoxy-4,4-dimethyl-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (34'o)



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (s, 2H), 6.22 (bs, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.75 (s, 3H), 3.72 (s, 3H), 3.25 (d, J = 17.9 Hz, 1H), 2.95 (dd, J = 17.9, 3.0 Hz, 1H), 2.77-2.66 (m, 1H), 2.59 (dd, J = 13.0, 7.2 Hz, 1H), 2.12 (t, J = 12.4 Hz, 1H), 1.64 (s. 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 172.2 (C), 172.1 (C), 152.6 (C), 148.1(C), 139.7 (C), 136.7 (C), 128.9 (C), 122.1 (CH), 119.2 (CH), 110.0 (CH), 60.6 (CH_3), 58.8 (C), 55.7 (CH_3), 52.8 (CH_3), 52.8 (CH_3), 49.5 (CH), 39.1 (CH_2), 38.2 (C), 35.0 (CH_2), 27.2 (CH_3), 20.8 (CH_3); HRMS-ESI calcd. for $C_{21}H_{26}O_6Na$ $[M+Na]^+$: 397.1627. Found: 397.1624. The structure was confirmed by COSY, NOESY, HMQC, and HMBC experiments.

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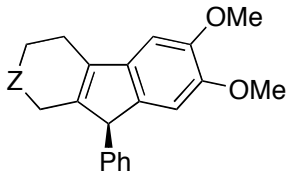
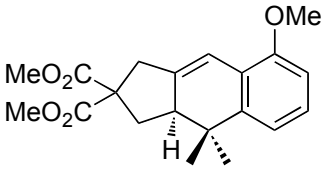
Dimethyl 6,7-Dimethoxy-9-phenyl-3,4-dihydro-1*H*-fluorene-2,2(9H)-dicarboxylate (35p'')



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 3H), 7.00 (dd, J = 8.3, 1.55 Hz, 2H), 6.76 (d, J = 9.6 Hz, 2H), 4.29 (s, 1H), 3.91 (s, 3H), 3.77 (s, 3H), 3.70 (s, 3H), 3.61 (s, 3H), 2.84 (d, J = 17.9 Hz, 1H), 2.70-2.48 (m, 3H), 2.35 (q, J = 6.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 171.6, 148.5, 147.2, 140.6, 140.4, 139.6, 137.0, 134.6, 128.6, 128.3, 126.7, 108.2, 102.0, 57.4, 56.3, 56.2, 54.1, 52.7, 52.5, 30.1, 28.1, 19.9; HRMS-ESI calcd. for $C_{25}H_{26}O_6Na$ $[M+Na]^+$: 445.1627. Found: 445.1617.

Dimethyl 8-methoxy-4,4-dimethyl-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (34q)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (dd, J = 8.1, 7.8 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.74 (bs, 1H), 6.72 (d, J = 8.1 Hz, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 3.70 (s, 3H), 3.31 (d, J = 18.2 Hz, 1H), 3.01 (dt, J = 18.2, 3.1 Hz, 1H), 2.72-2.65 (m, 1H), 2.60 (dd, J = 12.5, 8.1 Hz, 1H), 2.10 (t J = 12.5 Hz, 1H), 1.40 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 172.2 (C), 171.9 (C), 154.6 (C), 145.6 (C), 142.0 (C), 127.3 (CH), 122.9 (C), 116.1 (CH), 113.1 (CH), 108.5 (CH), 59.0 (C), 55.6 (CH_3), 52.8 ($2CH_3$), 48.0 (CH), 39.5 (CH_2), 36.9 (C), 34.8 (CH_2), 25.8 (CH_3), 21.5 (CH_3); HRMS-ESI calcd. for $C_{20}H_{24}O_5Na$ $[M+Na]^+$: 367.1521. Found: 367.1511. The structure was confirmed by COSY, NOESY, HMQC and HMBC experiments.

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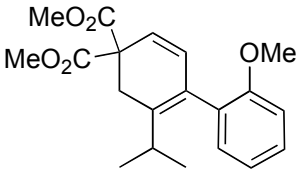
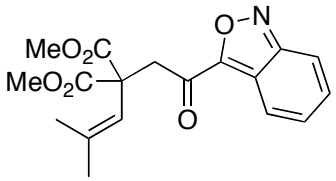
Dimethyl 5-isopropyl-4-(2-methoxyphenyl)cyclohexa-2,4-diene-1,1-dicarboxylate (36q)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7-23 (m, 1H), 6.97 (dd, J = 7.4, 1.8 Hz, 1H), 6.94-6.87 (m, 2H), 6.05 (d, J = 9.5 Hz, 1H), 5.81 (d, J = 9.5 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 2.87 (d, J= 5.4 Hz, 2H), 2.51 (hept, J = 6.9 Hz, 1H), 0.97 (d, J = 6.9 Hz, 3H), 0.93 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 171.5 (C), 171.2 (C), 156.9 (C), 139.0 (C), 131.5 (CH), 130.5 (CH), 129.3 (C), 127.3 (CH), 126.2 (C), 120.4 (CH), 119.2 (CH), 111.1 (CH), 55.5 (CH_3), 54.6 (C), 52.8 (CH_3), 52.7 (CH_3), 30.7 (CH), 28.8 (CH_2), 20.7 (CH_3), 19.6 (CH_3); HRMS-ESI calcd. for $C_{20}H_{24}O_5Na$ $[M+Na]^+$: 367.1521. Found: 367.1511. The structure was confirmed by COSY, NOESY, HMQC and HMBC experiments.

Dimethyl 2-(2-(Benzo[*c*]isoxazol-3-yl)-2-oxoethyl)-2-(3-methylbut-2-enyl)malonate (37)



Yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 9.6 Hz, 1H), 7.75 (d, J = 9.1 Hz, 1H), 7.42 (t, J = 7.2 Hz, 1H), 7.28 (overlap, 1H), 5.03 (tt, J = 1.5, 7.8 Hz, 1H), 3.84 (s, 2H), 3.80 (s, 6H), 2.86 (d, J = 7.8 Hz, 2H), 1.66 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.8, 170.9, 159.2, 157.6, 140.6, 137.1, 131.4, 128.8, 121.2, 119.32, 117.6, 116.0, 113.0, 55.5, 52.9, 42.3, 32.5, 30.9, 25.9, 17.8; HRMS-ESI calcd. for $C_{19}H_{21}NO_6Na$ $[M+Na]^+$: 382.1267. Found: 382.1272.

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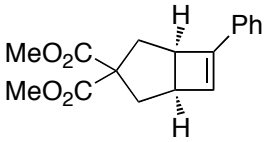
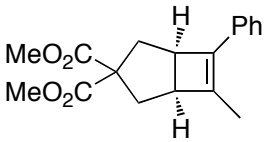
3.2. Cycloaddition of arylenynes with less substituted alkenes

(1*R,5*S**)-Dimethyl 7-Phenylbicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (39c'')**



White solid: mp = 68-70 ºC: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.15 (m, 5H), 6.01 (s, 1H); 3.63 (s, 3H), 3.56 (dd, *J* = 7.4, 3.5 Hz, 1H), 3.25 (dd, *J* = 7.5, 3.5 Hz, 1H), 3.15 (s, 3H), 2.76 (d, *J* = 13.5 Hz, 1H), 2.61 (d, *J* = 13.3 Hz, 1H) 1.95 (dd, *J* = 13.5, 7.5 Hz, 1H); 1.90 (dd, *J* = 13.3, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 171.9, 146.7, 133.3, 129.8, 128.3, 127.8, 124.6, 60.9, 52.9, 51.7, 45.7, 43.5, 35.4, 34.0; HRMS-CI calcd. for $C_{17}H_{19}O_4$ $[M+H]^+$: 287.1283. Found: 287.1274. The structure was confirmed by COSY, NOESY, HMQC and HMBC experiments.

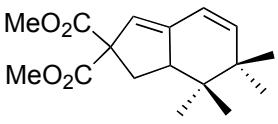
(1*R*,5*S*)-Dimethyl 6-Methyl-7-phenylbicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (39k'')



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.25 (m, 4H), 7.21-7.15 (m, 1H), 3.68 (s, 3H), 3.50-3.45 (m, 1H), 3.22 (s, 3H), 3.15-3.11 (m, 1H), 2.72 (dd, *J* = 28.8, 13.3 Hz, 1H), 2.02 (dd, *J* = 13.4, 7.2 Hz, 1H), 1.86 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.85 (dd, *J* = 2.8, 1.4 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 172.6, 172.4, 140.9, 138.5, 134.6, 128.2, 126.7, 125.6, 60.6, 52.8, 51.8, 46.3, 43.6, 34.6, 33.6, 13.9; HRMS-CI calcd. for $C_{28}H_{20}O_4$ $[M+H]^+$: 301.1440. Found: 301.1437. The structure was confirmed by COSY, NOESY, HMQC and HMBC experiments.

3.3 [2+2] of alkenyl substituted enynes

Dimethyl 6,6,7,7-Tetramethyl-7,7a-dihydro-1*H*-indene-2,2(6*H*)-dicarboxylate (41a)



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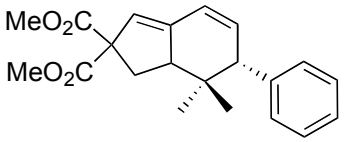
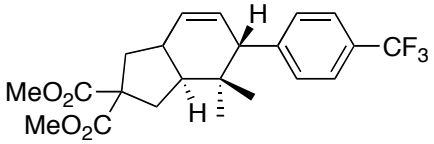
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (d, J = 9.6 Hz, 1H), 5.56 (d, J = 9.7 Hz, 1H), 5.53 (d, J = 2.4 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 2.10 (d, J = 1.5 Hz, 2H), 2.8 (d, J = 7.6 Hz, 2H), 1.86 (s, 3H), 1.80 (s, 3H), 1.71 (td, J = 2.4, 7.8 Hz, 1H), 2.62 (dd, J = 7.8, 13.2 Hz, 1H), 2.10 (dd, J = 13.3, 9.3 Hz, 1H), 1.01 (s, 3H), 0.98 (s, 3H), 0.89 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 171.6, 145.7, 144.2, 120.3, 119.6, 120.3, 119.6, 65.8, 52.7, 48.4, 40.0, 37.4, 33.2, 24.9, 23.7, 21.2, 17.0; HMRS-ESI calcd. for $C_{17}H_{24}O_4Na$ $[M+Na]^+$: 315.1572 Found: 315.1568.

(6*S*)-Dimethyl 7,7-Dimethyl-6-phenyl-7,7a-dihydro-1*H*-indene-2,2(6*H*)-dicarboxylate (41b)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 3H), 7.17 (d, J = 8.9 *Hz*, 2H), 6.50 (d, J= 9.9 Hz, 1H), 5.95 (dd, J= 5.6, 9.7 *Hz*, 1H), 5.74 (d, J= 2.5 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.22 (d, J= 5.23 Hz, 1H), 2.98 (t, J = 8.2 Hz, 1H), 2.53 (dd, J= 7.7, 13.3 Hz, 1H), 2.06 (dd, J = 13.2, 9.3 Hz, 1H), 0.94 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 171.4, 145.3, 139.9, 134.6, 130.2, 127.8, 127.6, 126.6, 122.6, 122.2, 65.3, 55.4, 52.7, 46.7, 33.0, 26.1, 23.1; HMRS-ESI calcd. for $C_{21}H_{24}O_4Na$ $[M+Na]^+$: 363.1572 Found: 363.1579.

(6*S*,7a*S*)-Dimethyl 7,7-Dimethyl-6-(4-(trifluoromethyl)phenyl)-3,3a,7,7a-tetrahydro-1*H*-indene-2,2(6*H*)-dicarboxylate (41c)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.1 Hz, 2H), 7.30 – 7.22 (m, 4H), 6.52 (d, J = 9.7 Hz, 1H), 5.90 (dd, J = 9.6, 5.6, 1H), 5.76 (d, J = 2.4, 1H), 5.30 (s, 1H), 3.78-3.70 (m, 7H), 3.26 (d, J = 5.5 Hz, 1H), 2.93-2.85 (m, 1H), 2.51 (dd, J = 13.2, 7.7 Hz, 1H), 2.04 (d, J = 2.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 171.2, 144.7, 144.2, 133.5, 130.5, 124.8, 123.4, 123.0, 65.3, 55.1, 52.8, 46.4, 35.8, 33.0,

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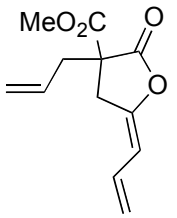
30.9, 29.7, 26.1, 23.1; HRMS-ESI calcd. for $C_{22}H_{23}O_4F_3Na$ $[M+Na]^+$: 431.1446. Found: 431.1434.

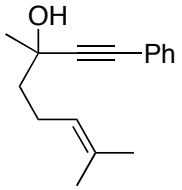
(*E*)-Methyl 3-Allyl-5-allylidene-2-oxotetrahydrofuran-3-carboxylate (42)



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (dt, J = 17.1, 10.6 Hz, 1H), 5.74-5.73 (m, 1H), 5.35 (dq, J = 1.53, 1.1, 0.76 Hz, 1H), 5.22 (d, J = 0.76 Hz, 1H), 5.20-5.18 (m, 1H), 5.14 (dq, J = 17.1, 0.65 Hz, 1H), 5.04 (dq, J = 10.2, 0.91 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 1H), 3.30 (dd, J = 17.1, 0.76 Hz, 1H), 2.92 (dd, J = 16.9, 0.91 Hz, 1H), 2.72 (ddt, J = 27.6, 7.6, 6.3, 1.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.9, 129.3, 121.2, 116.1, 106.7, 54.4, 53.5, 38.4, 34.4.

3.5 Application of the [4+2] cycloaddition reaction towards the total synthesis of the pycnanthuquinone

3,7-Dimethyl-1-Phenyloct-6-en-1-yn-3-ol (46r)[290]



At 0 ºC BuLi (2.4 M, 13.2 mL, 31.7 mmol) was added dropwise to a solution of phenylacetylene (3.23 g, 31.7 mmol) in THF (50 mL). After 1 h the mixture was cooled down to -30 ºC and the ketone (4.00 g, 31.7 mmol) was added and the mixture was allowed to warm to r. t (2 h). The mixture was diluted with EtOAc (50 mL), washed with water (2 x 20 mL), dried ($MgSO_4$) and the solvent was reduced under diminished pressure. The residue was purified by flash chromatography (hexanes/EtOAc 85:15) to yielded 6.28 g (87%) of a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.44 (m, 2H), 7.29-7.33 (m, 3H), 5.22 (tm, J = 6.8 Hz, 1H),

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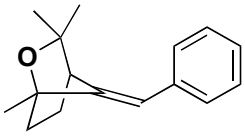
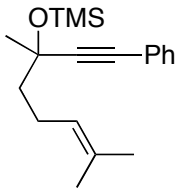
2.37 (dq, *J* = 16.1, 8.0 Hz, 1H), 2.27 (dq, *J* = 16.1, 8.0 Hz, 1H), 2.21 (s, 3H), 1.77-1.82 (m, 2H), 1.71 (s, 3H), 1.67 (s, 3H), 1.58 (s, 3H).

(*E*)-7-Benzylidene-1,3,3-Trimethyl-2-oxabicyclo[2.2.1]heptane (47)[290]



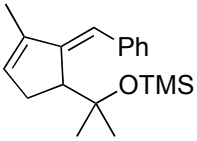
According to general procedure: Enyne (50 mg, 0.219 mmol) and complex **1g** (2.4 mg, 0.031 mmol) for 12 h in CH_2Cl_2. Flash chromatography (hexanes/EtOAc 99:1) yielded 31.2 mg, 62%: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.52 (m, 2H), 7.36-7.42 (m, 2H), 7.38-7.43 (m, 1H), 6.40 (d, *J* = 1.8 Hz, 1H), 3.75-3.78 (m, 1H), 2.14-2.22 (m, 1H), 1.78-1.90 (m, 1H), 1.46 (s, 3H), 1.40 (s, 3H), 1.36-1.40 (m, 1H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 138.4, 128.8, 128.6, 128.4, 128.1, 127.5, 125.0, 74.4, 71.9, 42.0, 31.9, 29.2, 27.9, 24.9, 20.7; HRMS-ESI. calcd. For $C_{16}H_{20}ONa$ $[M+Na]^+$: 251.1412. Found: 251.1419.

(3,7-Dimethyl-1-Phenyloct-6-en-1-yn-3-yloxy)trimethylsilane (46s)[290]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.46 (m, 2H), 7.32-7.35 (m, 2H), 5.20 (tm, *J* = 7.2 Hz, 1H), 2.20-2.28 (m, 2H), 1.69-1.81 (m, 2H), 1.72 (s, 3H), 1.67 (s, 3H), 1.56 (s, 3H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.6 (C), 131.4 (CH), 128.3 (CH), 128.1 (CH), 124.2 (CH), 123.2 (C), 93.4 (C), 84.3 (C), 69.7 (C), 45.2 (CH_2), 31.2 (CH_3), 25.7 (CH_3), 23.6 (CH_2), 17.6 (CH_3), 1.9 (CH_3).

(E)-(2-(2-Benzylidene-3-Methylcyclopent-3-enyl)propan-2-yloxy)trimethylsilane (48)[290]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.41 (m, 2H), 7.26-7.32 (m, 2H), 7.16-7.21 (m,

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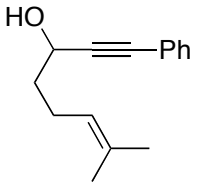
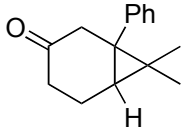
1H), 5.41-5.46 (m, 1H), 2.89 (d, J = 10.3 Hz, 1H), 2.76 (dd, J = 18.3, 6.3 Hz, 1H), 2.50 (ddt, J = 18.3, 10.0, 3.1 Hz, 1H), 1.77 (s, 3H), 1.18 (s, 3H), 0,90 (s, 3H), 0.0 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3 (C), 138.7 (C), 131.2 (C), 128.6 (CH), 128.2 (CH), 126.5 (CH), 126.3 (CH), 121,1 (CH), 78.2 (C), 44.8 (CH), 29.6 (CH_3), 26.8 (CH_3), 25.7 (CH_2), 21.0 (CH_3), 2.4 (CH_3); HRMS-ESI. calcd. for $C_{19}H_{28}OSiNa$ $[M+Na]^+$: 323.1807. Found: 323.1805.

7-Methyl-1-Phenyloct-6-en-1-yn-3-ol (46t)[290]



To a solution of tolylacetylene (750 mg, 7.34 mmol) was added Butyllithium (2.4 M, 3.06 mL, 7.34 mmol) dropwise at -78 ºC. The mixture was let to r. t. then cooled down to -40 ºC and 5-methylhex-4-enal (1.03 g, 7.34 mmol) was added. After 3 h at r. t. EtOAc (100 mL) was added and the mixture washed with water (50 mL) and brine (10 mL). The combined aqueous layers were extracted with EtOAc (20 mL), the organic layers dried ($MgSO_4$) and the solvent was reduced under diminished pressure. The residue was purified by flash chromatography (hexanes/EtOAc 95:5) yielded 1.34 g (85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.45 (m, 2H), 7.29-7.32 (m, 3H), 5.18 (tm, J = 7.0 Hz, 1H), 4.61 (q, J = 6.3 Hz, 1H), 2.30-2.20 (m, 2H), 1.98 (brs, 1H), 1.85 (m, 2H), 1.71 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.8 (C), 131.7 (CH), 128.4 (CH), 128.3 (CH), 123.3 (CH), 122.7 (C), 90.1 (C), 85.0 (C), 62.7 (CH), 37.9 (CH_2), 25.8 (CH_3), 23.9 (CH_2), 17.8 (CH_3).

7,7-dimethyl-1-phenylbicyclo[4.1.0]heptan-3-one (49)[290]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.33 (m, 2H), 7.18-7.21 (m, 3H), 2.74 (d, J = 17.7 Hz, 1H), 2.52 (d, J = 17.7 Hz, 1H), 2.43-2.54 (m, 1H), 2.35-2.40 (m, 1H), 2.25-2.32 (m, 1H), 1.69 (dddd, J = 16.7, 8.8, 5.8, 4.0 Hz, 1H), 1.48 (dd, J = 9.2, 6.1 Hz, 1H), 1.11 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.8 (C), 145.3 (C),

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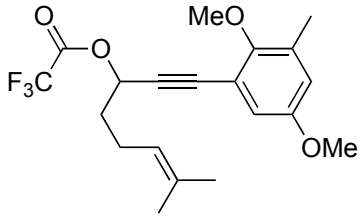
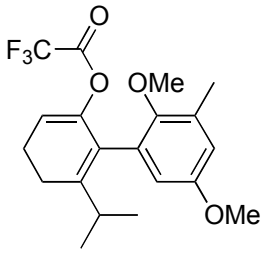
128.7 (CH), 128.4 (CH), 126.2 (CH), 45.2 (CH_2), 38.9 (CH_2), 34.6 (C), 25.4 (CH_3), 25.3 (C), 20.2 (CH_2), 16.7 (CH_3).

1-(2,5-Dimethoxy-3-Methylphenyl)-7-methyloct-6-en-1-yn-3-yl 2,2,2-trifluoroacetate (46u)[290]



To a mixture of acetic triflour acetic anhydride (4.37 g, 2.08 mmol), DMAP (127 mg, 1.04 mmol in pyridine (4 mL) was added 1-(2,5-dimethoxy-3-methylphenyl)-7-methyloct-6-en-1-yn-3-ol (150 mg, 0.52 mmol) at r. t. The mixture was stirred for 3 h then dilluted with EtOAc (30 mL) and washed with 10 % HCl (30 mL) and sat. $NaHCO_3$ (30 mL). The aqueous layer extracted with EtOAc (20 mL), the organic layers washed with brine (10 mL) dried ($MgSO_4$) and the solvent was reduced under diminished pressure. The residue was purified by flash chromatography (hexanes/EtOAc 95:5) yielded 159 mg (83%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, J = 3.2 Hz, 1H), 6.69 (d, J = 2.9 Hz, 1H), 5.16 (t, J = 7.2 Hz, 1H), 4.63 (t, J = 6.6 Hz, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 2.20-2.29 (m, 3H), 2.25 (s, 3H), 1.85 (q, J = 7.2 Hz, 2H), 1.70 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9 (d, J = 43 Hz), 155.0 (C), 153.6 (C), 132.7 (C), 132.4 (C), 123.3 (CH), 118.8 (CH), 117.9 (CH), 116.7 (C), 114.9 (CH), 114.7 (d, J = 284 Hz, CF_3), 93.9 (C), 81.4 (C), 62.7 (CH), 60.7 (CH_3), 55.5 (CH_3), 37.8, 25.7 (CH_3), 23.9 (CH_2), 17.7 (CH_3), 16.3 (CH_3).

6-(2,5-Dimethoxy-3-Methylphenyl)-5-isopropylcyclohexa-1,5-dienyl 2,2,2-trifluoroacetate (50)[290]



Enyne (40 mg, 0.104 mmol) and complex **1g** (2.4 mg, 0.031 mmol) for 30 min.

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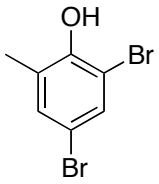
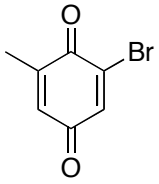
Column (DCM) yielded 37.2 mg (93%) (rf = 1.0). Due to its instability the set was used directly in the next reaction: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (d, J = 3.2 Hz, 1H), 6.33 (d, J = 3.2 Hz, 1H), 5.56 (t, J = 4.5 Hz, 1H), 3.70 (s, 3H), 3.54 (s, 3H), 2.68 (hept, J = 6.8 Hz, 1 H), 2.25-2.41 (m, 4H), 2.21 (s, 3H), 1.02 (d, J = 6.7 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8 (d, J = 42 Hz, C), 155.2 (C), 146.4 (C), 145.7 (C), 132.3 (C), 129.0 (C), 124.5 (C), 116.4 (CH), 114.3 (d, J = 284 Hz, CF_3), 114.2 (CH), 111.8 (CH), 60.2 (CH_3), 55.7 (CH_3), 31.3 (CH), 22.0 (CH_2), 21.8 (CH_2), 21.2 (CH_3), 20.5 (CH_3), 16.5 (CH_3). No further characterization was done due the instability of the compound.

2,5-Dibromo-3-Methylphenol (52)



To a solution of *o*-cresol (16.3 g, 151 mmol) in 90% glacial acetic (150 mL) was added bromine (48.2 g, 301 mmol). The reaction mixture was stirred at room temperature for 1 h then poured into 500 mL of water. The precipitate was filtered off and washed with water (3 x 250 mL) and dried. The remaining colorless solid (38.9 g, 97%) was pure enough to be used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 5.56 (s, 1H), 7.19 (s, 1H), 7.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1 (C), 133.3 (CH), 131.6 (C), 127.9 (CH), 112.4 (C), 110.8 (C), 16.9(CH_3).

2-Bromo-6-Methylcyclohexa-2,5-diene-1,4-dione (53)



To a suspension containing 24.0 g (90.3 mmol) 2,4-dibromo-6-methylphenol in acetic acid/ water (4:1, 50 mL) and acetonitrile (25 mL) was added a solution of CrO_3 (8.34 g, 83.4 mmol) in water (25 mL). The reaction mixture was heated to 60 ºC for 1.5 h, cooled to room temperature, diluted with of water (400 mL) and

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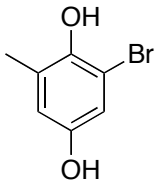
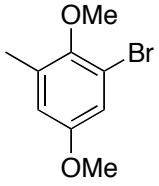
extracted with $CHCl_3$ (3 x 200 mL). The organic phase was dried ($MgSO_4$) and concentrated to yield 18.1 g (quant.) as bright orange crystals: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12 (s, 3H), 6.63 (m, 1H), 7.20 (d, J = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.1 (C), 180.1 (C), 145.9 (C), 138.3 (C), 137.5 (CH), 133.6 (CH), 17.1 (CH_3).

2-Bromo-6-Methylbenzene-1,4-diol



To a suspension of 14.0 g (69.7 mmol) of 2-bromo-6-methylcyclohexa-2,5-diene-1,4-dione in a mixture of ethanol (120 mL) and water (30 mL) was added Na_2SO_4 (14.5 g, 83.6 mmol) and the mixture was heated for 2 h to 50 ºC. After cooling down to r. t. the solvent was concentrated under diminished pressure and diluted with EtOAc (150 mL). The mixture was washed with water (2 x 100 mL), the aqueous layers extracted with EtOAc (2 x 30 mL), the organic layers dried ($MgSO_4$) and concentrated to yield 12.3 g (87%) as brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 4.94 (br s, 1H), 5.20 (s, 1H), 6.60 (d, J = 2.7 Hz, 1H), 6.82 (d, J = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1 (C), 145.1 (C), 126.9 (C), 118.2 (CH), 116.3 (CH), 110.1 (C), 17.3 (CH_3).
NMR data of the product according with Dr. Thorsten Lauterbach, unpublished results

1-Bromo-2,5-Dimethoxy-3-methylbenzene (54)



To a solution of 2-bromo-6-methylbenzene-1,4-diol (12.3 g, 53.2 mmol) in acetone (500 mL) of added dimethylsulfate (30.7 g, 221 mmol) and K_2CO_3 (33.6 g, 221 mmol). The reaction mixture was heated at reflux for 4 h, cooled to room

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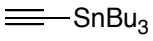
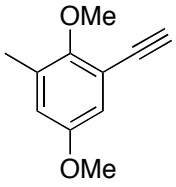
temperature and filtered. The filtrate was concentrated under diminished pressure and dissolved in ethyl acetate (300 mL) and washed with water (3 x 100 mL) dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 95:5) to yield 10.7 g (73%) of a yellowish oil (rf 0.6 in Hexanes/EtOAc 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.74 (s, 3H), 3.76 (s, 3H), 6.67 (d, J = 3.0 Hz, 1H), 6.92 (d, J = 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1 (C), 149.6 (C), 133.7 (C), 117.5 (C), 116.3 (CH), 115.8 (CH), 60.6 (CH_3), 55.9 (CH_3), 17.1 (CH_3).

Tributyl(Ethynyl)stannane



To a suspension of sodium ethylene in mineral oil (18 weight%) (7.00 g, 146 mmol) in THF (150 mL) was added dropwise tributylstannylchloride (33.2 g, 102 mmol). The mixture was stirred for 16 h, then water (10 mL) was added and the mixture filtered. After concentration of the solvent under diminished pressure to ca. 20 mL the residue was distillated (5 mbar, 105-115 ºC) to yield 15.2 g (47%) of a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.20 (s, 1H), 1.54-1.62 (m, 6H), 1.34 (sext, J = 7.4 Hz, 6H), 1.00-1.04 (m, 6H), 0.91 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 96.9 (CH), 89.1 (C), 28.9 (CH_2), 27.1 (CH_2), 13.8 (CH_2), 11.2 (CH_3).

1-Ethynyl-2,5-Dimethoxy-3-methylbenzene (55)



To a mixture of tetrakis triphenyphosphine palladium (1.25 g, 1.08 mmol) in toluene (75 mL) was added 1-bromo-2,5-dimethoxy-3-methylbenzene (5.00 g, 21.6 mmol) and ethynyl-tri-stannane (7.16 g, 22.7 mmol). The mixture was refluxed for 48 h. Then a solution of KF (5.0 g) in water (50 mL) was added and the mixture was stirred for further 2 h at r. t. The aqueous layer was separated, the mixture dried ($MgSO_4$), the solvent evaporated under diminished pressure. The residue was purified by flash chromatography (hexanes/EtOAc 98:2) to yield 3.52 g (92%) of a deep brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (d, J = 3.2 Hz, 1H), 6.73 (d, J =

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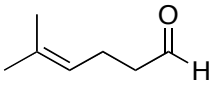
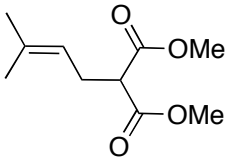
3.2 Hz, 1H), 3.84 (s, 3H), 3.74 (s, 3H), 3.75 (s, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0 (C), 154.3 (C), 132.6 (C), 118.4 (CH), 116.1 (C), 115.4 (CH), 80.8 (CH), 80.3 (C), 60.8 (CH_3), 55.6 (CH_3), 16.3 (CH_3).

5-Methylhex-4-Enal



2-Methylbut-3-en-2-ol and $Hg(OAc)_2$ were dissolved in etoxyethene (250 mL) and stirred for 6 days at r. t. Then the remaining ethoxyethene and formed diethylether was removed carefully under reduced pressure (500 mbar, 35 ºC) until ca 20 mL remained. The rest of the solvent and the remaining alcohol were distilled until 100 ºC (760 torr). The residue was filtered through cellite and cromatographed (Et_2O/Pentane 8:92) to give 3.55 g of the aldehyde (27%). Rf = 0.20 (2.5% EtOAc in hexane). The aldehyde contains 9.7% Et_2O and 3% starting material (2-methylbut-3-en-2-ol): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (t, J = 1.8 Hz, 1H), 5.11 (dsept, J = 7.0, 1.4 Hz, 1H), 2.48 (t, J = 7.2 Hz, 2H), 2.34 (t, J = 7.0 Hz, 2H), 1.71 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 202.7 (C), 133.3 (C), 122.1 (CH), 43.9 (CH_2), 25.4 (CH_3), 20.9 (CH_2), 17.3 (CH_3).

Dimethyl 2-(3-Methylbut-2-enyl)malonate (56)



Dimethylmalonate (39.9 g, 302 mmol) was added dropwise to a suspension of NaH (12.8 g, 302 mmol) in THF (150 mL). After 1 h the 1-bromo-3-methylbut-2-ene (15 g, 101 mmol) was added to the solution and stirred for 10 h. The mixture was poured onto Et_2O (200 mL) and washed with sat. $NaHCO_3$ (2 x 50 mL) and brine (50 mL). After drying over Na_2SO_4 and evaporation of the solvent the product was isolated by fractionized distillation (5 mbar, 105-110 ºC) to yield 14.5 g (24%) of a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.04 (tm, J = 7.3 Hz, 1H), 3.72 (s, 6H), 3.36 (t, J = 7.6 Hz, 2H), 2.59 (tm, J = 7.5 Hz), 1.67 (m, 3H), 1.62 (m, 3H).

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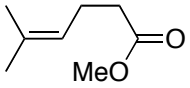
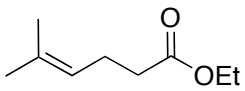
Methyl 5-Methylhex-4-enoate (57)



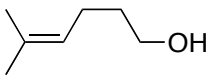
Dimethyl 2-(3-methylbut-2-enyl)malonate (14.5 g, 72.4 mmol), NaCl (5.93 g, 101 mmol) and water (2.61 g, 145 mmol) were added to DMSO (100 mL, deoxygenated by bubbling 1 h with Ar. The mixture was heated for 3 h under argon. The mixture was extracted with Et_2O (3 x 100 mL), the combined organic layers washed with water (100 mL) and brine (20 mL), dried ($MgSO_4$) and concentrated carefully under diminished pressure. Kugelrohr-distillation (48 mbar, 130 ºC) yielded 6.90 g (67%) of a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.05-5.11 (m, 1H), 3.37 (s, 3H), 2.29-2.35 (m, 4H), 1.68 (s, 3H), 1.63 (s, 3H).

Ethyl 5-Methylhex-4-enoate (60)



2-Methylbut-3-en-2-ol (25.0 g, 284 mmol), 1,1,1-triethoxyethane (138 g, 851 mmol) and propionic acid (2.10 g, 28.4 mmol) were heated neat under reflux for 6 h. Then 10% HCl (200 mL) was added dropwise. Et_2O (200 mL) was added and the aqueous layer separated. The organic layer was washed with sat. $NaHCO_3$ (3 x 100 mL) and brine (50 mL). After evaporation of the solvent the organic layer was filtered through a pad of silica (pentane/Et_2O 19:1) to yield 16.5 g (41%) of a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08-5.14 (m, 1H), 4.13 (q, J = 7.2 Hz, 2H), 2.30-2.35 (m, 4H), 1.69 (s, 3H), 1.63 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5 (C), 133.0 (C), 122.5 (CH), 60.2 (CH_2), 34.6 (CH_2), 25.7 (CH_3), 23.7 (CH_2), 17.7 (CH_3), 14.2 (CH_3).

5-Methylhex-4-En-1-ol (61)



a) Starting from methyl 5-methylhex-4-enoate: Methyl 5-methylhex-4-enoate (6.50 g, 45.7 mmol) was added dropwise to a suspension of $LiAlH_4$ (0.867 g, 22.9 mmol) in Et_2O (50 mL) and stirred for further 3 h at r. t. To the mixture then subsequently were added dropwise water (0.8 mL), 15% NaOH (0.8 mL) and water (2 mL). The

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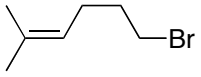
mixture was filtered and reduced with caution under diminished pressure to yield 5.25 g (quant.) of a colorless liquid.

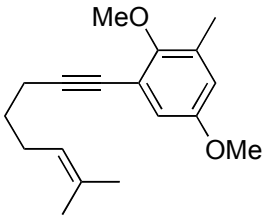
b) Starting from ethyl 5-methylhex-4-enoate: Like described before using ethyl 5-methylhex-4-enoate (12.0 g, 76.8 mmol), $LiAlH_4$ (1.46 g, 38.4 mmol) in Et_2O (250 mL) to yield 8.85 g (quant.) of the product. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 (tm, J = 7.2 Hz, 1H), 3.62 (t, J = 6.3 Hz, 2H), 2.05 (t, J = 6.4 Hz, 2H), 1.68 (brs, 3H), 1.61 (brs), 1.58-1.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2(C), 123.9 (CH), 62.7 (CH_2), 32.8 (CH_2), 25.7 (CH_3), 24.4 (CH_2), 17.6 (CH_3).

6-Bromo-2-Methylhex-2-ene (59)



Bromine (7.70 g, 48.2 mmol) was added to an ice cooled solution of PPh_3 (12.6 g, 48.1 mmol) in CH_2Cl_2 until a permanent yellow color appeared. Then pyridine (6.93 g, 87.7 mmol), bromine and 5-Methylhex-4-en-1-ol (5.00 g, 43.8 mmol) were added. The mixture was allowed to stir for 14 h. The mixture was poured onto water (100 mL) and extracted with pentane (2 x 50 mL). The organic layers were washed with aq. NH_4Cl and brine and dried (Na_2SO_4). While evaporation of the pentane at atmosphere pressure Ph_3PO precipitated. After adding of further pentane (50 mL) the Ph_3PO was filtered of. This procedure was repeated three times. It remained 5,55 g (65%) containing still 20% Ph_3PO: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (tm, J = 7.2 Hz, 1H), 3.40 (t, J = 6.3 Hz, 2H), 2.13 (t, J = 6.4 Hz, 2H), 1.88 (quint, J = 7.2 Hz, 2H), 1.70 (brs, 3H), 1.63 (brs); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.2 (C), 122.5 (CH), 33.6 (CH_2), 32.9 (CH_2), 26.5 (CH_3), 25.7 (CH_2), 17.8 (CH_3).

2,5-Dimethoxy-1-Methyl-3-(7-methyloct-6-en-1-ynyl)benzene (33aa)



To 1-ethynyl-2,5-dimethoxy-3-methylbenzene (1.6 g, 9.10 mmol) in THF (10 mL) was added dropwise butyllithium (3.6 mL of a 2.5 M solution in hexane, 9.1 mmol)

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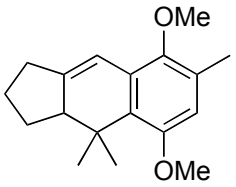
at -78 ºC. The mixture was let to r. t. and then cooled to -40 ºC and 6-bromo-2-methylhex-2-ene (1.77 g, 10.0 mmol) was added dropwise. The mixture was let to r. t. and DMF (20 mL) was added. The mixture was stirred for 18 h at r. t. then poured onto water (30 mL) and extracted twice with EtOAc (2 x 50 mL). The combined organic layers were washed with brine (20 mL) and dried ($MgSO_4$) and the solvent was reduced under diminished pressure. The residue was purified by flash chromatography (hexanes/EtOAc 95:5) 1.36 g (55%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (d, J = 3.3 Hz, 1H), 6.65 (d, J = 3.3 Hz, 1H), 5.14 (tm, J = 7.4 Hz, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 2.45 (t, J = 7.2 Hz, 2H), 2.13-2.25 (m, 2H), 2.23 (s, 3H), 1.85 (q, J = 7.3 Hz, 2H), 1.70 (brs, 3H), 1.64 (brs, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0 (C), 153.5 (C), 132.4 (C), 132.2 (C), 123.7 (CH), 118.0 (C), 116.9 (CH), 114.9 (CH), 94.3 (C), 60.5 (CH_3), 55.5 (CH_3), 29.0 (CH_2), 27.2 (CH_2), 19.2 (CH_3), 17.8 (CH_3), 16.3 (CH_3).

Compound 34aa



According to general conditions: Enyne, (50 mg, 0.184 mmol), Complex **1g** (7.1 mg, 0.092 mmol) in CH_2Cl_2 for 80 minutes at 80 ºC under microwave irradiation. Rf 0.30 (2.5% EtOAc in hexane), yield 43.3 mg (99%): ^{1}H NMR (400 MHz, C_6D_6) δ 6.95 (q, J = 2.5 Hz, 1H), 6.53 (s, 1H), 3.62 (s, 3H), 3.49 (s, 3H), 2.65 - 2.73 (m, 1H), 2.56-2.65 (m, 1H), 2.34-2.43 (m, 1H), 2.33 (s, 3H), 1.91 (s, 3H), 1.83-1.91 (m, 1H), 1.73-1.80 (m, 1H). 1.56 (dddd, J = 12.3, 10.9, 9.5, 4.4 Hz, 1H), 1.44-1.53 (m, 1H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 153.8 (C), 148.3 (C), 145.8 (C), 130.1 (C), 129.0 (C), 127.9 (CH), 59.6 (CH_3), 54.4 (CH_3), 51.2 (CH), 37.2 (C), 31.6 (CH_2), 27.4 (CH_3), 26.4 (CH_2), 24.2 (CH_2), 19.0 (CH_3), 15.1 (CH_3).

NMR data of the product according with Dr. Thorsten Lauterbach, unpublished results

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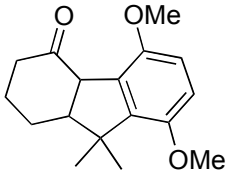
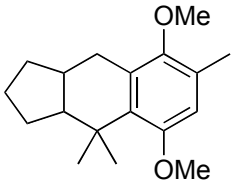
5,8-Dimethoxy-6,9,9-Trimethyl-2,3,9,9a-tetrahydro-1H-fluoren-4(4aH)-one (62)



To a mixture of 5,8-dimethoxy-4,4,7-trimethyl-2,3,3a,4-tetrahydro-1H-cyclopenta[*b*]naphthalene (25 mg, 92 μmol) and $NaHCO_3$ (19.3 mg, 223 μmol) in CH_2Cl_2 (1 mL) was added MCPBA (33.9 mg, 138 μmol). After stirring for 1 h the mixture was diluted with CH_2Cl_2 (10 mL), washed with sat. aq. $NHCO_3$ (sat.) (2 x 5 mL), dried (Na_2SO_4) and the solvent was reduced under diminished pressure. The residue was purified by flash chromatography (hexanes/EtOAc 95:5) to yield 15.9 mg (60%). The same reaction using water/CH_2Cl_2 (1:1) yielded in 23.5 mg (82%): ^{1}H NMR (400 MHz, C_6D_6) δ 6.45 (s, 1H), 4.02-4.06 (m, 1H), 3.39 (s, 3H), 3.38 (s, 3H), 2.31-2.39 (m, 2H), 2.02 (s, 3H), 2.15-2.23 (m, 1H), 2.03 (tt, J = 12.9, 3.9 Hz, 1H), 1.69 (s, 3H), 1.45-1.68 (m, 4H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 213.2 (C), 152.9 (C), 148.7 (C), 131.5 (C), 131.4 (C), 112.2 (CH), 59.4 (CH_3), 59.2 (CH_3, 54.0 (CH), 47.4 (CH), 42.2 (C), 35.4 (CH_2), 31.0 (CH_2), 29.3 (CH_3), 24.4 (CH_3), 16.9 (CH_2), 15.3 (CH_3).

5,8-Dimethoxy-4,4,7-Trimethyl-2,3,3a,4,9,9a-hexahydro-1H-cyclopenta[b]naphthalene (65)



5,8-dimethoxy-4,4,7-trimethyl-2,3,3a,4-tetrahydro-1H-cyclopenta[b]naphthalene (30.0 mg, 0.109 mmol) was added to a mixture of Pd/C in methanol (4 mL). A balloon filled with H_2 was added via syringe into the suspension and the mixture was stirred 16 h. The mixture was filtrated through a pad of silica and the solvent was evaporated to yield 30.0 mg (quant.) of an off white oil as a mixture of diastereoisomers (10:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (s, 1H), 3.77 (s, 3H), 3.67 (s, 3H), 2.75-2.87 (m, 1H), 2.26 (s, 3H), 2.25 - 2.30 (m, 2H), 1.69-1.80 (m, 3H), 1.52-1.63 (m, 2H), 1.43 (s, 3H), 1.31 (s, 3H), 1.21-1.32 (m, 2H); ^{13}C NMR

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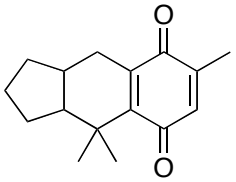
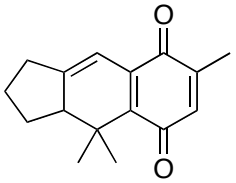
(100 MHz, $CDCl_3$) δ 155.4 (C), 150.0 (C), 130.9 (C), 130.9 (C), 127.7 (C), 111.7 (CH), 59.6 (CH_3), 55.4 (CH_3), 54.1 (CH), 36.2 (C), 32.9 (CH), 32.3 (CH_2), 31.0 (CH_3) 27.4 (CH_3), 26.7 (CH_2), 26.4 (CH_2), 23.1 (C), 20.9 (CH_2), 16.1 (CH_3).

4,4,7-Trimethyl-2,3,3a,4-Tetrahydro-1H-cyclopenta[b]naphthalene-5,8(9H,9aH)-dione (66)



5,8-dimethoxy-4,4,7-trimethyl-2,3,3a,4,9,9a-hexahydro-1H-cyclopenta[b]naphthalene (20 mg, 0.073 mmol) was added to a mixture of Cerium Ammonium Nitrate (20 mg, 0.36 mmol) in acetonitrile (3 mL). After 16 h the mixture was poured onto water (5 mL) and extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was reduced under diminished pressure. The residue was purified by flash chromatography (hexanes/EtOAc 85:15) to yielded 11.1 mg (62%) of a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 (d, J = 1.5 Hz, 1 H), 2.60 (dd, J = 20.6, 7.3 Hz, 1H), 1.98 (s, 3H), 1.90 (J = 20.6, 9.9 Hz, 1H), 1.51-1.62 (m, 6 H), 1.34 (s, 6H), 1.17-1.27 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 188.5 (C), 187.8 (C), 147.0 (C), 144.0 (C), 141.8 (C), 135.0 (CH), 53.3 (CH), 36.2 (C), 32.0 (CH), 31.6 (CH_2), 31.3 (CH_3), 26.0 (CH_3), 25.7 (CH_2), 25.3 (CH_2), 20.1 (CH_2), 15.3 (CH_3).

4,4,7-Trimethyl-2,3,3a,4-Tetrahydro-1*H*-cyclopenta[*b*]naphthalene-5,8-dione (64)



To a suspension of substrate **34aa** (0.05 g, 0.18 mmol) in dioxane (2 mL) was added silver oxide (0.09 g, 0.73 mmol). The oxidation was initiated by addition of HNO_3 6N (0.2 mL). Passed 20 minutes the reaction finished. Flash chromatography was carried out to purify the product (70%). The product decomposes rapidly and the

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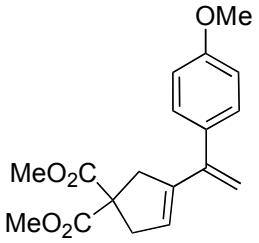
characterization resulted difficult to obtain. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (q, J = 2.4 Hz, 1H), 6.46 (q, J = 1.7 Hz, 1H), 2.88 (dd, overlap., J = 18.7, 6.4 Hz, 1H), 2.50-2.40 (m, 2H), 2.02 (d, J = 1.7 Hz, 3H), 1.96-1.90 (m, 2H), 1.55 (s, 3H), 1.57-1.52 (m, 2H), 0.92 (s, 3H). GC-Mass *m/z* 242.

4. Single/Double cleavage rearrangement

General method:

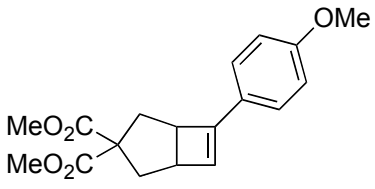
In a sealed tub for microwave reactor were added the substituted 1,6-enyne (0,050mg), the catalyst (0,05mol%) and the solvent (1 mL)

Dimethyl 3- (1-(4-Methoxyphenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (39a)



Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.21 (m, 2H), 6.89-6.85 (m, 2H), 5.49-5.45 (m, 1H), 5.13 (s, 1H), 5.11 (s, 1H), 3.83 (s, 3H), 3.79 (s, 6H), 3.30 (d, J = 1.4 Hz, 2H), 3.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 159.0, 144.8, 140.8, 133.7, 129.51, 127.2, 114.1, 113.3, 58.9, 55.3, 52.9, 41.3, 41.2; HRMS-ESI calcd. for $C_{18}H_{20}O_5Na$ $[M+Na]^+$: 339.1208. Found: 339.1198.

Dimethyl 6-(4-Methoxyphenyl)bicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (39''a)



Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 5.92 (s, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 3.61-3.57 (m, 1H), 3.33-3.28 (m, 1H), 3.26 (s, 3H), 2.78 (d, J = 13.2 Hz, 1H), 2.67 (d, J = 13.2 Hz, 1H), 2.00-1.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 159.0, 146.0, 126.9, 126.0,

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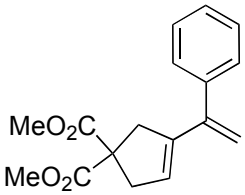
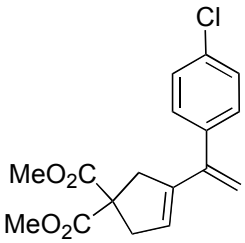
125.7, 60.6, 55.0, 52.5, 51.6, 45.5, 43.1, 35.3, 33.8; HRMS-ESI calcd. for $C_{18}H_{20}O_5Na$ $[M+Na]^+$: 339.1208. Found: 339.1198.

Dimethyl 3-(1-Phenylvinyl)cyclopent-3-ene-1,1-dicarboxylate (39b)



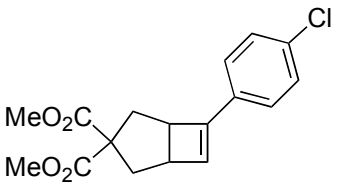
Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (m, 5H), 5.44 (t, J = 2.6 Hz, 1H), 5.19 (s, 1H), 5.13 (s, 1H), 3.77 (s, 6H), 3.30 (d, J = 1.9 Hz, 2H), 3.12 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 145.3, 141.3, 140.5, 128.5, 128.0, 127.4, 114.8, 58.9, 53.0, 41.3, 41.1; HRMS-ESI calcd. for $C_{17}H_{19}O_4$ $[M+H]^+$: 287.1283. Found: 287.1271.

Dimethyl 3-(1-(4-Chlorophenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (39c)



Brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 7.5 Hz, 2H), 7.23 (d, J = 7.5 Hz, 2H), 5.43 (s, 1H), 5.21 (s, 1H), 5.14 (s, 1H), 3.75 (s, 6H), 3.30 (s, 2H), 3.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 143.7, 139.7, 139.1, 132.6, 129.6, 127.7, 127.1, 115.1, 58.8, 53.0, 41.3, 41.1; HRMS-ESI calcd. for $C_{17}H_{170}O_4NaCl$ $[M+Na]^+$: 343.0713. Found: 343.0712.

Dimethyl 6-(4-Chlorophenyl)bicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (39''c)



Brown solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.18 (m, 4H), 6.08 (s, 1H), 3.77 (s, 3H), 3.63-3.58 (m, 1H), 3.35-3.30 (m, 1H), 3.27 (s, 3H), 2.76 (d, J = 13.6 Hz, 1H),

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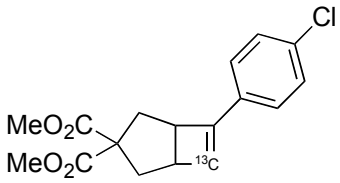
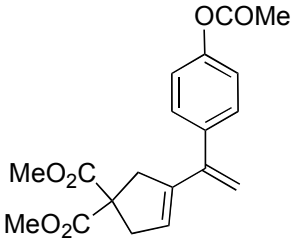
2.67 (d, J = 13.6 Hz, 1H), 2.06-1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 145.5, 130.3, 128.5, 128.0, 125.7, 60.8, 52.9, 51.9, 45.7, 43.6, 35.2, 33.9; HRMS-ESI calcd. for $C_{17}H_{170}O_4NaCl$ $[M+Na]^+$: 343.0713. Found: 343.0712.

^{13}C-Dimethyl 6-(4-Chlorophenyl)bicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (39''c-^{13}C)



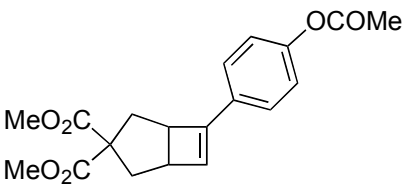
Brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.18 (m, 4H), 6.08 (d, J(^{13}C-H) = 168.9 Hz, 1H), 3.77 (s, 3H), 3.64-3.60 (m, 1H), 3.37-3.30 (m, 1H), 3.27 (s, 3H), 2.77 (d, J = 13.0 Hz, 1H), 2.68 (dd, J = 6.5, 13.0 Hz, 1H), 2.02 (dd, J = 7.1, 14.3 Hz, 1H), 1.99-1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.7.

Dimethyl 3-(1-(4-Acetoxyphenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (39d)



Light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, J = 2.2, 6.3 Hz, 2H), 7.03 (dd, J = 2.1, 6.5 Hz, 2H), 5.45 (t, J= 2.8 Hz, 1H), 5.18 (s, 1H), 5.13 (s, 1H), 3.77 (s, 6H), 3.29 (d, J = 1.7 Hz, 2H), 3.12 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 150.0, 144.3, 140.3, 138.7, 129.5, 127.5, 120.8, 115.0, 58.9, 53.0, 41.3, 41.1, 21.2. About the rapidly decomposition of the product, the mass could not be determined.

Dimethyl 6-(4-Acetoxyphenyl)bicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (39''d)



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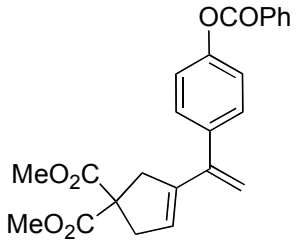
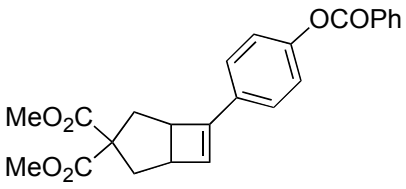
Light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 2.0, 6.8 Hz, 2H), 7.05 (dd, J = 2.0, 6.6 Hz, 2H), 6.07 (s, 1H), 3.70 (s, 3H), 3.63 (dd, J = 3.4, 7.3, 1H), 3.35 (dd, J = 3.4, 7.6 Hz, 1H), 3.26 (s, 3H), 2.80 (d, J = 12.7 Hz, 1H), 2.69 (d, J = 12.7 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 171.9, 150.2, 145.8, 131.2, 129.9, 125.7, 121.5, 60.9, 52.9, 51.9, 45.8, 43.5, 35.3, 34.0, 21.2; HRMS-ESI calcd. for $C_{17}H_{170}O_4NaCl$ $[M+Na]^+$: 343.0713. Found: 343.0712. About the rapidly decomposition of the product, the mass could not be determined.

Dimethyl 3-(1-(4-(Benzoyloxy)phenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (39e)



White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.1 Hz, 2H), 7.64 (t, J = 8.2 Hz, 1H), 7.52 (t, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 5.49 (bs, 1H), 5.19 (d, J = 16.1Hz, 2H), 3.78 (s, 6H), 3.31 (s, 2H), 3.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 140.1, 133.3, 129.9, 129.2, 128.3, 127.3, 125.7, 120.9, 114.8, 114.3, 58.6, 52.7, 41.1, 40.1. About the rapidly decomposition of the product, the mass could not be determined.

Dimethyl 6-(4-(Benzoyloxy)phenyl)bicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (39''e)



Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.2 (d, J = 7.5 Hz, 2H), 7.64 (d, J = 7.5 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.09 (s, 1H), 3.70 (s, 3H), 3.64 (dd, J = 7.4, 3.6 Hz, 1H), 3.35 (dd, J = 7.6, 3.4 Hz, 1H), 3.29 (s, 3H), 2.81 (d, J = 13.4 Hz, 1H), 2.70 (d, J = 13.4 Hz, 1H), 2.06-1.96

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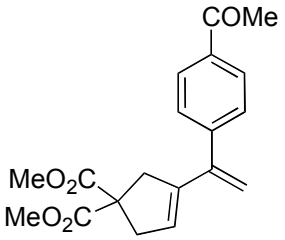
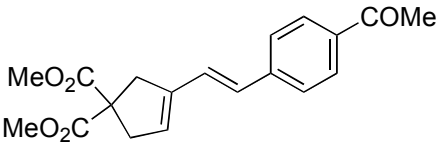
(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 171.7, 164.8, 150.2, 145.5, 133.4, 130.9, 129.9, 129.7, 128.3, 125.5, 121.4, 60.6, 51.6, 45.5, 43.2, 35.1, 33.7, 22.4, 13.9. About the rapidly decomposition of the product, the mass could not be determined.

Dimethyl 3-(1-(4-Acetylphenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (39f)



Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 5.43 (s, 1H), 5.28 (s, 1H), 5.20 (s, 1H), 3.76 (s, 6H), 3.35 (s, 2H), 3.18 (s, 2H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 144.7, 140.2, 128.9, 128.4, 127.9, 115.9, 59.0, 53.2, 41.6, 41.3, 29.9, 26.9; HRMS-ESI calcd. for $C_{19}H_{20}O_5Na$ $[M+Na]^+$: 351.1208. Found: 351.1208.

(*E*)-dimethyl 3-(4-Acetylstyryl)cyclopent-3-ene-1,1-dicarboxylate (39'f)



Yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 16.2 Hz, 1H), 6.49 (d, J = 16.4 Hz, 1H), 5.82 (s, 1H), 3.82 (s, 6H), 3.29 (s, 2H), 3.20 (s, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 142.1, 139.7, 136.1, 129.7, 129.0, 128.9, 127.1, 126.6, 59.0, 53.2, 41.3, 39.8, 26.8; HRMS-ESI calcd. for $C_{19}H_{20}O_5Na$ $[M+Na]^+$: 351.1208. Found: 351.1208.

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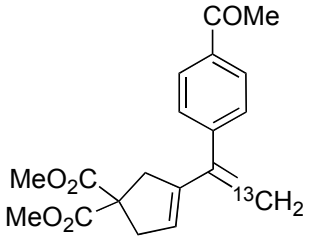
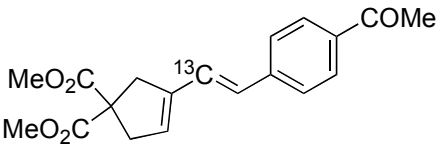
^{13}C-Dimethyl 3-(1-(4-Acetylphenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (39f-^{13}C)



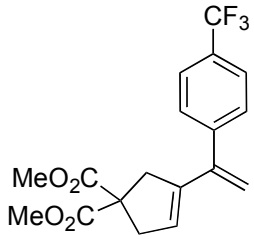
Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 5.43 (s, 1H), 5.28 (s, 1H), 5.20 (s, 1H), 3.76 (s, 6H), 3.35 (s, 2H), 3.18 (s, 2H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.9.

^{13}C-(*E*)-dimethyl 3-(4-Acetylstyryl)cyclopent-3-ene-1,1-dicarboxylate (39'f-^{13}C)



Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 16.2 Hz, 1H), 6.49 (d, J = 16.4 Hz, 1H), 5.82 (s, 1H), 3.82 (s, 6H), 3.29 (s, 2H), 3.20 (s, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.1.

Dimethyl 3-(1-(4-(Trifluoromethyl)phenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (39g)



Brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 5.37 (s, 1H), 5.25 (s, 1H), 5.16 (s, 1H), 3.77 (s, 6H), 3.30 (d, J = 1.8 Hz, 2H), 3.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 144.9, 144.3, 140.0, 128.8, 128.4, 127.8, 126.4, 125.5, 124.9, 115.8, 58.8, 53.0, 41.4, 41.1. The mass could not be determined because decomposed rapidly.

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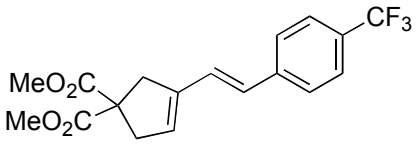
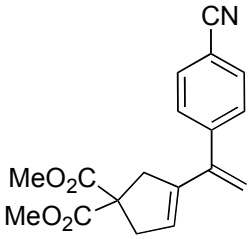
(*E*)-dimethyl 3-(4-(Trifluoromethyl)styryl)cyclopent-3-ene-1,1-dicarboxylate (39'g)



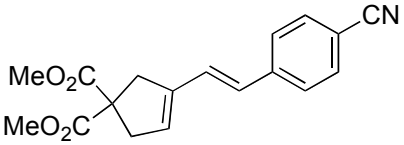
Brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 16.1 Hz, 1H), 6.45 (d, J = 16.1 Hz, 1H), 5.77 (s, 1H), 3.77 (s, 6H), 3.26 (s, 2H), 3.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 140.7, 139.4, 129.3, 128.5, 126.6, 126.4, 125.6, 125.5, 58.8, 53.0, 41.1, 39.6. The mass could not be determined because decomposed rapidly.

Dimethyl 3-(1-(4-Cyanophenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (39h)



Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 5.37 (s, 1H), 5.28 (s, 1H), 5.17 (s, 1H), 3.77 (s, 6H), 3.29 (s, 2H), 3.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 139.7, 131.9, 131.7, 129.2, 128.0, 116.3, 58.7, 53.0, 41.4, 41.0; HRMS-ESI calcd. for $C_{18}H_{17}NO_4Na$ $[M+Na]^+$: 334.1055. Found: 334.1042.

(*E*)-Dimethyl 3-(4-Cyanostyryl)cyclopent-3-ene-1,1-dicarboxylate (39'h)



White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 6.99 (d, J = 15.8 Hz, 1H), 6.42 (d, J = 16.0 Hz, 1H), 5.83 (s, 1H), 3.77 (s, 6H), 3.26 (s, 2H), 3.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 141.7, 139.3, 132.4, 130.4, 128.1, 127.8, 126.7, 125.1, 119.0, 110.5, 58.8, 53.1, 41.2, 39.5; HRMS-ESI calcd. for $C_{18}H_{17}NO_4Na$ $[M+Na]^+$: 334.1055. Found: 334.1048.

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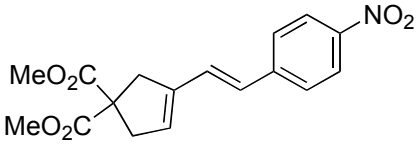
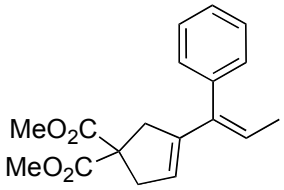
(*E*)-Dimethyl 3-(4-Nitrostyryl)cyclopent-3-ene-1,1-dicarboxylate (39'i)



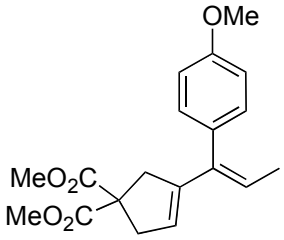
Yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.9 Hz, 2H), 7.50 (d, J = 8.9 Hz, 2H), 7.04 (d, J = 16.5 Hz, 1H), 6.47 (d, J = 16.5 Hz, 1H), 5.87 (s, 1H), 3.77 (s, 6H), 3.26 (s, 2H), 3.19 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 146.7, 143.8, 139.3, 130.8, 128.5, 127.7, 126.7, 124.0, 58.8, 53.1, 41.2, 39.5, 29.7; HRMS-ESI calcd. for $C_{17}H_{17}NO_6Na$ $[M+Na]^+$: 354.0953. Found: 354.0954.

(*Z*)-Dimethyl 3-(1-Phenylprop-1-enyl)cyclopent-3-ene-1,1-dicarboxylate (39j)



Yellow oil: (15:1 trans/cis) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.26 (m, 3H), 7.12 (d, J = 8.4 Hz, 2H), 5.75 (q, J = 7.2 Hz, 1H), 4.99 (s, 1H), 3.77 (s, 6H), 3.29 (s, 2H), 3.05 (s, 2H), 1.58 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 146.7, 138.4, 138.2, 129.0, 127.4, 126.2, 124.1, 58.3, 52.6, 40.5, 40.1, 31.6, 14.2; HRMS-ESI calcd. for $C_{18}H_{20}O_4Na$ $[M+Na]^+$: 323.1259. Found: 323.1250.

(*Z*)-Dimethyl 3-(1-(4-Methoxyphenyl)prop-1-enyl)cyclopent-3-ene-1,1-dicarboxylate (39k)



Brown oil, 45 %: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, J = 9.0 Hz, 2H), 6.87 (d, J = 9.0 Hz, 2H), 5.71 (q, J = 7.3 Hz, 1H), 5.00 (s, 1H), 3.81 (s, 6H), 3.75 (s, 6H), 3.25 (d, J = 2.2 Hz, 2H), 3.03 (s, 2H), 1.57 (d, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 158.3, 142.5, 138.4, 131.4, 130.6, 124.3, 113.4, 58.8, 55.2, 52.3,

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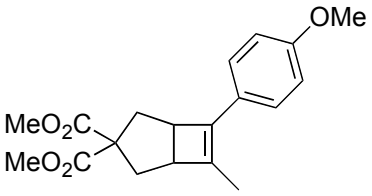
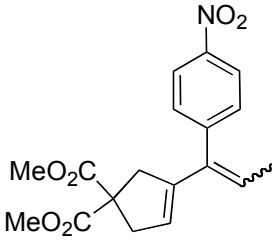
40.9, 40.7, 15.0; HRMS-ESI calcd. for $C_{19}H_{23}O_5$ $[M+H]^+$: 331.1545. Found: 331.1552.

Dimethyl 6-(4-Methoxyphenyl)-7-methylbicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (39''k



Brown oil**,** 46 %: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 3.80 (s, 3H), 3.68 (s, 3H), 3.48-3.39 (m, 1H), 3.25 (s, 3H), 3.15-3.07 (m, 1H), 2.71 (dd, J = 13.9, 25.6 Hz, 2H), 2.00 (dd, J = 7.7, 15.5 Hz, 1H), 1.84 (dd, J = 7.4, 15.5 Hz, 1H), 1.81 (t, J = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 171.4, 158.4, 138.0, 128.5, 127.7, 126.9, 113.7, 60.6, 55.2, 52.8, 51.9, 46.2, 43.6, 34.7, 33.6, 13.7; HRMS-ESI calcd. for $C_{19}H_{22}O_5Na$ $[M+Na]^+$: 353.1365. Found: 353.1369.

Dimethyl 3-(1-(4-Nitrophenyl)prop-1-enyl)cyclopent-3-ene-1,1-dicarboxylate (39l)



Brown oil (6:1 trans/cis): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 5.82 (q, J = 7.2 Hz, 1H), 4.90 (s, 1H), 3.76 (s, 6H), 3.27 (d, J = 1.8 Hz, 2H), 3.09 (s, 2H), 1.56 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 146.8, 146.3, 141.1, 137.2, 130.5, 128.5, 125.6, 125.0, 123.4, 58.8, 53.0, 40.9, 40.7, 15.0; HRMS-ESI calcd. for $C_{18}H_{19}NO_6Na$ $[M+Na]^+$: 368.1110. Found: 368.1109.

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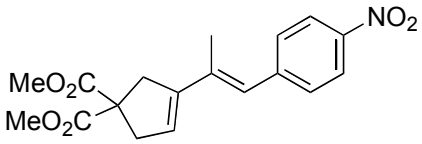
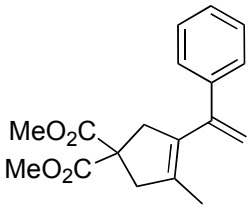
(*E*)-Dimethyl 3-(1-(4-Nitrophenyl)prop-1-en-2-yl)cyclopent-3-ene-1,1-dicarboxylate (39'l)



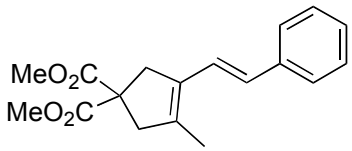
Brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 16.3 Hz, 1H), 6.47 (d, J = 16.0 Hz, 1H), 5.84 (s, 1H), 3.76 (d, J = 2.5 Hz, 6H), 3.52 (d, J = 17.0 Hz, 1H), 3.30 (dd, J = 2.2, 18.6 Hz, 1H), 3.13 (d, J = 20.0 Hz, 1H), 2.98 (d, J = 16.0 Hz, 1H), 1.03 (d, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 137.6, 133.2, 130.7, 129.0, 127.9, 126.9, 124.3, 63.2, 53.1, 52.7, 45.7, 40.9, 36.6, 15.9; HRMS-ESI calcd. for $C_{18}H_{19}NO_6Na$ $[M+Na]^+$: 368.1110. Found: 368.1120.

Dimethyl 3-Methyl-4-(1-phenylvinyl)cyclopent-3-ene-1,1-dicarboxylate (39m)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 3H), 7.14-7.09 (m, 2H), 6.12-6.00 (m, 2H), 3.74 (s, 6H), 2.74 (s, 2H), 2.68 (d, J = 5.9 Hz, 2H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 133.9, 128.9, 128.0, 68.9, 52.6, 46.5, 39.4, 33.4, 22.4. The mass could not be determined.

(*E*)-Dimethyl 3-Methyl-4-styrylcyclopent-3-ene-1,1-dicarboxylate (39'm)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.6 Hz, 2H), 7.35-7.27 (m, 3H), 6.97 (d, J = 16.5 Hz, 1H), 6.41 (d, J = 16.5 Hz, 1H), 3.76 (s, 6H), 3.28 (bs, 2H), 3.11 (bs, 2H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 147.2, 143.9, 137.7, 136.6, 131.1, 128.6, 126.6, 122.1, 61.7, 46.6, 41.1, 13.8. The mass could not be determined.

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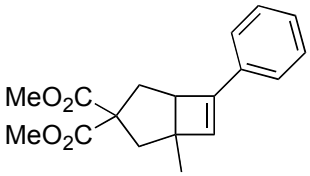
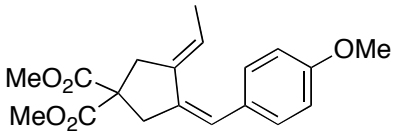
Dimethyl 1-Methyl-6-phenylbicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (39''m)



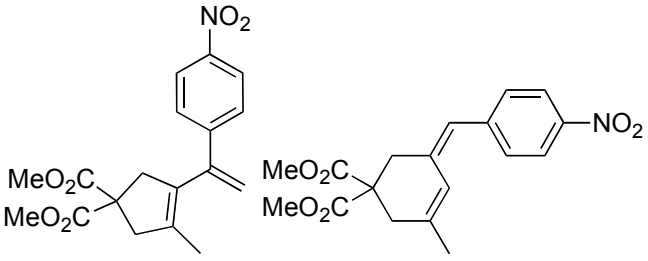
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.6 Hz, 1H), 7.34-7.21 (m, 3H), 7.11 (td, J = 7.6, 1.4 Hz, 1H), 6.50 (s, 1H), 3.76 (s, 3H), 3.64 (s, 3H), 2.80-2.74 (m, 2H), 2.43 (dt, J = 13.8, 2.8 Hz, 1H), 1.92-1.78 (m, 2H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 170.5, 147.2, 146.4, 126.7, 125.6, 124.3, 123.8, 120.7, 55.9, 52.9, 40.2, 35.6, 34.0, 21.4. The mass could not be determined.

(3*E*,4*Z*)-Dimethyl 3-Ethylidene-4-(4-methoxybenzylidene)cyclopentane-1,1-dicarboxylate (68)



Brown oil, 8 %: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 8.7, 2H), 6.82 (d, J = 8.7, 2H), 5.65 (t, J = 3.4, 1H), 5.43 (q, J = 7.1, 1H), 3.72 (s, 6H), 2.85 (s, 2H), 2.80 (d, J = 3.9, 2H), 1.11 (d, J = 7.3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 159.0, 138.5, 134.9, 128.5, 126.3, 113.7, 55.4, 53.0, 40.6, 32.7, 16.5; HRMS-ESI calcd. for $C_{19}H_{22}O_5Na$ $[M+Na]^+$: 353.1382. Found: 353.1382.

Dimethyl 3-Methyl-4-(1-(4-nitrophenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (38o and 69)



Brown oil. For **38p**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.7, 2H), 7.41 (d, J = 8.7, 2H), 6.38 (s, 1H), 6.29 (s, 1H), 3.77 (s, 6H), 3.13 (bs, 2H), 2.75 (bs, 2H), 1.92 (s, 3H); For **65**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.7, 2H), 7.48 (d, J = 8.7, 2H), 6.37 (s, 1H), 6.05 (s, 1H), 3.73 (s, 6H), 2.98 (bs, 2H), 2.75 (bs, 2H), 1.93

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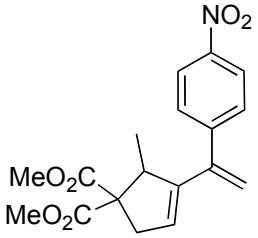
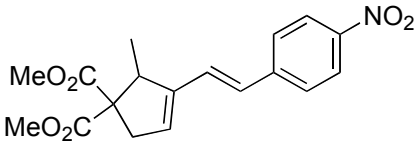
(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 145.9, 145.8, 144.33, 140.7, 138.1, 137.2, 135.9, 129.6, 129.4, 126.1, 124.5, 123.6, 123.5, 122.9, 119.9, 54.5, 52.9, 37.5, 36.5, 31.5, 24.0, 23.8; HRMS-ESI calcd. for $C_{18}H_{19}NO_6Na$ $[M+Na]^+$: 368.1110. Found: 368.1101.

Dimethyl 2-Methyl-3-(1-(4-nitrophenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (39p)



Brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 9.2 Hz, 2H), 7.47 (d, J = 9.2 Hz, 2H), 5.45 (s, 1H), 5.36 (t, J = 5.3 Hz, 1H), 5.30 (s, 3H), 3.76 (s, 3H), 3.74 (s, 3H), 3.40 (d, J = 18.2 Hz, 2H), 2.83 (dd, J = 3.6, 17.8 Hz, 2H), 1.03 (d, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 169.9, 147.6, 147.0, 146.0, 142.4, 128.8, 125.9, 123.0, 116.7, 64.1, 52.3, 52.1, 44.3, 38.2, 14.0; HRMS-ESI calcd. for $C_{18}H_{19}NO_6Na$ $[M+Na]^+$: 368.1110. Found: 368.1118.

(*E*)-Dimethyl 2-Methyl-3-(4-nitrostyryl)cyclopent-3-ene-1,1-dicarboxylate (39'p)



Brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 16.4 Hz, 1H), 6.59 (d, J = 16.4 Hz, 1H), 5.79 (t, J = 2.7 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.45 (d, J = 18.2 Hz, 2H), 2.89 (dd, J = 4.2, 18.2 Hz, 2H), 1.06 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.8, 146.4, 145.4, 143.6, 129.1, 127.7, 126.7, 126.4, 123.5, 64.5, 52.7, 52.3, 42.9, 37.9, 14.1; HRMS-ESI calcd. for $C_{18}H_{19}NO_6Na$ $[M+Na]^+$: 368.1110. Found: 368.1123.

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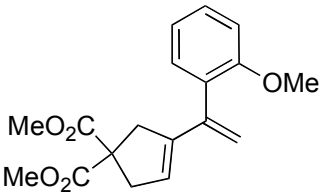
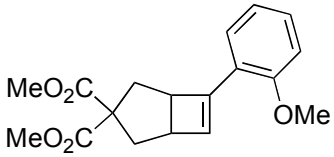
Dimethyl 3-(1-(2-Methoxyphenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (39r)



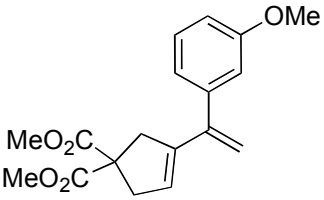
Colorless oil, 10 %: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (dd, J = 2.5, 8.0 Hz, 1H), 6.95-6.86 (m, 3H), 5.30 (s, 1H), 5.16 (t, J = 2.0 Hz, 1H), 5.08 (s, 1H), 3.76 (s, 6H), 3.75 (s, 3H), 3.31 (dd, J = 1.8, 3.5 Hz, 2H), 3.07 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 142.3, 140.7, 130.9, 128.8, 126.5, 126.0, 120.4, 115.4, 111.2, 55.9, 53.1, 41.4, 40.6; HRMS-ESI calcd. for $C_{18}H_{20}O_5Na$ $[M+Na]^+$: 339.1208. Found: 339.1214.

Dimethyl 6-(2-Methoxyphenyl)bicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (39''r)



Colorless oil, 88 %: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 7.9 Hz, 2H), 6.96 (td, J = 0.8, 7.5 Hz, 1H), 6.86 (d, J = 7.9 Hz, 1H), 6.15 (s, 1H), 3.86 (s, 3H), 3.71 (s, 3H), 3.68 (q, J = 3.7 Hz, 1H), 3.37 (q, J = 3.7 Hz, 1H), 3.28 (s, 3H), 2.83 (d, J = 13.2 Hz, 1H), 2.70 (d, J = 13.2 Hz, 1H), 2.01 (dd, J = 2.0, 13.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 172.1, 158.7, 143.6, 134.4, 128.9, 127.2, 122.3, 120.4, 110.5, 61.1, 55.2, 53.0, 51.8, 46.9, 44.6, 35.9, 34.7; HRMS-ESI calcd. for $C_{18}H_{20}O_5Na$ $[M+Na]^+$: 339.1208. Found: 339.1221.

Dimethyl 3-(1-(3-Methoxyphenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (39s)



Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.21 (m, 1H), 6.92-6.83 (m,, 3H), 5.49 (s, 1H), 5.18 (d, J = 14.6 Hz, 2H), 3.82 (s, 3H), 3.79 (s, 6H), 3.31 (s, 2H), 3.14

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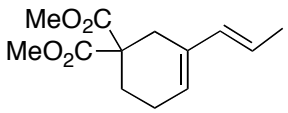
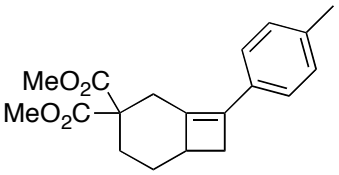
(s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 159.0, 145.2, 142.5, 140.2, 128.7, 127.3, 121.0, 114.7, 114.0, 113.0, 58.9, 55.5, 55.3, 53.0, 41.3, 41.1; HRMS-ESI calcd. for $C_{18}H_{20}O_5Na$ $[M+Na]^+$: 339.1214. Found: 339.1208.

(*E*)-Dimethyl 3-(Prop-1-enyl)cyclohex-3-ene-1,1-dicarboxylate (71a)



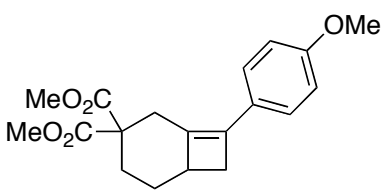
Colorless oil, 95 %: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (d, J = 16.0 Hz, 1H), 5.70-5.58 (m, 1H), 5.55 (bs, 1H), 3.72 (s, 6H), 2.67 (s, 2H), 2.18 (bs, 2H), 2.14 (d, J = 5.6 Hz, 2H), 1.76 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 133.6, 133.1, 124.7, 122.6, 53.5, 52.8, 30.4, 27.8, 22.9, 18.4; HRMS-ESI calcd. for $C_{13}H_{18}O_4Na$ $[M+Na]^+$: 261.1103. Found: 261.1113.

Dimethyl 8-*p*-Tolylbicyclo[4.2.0]oct-1(8)-ene-3,3-dicarboxylate (71b)



Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 3.74 (s, 3H), 3.57 (s, 3H), 2.82 (dt, J = 12.5, 3.8 Hz, 1H), 2.54-2.39 (m, 2H), 2.33 (s, 3H), 2.22 (ddd, J = 12.8, 2.7, 1.4 Hz, 1H), 2.13-2.03 (m, 2H), 1.85 (td, J = 14.0, 3.3 Hz, 1H), 1.25-1.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 170.9, 138.9, 136.6, 135.4, 133.0, 125.6, 56.6, 52.8, 52.4, 36.0, 34.3, 32.7, 29.7, 29.2, 21.3; HRMS-ESI calcd. for $C_{17}H_{170}O_4NaCl$ $[M+Na]^+$: 343.0713. Found: 343.0712.

Dimethyl 8-(4-Methoxyphenyl)bicyclo[4.2.0]oct-1(8)-ene-3,3-dicarboxylate(67c)



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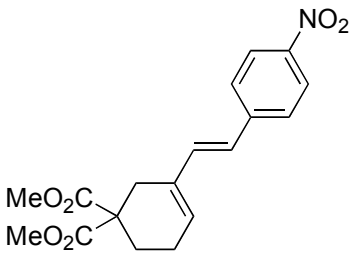
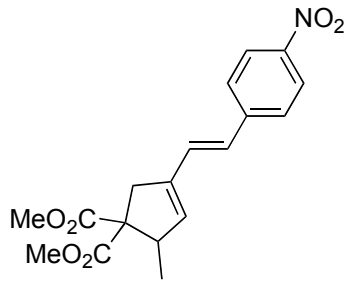
White sticky solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H), 3.74 (s, 3H), 3.57 (s, 3H), 2.81 (dt, J = 12.7, 3.8 Hz, 1H), 2.48-2.38 (m, 2H), 2.20 (d, J = 12.7 Hz, 1H), 2.12-2.04 (m, 2H), 1.85 (td, J = 13.8, 3.8 Hz, 1H), 1.29-1.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 170.9, 158.6, 137.4, 134.9, 134.8, 128.8, 127.0, 113.7, 56.5, 52.8, 52.4, 35.9, 34.4, 32.6, 31.6, 29.2, 22.7, 14.2; HRMS-ESI calcd. for $C_{17}H_{170}O_4NaCl$ $[M+Na]^+$: 343.0713. Found: 343.0712.

(*E*)-Dimethyl 3-(4-Nitrostyryl)cyclohex-3-ene-1,1-dicarboxylate (71d)



Orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 9.1 Hz, 2H), 7.51 (d, J = 9.1 Hz, 2H), 6.92 (d, J = 16.0 Hz, 1H), 6.55 (d, J = 16.0 Hz, 1H), 5.99 (t, J = 3.8 Hz, 1H), 3.76 (s, 6H), 2.84 (s, 2H), 2.33 (bs, 2H), 2.2 (t, J = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 146.5, 144.3, 135.6, 132.9, 132.0, 129.6, 126.6, 124.0, 123.6, 53.2, 52.9, 30.0, 27.3, 23.4.

(*R*,*E*)-Dimethyl 2-Methyl-4-(4-nitrostyryl)cyclopent-3-ene-1,1-dicarboxylate (72)



Orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.8 Hz, 2H), 7.55 (d, J = 8.8 Hz, 2H), 7.07 (d, J = 16.0 Hz, 1H), 6.51 (d, J = 16.0 Hz, 1H), 5.88 (s, 1H), 3.81 (d, J = 2.4 Hz, 6H), 3.74 (d, J = 3.9 Hz, 1H), 3.57 (d, J = 16.4 Hz, 1H), 3.03 (d, J = 16.4 Hz, 1H), 1.08 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 170.6,

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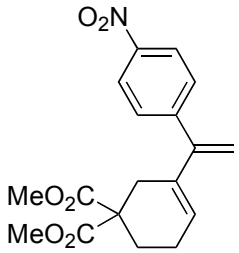
146.7, 143.8, 137.8, 137.5, 128.8, 127.7, 126.6, 124.1, 91.5, 63.2, 52.8, 45.5, 38.4, 29.7, 15.7.

Dimethyl 3-(1-(4-Nitrophenyl)vinyl)cyclohex-3-ene-1,1-dicarboxylate (71'd)



Orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.4 Hz, 2H), 7.3 (d, J = 8.4 Hz, 2H), 5.83 (q, J = 7.1 Hz, 2H), 4.91 (s, 1H), 3.77 (s, 6H), 3.28 (d, J = 1.7 Hz, 2H), 3.05 (bs, 2H), 2.24-2.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 146.9, 141.3, 137.2, 132.4, 130.5, 125.6, 123.6, 58.6, 53.0, 41.0, 31.6, 27.0, 24.0, 15.0.

5. New Silver(I) and Copper(I)-Complexes

General method for the synthesis of [LAgNCMe]SbF_6:

To a suspension of $AgSbF_6$ (300 mmol) in acetonitrile (5 mL) was added the phosphine ligand (300 mmol) dissolved in acetonitrile (5 mL). The reaction mixture was stirred for 2 h in the dark, then the solvent was reduced to 3 mL and the solution was filtered through a pad of Celite. Addition of Et_2O (2 mL) afforded the product as a white crystalline solid, which was filtered off and washed with pentane. Crystals were obtained by slow evaporation of CH_2Cl_2 at room temperature.

General method for the synthesis of [LCu(NCMe)$_n$]BF_4:

In a typical reaction, a flame dried 50 ml schlenck was charged with $[Cu(CH_3CN)_4]BF_4$ (100 mg, 0.318 mmol, 1 equiv) in 2 ml of dry CH_2Cl_2 and the whole was stirred under argon at room temperature. The desired phosphine ligand (0.318 mmol, 1 equiv.) was added and after stirring the mixture for 30 min, the solvent was removed to yield the corresponding copper(I) tetrafluoroborate complex as a white solid. Crystals were obtained by slow evaporation of a mixture of non-dried solvents at -4 ºC (Hexane/CH_2Cl_2, 10:1).

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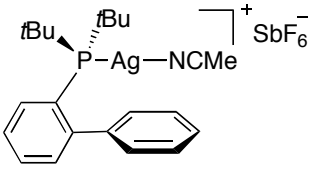
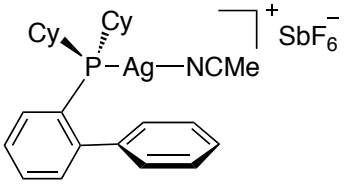
Complex 75a



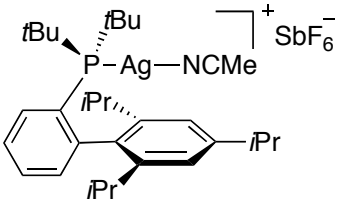
Yield = 80 %: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (t, J = 6.9 Hz, 1H), 7.69-7.50 (m, 5H), 7.34-7.29 (m, 1H), 7.25 (d, J = 6.9 Hz, 2H), 2.30 (s, 3H), 1.35 (s, 9H), 1.31 (s, 9H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 49.8 (d, J = 55.4 Hz), 45.34 (d, J = 55.4 Hz); HRMS- ESI calcd. for $C_{22}H_{30}AgNP$ $[M\text{-}SbF_6]^+$: 446.1167. Found: 446.1152; Elemental analysis (%) calcd. $C_{22}H_{30}AgF_6NPSb$: C, 38.68; H, 4.43; N, 2.05; found: C, 38.23; H, 4.31; N, 2.03.

Complex 75b



^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.65-7.49 (m, 6H), 7.32 (q, J = 4.3 Hz, 1H), 7.22 (d, J = 7.4 Hz, 2H), 2.25 (s, 3H), 2.21-2.05 (m, 2H), 1.93-1.54 (m, 13H), 1.41-1.05 (m, 9H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.61 (d, J = 56.3 Hz), 19.80 (d, J = 56.3 Hz); HRMS- ESI calcd. for $C_{26}H_{34}AgPN$ $[M\text{-}SbF_6]^+$: 498.1480. Found: 498.1483.

Complex 75c



Yield = 70%: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (td, J = 6.1, 2.4 Hz, 1H), 7.58-7.54 (m, 2H), 7.34-7.29 (m, 1H), 7.24 (s, 2H), 3.00 (dt, J = 13.8, 6.9 Hz, 1H), 2.38 (dt, J = 13.8, 6.9 Hz, 2H), 2.27 (s, 3H), 1.41-1.25 (m, 12H + 18H), 0.96 (d, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.2, 134.7, 134.2, 133.6, 132.5, 130.7, 127.5, 122.6, 119.2, 35.8, 34.0, 31.1, 26.3, 23.8, 23.1, 2.2; ^{31}P NMR (162 MHz,

$CDCl_3$) δ 48.1 (d, J = 52.5 Hz, 1H), 43.7 (d, J = 50.4 Hz, 1H); HRMS- ESI calcd. for $C_{31}H_{48}AgNP$ $[M\text{-}SbF_6]^+$: 572.2575. Found: 572.2569; Elemental analysis (%) calcd. $C_{31}H_{48}AgF_6NPSb$: C, 46.01; H, 5.98; N, 1.73; found: C, 46.31; H, 5.86; N, 1.76.

Table 1. Crystal data and structure refinement for **75c**.

Identification code	**75c**	
Empirical formula	C_{31} H_{48} Ag F_6 N P Sb	
Formula weight	809.29	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.6724(13) Å	a= 90°.
	b = 13.9088(13) Å	b= 97.995(4)°.
	c = 17.0756(15) Å	g = 90°.
Volume	3450.8(5) $Å^3$	
Z	4	
Density (calculated)	1.558 Mg/m^3	
Absorption coefficient	1.450 mm^{-1}	
F(000)	1632	
Crystal size	0.10 x 0.10 x 0.05 mm^3	
Theta range for data collection	2.82 to 39.41°.	
Index ranges	-24<=h<=24, -24<=k<=23, -30<=l<=29	
Reflections collected	84833	
Independent reflections	19438 [R(int) = 0.0518]	
Completeness to theta = 39.41°	94.3 %	
Absorption correction	SADABS (Bruker-Nonius)	
Max. and min. transmission	0.9311 and 0.8686	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19438 / 0 / 449	

Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0479, wR2 = 0.1059
R indices (all data)	R1 = 0.0645, wR2 = 0.1156
Largest diff. peak and hole	5.795 and -4.083 e.$Å^{-3}$

Table 2. Bond lengths [Å] and angles [°] for **75c**.

Ag(1)-N(1)	2.1100(18)
Ag(1)-P(1)	2.3583(5)
P(1)-C(1)	1.8296(16)
P(1)-C(22)	1.8842(19)
P(1)-C(26)	1.885(2)
C(1)-C(2)	1.405(2)
C(1)-C(6)	1.417(2)
N(1)-C(30)	1.138(3)
C(2)-C(3)	1.390(3)
C(3)-C(4)	1.385(3)
C(4)-C(5)	1.388(3)
C(5)-C(6)	1.401(2)
C(6)-C(7)	1.508(2)
C(7)-C(8)	1.412(2)
C(7)-C(12)	1.416(2)
C(8)-C(9)	1.397(3)
C(8)-C(13)	1.517(2)
C(9)-C(10)	1.394(3)
C(10)-C(11)	1.385(3)
C(10)-C(16)	1.535(3)
C(10)-C(16')	1.614(5)
C(11)-C(12)	1.396(2)
C(12)-C(19)	1.518(3)
C(13)-C(14)	1.536(3)
C(13)-C(15)	1.536(3)

C(16)-C(17)	1.418(10)
C(16)-C(18)	1.490(9)
C(16')-C(18')	1.33(2)
C(16')-C(17')	1.704(15)
C(19)-C(20)	1.530(3)
C(19)-C(21)	1.532(3)
C(22)-C(25)	1.535(3)
C(22)-C(23)	1.538(3)
C(22)-C(24)	1.539(3)
C(26)-C(28)	1.531(3)
C(26)-C(29)	1.533(3)
C(26)-C(27)	1.538(3)
C(30)-C(31)	1.446(3)
Sb(1)-F(4')	1.669(10)
Sb(1)-F(3')	1.695(9)
Sb(1)-F(5A)	1.728(6)
Sb(1)-F(6A)	1.831(4)
Sb(1)-F(1A)	1.8440(18)
Sb(1)-F(2A)	1.855(2)
Sb(1)-F(4A)	1.897(3)
Sb(1)-F(3A)	1.941(5)
Sb(1)-F(5')	1.993(8)
Sb(1)-F(6')	2.004(12)
N(1)-Ag(1)-P(1)	168.01(5)
C(1)-P(1)-C(22)	107.66(8)
C(1)-P(1)-C(26)	107.36(8)
C(22)-P(1)-C(26)	112.27(9)
C(1)-P(1)-Ag(1)	110.57(5)
C(22)-P(1)-Ag(1)	108.55(6)
C(26)-P(1)-Ag(1)	110.41(6)
C(2)-C(1)-C(6)	118.56(15)
C(2)-C(1)-P(1)	118.62(13)

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C(6)-C(1)-P(1)	122.77(12)
C(30)-N(1)-Ag(1)	171.70(18)
C(3)-C(2)-C(1)	122.03(17)
C(4)-C(3)-C(2)	119.21(16)
C(3)-C(4)-C(5)	119.82(16)
C(4)-C(5)-C(6)	122.07(17)
C(5)-C(6)-C(1)	118.30(15)
C(5)-C(6)-C(7)	115.58(14)
C(1)-C(6)-C(7)	126.12(14)
C(8)-C(7)-C(12)	118.92(15)
C(8)-C(7)-C(6)	119.92(14)
C(12)-C(7)-C(6)	120.74(14)
C(9)-C(8)-C(7)	119.35(16)
C(9)-C(8)-C(13)	118.94(17)
C(7)-C(8)-C(13)	121.56(15)
C(10)-C(9)-C(8)	122.19(19)
C(11)-C(10)-C(9)	117.48(18)
C(11)-C(10)-C(16)	117.7(2)
C(9)-C(10)-C(16)	124.2(2)
C(11)-C(10)-C(16')	123.7(3)
C(9)-C(10)-C(16')	113.7(3)
C(16)-C(10)-C(16')	31.3(2)
C(10)-C(11)-C(12)	122.68(17)
C(11)-C(12)-C(7)	119.07(16)
C(11)-C(12)-C(19)	118.36(15)
C(7)-C(12)-C(19)	122.47(14)
C(8)-C(13)-C(14)	113.65(16)
C(8)-C(13)-C(15)	109.49(14)
C(14)-C(13)-C(15)	109.67(16)
C(17)-C(16)-C(18)	111.6(6)
C(17)-C(16)-C(10)	116.4(4)
C(18)-C(16)-C(10)	110.0(4)

C(18')-C(16')-C(10)	119.9(9)
C(18')-C(16')-C(17')	122.9(9)
C(10)-C(16')-C(17')	101.0(6)
C(12)-C(19)-C(20)	109.67(17)
C(12)-C(19)-C(21)	112.80(16)
C(20)-C(19)-C(21)	109.53(18)
C(25)-C(22)-C(23)	107.50(18)
C(25)-C(22)-C(24)	108.75(17)
C(23)-C(22)-C(24)	109.57(16)
C(25)-C(22)-P(1)	105.49(13)
C(23)-C(22)-P(1)	117.51(14)
C(24)-C(22)-P(1)	107.69(14)
C(28)-C(26)-C(29)	108.36(18)
C(28)-C(26)-C(27)	109.15(16)
C(29)-C(26)-C(27)	107.89(17)
C(28)-C(26)-P(1)	115.95(14)
C(29)-C(26)-P(1)	107.99(13)
C(27)-C(26)-P(1)	107.24(14)
N(1)-C(30)-C(31)	179.6(3)
F(4')-Sb(1)-F(3')	106.6(12)
F(4')-Sb(1)-F(5A)	110.7(7)
F(3')-Sb(1)-F(5A)	142.6(10)
F(4')-Sb(1)-F(6A)	153.8(7)
F(3')-Sb(1)-F(6A)	47.3(9)
F(5A)-Sb(1)-F(6A)	95.4(5)
F(4')-Sb(1)-F(1A)	93.2(4)
F(3')-Sb(1)-F(1A)	90.9(4)
F(5A)-Sb(1)-F(1A)	90.3(4)
F(6A)-Sb(1)-F(1A)	89.53(19)
F(4')-Sb(1)-F(2A)	86.3(4)
F(3')-Sb(1)-F(2A)	89.2(4)
F(5A)-Sb(1)-F(2A)	89.9(4)

F(6A)-Sb(1)-F(2A)	90.9(2)
F(1A)-Sb(1)-F(2A)	179.52(17)
F(4')-Sb(1)-F(4A)	19.5(7)
F(3')-Sb(1)-F(4A)	125.7(10)
F(5A)-Sb(1)-F(4A)	91.7(3)
F(6A)-Sb(1)-F(4A)	172.8(4)
F(1A)-Sb(1)-F(4A)	89.12(14)
F(2A)-Sb(1)-F(4A)	90.47(17)
F(4')-Sb(1)-F(3A)	66.6(7)
F(3')-Sb(1)-F(3A)	40.3(10)
F(5A)-Sb(1)-F(3A)	176.9(4)
F(6A)-Sb(1)-F(3A)	87.4(4)
F(1A)-Sb(1)-F(3A)	88.4(3)
F(2A)-Sb(1)-F(3A)	91.3(3)
F(4A)-Sb(1)-F(3A)	85.5(2)
F(4')-Sb(1)-F(5')	88.0(7)
F(3')-Sb(1)-F(5')	164.8(10)
F(5A)-Sb(1)-F(5')	22.8(4)
F(6A)-Sb(1)-F(5')	118.0(5)
F(1A)-Sb(1)-F(5')	92.7(4)
F(2A)-Sb(1)-F(5')	87.4(4)
F(4A)-Sb(1)-F(5')	69.1(4)
F(3A)-Sb(1)-F(5')	154.5(4)
F(4')-Sb(1)-F(6')	166.9(7)
F(3')-Sb(1)-F(6')	86.2(10)
F(5A)-Sb(1)-F(6')	56.4(6)
F(6A)-Sb(1)-F(6')	39.0(5)
F(1A)-Sb(1)-F(6')	89.5(4)
F(2A)-Sb(1)-F(6')	91.0(4)
F(4A)-Sb(1)-F(6')	148.1(6)
F(3A)-Sb(1)-F(6')	126.4(6)
F(5')-Sb(1)-F(6')	79.1(6)

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Symmetry transformations used to generate equivalent atoms:

Table 3. Torsion angles [°] for **75c**.

N(1)-Ag(1)-P(1)-C(1)	159.9(3)
N(1)-Ag(1)-P(1)-C(22)	42.1(3)
N(1)-Ag(1)-P(1)-C(26)	-81.4(3)
C(22)-P(1)-C(1)-C(2)	-62.56(17)
C(26)-P(1)-C(1)-C(2)	58.52(16)
Ag(1)-P(1)-C(1)-C(2)	179.02(13)
C(22)-P(1)-C(1)-C(6)	120.00(15)
C(26)-P(1)-C(1)-C(6)	-118.93(15)
Ag(1)-P(1)-C(1)-C(6)	1.57(16)
P(1)-Ag(1)-N(1)-C(30)	-6.0(16)
C(6)-C(1)-C(2)-C(3)	-0.9(3)
P(1)-C(1)-C(2)-C(3)	-178.45(15)
C(1)-C(2)-C(3)-C(4)	0.8(3)
C(2)-C(3)-C(4)-C(5)	0.2(3)
C(3)-C(4)-C(5)-C(6)	-1.2(3)
C(4)-C(5)-C(6)-C(1)	1.2(3)
C(4)-C(5)-C(6)-C(7)	-178.18(16)
C(2)-C(1)-C(6)-C(5)	-0.1(2)
P(1)-C(1)-C(6)-C(5)	177.35(13)
C(2)-C(1)-C(6)-C(7)	179.17(16)
P(1)-C(1)-C(6)-C(7)	-3.4(2)
C(5)-C(6)-C(7)-C(8)	85.53(19)
C(1)-C(6)-C(7)-C(8)	-93.8(2)
C(5)-C(6)-C(7)-C(12)	-86.9(2)
C(1)-C(6)-C(7)-C(12)	93.8(2)
C(12)-C(7)-C(8)-C(9)	-5.5(3)
C(6)-C(7)-C(8)-C(9)	-178.08(18)

C(12)-C(7)-C(8)-C(13)	169.88(15)
C(6)-C(7)-C(8)-C(13)	-2.7(2)
C(7)-C(8)-C(9)-C(10)	1.7(4)
C(13)-C(8)-C(9)-C(10)	-173.8(2)
C(8)-C(9)-C(10)-C(11)	3.2(4)
C(8)-C(9)-C(10)-C(16)	-167.2(3)
C(8)-C(9)-C(10)-C(16')	158.8(3)
C(9)-C(10)-C(11)-C(12)	-4.4(4)
C(16)-C(10)-C(11)-C(12)	166.7(2)
C(16')-C(10)-C(11)-C(12)	-157.4(3)
C(10)-C(11)-C(12)-C(7)	0.6(3)
C(10)-C(11)-C(12)-C(19)	177.1(2)
C(8)-C(7)-C(12)-C(11)	4.4(2)
C(6)-C(7)-C(12)-C(11)	176.90(16)
C(8)-C(7)-C(12)-C(19)	-171.94(16)
C(6)-C(7)-C(12)-C(19)	0.6(2)
C(9)-C(8)-C(13)-C(14)	-40.4(3)
C(7)-C(8)-C(13)-C(14)	144.15(17)
C(9)-C(8)-C(13)-C(15)	82.6(2)
C(7)-C(8)-C(13)-C(15)	-92.8(2)
C(11)-C(10)-C(16)-C(17)	-168.3(5)
C(9)-C(10)-C(16)-C(17)	2.1(6)
C(16')-C(10)-C(16)-C(17)	81.6(7)
C(11)-C(10)-C(16)-C(18)	63.5(6)
C(9)-C(10)-C(16)-C(18)	-126.1(6)
C(16')-C(10)-C(16)-C(18)	-46.6(6)
C(11)-C(10)-C(16')-C(18')	-5.3(8)
C(9)-C(10)-C(16')-C(18')	-159.1(7)
C(16)-C(10)-C(16')-C(18')	83.5(8)
C(11)-C(10)-C(16')-C(17')	-143.9(4)
C(9)-C(10)-C(16')-C(17')	62.2(5)
C(16)-C(10)-C(16')-C(17')	-55.1(5)

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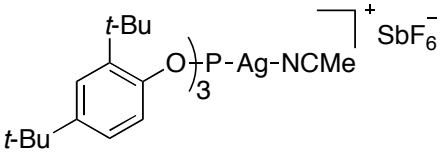
C(11)-C(12)-C(19)-C(20)	-73.0(2)
C(7)-C(12)-C(19)-C(20)	103.34(19)
C(11)-C(12)-C(19)-C(21)	49.4(2)
C(7)-C(12)-C(19)-C(21)	-134.29(18)
C(1)-P(1)-C(22)-C(25)	-66.54(14)
C(26)-P(1)-C(22)-C(25)	175.51(13)
Ag(1)-P(1)-C(22)-C(25)	53.18(14)
C(1)-P(1)-C(22)-C(23)	53.21(18)
C(26)-P(1)-C(22)-C(23)	-64.74(18)
Ag(1)-P(1)-C(22)-C(23)	172.92(15)
C(1)-P(1)-C(22)-C(24)	177.45(13)
C(26)-P(1)-C(22)-C(24)	59.50(16)
Ag(1)-P(1)-C(22)-C(24)	-62.84(14)
C(1)-P(1)-C(26)-C(28)	-83.19(16)
C(22)-P(1)-C(26)-C(28)	34.94(17)
Ag(1)-P(1)-C(26)-C(28)	156.21(13)
C(1)-P(1)-C(26)-C(29)	38.56(15)
C(22)-P(1)-C(26)-C(29)	156.69(14)
Ag(1)-P(1)-C(26)-C(29)	-82.04(14)
C(1)-P(1)-C(26)-C(27)	154.60(12)
C(22)-P(1)-C(26)-C(27)	-87.28(14)
Ag(1)-P(1)-C(26)-C(27)	34.00(14)
Ag(1)-N(1)-C(30)-C(31)	-113(41)

Complex 75d



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J1/42.1 Hz, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.22 (dd, J = 8.4, 2.1 Hz, 1H), 2.13 (s, 3H), 1.44 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 146.5, 139.1, 125.2, 124.3, 118.8, 68.1, 35.0, 34.0, 30.0, 25.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 112 (br d, J (^{31}P-Ag) = 110 Hz).

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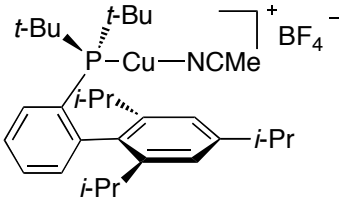
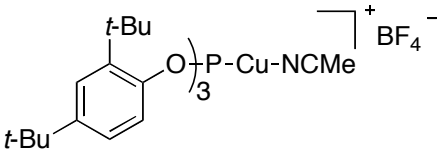
Complex 76c



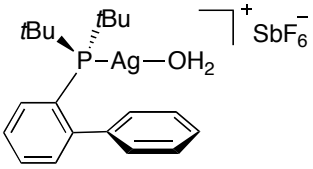
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, 1H), 7.51 (m, 2H), 7.31 (m, 1H), 7.29 (s, 2H), 3.01 (m, J= 6.7 Hz, 1H), 2.37 (m, J = 6.7 Hz, 2H), 2.28 (s, 3H, CH_3CN), 1.34-1.28 (d, 18H, *t*Bu, 12H, *i*Pr), 0.95 (d, J = 6.7 Hz, 6H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.5.

Complex 76d



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J1/42.3 Hz, 1H), 7.29 (d, J = 6.5 Hz, 1H), 7.20 (dd, J = 6.5, 2.3 Hz, 1H), 2.1 (s, 3H), 1.40 (s, 9H), 1.32 (s, 9H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 116.2.

Complex 77a



To a suspension of **81a** in non-dried dichloromethane was added benzene and the mixture was stirred for 1h. After this time the solvent was removed under reduced pressure. Crystals were obtained by slow evaporation of dichloromethane and benzene: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (t, J = 6.9 Hz, 1H), 7.67-7.40 (m, 5H), 7.33-7.28 (m, 1H), 7.25 (d, J = 6.9 Hz, 2H), 2.22 (s, 2H), 1.36 (s, 9H), 1.32 (s, 9H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 50.09 (d, J = 53.0 Hz), 45.53 (d, J = 53.0 Hz).

Table 1. Crystal data and structure refinement for **77a**.

Identification code	**77a**
Empirical formula	C_{40} H_{58} Ag_2 B_2 F_8 O_2 P_2

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Formula weight	1022.16	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.8891(6) Å	a= 90°.
	b = 11.0560(4) Å	b= 102.002(2)°.
	c = 26.9396(10) Å	g = 90°.
Volume	4337.7(3) $Å^3$	
Z	4	
Density (calculated)	1.565 Mg/m^3	
Absorption coefficient	1.044 mm^{-1}	
F(000)	2080	
Crystal size	0.20 x 0.10 x 0.10 mm^3	
Theta range for data collection	2.53 to 40.00°.	
Index ranges	-7<=h<=26, -19<=k<=19, -48<=l<=41	
Reflections collected	81170	
Independent reflections	24754 [R(int) = 0.0233]	
Completeness to theta = 40.00°	92.0 %	
Absorption correction	SADABS (Bruker-Nonius)	
Max. and min. transmission	0.9028 and 0.8183	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	24754 / 6 / 545	
Goodness-of-fit on F^2	1.079	
Final R indices [I>2sigma(I)]	R1 = 0.0296, wR2 = 0.0759	
R indices (all data)	R1 = 0.0373, wR2 = 0.0800	
Largest diff. peak and hole	2.276 and -1.198 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **77a**.

Ag(1B)-O(1B)	2.1664(9)

Ag(1B)-P(1B)	2.3615(3)
P(1B)-C(1B)	1.8265(10)
P(1B)-C(17B)	1.8725(10)
P(1B)-C(13B)	1.8805(10)
C(1B)-C(2B)	1.4038(14)
C(1B)-C(6B)	1.4097(13)
C(2B)-C(3B)	1.3832(16)
C(3B)-C(4B)	1.3876(17)
C(4B)-C(5B)	1.3849(18)
C(5B)-C(6B)	1.4017(15)
C(6B)-C(7B)	1.4900(15)
C(7B)-C(12B)	1.3984(15)
C(7B)-C(8B)	1.3999(15)
C(8B)-C(9B)	1.3920(18)
C(9B)-C(10B)	1.393(2)
C(10B)-C(11B)	1.392(2)
C(11B)-C(12B)	1.3905(18)
C(13B)-C(15B)	1.5304(15)
C(13B)-C(16B)	1.5334(16)
C(13B)-C(14B)	1.5441(16)
C(17B)-C(20B)	1.5305(15)
C(17B)-C(18B)	1.5347(15)
C(17B)-C(19B)	1.5351(16)
Ag(1A)-O(1A)	2.1553(9)
Ag(1A)-P(1A)	2.3532(3)
P(1A)-C(1A)	1.8284(10)
P(1A)-C(13A)	1.8718(10)
P(1A)-C(17A)	1.8800(10)
C(1A)-C(2A)	1.4035(14)
C(1A)-C(6A)	1.4108(13)
C(2A)-C(3A)	1.3854(15)
C(3A)-C(4A)	1.3905(16)

C(4A)-C(5A)	1.3850(17)
C(5A)-C(6A)	1.4037(14)
C(6A)-C(7A)	1.4901(14)
C(7A)-C(12A)	1.3981(16)
C(7A)-C(8A)	1.4007(15)
C(8A)-C(9A)	1.3922(17)
C(9A)-C(10A)	1.394(2)
C(10A)-C(11A)	1.390(2)
C(11A)-C(12A)	1.3899(18)
C(13A)-C(15A)	1.5283(15)
C(13A)-C(14A)	1.5322(14)
C(13A)-C(16A)	1.5328(16)
C(17A)-C(18A)	1.5312(15)
C(17A)-C(19A)	1.5331(15)
C(17A)-C(20A)	1.5438(17)
B(1B)-F(2B)	1.317(3)
B(1B)-F(4B)	1.387(3)
B(1B)-F(1B)	1.418(3)
B(1B)-F(3B)	1.439(3)
F(1B)-B(1B')	1.371(9)
F(2B)-B(1B')	1.342(8)
B(1B')-F(4B')	1.356(9)
B(1B')-F(3B')	1.423(9)
B(1A)-F(1A)	1.3413(18)
B(1A)-F(3A)	1.3915(16)
B(1A)-F(4A)	1.3921(18)
B(1A)-F(2A)	1.4284(15)
O(1B)-Ag(1B)-P(1B)	162.47(3)
C(1B)-P(1B)-C(17B)	103.65(5)
C(1B)-P(1B)-C(13B)	108.06(5)
C(17B)-P(1B)-C(13B)	113.90(5)
C(1B)-P(1B)-Ag(1B)	114.55(3)

C(17B)-P(1B)-Ag(1B)111.81(3)
C(13B)-P(1B)-Ag(1B)105.09(3)
C(2B)-C(1B)-C(6B) 118.34(9)
C(2B)-C(1B)-P(1B) 119.30(7)
C(6B)-C(1B)-P(1B) 122.24(8)
C(3B)-C(2B)-C(1B) 121.96(10)
C(2B)-C(3B)-C(4B) 119.63(11)
C(5B)-C(4B)-C(3B) 119.37(10)
C(4B)-C(5B)-C(6B) 121.88(10)
C(5B)-C(6B)-C(1B) 118.76(10)
C(5B)-C(6B)-C(7B) 117.76(9)
C(1B)-C(6B)-C(7B) 123.47(9)
C(12B)-C(7B)-C(8B) 118.80(11)
C(12B)-C(7B)-C(6B) 120.80(10)
C(8B)-C(7B)-C(6B) 120.36(9)
C(9B)-C(8B)-C(7B) 120.47(11)
C(8B)-C(9B)-C(10B) 120.23(12)
C(11B)-C(10B)-C(9B)119.62(12)
C(12B)-C(11B)-C(10B)120.19(13)
C(11B)-C(12B)-C(7B)120.65(12)
C(15B)-C(13B)-C(16B)109.94(10)
C(15B)-C(13B)-C(14B)107.93(9)
C(16B)-C(13B)-C(14B)107.96(9)
C(15B)-C(13B)-P(1B)117.14(7)
C(16B)-C(13B)-P(1B)107.17(7)
C(14B)-C(13B)-P(1B)106.33(7)
C(20B)-C(17B)-C(18B)108.08(9)
C(20B)-C(17B)-C(19B)109.86(9)
C(18B)-C(17B)-C(19B)109.08(10)
C(20B)-C(17B)-P(1B)115.88(8)
C(18B)-C(17B)-P(1B)105.59(7)
C(19B)-C(17B)-P(1B)108.12(7)

O(1A)-Ag(1A)-P(1A)165.80(3)

C(1A)-P(1A)-C(13A)103.94(4)

C(1A)-P(1A)-C(17A)108.22(5)

C(13A)-P(1A)-C(17A)113.34(4)

C(1A)-P(1A)-Ag(1A)113.57(3)

C(13A)-P(1A)-Ag(1A)111.62(3)

C(17A)-P(1A)-Ag(1A)106.27(4)

C(2A)-C(1A)-C(6A) 118.16(9)

C(2A)-C(1A)-P(1A) 119.67(7)

C(6A)-C(1A)-P(1A) 122.06(7)

C(3A)-C(2A)-C(1A) 121.98(10)

C(2A)-C(3A)-C(4A) 119.77(10)

C(5A)-C(4A)-C(3A) 119.16(10)

C(4A)-C(5A)-C(6A) 121.88(10)

C(5A)-C(6A)-C(1A) 118.97(9)

C(5A)-C(6A)-C(7A) 117.27(9)

C(1A)-C(6A)-C(7A) 123.76(9)

C(12A)-C(7A)-C(8A)119.00(10)

C(12A)-C(7A)-C(6A)120.78(10)

C(8A)-C(7A)-C(6A) 120.18(10)

C(9A)-C(8A)-C(7A) 120.38(12)

C(8A)-C(9A)-C(10A)120.17(13)

C(11A)-C(10A)-C(9A)119.62(12)

C(12A)-C(11A)-C(10A)120.41(14)

C(11A)-C(12A)-C(7A)120.39(13)

C(15A)-C(13A)-C(14A)107.97(9)

C(15A)-C(13A)-C(16A)110.08(9)

C(14A)-C(13A)-C(16A)109.01(9)

C(15A)-C(13A)-P(1A)115.20(8)

C(14A)-C(13A)-P(1A)105.85(7)

C(16A)-C(13A)-P(1A)108.52(7)

C(18A)-C(17A)-C(19A)110.09(10)

C(18A)-C(17A)-C(20A)	107.63(9)
C(19A)-C(17A)-C(20A)	107.94(9)
C(18A)-C(17A)-P(1A)	106.84(7)
C(19A)-C(17A)-P(1A)	117.32(7)
C(20A)-C(17A)-P(1A)	106.60(8)
F(2B)-B(1B)-F(4B)	111.5(2)
F(2B)-B(1B)-F(1B)	111.71(17)
F(4B)-B(1B)-F(1B)	110.1(2)
F(2B)-B(1B)-F(3B)	112.0(2)
F(4B)-B(1B)-F(3B)	107.18(18)
F(1B)-B(1B)-F(3B)	104.09(19)
B(1B')-F(1B)-B(1B)	14.9(3)
B(1B)-F(2B)-B(1B')	15.7(3)
F(2B)-B(1B')-F(4B')	117.6(6)
F(2B)-B(1B')-F(1B)	113.1(6)
F(4B')-B(1B')-F(1B)	106.6(6)
F(2B)-B(1B')-F(3B')	91.1(6)
F(4B')-B(1B')-F(3B')	111.6(7)
F(1B)-B(1B')-F(3B')	116.8(5)
F(1A)-B(1A)-F(3A)	111.59(12)
F(1A)-B(1A)-F(4A)	110.83(11)
F(3A)-B(1A)-F(4A)	109.69(12)
F(1A)-B(1A)-F(2A)	110.25(12)
F(3A)-B(1A)-F(2A)	106.18(10)
F(4A)-B(1A)-F(2A)	108.14(11)

Table 3. Torsion angles [°] for **77a**.

O(1B)-Ag(1B)-P(1B)-C(1B)	-149.03(9)
O(1B)-Ag(1B)-P(1B)-C(17B)	93.45(10)
O(1B)-Ag(1B)-P(1B)-C(13B)	-30.60(10)

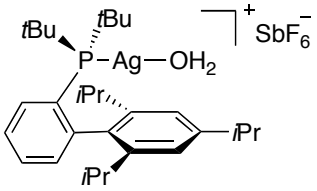
C(17B)-P(1B)-C(1B)-C(2B)	-72.06(9)
C(13B)-P(1B)-C(1B)-C(2B)	49.12(9)
Ag(1B)-P(1B)-C(1B)-C(2B)	165.85(7)
C(17B)-P(1B)-C(1B)-C(6B)	103.94(9)
C(13B)-P(1B)-C(1B)-C(6B)	-134.88(8)
Ag(1B)-P(1B)-C(1B)-C(6B)	-18.15(9)
C(6B)-C(1B)-C(2B)-C(3B)	-0.42(16)
P(1B)-C(1B)-C(2B)-C(3B)	175.74(9)
C(1B)-C(2B)-C(3B)-C(4B)	-1.54(17)
C(2B)-C(3B)-C(4B)-C(5B)	1.72(17)
C(3B)-C(4B)-C(5B)-C(6B)	0.04(17)
C(4B)-C(5B)-C(6B)-C(1B)	-1.99(15)
C(4B)-C(5B)-C(6B)-C(7B)	177.53(10)
C(2B)-C(1B)-C(6B)-C(5B)	2.13(14)
P(1B)-C(1B)-C(6B)-C(5B)	-173.91(8)
C(2B)-C(1B)-C(6B)-C(7B)	-177.36(9)
P(1B)-C(1B)-C(6B)-C(7B)	6.60(14)
C(5B)-C(6B)-C(7B)-C(12B)	73.06(13)
C(1B)-C(6B)-C(7B)-C(12B)	-107.44(12)
C(5B)-C(6B)-C(7B)-C(8B)	-104.92(12)
C(1B)-C(6B)-C(7B)-C(8B)	74.57(13)
C(12B)-C(7B)-C(8B)-C(9B)	0.96(16)
C(6B)-C(7B)-C(8B)-C(9B)	178.99(10)
C(7B)-C(8B)-C(9B)-C(10B)	0.48(18)
C(8B)-C(9B)-C(10B)-C(11B)	-1.2(2)
C(9B)-C(10B)-C(11B)-C(12B)	0.5(2)
C(10B)-C(11B)-C(12B)-C(7B)	0.9(2)
C(8B)-C(7B)-C(12B)-C(11B)	-1.67(18)
C(6B)-C(7B)-C(12B)-C(11B)	-179.69(11)
C(1B)-P(1B)-C(13B)-C(15B)	-82.45(9)
C(17B)-P(1B)-C(13B)-C(15B)	32.13(10)
Ag(1B)-P(1B)-C(13B)-C(15B)	154.84(8)

C(1B)-P(1B)-C(13B)-C(16B)	41.58(9)
C(17B)-P(1B)-C(13B)-C(16B)	156.15(8)
Ag(1B)-P(1B)-C(13B)-C(16B)	-81.14(8)
C(1B)-P(1B)-C(13B)-C(14B)	156.84(7)
C(17B)-P(1B)-C(13B)-C(14B)	-88.58(8)
Ag(1B)-P(1B)-C(13B)-C(14B)	34.13(7)
C(1B)-P(1B)-C(17B)-C(20B)	52.97(9)
C(13B)-P(1B)-C(17B)-C(20B)	-64.20(9)
Ag(1B)-P(1B)-C(17B)-C(20B)	176.86(7)
C(1B)-P(1B)-C(17B)-C(18B)	-66.61(8)
C(13B)-P(1B)-C(17B)-C(18B)	176.23(7)
Ag(1B)-P(1B)-C(17B)-C(18B)	57.28(8)
C(1B)-P(1B)-C(17B)-C(19B)	176.75(8)
C(13B)-P(1B)-C(17B)-C(19B)	59.59(9)
Ag(1B)-P(1B)-C(17B)-C(19B)	-59.36(8)
O(1A)-Ag(1A)-P(1A)-C(1A)	-152.56(14)
O(1A)-Ag(1A)-P(1A)-C(13A)	90.33(14)
O(1A)-Ag(1A)-P(1A)-C(17A)	-33.70(14)
C(13A)-P(1A)-C(1A)-C(2A)	-74.36(9)
C(17A)-P(1A)-C(1A)-C(2A)	46.40(9)
Ag(1A)-P(1A)-C(1A)-C(2A)	164.14(7)
C(13A)-P(1A)-C(1A)-C(6A)	101.86(8)
C(17A)-P(1A)-C(1A)-C(6A)	-137.38(8)
Ag(1A)-P(1A)-C(1A)-C(6A)	-19.64(9)
C(6A)-C(1A)-C(2A)-C(3A)	-0.70(15)
P(1A)-C(1A)-C(2A)-C(3A)	175.66(9)
C(1A)-C(2A)-C(3A)-C(4A)	-1.74(17)
C(2A)-C(3A)-C(4A)-C(5A)	2.15(17)
C(3A)-C(4A)-C(5A)-C(6A)	-0.14(17)
C(4A)-C(5A)-C(6A)-C(1A)	-2.29(15)
C(4A)-C(5A)-C(6A)-C(7A)	176.89(10)
C(2A)-C(1A)-C(6A)-C(5A)	2.66(14)

P(1A)-C(1A)-C(6A)-C(5A)	-173.62(8)
C(2A)-C(1A)-C(6A)-C(7A)	-176.47(9)
P(1A)-C(1A)-C(6A)-C(7A)	7.26(14)
C(5A)-C(6A)-C(7A)-C(12A)	74.55(14)
C(1A)-C(6A)-C(7A)-C(12A)	-106.31(12)
C(5A)-C(6A)-C(7A)-C(8A)	-103.14(12)
C(1A)-C(6A)-C(7A)-C(8A)	76.00(14)
C(12A)-C(7A)-C(8A)-C(9A)	1.16(17)
C(6A)-C(7A)-C(8A)-C(9A)	178.89(10)
C(7A)-C(8A)-C(9A)-C(10A)	0.17(19)
C(8A)-C(9A)-C(10A)-C(11A)	-0.9(2)
C(9A)-C(10A)-C(11A)-C(12A)	0.3(2)
C(10A)-C(11A)-C(12A)-C(7A)	1.0(2)
C(8A)-C(7A)-C(12A)-C(11A)	-1.75(19)
C(6A)-C(7A)-C(12A)-C(11A)	-179.47(12)
C(1A)-P(1A)-C(13A)-C(15A)	51.53(8)
C(17A)-P(1A)-C(13A)-C(15A)	-65.72(9)
Ag(1A)-P(1A)-C(13A)-C(15A)	174.33(7)
C(1A)-P(1A)-C(13A)-C(14A)	-67.68(8)
C(17A)-P(1A)-C(13A)-C(14A)	175.07(7)
Ag(1A)-P(1A)-C(13A)-C(14A)	55.12(8)
C(1A)-P(1A)-C(13A)-C(16A)	175.44(7)
C(17A)-P(1A)-C(13A)-C(16A)	58.19(9)
Ag(1A)-P(1A)-C(13A)-C(16A)	-61.76(8)
C(1A)-P(1A)-C(17A)-C(18A)	43.05(9)
C(13A)-P(1A)-C(17A)-C(18A)	157.77(8)
Ag(1A)-P(1A)-C(17A)-C(18A)	-79.27(8)
C(1A)-P(1A)-C(17A)-C(19A)	-81.03(9)
C(13A)-P(1A)-C(17A)-C(19A)	33.69(11)
Ag(1A)-P(1A)-C(17A)-C(19A)	156.65(8)
C(1A)-P(1A)-C(17A)-C(20A)	157.91(7)
C(13A)-P(1A)-C(17A)-C(20A)	-87.37(8)

Ag(1A)-P(1A)-C(17A)-C(20A)	35.59(8)
F(2B)-B(1B)-F(1B)-B(1B')	79.6(16)
F(4B)-B(1B)-F(1B)-B(1B')	-156.0(18)
F(3B)-B(1B)-F(1B)-B(1B')	-41.4(16)
F(4B)-B(1B)-F(2B)-B(1B')	163.9(18)
F(1B)-B(1B)-F(2B)-B(1B')	-72.4(16)
F(3B)-B(1B)-F(2B)-B(1B')	43.9(16)
B(1B)-F(2B)-B(1B')-F(4B')	-40.2(12)
B(1B)-F(2B)-B(1B')-F(1B)	84.7(17)
B(1B)-F(2B)-B(1B')-F(3B')	-155.4(19)
B(1B)-F(1B)-B(1B')-F(2B)	-77.1(15)
B(1B)-F(1B)-B(1B')-F(4B')	53.6(15)
B(1B)-F(1B)-B(1B')-F(3B')	179(2)

Complex 77b



To a suspension of **81c** in the minimal amount of non-dry dichloromethane was added non-dried *p*-xylene and the mixture was stirred during 1 h. After this time the solvent was removed under reduced pressure. Crystals were obtained by slow evaporation of dichloromethane: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (td, J = 6.1, 2.4 Hz, 1H), 7.58-7.54 (m, 2H), 7.34-7.29 (m, 1H), 7.24 (s, 2H), 3.03 (dt, J = 13.8, 6.9 Hz, 1H), 2.76 (bs, 2H), 2.38 (dt, J = 13.8, 6.9 Hz, 2H), 1.41-1.25 (m, 12H + 18H), 0.96 (d, J = 6.6 Hz, 6H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 49.0 (d, J = 55.9 Hz, 1H), 44.3 (d, J = 53.8 Hz, 1H).

Table 1. Crystal data and structure refinement for **77b**.

Identification code	**77b**

Empirical formula	C_{29} H_{47} Ag F_6 O P Sb	
Formula weight	786.26	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.5534(7) Å	a= 90.00 °.
	b = 27.242(2) Å	b = 103.609(2) °.
	c = 13.0391(9) Å	g = 90.00 °.
Volume	3298.2(4) $Å^3$	
Z	4	
Density (calculated)	1.583 Mg/m^3	
Absorption coefficient	1.515 mm^{-1}	
F(000)	1584	
Crystal size	0.30 x 0.20 x 0.20 mm^3	
Theta range for data collection	2.65 to 39.25 °.	
Index ranges	-17 <=h<=16 ,-46 <=k<=48 ,-23 <=l<=22	
Reflections collected	18979	
Independent reflections	16758 [R(int) = 0.0298]	
Completeness to theta =39.25 °	0.973 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7515 and 0.6592	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18979 / 0 / 366	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0244 , wR2 = 0.0614	
R indices (all data)	R1 = 0.0301 , wR2 = 0.0641	
Largest diff. peak and hole	1.629 and -0.714 $e.Å^{-3}$	

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Table 2. Bond lengths [Å] and angles [°] for **77b**.

Bond lengths----	
Sb1-F2	1.8642(8)
Sb1-F1	1.8707(8)
Sb1-F3	1.872(8)
Sb1-F6	1.8748(8)
Sb1-F5	1.889(7)
Sb1-F4	1.895(8)
Ag1-O1	2.1766(9)
Ag1-P1	2.3656(3)
P1-C1	1.8357(9)
P1-C22	1.8763(11)
P1-C26	1.8951(11)
C1-C2	1.4073(13)
C1-C6	1.4185(13)
C2-C3	1.3844(14)
C3-C4	1.3877(15)
C4-C5	1.3905(14)
C5-C6	1.4029(13)
C6-C7	1.5027(12)
C7-C8	1.4108(13)
C7-C12	1.4187(12)
C8-C9	1.4023(14)
C8-C13	1.527(14)
C9-C10	1.3888(14)
C10-C11	1.4003(14)
C10-C16	1.5245(14)
C11-C12	1.4057(13)
C12-C19	1.5241(13)
C13-C15	1.5347(16)
C13-C14	1.5368(17)

C16-C17	1.5205(18)
C16-C18	1.528(18)
C19-C21	1.5303(14)
C19-C20	1.5348(14)
C22-C25	1.5316(19)
C22-C24	1.5318(16)
C22-C23	1.5348(16)
C26-C28	1.5379(19)
C26-C27	1.5398(16)
C26-C29	1.5402(16)

Angles----------

F2-Sb1-F1	177.62(5)
F2-Sb1-F3	90.43(5)
F1-Sb1-F3	90.97(4)
F2-Sb1-F6	90.98(4)
F1-Sb1-F6	90.92(4)
F3-Sb1-F6	90.98(4)
F2-Sb1-F5	89.36(4)
F1-Sb1-F5	89.22(4)
F3-Sb1-F5	179.29(4)
F6-Sb1-F5	89.71(4)
F2-Sb1-F4	89.24(4)
F1-Sb1-F4	88.83(4)
F3-Sb1-F4	90.13(4)
F6-Sb1-F4	178.87(4)
F5-Sb1-F4	89.18(4)
O1-Ag1-P1	159.74(3)
C1-P1-C22	105.65(4)
C1-P1-C26	107.66(5)
C22-P1-C26	112.93(5)
C1-P1-Ag1	112.47(3)

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C22-P1-Ag1	109.55(4)
C26-P1-Ag1	108.61(3)
C2-C1-C6	118.38(8)
C2-C1-P1	118.32(7)
C6-C1-P1	123.25(7)
C3-C2-C1	122.09(9)
C2-C3-C4	119.49(9)
C3-C4-C5	119.55(9)
C4-C5-C6	121.99(9)
C5-C6-C1	118.39(8)
C5-C6-C7	117.38(8)
C1-C6-C7	124.19(8)
C8-C7-C12	119.60(8)
C8-C7-C6	119.79(8)
C12-C7-C6	120.56(8)
C9-C8-C7	118.79(8)
C9-C8-C13	119.03(8)
C7-C8-C13	122.08(8)
C10-C9-C8	122.57(9)
C9-C10-C11	118.06(9)
C9-C10-C16	119.94(9)
C11-C10-C16	121.96(9)
C10-C11-C12	121.54(9)
C11-C12-C7	119.17(8)
C11-C12-C19	120.11(8)
C7-C12-C19	120.40(8)
C8-C13-C15	113.58(9)
C8-C13-C14	110.58(9)
C15-C13-C14	108.30(10)
C17-C16-C10	111.72(10)
C17-C16-C18	110.22(10)
C10-C16-C18	112.14(10)

C12-C19-C21	114.07(8)
C12-C19-C20	109.06(8)
C21-C19-C20	109.80(9)
C25-C22-C24	108.23(10)
C25-C22-C23	108.89(11)
C24-C22-C23	110.01(9)
C25-C22-P1	105.37(7)
C24-C22-P1	114.78(8)
C23-C22-P1	109.34(8)
C28-C26-C27	107.67(10)
C28-C26-C29	109.54(11)
C27-C26-C29	107.74(9)
C28-C26-P1	107.34(7)
C27-C26-P1	107.23(9)
C29-C26-P1	116.97(8)

Table 3. Torsion angles [°] for **77b**.

O1-Ag1-P1-C1	165.24(8)
O1-Ag1-P1-C22	-77.59(9)
O1-Ag1-P1-C26	46.18(9)
C22-P1-C1-C2	74.43(9)
C26-P1-C1-C2	-46.49(9)
Ag1-P1-C1-C2	-166.10(7)
C22-P1-C1-C6	-108.15(8)
C26-P1-C1-C6	130.93(8)
Ag1-P1-C1-C6	11.32(9)
C6-C1-C2-C3	-1.41(15)
P1-C1-C2-C3	176.14(8)
C1-C2-C3-C4	-1.38(16)
C2-C3-C4-C5	2.06(16)

C3-C4-C5-C6	0.05(16)
C4-C5-C6-C1	-2.83(15)
C4-C5-C6-C7	175.01(9)
C2-C1-C6-C5	3.42(13)
P1-C1-C6-C5	-173.99(7)
C2-C1-C6-C7	-174.25(8)
P1-C1-C6-C7	8.33(13)
C5-C6-C7-C8	-79.54(11)
C1-C6-C7-C8	98.15(11)
C5-C6-C7-C12	98.05(10)
C1-C6-C7-C12	-84.25(11)
C12-C7-C8-C9	5.65(13)
C6-C7-C8-C9	-176.74(9)
C12-C7-C8-C13	-170.60(9)
C6-C7-C8-C13	7.02(13)
C7-C8-C9-C10	-1.82(15)
C13-C8-C9-C10	174.54(10)
C8-C9-C10-C11	-2.15(16)
C8-C9-C10-C16	179.91(10)
C9-C10-C11-C12	2.31(15)
C16-C10-C11-C12	-179.80(10)
C10-C11-C12-C7	1.48(14)
C10-C11-C12-C19	-172.09(9)
C8-C7-C12-C11	-5.49(13)
C6-C7-C12-C11	176.91(8)
C8-C7-C12-C19	168.05(8)
C6-C7-C12-C19	-9.55(12)
C9-C8-C13-C15	36.92(14)
C7-C8-C13-C15	-146.84(10)
C9-C8-C13-C14	-85.07(12)
C7-C8-C13-C14	91.16(12)
C9-C10-C16-C17	119.75(11)

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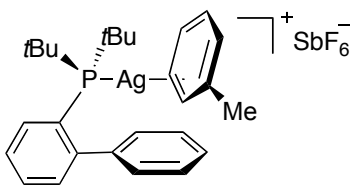
C11-C10-C16-C17	-58.10(14)
C9-C10-C16-C18	-115.93(12)
C11-C10-C16-C18	66.22(14)
C11-C12-C19-C21	-38.62(12)
C7-C12-C19-C21	147.90(9)
C11-C12-C19-C20	84.54(11)
C7-C12-C19-C20	-88.95(10)
C1-P1-C22-C25	72.96(9)
C26-P1-C22-C25	-169.62(8)
Ag1-P1-C22-C25	-48.41(8)
C1-P1-C22-C24	-46.00(10)
C26-P1-C22-C24	71.42(10)
Ag1-P1-C22-C24	-167.37(7)
C1-P1-C22-C23	-170.15(9)
C26-P1-C22-C23	-52.73(10)
Ag1-P1-C22-C23	68.48(9)
C1-P1-C26-C28	-45.07(9)
C22-P1-C26-C28	-161.30(8)
Ag1-P1-C26-C28	76.96(8)
C1-P1-C26-C27	-160.52(8)
C22-P1-C26-C27	83.24(9)
Ag1-P1-C26-C27	-38.49(9)
C1-P1-C26-C29	78.43(10)
C22-P1-C26-C29	-37.80(11)
Ag1-P1-C26-C29	-159.53(9)

Complex 79a



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Complex **6b** was dissolved in the minimal amount of dry dichloromethane, and then anhydrous toluene was added. The mixture was stirred 1 h at room temperature. After this time the solvent was removed under reduced pressure. Crystals were obtained from slow evaporation of a mixture CH_2Cl_2/toluene: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (t, J = 6.5 Hz, 1H), 7.63 (q, J = 6.2 Hz, 3H), 7.53 (t, J = 6.8 Hz, 2H), 7.31 (dd, J = 9.3, 4.3 Hz, 1H), 7.26 (t, J = 7.2 Hz, 4H), 7.18 (d, J = 7.8 Hz, 2H), 7.14 (d, J = 7.2 Hz, 1H), 2.35 (s, 3H), 1.34 (s, 9H), 1.30 (s, 9H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 50.9 (d, J = 54.9 Hz), 46.2 (d, J = 54.9 Hz).

Table 1. Crystal data and structure refinement for **79a**.

Identification code	**79a**	
Empirical formula	C_{27} H_{35} Ag F_6 P Sb	
Formula weight	734.14	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.9215(16) Å	a= 90°.
	b = 24.860(4) Å	b= 96.472(7)°.
	c = 11.613(2) Å	g = 90°.
Volume	2846.1(8) Å^3	
Z	4	
Density (calculated)	1.713 Mg/m^3	
Absorption coefficient	1.747 mm^{-1}	
F(000)	1456	
Crystal size	0.40 x 0.40 x 0.10 mm^3	
Theta range for data collection	2.86 to 39.34°.	
Index ranges	-17<=h<=13, -43<=k<=43, -17<=l<=14	
Reflections collected	45398	
Independent reflections	12998 [R(int) = 0.0837]	
Completeness to theta = 39.34°	76.8 %	
Absorption correction	SADABS (Bruker-Nonius)	

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Max. and min. transmission	0.8447 and 0.5416
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12998 / 0 / 332
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0888, wR2 = 0.2499
R indices (all data)	R1 = 0.1326, wR2 = 0.2847
Largest diff. peak and hole	4.723 and -2.285 e.Å^{-3}

Table 2. Bond lengths [Å] and angles [°] for **79a**.

Ag(1)-C(3A)	2.366(6)
Ag(1)-P(1)	2.3864(13)
Ag(1)-C(2A)	2.474(5)
P(1)-C(1)	1.828(5)
P(1)-C(17)	1.872(6)
P(1)-C(13)	1.883(6)
C(1)-C(6)	1.401(7)
C(1)-C(2)	1.410(6)
C(2)-C(3)	1.406(7)
C(2)-C(7)	1.497(7)
C(3)-C(4)	1.379(8)
C(4)-C(5)	1.388(8)
C(5)-C(6)	1.400(8)
C(7)-C(12)	1.386(9)
C(7)-C(8)	1.397(9)
C(8)-C(9)	1.390(8)
C(9)-C(10)	1.403(10)
C(10)-C(11)	1.390(10)
C(11)-C(12)	1.395(8)
C(13)-C(14)	1.534(9)
C(13)-C(15)	1.537(10)
C(13)-C(16)	1.537(8)

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C(17)-C(20)	1.518(9)
C(17)-C(19)	1.531(9)
C(17)-C(18)	1.537(9)
C(1A)-C(6A)	1.402(8)
C(1A)-C(2A)	1.409(9)
C(1A)-C(7A)	1.484(11)
C(2A)-C(3A)	1.392(10)
C(3A)-C(4A)	1.397(8)
C(4A)-C(5A)	1.389(9)
C(5A)-C(6A)	1.382(11)
Sb(1)-F(3)	1.854(5)
Sb(1)-F(6)	1.855(5)
Sb(1)-F(5)	1.862(5)
Sb(1)-F(2)	1.869(4)
Sb(1)-F(1)	1.874(4)
Sb(1)-F(4)	1.880(4)
C(3A)-Ag(1)-P(1)	158.82(13)
C(3A)-Ag(1)-C(2A)	33.3(2)
P(1)-Ag(1)-C(2A)	150.24(16)
C(1)-P(1)-C(17)	105.0(3)
C(1)-P(1)-C(13)	108.0(3)
C(17)-P(1)-C(13)	114.4(3)
C(1)-P(1)-Ag(1)	111.85(15)
C(17)-P(1)-Ag(1)	108.43(19)
C(13)-P(1)-Ag(1)	109.21(19)
C(6)-C(1)-C(2)	118.5(4)
C(6)-C(1)-P(1)	120.3(3)
C(2)-C(1)-P(1)	121.2(4)
C(3)-C(2)-C(1)	118.5(4)
C(3)-C(2)-C(7)	116.1(4)
C(1)-C(2)-C(7)	125.4(4)
C(4)-C(3)-C(2)	122.2(5)

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C(3)-C(4)-C(5)	119.8(5)
C(4)-C(5)-C(6)	118.9(5)
C(5)-C(6)-C(1)	122.1(5)
C(12)-C(7)-C(8)	119.0(5)
C(12)-C(7)-C(2)	120.0(5)
C(8)-C(7)-C(2)	120.6(5)
C(9)-C(8)-C(7)	121.1(6)
C(8)-C(9)-C(10)	119.4(6)
C(11)-C(10)-C(9)	119.5(5)
C(10)-C(11)-C(12)	120.4(6)
C(7)-C(12)-C(11)	120.4(6)
C(14)-C(13)-C(15)	108.2(6)
C(14)-C(13)-C(16)	108.4(5)
C(15)-C(13)-C(16)	109.8(6)
C(14)-C(13)-P(1)	107.1(4)
C(15)-C(13)-P(1)	105.9(4)
C(16)-C(13)-P(1)	117.1(5)
C(20)-C(17)-C(19)	109.9(5)
C(20)-C(17)-C(18)	108.3(6)
C(19)-C(17)-C(18)	108.6(6)
C(20)-C(17)-P(1)	115.4(5)
C(19)-C(17)-P(1)	108.6(5)
C(18)-C(17)-P(1)	105.9(4)
C(6A)-C(1A)-C(2A)	116.9(7)
C(6A)-C(1A)-C(7A)	122.2(6)
C(2A)-C(1A)-C(7A)	120.8(6)
C(3A)-C(2A)-C(1A)	121.8(5)
C(3A)-C(2A)-Ag(1)	69.0(3)
C(1A)-C(2A)-Ag(1)	103.5(4)
C(2A)-C(3A)-C(4A)	119.8(6)
C(2A)-C(3A)-Ag(1)	77.6(3)
C(4A)-C(3A)-Ag(1)	98.9(4)

C(5A)-C(4A)-C(3A)	118.9(7)
C(6A)-C(5A)-C(4A)	121.1(5)
C(5A)-C(6A)-C(1A)	121.5(6)
F(3)-Sb(1)-F(6)	90.2(3)
F(3)-Sb(1)-F(5)	178.4(2)
F(6)-Sb(1)-F(5)	90.5(3)
F(3)-Sb(1)-F(2)	89.7(3)
F(6)-Sb(1)-F(2)	179.3(3)
F(5)-Sb(1)-F(2)	89.6(2)
F(3)-Sb(1)-F(1)	91.1(2)
F(6)-Sb(1)-F(1)	89.8(2)
F(5)-Sb(1)-F(1)	90.3(2)
F(2)-Sb(1)-F(1)	90.9(3)
F(3)-Sb(1)-F(4)	88.8(2)
F(6)-Sb(1)-F(4)	90.0(2)
F(5)-Sb(1)-F(4)	89.9(2)
F(2)-Sb(1)-F(4)	89.3(3)
F(1)-Sb(1)-F(4)	179.7(3)

Table 3. Torsion angles [°] for **79a**.

C(3A)-Ag(1)-P(1)-C(1)	167.9(5)
C(2A)-Ag(1)-P(1)-C(1)	-110.4(3)
C(3A)-Ag(1)-P(1)-C(17)	-76.7(5)
C(2A)-Ag(1)-P(1)-C(17)	4.9(3)
C(3A)-Ag(1)-P(1)-C(13)	48.4(5)
C(2A)-Ag(1)-P(1)-C(13)	130.1(3)
C(17)-P(1)-C(1)-C(6)	71.0(6)
C(13)-P(1)-C(1)-C(6)	-51.4(6)
Ag(1)-P(1)-C(1)-C(6)	-171.6(5)
C(17)-P(1)-C(1)-C(2)	-109.2(5)

C(13)-P(1)-C(1)-C(2)	128.4(5)
Ag(1)-P(1)-C(1)-C(2)	8.3(6)
C(6)-C(1)-C(2)-C(3)	-1.1(9)
P(1)-C(1)-C(2)-C(3)	179.1(5)
C(6)-C(1)-C(2)-C(7)	178.9(6)
P(1)-C(1)-C(2)-C(7)	-1.0(9)
C(1)-C(2)-C(3)-C(4)	0.7(10)
C(7)-C(2)-C(3)-C(4)	-179.2(6)
C(2)-C(3)-C(4)-C(5)	-0.3(11)
C(3)-C(4)-C(5)-C(6)	0.3(11)
C(4)-C(5)-C(6)-C(1)	-0.7(11)
C(2)-C(1)-C(6)-C(5)	1.1(10)
P(1)-C(1)-C(6)-C(5)	-179.1(6)
C(3)-C(2)-C(7)-C(12)	-77.5(7)
C(1)-C(2)-C(7)-C(12)	102.6(7)
C(3)-C(2)-C(7)-C(8)	95.5(7)
C(1)-C(2)-C(7)-C(8)	-84.5(7)
C(12)-C(7)-C(8)-C(9)	1.9(8)
C(2)-C(7)-C(8)-C(9)	-171.1(5)
C(7)-C(8)-C(9)-C(10)	-1.7(8)
C(8)-C(9)-C(10)-C(11)	0.1(8)
C(9)-C(10)-C(11)-C(12)	1.3(8)
C(8)-C(7)-C(12)-C(11)	-0.4(8)
C(2)-C(7)-C(12)-C(11)	172.6(5)
C(10)-C(11)-C(12)-C(7)	-1.1(8)
C(1)-P(1)-C(13)-C(14)	-154.0(4)
C(17)-P(1)-C(13)-C(14)	89.5(5)
Ag(1)-P(1)-C(13)-C(14)	-32.2(4)
C(1)-P(1)-C(13)-C(15)	-38.7(5)
C(17)-P(1)-C(13)-C(15)	-155.2(4)
Ag(1)-P(1)-C(13)-C(15)	83.1(4)
C(1)-P(1)-C(13)-C(16)	84.1(5)

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C(17)-P(1)-C(13)-C(16)	-32.4(6)
Ag(1)-P(1)-C(13)-C(16)	-154.1(4)
C(1)-P(1)-C(17)-C(20)	-54.9(5)
C(13)-P(1)-C(17)-C(20)	63.3(5)
Ag(1)-P(1)-C(17)-C(20)	-174.6(4)
C(1)-P(1)-C(17)-C(19)	-178.7(4)
C(13)-P(1)-C(17)-C(19)	-60.5(5)
Ag(1)-P(1)-C(17)-C(19)	61.6(4)
C(1)-P(1)-C(17)-C(18)	64.9(5)
C(13)-P(1)-C(17)-C(18)	-177.0(4)
Ag(1)-P(1)-C(17)-C(18)	-54.9(4)
C(6A)-C(1A)-C(2A)-C(3A)	-1.8(8)
C(7A)-C(1A)-C(2A)-C(3A)	-178.2(6)
C(6A)-C(1A)-C(2A)-Ag(1)	-75.3(6)
C(7A)-C(1A)-C(2A)-Ag(1)	108.3(6)
P(1)-Ag(1)-C(2A)-C(3A)	-139.4(3)
C(3A)-Ag(1)-C(2A)-C(1A)	119.3(5)
P(1)-Ag(1)-C(2A)-C(1A)	-20.1(6)
C(1A)-C(2A)-C(3A)-C(4A)	0.0(8)
Ag(1)-C(2A)-C(3A)-C(4A)	93.2(5)
C(1A)-C(2A)-C(3A)-Ag(1)	-93.2(5)
P(1)-Ag(1)-C(3A)-C(2A)	116.7(5)
P(1)-Ag(1)-C(3A)-C(4A)	-2.1(9)
C(2A)-Ag(1)-C(3A)-C(4A)	-118.8(6)
C(2A)-C(3A)-C(4A)-C(5A)	1.6(8)
Ag(1)-C(3A)-C(4A)-C(5A)	82.3(6)
C(3A)-C(4A)-C(5A)-C(6A)	-1.3(9)
C(4A)-C(5A)-C(6A)-C(1A)	-0.5(9)
C(2A)-C(1A)-C(6A)-C(5A)	2.1(9)
C(7A)-C(1A)-C(6A)-C(5A)	178.4(6)

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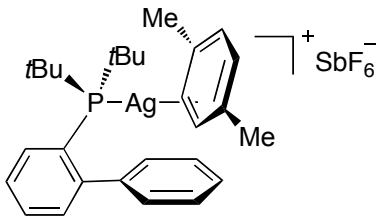
Complex 79b



Complex **89b** was dissolved in the minimal amount of dry dichloromethane. At this point, anhydrous *p*-xylene was added and the mixture was stirred 1 h at room temperature. After this time the solvent was removed under reduced pressure. Crystals were obtained from slow evaporation of a mixture *p*-xilene/$CHCl_3$: ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 10.3, 4.5 Hz, 1H), 7.63 (d, J = 6.8 Hz, 3H), 7.53 (dd, J = 14.0, 7.0 Hz, 2H), 7.33 – 7.29 (m, 1H), 7.27 (d, J = 2.1 Hz, 2H), 7.06 (s, 4H), 2.31 (s, 6H), 1.34 (s, 9H), 1.30 (s, 9H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 51.00 (d, J = 55.0 Hz), 46.25 (d, J = 55.1 Hz).

Table 1. Crystal data and structure refinement for **79b**.

Identification code	**79b**	
Empirical formula	C_{28} H_{37} Ag F_6 P Sb	
Formula weight	748.17	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.9651(5) Å	α= 90°.
	b = 25.1777(13) Å	β= 92.159(3)°.
	c = 11.8128(7) Å	γ = 90°.
Volume	2961.7(3) $Å^3$	
Z	4	
Density (calculated)	1.678 Mg/m^3	
Absorption coefficient	1.681 mm^{-1}	
F(000)	1488	
Crystal size	0.20 x 0.10 x 0.10 mm^3	
Theta range for data collection	2.73 to 39.72°.	

Index ranges	-17<=h<=16, -43<=k<=45, -13<=l<=21
Reflections collected	65948
Independent reflections	17095 [R(int) = 0.0353]
Completeness to theta = 39.72°	94.8 %
Absorption correction	SADABS (Bruker-Nonius)
Max. and min. transmission	0.8499 and 0.7298
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	17095 / 10 / 393
Goodness-of-fit on F^2	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0309, wR2 = 0.0650
R indices (all data)	R1 = 0.0591, wR2 = 0.0774
Largest diff. peak and hole	1.904 and -1.468 e.Å^{-3}

Table 2. Bond lengths [Å] and angles [°] for **79b**.

Ag(1)-C(21)	2.367(8)
Ag(1)-C(22)	2.387(7)
Ag(1)-P(1)	2.4023(4)
Ag(1)-C(21')	2.464(6)
Ag(1)-C(22')	2.492(6)
P(1)-C(1)	1.8302(14)
P(1)-C(13)	1.8751(16)
P(1)-C(17)	1.8802(15)
C(1)-C(2)	1.406(2)
C(1)-C(6)	1.411(2)
C(2)-C(3)	1.389(2)
C(3)-C(4)	1.388(3)
C(4)-C(5)	1.387(2)
C(5)-C(6)	1.400(2)
C(6)-C(7)	1.493(2)
C(7)-C(8)	1.401(2)
C(7)-C(12)	1.401(2)

C(8)-C(9)	1.392(2)
C(9)-C(10)	1.386(3)
C(10)-C(11)	1.389(3)
C(11)-C(12)	1.393(2)
C(13)-C(16)	1.530(2)
C(13)-C(14)	1.532(2)
C(13)-C(15)	1.537(2)
C(17)-C(18)	1.534(3)
C(17)-C(20)	1.539(2)
C(17)-C(19)	1.542(2)
C(21)-C(22)	1.3900
C(21)-C(26)	1.3900
C(22)-C(23)	1.3900
C(23)-C(24)	1.3900
C(23)-C(27)	1.517(4)
C(24)-C(25)	1.3900
C(25)-C(26)	1.3900
C(26)-C(28)	1.517(5)
C(21')-C(22')	1.3900
C(21')-C(26')	1.3900
C(22')-C(23')	1.3900
C(23')-C(24')	1.3900
C(23')-C(27')	1.525(4)
C(24')-C(25')	1.3900
C(25')-C(26')	1.3900
C(26')-C(28')	1.515(4)
Sb(1)-F(3)	1.8575(14)
Sb(1)-F(4)	1.8610(13)
Sb(1)-F(5)	1.8611(14)
Sb(1)-F(2)	1.8633(13)
Sb(1)-F(6)	1.8734(15)
Sb(1)-F(1)	1.8776(13)

C(21)-Ag(1)-C(22)	34.00(10)
C(21)-Ag(1)-P(1)	160.72(12)
C(22)-Ag(1)-P(1)	146.68(13)
C(21)-Ag(1)-C(21')	2.69(15)
C(22)-Ag(1)-C(21')	33.4(2)
P(1)-Ag(1)-C(21')	158.37(9)
C(21)-Ag(1)-C(22')	33.74(19)
C(22)-Ag(1)-C(22')	7.31(11)
P(1)-Ag(1)-C(22')	142.79(13)
C(21')-Ag(1)-C(22')	32.57(8)
C(1)-P(1)-C(13)	104.47(7)
C(1)-P(1)-C(17)	107.64(7)
C(13)-P(1)-C(17)	113.97(7)
C(1)-P(1)-Ag(1)	113.14(5)
C(13)-P(1)-Ag(1)	109.85(5)
C(17)-P(1)-Ag(1)	107.84(5)
C(2)-C(1)-C(6)	118.51(13)
C(2)-C(1)-P(1)	120.08(12)
C(6)-C(1)-P(1)	121.40(10)
C(3)-C(2)-C(1)	121.64(16)
C(4)-C(3)-C(2)	119.53(15)
C(5)-C(4)-C(3)	119.69(14)
C(4)-C(5)-C(6)	121.69(15)
C(5)-C(6)-C(1)	118.92(13)
C(5)-C(6)-C(7)	116.21(13)
C(1)-C(6)-C(7)	124.87(12)
C(8)-C(7)-C(12)	118.91(14)
C(8)-C(7)-C(6)	119.96(13)
C(12)-C(7)-C(6)	120.96(13)
C(9)-C(8)-C(7)	120.33(15)
C(10)-C(9)-C(8)	120.33(15)
C(9)-C(10)-C(11)	119.93(15)

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C(10)-C(11)-C(12)	120.17(16)
C(11)-C(12)-C(7)	120.33(15)
C(16)-C(13)-C(14)	109.92(14)
C(16)-C(13)-C(15)	108.95(14)
C(14)-C(13)-C(15)	108.43(14)
C(16)-C(13)-P(1)	108.33(11)
C(14)-C(13)-P(1)	115.23(11)
C(15)-C(13)-P(1)	105.77(11)
C(18)-C(17)-C(20)	110.17(15)
C(18)-C(17)-C(19)	107.72(14)
C(20)-C(17)-C(19)	107.91(14)
C(18)-C(17)-P(1)	106.09(12)
C(20)-C(17)-P(1)	117.41(11)
C(19)-C(17)-P(1)	107.15(10)
C(22)-C(21)-C(26)	120.0
C(22)-C(21)-Ag(1)	73.8(2)
C(26)-C(21)-Ag(1)	101.8(2)
C(21)-C(22)-C(23)	120.0
C(21)-C(22)-Ag(1)	72.2(3)
C(23)-C(22)-Ag(1)	102.5(3)
C(22)-C(23)-C(24)	120.0
C(22)-C(23)-C(27)	119.1(4)
C(24)-C(23)-C(27)	120.9(4)
C(25)-C(24)-C(23)	120.0
C(24)-C(25)-C(26)	120.0
C(25)-C(26)-C(21)	120.0
C(25)-C(26)-C(28)	127.4(8)
C(21)-C(26)-C(28)	111.9(8)
C(22')-C(21')-C(26')	120.0
C(22')-C(21')-Ag(1)	74.8(2)
C(26')-C(21')-Ag(1)	102.3(2)
C(21')-C(22')-C(23')	120.0

C(21')-C(22')-Ag(1)	72.6(2)
C(23')-C(22')-Ag(1)	103.3(2)
C(22')-C(23')-C(24')	120.0
C(22')-C(23')-C(27')	122.6(4)
C(24')-C(23')-C(27')	117.4(4)
C(25')-C(24')-C(23')	120.0
C(26')-C(25')-C(24')	120.0
C(25')-C(26')-C(21')	120.0
C(25')-C(26')-C(28')	112.7(6)
C(21')-C(26')-C(28')	127.3(6)
F(3)-Sb(1)-F(4)	89.18(8)
F(3)-Sb(1)-F(5)	179.00(8)
F(4)-Sb(1)-F(5)	89.87(9)
F(3)-Sb(1)-F(2)	90.70(8)
F(4)-Sb(1)-F(2)	179.79(9)
F(5)-Sb(1)-F(2)	90.25(9)
F(3)-Sb(1)-F(6)	90.56(8)
F(4)-Sb(1)-F(6)	91.14(8)
F(5)-Sb(1)-F(6)	89.77(8)
F(2)-Sb(1)-F(6)	89.04(7)
F(3)-Sb(1)-F(1)	90.56(7)
F(4)-Sb(1)-F(1)	90.60(8)
F(5)-Sb(1)-F(1)	89.13(6)
F(2)-Sb(1)-F(1)	89.22(7)
F(6)-Sb(1)-F(1)	177.94(7)

Table 3. Torsion angles [°] for **79b**.

C(21)-Ag(1)-P(1)-C(1)	175.1(3)
C(22)-Ag(1)-P(1)-C(1)	-107.8(2)
C(21')-Ag(1)-P(1)-C(1)	178.8(3)

C(22')-Ag(1)-P(1)-C(1)	-118.5(2)
C(21)-Ag(1)-P(1)-C(13)	-68.6(3)
C(22)-Ag(1)-P(1)-C(13)	8.6(2)
C(21')-Ag(1)-P(1)-C(13)	-64.8(3)
C(22')-Ag(1)-P(1)-C(13)	-2.2(2)
C(21)-Ag(1)-P(1)-C(17)	56.1(3)
C(22)-Ag(1)-P(1)-C(17)	133.3(2)
C(21')-Ag(1)-P(1)-C(17)	59.9(3)
C(22')-Ag(1)-P(1)-C(17)	122.6(2)
C(13)-P(1)-C(1)-C(2)	72.59(14)
C(17)-P(1)-C(1)-C(2)	-48.91(14)
Ag(1)-P(1)-C(1)-C(2)	-167.96(11)
C(13)-P(1)-C(1)-C(6)	-106.17(13)
C(17)-P(1)-C(1)-C(6)	132.33(12)
Ag(1)-P(1)-C(1)-C(6)	13.28(13)
C(6)-C(1)-C(2)-C(3)	-0.1(2)
P(1)-C(1)-C(2)-C(3)	-178.89(13)
C(1)-C(2)-C(3)-C(4)	0.6(3)
C(2)-C(3)-C(4)-C(5)	-0.3(3)
C(3)-C(4)-C(5)-C(6)	-0.6(3)
C(4)-C(5)-C(6)-C(1)	1.1(2)
C(4)-C(5)-C(6)-C(7)	-178.80(14)
C(2)-C(1)-C(6)-C(5)	-0.8(2)
P(1)-C(1)-C(6)-C(5)	178.03(11)
C(2)-C(1)-C(6)-C(7)	179.13(14)
P(1)-C(1)-C(6)-C(7)	-2.1(2)
C(5)-C(6)-C(7)-C(8)	-75.76(19)
C(1)-C(6)-C(7)-C(8)	104.35(17)
C(5)-C(6)-C(7)-C(12)	99.44(16)
C(1)-C(6)-C(7)-C(12)	-80.45(19)
C(12)-C(7)-C(8)-C(9)	-0.1(2)
C(6)-C(7)-C(8)-C(9)	175.15(15)

C(7)-C(8)-C(9)-C(10)	-0.6(3)
C(8)-C(9)-C(10)-C(11)	1.0(3)
C(9)-C(10)-C(11)-C(12)	-0.6(3)
C(10)-C(11)-C(12)-C(7)	-0.2(2)
C(8)-C(7)-C(12)-C(11)	0.5(2)
C(6)-C(7)-C(12)-C(11)	-174.71(14)
C(1)-P(1)-C(13)-C(16)	-177.54(11)
C(17)-P(1)-C(13)-C(16)	-60.33(12)
Ag(1)-P(1)-C(13)-C(16)	60.81(11)
C(1)-P(1)-C(13)-C(14)	-53.97(14)
C(17)-P(1)-C(13)-C(14)	63.24(14)
Ag(1)-P(1)-C(13)-C(14)	-175.62(11)
C(1)-P(1)-C(13)-C(15)	65.78(12)
C(17)-P(1)-C(13)-C(15)	-177.01(10)
Ag(1)-P(1)-C(13)-C(15)	-55.88(11)
C(1)-P(1)-C(17)-C(18)	-41.38(12)
C(13)-P(1)-C(17)-C(18)	-156.75(11)
Ag(1)-P(1)-C(17)-C(18)	81.00(11)
C(1)-P(1)-C(17)-C(20)	82.25(15)
C(13)-P(1)-C(17)-C(20)	-33.12(16)
Ag(1)-P(1)-C(17)-C(20)	-155.37(12)
C(1)-P(1)-C(17)-C(19)	-156.25(12)
C(13)-P(1)-C(17)-C(19)	88.38(13)
Ag(1)-P(1)-C(17)-C(19)	-33.87(13)
P(1)-Ag(1)-C(21)-C(22)	106.7(5)
C(21')-Ag(1)-C(21)-C(22)	76(5)
C(22')-Ag(1)-C(21)-C(22)	13.1(2)
C(22)-Ag(1)-C(21)-C(26)	-118.12(7)
P(1)-Ag(1)-C(21)-C(26)	-11.4(5)
C(21')-Ag(1)-C(21)-C(26)	-43(5)
C(22')-Ag(1)-C(21)-C(26)	-104.99(19)
C(26)-C(21)-C(22)-C(23)	0.0

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Ag(1)-C(21)-C(22)-C(23)	-94.4(3)
C(26)-C(21)-C(22)-Ag(1)	94.4(3)
P(1)-Ag(1)-C(22)-C(21)	-144.8(2)
C(21')-Ag(1)-C(22)-C(21)	-4.7(3)
C(22')-Ag(1)-C(22)-C(21)	-82.5(16)
C(21)-Ag(1)-C(22)-C(23)	117.82(8)
P(1)-Ag(1)-C(22)-C(23)	-27.0(2)
C(21')-Ag(1)-C(22)-C(23)	113.1(3)
C(22')-Ag(1)-C(22)-C(23)	35.3(15)
C(21)-C(22)-C(23)-C(24)	0.0
Ag(1)-C(22)-C(23)-C(24)	-76.5(2)
C(21)-C(22)-C(23)-C(27)	-179.9(5)
Ag(1)-C(22)-C(23)-C(27)	103.6(4)
C(22)-C(23)-C(24)-C(25)	0.0
C(27)-C(23)-C(24)-C(25)	179.9(6)
C(23)-C(24)-C(25)-C(26)	0.0
C(24)-C(25)-C(26)-C(21)	0.0
C(24)-C(25)-C(26)-C(28)	-170.1(9)
C(22)-C(21)-C(26)-C(25)	0.0
Ag(1)-C(21)-C(26)-C(25)	77.9(2)
C(22)-C(21)-C(26)-C(28)	171.5(8)
Ag(1)-C(21)-C(26)-C(28)	-110.5(7)
C(21)-Ag(1)-C(21')-C(22')	-114(5)
C(22)-Ag(1)-C(21')-C(22')	-13.4(2)
P(1)-Ag(1)-C(21')-C(22')	93.8(4)
C(21)-Ag(1)-C(21')-C(26')	128(5)
C(22)-Ag(1)-C(21')-C(26')	-131.5(2)
P(1)-Ag(1)-C(21')-C(26')	-24.3(4)
C(22')-Ag(1)-C(21')-C(26')	-118.11(6)
C(26')-C(21')-C(22')-C(23')	0.0
Ag(1)-C(21')-C(22')-C(23')	-95.6(2)
C(26')-C(21')-C(22')-Ag(1)	95.6(2)

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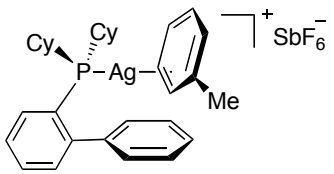
C(21)-Ag(1)-C(22')-C(21')	4.4(3)
C(22)-Ag(1)-C(22')-C(21')	91.0(17)
P(1)-Ag(1)-C(22')-C(21')	-142.54(17)
C(21)-Ag(1)-C(22')-C(23')	122.1(3)
C(22)-Ag(1)-C(22')-C(23')	-151.3(17)
P(1)-Ag(1)-C(22')-C(23')	-24.88(18)
C(21')-Ag(1)-C(22')-C(23')	117.66(7)
C(21')-C(22')-C(23')-C(24')	0.0
Ag(1)-C(22')-C(23')-C(24')	-77.4(2)
C(21')-C(22')-C(23')-C(27')	-179.2(5)
Ag(1)-C(22')-C(23')-C(27')	103.4(4)
C(22')-C(23')-C(24')-C(25')	0.0
C(27')-C(23')-C(24')-C(25')	179.2(5)
C(23')-C(24')-C(25')-C(26')	0.0
C(24')-C(25')-C(26')-C(21')	0.0
C(24')-C(25')-C(26')-C(28')	-179.6(7)
C(22')-C(21')-C(26')-C(25')	0.0
Ag(1)-C(21')-C(26')-C(25')	79.4(2)
C(22')-C(21')-C(26')-C(28')	179.6(8)
Ag(1)-C(21')-C(26')-C(28')	-101.0(8)

Complex 79c



Complex **81b** was dissolved in the minimal amount of dry dichloromethane, and then was added anhydrous toluene and the mixture was stirred 3h at room temperature. After this time the solvent was removed under reduced pressure. Crystals were obtained from slow evaporation of a mixture CH_2Cl_2/Toluene: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65-7.45 (m, 6H), 7.32 (q, J = 4.3 Hz, 1H), 7.30-7.13

(m, 7H), 2.36 (s, 3H), 2.21-2.05 (m, 2H), 1.93-1.54 (m, 10H), 1.41-1.05 (m, 10H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.7 (d, J = 56.3 Hz), 19.9 (d, J = 56.3 Hz).

Table 1. Crystal data and structure refinement for **79c**.

Identification code	**79c**	
Empirical formula	C_{31} H_{39} Ag F_6 P Sb	
Formula weight	786.21	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 10.4129(7) Å	a= 90.00 °.
	b = 16.2701(11) Å	b = 96.020(3) °.
	c = 18.3470(18) Å	g = 90.00 °.
Volume	3091.2(4) Å^3	
Z	4	
Density (calculated)	1.689 Mg/m^3	
Absorption coefficient	1.615 mm^{-1}	
F(000)	1568	
Crystal size	0.30 x 0.20 x 0.03 mm^3	
Theta range for data collection	2.67 to 35.00 °.	
Index ranges	-16 <=h<=14 ,-26 <=k<=26 ,-29 <=l<=19	
Reflections collected	8674	
Independent reflections	7871 [R(int) = 0.0893]	
Completeness to theta =35.00 °	0.984 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9532 and 0.6430	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8674 / 2 / 362	

Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0782 , wR2 = 0.1889
R indices (all data)	R1 = 0.0839 , wR2 = 0.1995
Largest diff. peak and hole	4.679 and -4.826 e.Å^{-3}

Table 2. Bond lengths [Å] and angles [°] for **79c**.

Bond lengths----	
Ag1-C25	2.322(6)
Ag1-P1	2.371(14)
Ag1-C26	2.626(6)
Ag1-C30	2.696(8)
P1-C1	1.827(6)
P1-C19	1.852(6)
P1-C13	1.856(6)
C1-C6	1.398(8)
C1-C2	1.409(8)
C2-C3	1.384(9)
C3-C4	1.384(11)
C4-C5	1.402(10)
C5-C6	1.4(9)
C6-C7	1.483(8)
C7-C12	1.393(9)
C7-C8	1.41(8)
C8-C9	1.405(10)
C9-C10	1.377(12)
C10-C11	1.399(10)
C11-C12	1.39(9)
C13-C18	1.487(9)
C13-C14	1.545(9)
C14-C15	1.511(10)
C15-C16	1.514(11)

C16-C17	1.521(12)
C17-C18	1.542(10)
C19-C20	1.531(8)
C19-C24	1.533(9)
C20-C21	1.53(10)
C21-C22	1.508(11)
C22-C23	1.542(11)
C23-C24	1.519(10)
C25-C26	1.39(11)
C25-C30	1.4(11)
C26-C27	1.404(10)
C27-C28	1.375(11)
C28-C29	1.391(13)
C29-C30	1.399(11)
C29-C31	1.516(12)
Sb1-F1	1.861(5)
Sb1-F6	1.865(5)
Sb1-F3	1.868(4)
Sb1-F2	1.87(5)
Sb1-F4	1.87(5)
Sb1-F5	1.871(5)

Angles----------

C25-Ag1-P1	165.49(18)
C25-Ag1-C26	31.9(3)
P1-Ag1-C26	141.23(18)
C25-Ag1-C30	31.3(2)
P1-Ag1-C30	137.85(17)
C26-Ag1-C30	53.9(2)
C1-P1-C19	104.4(3)
C1-P1-C13	103.4(3)
C19-P1-C13	106.4(3)

C1-P1-Ag1	114.81(18)
C19-P1-Ag1	112.80(17)
C13-P1-Ag1	114.0(2)
C6-C1-C2	119.7(5)
C6-C1-P1	123.9(4)
C2-C1-P1	116.0(4)
C3-C2-C1	120.9(6)
C2-C3-C4	119.5(6)
C3-C4-C5	120.4(6)
C6-C5-C4	120.5(6)
C1-C6-C5	118.9(5)
C1-C6-C7	123.3(5)
C5-C6-C7	117.7(5)
C12-C7-C8	118.6(6)
C12-C7-C6	120.0(5)
C8-C7-C6	121.2(6)
C9-C8-C7	119.0(6)
C10-C9-C8	121.5(6)
C9-C10-C11	119.8(6)
C12-C11-C10	119.1(7)
C11-C12-C7	122.0(6)
C18-C13-C14	112.0(6)
C18-C13-P1	112.8(4)
C14-C13-P1	110.2(4)
C15-C14-C13	111.0(6)
C14-C15-C16	112.2(6)
C15-C16-C17	111.6(7)
C16-C17-C18	112.2(6)
C13-C18-C17	112.4(6)
C20-C19-C24	108.1(5)
C20-C19-P1	110.8(4)
C24-C19-P1	112.5(4)

C21-C20-C19	110.8(6)
C22-C21-C20	112.1(6)
C21-C22-C23	109.5(5)
C24-C23-C22	112.0(6)
C23-C24-C19	110.8(5)
C26-C25-C30	119.8(6)
C26-C25-Ag1	86.2(4)
C30-C25-Ag1	89.2(4)
C25-C26-C27	119.3(6)
C25-C26-Ag1	61.9(3)
C27-C26-Ag1	103.5(4)
C28-C27-C26	120.1(7)
C27-C28-C29	121.5(7)
C28-C29-C30	118.3(6)
C28-C29-C31	121.8(9)
C30-C29-C31	119.8(10)
C29-C30-C25	120.8(7)
C29-C30-Ag1	103.5(4)
C25-C30-Ag1	59.5(4)
F1-Sb1-F6	90.6(3)
F1-Sb1-F3	90.1(2)
F6-Sb1-F3	179.2(3)
F1-Sb1-F2	91.2(3)
F6-Sb1-F2	90.5(3)
F3-Sb1-F2	89.4(3)
F1-Sb1-F4	89.2(3)
F6-Sb1-F4	90.2(3)
F3-Sb1-F4	89.9(3)
F2-Sb1-F4	179.2(3)
F1-Sb1-F5	179.1(3)
F6-Sb1-F5	89.6(3)
F3-Sb1-F5	89.7(3)

F2-Sb1-F5	89.7(3)
F4-Sb1-F5	89.9(2)

Table 3. Torsion angles [°] for **79c**.

C25-Ag1-P1-C1	-161.3(8)
C26-Ag1-P1-C1	145.7(3)
C30-Ag1-P1-C1	-125.8(3)
C25-Ag1-P1-C19	79.3(8)
C26-Ag1-P1-C19	26.3(3)
C30-Ag1-P1-C19	114.8(3)
C25-Ag1-P1-C13	-42.3(8)
C26-Ag1-P1-C13	-95.3(3)
C30-Ag1-P1-C13	-6.8(3)
C19-P1-C1-C6	123.4(5)
C13-P1-C1-C6	-125.4(5)
Ag1-P1-C1-C6	-0.6(5)
C19-P1-C1-C2	-49.3(5)
C13-P1-C1-C2	61.8(5)
Ag1-P1-C1-C2	-173.3(4)
C6-C1-C2-C3	-0.4(8)
P1-C1-C2-C3	172.6(5)
C1-C2-C3-C4	-1.7(10)
C2-C3-C4-C5	1.7(11)
C3-C4-C5-C6	0.5(11)
C2-C1-C6-C5	2.6(8)
P1-C1-C6-C5	-169.9(4)
C2-C1-C6-C7	-174.6(5)
P1-C1-C6-C7	12.9(8)
C4-C5-C6-C1	-2.7(9)
C4-C5-C6-C7	174.7(6)

C1-C6-C7-C12	59.5(8)
C5-C6-C7-C12	-117.8(7)
C1-C6-C7-C8	-124.9(6)
C5-C6-C7-C8	57.9(8)
C12-C7-C8-C9	-1.1(10)
C6-C7-C8-C9	-176.8(6)
C7-C8-C9-C10	-0.3(12)
C8-C9-C10-C11	2.3(12)
C9-C10-C11-C12	-2.7(11)
C10-C11-C12-C7	1.3(11)
C8-C7-C12-C11	0.6(10)
C6-C7-C12-C11	176.4(6)
C1-P1-C13-C18	-171.6(5)
C19-P1-C13-C18	-62.0(6)
Ag1-P1-C13-C18	63.0(5)
C1-P1-C13-C14	62.4(5)
C19-P1-C13-C14	172.1(5)
Ag1-P1-C13-C14	-62.9(5)
C18-C13-C14-C15	54.6(8)
P1-C13-C14-C15	-179.0(6)
C13-C14-C15-C16	-55.1(10)
C14-C15-C16-C17	54.5(10)
C15-C16-C17-C18	-52.0(11)
C14-C13-C18-C17	-52.9(9)
P1-C13-C18-C17	-177.8(6)
C16-C17-C18-C13	52.0(11)
C1-P1-C19-C20	-162.0(4)
C13-P1-C19-C20	89.1(4)
Ag1-P1-C19-C20	-36.7(4)
C1-P1-C19-C24	-40.8(4)
C13-P1-C19-C24	-149.8(4)
Ag1-P1-C19-C24	84.4(4)

C24-C19-C20-C21	58.8(7)
P1-C19-C20-C21	-177.5(4)
C19-C20-C21-C22	-58.5(7)
C20-C21-C22-C23	54.5(8)
C21-C22-C23-C24	-54.5(8)
C22-C23-C24-C19	57.8(7)
C20-C19-C24-C23	-58.8(7)
P1-C19-C24-C23	178.6(5)
P1-Ag1-C25-C26	-71.3(10)
C30-Ag1-C25-C26	-119.9(6)
P1-Ag1-C25-C30	48.7(11)
C26-Ag1-C25-C30	119.9(6)
C30-C25-C26-C27	3.3(10)
Ag1-C25-C26-C27	90.2(6)
C30-C25-C26-Ag1	-86.9(6)
P1-Ag1-C26-C25	157.7(4)
C30-Ag1-C26-C25	33.8(4)
C25-Ag1-C26-C27	-116.3(7)
P1-Ag1-C26-C27	41.4(6)
C30-Ag1-C26-C27	-82.5(5)
C25-C26-C27-C28	-1.2(10)
Ag1-C26-C27-C28	63.9(7)
C26-C27-C28-C29	-1.4(11)
C27-C28-C29-C30	1.9(11)
C27-C28-C29-C31	-178.1(8)
C28-C29-C30-C25	0.1(10)
C31-C29-C30-C25	-179.8(8)
C28-C29-C30-Ag1	-62.1(7)
C31-C29-C30-Ag1	117.9(7)
C26-C25-C30-C29	-2.8(10)
Ag1-C25-C30-C29	-87.9(6)
C26-C25-C30-Ag1	85.2(6)

C25-Ag1-C30-C29	118.0(7)
P1-Ag1-C30-C29	-45.7(5)
C26-Ag1-C30-C29	83.5(5)
P1-Ag1-C30-C25	-163.7(4)
C26-Ag1-C30-C25	-34.5(4)

KINETIC DATA

Kinetics studies for skeletal rearrangement using complex **4e**:

Variation in the area of the olefinic H at 4.93 ppm was observed. As internal standard the signal of $CHCl_3$ at 7.26 ppm, ws used.

T = 233 K

Time (s)	Ln A
180	0
360	-0,008169278
540	-0,009424269
720	-0,013121714
900	-0,022894081
1080	-0,027700131
1260	-0,032590343
1440	-0,035758793
1620	-0,0420029
1800	-0,047080077
1980	-0,053242561
2160	-0,062223337
2340	-0,066295798
2520	-0,069798196
2700	-0,079621296
2880	-0,08889679

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3060	-0,094348043
3240	-0,108360567
3420	-0,117937048
3600	-0,123105927
3780	-0,129144458
3960	-0,135484155
4140	-0,147228196
4320	-0,15548023
4500	-0,168690878
4680	-0,182852498
4860	-0,181795295
5040	-0,19058924
5220	-0,205252063
5400	-0,21137186
5580	-0,221235373
5760	-0,227337333
5940	-0,239401244
6120	-0,250527595
6300	-0,25875389
6480	-0,263191106
6660	-0,277990521
6840	-0,280731616
7020	-0,293473477
7200	-0,29973711
7380	-0,30723873

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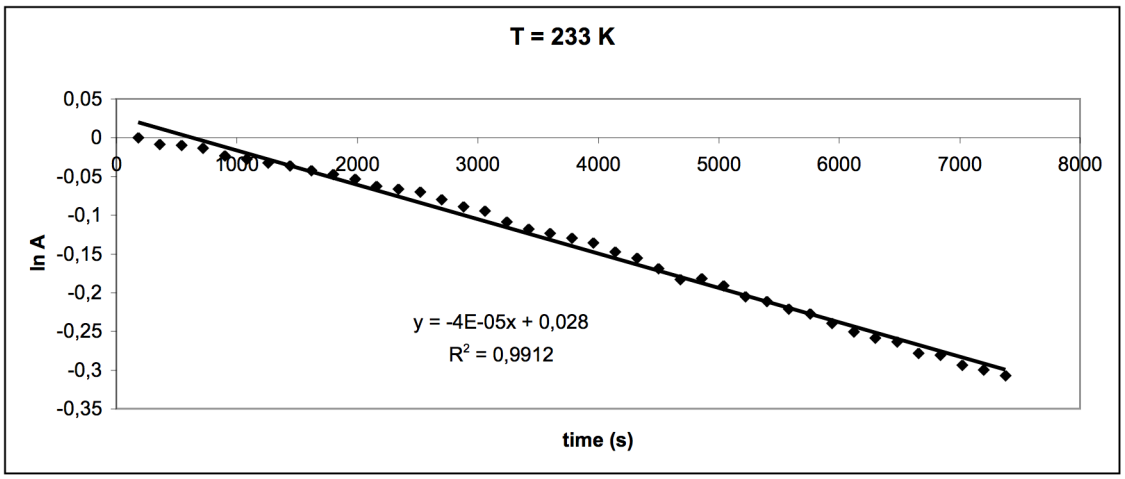

Ln A = 0.028 + (-0.00004)t

r = 0.995

T = 243 K

Time (s)	Ln A
180	0
360	-0,019208304
540	-0,038548539
720	-0,05463466
900	-0,070493282
1080	-0,083908922
1260	-0,096655184
1440	-0,109035036
1620	-0,115838552
1800	-0,123751939
1980	-0,130000491
2160	-0,133667402
2340	-0,136703275

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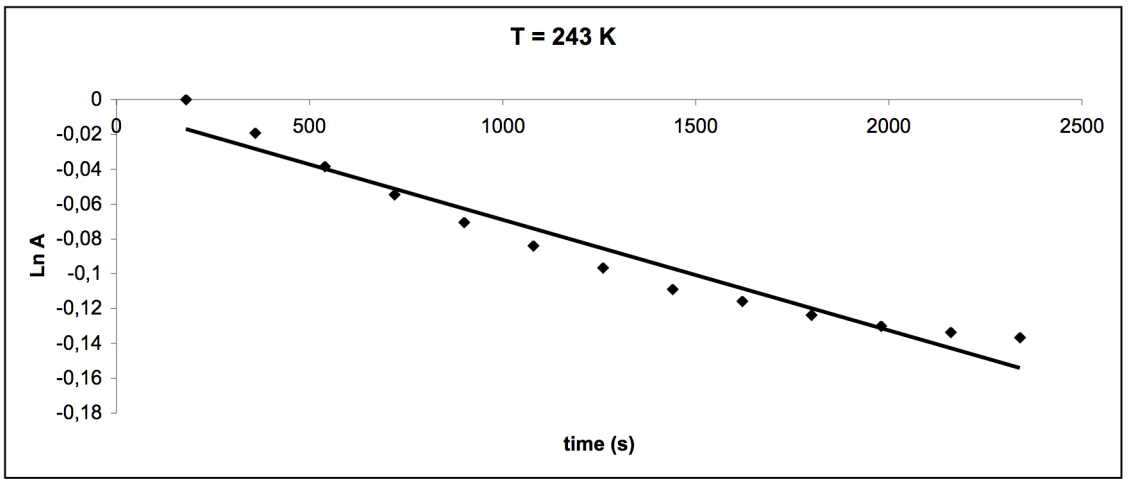
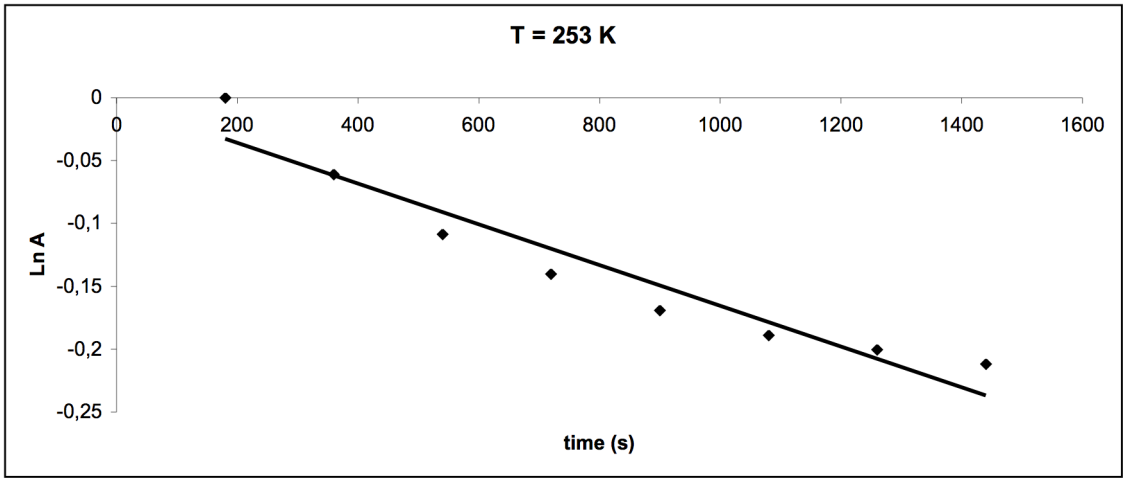


Ln A = -0.0055 + (-0.00006)t

r = 0.974

T = 253 K

Time (s)	Ln A
180	0
360	-0,061049149
540	-0,108739552
720	-0,140125659
900	-0,169018832
1080	-0,189208417
1260	-0,200528706
1440	-0,211801862



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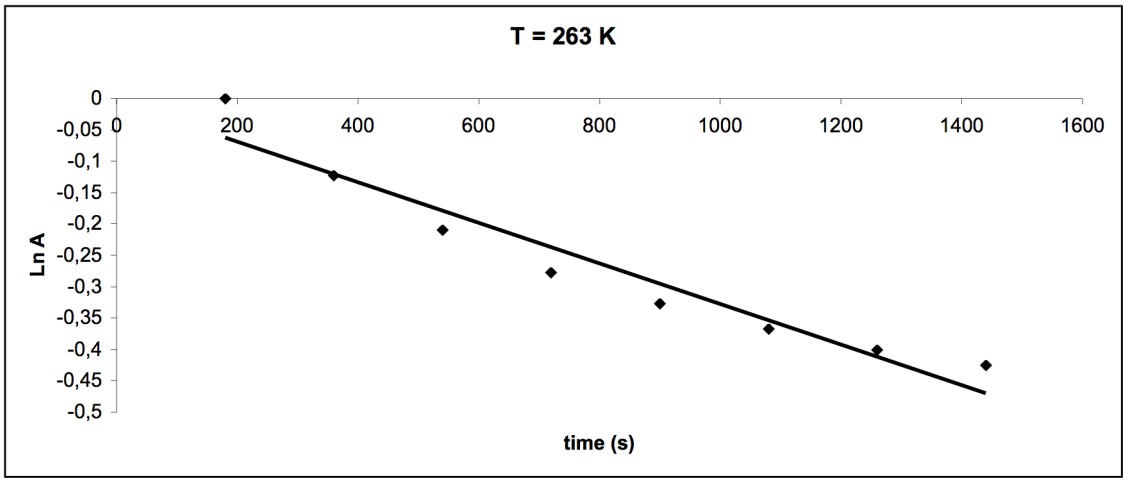
Ln A = -0.0038 + (-0.0002)t

r = 0.961

T = 263 K

Time (s)	Ln A
180	0
360	-0,122439987
540	-0,209705498
720	-0,277238134
900	-0,326752824
1080	-0,367494695
1260	-0,400853757
1440	-0,425219957



Ln A = -0.0042 + (-0.0003)t

r = 0.968

T = 273 K

Time (s)	Ln A
180	0
360	-0,620822798

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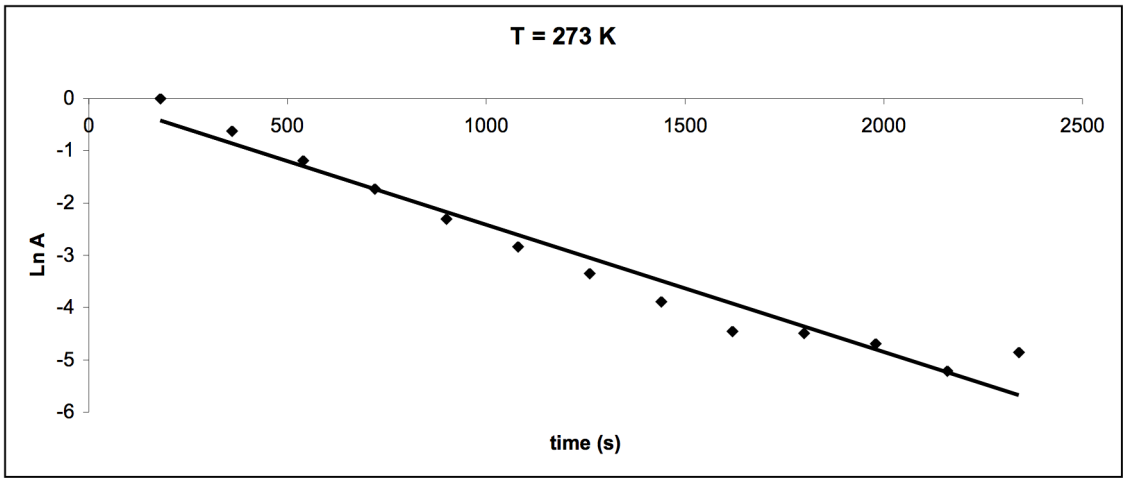
540	-1,192446159
720	-1,729647014
900	-2,301295924
1080	-2,839087564
1260	-3,343645712
1440	-3,885089004
1620	-4,456233073
1800	-4,493271093
1980	-4,691272885
2160	-5,213608639



Ln A = 0.0191 + (-0.0024)t

r = 0.978

T = 283 K

Time (s)	Ln A
180	0
360	-1,49153044
540	-2,789319911
720	-3,245117136

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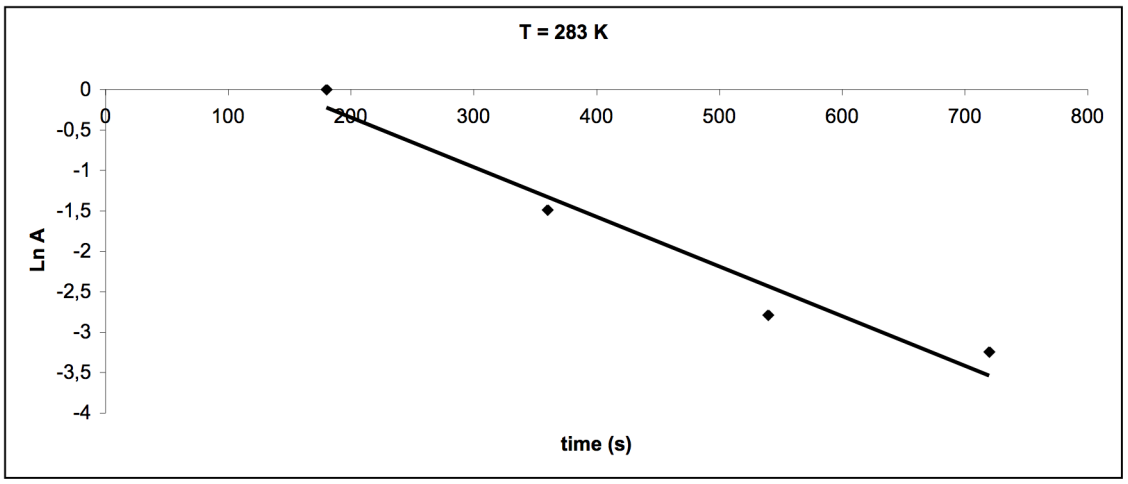

Ln A = 0.8768 + (-0.0061)t

r = 0.977

Eyring Equation: Activation Parameters

T (K)	k(s^{-1})	*k*/T	1/T	Ln *k*/T
283	0,0061	2,15548E-05	0,003533569	-10,74491341
273	0,0026	9,52381E-06	0,003663004	-11,56171563
263	0,0003	1,14068E-06	0,003802281	-13,68388212
253	0,0002	7,90514E-07	0,003952569	-14,05058268
243	0,00006	2,46914E-07	0,004115226	-15,21422744
233	0,00004	1,71674E-07	0,004291845	-15,57766956

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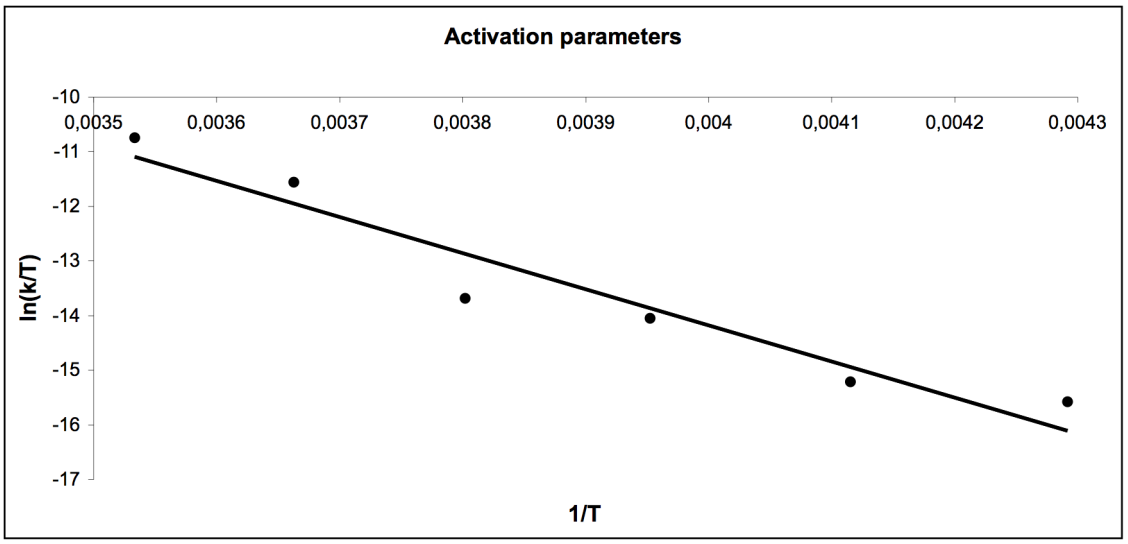

Linear fit: ln (*k*/T) = 12.284 + (-6616)/T

r = 0.96

Activation Parameters:

$\Delta H^{\neq}$ = 13.1 ± 0.5 Kcal/mol

$\Delta S^{\neq}$ = -22.8 ± 2.1 cal/mol

$\Delta G^{\neq}_{298}$ = 19.9 ± 2.1 Kcal/mol

Kinetics studies for skeletal rearrangement using complex **4f**:

Variation in the area of the olefinic H at 8.93 ppm was observed. As internal standard the signal of $CHCl_3$ at 7.26 ppm, was used.

T = 223 K

Time (s)	**Ln A**
300	0
600	-0,013398358
900	-0,02084475
1200	-0,036409867

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1500	-0,061374465
1800	-0,07672123
2100	-0,093324353
2400	-0,103788419
2700	-0,123961332
3000	-0,14217435
3300	-0,157093673
3600	-0,172947233
3900	-0,200594698
4200	-0,220377381
4500	-0,233633378
4800	-0,255235534
5100	-0,278761975
5400	-0,300042144
5700	-0,313987719
6000	-0,339091865
6300	-0,34983411
6600	-0,373019215
6900	-0,38905942
7200	-0,396341356
7500	-0,417444576
7800	-0,441952759
8100	-0,443405321
8400	-0,471869369
8700	-0,491472444
9000	-0,492404669
9300	-0,514318383
9600	-0,534851958
9900	-0,527390399
10200	-0,541446356
10500	-0,562424228
10800	-0,573561327

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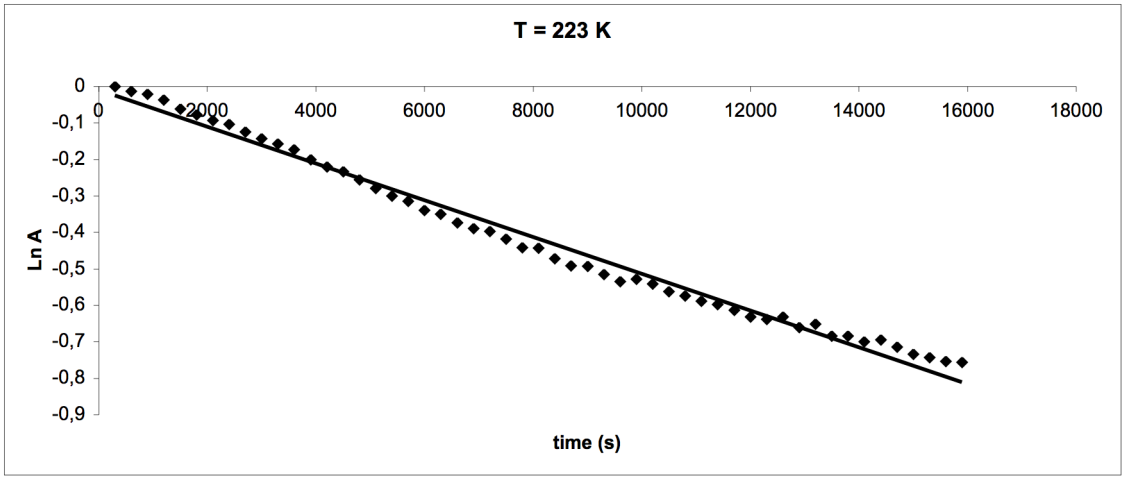
11100	-0,588145929
11400	-0,597913367
11700	-0,613620914
12000	-0,631079835
12300	-0,638032298
12600	-0,631222698
12900	-0,660836828
13200	-0,65098848
13500	-0,684013024
13800	-0,684286552
14100	-0,700151655
14400	-0,694892703
14700	-0,713556032
15000	-0,73358175
15300	-0,743112935
15600	-0,753776552
15900	-0,75580374



Ln A = -0.01 + (-0.00005)t

r = 0.993

T = 233 K

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Time (s)	Ln A
300	0
600	-0,065448802
900	-0,121669453
1200	-0,177342374
1500	-0,231226128
1800	-0,293765875
2100	-0,348770552
2400	-0,396225426
2700	-0,451026441
3000	-0,496318036
3300	-0,556321719
3600	-0,588480906
3900	-0,633776992
4200	-0,69518726
4500	-0,736119402
4800	-0,782133598
5100	-0,808941944
5400	-0,876969062
5700	-0,915363662
6000	-0,952643561
6300	-0,997088725
6600	-1,05299286
6900	-1,077877743
7200	-1,126434769
7500	-1,165951528
7800	-1,194342657

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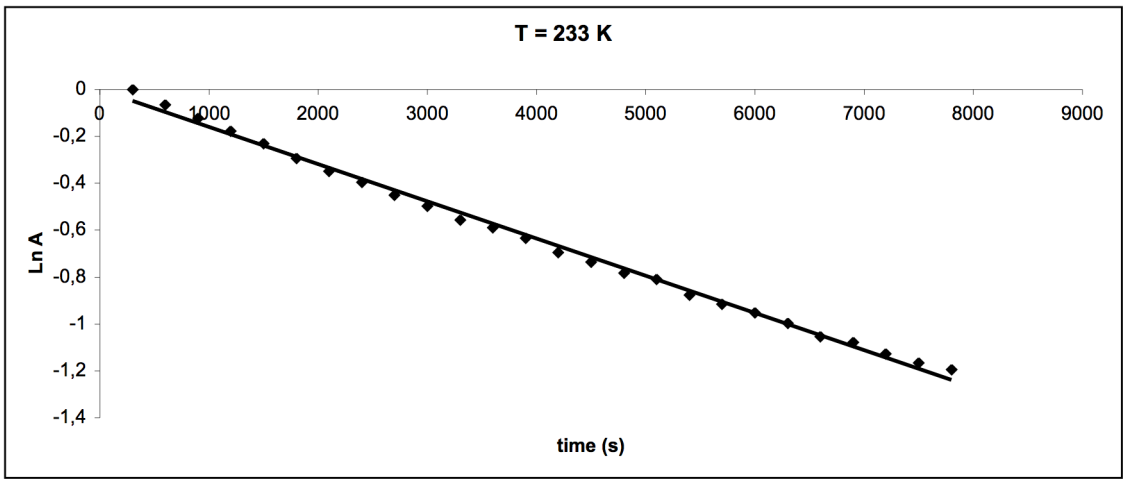

Ln A = -0.0019 + (-0.0002)t

r = 0.998

T = 243 K

Time (s)	Ln A
300	0
600	-0,207305882
900	-0,39156812
1200	-0,568309973
1500	-0,743403118
1800	-0,915845831
2100	-1,093974062
2400	-1,275651422
2700	-1,463114932
3000	-1,660126127
3300	-1,851184686
3600	-2,068026937
3900	-2,294081353
4200	-2,502586013
4500	-2,705872574
4800	-2,982934515
5100	-3,226857595

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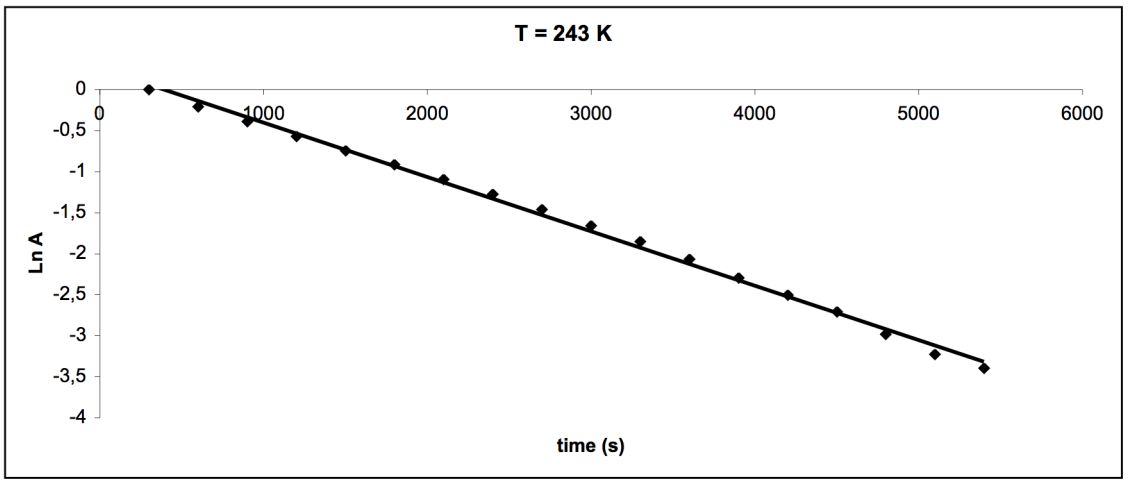
5400	-3,39617999



Ln A = 0.2569 + (-0.0007)t

r = 0.998

T = 253 K

Time (s)	Ln A
300	0
600	-0,583862375
900	-1,185468405
1200	-1,788492811
1500	-2,45143319
1800	-3,184691813
2100	-4,792102355
2700	-5,215447889

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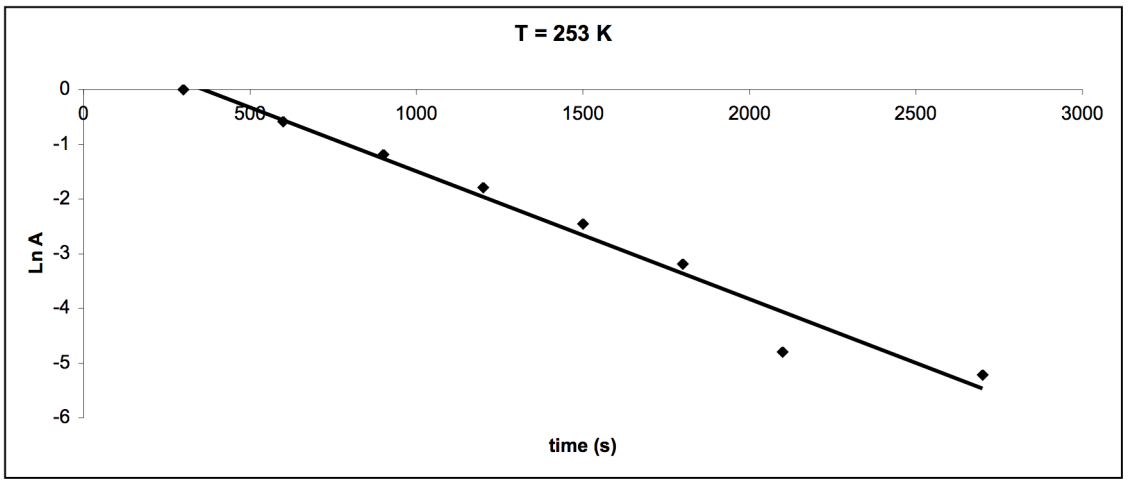

Ln A = 0.838 + (-0.0023)t

r = 0.985

T = 263 K

Time (s)	Ln A
300	0
600	-0,439361143
900	-0,926204713
1200	-1,451101718
1500	-1,964114854
1800	-2,434882961
2100	-2,965765787
2400	-3,507591765
2700	-3,857866314
3000	-4,101550462
3300	-4,760888761

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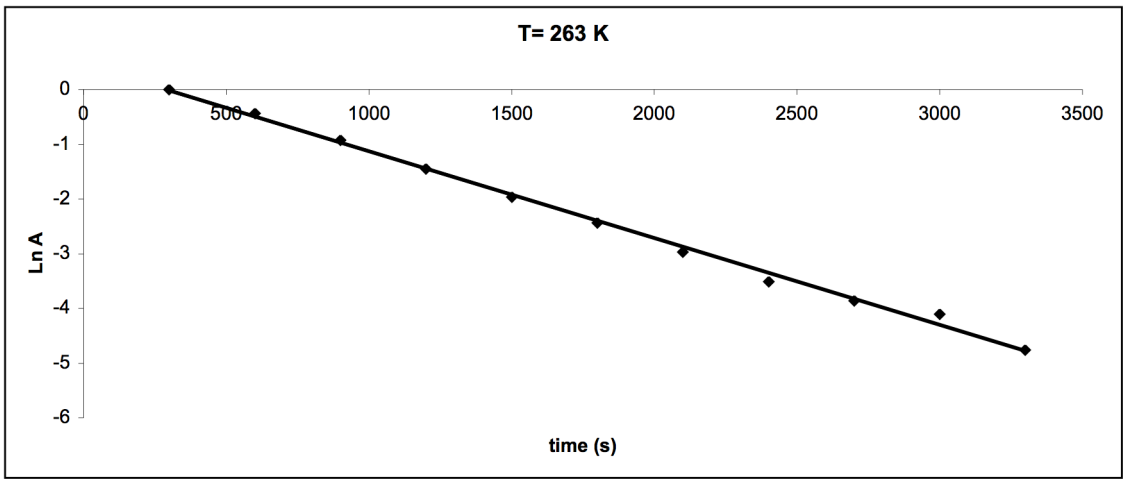
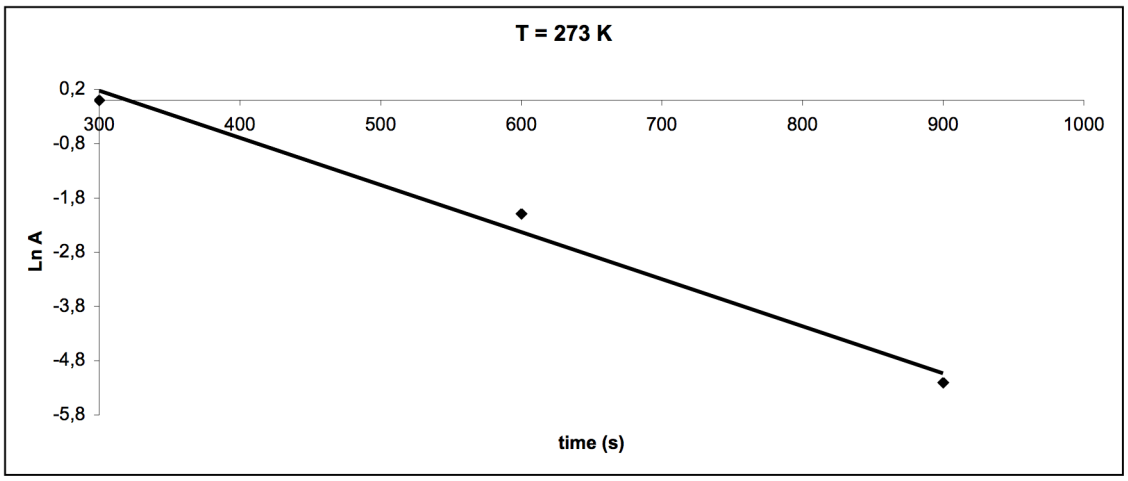


Ln A = 0.4553 + (-0.0016)t

r = 0.998

T = 273 K

Time (s)	Ln A
300	0
600	-2,089265641
900	-5,205373621



Ln A = 2.7738 + (-0.0087)t

r = 0.998

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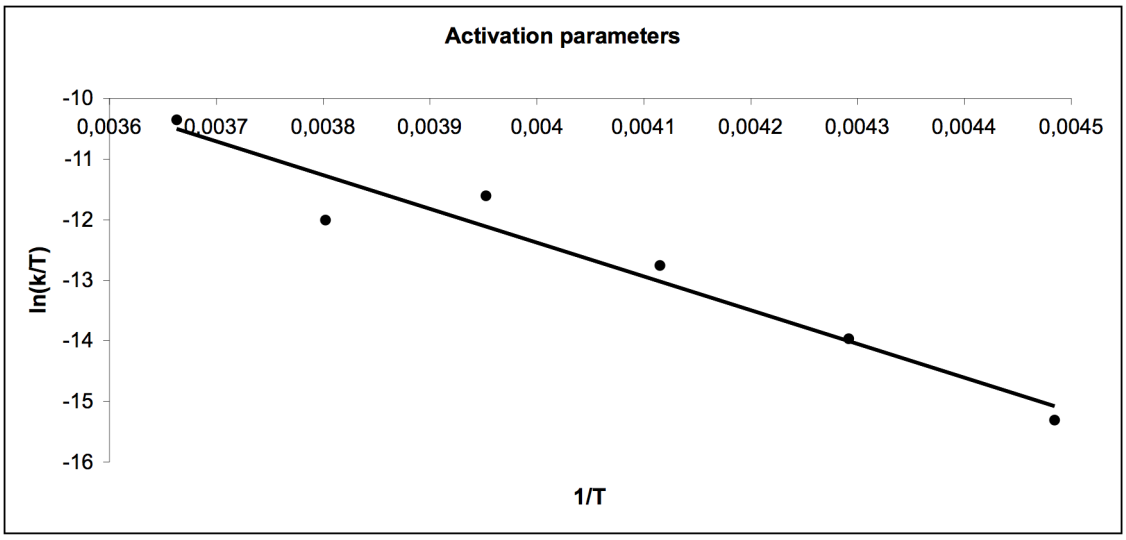
Eyring Equation: Activation Parameters

T (K)	k(s^{-1})	*k*/T	1/T	Ln *k*/T
273	0,0087	3,18681E-05	0,003663004	-10,35390405
263	0,0016	6,08365E-06	0,003802281	-12,00990568
253	0,0023	9,09091E-06	0,003952569	-11,60823564
243	0,0007	2,88066E-06	0,004115226	-12,75749167
233	0,0002	8,58369E-07	0,004291845	-13,96823164
223	0,00005	2,24215E-07	0,004484305	-15,31065932



Linear fit: ln (*k*/T) = 9.9071 + (-5572)/T

r = 0.97

Activation Parameters:

$\Delta H^{\neq}$ = 11.1 ± 0.3 Kcal/mol

$\Delta S^{\neq}$ = -27.5 ± 1.4 cal/mol

$\Delta G^{\neq}_{298}$ = 19.3 ± 1.5 Kcal/mol

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