Gold-Catalyzed Cycloisomerization Strategies to Carbocycles from Alkynes

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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ABSTRACT

The work in this thesis was undertaken in Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences in Nanyang Technological University from January 2010 to March 2014 under the supervision of Prof. Philip Wai Hong Chan.

The work of this thesis has been directed towards establishing gold-catalyzed intramolecular cyclization as novel synthetic strategies to carbocycles. This thesis is divided into three parts:

- Part I consists of Chapter I, which gives an introduction to gold catalysis and its application in the cycloisomerization of 1,*n*-enyne esters and 1,*n*-diyne carbonates and esters.
- Part II is aimed at exploring novel gold-catalyzed cyclization of 1,*n*-diyne esters and carbonates for the preparation of synthetically useful cyclic organic compounds. Chapter II addresses an efficient gold-catalyzed, expedient and chemoselective approach for the transformation of 1,6-diyne carbonates and esters to 2,4a-dihydro-1*H*-fluorenes which could be found in a lot of natural and synthetic compounds and functional materials. Chapter III describes an efficient gold-catalyzed cyclization strategy to structurally diverse 1*H*-cyclopenta[*b*]naphthalenes, cyclopenten-2-yl *δ*-ciketones and bicyclo[3.2.0]hepta-1,5-dienes.
- Part III contains the experimental data (Chapter V) and references (Chapter VI) pertaining to this thesis.

ABBREVIATIONS

Ac	acetate
Ar	aryl
Bu	butyl
Cbz	benzyloxycarbonyl
DCE	1,2-dichloroethane
DMAP	4-(dimethylamino)pyridine
ee	enantiomeric excess
equiv	equivalent
h	hour
IPr	1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
LDA	lithium diisopropylamide
Me	methyl
min	minute
m.p.	melting point
NMR	nuclear magnetic resonance
Nu	nucleophile
OMe	methoxyl
OTf	triflouromethanesulfonate
Ph	phenyl
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
Ts	*p*-methylphenylsulfonyl
α	alpha

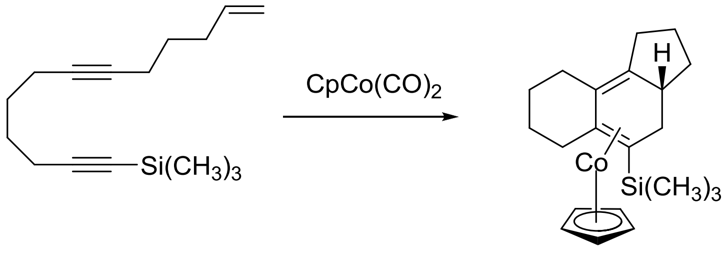
β	beta
δ	delta

Chapter I. Gold-Catalyzed Cycloisomerization of 1,*n*-Enyne Esters and 1,*n*-Diyne Carbonates and Esters

1.1 Introduction

Carbon-carbon bond forming reactions leading to the construction of carbocyclic structures are one of the most important fundamental pursuits in synthetic organic chemistry. This is because of the utility of carbocycles as building blocks in organic synthesis and their role as key structural features in many natural products and functional materials, selected examples of which are shown in Figure 1.1.[1]

A large majority of carbon-carbon bond formation reactions that lead to the generation of a carbocycle can be achieved by either free radical or pericyclic chemistry.[2] Another synthetic approach that has also been extensively explored is transition metal-catalyzed functional group transformations. In this area, intramolecular carbon-carbon bond formation reactions have attracted particular attention due to the atom- and step-economical nature of such synthetic methods. One of the early examples of this is the work of Vollhardt and co-workers, who demonstrated that by using $CpCo(CO)_2$ as a reagent, cyclization of enediyne **1** to the tricyclic product **2** could be achieved in 85% yield (Scheme 1.1).[3]

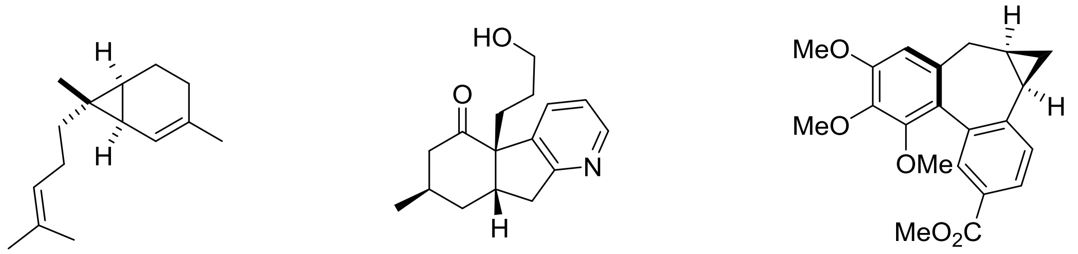


1

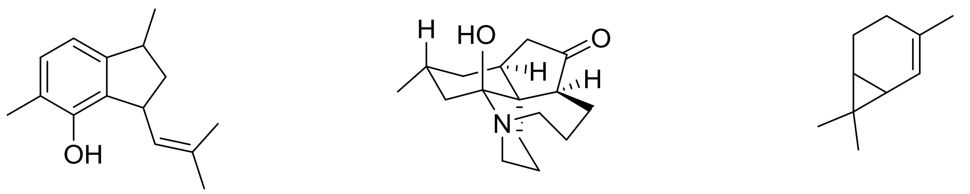
2

85% yield

Scheme 1.1 Intramolecular cyclization of enediyne with terminal double bond



Sesquicarene (+)-Lycopladine Allocolchicinoid



Jungianol (+)-Fawcettimine 2-Carene

Figure 1.1 Examples of natural products containing the carbocyclic motif

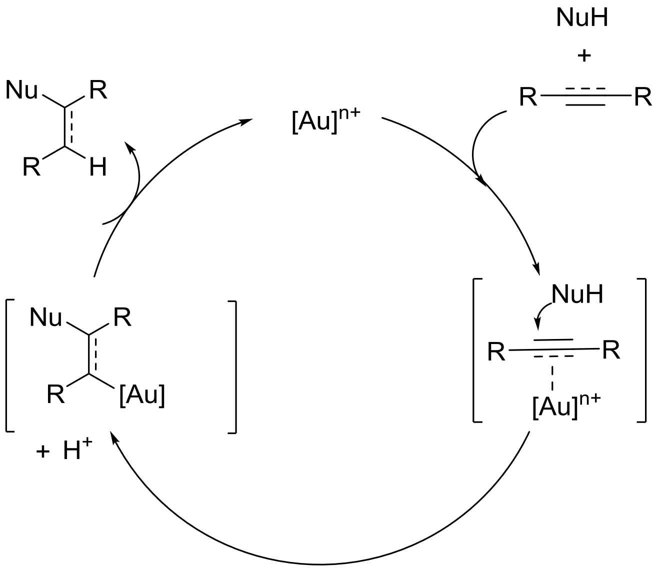
More recently, the establishing of novel catalytic synthetic routes to carbocycles has included the use of readily available gold catalysts.[4] Typically, the gold complexes and salts were shown to activate the π bonds of alkenes, alkynes and allenes that made them susceptible to subsequent attack by a carbonucleophile to form the new carbon-carbon bond and generation of the carbocycle. This Introduction will focus on the advances made in the development of gold-catalyzed reactions of 1,*n*-enyne and 1,*n*-diyne carbonates and esters as highly efficient and selective methods for stereoseletive carbocyclic ring formation.

1.2 Gold as a Lewis Acidic Catalyst

Traditionally, gold was seen as both a catalytically inactive and economically unviable catalyst due to its high monetary value. Added to this, early reports using gold as a catalyst did not show it to be superior to other metal catalysts. For these three main factors, the field of hetero- and homogeneous gold catalysis was neglected for much of the last century. However, this all changed in 1973 when Bond and co-workers reported the hydrogenation of olefins over a supported gold catalyst.[5] Since this initial discovery, the number of reports describing gold as an efficient catalyst which either matches or exceeds other metal complexes to mediate organic transformations has exponentially increased year on year.[6]

Gold is naturally more abundant than palladium, platinum and rhodium. Metallic complexes and salts of the Group 11 element are both tolerant to air and moisture. Gold(0), gold(I), and gold(III) are the most common oxidation states arriving from the outer $5d^{10}6s^1$ electronic configuration of the element. Of the three possible oxidation states, complexes and salts of Au(I) and Au(III) exhibit highly selective Lewis acidic activity with a high affinity for π bonds of alkenes, alkynes and allenes. This π-acidity of cationic gold complexes is due to relativistic effects, which results from contraction and lowering in energy of the lowest unoccupied molecular orbital (LUMO) of the 6s orbital of Au, the primary acceptor of electron density from the highest occupied molecular orbital (HOMO) π orbital of π bonds.[7]

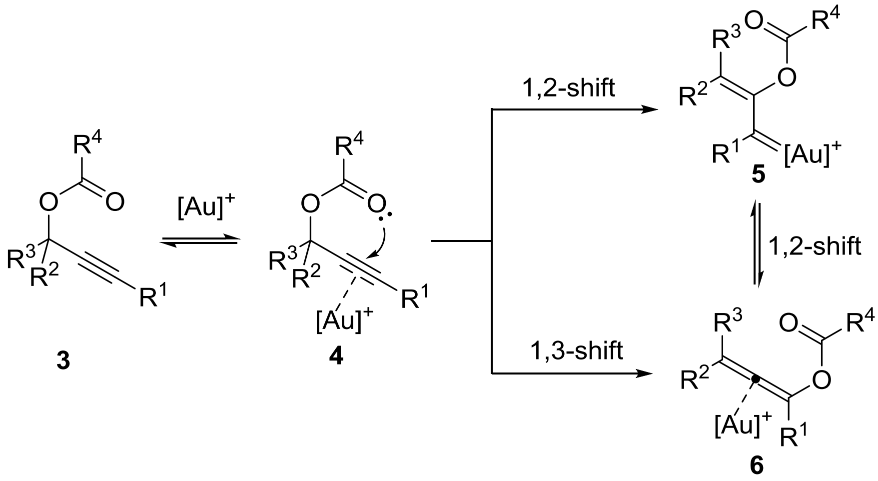
A common reactivity pattern in gold catalysis is activation of the carbon-carbon multiple bond of an alkyne, alkene or allene by the metal. This is followed by attack by a nucleophile and, typically, proto-deauration to release the Lewis acid catalyst and the product. The general mechanism in gold catalysis, whereby the oxidation state of the metal center does not change, is shown in Scheme 1.2.



Scheme 1.2 General mechanism for gold catalysis

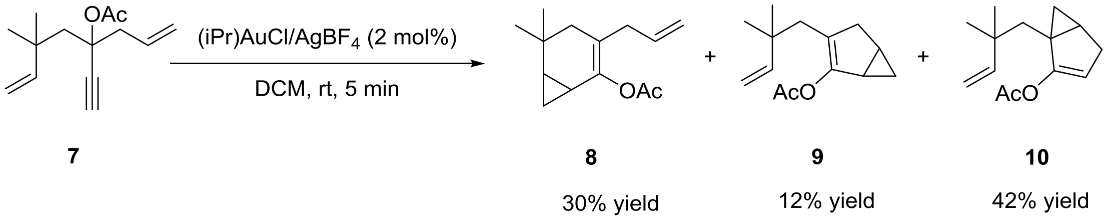
1.3 Gold-Catalyzed Cycloisomerization of 1,*n*-Enyne Esters

Gold-catalyzed migration reactions of propargylic esters have emerged as a powerful tool for the synthesis of natural products and complex molecules, which can not easily be achieved by conventional methods during the last decade.[8] One rapidly developing and interesting area within the field is the migration of 1,*n*-enyne esters in which the carbonyl group acts as a nucleophile by adding onto the gold activated alkyne. This results in either 1,2 or 1,3-acyloxy migration to provide the respective gold carbenoid species **5** or allene intermediate **6** (Scheme 1.3). Further functionalization of these newly formed intermediates can then give the opportunity to develop a wide range of transformations, the recent progress of which is discussed in this section.



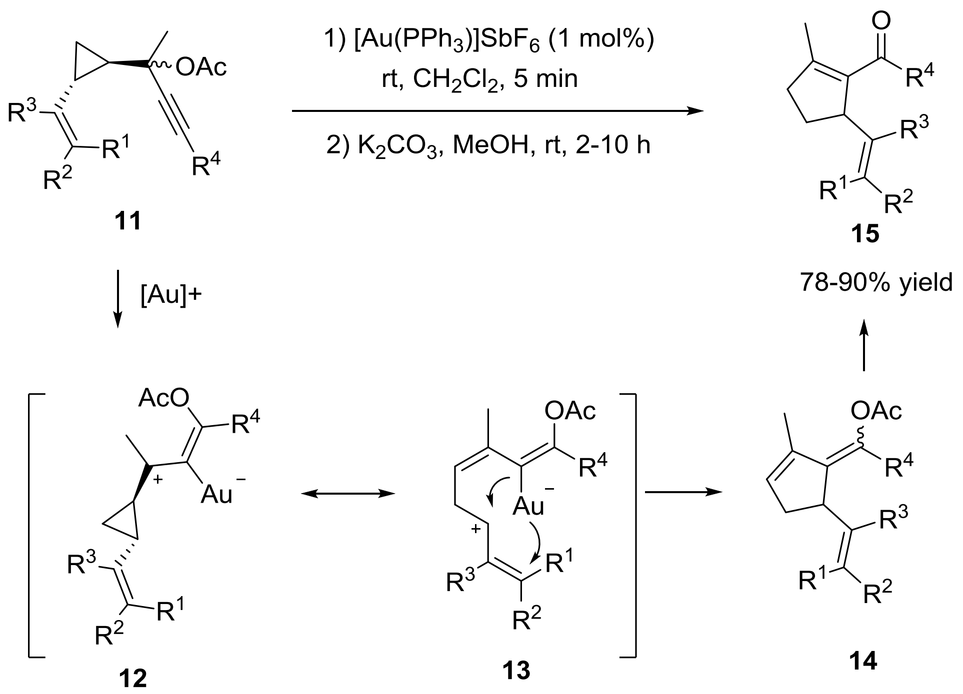
Scheme 1.3 Gold-catalyzed reactivities of 1,*n*-enyne carboxylates

In 2006, Nolan and co-workers[9] reported (NHC)-Au(I) (NHC = *N*-heterocyclic carbene)-catalyzed cyclization of enyne propargylic ester **7** to form bicyclo[3.1.0]hexene **10** in 42% yield (Scheme 1.4). In this work, it appeared that the formation of the [3.1.0] bicyclic derivative required very specific steric and electronic properties from the ancillary ligand at the gold center.

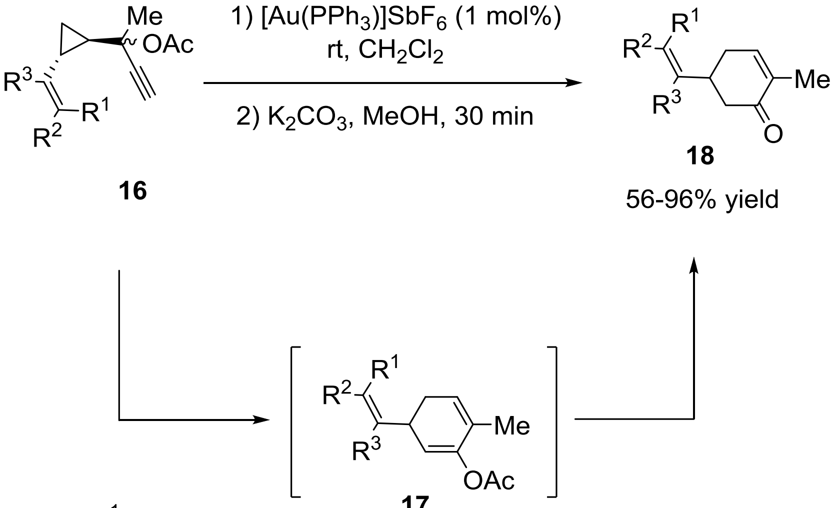


Scheme 1.4 Gold-catalyzed cyclization of 1,5-enyne esters to bicyclo[3.1.0]hexane

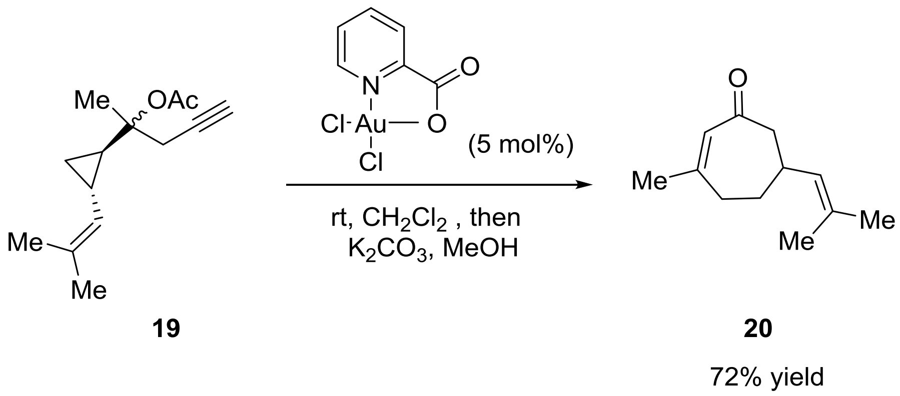
Following this work, Goeke, Nevado, Wang and co-workers[10] reported that gold-catalyzed Rautenstrauch rearrangement[11] of 1-cyclopropylpropargylic esters **11**, **16**, and **19** gave cyclopentenyl ketones **15**, cyclohexenones **18** and cycloheptenone **20** (Scheme 1.5). In this work, the formation of the cyclopentenyl ketones **15** in 78-90% yield was reported to proceed via the cationic vinyl gold species **12** and its resonance structure **13**. In this latter species, cyclization at the allyl cationic position may occur,



R^1 = H, Me
R^2 = Me, Phenyl
R^3 = H, Me
R^4 = Me, cyclopropyl



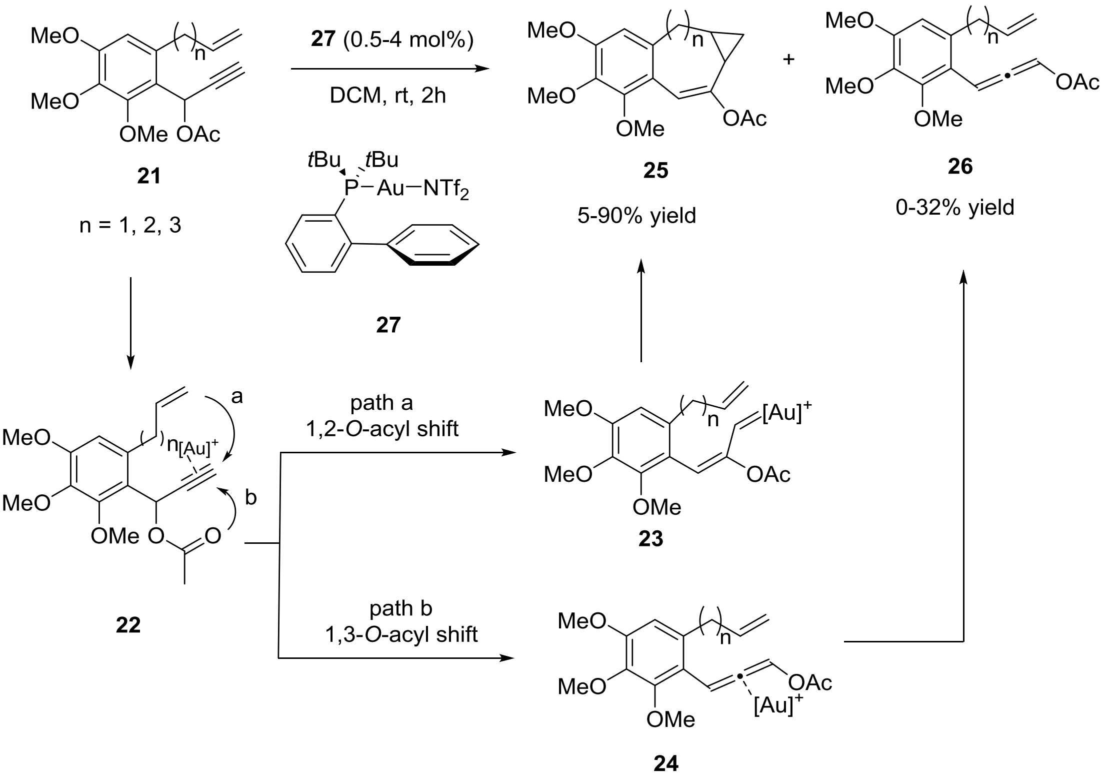
R^1 = H, alkyl
R^2 = alkyl, aryl
R^3 = H, Me



Scheme 1.5 Gold-catalyzed cycloisomerization of cyclopropyl alkynyl acetates to 5-, 6-, and 7-membered carbocycles

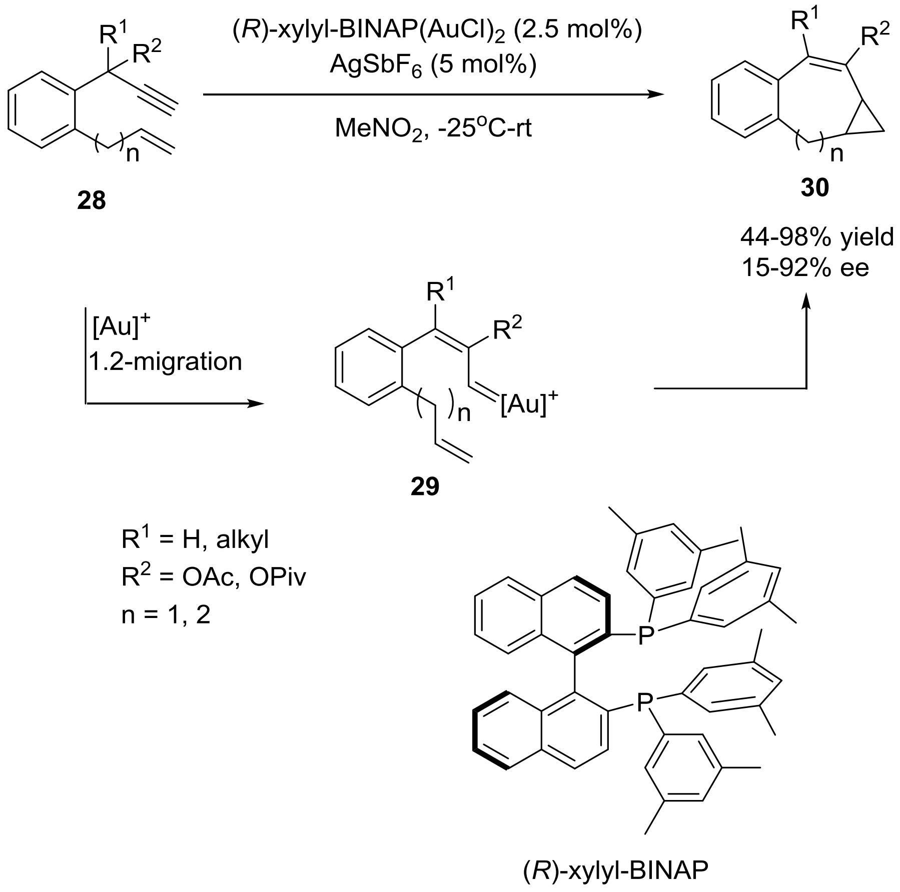
but only trienyl acetate **14** was obtained in almost quantitative yield and as a mixture of *cis* and *trans* isomers. Finally, cyclopentenyl ketones **15** could be abtained via deacylation of the vinyl acetate **14**. On the other hand, substrates **16** and **19** cyclised smoothly affording cyclohexenone **18** and cycloheptenone **20** in 56-96% yield and 72% yield, respectively. In addition, optically active propargyl acetates could be converted to the enantioenriched cyclohexenones and cyclopentenyl ketones through this method.

At about the same time, Hanna, Goff, and Boyer reported that Au(I)-catalyzed cycloisomerization of 1,7 and 1,8-enyne propargylic acetates **21** provided tricyclic enol esters **25** in 5-90% yield (Scheme 1.6).[12] In their work, the mechanism was proposed to involve either 1,2 or 1,3-acyloxy shift to give the corresponding gold carbenoid intermediate **23** or gold(I)-activated allene species **24**. Further functionalization of these intermediates was then proposed to lead to the tricyclic derivative **25** and allene acetate **26**, respectively. The **25/26** ratio was thought to mainly depend on the ring size. For *n* = 1, ring closure of intermediate **23** occurred exclusively, giving the cycloheptyl derivative **25**. For *n* = 2 and 3, the strain incurred in forming eight- and nine-membered rings was reported to make path a more difficult and this was pointed to the formation of allenyl acetates **26.**



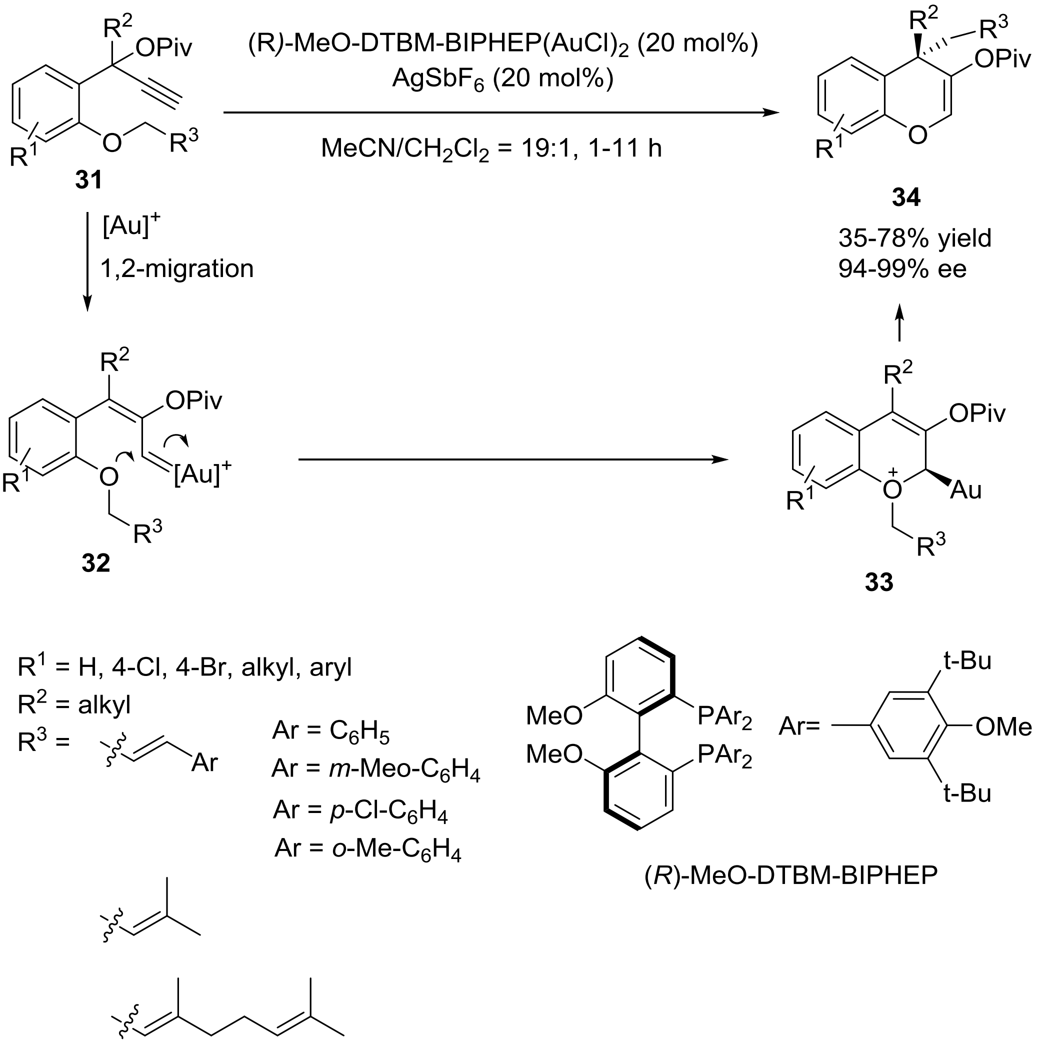
Scheme 1.6 Gold-catalyzed cycloisomerization of 1,7- and 1,8-enynes to allocolchicinoids

In 2009, Toste and co-workers[13] described a cascade process involving gold-catalyzed asymmetric intramolecular alkene cyclopropanation for the enantioselective synthesis of 7- and 8-membered rings **30** in 44-98% yield and with ee (ee = enantiomeric excess) values up to 92% (Scheme 1.7). In this study, an initial 1,2-migration of the propargyl ester occurred allowing for the formation of the carbenoid intermediate **29** and then followed by the cyclopropanation to give the product **30**. This work greatly expanded the class of enantioselective transformations of transition metal-catalyzed enyne cycloisomerization reactions which were usually limited to the synthesis of 5- and 6-membered rings.



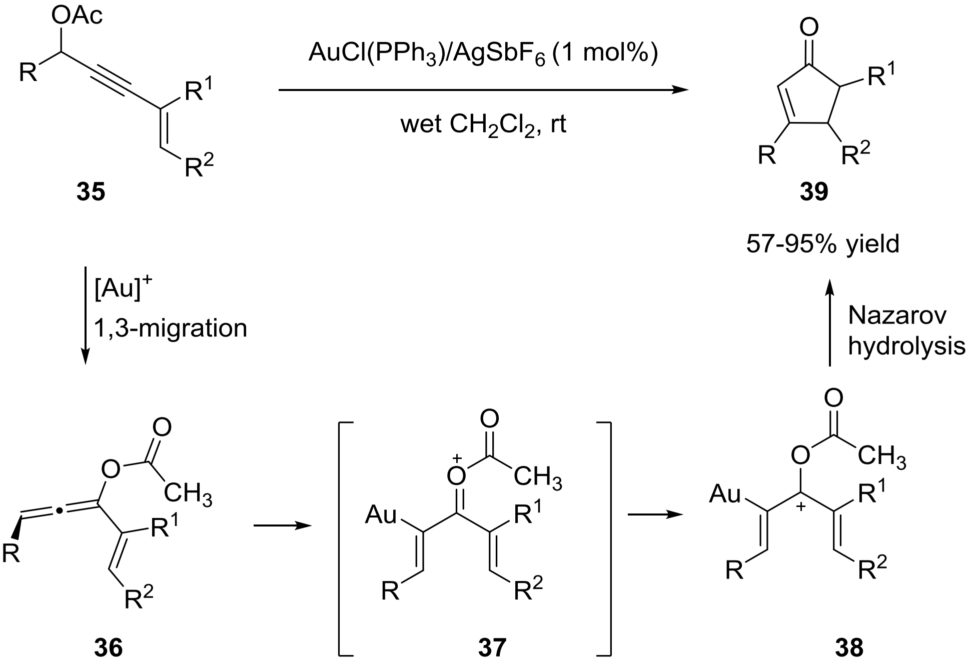
Scheme 1.7 Asymmetric synthesis of medium-sized rings from enyne proparylic acetate by intramolecular gold-catalyzed cyclopropanation

In the same year, Toste and co-workers[14] reported gold-catalyzed enantioselective synthesis of benzopyrans **34** in 35-78% yield and 94-99% ee (Scheme 1.8). As one of the few examples of enantioselective transformations involving transition metal carbenoid intermediates, this work provided benzopyrans containing quaternary stereocenters with excellent enantioselectivity. In the proposed mechanism, it was suggested that the gold(I)-promoted 1,2-migration of propargyl ester **31** gave the corresponding gold(I) carbenoid species **32**, which was subsequently attacked by the ethereal oxygen to generate oxonium intermediate **33**. Further rearrangement of this adduct was proposed to give the benzopyran **34**. This work significantly extended the scope of enantioseletive tranformations of transition metal carbenoid intermediates which were formed via 1,2- migration of propargyl esters.



Scheme 1.8 Gold-catalyzed enantioselective synthesis of benzopyrans

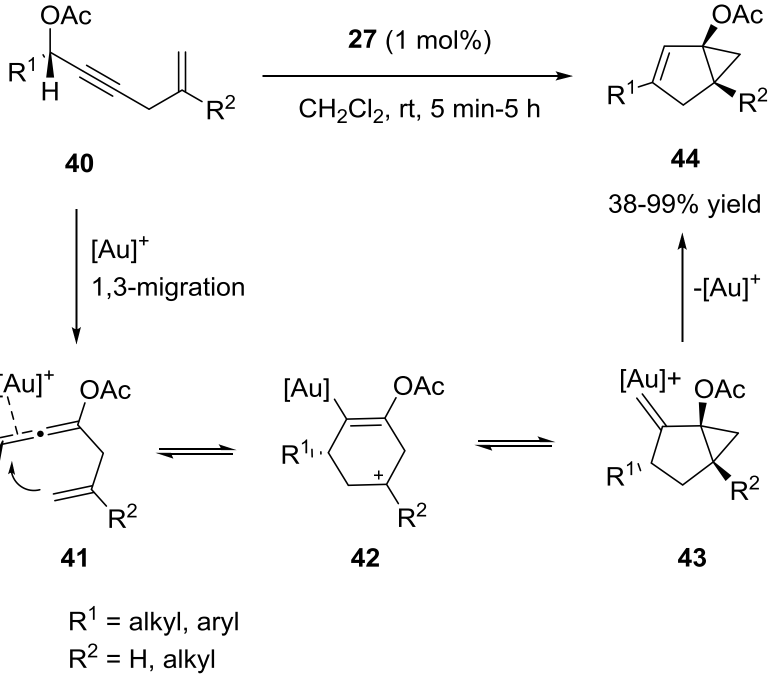
In 2006, the Zhang group reported an efficient method for the preparation of various cyclopentenones **39** in 57-95% yield from enynyl acetates **35** (Scheme 1.9).[15] In this work, they proposed the mechanism involved tandem Au(I)-catalyzed [3,3] sigmatropic rearrangement and Nazarov cyclization of the resulting allenic ester **36**. The substrate scope of this reaction was found to be broad and flexible, allowing for excellent control of the double bond position in the cyclopentenone ring that addressed such limitations in previous Nazarov cyclization approaches to cyclopentenones.



R = alkyl
R^1 = H, alkyl, aryl
R^2 = H, alkyl

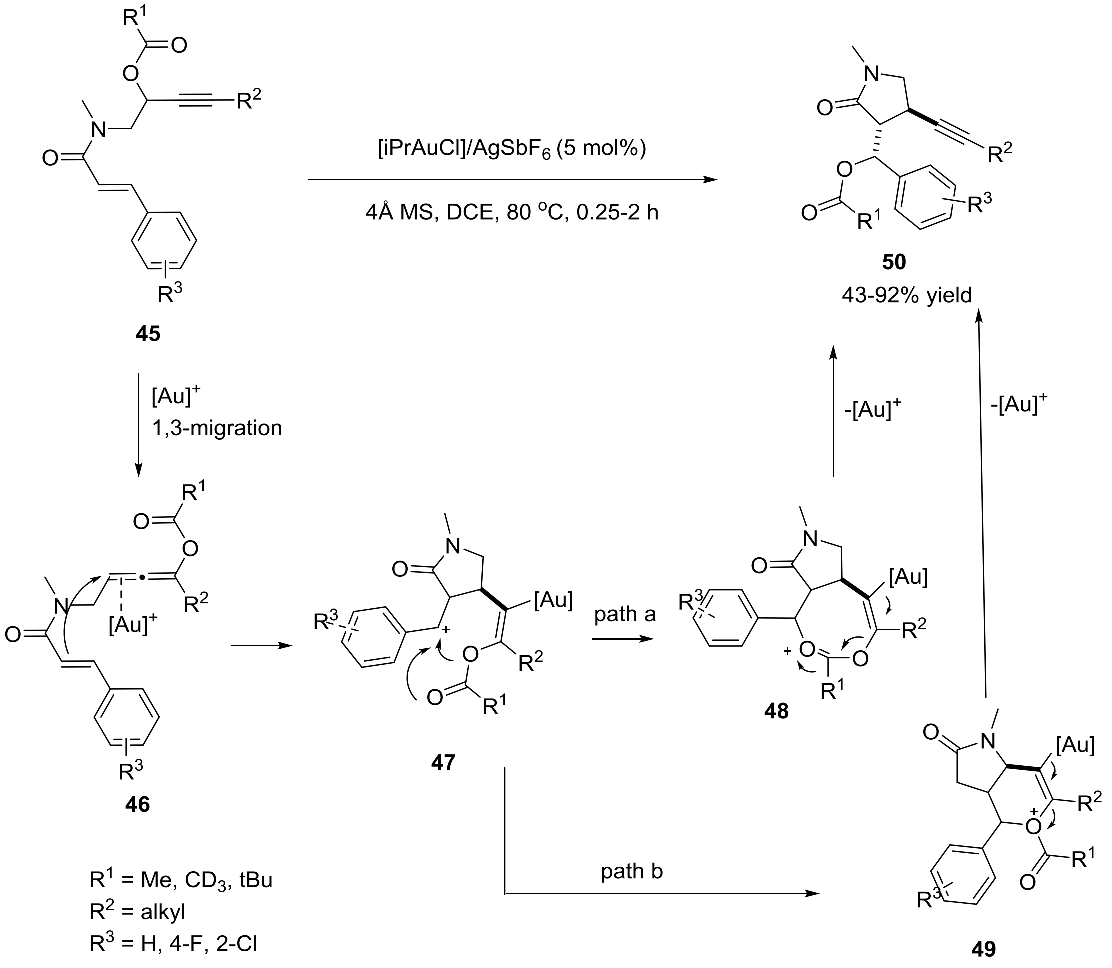
Scheme 1.9 Gold-catalyzed cycloisomerization of enynyl acetates to cyclopentenones

In the same year, Gagosz and co-workers developed an efficient method for the cycloisomerization of 5-en-2-yn-1-yl acetates **40** to acetoxy bicyclo[3.1.0]hexenes **44** in 38-99% yield (Scheme 2.0).[16] They proposed the mechanism to follow initial gold activation of the triple bond in the substrate to provide the allene intermediate **41** through a [3,3]-sigmatropic rearrangement. The allene intermediate was then further activated by the gold catalyst to induce nucleophilic attack of the pendant alkene to form the cationic gold species **42**, which could be converted to the gold carbenoid adduct **43** assisted by electron donation from the gold center. A final hydride shift in the gold carbenoid complex was thought to release the gold catalyst and produce the bicycle[3.1.0]hexane **44**. The presence of the acetoxy functionality at the ring junction allowed for the cycloisomerized product being further converted to 2-cycloalken-1-ones and cyclohexenones, which were noted as important building blocks in a number of total synthesis strategies.



Scheme 1.10 Gold-catalyzed isomerization of 5-en-2-yn-1-yl acetates to acetoxy bicyclo[3.1.0]hexenes

More recently, Hashmi and co-workers reported the first example of long-range 1,6-acyloxy migration in enyne ester **45** that gave 3,4-disubstituted pyrrolidin-2-ones **50** in 43-92% yield (Scheme 1.11).[17] In this work, it was proposed the mechanism involved tandem 1,3-acyloxy migration of enyne ester to form the allene intermediate **46**. Subsequent nucleophilic attack of the the pendant alkene onto the gold-activated allene species was suggested to lead to intermediate **47**. The intermediate **47** could be further converted to intermediates **48** and **49** via pathways a and b. Both pathways could lead to the formation of product **50**. This long-range 1,6-acyloxy migration was an intramolecular reaction without elimination of the acyloxy group, which was supported by crossover experiments. In addition, the transformation was demonstrated to access diastereomerically pure 3,4-disubstituted pyrrolidin-2-ones.

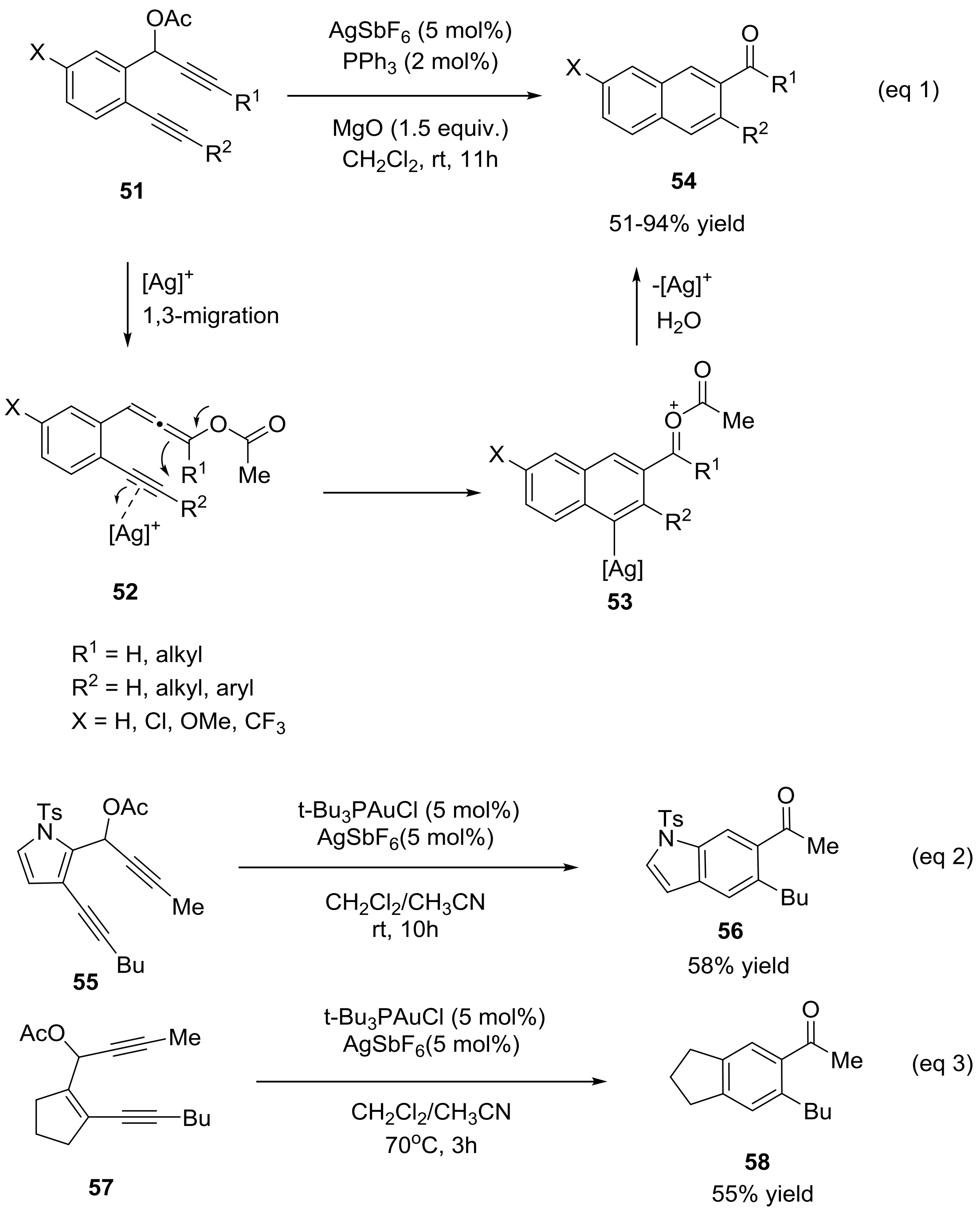


Scheme 1.11 Gold-catalyzed 1,6-acyloxy migration leading to 3,4-disubstituted pyrrolidin-2-ones

1.4 Gold-Catalyzed Cycloisomerization of 1,*n*-Diyne Carbonates and Esters

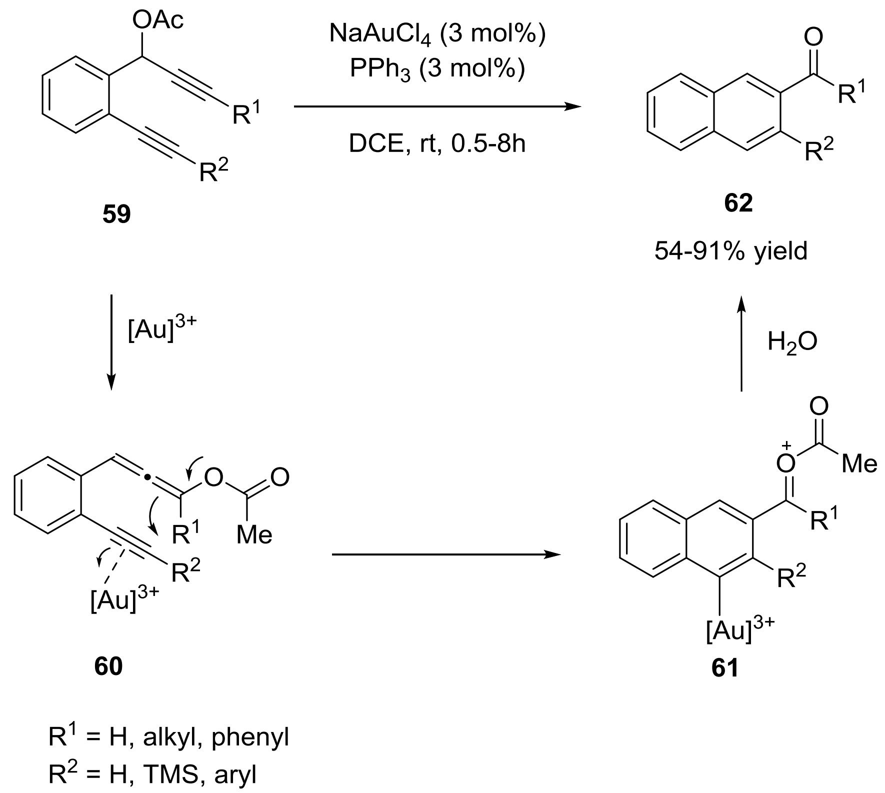
In recent years, there has been a large number of elegant methods describing cycloisomerization of 1,*n*-diynes containing a carboxylic ester or carbonate moiety at one of the propargylic positions to synthetically useful cyclic compounds.[18] The mechanism typically involves 1,2- or 1,3-acyloxy migration.[19, 20] It is well known that terminal or electronically demanding alkynes react via a 1,2-migration pathway, whereas internal alkynes react by a 1,3-migration pathway.[19] The recent progress in this field is discussed in this section.

In 2006, Toste and co-workers reported the gold-catalyzed cyclization of alkyne propargylic esters **55** and **57** to form aryl ketones **56** and **58** in 58% and 55% yield, respectively (Scheme 1.12).[18f] In their initial work, they found silver as catalyst could achieve aryl ketones **54** in 51-94% yield from alkyne propargylic esters **51**. In most cases, the silver-catalyzed naphthyl ketone synthesis proceeded as well or better than the gold(I)-catalyzed version. However, rearrangement of pyrroles **55** and enediynes **57** failed to produce the desired aromatic ketones (Scheme 1.12, eq 2 and 3). In these cases, they found *t*-Bu_3PAuCl could serve as effective catalyst to deliver indoles **56** and acetophenones **58** from those respective substrates. Mechanistically, it was proposed that 1,3-migration of the ester functional group and subsequent activation of the remaining alkyne by the metal catalyst induced 6-*endo*-dig addition of the allenyl ester **52**. Further hydrolysis of the oxocarbenium ion interrmediate **53** gave the aromatic ketone **54**. In view of the acetic acid generated after hydrolysis possibly consuming the silver catalyst during the course of reaction, it was found addition of MgO could improve the reaction yield for the reason that it can serve as an acid scavenger during the reaction. To further support the mechanism, the allene intermediate was successfully isolated and resubjected to the reacition conditions to afford the expected naphthyl ketone in excellent yield. Overall, the reaction conditions were reported to be moisture- and air-tolerant, allowing a variety of substrates being converted to the corresponding aryl ketones under mild conditions. In this work, the limitations of Ag catalysis were addressed simply through the use of Au(I) catalysis.



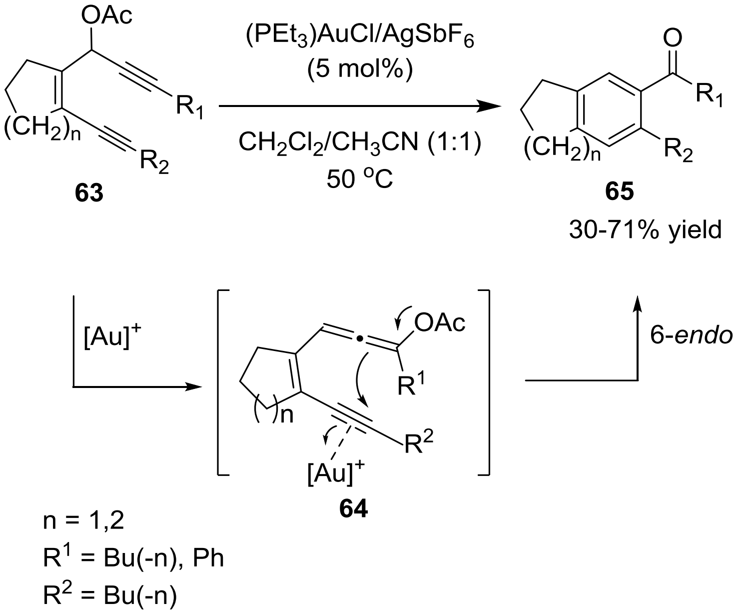
Scheme 1.12 Gold-catalyzed tandem [3,3]-sigmatropic rearrangement and formal Myers-Saito cyclization[21] of alkyne propargylic esters to aromatic ketones

At about the same time, Oh and Kim reported a similar method for the cycloisomerization of alkyne propargylic acetates **59** to obtain 2-acyl-3-arylnaphthalenes **62** in 54-91% yield (Scheme 1.13).[22] In the reported mechanism study, a similar pathway was proposed involving initial 1,3-migration of the ester functional group of diyne ester of **59** to give allene intermediate **60**. Further hydrolysis of the oxocarbenium ion intermediate **61** gave the aromatic ketone **62**. In addition, the approach was much simpler and more environmentally benign in terms of reaction conditions because of neither a co-catalyst nor additive was necessary.



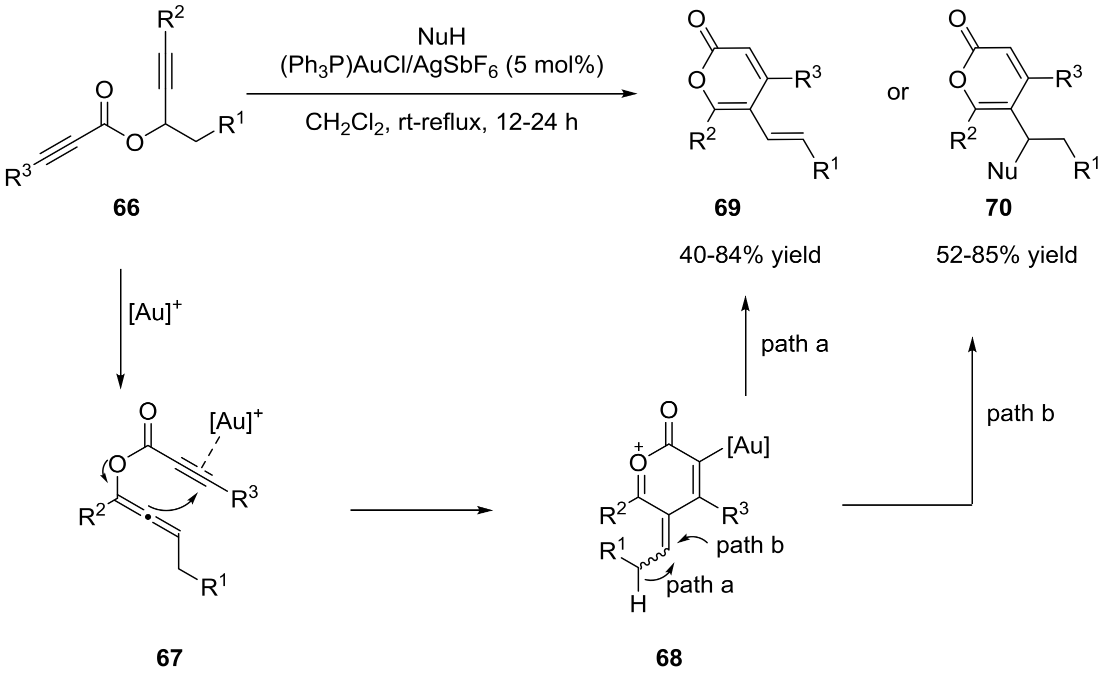
Scheme 1.13 Gold-catalyzed cyclization of alkyne propargylic acetates to 2-acyl-3-arylnaphthalenes

In 2007, Oh and Kim extended this approach to the cycloisomerization of alkyne propargylic esters **63** without a structurally rigid phenyl group as a cyclic linker to obtain cyclization product **65** in 30-71% yield (Scheme 1.14).[18e] In the reported mechanism study, a similar pathway was proposed involving initial 1,3-migration of the ester functional group of diyne ester **63** to give the allene intermediate **64**. Further functionalization of this intermediate then gave the aromatic ketones **65**. In addition, the approach provided a rapid route to valuable building blocks for polycyclic compound synthesis by simply modifying the substrate. Overall, the method described a convenient method for the formation of the 2-acyl-1,3-butadiene skeleton from gold-catalyzed cyclization of alkyne propargylic acetates.



Scheme 1.14 Gold-catalyzed cyclization of alkyne propargylic esters with fixed orientations of reacting alkyne and propargylic groups

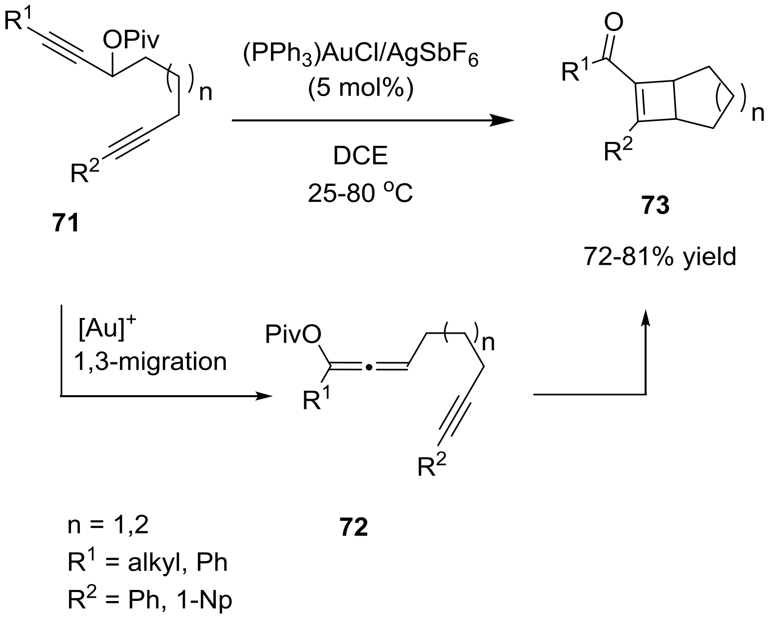
In the same year, Schreiber and co-workers reported the synthesis of trisubstituted pyrones **69** and **70** from diyne esters **66** in 40-84% and 52-85% yield, respectively (Scheme 1.15).[18d] The work was inspired by the earlier report of Toste and co-workers for the synthesis of aromatic ketones involving [3,3] sigmatropic rearrangement followed by 6-*endo*-dig cyclization cascade reaction of alkyne propargylic esters **55**. It was postulated that the propargyl propiolate **66** was firstly converted to the allene ester **67** by 1,3-acyloxy migration. This intermediate **67** was then transformed to the oxocarbenium intermediate **68** similar to that reported by Toste and co-workers. Elimination of a proton and demetalation was thought to lead to the vinyl pyrones **69**, while trapping attack using an electronic rich arene as a nucleophile gave **70**. Overall, this method provided an alternative way for the preparation of pyrones.



R^1 = H, alkyl, aryl
R^2 = alkyl, aryl
R^3 = alkyl, phenyl
Nu = aryl, furan, indole

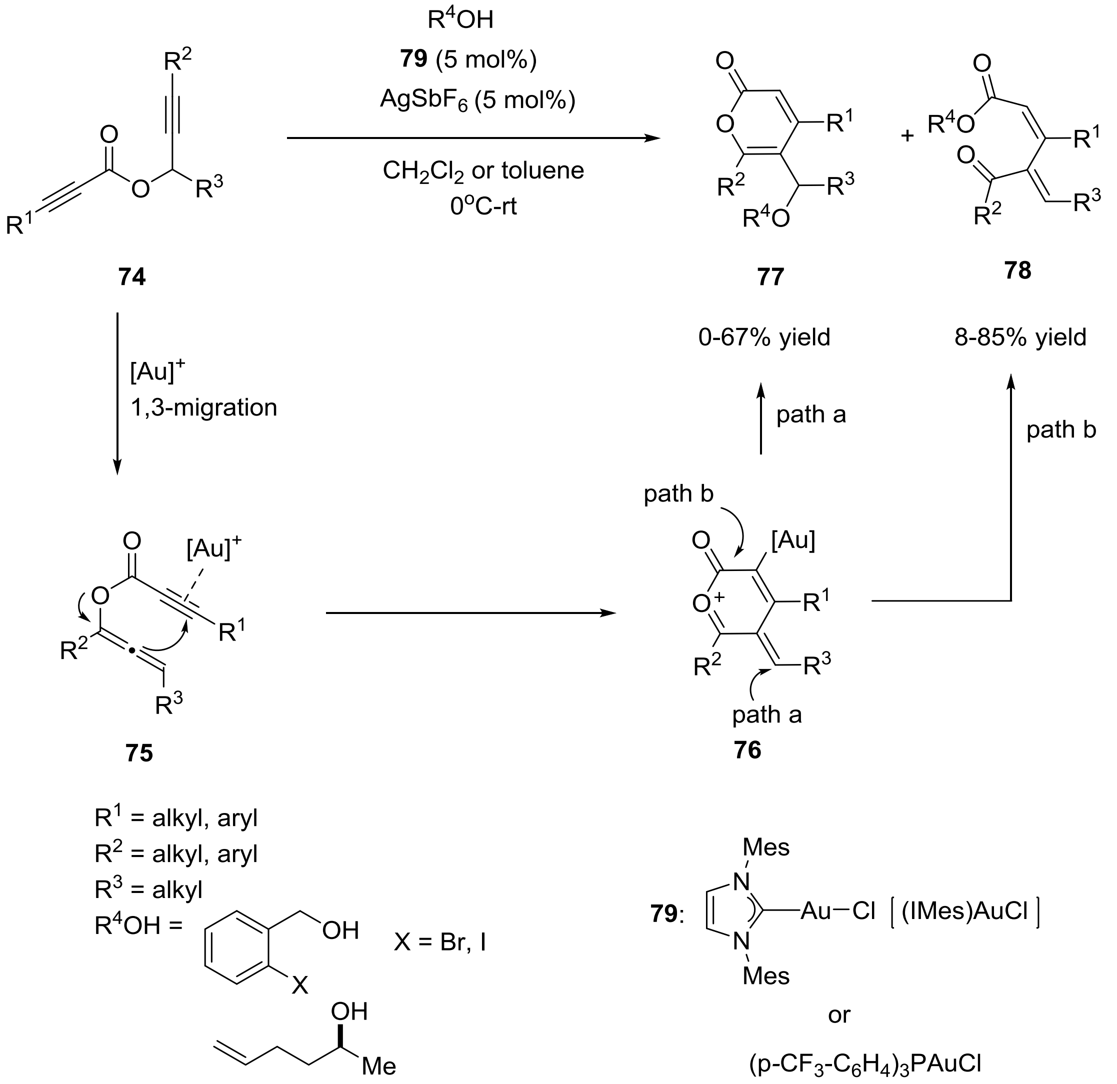
Scheme 1.15 Syntheses of trisubstituted pyrones by gold-catalyzed cascade reactions

In 2008, Oh and Kim reported the synthesis of fused bicyclic compounds **73** from alkyne propargylic pivaloates **71** in 72-81% yield (Scheme 1.16).[23] In this work, propargylic alkyne **71** was activated by the gold catalyst to afford allene intermediate **72** by 1,3-acyloxy migration, followed by direct [2+2] pathway leading to the [3.2.0] and [4.2.0] bicycles **73**. As a whole, the method provided an efficient and easy way for the preparation of valuable building blocks for polycyclic compounds.



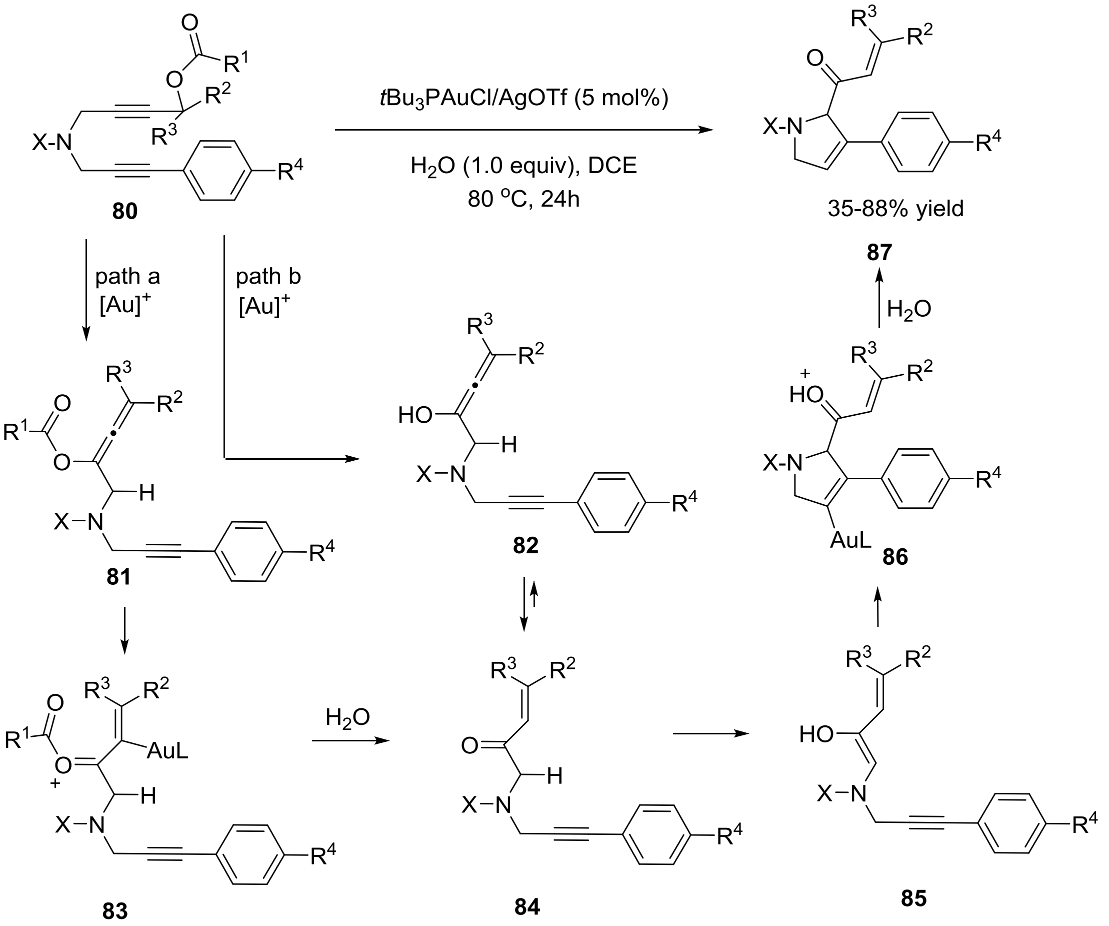
Scheme 1.16 Gold(I)-catalyzed cyclization of alkyne-pivaloates to fused bicyclic compounds

In 2009, the same group described an extension of this work by using an alcohol as the nucleophile to provide **77** and **78** in up to 85% yield (Scheme 1.17).[18c] In this work, the propargyl propiolate **74** was transferred to enyne allene intermediate **75** via 1,3-migration and then followed by the formation of the oxocarbenium **76** by a 6-*endo*-dig cyclization. Compounds **77** and **78** could be achieved by trapping of the intermediate **76** by an alcohol nucleophile at two distinct positions (pathways a and b). The distribution of the two products was adjusted by varying the ligand which could tune the electron-density of the gold(I) catalyst. In their study of the regioselectivity, three factors were considered. Firstly, it was found that the more electron-donating ligand could facilitate the formation of ketoester **78**. Secondly, since the linear coordinative pattern of the gold complex, the steric effects of different ligands did not influence the regioselectivity of the reaction. Finally, the size of the nucleophile could also affect the regioselectivity of the reaction. It was found that the larger secondary alcohol preferentially attacked the carbonyl of intermediate **76** affording the ketoester **78** as the major product.



Scheme 1.17 Gold(I)-catalyzed cascade reactions of propargyl propiolates

In 2011, Shi and co-workers reported the first example in which gold-catalyzed cycloisomerization of internal 1,6-diyne esters **80** connected by a nitrogen atom gave nitrogen-containing five-membered heterocyclic rings **87** in 35-88% yield (Scheme 1.18).[24] In this work, it was proposed that this reaction was likely to proceed via two possible pathways. In pathway a, 1,6-diyne ester **80** was activated by gold catalyst to give allene intermediate **81** via [3,3]-sigmatropic rearrangement and then followed by the formation of oxonium intermediate **83** which could undergo hydrolysis to give enone **84**. The enone **84** could undergo a Lewis acid catalyzed enolization to give intermediate **85**. Further activation of the remaining alkyne moiety of intermediate **85** by the gold complex could lead to a 5-*endo*-dig cycloaddition to give intermediate **86**. The hydrolysis of intermediate **86** provided product **87**.

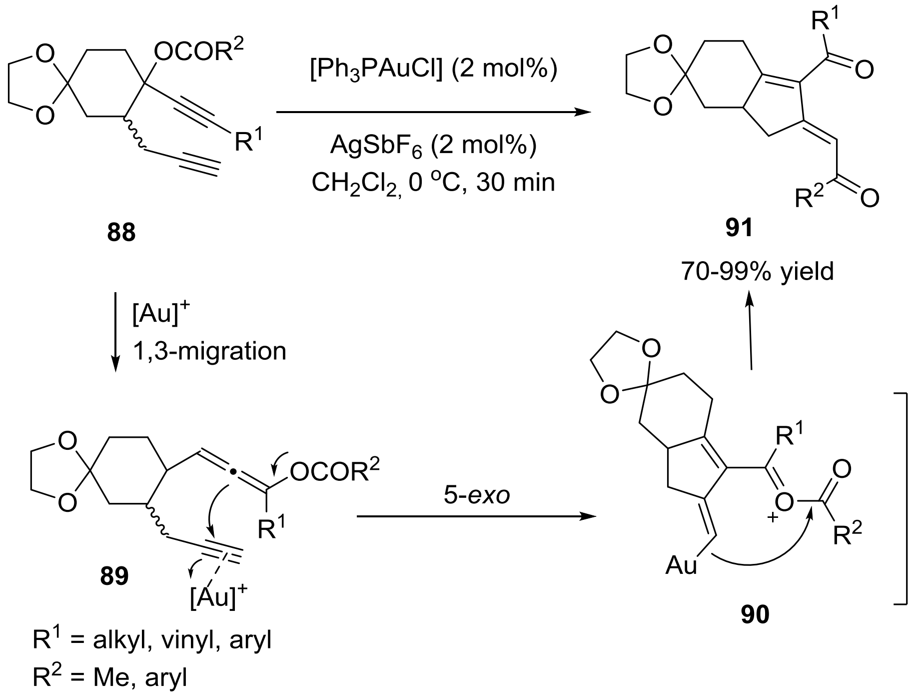


$R^1 = CH_3$, tBu
R^2 = alkyl, $PhCH_2$, $BnOCH_2$, $PhCH_2CH_2$
R^3 = H, alkyl
R^4= H, CH_3
X = Ts, Ns, Bs

Scheme 1.18 Gold(I)-catalyzed cycloisomerization of 1,6-diynes to 2,3-disubstituted 3-pyrroline derivatives

On the other hand, path b was proposed to involve a Meyer-Schuster-like rearrangement[25] with intermediate **82** being achieved by nucleophilic attack of water on the alkyne moiety of 1,6-diyne ester **80** and subsequent release of AcO^- group. This intermediate **82** could further tautomerize to the conjugated enone **84** and then gave the product **87** via a few steps. For this reaction, the key species in the catalytic cycle was the corresponding alkynyl enone **84**. The limitation of this method was that the substrates must be internal 1,6-diynes, otherwise the intermediate enone **84** was formed rather than the cyclization product.

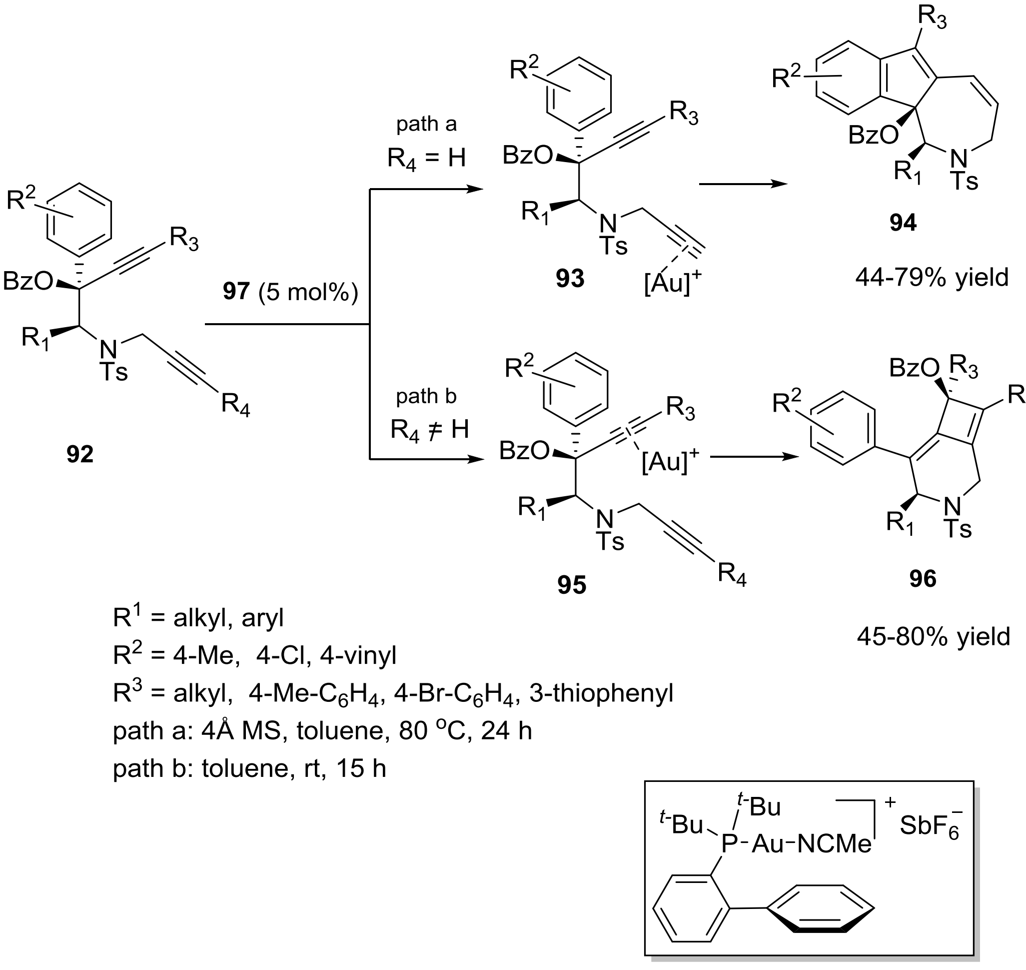
Fensterbank, Gandon, Malacria and co-workers described the transformation of 1,6-diyne esters **88** containing a terminal alkyne functionality to δ-diketones **91** in 70-99% yield (Scheme 1.19).[18a] In this study, it was proposed that 1,6-diyne ester **88** was activated by the gold catalyst to give allene intermediate **89** via 1,3-migration.



Scheme 1.19 Gold-catalyzed cyclization of propargylic esters to δ-diketones

The pendant alkyne was activated by the gold catalyst again and following nucleophilic attack of the allene ester, gave intermediate **90**. Trapping the acylium ion via an unprecedented Au-triggered 1,5-acyl shift was proposed to give the final product **91**. In this work, the limitation was that when a disubstituted propargyl ester moiety was used, the second triple bond must be monosubstituted. On the other hand, all the substrates gave δ-diketones containing an *E* exocyclic double bond geometry.

Chan and co-workers explored a cascade process involving gold-catalyzed cycloisomerization of 1,7-diyne benzoates **92** to afford two different cyclization products **94** and **96** in 44-79% and 45-80% yield, respectively, depending on the substitution pattern of the tethered alkyne moiety (Scheme 1.20).[26] This protocol

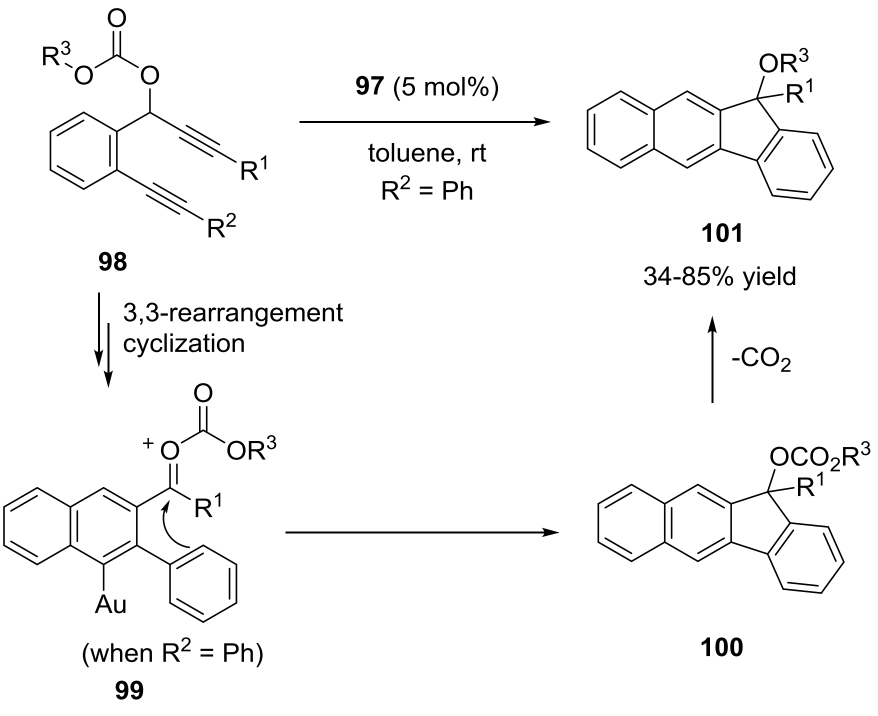


R^1 = alkyl, aryl
R^2 = 4-Me, 4-Cl, 4-vinyl
R^3 = alkyl, 4-Me-C_6H_4, 4-Br-C_6H_4, 3-thiophenyl
path a: 4Å MS, toluene, 80 °C, 24 h
path b: toluene, rt, 15 h

97

Scheme 1.20 Gold-catalyzed cycloisomerization pathways of 1,7-diyne benzoates provided a tandem process which allowed for the activation of either alkyne moiety of the 1,7-diyne ester allowed for the synthesis of a variety of cycloisomerization products. In path a, the less sterically encumbered terminal alkyne was preferably activated. This gave the putative Au(I)-coordinated species **93** generated in situ, which was susceptible to a concerted 5-endo-dig followed by a 7-endo-dig cyclization process triggered by nucleophilic attack by an appropriately placed aryl moiety to provide the indeno[1,2-*c*]azepine ring system. In path b, it was proposed that activation of the triple bond next to the ester could give the bicyclic product **96** via 1,3-acyloxy migration and Prins-type cyclization.

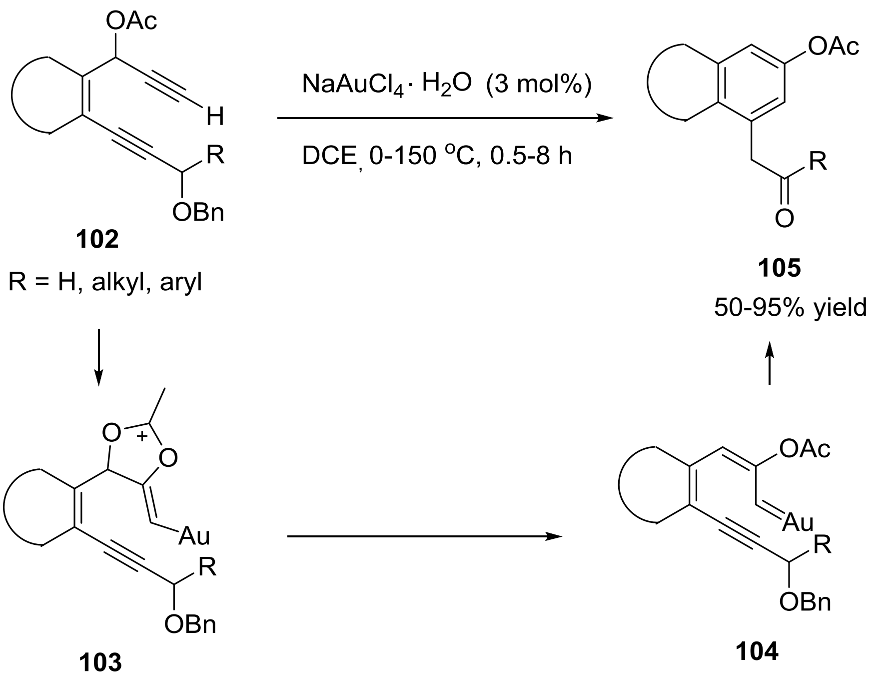
In 2012, Liu and co-workers reported a gold-catalyzed cascade cyclization of 1,6-diynyl carbonates **98** leading to benzo[b]fluorenes **101** in 34-85% yield by



R^1 = alkyl, aryl
R^2 = alkyl, aryl
R^3 = allyl, alkyl, Bn

Scheme 1.21 Gold-catalyzed cascade cyclization of 1,6-diynyl carbonates to benzo[*b*]fluorenes arylation of oxocarbenium ion intermediates, which subsequently underwent decarboxylative etherification (Scheme 1.21).[27] In this work, the use of a carbonate instead of an ester moiety in the substrate design was thought to provide increased stability of the resulting oxocarbenium ion intermediate **99,** thus allowing further reaction with a nucleophile to give intermediate **100** which could provide product **101** by releasing CO_2. The novelty in this mechanism was that it was the first decarboxylative etherification by using of gold catalysts compared to those with other transition metals such as rhodium and palladium.[28]

More recently, Oh and co-workers reported gold-catalyzed cycloisomerization of substituted propargyl acetates **102** to 2-acetoxynaphthalene derivatives **105** in 50-95% yield (Scheme 1.22).[29] In this work, substituted propargyl acetates **102** was activated



Scheme 1.22 Gold-catalyzed cycloisomerization of substituted propargyl acetates to gold carbenes

by the gold(III) catalyst to give intermediate **103** followed by the subsequent formation of carbenoid intermediate **104** via a 1,2-acyloxy shift. Finally, the gold-carbenoid species **104** underwent an ene-type reaction with the pendant triple bond to provide a variety of 2-acetoxynaphthlene derivatives **105**. As a whole, this protocol could provide an important structural motif for complex multi-functional organic materials.

1.5 Proposed work

The work of this thesis has been directed toward providing novel synthetic methodologies for the synthesis of carbocyclic compounds which could be found in a lot of natural and synthetic compounds and functional materials. This will be accomplished by exploring 1,*n*-diyne ester cycloisomerizations catalyzed by complexes of gold(I) and gold(III), which have became one of the most efficient and atom-economical method for complex molecule synthesis in one step.

Thus, the aim of this project has been to establish new gold-catalyzed protocols for the construction of 2,4a-dihydro-1*H*-fluorenes, 1*H*-cyclopenta[b]naphthalenes, δ-diketones and 4,7-diphenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl acetates from 1,6-diyne esters and carbonates (Figure 1.2). It is envisioned that a synthetic route to 2,4a-dihydro-1*H*-fluorenes can be developed from 1,6-diyne esters **111**. We surmise that a 1,2-acyloxy migration step may be initiated by activation of alkynes by gold complexes, and further functionalization to give the 2,4a-dihydro-1*H*-fluorenes. On the other hand, if we tune the substrate **111** which contains a terminal propargyl alkyne to substrate **128** which contains an internal propargyl alkyne, we surmise that new carbocyclic compounds could be achieved by 1,3-acyloxy migration. In addition, inspired by the previous work, we envision that by utilizing internal 1,6-diyne **128** in which the phenyl substituent was replaced with isoprenyl, a synthetic route to 4,7-diphenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl acetates may be achieved.

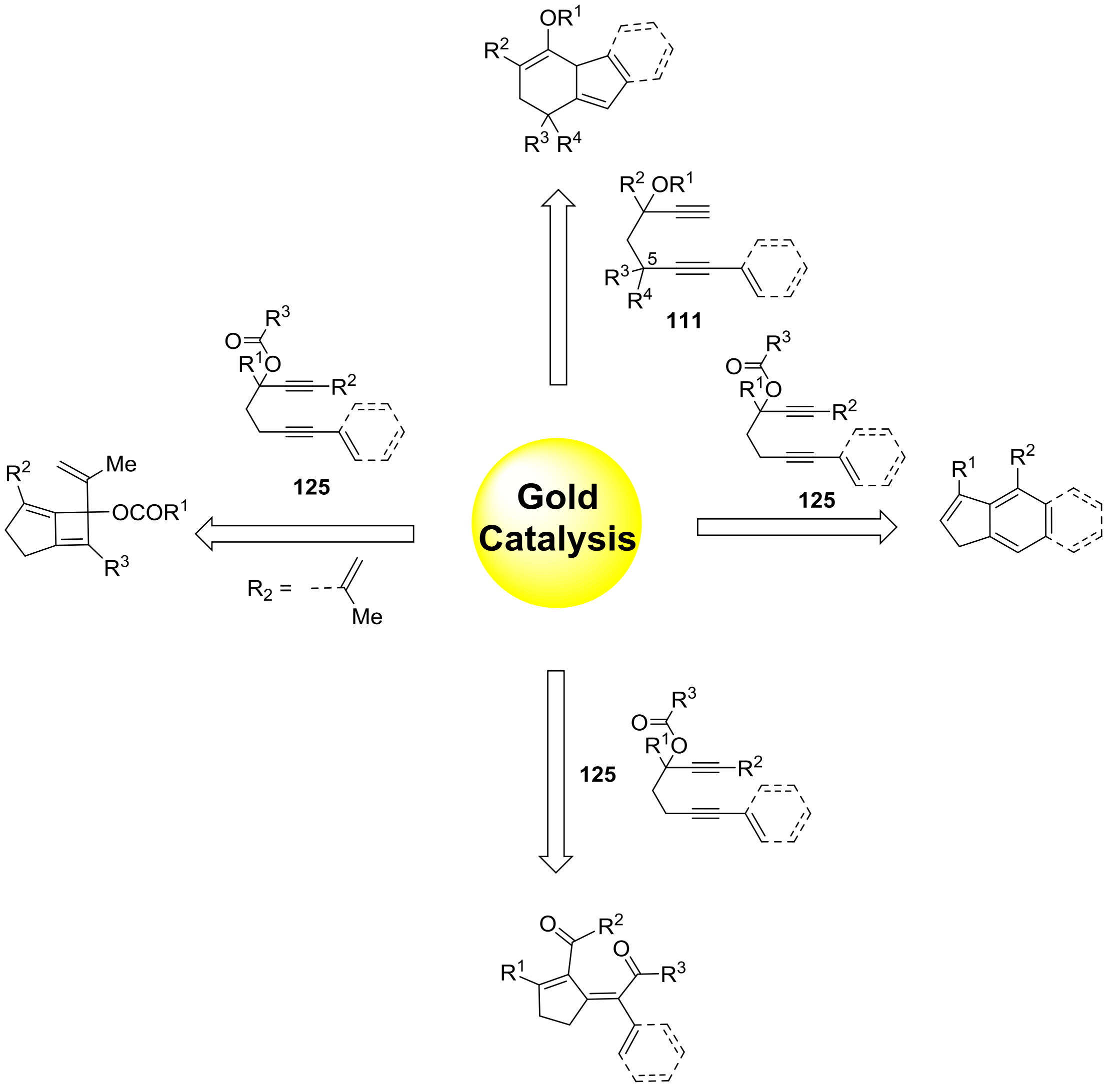
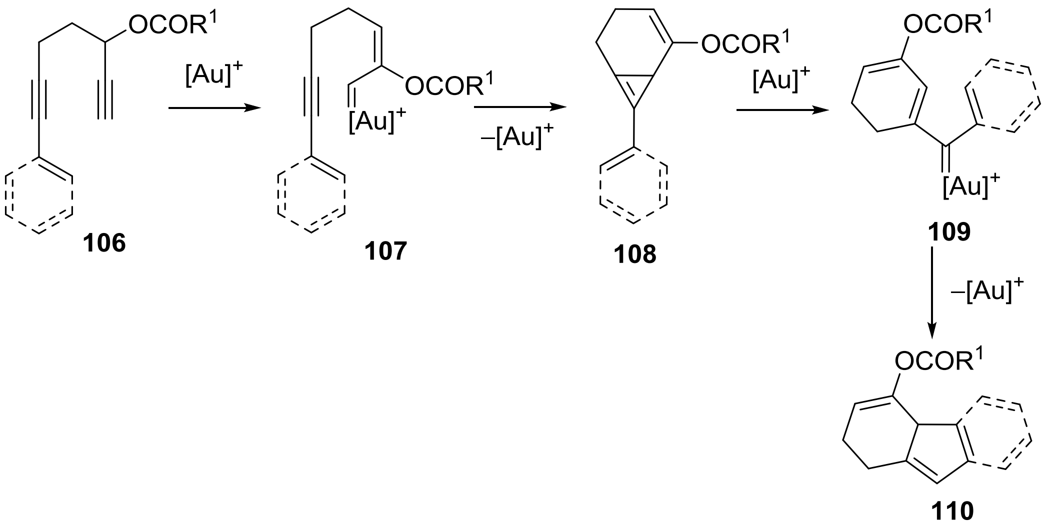


Figure 1.2 Gold-catalyzed synthesis of complex molecules from 1,6-diyne esters and carbonates

Chapter II. Gold-Catalyzed Cycloisomerization of 1,6-Diyne Carbonates and Esters to 2,4a-Dihydro-1*H*-fluorenes

2.1 Introduction

In contrast to the cycloisomerization chemistry of 1,*n*-enyne esters, there have so far been few reported examples of the reactions of 1,*n*-diyne carbonates and esters involving a 1,2-acyloxy migration step which is initiated by gold catalyst. For the reason above, we started to focus on the chemistry of cycloisomerization of 1,6-diyne carbonates and esters **106** (Scheme 2.1). We proposed that substrates like this having a terminal carbonate C≡C bond or a C≡C bond next to an ester would be preferentially initiated by 1,2-acyloxy migration for the reason of being less sterically hindered which may allow for the pendent alkyne moiety reacting toward the carbenoid **107** formed. The formation of cyclopropene intermediate **108** followed by formation of gold carbenoid species **109** is extremely rare in gold chemistry until now. This intermediate **109** could give the desired 2,4a-dihydro-1*H*-fluorene derivatives by Narazov cyclization.[30-33] In this work, we would provide an efficient method which

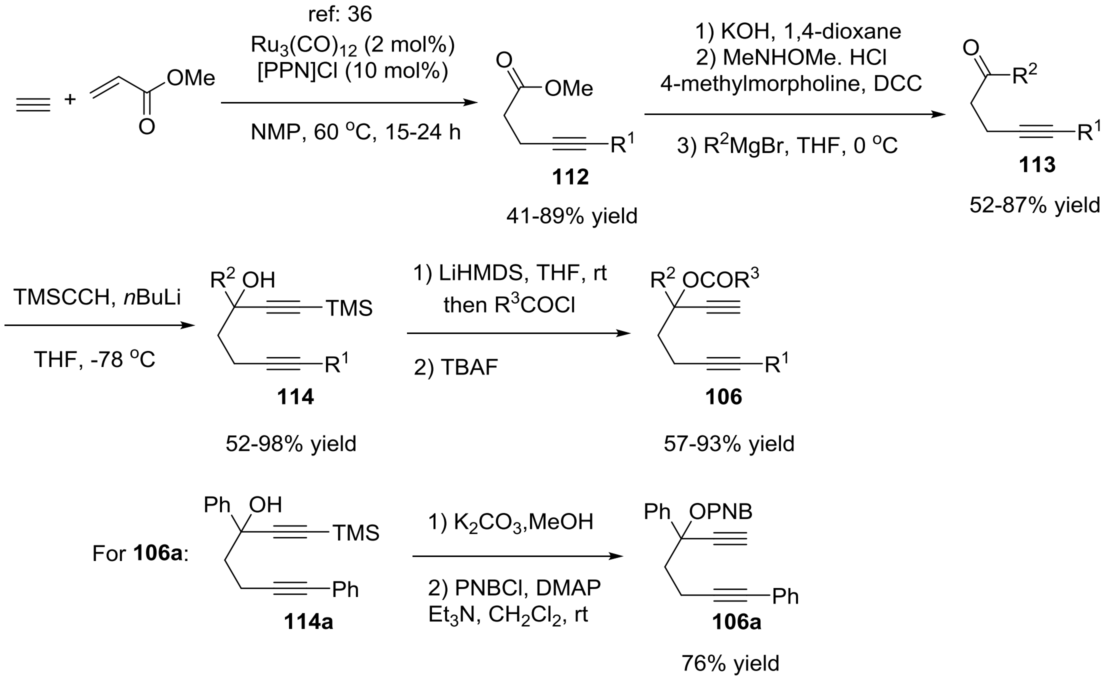


Scheme 2.1 Gold(I) catalyzed cyclization of 1,*n*-diyne carbonates and esters

allows for the formation of this carbocyclic motif which could be found in a vast number of synthetic compounds and functional materials.[34] An ONIOM computational study about the reaction selectivity was also provided via using two different levels of quantum mechanical methods (ONIOM(QM:QM')).[36]

2.2 Results and Discussion

All 1,6-diyne carbonates and esters studied in this work were prepared as shown in Scheme 2.2. This involved conjugate addition of terminal alkynes to methyl acrylates catalyzed by the ruthenium complex $Ru_3(CO)_{12}$ in the presence of bis(triphenylphosphine)iminium chloride ([PPN]Cl) to give moderate to high yields (41-89%) of alkynyl ester **112**.[37] The alkynyl ester was then converted to ketone **113** in 52-87% yield via formation of the carboxylic acid under basic conditions and subsequent convertion to the Weinreb amide in the presence of *N*-methylmorpholine, *N*,*O*-dimethylhydroxylamine.HCl and *N*,*N*-dicyclohexylcarbodiimide. This was followed by reaction with the Grignard reagent. The ketone **113** obtained was then protected by trimethylsilane to give (trimethylsilyl)hepta-1,6-diyn-3-ol **114** in 52-98% yield. The alcohol **114** was then subjected to R_3COCl and TBAF to afford the desired substrate **106** in 57-93% yield. For substrate **106a**, the ester was afforded in 76% yield by treatment of **114a** with K_2CO_3 in MeOH followed by PNBCl in the presence of DMAP and Et_3N in dichloromethane.



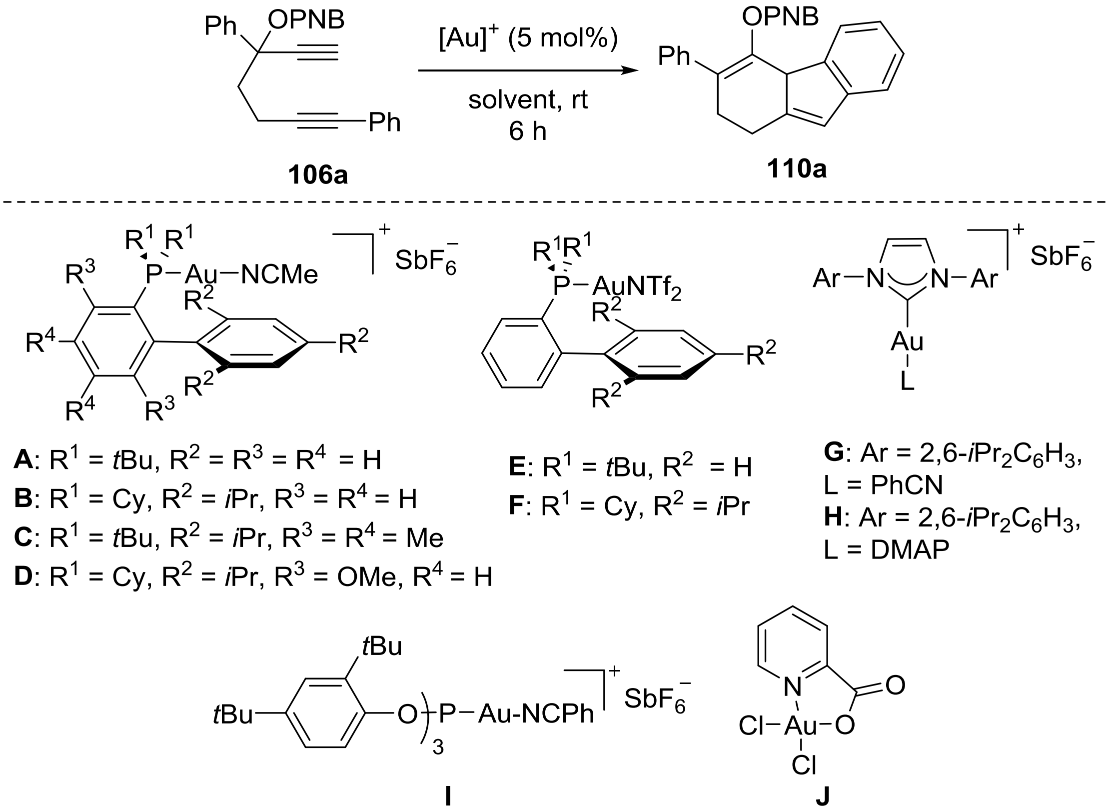
Scheme 2.2 Synthesis of **106**

We commenced our study by using 1,6-diyne ester **106a** to optimise the reaction conditions (Table 2.1).[37] In our initial study, we found that treating **106a** with 5 mol % of Au(I) catalyst **A** in dichloromethane for 6 h at room temperature gave **110a** in 71% yield (entry 1). The structure of **110a** was confirmed by ^{1}H NMR and X-ray crystallography (Figure 2.1).[38] We found that using the gold(I) complex **C** which was more sterically crowed could improve the yield to 78%. (entry 3). On the other hand, we found that using the gold(I) phosphine complexes **B** and **D-F**, NHC-gold(I) (NHC = N-heterocyclic carbene) complex **G**, and gold(I) phosphite complex **I** gave the product in 12-67% yield (entries 2, 4-6, 9 and 11).[39] While changing the catalyst to Au(I) phoshine complexes **E** and **F**, we recovered the substrates in 70 and 50% yield, respectively (entries 5 and 6). Using the catalyst gold(I) phoshine complex **C**, we found that **110a** formed in 27% yield by using toluene as solvent (entry 13). On the other hand, we also did the control experiment finding that no reaction occurred using NHC-gold(I) complex **H** , AuCl, PPh_3AuCl or Au(I) complex **C** or gold(III) complex

J, or in reaction medium like acetonitrile and THF which is polar (entries 7, 8, 10, 12, 14 and 15). Based on the results above, the cyclization of **106a** catalyzed by **C** (5 mol %) in dichloromethane for 6 h at room temperature gave the best yield.

With the opitmised reaction condition in hand, we turned to the substrate scope study by examing various 1,6-diyne carbonates and esters. In providing the results summarized in Table 2.2 we found that a variety of substrates **106b-y** could give the

Table 2.1 Optimization of reaction conditions[a]



entry	catalyst	solvent	yield (%)[b]
1	**A**	CH_2Cl_2	71
2	**B**	CH_2Cl_2	67
3	**C**	CH_2Cl_2	78
4	**D**	CH_2Cl_2	52

Table 2.1 (*continued*)

entry	catalyst	solvent	yield (%)[b]
5	**E**	CH_2Cl_2	12(70)[c]
6	**F**	CH_2Cl_2	38(50)[c]
7	Ph_3PAuCl	CH_2Cl_2	-[d]
8	AuCl	CH_2Cl_2	-[d]
9	**G**	CH_2Cl_2	62
10	**H**	CH_2Cl_2	-[d]
11	**I**	CH_2Cl_2	50
12	**J**	CH_2Cl_2	-[d]
13	**C**	PhMe	27
14	**C**	MeCN	-[d]
15	**C**	THF	-[d]

[a] All reactions were performed at the 0.2 mmol scale with catalyst:1a ratio = 1:20 in given solvent at room temperature for 6 h. PNB = *p*-nitrobenzoyl. [b] Isolated yield. [c] Reaction carried out at room temperature for 24 h; values in parentheses denote the yield of recovered starting material. [d] No reaction based on TLC and ^1H NMR analysis of the crude mixture.

corresponding 2,4a-dihydro-1*H*-fluorenes in 44-93% yield. For the substrates with a Bz (**106b**), Ac (**106c**), Cbz (**106d**) or Boc (**106e**) rather than a PNB migrating group could give the corresponding 2,4a-dihydro-1*H*-fluorenes **110b-e** in 52-80% yield. Similarly, using 1,6-diyne esters containing a pendant aryl (**106f-o** and **106q-r**), thiophene (**106p**) or cyclohexene (**106s**) group could give the tri-, tetra- and

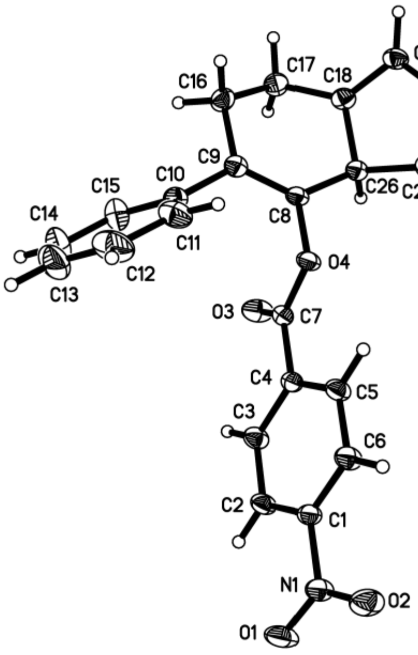
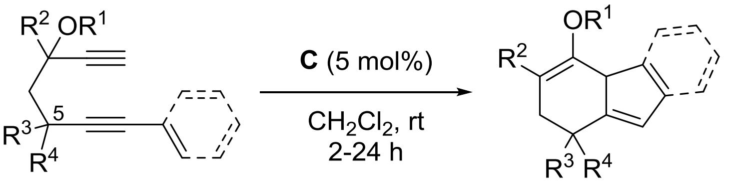


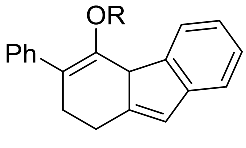
Figure 2.1 ORTEP drawing of **110a** with thermal ellipsoids at 50% probability levels[35]

pentacyclic adducts in 47-83% yield. Different aryl motifs on the benzoate carbon center of the benzoate almost have no influence on the reaction with **110t-v** achieved in 53-76% yield. Substrates containing a cyclopropane ring on the benzoate carbon center (**106w** and **106x**) or methyl groups at the C5 position (**106y**) were the only exceptions. For these reactions, both **C** and **G** as the gold(I) catalyst could give almost the same product yields except that in the latter conditions fewer impurities were found. Obviously, all the cycloisomerizations indicated that the ring-forming process takes place in a highly selective manner with the 1,4-diene isomer of the adduct being formed only. In addition, except for some unkown decomposition products, we have not found any other cyclic compounds which could be generated from an 1,3-acyloxy migration step or concerted double cyclization pathway by ^{1}H NMR analysis of the crude mixtures.

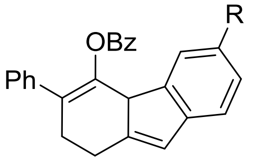
Table 2.2 Cycloisomerization of 1,6-diyne carbonates and esters **106b-y** catalyzed by **C**[a]



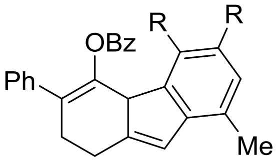
106 **110**



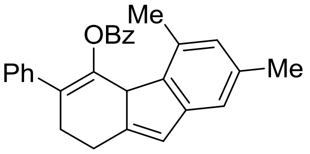
110b: R = Bz (80%)
110c: R = Ac (71%)
110d: R = Cbz (55%)
110e: R = Boc (52%)



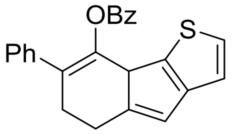
110f: R = Me (83%)
110g: R = OMe (71%)
110h: R = *n*Pent (81%)
110i: R = Ph (77%)
110j: R = vinyl (47%)
110k: R = F (64%)
110l: R = Br (55%)



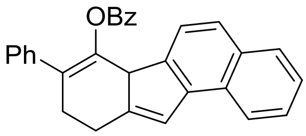
110m: R = H (80%)
110n: R = Me (77%)



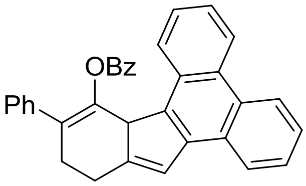
110o: (83 %)



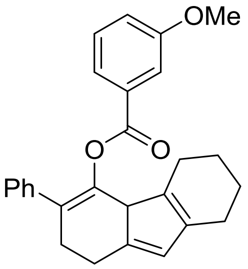
110p: (72%)



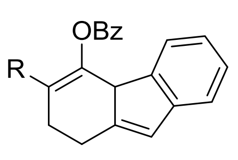
110q: (77%)



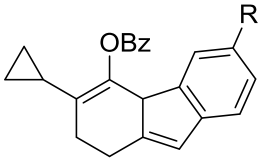
110r: (71%)



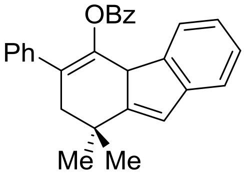
110s: (57%)



110t: R = 4-ClC$_6$H$_4$ (76%)
110u: R = 4-vinylC$_6$H$_4$ (60%)
110v: R = 1-naphthalenyl (53%)[b]



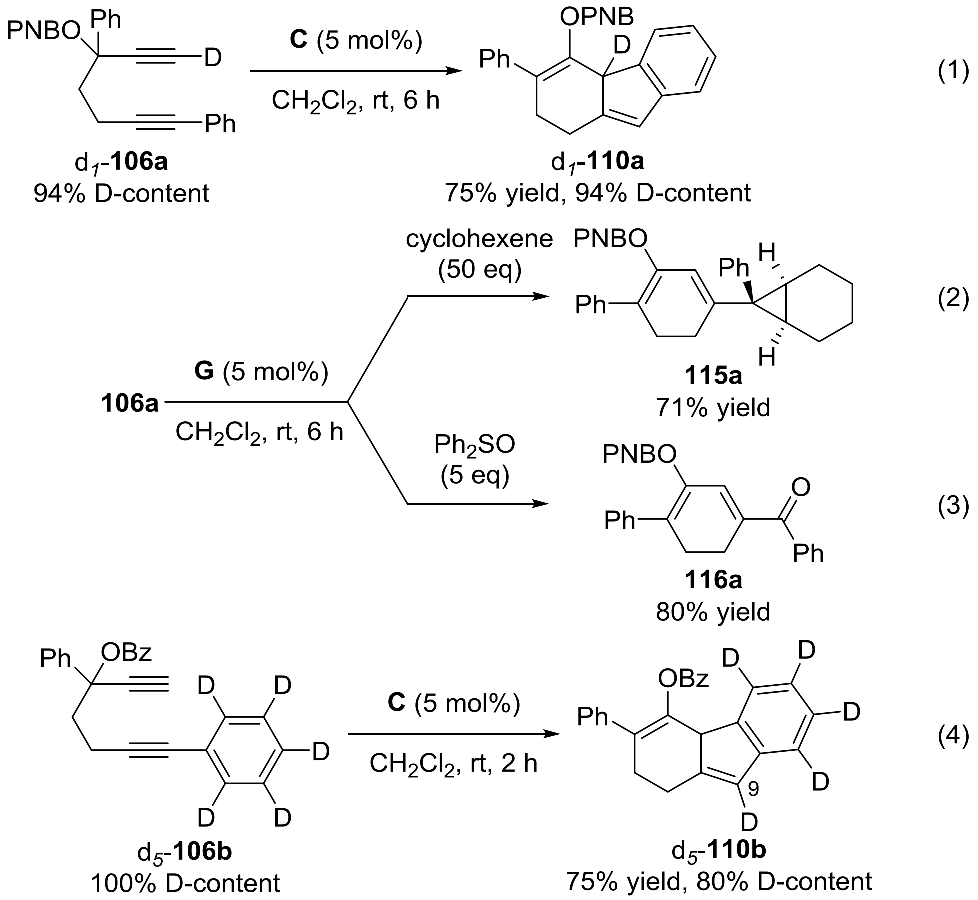
110w: R = H (47%)[c]
110x: R = OMe (44%)[c]



110y: (93%)[c]

[a] All reactions were performed at the 0.2 mmol scale with **C**:1 ratio = 1:20 in CH$_2$Cl$_2$ at room temperature for 2-24 h. Values in parentheses denote isolated product yields. [b] Isolated as an inseparable mixture of diastereomers in a ratio = 1.1:1. [c] Reaction carried out with NHC-gold(I) complex **G** as the catalyst.

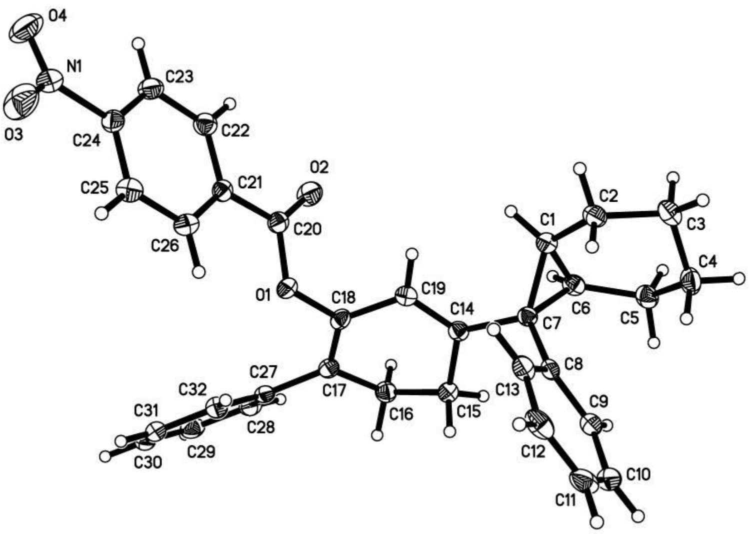
To further verify the mechanism proposed in Scheme 2.1, we commenced the following mechanistic experiments (Scheme 2.3).



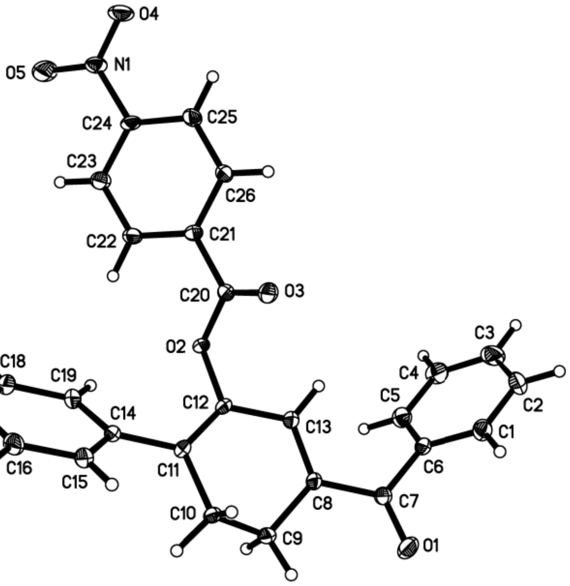
Scheme 2.3 Control experiments with **106a**, d_1-**106a** and d_5-**106b** catalyzed by **C** or **G**

Firstly we focused on the convertion of d_1-**106a** in reaction medium dichloromethane with 5 mol % of **C** under the conditions described in Scheme 2.3, eq 1 since recent works showing that the likely containment of gold(I)-activated alkynylgold(I) species in alkyne cycloisomerizations catalyzed by the metal catalyst[40]. This gave d_1-**110a** in 75% yield and with a D content of 94% via ^{1}H NMR measurements which provided a way to rule out the possibility of containing a dual activation pathway in which the alkyne terminus of **106** was activated by two molecules of the Au(I) catalyst. In addition, we also tested reactions of **106a** which were repeated with cyclohexene and Ph_2SO catalyzed by NHC-gold(I) **G** under the standard conditions and this could support the the participation of the gold carbenoid intermediate **107** (Scheme 2.3, eq 2 and 3).[41,42] In the reactions tested above, the cyclopropane and ketone adducts **115a** and **116a** as the anticipated trapping products, was achieved in yields of 71% and 80%. The structures of the 4-((1*R**,6*S**,7*S**)-7-phenylbicyclo[4.1.0]heptan-7-yl)-5,6-dihydro-[1,1'-biphenyl]-2-yl 4-nitrobenzoate (**115a**) and 4-benzoyl-5,6-dihydro-[1,1'-biphenyl]-2-yl 4-nitrobenzoate (**116a**) were determined by ^{1}H NMR spectroscopic measurements and X-ray crystallography (Figure 2.2).[43] We also did a control experiment to support the proton source generated in the protodeauration process which would lead to product was likely come from the Nazarov cyclization step which drived by the regeneration of aromaticity or alkene bond (Scheme 2.3, eq 4).[32] We also found that subjecting d_5-**106b** to the gold(I) catalyst **C** could give d_5-**110b** in 75% yield and with a D content of 80% at the C9 position of the adduct under the standard conditions depicted in Scheme 2.3, eq 4, as determined by ^{1}H NMR measurements.

A tentative mechanism for the formation of 2,4a-dihydro-1*H*-fluorene catalyzed by gold(I) is outlined in Scheme 2.4. We began our study by using **106b** as an example, we propose that the reaction was initiated by activation of the alkyne next to the ester by the Au(I) catalyst to give **117**. This was followed by syn 1,2-migration of the carboxylate group to generate gold carbenoid **119** via **118**. The gold carbenoid formed was then trapped by the pendent C≡C bond which could give the cyclopropene intermediate **120**.[31] Further coordination of the π- acidic metal complex to the alkene bond of the bicyclic adduct could produce the Au(I)-activated



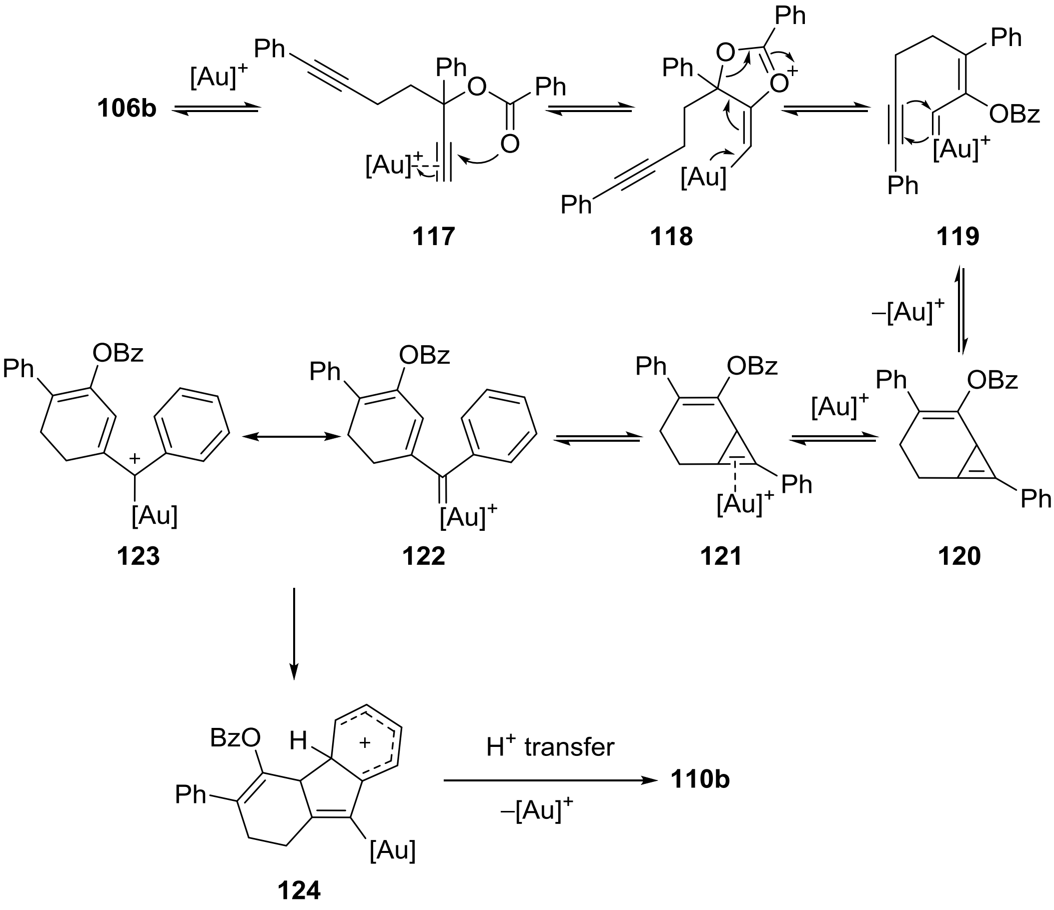
(a) **115a**



(b) **116a**

Figure 2.2 ORTEP drawing of (a) **115a** and (b) **116a** with thermal ellipsoids at 50% probability levels[43]

species **121**. Followed by the electrophilic ring-opening of the cyclopropenyl gold moiety in **121,** the second gold carbenoid **122** and its resonance form **123** could be achieved. The active species formed would then undergo Nazarov cyclization,[32] and give **110b** via re-aromatization of the ensuing Wheland-type intermediate **124** followed by protodeauration.



Scheme 2.4 Proposed mechanism for gold(I)-catalyzed cycloisomerization of 1,6-diyne carbonates and esters represented by **106b**

To verify mechanism shown in Scheme 2.4, two-layer ONIOM(QM:QM')[32] computational studies using Gaussian 09[44] was done by Prof. Hirao, Hajime of this Division. The B3LYP functional was used for both QM layers,[45] in combination with three different basis sets, i.e. LANL2MB (B1), [SDD(for Au),6-31G*(for others)] (B2), and [LANL2TZ(f)(for Au),6-311+G(d,p)(for others)] (B3).[46-48] Both geometry optimization study and frequency calculation study were performed at the ONIOM(B3LYP/B2:B3LYP/B1) level, and single-point energy calculations were done on optimized geometries at the ONIOM(B3LYP/B3:B3LYP/B1) level; in addition, the dichloromethane reaction medium effect was considered with the IEFPCM (integral equation formalism variant of the polarizable continuum model) method.[49] Molecules were drawn by UCSF Chimera.[50] The ONIOM calculations provided different transition states and intermediates during the reaction pathway from **106b** to **110b**. The calculation results also show that the formation of an intermediate containing a six-membered ring (**Int3**) between **119** and **121** through a transition state for ring closure (**TS3**). The mechanism we delineated has a special feature which is that **Int3** undergoes another ring closure to provide a unique cyclopropene adduct **Int4** (**121** in Figure 2.3) through **TS4a** invovling an energy barrier of 11.1 kcal/mol. The calculation also shows that a cyclopropene ring-opening step is followed via **TS5** which has an energy barrier of 11.3 kcal/mol. Based on the study above, it was found that the relative ease in which the cyclopropene intermediate can undergo ring-opening would make trapping of the cyclic adduct experimentally less likely, although its transient formation is reasonable. The calculation results further suggest that an alternative pathway from **Int3** via **TS4b** to **Int5** may involves gold migration, as shown in Figure 2.3. Focused on the structure of **TS4b**, it could be found that this transition state has a four-membered ring geometry which allows 1,3-migration efficiently. In contrast, **TS4b** is a little bit higher in energy than **TS4a** and this gold migration pathway should be slightly less favorable than that involving cyclopropene formation via **TS4a**. In this transformation, Nazarov cyclization, from **Int6** to **Int7**, has the highest energy barrier (22.1 kcal/mol), suggesting that the prior intermediates (**Int5** and **Int6** (**122** in Scheme 2.4)) should be relatively long-lived. Once the formation of Wheland-type intermediate **Int7** (**124** in Scheme 2.4) was furnished, the benzoyl group was found to play a key role in

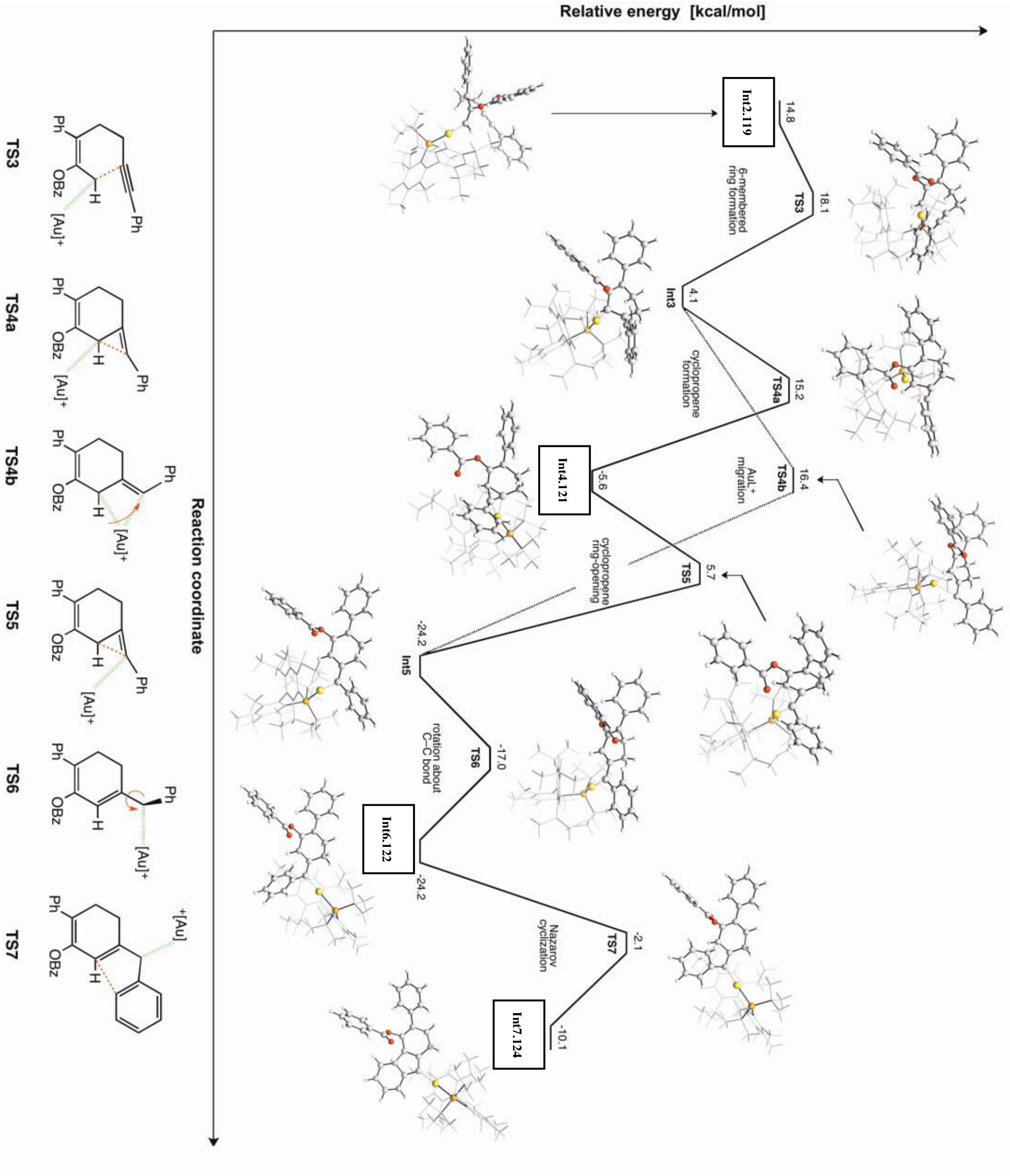


Figure 2.3 Reaction energy diagram (in kcal/mol) for the middle stage of the reaction, as obtained at the ONIOM(B3LYP/B3:B3LYP/B1)-PCM//ONIOM(B3LYP/B2:B3LYP/B1) level with zero-point energy corrections. An alternative pathway between Int3 and Int5 via TS4b is indicated by a dotted line. In the 3-D figures, H, C, O, P, and Au atoms are colored white, grey, red, orange, and gold, respectively. The ball-and-stick representation is used for the high-level QM layer and the stick representation is used for the rest of the system. Schematic drawings of the transition states along with Int3 and Int5 are also given below the energy diagram. Relative energy values are given with respect to the energy of isolated **106b** and $[AuL(NCCH_3)]^+$ from catalyst **C**.

assisting the 1,3-proton migration by accepting and donating the proton appropriately to give the desired product. The calculation study is consistent with the experiment results that the preferential formation of **115a** and **116a** and the high D content found at the C9 position of d_5-**110b**.

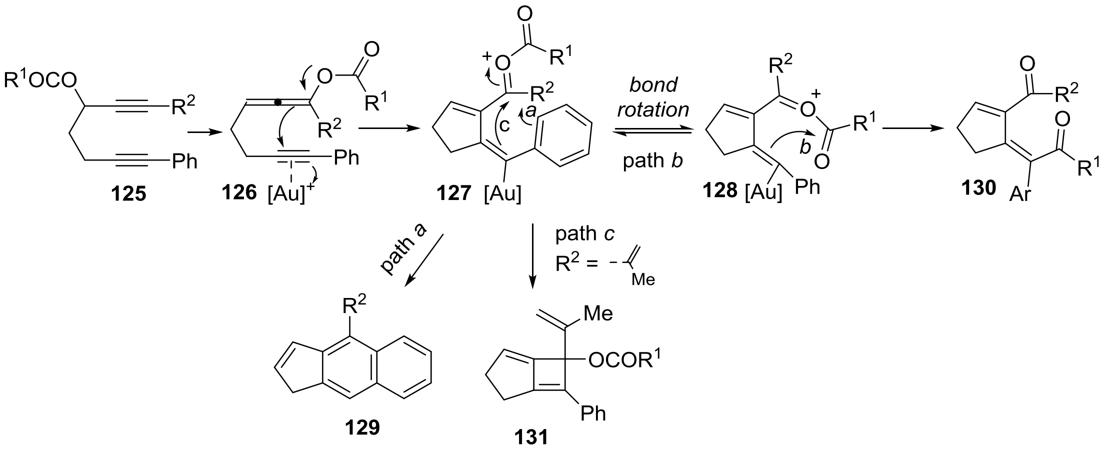
2.3 Conclusion

In conclustion, we have achieved an efficient method for the formation of highly functionalized 2,4a-dihydro-1*H*-fluorenes from 1,6-diyne carbonates and esters via a gold(I)-catalyzed strategy. In our studies, we found that the transformation was initiated by a 1,2-acyloxy migration which was not seen in previous research about this type of substrates. Surprisingly, we have also found that the reaction possibly involves a cyclopropene intermediate formation step which has been rarely reported in gold catalysis. Further study on the scope of this reaction and the corresponding applications are in progress and hopefully will be reported in future.

Chapter III. Gold-Catalyzed Cycloisomerization of 1,6-Diyne Esters to 1*H*-Cyclopenta[*b*]naphthalenes, Bicyclo[3.2.0]hepta-1,5-dienes and Cyclopenten-2-yl *δ*-Diketones

3.1 Introduction

In line with our present investigations in the field of gold-catalyzed alkyne cycloisomerizations,[51] we were interested in assessing 1,6-diyne esters possessing two internal alkyne moieties (Scheme 3.1). It was anticipated that these substrates would be prone to a 1,3-acyloxy shift; in contrast to having a terminal alkyne next to the ester. Activation of the pendant internal alkyne in **126**, by either a gold(I) or gold(III) catalyst was posited to result in a 5-*exo-dig* cyclization to give putative vinyl-gold intermediate **127**, with three possible succeeding outcomes: In the presence of a gold(I) catalyst, nucleophilic attack of the oxocarbenium species by the tethered phenyl group to 1*H*-cyclopenta[*b*]naphthalenes **129** (Scheme 3.1, path a). On the other hand, we envisioned a 1,5-acyl migration leading to *δ*-diketones **130** might be observed on utilization of a gold(III) catalyst (Scheme 3.1, path b). Finally, a Prins-type step-wise [2 + 2]-cycloaddition may occure to afford



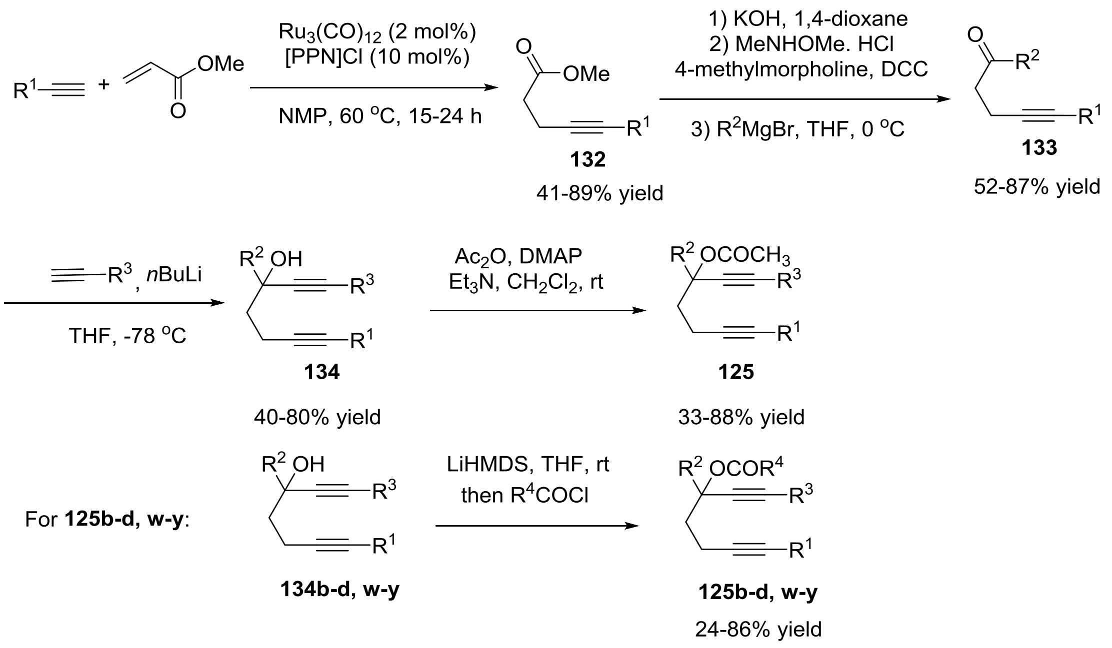
Scheme 3.1 Gold-catalyzed reaction pathways of 1,*n*-diyne esters.

bicyclo[3.2.0]hepta-1,5-dienes **131** when R^2 = isoprenyl in the substrate (Scheme 3.1, path c). Herein, we report our research in this chemistry, which permits expedient and divergent access to three different structural motifs; the carbocyclic scaffolds which may be found in bioactive molecules, functional materials, and their building blocks.[52,53]

3.2 Results and Discussion

All 1,6-diyne carbonates and esters studied in this work were prepared as shown in Scheme 3.2. This involved conjugate addition of terminal alkynes to methyl acrylates catalyzed by the ruthenium complex $Ru_3(CO)_{12}$ in the presence of [PPN]Cl to give alkynyl ester **132** in 41-89% yield. The alkynyl ester was then converted to the ketone **133** in 52-87% yield via formation of the carboxylic acid under basic conditions and subsequent conversion to the Weinreb amide in the presence of *N*-methylmorpholine, *N*,*O*-dimethylhydroxylamine.HCl and *N*,*N*-dicyclohexylcarbodiimide. This was followed by reaction with the Grignard reagent. The ketone **133** obtained was then converted to compound **134** in 40-80% yield. The alcohol **134** was then subjected to R_3COCl to afford the desired substrate **125** in 33-88% yield. For substrates **125b-d, z-β**, the esters were afforded in 24-86% yield by treatment of **134b-d, z-β** with Ac_2O in the presence of DMAP and Et_3N in dichloromethane.

We commenced our investigations by examining the gold-catalyzed cycloisomerization of 1,6-diyne ester **125a** to establish the reaction conditions (Table 3.1). Initially this revealed that the treatment of **125a** with 5 mol % of phosphine-gold(I) catalyst **A** in CH_2Cl_2 at room temperature for 2 h afforded the tricyclic 1*H*-cyclopenta[*b*]naphthalene **129a** in 64% yield (entry 1). Replacing the phosphine for

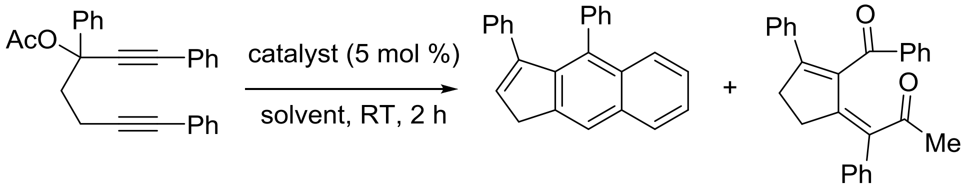


Scheme 3.2 Synthesis of 1,6-diyne esters

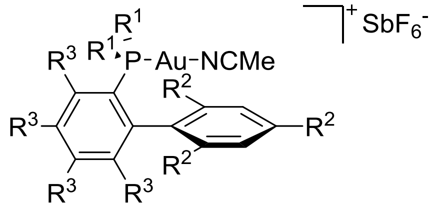
an NHC ligand in complex **B** resulted in an improvement in yield of **129a** (69%, entry 2). Substituting the axial nitrile ligand with triflimide (NTf_2) in catalysts **C** and **D** afforded similar selectivity for **129a**, but offered no improvement over **B** (56 and 58% yield, entries 3 and 4). With **B** as the catalyst, a similar outcome was found when the reaction was repeated with toluene, MeCN and THF in place of CH_2Cl_2 as the solvent, furnishing product yields of 18–62% (entries 5–7). With Ph_3PAuCl as the catalyst, no detectable reaction over 24 h, and treatment with $AgSbF_6$ met with decomposition (entries 8 and 11). Further reactions with both AuCl and $PtCl_2$, over a period of 24 h, also did not afford **129a**. However, remarkably these catalysts did lead to the selective formation of **130a** in 68 and 50%, respectively (entries 9 and 10).[54] The structure of both products was determined by ^1H NMR spectroscopic measurements and X-ray crystallography (Figure 3.1).[55] The efficiency of which was enhanced by employing the gold(III) catalyst **E** over 2 h, with **130a** obtained in 83% yield (entry 12). Again, as with **E**, varying the solvent gave no improvement with product yields of 50–73% afforded from reactions in toluene, MeCN and THF (entries 13–15).

With gold(I) complex **B** and gold(III) complex **E** established as the optimal catalysts for the selective isomerization of **125a** to **129a** and **130a**, respectively,

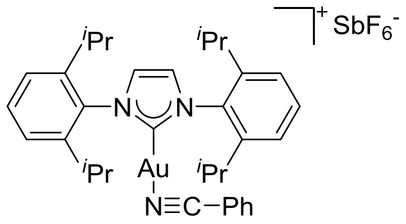
Table 3.1 Optimization of reaction conditions [a]



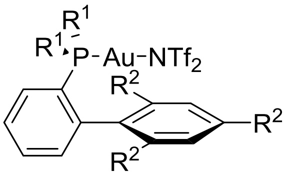
125a **129a** **130a**



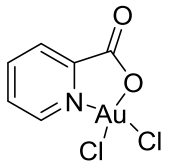
A: R^1 = ^{t}Bu, R^2 = R^3 = H



B



C: R^1 = Cy, R^2 = ^{i}Pr
D: R^1 = ^{t}Bu, R^2 = H



E

entry	catalyst	solvent	yield (%)[b]	
			129a	**130a**
1[c]	**A**	CH_2Cl_2	64	-
2	**B**	CH_2Cl_2	69	-
3	**C**	CH_2Cl_2	56	-
4	**D**	CH_2Cl_2	58	-
5	**B**	toluene	43	-
6	**B**	MeCN	62	

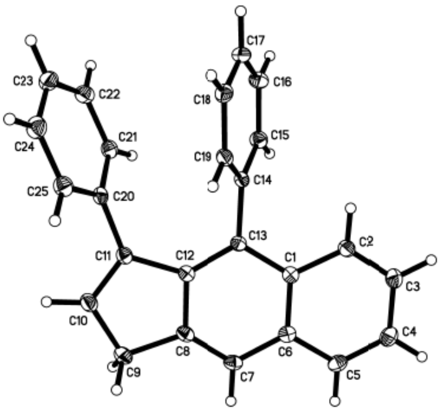
Table 3.1 (*continued*)

entry	catalyst	solvent	yield (%)[b]	
			129a	**130a**
7	**B**	THF	18[c]	-
8	Ph_3PAuCl	CH_2Cl_2	-[c,d]	-
9	AuCl	CH_2Cl_2	-	68[c]
10	$PtCl_2$	CH_2Cl_2	-	50[c]
11	$AgSbF_6$	CH_2Cl_2	-[e]	-
12	**E**	CH_2Cl_2	-	83
13	**E**	toluene	-	73
14	**E**	MeCN	-	62
15	**E**	THF	-	50[c]

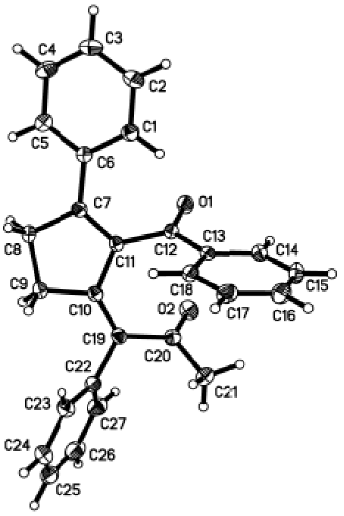
[a] All reactions were performed on a 0.2 mmol scale with a catalyst:**125** ratio of 1:20 at RT. [b] Isolated yield. [c] Reaction was conducted at RT for 24 h. [d] No reaction based on ^1H NMR analysis of the crude mixture. [e] Decomposition observed based on ^1H NMR measurements and TLC analysis of the crude mixture.

the scope of the procedures was assessed with a panel of 1,6-diyne esters (Table 3.2). In general, these experiments indicated tolerance towards a broad range of substrates **125**, furnishing a variety of substituted 1*H*-cyclopenta[*b*]naphthalenes and derivatives **129**, and δ-diketones **130** in up to 90% yield. Reactions with substrates containing a Bz (**125b**) and cyclopropanecarbonyl (**125d**) instead of an Ac migrating group were very well tolerated, affording the corresponding products **129a**, **130b** and **130d** in 65–73% yield. Replacement of the propargylic phenyl moiety with 4-chlorophenyl (**125g**) or an aliphatic cyclopropyl (**125f**) group also gave **129f** and **129g**, and **130f** and **130g** in good yield (50–71%). Substituent changes at the alkynyl positions with 4-fluorophenyl (**125h**) and 3-thiophenyl (**125j**) afforded **129h** and **129j**, and **130h** and **130j** in good to excellent yield (59–86%). Altering the substitution of the pendant alkynyl position with 4-fluorophenyl (**125m**), 4-bromophenyl (**125n**), 4-n-pentylphenyl (**125o**), 4-methylphenyl (**125p**), 2-methylphenyl (**125q**), 3,5-dimethylphenyl (**125r**) and 2-thiophenyl (**125u**) was also well tolerated, affording **129m–q**, **129r**, **129u**, **130m–q**, **130r**, and **130u** in 52–81% yield.

Changing the pendant phenyl moiety with a bulkier 1-naphthalenyl (**125s**) substituent afforded **129s** and **130s** in moderate yields (45–53%). While exchanging the propargylic phenyl group with a methyl (**125e**) gave **129e** in good yields of 67%, the analogous reaction catalyzed by Au(III) complex **E** afforded **130e** in a poor yield of 23%. On the other hand, a 4-methylphenyl substituent at the alkynyl position (**125i**) or a 3-thiophenyl group at the pendant alkynyl position (**125t**) gave moderate to low yields of **129i** and **129t** (41 and 10%), but high yields of **130i** and **130t** (71 and 74%). In contrast, the reaction with pivaloyl ester (**125c**) with **B** gave **129a** in 90% yield, but treatment with **E** met with decomposition. Finally, no reaction and decomposition for the respective reactions of substrates bearing an electron-rich PMB group in the alkynyl position (**125k**) or an alphalic *n*-butyl (**125l**). Subsequently, we found that when the alkynyl phenyl substituent of **125a** was replaced with an isoprenyl group (**125v**) a markedly different reaction outcome was observed; the gold(I) catalyst **A**, in toluene at room temperature over 2 h, led to the formation of a mixture of the δ-diketone **130v** and bicyclo[3.2.0]hepta-1,5-diene **131v** (Table 3.3). The structure of **131v** was determined by NMR spectroscopic measurements and X-ray crystallography (Figure 3.2).[55] With this result we extended our investigation to



(a) **129a**



(b) **130a**

Figure 3.1 ORTEP drawing of (a) **129a** and (b) **130a** with thermal ellipsoids at 50% probability levels[55]

establish reaction conditions for this cyclobutene forming reaction. The reaction with **A** initially gave **130v** and **131v** in 25 and 40% yield, respectively in product

Table 3.2 Cycloisomerization of 1,6-diyne esters **125a**–**125u** catalyzed by **B** and **F**^{a}

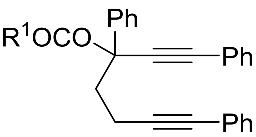
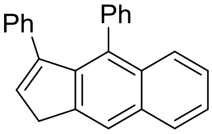
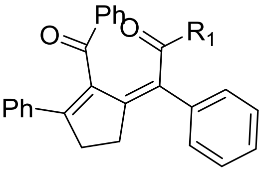
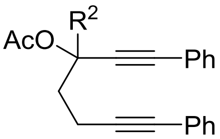
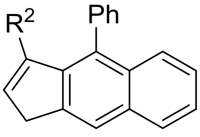
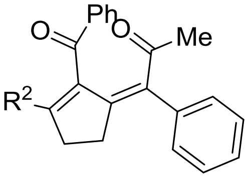
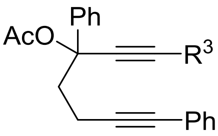
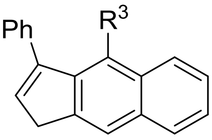
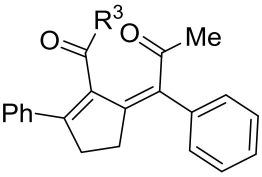
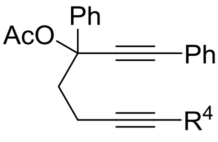
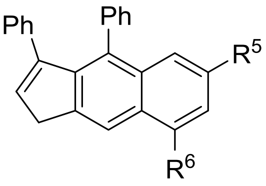
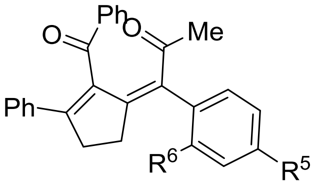
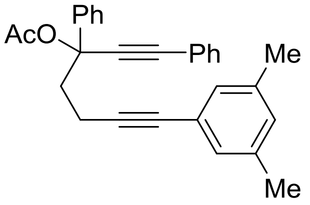
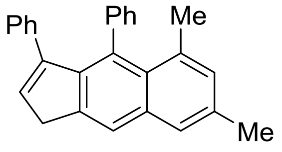
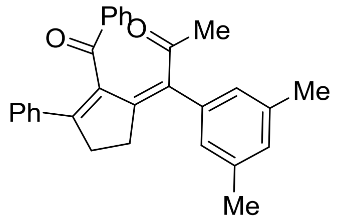
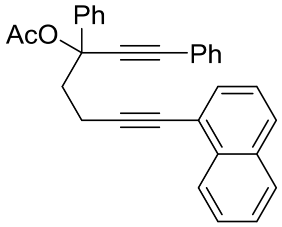
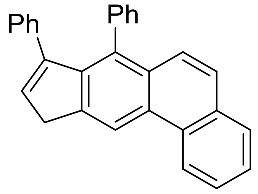
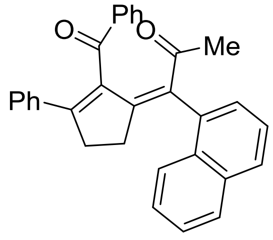
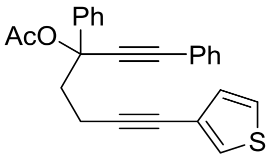
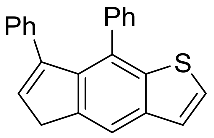
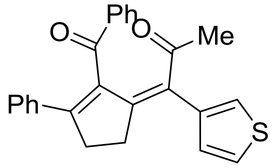
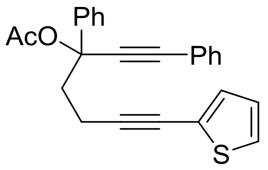
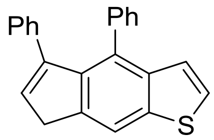
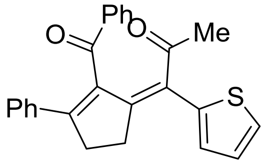
substrate **125**	product **129**	product **130**
		
125a: R^1 = Me **125b**: R^1 = Bn **125c**: R^1 = ^{t}Bu **125d**: R^1 = cyclopropyl	**129a** (69%) **129a** (65%) **129a** (90%) **129a** (73%)	**130a** (83%) **130b** (68%) **130c** (- ^{d}) **130d (**67%)
		
125e: R^2 = Me **125f**: R^2 = cyclopropyl **125g**: R^2 = 4-ClC$_6$H$_4$	**129e** (67%) **129f** (60%) **129g** (71%)	**130e** (23%) **130f** (50%) **130g** (50%)
		
125h: R^3 = 4-FC$_6$H$_4$ **125i**: R^3 = 4-MeC$_6$H$_4$ **125j**: R^3 = 3-thiophenyl **125k**: R^3 = 4-MeOC$_6$H$_4$ **125l**: R^3 = ^{n}Bu	**129h** (86%) **129i** (41%) **129j** (59%) **129k** (- ^{e}) **129l** (- ^{d})	**130h** (78%) **130i** (71%) **130j** (70%) **130k** (- ^{e}) **130l** (- ^{d})
		
125m: R^4 = 4-FC$_6$H$_4$ **125n**: R^4 = 4-BrC$_6$H$_4$ **125o**: R^4 = 4-^{n}PentC$_6$H$_4$ **125p**: R^4 = 4-MeC$_6$H$_4$ **125q**: R^4 = 2-MeC$_6$H$_4$	**129m**: R^5 = F, R^6 = H (65%) **129n**: R^5 = Br, R^6 = H (81%) **129o**: R^5 = ^{n}Pent, R^6 = H (57%) **129p**: R^5 = Me, R^6 = H (68%) **129q**: R^6 = H, R^6 = Me (81%)	**130m** (68%) **130n** (81%) **130o** (78%) **130p** (78%) **130q** (54%)

Table 3.2 (*continued*)

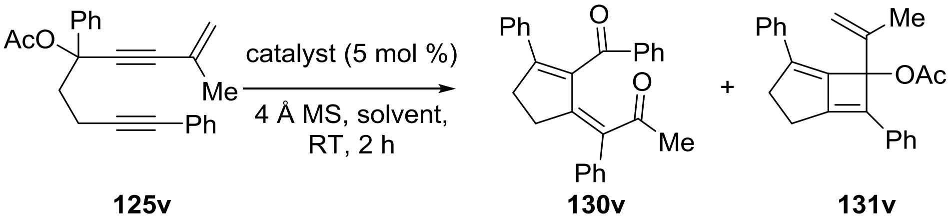
substrate **125**	product **129**	product **130**
 **125r**	 **129r** (53%)	 **130r** (70%)
 **125s**	 **129s** (53%)	 **130s** (45%)
 **125t**	 **129t** (10%)	 **130t** (74%)
 **125u**	 **129u** (52%)	 **130u** (71%)

[a] All reactions performed at the 0.2 mmol scale with catalyst:**125** ratio = 1:20 in anhydrous pentane at RT for 12-30 h. Values in parentheses denote isolated product yield. [b] Decomposed during purification by flash column chromatography on silica gel. [c] No reaction detected based on ^{1}H NMR analysis of the crude mixture.

chemoselectivity or yield was obtained by: (1) utilising an NHC-gold(I) catalyst **B**, a gold(III) catalyst **E**; (2) or by extending the reaction time to 24 h (entries 3 and 5). In each case, the cycloadducts **130v** and **131v** were furnished in respective yields of 29-34 and 13-57%. Similarly, with AuCl as the catalyst, the reaction afforded a lower product yield and product selectivity (**130v**: 31%, **131v**: 36%, entry 6). In contrast, the gold(I) triflimide catalyst **C** gave a comparable yield to **A** with **130v** and **131v** afforded in 35 and 57% yield (entry 4). The effect of solvent on the reaction with **A** as the catalyst was also assessed (entries 7–12). With CH_2Cl_2, benzene, hexane or cyclohexane as the reaction medium, both **130v** and **131v** were obtained in respective yields of 8–40 and 25–67% (entries 7–10). An optimal result in selectivity and product yield was found when *n*-pentane was employed as the solvent over 24 h (entry 12). Under these conditions, the δ-diketone **130v** and cyclobutene **131v** adducts were provided in 13 and 72% yield, respectively.

With the optimal catalyst **A**, we next sought to establish the substrate scope for

Table 3.3 Optimization of reaction conditions[a]



entry	catalyst	solvent	yield of **130v** (%)[b]	yield of **131v** (%)[b]
1[c]	**A**	toluene	25	40
2	**A**	toluene	35	61
3	**B**	toluene	31[d]	13[d]

Table 3.3 (*continued*)

4	**C**	toluene	35[d]	57[d]
5	**E**	toluene	34	57
6	AuCl	toluene	31[d]	36[d]
7	**A**	CH_2Cl_2	40	27
8	**A**	benzene	23	25
9	**A**	hexane	8[d]	59[d]
10	**A**	CyH	25[d]	67[d]
11	**A**	pentane	16[d]	68[d]
12	**A**	pentane[e]	13[d]	72[d]

[a] All reactions were performed on a 0.2 mmol scale with a catalyst:**125v** ratio of 1:20 at RT for 2 h. [b] Isolated yield. [c] Reaction conducted without 4 Å MS. [d] Reaction was conducted at RT for 24 h. [e] Solvent dried over 4 Å MS.

this transformation (Table 3.4). Overall, the tolerance of substrate structure was

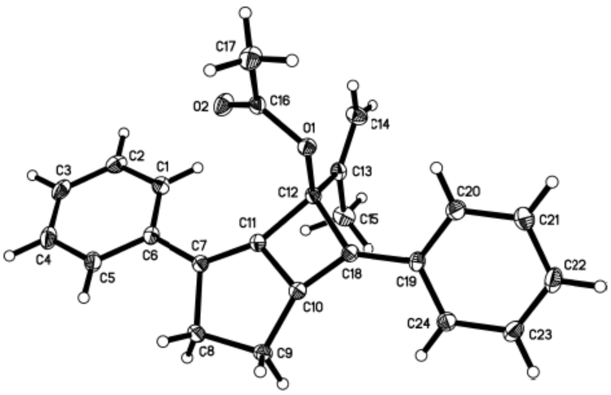
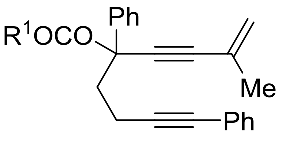
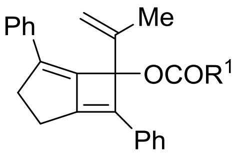
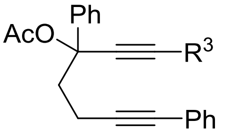
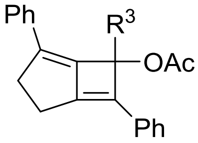
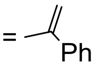
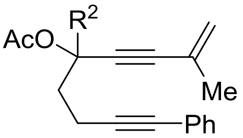
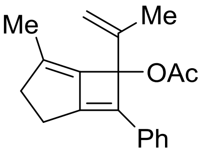
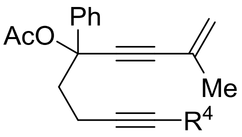
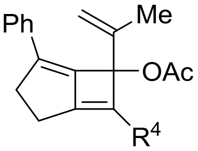


Figure 3.2 ORTEP drawing of **131v** with thermal ellipsoids at 50% probability levels[55]

found to be broad, providing the corresponding cyclobutene adducts **131v–ξ** in up to 78% yield. Changing the Ac migrating group (**125v**) for Bz (**125w**), was moderately tolerated affording **131w** in 48%. In contrast, reaction where the identity of the migrating group was a Piv (**125x**) and cyclopropanecarbonyl moiety (**125y**), a poorer yield of 24% and 31% was obtained. Exchanging the propargylic phenyl for a methyl substituent (**125γ**) gave a product which decomposed upon attempts at purification by flash chromatography on silica gel. Replacement of the propargylic phenyl moiety with 4-chlorophenyl or 1-naphthalenyl group gave **125z** and **125β** in poor yields of 26-34%. Altering the propargylic phenyl with 4-methylphenyl gave **125α** in 63% yield. On the other hand, replacing the vinylogous methyl substitution to *n*-hexyl (**125δ**) gave **131δ** in a comparable 68% yield, but phenyl (**125ε**) resulted in no reaction. Modifying the pendant alkynyl group with a broad range of aromatic motifs (**125ζ–λ**) was found to have no influence on the course of the reaction. Under the standard conditions, substrates with an electron-withdrawing (**125ζ**) or electron-donating **(125η-125λ)** substituent at various positions of the phenyl group at this position were found to give the corresponding cyclobutene adducts **131ζ-131λ** in 60-75% yield. Likewise, reactions with a 1-naphthalenyl (**125μ**), 2-thiophenyl (**125ν**) or 9-phenanthrenyl (**125ξ**) motif at this position of the starting acetate afforded the corresponding adducts **131μ-131ξ** in 65-78% yield.

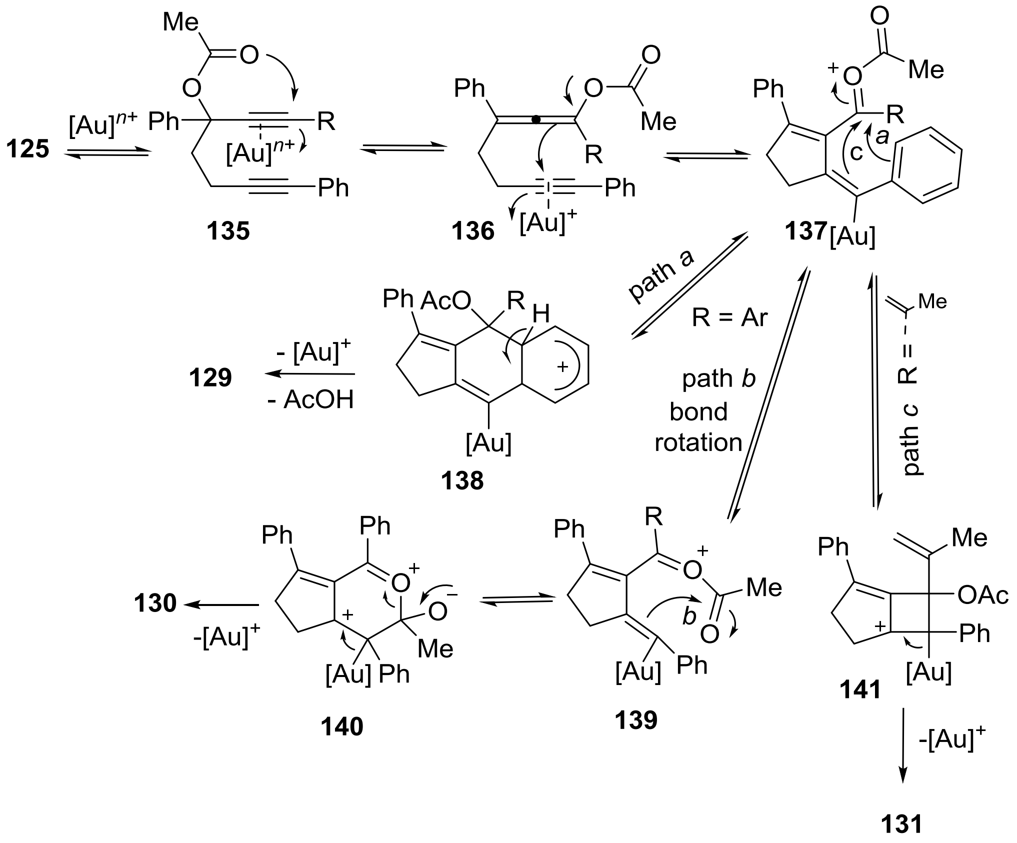
A tentative mechanism for the present Au(I)- and Au(III)-catalyzed 1*H*-cyclopenta[*b*]naphthalene **129**, δ-diketone **130** and bicyclo[3.2.0]hepta-1,5-diene **131** forming reactions is presented in Scheme 3.3. It is proposed that the reaction pathway may initially proceed by activation of the estereal alkyne moiety in the substrate by the Group 11 metal catalyst to give the gold-coordinated complex **135**. This may lead to 1,3-acyloxy migration and generation of the allene intermediate **136**. Subsequent

Table 3.4 Cycloisomerization of 1,6-diyne esters **125v–125ξ** catalyzed by **A**[a]

substrate **125**	product **131**	substrate **125**	product **131**
			
125v: R^1 = Me **125w**: R^1 = Bn **125x**: R^1 = ^{t}Bu **125y**: R^1 = cyclopropyl	**131v** (72%) **131w** (48%) **131x** (24%) **131y** (31%)	**125δ**: R^3 = 2-heptenyl **125ε**: R^3 = 	**131δ** (68%) **131ε**[c]
			
125z: R^2= 4-ClC_6H_4 **125α**: R^2 = 4-MeC_6H_4 **125β**: R^2 = 1-naphthalenyl **125γ**: R^2 = Me	**131z** (34%) **131α** (63%) **131β** (26%) **131γ** (–[b])	**125ζ**: R^4 = 4-FC_6H_4 **125η** : R^4 = 4-MeC_6H_4 **125θ**: R^4 = 4-^{n}PentC_6H_4 **125ι**: R^4 = 2-MeC_6H_4 **125κ**: R^4 = 3,5-$Me_2C_6H_3$ **125λ**: R^4 = 2,4,5-$Me_3C_6H_2$ **125μ**: R^4 = 1-naphthalenyl **125ν** : R^4 = 2-thiophenyl **125ξ**: R^4 = 9-phenanthrenyl	**131ζ** (68%) **131η** (69%) **131θ** (60%) **131ι** (75%) **131κ** (60%) **131λ** (72%) **131μ** (78%) **131ν** (69%) **131ξ** (65%)

[a] All reactions performed at the 0.2 mmol scale with catalyst:**125** ratio = 1:20 in anhydrous pentane at RT for 12-30 h. Values in parentheses denote isolated product yield. [b] Decomposed during purification by flash column chromatography on silica gel. [c] No reaction detected based on ^{1}H NMR analysis of the crude mixture.

5-*exo-dig* cyclization of this newly formed adduct involving anti addition of the allenic moiety to the C≡C bond in the ester would then provide the putative vinyl gold complex **137**. At this point, a divergence in the reactivity mode might occur depending on the nature of the gold catalyst and the substitution pattern of the substrate. In the presence of the Au(I) catalyst **B**, a Friedel-Crafts-type reaction involving attack of the pendant phenyl group to the oxocarbenium moiety in **137** may proceed in substrates where R = Ar (Scheme 3.3, path a).[56] This could be due to unfavorable steric interactions between these two side-chains restricting the rate of rotation the oxonium motif in the adduct. Protodeauration followed by re-aromatization of the ensuing Wheland intermediate **138** would then deliver **129**. On the other hand, it is possible that the same steric interactions might be anticipated to be less so in the analogous intermediate generated from reaction of the substrate with the gold(III) complex **E**. As a result, rotation of the oxonium side chain in **137** can now take place more readily to give **139** and better orbital overlap between the HOMO of the vinyl gold bond and the LUMO of the carbonyl carbon center offered by this latter conformer (Scheme 3.3, path b).[57] Deauration of the resulting organogold adduct **140** would then regenerate the gold(III) catalyst and give the *cis*-cyclopentene **130**. In contrast, it might be that there is a similar degree of restricted rate of rotation of the oxocarbenium side-chain in adducts of **137** generated from reaction of substrates containing an isoprenyl group at R with the Au(I) catalyst **A**. Moreover, the spatial volume occupied by the isoprenyl substituent may also be sufficient to hinder approach of the phenyl group to the oxonium moiety in the vinyl gold intermediate. Consequently, this may allow for the competitive Prins-type [2 + 2]-cyclization to proceed, involving attack of the oxocarbenium carbon center by the vinyl gold moiety in **137** (Scheme 3.3, path c).[58,59] Deauration of the resulting alkyl gold species **141** would release the gold(I) catalyst and afford the bicyclic adduct **131**.



Scheme 3.3 Proposed mechanism for the gold(I)-catalyzed cycloisomerization of 1,6-diyne esters **125**

While the mechanistic premise put forward for the observed product chemoselectivities is speculative, it would be in good agreement with a number of experiments examined in this work. First is the gold(III) complex **E**-mediated reaction of **125c** leading to decomposition where, presumably, it could now be due to the presence of the bulky *t*-Bu ester group in the substrate restricting the rate of rotation of the oxonium side chain in **137** upon its formation. Likewise, the same type of unfavorable steric interactions in vinyl gold species **137** generated from substrates with a pendant alkynyl phenyl group possessing an *o*-substituent, as in **125q** (2-methylphenyl) and **125s** (1-naphthalenyl) would explain the lower product yields found for these reactions. The observed increase in selectivity in favor of the fused cyclobutene **131** in reactions catalyzed by Au(I) complex **A** with *n*-pentane as the solvent would also be consistent with the poor ability of non-polar solvents to stabilize the cationic intermediate **137** sufficiently for bond rotation to occur.

3.3 Conclusion

In summary, we have described an efficient strategy for the synthesis of a variety of 1*H*-cyclopenta[*b*]naphthalenes, *cis*-cyclopenten-2-yl *δ*-diketones and bicyclo[3.2.0]hepta-1,5-dienes by gold-catalyzed cycloisomerization of 1,6-diyne esters. The reaction conditions were shown to tolerate a broad substrate scope, providing products containing scaffolds of potential utility in medicinal chemistry and as functional materials. Our studies showed that effective and divergent chemoselectivity was possible by harnessing the inherent differences in electronic and steric properties of NHC-gold(I), phosphine-gold(I) and gold(III) complexes. Following an initial 1,3-acyloxy migration/5-*exo-dig* sequence, we demonstrated that phenyl or vinyl substituents at the estereal alkynyl position in the substrate enabled the respective formation of the 1*H*-cyclopenta[*b*]naphthalene and bicyclo[3.2.0]hepta-1,5-diene products. The latter, formed by a Prins-type [2 + 2]-cycloaddition, possessed a stable fused cyclobutene moiety. We also showed that the use of the more Lewis acidic gold(III) catalyst led to chemoselective formation of *cis*-cyclopenten-2-yl *δ*-diketones via 1,5-acyl migration following the 1,3-acyloxy migration/5-*exo-dig* cyclization pathway. Efforts to explore the scope and synthetic applications of the present reactions are in progress and will be reported in due course.

Chapter IV. Concluding Remarks

Gold-catalyzed intramolecular based approaches for the synthesis of 2,4a-dihydro-1*H*-fluorene, 1*H*-Cyclopenta[*b*]naphthalenes, bicyclo[3.2.0]hepta-1,5-dienes and cyclopenten-2-yl *δ*-diketones from 1.6-diyne esters or carbonates have been established (Figure 4.1). An efficient method to functionalized 2,4a-dihydro-1*H*-fluorene from 1,6-diyne carbonates and esters **106** involving a 1,2-acyloxy migration step which was seldom seen in this type of substrates previously. The possibility of cyclopropene intermediate formation in situ which has remained rare in gold catalysis was proposed. In addition, a synthetic method to prepare 1*H*-cyclopenta[*b*]naphthalenes, bicyclo[3.2.0]hepta-1,5-dienes and cyclopenten-2-yl *δ*-diketones from gold-catalyzed cycloisomerization reactions of 1,6-diyne esters **125** was described. In our study, we found that the tandem process was initiated by a 1,3-migration leading to the formation of an allene intermediate, which can be further converted to oxocarbenium ion intermediates followed by a further reaction with a nucleophile, thus a sketetal reorganization could be achieved. In this text, the work we did as a whole is a very compresensive study in gold-catalyzed cycloisomerization of 1,6-diyne esters and carbonates. Included are the different reaction mechanisms.

In Chapter II, a novel strategy to 2,4a-dihydro-1*H*-fluorenes that relied on a gold-catalyzed cycloisomerization reactions of 1,6-diyne carbonates and esters was described. For the cycloisomerization of 1,6-diyne carbonates and esters **106** (Figure 4.1), in which containing a sterically less hindered terminal carbonate or a C≡C bond next to ester, 1,2-acyloxy migration and subsequent trapping of the ensuing gold carbenoid by the remaining alkyne moiety would be likely happen. Cycloreversion of the resulting cyclopropene intermediate in gold catalysis is extremely rare and then give the gold carbenoid species followed by Narazov cyclization would then be expected to provide 2,4a-dihydro-1*H*-fluorene derivatives. In this work, the details of the chemistry that offers an expedient and chemoselective approach to this carbocyclic motif in good to excellent yields would be described. Computational studies about the origin of the reaction selectivity was done by Prof. Hirao, Hajime of this Division using two different levels of quantum mechanical methods (ONIOM(QM:QM')).

In Chapter III, a synthetic method to prepare 1*H*-cyclopenta[*b*]naphthalenes, bicyclo[3.2.0]hepta-1,5-dienes and cyclopenten-2-yl δ-diketones from gold-catalyzed cycloisomerization reactions of 1,6-diyne esters was described. It is proposed that the reaction pathway may initially proceed by catalyst activation of the alkyne moiety next to the ester of the 1,6-diyne in complex **135**. This may then result in a 1,3-acyloxy migration generating the allene intermediate **136**. We propose that the pendant alkyne, activated by the gold catalyst, would undergo subsequent nucleophilic attack by the allene that results in 5-*exo-dig* cyclization and formation of the putative oxocarbenium-containing vinyl-gold adduct **137**. At this point, we suggest a divergence in the reactivity mode depending on the nature of the gold catalyst and the substitution pattern of the substrate. One proposed pathway may consist of cyclization by attack by the pendant phenyl group on the oxocarbenium of **137**.[53] (Scheme 3.3, path a). On the other hand, bond rotation of **137** to **139** would potentially trigger either a 1,5 migration, as shown in Scheme 3.3, paths b. After 1,5 migration, this might induce nucleophilic attack of the vinyl gold motif on to the carbonyl carbon center in **139** when R = Ar (Scheme 3.3, path b).[54] Cycloreversion of the resulting pyrylium species **140** followed by protodeauration would then deliver the δ-diketone **130**. In substrates where R = isoprenyl, Prins type cyclization of the vinyl gold moiety to the oxonium carbon center in **139** would give the intermediate **141**, which upon protodeauration, provide the product **131** (Scheme 3.3, path c).[58, 59]

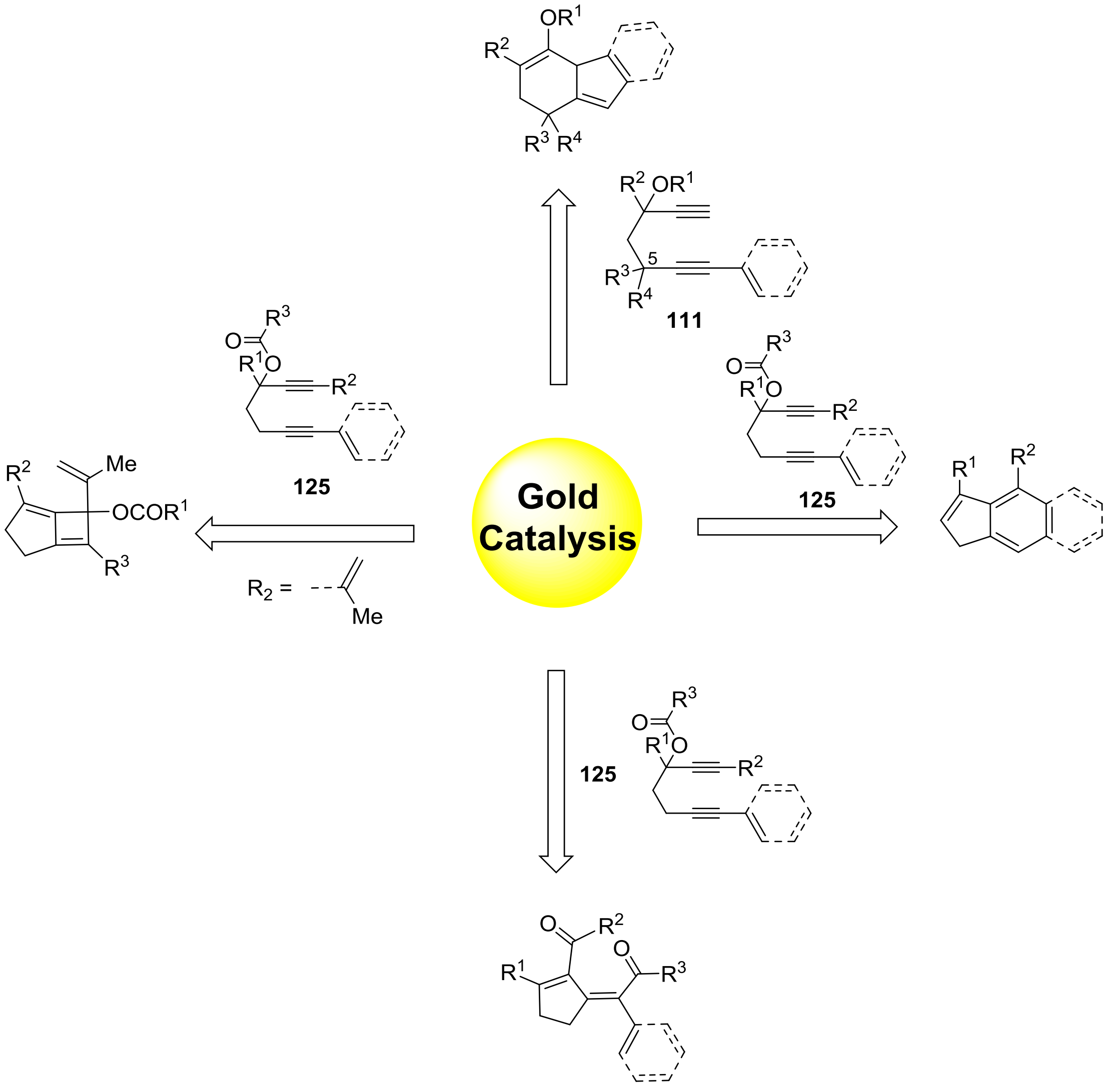


Figure 1.2 Gold-catalyzed synthesis of complex molecules from 1,6-diyne esters and carbonates

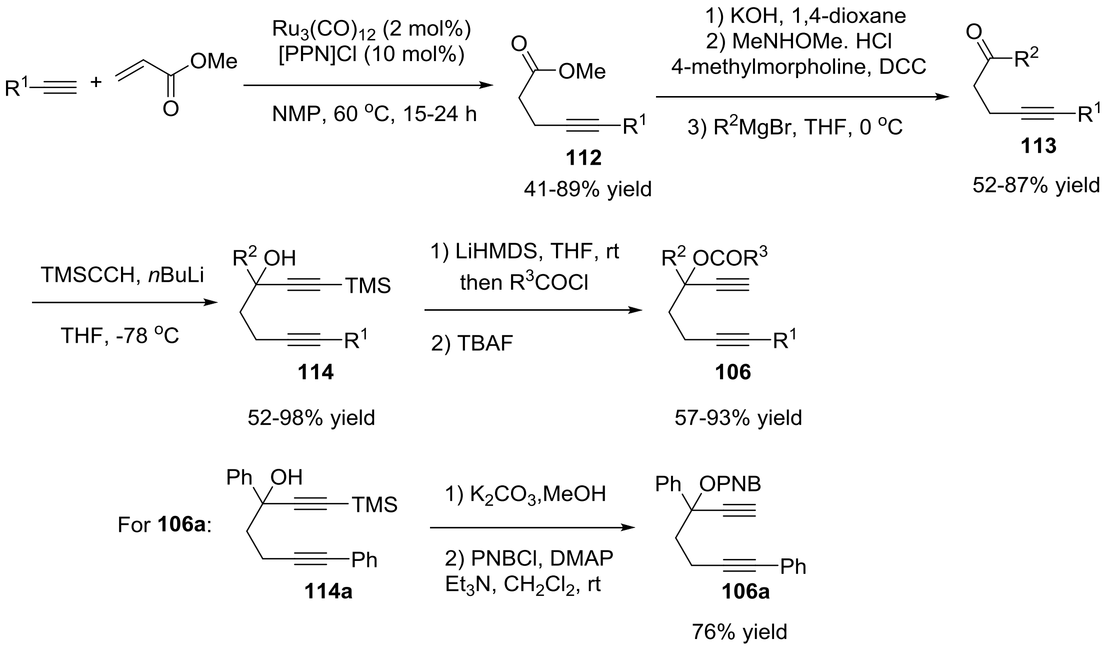
Chapter V. Experimental Section

5.1 General Remarks

All reactions were performed under an argon atmosphere. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Solvents were purified following standard literature procedures. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plate. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and gradient solvent system (EtOAc: *n*-hexane as eluant). ^{1}H and ^{13}C NMR spectra were measured on 400 MHz spectrometers. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), brs (broad singlet), d (doublet), t (triplet), dd (doublet of doublets), q (quartet) or m (multiplet). The number of protons (n) for a given resonance is indicated by nH and coupling constants are reported as a J value in Hz. Infrared spectra were recorded on a FTIR spectrometer. Solid samples were examined as a thin film between NaCl salt plates. High resolution mass spectra (HRMS) were obtained on a LC/HRMS mass spectrometer.

5.2 Gold-Catalyzed Cycloisomerization of 1,6-Diyne Carbonates and Esters to 2,4a-Dihydro-1*H*-fluorenes

General Routes for the Preparation of 1,6-Diyne Carbonates and Esters

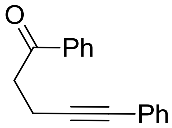


5.2.1. General Procedure for the Preparation of Ketones 113 from 112

To a solution of **112** (5.0 mmol) in 1,4-dioxane (15 mL) was added 15 mL of aqueous KOH 1M solution and the mixture was vigorously stirred at room temperature until completion (TLC, 1-2 hours). The reaction mixture was extracted with Et_2O (20 mL x 2) and this organic layer was discharged. To the aqueous phase was added 5% HCl until pH=2 and was extracted with EA (3 x 30 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, concentrated *in vacuo* and the resulting carboxylic acids in near quantitative yield was directly employed in the next reaction.

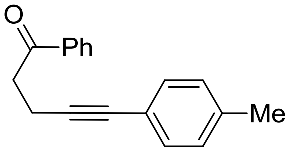
The resulting carboxylic acid was dissolved in 30 ml CH_2Cl_2, *N*-methylmorpholine (1.1 eq), *N*,*O*-dimethylhydroxylamine.HCl (1.1 eq) and *N*,*N*-dicyclohexylcarbodiimide (1.1 eq mmol) were added accordingly. The reaction mixture was stirred at room temperature for 15 hours, then filtered through Celite and concentrated under reduced pressure. The crude mixture was then purified by flash chromatography on silica gel (eluent: *n*hexane: EtOAc = 3:2) to give Weinreb amides as colorless liquid. To a solution of Weinreb amides in THF (15 mL) was added R_2MgBr (2 eq) at 0 ^{o}C. The resulting solution was stirred at room temperature for 2 hours then quenched by addition of saturated NH_4Cl (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*hexane: EtOAc: DCM = 50:1:1) to give ketones **113** (52-87% yield over 3 steps).

1,5-diphenylpent-4-yn-1-one (113a)[60]



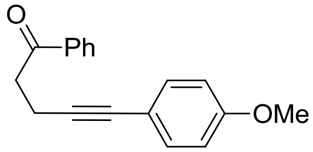
Yield 71%; yellow solid, mp = 73-74 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.86 (t, 2H, *J* = 7.0 Hz), 3.22 (t, 2H, *J* = 7.0 Hz), 7.27-7.28 (m, 3H), 7.39-7.41 (m, 2H), 7.46-7.50 (m, 2H), 7.56-7.60 (m, 1H), 8.00 (d, 2H, *J* = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 14.4, 37.9, 81.1, 89.9, 123.7, 127.8, 128.1, 128.2, 128.7, 131.6, 133.3, 136.6, 198.0.

1-phenyl-5-(p-tolyl)pent-4-yn-1-one (113b)



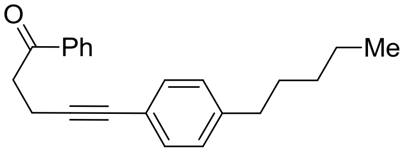
Yield 77%; pale-yellow solid, mp = 55-56 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.27 (s, 3H), 2.80 (t, 2H, *J* = 7.6 Hz), 3.22 (t, 2H, *J* = 7.6 Hz), 7.03 (d, 2H, *J* = 7.8 Hz), 7.27 (d, 2H, *J* = 8.1 Hz), 7.39-7.42 (m, 2H), 7.49-7.53 (m, 1H), 7.92-7.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz): 14.4, 21.4, 37.9, 81.2, 88.2, 120.7, 128.1, 128.7, 129.1, 131.5, 133.3, 136.6, 137.7, 198.0; IR (NaCl, neat) *v*: 3017, 2920, 2399, 1688, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{17}O$ (M^{+}+ H): 249.1279, found: 249.1282.

5-(4-methoxyphenyl)-1-phenylpent-4-yn-1-one (113c)



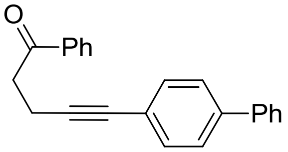
Yield 56%; pale-yellow solid, mp = 56-57 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.84 (t, 2H, *J* = 7.6 Hz), 3.29 (t, 2H, *J* = 7.6 Hz), 3.76 (s, 3H), 6.81 (d, 2H, *J* = 8.7 Hz), 7.35 (d, 2H, *J* = 8.7 Hz), 7.46 (t, 2H, *J* = 7.6 Hz), 7.57 (t, 1H, *J* = 7.4 Hz), 7.03 (d, 2H, *J* = 7.4 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 14.4, 37.9, 55.2, 80.9, 87.4, 113.9, 115.8, 128.1, 128.7, 133.0, 133.2, 136.6, 159.2, 198.0; IR (NaCl, neat) *v*: 3017, 2399, 1686, 1508, 1246, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{17}O_2$ (M$^+$+ H): 265.1229, found: 265.1221.

5-(4-pentylphenyl)-1-phenylpent-4-yn-1-one (113d)



Yield 79%; pale-yellow solid, mp = 58-59 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.87 (t, 3H, *J* = 7.1 Hz), 1.25-1.34 (m, 4H), 1.53-1.60 (m, 2H), 2.54 (t, 2H, *J* = 7.6 Hz), 2.82 (t, 2H, *J* = 7.6 Hz), 3.26 (t, 2H, *J* = 7.6 Hz), 7.06 (d, 2H, *J* = 8.1Hz), 7.29 (d, 2H, *J* = 8.1 Hz), 7.41-7.45 (m, 2H), 7.51-7.55 (m, 1H), 7.95-7.97 (m, 2H); ^{13}C NMR (CDCl$_3$, 100MHz): 14.1, 14.4, 22.6, 31.0, 31.5, 35.8, 37.9, 81.2, 88.1, 120.8, 128.1, 128.4, 128.7, 131.5, 133.2, 136.6, 142.8, 198.0; IR (NaCl, neat) *v*: 3019, 2930, 2399, 1686, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{25}O$ (M$^+$+ H): 305.1905, found: 305.1896.

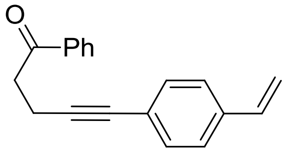
5-([1,1'-biphenyl]-4-yl)-1-phenylpent-4-yn-1-one (113e)



Yield 81%; pale-yellow solid, mp = 98-99 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.90 (t, 2H, *J* = 7.2 Hz), 3.35 (t, 2H, *J* = 7.2 Hz), 7.36 (t, 1H, *J* = 7.4 Hz), 7.43-7.61 (m, 11H), 8.02 (d, 2H, *J* = 7.4 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 14.5, 37.9, 81.0, 89.7, 122.7, 126.9, 127.0, 127.6, 128.1, 128.7, 128.9, 132.1, 133.3, 136.6, 140.4, 140.5, 198.0; IR

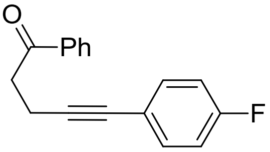
(NaCl, neat) *v*: 3018, 2399, 1686, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{23}H_{19}O$ (M^{+}+ H): 311.1436, found: 311.1429.

1-phenyl-5-(4-vinylphenyl)pent-4-yn-1-one (113f)



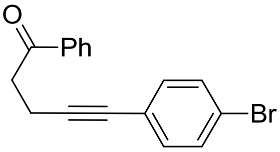
Yield 74%; yellow solid, mp = 50-51 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.86 (t, 2H, *J* = 7.6 Hz), 3.29 (t, 2H, *J* = 7.2 Hz), 5.27 (d, 1H, *J* = 10.9 Hz), 5.74 (d, 1H, *J* = 17.6 Hz), 6.69 (dd, 1H, *J* = 17.6, 10.9 Hz), 7.31-7.38 (m, 4H), 7.44-7.48 (m, 2H), 7.56 (t, 1H, *J* = 7.4 Hz), 7.98 (d, 2H, *J* = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 14.4, 37.8, 81.1, 89.7, 114.5, 123.1, 126.1, 128.1, 128.7, 131.8, 133.3, 136.3, 136.6, 137.0, 197.9; IR (NaCl, neat) *v*: 3017, 2399, 1686, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{17}O$ (M^{+}+ H): 261.1279, found: 261.1290.

5-(4-fluorophenyl)-1-phenylpent-4-yn-1-one (113g)



Yield 85%; yellow solid, mp = 69-70 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.80 (t, 2H, *J* = 7.3 Hz), 3.24 (t, 2H, *J* = 7.3 Hz), 6.90-6.95 (m, 2H), 7.31-7.41 (m, 2H), 7.43-7.50 (m, 2H), 7.51-7.54 (m, 1H), 7.93-7.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz): 14.3, 37.8, 80.1, 88.8, 115.4 (1C, d, J $_{C\text{-}F}$ = 8.3), 119.9, 119.9, 128.1, 128.7, 133.3, 133.5, 136.6, 162.2 (1C, d, J $_{C\text{-}F}$ = 249.1), 197.8; IR (NaCl, neat) *v*: 3019, 2397, 1686, 1506, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{14}OF$ (M^{+}+ H): 253.1029, found: 253.1024.

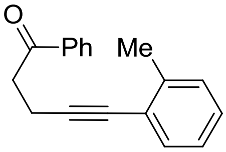
5-(4-bromophenyl)-1-phenylpent-4-yn-1-one (113h)



Yield 76%; yellow solid, mp = 82-83 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.74 (t, 2H, *J* = 7.6 Hz), 3.21 (t, 2H, *J* = 7.6 Hz), 7.13 (d, 2H, *J* = 8.5 Hz), 7.30 (d, 2H, *J* = 8.5 Hz), 7.37 (t, 2H, *J* = 7.8 Hz), 7.46-7.50 (m, 1H), 7.89 (d, 2H, *J* = 7.2 Hz); ^{13}C NMR

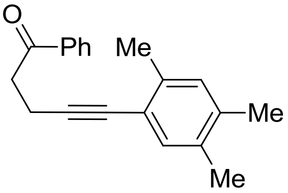
(CDCl$_3$, 100MHz): 14.3, 37.7, 80.1, 90.2, 121.9, 122.6, 128.1, 128.7, 131.4, 133.1, 133.3, 136.5, 197.8; HRMS (ESI) calcd. for $C_{17}H_{14}OBr$ (M^++ H): 313.0228, found: 313.0230.

1-phenyl-5-(o-tolyl)pent-4-yn-1-one (113i)



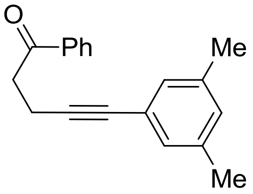
Yield 69%; pale-yellow solid, mp = 67-68 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.41 (s, 3H), 2.91 (t, 2H, *J* = 7.3 Hz), 3.32 (t, 2H, *J* = 7.3 Hz), 7.09-7.18 (m, 3H), 7.38 (d, 1H, *J* = 7.3 Hz), 7.45-7.59 (m, 3H), 8.00 (dd, 2H, *J* = 8.3, 1.4 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 14.7, 20.8, 38.1, 80.1, 123.5, 125.6, 127.8, 128.2, 128.8, 129.4, 132.0, 133.4, 136.7, 140.1, 198.1; IR (NaCl, neat) *v*: 3017, 2399, 1686, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{17}O$ (M^++ H): 249.1279, found: 249.1271.

1-phenyl-5-(2,4,5-trimethylphenyl)pent-4-yn-1-one (113j)



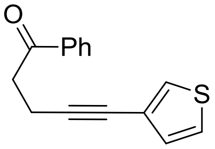
Yield 85%; yellow solid, mp = 89-90 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.20 (s, 3H), 2.23 (s, 3H), 2.38 (s, 3H), 2.92 (t, 2H, *J* = 7.6 Hz), 3.32 (t, 2H, *J* = 7.0 Hz), 6.96 (s, 1H), 7.18 (s, 1H), 7.47-7.51 (m, 2H), 7.57-7.61 (m, 1H), 8.02 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 14.6, 19.1, 19.6, 20.1, 38.1, 80.2, 91.7, 120.7, 128.1, 128.7, 130.8, 132.9, 133.2, 133.5, 136.4, 136.7, 137.3, 198.0; IR (NaCl, neat) *v*: 3017, 2918, 2399, 2222, 1686, 1449, 1362, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{21}O$ (M^++ H): 277.1592, found: 277.1588.

5-(3,5-dimethylphenyl)-1-phenylpent-4-yn-1-one (113k)



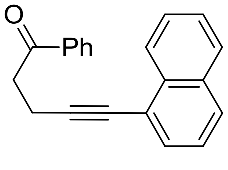
Yield 81%; white solid, mp = 82-83 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.28 (s, 6H), 2.86 (t, 2H, *J* = 7.4 Hz), 3.30 (t, 2H, *J* = 7.4 Hz), 6.92 (s, 1H), 7.06 (s, 2H), 7.46-7.50 (m, 2H), 7.57-7.60 (m, 1H), 8.01 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 14.4, 21.1, 37.9, 81.4, 88.2, 123.3, 128.1, 128.7, 129.4, 129.7, 133.3, 136.6, 137.7, 198.0; IR (NaCl, neat) *v*: 3019, 2918, 2399, 1688, 1215 cm^{-1}; HRMS (ESI) calcd. for C$_{19}$H$_{19}$O (M$^+$+ H): 263.1436, found: 263.1436.

1-phenyl-5-(thiophen-3-yl)pent-4-yn-1-one (113l)



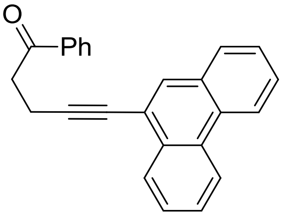
Yield 52%; pale-yellow solid, mp = 67-68 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.81 (t, 2H, *J* = 7.6 Hz), 3.25 (t, 2H, *J* = 7.6 Hz), 7.06 (dd, 1H, *J* = 5.0, 1.0 Hz), 7.19 (dd, 1H, *J* = 5.0, 3.0 Hz), 7.34 (d, 1H, *J* = 2.8 Hz), 7.43 (t, 2H, *J* = 7.8 Hz), 7.54 (t, 1H, *J* = 7.4 Hz), 7.95 (d, 2H, *J* = 7.4 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 14.3, 37.8, 76.3, 88.6, 122.7, 125.2, 128.0, 128.1, 128.7, 130.0, 133.3, 136.5, 197.8; IR (NaCl, neat) *v*: 3017, 2913, 2399, 1682, 1358, 1215 cm^{-1}; HRMS (ESI) calcd. for C$_{15}$H$_{13}$OS (M$^+$+ H): 241.0687, found: 241.0681.

5-(naphthalen-1-yl)-1-phenylpent-4-yn-1-one (113m)



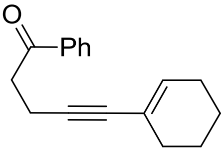
Yield 85%; yellow solid, mp = 115-116 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 3.05 (t, 2H, *J* = 7.0 Hz), 3.39 (t, 2H, *J* = 7.8 Hz), 7.40-7.61 (m, 6H), 7.68 (d, 1H, *J* = 7.1 Hz), 7.79-7.86 (m, 4H), 7.95 (d, 2H, *J* = 7.6 Hz), 8.40 (d, 1H, *J* = 8.1 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 14.8, 38.0, 79.2, 94.1, 121.5, 125.3, 126.4, 126.7, 128.2, 128.3, 128.3, 128.7, 130.2, 133.3, 133.3, 133.6, 136.7, 198.0; IR (NaCl, neat) *v*: 3017, 2399, 1686, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{17}O$ (M^++ H): 285.1279, found: 285.1287.

5-(phenanthren-9-yl)-1-phenylpent-4-yn-1-one (113n)



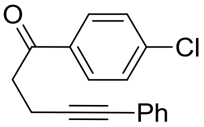
Yield 76%; yellow solid, mp = 150-151 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ 3.06 (t, 2H, *J* = 7.2 Hz), 3.45 (t, 2H, *J* = 7.2 Hz), 7.48-7.70 (m, 7H), 7.83 (d, 1H, *J* = 7.8 Hz), 7.94 (s, 1H), 8.05 (d, 2H, *J* = 7.6 Hz), 8.42-8.44 (m, 1H), 8.63-8.68 (m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz): 14.8, 38.0, 79.3, 93.6, 120.0, 122.6, 122.7, 126.9, 127.0, 127.0, 127.2, 128.1, 128.4, 128.7, 130.1, 131.3, 131.4, 131.5, 133.3, 136.6, 198.0; IR (NaCl, neat) *v*: 3017, 2399, 1686, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{19}O$ (M^++ H): 335.1436, found: 335.1420.

5-(cyclohex-1-en-1-yl)-1-phenylpent-4-yn-1-one (113o)



Yield 59%; pale-yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 1.53-1.61 (m, 4H), 2.04-2.09 (m, 4H), 2.72 (t, 2H, *J* = 7.6 Hz), 3.22 (t, 2H, *J* = 7.6 Hz), 5.99-6.01 (m, 1H), 7.43-7.47 (m, 2H), 7.53-7.57 (m, 1H), 7.96 (d, 2H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 14.2, 21.6, 22.4, 25.6, 29.5, 82.8, 85.9, 120.8, 128.0, 128.6, 133.2, 133.7, 136.6, 198.1; IR (NaCl, neat) *v*: 3019, 2918, 2399, 1686, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{19}O$ (M^++ H): 239.1436, found: 239.1442.

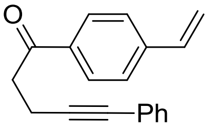
1-(4-chlorophenyl)-5-phenylpent-4-yn-1-one (113p)



Yield 71%; pale-yellow solid, mp = 56-57 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.82 (t, 2H, *J* = 7.6 Hz), 3.23 (t, 2H, *J* = 7.6 Hz), 7.23-7.26 (m, 3H), 7.35-7.41 (m, 4H), 7.88

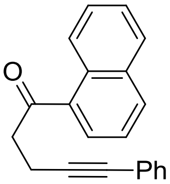
(dd, 2H, *J* = 8.6, 1.8 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 14.3, 37.8, 81.2, 88.8, 123.6, 127.8, 128.3, 129.0, 129.5, 131.6, 134.9, 139.7, 196.7; IR (NaCl, neat) *ν*: 3019, 2399, 1686, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{14}OCl$ (M$^+$+ H): 269.0733, found: 269.0731.

5-phenyl-1-(4-vinylphenyl)pent-4-yn-1-one (113q)



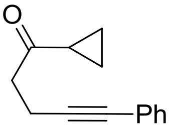
Yield 63%; white solid, mp = 85-86 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.85 (t, 2H, *J* = 7.2 Hz), 3.27 (t, 2H, *J* = 7.2 Hz), 5.40 (d, 1H, *J* = 10.9 Hz), 5.88 (d, 1H, *J* = 17.6 Hz), 6.76 (dd, 1H, *J* = 17.6, 10.9 Hz), 7.27-7.29 (m, 3H), 7.41-7.48 (m, 4H), 7.96 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 14.4, 37.8, 81.2, 89.1, 116.9, 123.8, 126.4, 127.8, 128.3, 128.5, 131.6, 135.7, 135.9, 142.2, 197.3; IR (NaCl, neat) *ν*: 3017, 2399, 1686, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{17}O$ (M$^+$+ H): 261.1279, found: 261.1285.

1-(naphthalen-1-yl)-5-phenylpent-4-yn-1-one (113r)



Yield 76%; colorless oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.91 (t, 2H, *J* = 7.6 Hz), 3.33 (t, 2H, *J* = 7.6 Hz), 7.24-7.27 (m, 3H), 7.37-7.59 (m, 5H), 7.83-7.86 (m, 2H), 7.95 (d, 1H, *J* = 8.2 Hz), 7.95 (d, 1H, *J* = 8.5 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 15.0, 41.0, 81.4, 89.0, 123.7, 124.5, 125.9, 126.6, 127.8, 127.8, 128.1, 128.3, 128.5, 130.2, 131.7, 132.9, 134.0, 135.5, 202.2; IR (NaCl, neat) *ν*: 3017, 2400, 1682, 1508 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{17}O$ (M$^+$+ H): 285.1279, found: 285.1275.

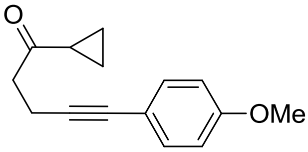
1-cyclopropyl-5-phenylpent-4-yn-1-one (113s)



Yield 58%; yellow oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.83-0.87 (m, 2H), 1.01-1.05 (m, 2H), 1.87-1.93 (m, 1H), 2.65 (dd, 1H, *J* = 8.4, 6.2 Hz), 2.83 (dd, 1H, *J* = 7.8, 5.6

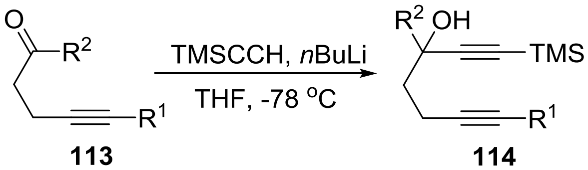
Hz), 7.23-7.27 (m, 3H), 7.35-7.38 (m, 2H); ^{13}C NMR (CDCl$_3$, 100MHz): 10.8, 14.1, 20.5, 42.1, 80.9, 88.9, 123.7, 127.7, 128.2, 131.6, 208.6; IR (NaCl, neat) *v*: 3019, 2399, 1686, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{15}O$ (M^++ H): 199.1123, found: 199.1118.

1-cyclopropyl-5-(4-methoxyphenyl)pent-4-yn-1-one (113t)



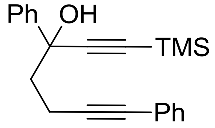
Yield 61%; colorless oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.87-0.91 (m, 2H), 1.03-1.07 (m, 2H), 1.92-1.98 (m, 1H), 2.66 (t, 2H, *J* = 8.0 Hz), 2.87 (t, 2H, *J* = 8.0 Hz), 3.78 (s, 3H), 6.80 (d, 2H, *J* = 8.7 Hz), 7.31 (d, 2H, *J* = 8.7 H); ^{13}C NMR (CDCl$_3$, 100MHz): 10.8, 14.1, 20.5, 42.3, 55.2, 80.6, 87.2, 113.8, 115.8, 132.9, 159.1, 208.8; IR (NaCl, neat) *v*: 3017, 2399, 1686, 1508, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{16}O_2Na$ (M^++ Na): 251.1048, found: 251.1042.

5.2.2. General Procedure for the Preparation of (trimethylsilyl)hepta-1,6-diyn-3-ol 114 from 113



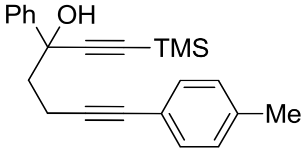
To a stirred solution of ethynyltrimethylsilane (0.353 mL, 2.5 mmol) in 10 mL of THF was added *n*-butyllithium (1.0 mL, 2.5 mmol, 2.5 M in cyclohexane) under argon at −78 °C. The resulting solution was stirred at −78 °C for 1 hour. A solution of ketone **113** (1.25 mmol) in THF (5 mL) was subsequently slowly added to the resulting solution at −78 °C and the reaction mixture was slowly warmed up to room temperature and stirred for a further 3 h. The reaction mixture was quenched by addition of water (10 mL) and extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO$_4$, concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*hexane: EtOAc: DCM = 50:1:2) to give (trimethylsilyl)hepta-1,6-diyn-3-ol **114** in 52-98% yield.

3,7-diphenyl-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114a)



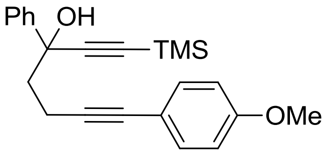
Yield 94%; yellow solid, mp = 75-76 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.32 (s, 9H), 2.23-2.39 (m, 2H), 2.59-2.79 (m, 2H), 3.01 (s, 1H), 7.30-7.44 (m, 8H), 7.71 (d, 2H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 0.1, 15.5, 44.3, 73.1, 81.2, 89.7, 91.5, 107.1, 123.9, 125.6, 127.7, 128.0, 128.3, 128.4, 131.7, 144.0; IR (NaCl, neat) *v*: 3445, 3019, 2961, 2168, 1601, 1491, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{23}Si$ (M^+–OH): 315.1569, found: 315.1572.

3-phenyl-7-(p-tolyl)-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114b)



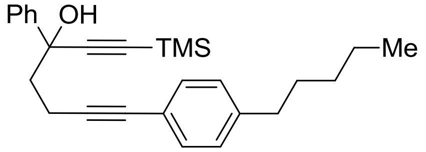
Yield 81%; yellow solid, mp = 92-92 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.29 (s, 9H), 2.19-2.26 (m, 1H), 2.29-2.35 (m, 1H), 2.37 (s, 3H), 2.54-2.62 (m, 1H), 2.68-2.75 (m, 1H), 2.77 (s, 1H), 7.12 (d, 2H, *J* = 7.8 Hz), 7.31 (d, 2H, *J* = 8.0 Hz), 7.36 (d, 1H, *J* = 7.3 Hz), 7.42 (t, 2H, *J* = 7.2 Hz), 7.69 (d, 2H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 0.0, 15.5, 21.4, 44.2, 73.1, 81.1, 88.7, 91.5, 106.9, 120.7, 125.5, 127.9, 128.3, 129.0, 131.4, 137.6, 143.9; IR (NaCl, neat) *v*: 3520, 3019, 2961, 2168, 1508, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{23}H_{25}Si$ (M^+–OH): 329.1726, found: 329.1724.

7-(4-methoxyphenyl)-3-phenyl-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114c)



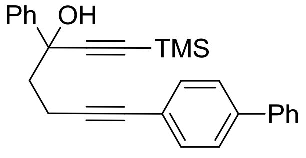
Yield 81%; colorless oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.28 (s, 9H), 2.17-2.34 (m, 2H), 2.52-2.60 (m, 1H), 2.65-2.74 (m, 1H), 2.97 (s, 1H), 3.78 (s, 3H), 6.82 (d, 2H, *J* = 8.3 Hz), 7.32-7.42 (m, 5H), 7.68 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 0.0, 15.5, 44.3, 55.2, 73.1, 80.8, 87.9, 91.4, 107.0, 113.9, 116.0, 125.5, 127.9, 128.3, 132.9, 144.0, 159.1; IR (NaCl, neat) *v*: 3449, 3019, 2961, 2399, 2167, 1607, 1508 cm^{-1}; HRMS (ESI) calcd. for $C_{23}H_{25}OSi$ (M^+–OH): 345.1675, found: 345.1680.

7-(4-pentylphenyl)-3-phenyl-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114d)



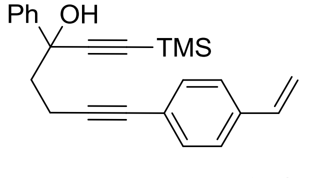
Yield 72%; yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.29 (s, 9H), 0.94 (t, 3H, J = 7.0 Hz), 1.33-1.41 (m, 4H), 1.60-1.68 (m, 2H), 2.18-2.24 (m, 1H), 2.26-2.36 (m, 1H), 2.54-2.63 (m, 3H), 2.68-2.76 (m, 1H), 2.83 (s, 1H), 7.12 (d, 2H, J = 8.0 Hz), 7.32-7.43 (m, 5H), 7.69 (d, 2H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 0.0, 14.1, 15.5, 22.6, 31.0, 31.5, 35.8, 44.3, 73 .1, 81.2, 88.7, 91.4, 107.0, 120.9, 125.5, 127.9, 128.4, 131.5, 142.7, 143.9; IR (NaCl, neat) v: 3520, 3019, 2930, 2168, 1508, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{33}Si$ (M^+–OH): 385.2352, found: 385.2350.

7-([1,1'-biphenyl]-4-yl)-3-phenyl-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114e)



Yield 88%; yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.30 (s, 9H), 2.21-2.29 (m, 1H), 2.31-2.39 (m, 1H), 2.58-2.66 (m, 1H), 2.71-2.80 (m, 2H), 7.34-7.49 (m, 8H), 7.55 (d, 2H, J = 8.2 Hz), 7.61 (d, 2H, J = 7.4 Hz), 7.71 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 0.0, 15.6, 44.2, 73.1, 80.9, 90.3, 91.6, 106.9, 122.8, 125.5, 126.9, 127.0, 127.6, 128.0, 128.4, 128.9, 132.0, 140.4, 140.5, 143.9; IR (NaCl, neat) v: 3452, 3019, 2961, 2399, 2168,1508 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{27}Si$ (M^+–OH): 391.1882, found: 391.1881.

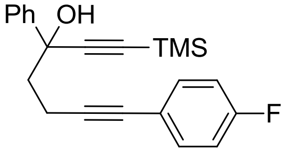
3-phenyl-1-(trimethylsilyl)-7-(4-vinylphenyl)hepta-1,6-diyn-3-ol (114f)



Yield 85%; yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.29 (s, 9H), 2.19-2.26 (m, 1H), 2.29-2.36 (m, 1H), 2.55-2.63 (m, 1H), 2.68-2.76 (m, 1H), 2.82 (s, 1H), 5.29 (d, 1H, J = 10.9 Hz), 5.76 (d, 1H, J = 17.6 Hz), 6.71 (dd, 1H, J = 17.6, 10.9 Hz), 7.33-7.43 (m, 7H), 7.69 (d, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 0.0, 15.5, 44.2, 73.1, 81.0, 90.3, 91.5, 106.9, 114.4, 123.2, 125.5, 126.1, 128.0, 128.4, 131.8, 136.4, 136.9, 143.9;

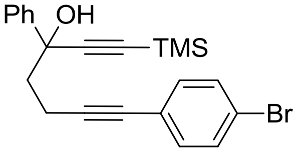
IR (NaCl, neat) *v*: 3439, 3018, 2961, 2168, 1601, 1246 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{25}Si$ (M^+–OH): 341.1726, found: 341.1727.

7-(4-fluorophenyl)-3-phenyl-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114g)



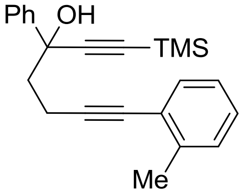
Yield 80%; yellow oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.22 (s, 9H), 2.11-2.19 (m, 1H), 2.21-2.28 (m, 1H), 2.46-2.55 (m, 1H), 2.59-2.67 (m, 1H), 2.74 (s, 1H), 6.92 (t, 2H, *J* = 8.7 Hz), 7.28-7.37 (m, 5H), 7.62 (d, 2H, *J* = 7.3 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 0.0, 15.4, 44.1, 73.0, 79.9, 89.2, 91.5, 106.9, 115.4 (1C, d, J $_{C\text{-}F}$ = 21.8), 119.9 (1C, d, J $_{C\text{-}F}$ = 3.3), 125.5, 128.0, 128.3, 133.3 (1C, d, J $_{C\text{-}F}$ = 8.3), 143.9, 162.1 (1C, d, J $_{C\text{-}F}$ = 246.8); IR (NaCl, neat) *v*: 3445, 3017, 2961, 2168, 1601, 1508, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{22}FSi$ (M^+–OH): 333.1475, found: 333.1481.

7-(4-bromophenyl)-3-phenyl-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114h)



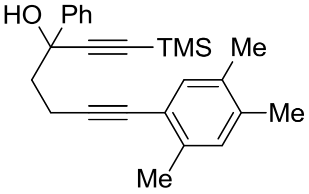
Yield 87%; yellow oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.26 (s, 9H), 2.15-2.22 (m, 1H), 2.24-2.32 (m, 1H), 2.50-2.58 (m, 1H), 2.62-2.69 (m, 1H), 2.71 (s, 1H), 7.21-7.23 (m, 2H), 7.30-7.41 (m, 5H), 7.65-7.67 (m, 2H); ^{13}C NMR (CDCl$_3$, 100MHz): 0.0, 15.4, 44.0, 73.0, 80.0, 90.9, 91.6, 106.8, 121.8, 122.8, 125.5, 128.0, 128.4, 131.4, 133.0, 143.8; IR (NaCl, neat) *v*: 3445, 3019, 2961, 2168, 1487, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{22}BrSi$ (M^+–OH): 393.0674, found: 393.0688.

3-phenyl-7-(o-tolyl)-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114i)



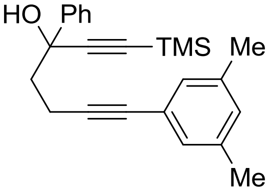
Yield 87%; colorless oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.30 (s, 9H), 2.21-2.29 (m, 1H), 2.31-2.39 (m, 1H), 2.45 (s, 3H), 2.60-2.68 (m, 1H), 2.74-2.83 (m, 1H), 2.85 (s, 1H), 7.12-7.21 (m, 3H), 7.34-7.45 (m, 4H), 7.70-7.72 (m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz): 0.0, 15.7, 20.8, 44.4, 73.1, 80.0, 91.5, 93.4, 106.9, 123.5, 125.5, 127.7, 128.0, 128.4, 129.4, 131.9, 140.0, 144.0; IR (NaCl, neat) *v*: 3447, 3019, 2961, 2168, 1487, 1450, 1246, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{23}H_{25}Si$ (M^+–OH): 329.1726, found: 329.1726.

3-phenyl-7-(2,4,5-trimethylphenyl)-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114j)



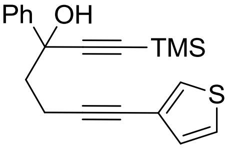
Yield 80%; colorless oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.32 (s, 9H), 2.23-2.26 (m, 7H), 2.31-2.40 (m, 1H), 2.42 (s, 3H), 2.60-2.68 (m, 1H), 2.74-2.83 (m, 1H), 2.90 (s, 1H), 6.99 (s, 1H), 7.19 (s, 1H), 7.35-7.38 (m, 1H), 7.42-7.45 (m, 2H), 7.72 (d, 2H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 0.0, 15.7, 19.1, 19.6, 20.2, 44.5, 73.2, 80.3, 91.4, 92.2, 120.7, 125.5, 127.9, 128.4, 130.8, 132.9, 133.5, 136.3, 137.2, 144.0; IR (NaCl, neat) *v*: 3520, 3019, 2961, 2168, 1450, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{29}Si$ (M^+–OH): 257.2039, found: 257.2036.

7-(3,5-dimethylphenyl)-3-phenyl-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114k)



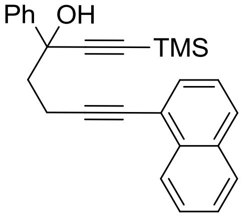
Yield 89%; colorless oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.29 (s, 9H), 2.18-2.25 (m, 1H), 2.28-2.36 (m, 7H), 2.53-2.61 (m, 1H), 2.67-2.76 (m, 1H), 2.83 (s, 1H), 6.94 (s, 1H), 7.05 (s, 2H), 7.33-7.36 (m, 1H), 7.40-7.44 (m, 2H), 7.69 (d, 2H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 0.0, 15.5, 21.1, 44.2, 73.1, 81.4, 88.7, 91.4, 106.9, 123.4, 125.5, 127.9, 128.3, 129.3, 129.6, 137.7, 143.9; IR (NaCl, neat) *v*: 3448, 3019, 2961, 2168, 1450, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{27}Si$ (M^+–OH): 343.1882, found: 343.1883.

3-phenyl-7-(thiophen-3-yl)-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114l)



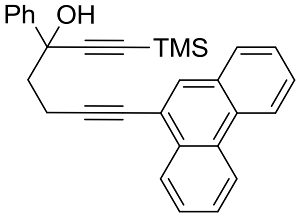
Yield 53%; yellow solid, mp = 52-53 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.28 (s, 9H), 2.16-2.24 (m, 1H), 2.26-2.34 (m, 1H), 2.51-2.60 (m, 1H), 2.64-2.73 (m, 1H), 2.81 (s, 1H), 7.06-7.08 (m, 1H), 7.21-7.23 (m, 1H), 7.32-7.42 (m, 4H), 7.66-7.68 (m, 2H); ^{13}C NMR (CDCl$_3$, 100MHz): 0.0, 15.4, 44.1, 73.0, 76.1, 89.1, 91.5, 106.9, 122.8, 125.1, 125.5, 127.8, 128.0, 128.4, 130.0, 143.9; IR (NaCl, neat) *v*: 3429, 3019, 2961, 2168, 1450, 1246, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{21}SSi$ (M^+–OH): 321.1133, found: 321.1126.

7-(naphthalen-1-yl)-3-phenyl-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114m)



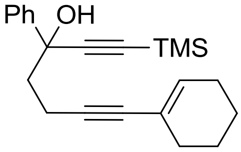
Yield 84%; yellow oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.31 (s, 9H), 2.32-2.49 (m, 2H), 2.73-2.81 (m, 2H), 2.86-2.94 (m, 1H), 7.35-7.46 (m, 4H), 7.51-7.61 (m, 2H), 7.65 (d, 1H, *J* = 7.1 Hz), 7.74 (d, 2H, *J* = 7.7 Hz), 7.80 (d, 1H, *J* = 8.2 Hz), 7.86 (d, 1H, *J* = 8.0 Hz), 8.37 (d, 1H, *J* = 8.2 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 0.0, 15.8, 44.4, 73.1, 79.1, 91.7, 94.6, 106.9, 121.5, 125.3, 125.5, 126.3, 126.3, 126.6, 128.0, 128.1, 128.3, 128.4, 130.1, 133.2, 133.5, 144.0; IR (NaCl, neat) *v*: 3429, 3061, 2961, 2168, 1450, 1246 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{25}Si$ (M^+–OH): 365.1726, found: 365.1734.

7-(phenanthren-9-yl)-3-phenyl-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114n)



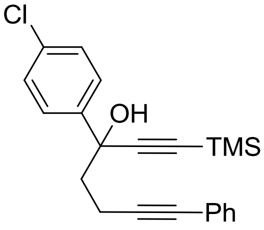
Yield 81%; yellow oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.34 (s, 9H), 2.37-2.44 (m, 1H), 2.47-2.54 (m, 1H), 2.78-2.86 (m, 2H), 2.91-2.99 (m, 1H), 7.38 (t, 1H, *J* = 7.2 Hz), 7.46 (t, 2H, *J* = 7.6 Hz), 7.59-7.78 (m, 6H), 7.85 (d, 1H, *J* = 7.7 Hz), 7.96 (s, 1H), 8.48-8.50 (m, 1H), 8.64-8.69 (m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz): 0.1, 15.9, 44.4, 73.2, 79.3, 91.7, 94.3, 106.9, 120.2, 122.6, 122.8, 125.6, 126.9, 127.0, 127.0, 127.1, 127.2, 128.1, 128.4, 128.5, 130.1, 131.4, 131.5, 131.5, 144.0; IR (NaCl, neat) *v*: 3431, 3061, 2961, 2168, 1952, 1491, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{30}H_{27}Si$ (M^+–OH): 415.1882, found: 415.1875.

7-(cyclohex-1-en-1-yl)-3-phenyl-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114o)



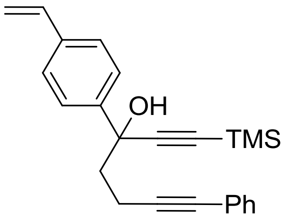
Yield 77%; yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.24 (s, 9H), 1.56-1.63 (m, 4H), 2.02-2.12 (m, 5H), 2.15-2.22 (m, 1H), 2.38-2.46 (m, 1H), 2.53-2.61 (m, 1H), 2.89 (s, 1H), 6.00 (s, 1H), 7.27-7.38 (m, 3H), 7.62 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 0.0, 15.3, 21.6, 22.4, 25.6, 29.5, 44.3, 73.1, 82.9, 86.5, 91.2, 107.0, 120.8, 125.4, 127.8, 128.2, 133.6, 143.9; IR (NaCl, neat) *v*: 3418, 2961, 2930, 2168, 1450, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{27}Si$ (M^+–OH): 319.1882, found: 319.1889.

3-(4-chlorophenyl)-7-phenyl-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114p)



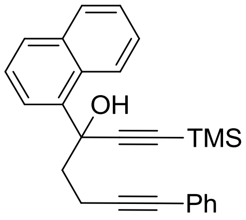
Yield 87%; yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.28 (s, 9H), 2.14-2.22 (m, 1H), 2.24-2.31 (m, 1H), 2.53-2.61 (m, 1H), 2.65-2.74 (m, 1H), 2.99 (s, 1H), 7.28-7.31 (m, 3H), 7.35-7.41 (m, 4H), 7.59-7.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz): 0.0, 15.4, 44.1, 72.6, 81.3, 89.3, 91.9, 106.4, 123.7, 127.1, 127.8, 128.3, 128.4, 131.6, 133.8, 142.5; IR (NaCl, neat) *v*: 3412, 3019, 2961, 2168, 1491, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{22}ClSi$ (M^+–OH): 349.1179, found: 349.1175.

7-phenyl-1-(trimethylsilyl)-3-(4-vinylphenyl)hepta-1,6-diyn-3-ol (114q)



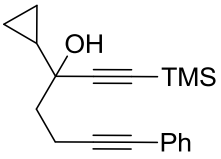
Yield 83%; yellow oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.31 (s, 9H), 2.20-2.27 (m, 1H), 2.29-2.37 (m, 1H), 2.55-2.63 (m, 1H), 2.68-2.76 (m, 1H), 2.85 (s, 1H), 5.31 (d, 1H, *J* = 11.3 Hz), 5.81 (d, 1H, *J* = 17.6 Hz), 6.78 (dd, 1H, *J* = 17.6, 10.9 Hz), 7.29-7.31 (m, 3H), 7.40-7.46 (m, 4H), 7.64 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 0.0, 15.4, 44.1, 72.9, 81.1, 89.5, 91.5, 106.9, 114.3, 123.8, 125.8, 126.2, 127.7, 128.3, 131.6, 136.4, 137.3, 143.4; IR (NaCl, neat) *v*: 3429, 3019, 2961, 2399, 2168, 1491, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{25}Si$ (M^+−OH): 341.1726, found: 341.1722.

3-(naphthalen-1-yl)-7-phenyl-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114r)



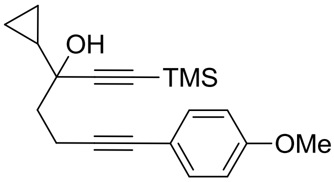
Yield 52%; yellow oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.26 (s, 9H), 2.55-2.77 (m, 4H), 2.94 (s, 1H), 7.26-7.28 (m, 3H), 7.35-7.37 (m, 2H), 7.47-7.57 (m, 3H), 7.84 (d, 1H, *J* = 8.1 Hz), 7.90 (d, 1H, *J* = 7.5 Hz), 8.01 (d, 1H, *J* = 7.2 Hz), 8.82 (d, 1H, *J* = 8.6 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): -0.1, 15.4, 41.8, 73.2, 81.1, 89.6, 92.3, 107.5, 123.8, 123.9, 124.9, 125.5, 126.2, 127.7, 128.2, 129.1, 129.4, 129.9, 131.5, 134.7, 138.3; IR (NaCl, neat) *v*: 3433, 3019, 2961, 2168, 1508, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{25}Si$ (M^+−OH): 365.1726, found: 365.1722.

3-cyclopropyl-7-phenyl-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114s)



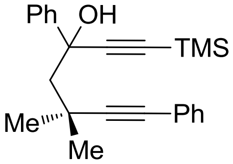
Yield 68%; colorless oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.16 (s, 9H), 0.44-0.63 (m, 4H), 1.08-1.13 (m, 1H), 2.08-2.14 (m, 2H), 2.32 (s, 1H), 2.67-2.71 (m, 2H), 7.25-7.28 (m, 3H), 7.37-7.40 (m, 2H); ^{13}C NMR (CDCl$_3$, 100MHz): 0.0, 1.2, 2.9, 15.2, 20.5, 31.5, 41.6, 73.2, 80.9, 90.0, 90.3, 104.4, 123.9, 127.7, 128.3, 131.6; IR (NaCl, neat) *ν*: 3424, 3019, 2961, 2168, 1491, 1246 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{23}Si$ (M^+–OH): 279.1569, found: 279.1560.

3-cyclopropyl-7-(4-methoxyphenyl)-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114t)



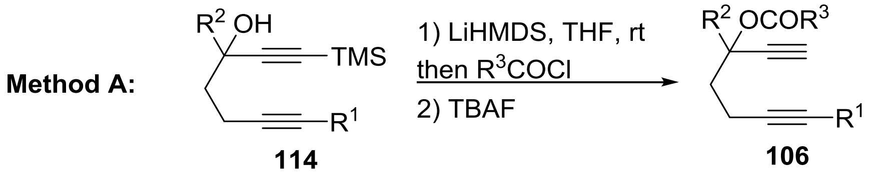
Yield 98%; colorless oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.10 (s, 9H), 0.35-0.50 (m, 3H), 0.53-0.58 (m, 1H), 1.02-1.09 (m, 1H), 2.00-2.10 (m, 2H), 2.44 (s, 1H), 2.59-2.64 (m, 2H), 3.71 (s, 3H), 6.74 (d, 2H, *J* = 8.7 Hz), 7.26 (d, 2H, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): -0.1, 1.1, 2.8, 15.1, 20.4, 41.7, 55.2, 73.1, 80.5, 88.3, 90.1, 104.5, 113.8, 116.0, 132.9, 159.1; IR (NaCl, neat) *ν*: 3452, 3019, 2961, 2168, 1491, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{25}OSi$ (M^+–OH): 309.1675, found: 309.1681.

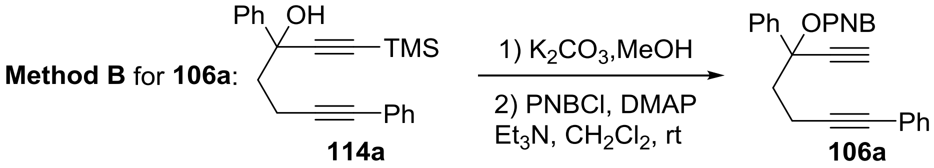
5,5-dimethyl-3,7-diphenyl-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (114u)



Yield 97%; colorless oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.26 (s, 9H), 1.38 (s, 3H), 1.71 (s, 3H), 2.13 (d, 1H, *J* = 14.4 Hz), 2.25 (d, 1H, *J* = 14.4 Hz), 4.50 (s, 1H), 7.31-7.35 (m, 4H), 7.42-7.50 (m, 4H), 7.76 (d, 2H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): -0.2, 30.5, 30.6, 32.6, 56.9, 72.3, 83.7, 91.4, 96.3, 108.6, 123.1, 125.4, 127.5, 128.1, 128.2, 128.3, 131.6, 145.6; IR (NaCl, neat) *ν*: 3507, 2967, 2961, 1952, 1601, 1491, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{27}Si$ (M^+–OH): 343.1882, found: 343.1890.

5.2.3. General Procedures for the Preparation of 1,6-Diyne Carbonates and Esters 106





Method A:

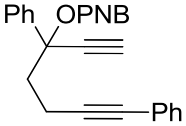
To a solution of (trimethylsilyl)hepta-1,6-diyn-3-ol **114** (1 mmol) in anhydrous THF (8 mL) was added LiHMDS (1.5 mL, 1.5 mmol, 1.0M in THF) under an argon atmosphere at room temperature, The reaction solution was stirred for a further 20 min at room temperature, then R^3COCl (1.5 mmol) was added and the reaction mixture was stirred at room temperature for 30 min. Upon completion (indicated by TLC), TBAF (1.5 mL,1.5 mmol, 1.0 M in THF) was added and the solution was stirred for 1 h at room temperature when TLC indicated that the reaction was complete. Water was added (10 mL), and the solution was extracted with EtOAc (3x 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*hexane: EtOAc: DCM = 50:1:1) to yield the desired product **106** (57-93% yield).

Method B:

To a solution of (trimethylsilyl)hepta-1,6-diyn-3-ol **114a** (2 mmol) in MeOH (15 mL) was added K_2CO_3 (0.829g, 6 mmol) at room temperature, the reaction mixture was stirred at room temperature for 1-3 hours when TLC indicated that the reaction was complete. The solution was concentrated under reduced pressure then water (15 mL) was added, extracted with EtOAc (3x 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to yield the crude 3,7-diphenylhepta-1,6-diyn-3-ol as pale-yellow oil was used in the next step without further purification.

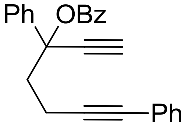
To a solution of 3,7-diphenylhepta-1,6-diyn-3-ol and DMAP (0.2 mmol) in CH_2Cl_2 (15 mL) was added Et_3N (0.557 mL, 4 mmol), then 4-nitrobenzoyl chloride (0.557 g, 3 mmol). The reaction mixture was stirred at room temperature for 15-24 hours. Upon completion (indicated by TLC), the reaction mixture was quenched by addition of saturated $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (2x 20 mL). The combined organic layers were washed with brine (15 mL), dried over $MgSO_4$, concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*hexane:EtOAc:DCM = 100:3:5) to yield the desired product **106a** in 76% yield over 2 steps.

3,7-diphenylhepta-1,6-diyn-3-yl 4-nitrobenzoate (106a)



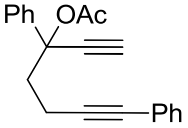
Yield 76%; white solid, mp = 143-144 °C; ^1H NMR ($CDCl_3$, 400MHz): δ 2.42-2.49 (m, 1H), 2.56-2.63 (m, 1H), 2.67-2.74 (m, 1H), 2.79-2.86 (m, 1H), 2.99 (s, 1H), 7.24-7.41 (m, 8H), 7.63 (d, 2H, *J* = 7.5 Hz), 8.17-8.23 (m, 4H); ^{13}C NMR ($CDCl_3$, 100MHz): 15.4, 43.3, 78.3, 79.7, 80.3, 81.2, 88.7, 123.6, 123.6, 125.2, 127.9, 128.3, 128.6, 128.7, 130.9, 131.5, 135.5, 139.7, 150.6, 162.3; IR (NaCl, neat) *v*: 3302, 3019, 2120, 1734, 1528, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{20}NO_4$ (M^++H): 410.1392, found: 410.1397.

3,7-diphenylhepta-1,6-diyn-3-yl benzoate (106b)



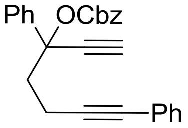
Yield 95%; yellow oil; ^1H NMR ($CDCl_3$, 400MHz): δ 2.46-2.52 (m, 1H), 2.64-2.78 (m, 2H), 2.85-2.92 (m, 1H), 2.98 (s, 1H), 7.31-7.47 (m, 10H), 7.59 (t, 1H, *J* = 7.3 Hz), 7.69 (d, 2H, *J* = 7.5 Hz), 8.14 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 15.4, 43.8, 77.7, 78.4, 81.0, 81.1, 89.0, 123.8, 125.2, 127.8, 128.3, 128.5, 128.6, 129.8, 130.3, 131.6, 133.3, 140.5, 164.0; IR (NaCl, neat) *v*: 3302, 3019, 2120, 1734, 1601, 1273 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{21}O_2$ (M^++H): 365.1542, found: 365.1537.

3,7-diphenylhepta-1,6-diyn-3-yl acetate (106c)



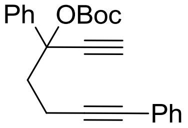
Yield 88%; colorless oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.11 (s, 3H), 2.27-2.39 (m, 1H), 2.49-2.58 (m, 2H), 2.66-2.78 (m, 1H), 2.92 (s, 1H), 7.29-7.42 (m, 8H), 7.59 (d, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 15.2, 21.7, 43.4, 76.9, 77.8, 81.0, 88.8, 123.8, 125.1, 127.8, 128.2, 128.3, 128.6, 131.6, 140.4, 168.4; IR (NaCl, neat) v: 3302, 3019, 2120, 1736, 1601, 1273 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{19}O_2$ (M^++H): 303.1385, found: 303.1374.

benzyl (3,7-diphenylhepta-1,6-diyn-3-yl) carbonate (106d)



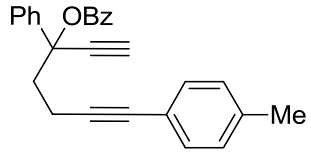
Yield 79%; colorless oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.35-2.40 (m, 1H), 2.53-2.65 (m, 2H), 2.74-2.83 (m, 1H), 2.99 (s, 1H), 5.15 (s, 2H), 7.28-7.46 (m, 13H), 7.66 (d, 1H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 15.3, 43.4, 69.7, 78.0, 80.3, 80.5, 81.0, 88.5, 123.7, 125.3, 127.7, 128.2, 128.4, 128.6, 128.6, 131.6, 135.1, 139.8, 152.5; IR (NaCl, neat) v: 3447, 3302, 3019, 2278, 1753, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{22}O_3Na$ (M^++ Na): 417.1467, found: 417.1465.

tert-butyl (3,7-diphenylhepta-1,6-diyn-3-yl) carbonate (106e)



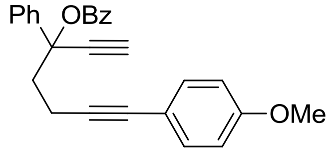
Yield 91%; colorless oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 1.40 (s, 9H), 2.24-2.32 (m, 1H), 2.46-2.55 (m, 2H), 2.66-2.74 (m, 1H), 2.90 (s, 1H), 7.24-7.40 (m, 8H), 7.59-7.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz): 15.3, 27.7, 43.7, 77.4, 79.3, 80.9, 82.8, 88.7, 123.8, 125.0, 127.7, 128.2, 128.3, 128.5, 131.6, 140.6, 150.8; IR (NaCl, neat) v: 3302, 2278, 2120, 1753 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{24}O_3Na$ (M^++ Na): 383.1623, found: 383.1608.

3-phenyl-7-(p-tolyl)hepta-1,6-diyn-3-yl benzoate (106f)



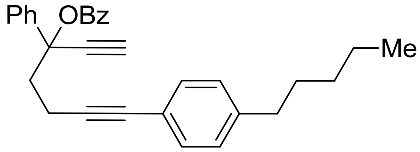
Yield 93%; colorless oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.37 (s, 3H), 2.45-2.51 (m, 1H), 2.63-2.77 (m, 2H), 2.84-2.91 (m, 1H), 2.98 (s, 1H), 7.13 (d, 2H, *J* = 7.6 Hz), 7.32-7.48 (m, 7H), 7.59 (t, 1H, *J* = 7.2 Hz), 7.68 (d, 2H, *J* = 7.6 Hz), 8.14 (d, 2H, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 15.4, 21.5, 43.9, 77.6, 78.4, 81.0, 81.1, 88.1, 120.7, 125.2, 128.3, 128.5, 128.6, 129.1, 129.8, 130.3, 131.5, 133.3, 137.8, 140.5, 164.0; IR (NaCl, neat) *v*: 3302, 2232, 2120, 1734 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{23}O_2$ (M^++H): 379.1698, found: 379.1689.

7-(4-methoxyphenyl)-3-phenylhepta-1,6-diyn-3-yl benzoate (106g)



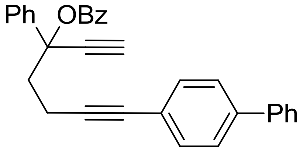
Yield 82%; colorless oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.41-2.48 (m, 1H), 2.59-2.73 (m, 2H), 2.80-2.87 (m, 1H), 2.95 (s, 1H), 3.80 (s, 3H), 6.82-6.84 (m, 2H), 7.31-7.46 (m, 7H), 7.56-7.66 (m, 3H), 8.10-8.12 (m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz): 15.4, 43.9, 55.3, 77.5, 78.4, 80.8, 81.0, 87.3, 113.9, 115.9, 125.1, 128.3, 128.5, 128.6, 129.8, 130.3, 132.9, 133.2, 140.5, 159.2, 164.0; IR (NaCl, neat) *v*: 3302, 3019, 2120, 1734, 1508, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{23}O_3$ (M^++H): 395.1647, found: 395.1653.

7-(4-pentylphenyl)-3-phenylhepta-1,6-diyn-3-yl benzoate (106h)



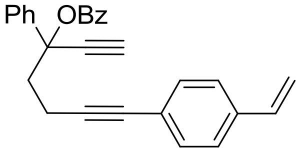
Yield 93%; pale-yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.96 (t, 3H, *J* = 7.0 Hz), 1.35-1.43 (m, 4H), 1.62-1.70 (m, 2H), 2.46-2.53 (m, 1H), 2.62-2.79 (m, 4H), 2.86-2.93 (m, 1H), 2.99 (s, 1H), 7.16 (d, 2H, *J* = 7.9 Hz), 7.34-7.48 (m, 7H), 7.60 (t, 1H, *J* = 7.2 Hz), 7.70 (d, 2H, *J* = 8.0 Hz), 8.16 (d, 2H, *J* = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 14.2, 15.5, 22.6, 31.0, 31.5, 35.9, 43.9, 77.6, 78.5, 81.0, 81.2, 88.2, 120.9, 125.2, 128.3, 128.4, 128.5, 128.6, 129.9, 130.4, 131.5, 133.3, 140.5, 142.8, 164.0; IR (NaCl, neat) *v*: 3300, 2930, 2232, 2120, 1964, 1732, 1269, 1094 cm^{-1}; HRMS (ESI) calcd. for $C_{31}H_{30}O_2Na$ (M^++Na): 457.2144, found: 457.2144.

7-([1,1'-biphenyl]-4-yl)-3-phenylhepta-1,6-diyn-3-yl benzoate (106i)



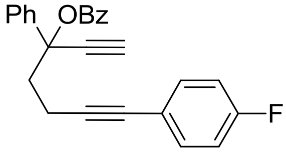
Yield 88%; pale-yellow oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.48-2.53 (m, 1H), 2.67-2.79 (m, 2H), 2.87-2.94 (m, 1H), 2.99 (s, 1H), 7.24-7.51 (m, 10H), 7.56-7.71 (m, 7H), 8.14-8.16 (m, 2H); ^{13}C NMR (CDCl$_3$, 100MHz): 15.5, 43.8, 77.6, 78.4, 81.0, 81.0, 89.7, 122.7, 125.2, 127.0, 127.0, 127.6, 128.3, 128.5, 128.7, 128.9, 129.9, 130.3, 132.0, 133.3, 140.5, 140.5, 164.1; IR (NaCl, neat) *v*: 3302, 3019, 2120, 1734, 1451, 1273 cm^{-1}; HRMS (ESI) calcd. for $C_{32}H_{20}O_2Na$ (M^++Na): 463.1674, found: 463.1666.

3-phenyl-7-(4-vinylphenyl)hepta-1,6-diyn-3-yl benzoate (106j)



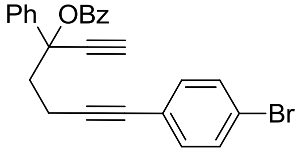
Yield 85%; pale-yellow solid, mp = 74-75 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.45-2.51 (m, 1H), 2.64-2.77 (m, 2H), 2.85-2.91 (m, 1H), 2.98 (s, 1H), 5.30 (d, 1H, *J* = 10.9 Hz), 5.78 (d, 1H, *J* = 17.6 Hz), 6.73 (dd, 1H, *J* = 17.6, 10.9 Hz), 7.33-7.47 (m, 9H), 7.57-7.69 (m, 3H), 8.12-8.14 (m, 2H); ^{13}C NMR (CDCl$_3$, 100MHz): 15.5, 43.8, 77.6, 78.4, 81.0, 81.1, 89.7, 114.5, 123.1, 125.2, 126.1, 128.3, 128.5, 128.6, 129.8, 130.3, 131.8, 133.3, 136.3, 137.0, 140.5, 164.0; IR (NaCl, neat) *v*: 3302, 3019, 2120, 1734, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{23}O_2$ (M^++H): 391.1698, found: 391.1706.

7-(4-fluorophenyl)-3-phenylhepta-1,6-diyn-3-yl benzoate (106k)



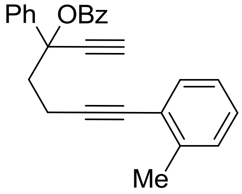
Yield 77%; pale-yellow solid, mp = 125-126 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.44-2.50 (m, 1H), 2.61-2.78 (m, 2H), 2.82-2.89 (m, 1H), 2.98 (s, 1H), 6.98-7.02 (m, 2H), 7.33-7.47 (m, 7H), 7.57-7.61 (m, 1H), 7.68 (d, 2H, J = 7.4 Hz) 8.13 (d, 2H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 15.3, 43.7, 77.7, 78.4, 80.0, 81.0, 88.6, 115.4 (1C, d, $J_{C\text{-}F}$ = 21.9), 119.8 (1C, d, $J_{C\text{-}F}$ = 3.3), 125.2, 128.3, 128.5, 128.6, 129.8, 130.3, 133.3, 133.4, 140.4, 162.2 (1C, d, $J_{C\text{-}F}$ = 8247.0), 164.0; IR (NaCl, neat) v: 3302, 3019, 2120, 1734, 1508, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{20}O_2F$ (M^++H): 383.1447, found: 383.1454.

7-(4-bromophenyl)-3-phenylhepta-1,6-diyn-3-yl benzoate (106l)



Yield 94%; white solid, mp = 138-139 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.41-2.47 (m, 1H), 2.58-2.73 (m, 2H), 2.79-2.86 (m, 1H), 2.95 (s, 1H), 7.23 (d, 2H, J = 8.2 Hz), 7.30-7.45 (m, 7H), 7.57 (t, 1H, J = 7.2 Hz), 7.65 (d, 2H, J = 7.4 Hz), 8.10 (d, 2H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 15.4, 43.5, 77.6, 78.3, 80.1, 80.9, 90.2, 121.9, 122.7, 125.1, 128.3, 128.5, 128.6, 129.8, 130.3, 131.5, 133.1, 133.3, 140.4, 164.0; IR (NaCl, neat) v: 3302, 3019, 2120, 1734, 1273 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{20}O_2Br$(M^++H): 443.0647, found: 443.0646.

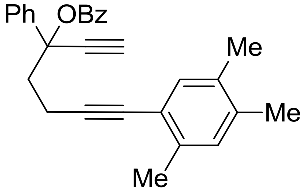
3-phenyl-7-(o-tolyl)hepta-1,6-diyn-3-yl benzoate (106m)



Yield 87%; yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.47-2.54 (m, 4H), 2.70-2.81 (m, 2H), 2.91-2.97 (m, 1H), 3.00 (s, 1H), 7.14-7.23 (m, 3H), 7.35-7.48 (m, 6H), 7.60 (t, 1H, J = 7.4 Hz), 7.70 (d, 2H, J = 7.3 Hz), 8.15 (d, 2H, J = 7.3 Hz); ^{13}C NMR

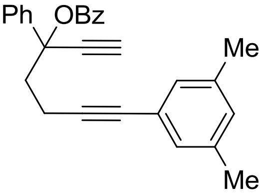
(CDCl$_3$, 100MHz): 15.6, 20.8, 44.0, 77.7, 78.5, 80.0, 81.0, 92.8, 123.5, 125.2, 125.5, 127.8, 128.3, 128.5, 128.7, 129.4, 129.8, 130.3, 131.9, 133.3, 140.0, 140.5, 164.1; IR (NaCl, neat) *v*: 3302, 3019, 2120, 1734, 1273 cm^{-1}; IR (NaCl, neat) *v*: 3300, 3019, 2120, 1734, 1450, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{23}O_2$ (M$^+$+H): 379.1698, found: 379.1707.

3-phenyl-7-(2,4,5-trimethylphenyl)hepta-1,6-diyn-3-yl benzoate (106n)



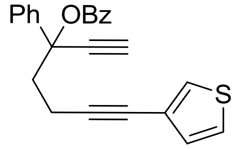
Yield 93%; colorless oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.22 (s, 3H), 2.25 (s, 3H), 2.39 (s, 3H), 2.46-2.52 (m, 1H), 2.67-2.78 (m, 2H), 2.87-2.94 (m, 1H), 2.98 (s, 1H), 6.99 (s, 1H), 7.18 (s, 1H), 7.34-7.48 (m, 5H), 7.58-7.62 (m, 1H), 7.69 (d, 2H, *J* = 8.0 Hz), 8.14 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 15.6, 19.1, 19.6, 20.1, 44.1, 77.6, 78.5, 80.1, 81.0, 91.5, 120.6, 125.2, 128.3, 128.5, 128.6, 129.8, 130.3, 130.8, 132.9, 133.3, 133.6, 136.4, 137.2, 140.5, 164.1; IR (NaCl, neat) *v*: 3302, 3019, 2120, 1734, 1273 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{27}O_2$ (M$^+$+H): 407.2011, found: 407.2012.

7-(3,5-dimethylphenyl)-3-phenylhepta-1,6-diyn-3-yl benzoate (106o)



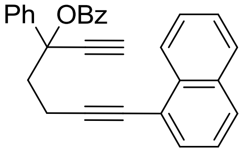
Yield 95%; colorless oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.29 (s, 3H), 2.42-2.48 (m, 1H), 2.60-2.73 (m, 2H), 2.80-2.87 (m, 1H), 2.96 (s, 1H), 6.94 (s, 1H), 7.03 (s, 2H), 7.31-7.46 (m, 5H), 7.56-7.60 (m, 1H), 7.65 (d, 2H, *J* = 7.3 Hz), 8.12 (d, 2H, *J* = 7.3 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 15.4, 21.1, 43.8, 77.5, 78.4, 81.0, 81.3, 88.1, 123.3, 125.1, 128.3, 128.5, 128.6, 129.3, 129.7, 129.8, 130.3, 133.2, 137.8, 140.5, 164.0; IR (NaCl, neat) *v*: 3302, 3019, 2120, 1734, 1601, 1450, 1109 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{25}O_2$ (M$^+$+H): 393.1855, found: 393.1850.

3-phenyl-7-(thiophen-3-yl)hepta-1,6-diyn-3-yl benzoate (106p)



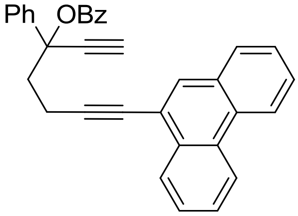
Yield 91%; colorless oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.43-2.49 (m, 1H), 2.61-2.75 (m, 2H), 2.81-2.88 (m, 1H), 2.97 (s, 1H), 7.08 (d, 1H, *J* = 5.0 Hz), 7.23-7.26 (m, 1H), 7.32-7.47 (m, 6H), 7.59 (t, 1H, *J* = 7.4 Hz), 7.67 (d, 2H, *J* = 7.4 Hz), 8.13 (d, 2H, *J* = 7.7 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 15.4, 43.7, 76.2, 77.6, 78.4, 81.0, 88.5, 122.7, 125.2, 127.9, 128.3, 128.5, 128.6, 129.8, 130.0, 130.3, 133.3, 140.4, 164.0; IR (NaCl, neat) *v*: 3287, 3019, 2120, 1734, 1273 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{19}O_2S$ (M$^+$+H): 371.1106, found: 371.1104.

7-(naphthalen-1-yl)-3-phenylhepta-1,6-diyn-3-yl benzoate (106q)



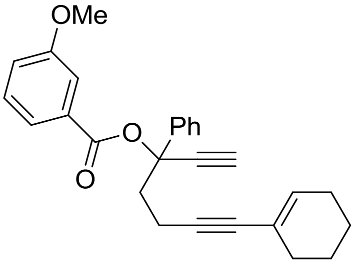
Yield 84%; white solid, mp = 105-106 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.55-2.64 (m, 1H), 2.80-2.88 (m, 2H), 2.98-3.09 (m, 2H), 7.34-7.45 (m, 6H), 7.51-7.60 (m, 3H), 7.64-7.72 (m, 3H), 7.82 (d, 1H, *J* = 8.2 Hz), 7.86 (d, 1H, *J* = 7.8 Hz), 8.13-8.15 (m, 2H), 8.37 (d, 1H, *J* = 7.7 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 15.8, 44.0, 77.7, 78.5, 79.1, 81.0, 93.9, 121.4, 125.2, 125.3, 126.3, 126.3, 126.6, 128.2, 128.3, 128.5, 128.7, 129.8, 130.2, 130.3, 133.2, 133.3, 133.5, 140.5, 164.0; IR (NaCl, neat) *v*: 3302, 3019, 2278, 1734, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{30}H_{23}O_2$ (M$^+$+H): 415.1698, found: 415.1698.

7-(phenanthren-9-yl)-3-phenylhepta-1,6-diyn-3-yl benzoate (106r)



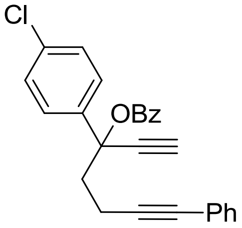
Yield 89%; yellow solid, mp = 73-75 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.59-2.68 (m, 1H), 2.83-2.92 (m, 2H), 3.02-3.13 (m, 2H), 7.36-7.46 (m, 5H), 7.55-7.74 (m, 7H), 7.85 (d, 1H, *J* = 7.7 Hz), 7.96 (s, 1H), 8.16 (d, 2H, *J* = 7.6 Hz), 8.48-8.50 (m, 1H), 8.65-8.71 (m, 2H); ^{13}C NMR (CDCl$_3$, 100MHz): 15.8, 43.9, 77.7, 78.5, 79.3, 81.0, 93.6, 120.1, 122.6, 122.8, 125.2, 126.9, 127.0, 127.0, 127.3, 128.4, 128.5, 128.7, 129.9, 130.1, 130.1, 130.3, 131.3, 131.4, 131.5, 133.3, 140.5, 164.1; IR (NaCl, neat) *v*: 3302, 3019, 2278, 1734, 1450, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{34}H_{25}O_2$ (M$^+$+H): 465.1855, found: 465.1846.

7-(cyclohex-1-en-1-yl)-3-phenylhepta-1,6-diyn-3-yl 3-methoxybenzoate (106s)



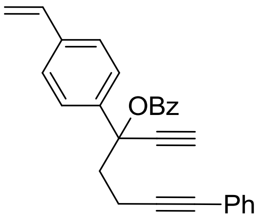
Yield 86%; colorless oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 1.55-1.63 (m, 4H), 2.07-2.08 (m, 4H), 2.32-2.39 (m, 1H), 2.46-2.54 (m, 1H), 2.57-2.63 (m, 1H), 2.64-2.75 (m, 1H), 2.93 (s, 1H), 3.83 (s, 3H), 6.01 (s, 1H), 7.13 (dd, 1H, *J* = 8.2, 2.0 Hz), 7.29-7.39 (m, 4H), 7.57-7.62 (m, 3H), 7.70 (d, 2H, *J* = 7.7 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 15.2, 21.6, 22.4, 25.6, 29.5, 44.0, 55.4, 77.5, 78.5, 80.9, 82.8, 85.8, 114.3, 119.7, 120.8, 122.1, 125.1, 128.2, 128.5, 129.5, 131.6, 133.7, 140.4, 159.6, 163.9; IR (NaCl, neat) *v*: 3302, 3019, 2940, 2120, 1728, 1273, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{27}O_3$ (M$^+$+H): 399.1960, found: 399.1956.

3-(4-chlorophenyl)-7-phenylhepta-1,6-diyn-3-yl benzoate (106t)



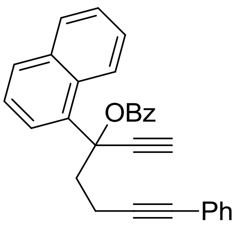
Yield 82%; colorless oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.38-2.50 (m, 1H), 2.63-2.73 (m, 2H), 2.81-2.92 (m, 1H), 2.98 (s, 1H), 7.30-7.46 (m, 9H), 7.57-7.62 (m, 3H) 8.11 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 15.4, 43.6, 77.9, 78.0, 80.5, 81.3, 88.7, 123.7, 126.7, 127.9, 128.3, 128.6, 128.8, 129.8, 130.0, 131.6, 133.4, 134.2, 139.1, 164.0; IR (NaCl, neat) *v*: 3302, 3019, 2288, 1734, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{20}O_2Cl$ (M$^+$+H): 399.1152, found: 399.1137.

7-phenyl-3-(4-vinylphenyl)hepta-1,6-diyn-3-yl benzoate (106u)



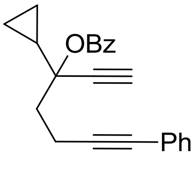
Yield 81%; colorless oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.45-2.51 (m, 1H), 2.63-2.77 (m, 2H), 2.84-2.90 (m, 1H), 2.98 (s, 1H), 5.29 (d, 1H, *J* = 10.9 Hz), 5.78 (d, 1H, *J* = 17.6 Hz), 6.75 (dd, 1H, *J* = 17.6, 10.9 Hz), 7.30-7.31 (m, 3H), 7.41-7.46 (m, 6H), 7.57-7.65 (m, 3H), 8.13 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 15.4, 43.6, 77.7, 78.3, 80.9, 81.1, 88.9, 114.6, 123.7, 125.5, 126.5, 127.8, 128.3, 128.5, 129.8, 130.3, 131.6, 133.3, 136.3, 137.7, 139.9, 164.1; IR (NaCl, neat) *v*: 3302, 3019, 2120, 1734, 1273, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{23}O_2$ (M$^+$+H): 391.1698, found: 391.1698.

3-(naphthalen-1-yl)-7-phenylhepta-1,6-diyn-3-yl benzoate (106v)



Yield 87%; yellow oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.64-2.80 (m, 2H), 2.96-3.06 (m, 2H), 3.17-3.24 (m, 1H), 7.27-7.29 (m, 3H), 7.36-7.43 (m, 6H), 7.51-7.58 (m, 2H), 7.84-7.88 (m, 2H), 8.12 (d, 2H, *J* = 7.6 Hz), 8.25 (d, 1H, *J* = 7.2 Hz), 8.58-8.61 (m, 1H); ^{13}C NMR (CDCl$_3$, 100MHz): 15.7, 40.9, 77.9, 80.8, 81.1, 81.8, 89.0, 123.7, 124.7, 125.0, 125.4, 126.3, 126.4, 127.7, 128.2, 128.5, 129.2, 129.6, 129.8, 129.9, 130.0, 131.5, 133.2, 134.5, 134.8, 163.8; IR (NaCl, neat) *v*: 3302, 3019, 2278, 1734, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{30}H_{23}O_2$ (M$^+$+H): 415.1698, found: 415.1691.

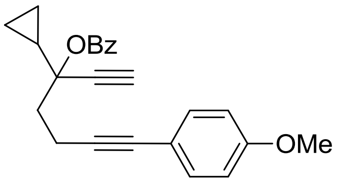
3-cyclopropyl-7-phenylhepta-1,6-diyn-3-yl benzoate (106w)



Yield 86%; colorless oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.57-0.67 (m, 3H), 0.93-0.99 (m, 1H), 1.46-1.53 (m, 1H), 2.38-2.45 (m, 1H), 2.55 (s, 1H), 2.61-2.74 (m, 3H), 7.20-

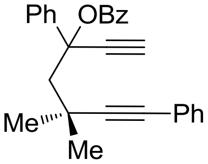
7.22 (m, 3H), 7.30-7.40 (m, 4H), 7.49 (t, 1H, *J* = 7.4 Hz), 7.98-8.00 (m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz): 3.0, 3.6, 15.1, 17.9, 39.5, 75.9, 79.0, 80.8, 80.9, 89.2, 123.8, 127.6, 128.2, 128.4, 129.7, 130.8, 131.5, 132.9, 164.7; IR (NaCl, neat) *v*: 3302, 3019, 2120, 1722, 1450 cm^{-1}; HRMS (ESI) calcd. for $C_{23}H_{21}O_2$ (M^++H): 329.1542, found: 329.1534.

3-cyclopropyl-7-(4-methoxyphenyl)hepta-1,6-diyn-3-yl benzoate (106x)



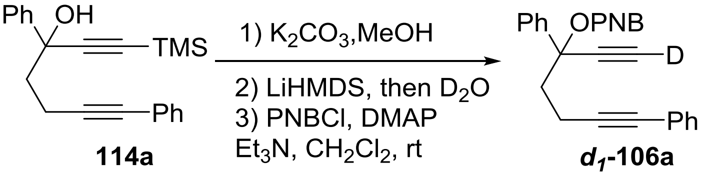
Yield 89%; colorless oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.61-0.71 (m, 3H), 0.98-1.04 (m, 1H), 1.51-1.58 (m, 1H), 2.42-2.49 (m, 1H), 2.61 (s, 1H), 2.65-2.77 (m, 3H), 3.78 (s, 3H), 6.78-6.81 (m, 2H), 7.28-7.31 (m, 2H), 7.40-7.43 (m, 2H), 7.52-7.56 (m, 1H), 8.03-8.06 (m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz): 3.0, 3.6, 15.1, 17.9, 39.7, 55.2, 75.9, 79.1, 80.6, 80.9, 87.6, 113.8, 115.9, 128.4, 129.7, 130.9, 132.9, 132.9, 159.1, 164.6; IR (NaCl, neat) *v*: 3302, 3019, 2120, 1722, 1527, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{23}O_3$ (M^++H): 359.1647, found: 359.1641.

5,5-dimethyl-3,7-diphenylhepta-1,6-diyn-3-yl benzoate (106y)



Yield 91%; colorless oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 1.53 (s, 3H), 1.55 (s, 3H), 2.46 (d, 1H, *J* = 14.7 Hz), 2.71 (d, 1H, *J* = 14.7 Hz), 3.00 (s, 1H), 7.26-7.42 (m, 10H), 7.53 (t, 1H, *J* = 7.4 Hz), 7.74 (d, 2H, *J* = 7.8 Hz), 8.19 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 31.0, 31.1, 31.5, 55.3, 78.1, 78.4, 81.2, 82.2, 97.4, 124.2, 125.3, 127.5, 128.0, 128.1, 128.4, 128.5, 129.9, 130.6, 131.6, 133.0, 142.2, 164.2; IR (NaCl, neat) *v*: 3300, 3019, 2120, 1730, 1273, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{25}O_2$ (M^++H): 393.1855, found: 393.1859.

5.2.4. General Procedures for the Preparation of 1,6-Diyne Esters d_1-106a

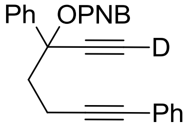


To a solution of (trimethylsilyl)hepta-1,6-diyn-3-ol **114** (1 mmol) in MeOH (10 mL) was added K_2CO_3 (0.415g, 3 mmol) at room temperature, the reaction mixture was stirred at room temperature for 1-3 hours when TLC indicated that the reaction was complete. The solution was concentrated under reduced pressure then water (10 mL) was added, extracted with EtOAc (3x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure to yield the crude 3,7-diphenylhepta-1,6-diyn-3-ol as pale-yellow oil was used in the next step without further purification.

To a solution of 3,7-diphenylhepta-1,6-diyn-3-ol in anhydrous THF (8 mL) was added LiHMDS (4 mL, 4 mmol, 1.0M in THF) under an argon atmosphere at room temperature, The reaction solution was stirred for a further 30 min at room temperature, D_2O (1 mL) was added, the resulting mixture was stirred at room temperature for 30 min, then diluted with CH_2Cl_2 , dried over $MgSO_4$ and concentrated under reduced pressure. The residue was used in the next step without further purification.

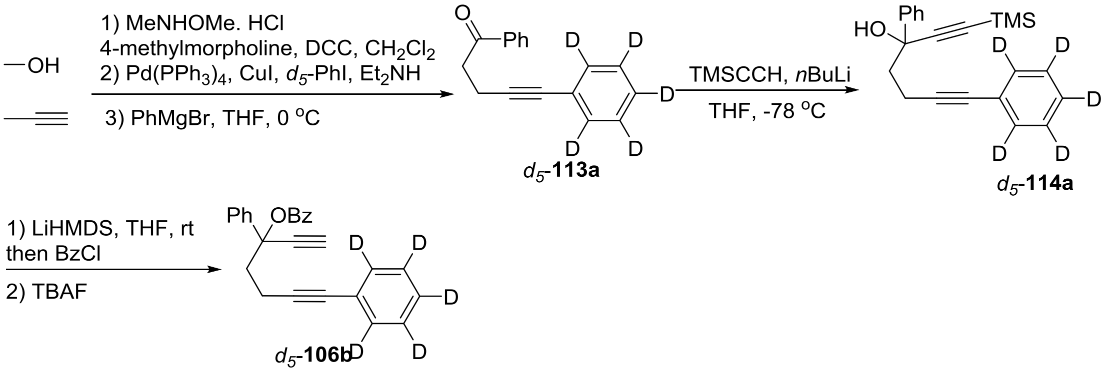
To a solution of deuterio-3,7-diphenylhepta-1,6-diyn-3-ol and DMAP (0.1 mmol) in CH_2Cl_2 (8 mL) was added Et_3N (0.278 mL, 4 mmol), then 4-nitrobenzoyl chloride (0.278 g, 1.5 mmol). The reaction mixture was stirred at room temperature for 15 hours. Upon completion (indicated by TLC), the reaction mixture was quenched by addition of saturated $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (2x 15 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*hexane:EtOAc:DCM = 100:3:5) to yield the desired product **106a** in 66% yield over 3 steps.

Deuterio-3,7-diphenylhepta-1,6-diyn-3-yl 4-nitrobenzoate (*d₁*-106a)



Yield 66%; Yellow solid, mp = 152-153 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.43-2.50 (m, 1H), 2.57-2.65 (m, 1H), 2.69-2.76 (m, 1H), 2.80-2.88 (m, 1H), 7.28-7.43 (m, 8H), 7.64 (d, 2H, J = 7.4 Hz), 8.19-8.25 (m, 4H); ^{13}C NMR ($CDCl_3$, 100MHz): 15.4, 43.3, 79.7, 81.2, 88.7, 123.6, 123.6, 125.2, 127.9, 128.3, 128.6, 128.7, 130.9, 131.5, 135.6, 139.7, 150.6, 162.3; IR (NaCl, neat) *v*: 3019, 2120, 1734, 1528, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{19}DNO_4$ (M^++H): 411.1455, found: 411.1450.

5.2.5. General Procedures for the Preparation of 1,6-Diyne Esters *d₅*-106b



The commercial avalibale 4-Pentynoic acid (0.490g, 5 mmol) was dissolved in 15 ml CH_2Cl_2, *N*-methylmorpholine (1.1 eq), *N*,*O*-dimethylhydroxylamine.HCl (1.1 eq) and *N*,*N*-dicyclohexylcarbodiimide (1.1 eq mmol) were added accordingly. The reaction mixture was stirred at room temperature for 15 hours, then filtered through Celite and concentrated under reduced pressure. The crude mixture was then purified by flash chromatography on silica gel (eluent: *n*hexane:EtOAc = 3:2) to give Weinreb amides 0.579 g in 82% yield as colorless liquid.

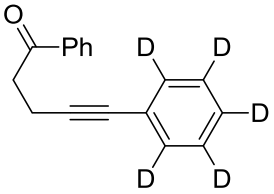
A solution of iodobenzene-*d₅* (0.517 mL, 4.62 mmol), $Pd(PPh_3)_4$ (97 mg, 0.02 eq) and CuI (40 mg, 0.05 eq) in Et_2NH (10 mL) was stirred at room temperature for 5 minutes. To the resulting mixture, a solution of Weinreb amides (0.579 g, 4.2 mmol) in Et_2NH (5 mL) was added. The reaction mixture was stirred at room temperature for 4 hours. Then, the reaction was quenched by addition of saturated NH_4Cl (20 mL) and extracted with EtOAc (3x20 mL). The combined organic layers were washed with brine (15 mL), dried over $MgSO_4$, concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent:*n*hexane:EtOAc = 3:2) to give Weinreb amides 0.654 g in 70% yield as colorless oil.

To a solution of Weinreb amides (0.654 g, 2.94 mmol) in anhydrous THF (12 mL) was added PhMgBr (5.88 mL, 5.88 mmol, 1.0 M in THF) at 0 ^{o}C. The resulting solution was stirred at room temperature for 2 hours then quenched by addition of saturated NH_4Cl (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*hexane:EtOAc:DCM = 50:1:2) to give ketones d_5-**113a** in 92% yield as white solid.

To a stirred solution of ethynyltrimethylsilane (0.283 mL, 2.0 mmol) in 10 mL of THF was added *n*-butyllithium (0.8 mL, 2.0 mmol, 2.5 M in cyclohexane) under argon at −78 °C. The resulting solution was stirred at −78 °C for 1 hour. A solution of ketone d_5-**113a** (1.0 mmol) in THF (5 mL) was subsequently slowly added to the resulting solution at −78 °C and the reaction mixture was slowly warmed up to room temperature and stirred for a further 3 h. The reaction mixture was quenched by addition of water (10 mL) and extracted with EtOAc (2 x 15 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*hexane:EtOAc: DCM = 50:1:2) to give d_5-**114a** in 85% yield.

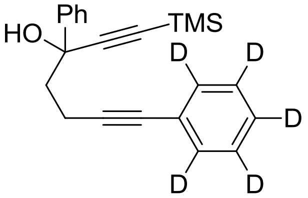
To a solution of d_5-**114a** (0.6 mmol) in anhydrous THF (5 mL) was added LiHMDS (0.9 mL, 0.9 mmol, 1.0M in THF) under an argon atmosphere at room temperature, The reaction solution was stirred for a further 20 min at room temperature, then BzCl (0.9 mmol) was added and the reaction mixture was stirred at room temperature for 30 min. Upon completion (indicated by TLC), TBAF (0.9 mL, 0.9 mmol, 1.0 M in THF) was added and the solution was stirred for 1 h at room temperature when TLC indicated that the reaction was complete. Water was added (10 mL), and the solution was extracted with EtOAc (3x 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*hexane: EtOAc: DCM = 50:1:1) to yield the desired product d_5-**106b** in 96% yield.

Deuterio-1,5-diphenylpent-4-yn-1-one (*d*$_5$-113a)



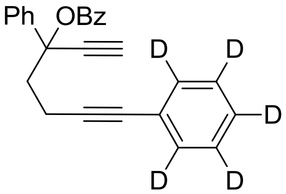
Yield 52.8%; white solid, mp = 73-74 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.81-2.85 (m, 2H), 3.24-3.28 (d, 2H), 7.42-7.45 (m, 2H), 7.52-7.56 (m, 1H), 7.96 (d, 2H, *J* = 8.6 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 14.3, 37.8, 81.1, 89.0, 123.5, 127.0, 127.3, 127.5, 127.8, 128.1, 128.7, 131.0, 131.2, 131.5, 133.3, 136.6, 197.9; IR (NaCl, neat) *v*: 3017, 2399, 1688, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{10}D_5O$ (M$^+$+H): 240.1437, found: 240.1442.

Deuterio-3,7-diphenyl-1-(trimethylsilyl)hepta-1,6-diyn-3-ol (*d*$_5$-114a)



Yield 85%; yellow oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.29 (s, 9H), 2.19-2.26 (m, 1H), 2.29-2.36 (m, 1H), 2.55-2.63 (m, 1H), 2.68-2.76 (m, 1H), 2.80 (s, 1H), 7.33-7.43 (m, 3H), 7.96 (d, 2H, *J* = 7.3 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 0.0, 15.5, 44.2, 73.1, 81.0, 89.6, 91.5, 106.9, 123.6, 125.5, 127.5, 127.7, 128.0, 128.4, 130.9, 131.2, 131.4, 143.9; IR (NaCl, neat) *v*: 3520, 3019, 2961, 2168, 1450, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{18}D_5Si$ (M$^+$–OH): 320.1883, found: 320.1884.

Deuterio-3,7-diphenylhepta-1,6-diyn-3-yl benzoate (*d*$_5$-106b)

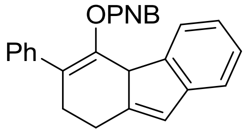


Yield 96%; colorless oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.47-2.53 (m, 1H), 2.66-2.79 (m, 2H), 2.86-2.93 (m, 1H), 2.99 (s, 1H), 7.34-7.48 (m, 5H), 7.60 (t, 1H, *J* = 7.4 Hz), 7.69-7.71 (m, 2H), 8.14-8.16 (m, 2H); ^{13}C NMR (CDCl$_3$, 100MHz): 15.4, 43.8, 77.7, 78.5, 81.0, 81.1, 89.0, 123.6, 125.2, 128.3, 128.5, 128.7, 129.9, 130.3, 133.3, 140.5, 164.1; IR (NaCl, neat) *v*: 3302, 3019, 2120, 1734, 1450, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{16}D_5O2$ (M^++H): 370.1855, found: 370.1856.

Representative Experimental Procedure for Gold Complexes C Catalyzed Cycloisomerization of 1,6-Diyne Carbonates and Esters 106a-y

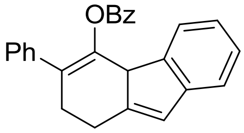
To a solution of 1,6-Diyne Carbonates or Esters **106** (0.2 mmol) in anhydrous CH_2Cl_2 (4 mL) was added gold(I) complex **C** (10 μmol) under an argon atmosphere. The reaction mixture was stirred at 80 °C for 2-24 h when TLC indicated that the reaction was complete. The solution was concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*hexane:EtOAc:DCM = 50:1:1) to give the product **110** in 44-93% yield.

3-phenyl-2,4a-dihydro-1H-fluoren-4-yl 4-nitrobenzoate (110a)



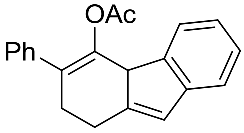
Reaction time 6h, yield 78%; yellow solid, mp = 85-86 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.65-2.73 (m, 1H), 2.81 (dd, 1H, *J* = 16.8, 5.7 Hz), 2.93-3.03 (m, 2H), 4.61 (s, 1H), 6.61 (s, 1H), 7.00 (t, 1H, *J* = 7.4 Hz), 7.12-7.35 (m, 8H), 8.11 (d, 2H, *J* = 8.8 Hz), 8.26 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 25.9, 34.5, 50.5, 120.9, 123.8, 124.1, 124.2, 127.3, 127.4, 127.7, 128.1, 128.2, 131.1, 134.8, 137.9, 140.9, 141.8, 145.3, 148.9, 150.8, 163.1; IR (NaCl, neat) *v*: 3018, 1734, 1601, 1528, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{19}NO_4Na$ (M^++Na): 432.1212, found: 432.4210.

3-phenyl-2,4a-dihydro-1H-fluoren-4-yl benzoate (110b)



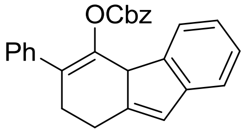
Reaction time 2h, yield 80%; pale-yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.61-2.70 (m, 1H), 2.81 (dd, 1H, *J* = 16.8, 6.4 Hz), 2.89-3.02 (m, 2H), 4.65 (s, 1H), 6.57 (s, 1H), 6.99 (t, 1H, *J* = 7.4 Hz), 7.09-7.13 (m, 1H), 7.17-7.25 (m, 6H), 7.31 (d, 1H, *J* = 7.4 Hz), 7.41 (t, 2H, *J* = 7.6 Hz), 7.55 (t, 1H, *J* = 7.4 Hz), 7.98 (d, 2H, *J* = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 26.0, 34.5, 50.8, 120.6, 123.9, 124.2, 124.5, 127.1, 127.2, 127.4, 127.8, 128.1, 128.6, 129.5, 130.1, 133.4, 138.3, 141.1, 142.2, 145.3, 149.4, 165.0; IR (NaCl, neat) *v*: 3019, 1734, 1451, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{21}O_2$ (M^++H): 365.1542, found: 365.1549.

3-phenyl-2,4a-dihydro-1H-fluoren-4-yl acetate (110c)



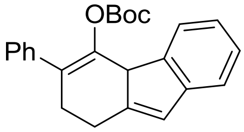
Reaction time 2h, yield 71%; Colorless oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.04 (s, 3H), 2.56-2.65 (m, 1H), 2.72 (dd, 1H, *J* = 16.4, 5.7 Hz), 2.85-2.92 (s, 2H), 4.43 (s, 1H), 6.55 (s, 1H), 7.11-7.37 (m, 9H); ^{13}C NMR ($CDCl_3$, 100MHz): 20.9, 25.9, 34.3, 50.7, 120.7, 123.9, 124.1, 124.2, 127.1, 127.2, 127.8, 128.1, 138.5, 140.8, 142.1, 145.2, 149.2, 169.2; IR (NaCl, neat) *v*: 3019, 1753, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{19}O_2$ (M^++H): 303.1385, found: 303.1386.

Benzyl (3-phenyl-2,4a-dihydro-1H-fluoren-4-yl) carbonate (110d)



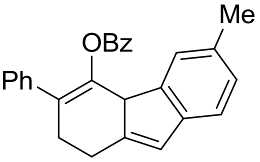
Reaction time 2h, yield 55%; colorless oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.56-2.66 (m, 1H), 2.71 (dd, 1H, *J* = 13.4, 3.4 Hz), 2.82-2.89 (m, 2H), 4.45 (s, 1H), 5.10 (dd, 2H, *J* = 12.2, 4.7 Hz), 6.54 (s, 1H), 7.03 (t, 1H, *J* = 7.4 Hz), 7.16-7.38 (m, 13H); ^{13}C NMR ($CDCl_3$, 100MHz): 25.9, 34.3, 50.5, 70.0, 120.6, 124.2, 124.3, 124.5, 127.2, 127.2, 127.6, 127.8, 128.1, 128.2, 128.5, 128.6, 135.1, 137.8, 141.1, 141.8, 144.9, 148.7, 152.9; IR (NaCl, neat) *v*: 3019, 1753, 1234 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{23}O_3$ (M$^+$+H): 395.1647, found: 395.1647.

tert-butyl (3-phenyl-2,4a-dihydro-1H-fluoren-4-yl) carbonate (110e)



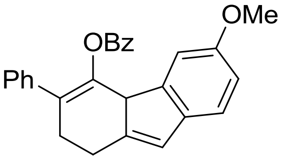
Reaction time 2h, yield 52%; colorless oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 1.31 (s, 9H), 2.61-2.72 (m, 2H), 2.87-2.89 (m, 2H), 4.40 (s, 1H), 6.54 (s, 1H), 7.11 (t, 1H, *J* = 7.2 Hz), 7.20-7.30 (m, 7H), 7.48 (d, 2H, *J* = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 25.9, 27.5, 34.2, 50.8, 82.8, 120.5, 124.0, 124.2, 124.5, 127.0, 127.1, 127.2, 127.8, 128.1, 138.3, 141.1, 142.1, 144.9, 148.9, 151.0; IR (NaCl, neat) *v*: 3019, 1753, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{25}O_3$ (M$^+$+H): 361.1804, found: 361.1809.

6-methyl-3-phenyl-2,4a-dihydro-1H-fluoren-4-yl benzoate (110f)



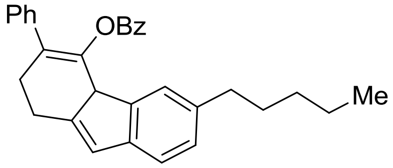
Reaction time 2h, yield 83%; yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.15 (s, 3H), 2.61-2.68 (m, 1H), 2.80 (dd, 1H, *J* = 16.8, 6.0 Hz), 2.87-3.00 (m, 2H), 4.60 (s, 1H), 6.53 (s, 1H), 7.03-7.23 (m, 8H), 7.41 (t, 2H, *J* = 7.6 Hz), 7.55 (t, 1H, *J* = 7.2 Hz), 8.00 (d, 2H, *J* = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 21.4, 26.0, 34.5, 50.6, 120.2, 123.7, 125.7, 127.0, 127.4, 127.8, 127.8, 128.1, 128.5, 129.6, 130.1, 133.4, 133.6, 138.4, 141.1, 142.4, 142.6, 148.3, 165.0; IR (NaCl, neat) *v*: 3019, 1722, 1601, 1451, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{23}O_2$ (M$^+$+H): 379.1698, found: 379.1704.

6-methoxy-3-phenyl-2,4a-dihydro-1H-fluoren-4-yl benzoate (110g)



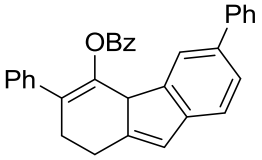
Reaction time 24h, yield 71%; yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.66-2.74 (m, 1H), 2.83 (dd, 1H, *J* = 16.8, 6.4 Hz), 2.89-3.02 (m, 2H), 3.47 (s, 3H), 4.63 (s, 1H), 6.53 (s, 1H), 6.82 (dd, 1H, *J* = 8.2, 2.3 Hz), 6.86 (d, 1H, *J* = 1.5 Hz), 7.13-7.17 (m, 1H), 7.21-7.28 (m, 5H), 7.44 (t, 2H, *J* = 7.6 Hz), 7.58 (t, 1H, *J* = 7.4 Hz), 8.04 (dd, 1H, *J* = 8.4, 1.2 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 25.9, 34.5, 50.7, 55.1, 110.8, 113.3, 120.8, 123.3, 127.1, 127.5, 127.8, 128.1, 128.6, 129.4, 130.1, 133.5, 138.2, 138.3, 140.8, 143.8, 147.0, 157.2, 164.9; IR (NaCl, neat) *v*: 3019, 1722, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{23}O_3$ (M$^+$+H): 395.1647, found: 395.1645.

6-pentyl-3-phenyl-2,4a-dihydro-1H-fluoren-4-yl benzoate (110h)



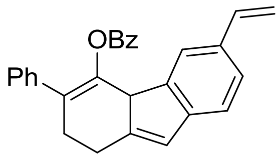
Reaction time 2h, yield 81%; yellow oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.84 (t, 3H, *J* = 7.0 Hz), 1.20-1.22 (m, 4H), 1.38-1.42 (m, 2H), 2.43 (t, 3H, *J* = 7.3 Hz), 2.67-2.73 (m, 1H), 2.84 (dd, 1H, *J* = 16.6, 6.4 Hz), 2.91-3.04 (m, 2H), 4.65 (s, 1H), 6.57 (s, 1H), 7.06-7.17 (m, 3H), 7.21-7.28 (m, 5H), 7.45 (t, 2H, *J* = 7.7 Hz), 7.60 (t, 1H, *J* = 7.4 Hz), 8.05 (d, 2H, *J* = 7.7 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 14.0, 22.5, 26.0, 31.1, 31.4, 34.5, 35.8, 50.5, 120.2, 123.7, 124.9, 127.0, 127.2, 127.3, 127.8, 128.1, 128.5, 129.6, 130.1, 133.4, 138.4, 138.9, 141.0, 142.3, 142.8, 148.3, 164.9; IR (NaCl, neat) *v*: 3019, 1987, 1722, 1601, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{31}H_{31}O_2$ (M$^+$+H): 435.2324, found: 435.2328.

3,6-diphenyl-2,4a-dihydro-1H-fluoren-4-yl benzoate (110i)



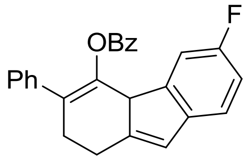
Reaction time 6h, yield 77%; yellow solid, mp = 65-66 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.72-2.78 (m, 1H), 2.87 (dd, 1H, *J* = 16.7, 6.4 Hz), 2.95-3.08 (m, 2H), 4.74 (s, 1H), 6.64 (s, 1H), 7.16-7.32 (m, 10H), 7.40 (d, 1H, *J* = 7.8 Hz), 7.45-7.54 (m, 4H), 7.63 (t, 1H, *J* = 7.4 Hz), 8.10 (d, 2H, *J* = 7.4 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 26.1, 34.4, 50.6, 120.8, 123.5, 123.6, 126.0, 126.7, 126.7, 127.1, 127.4, 127.8, 128.1, 128.5, 128.7, 129.5, 130.2, 133.5, 136.9, 138.3, 140.7, 141.2, 142.8, 144.5, 149.8, 164.9; IR (NaCl, neat) *v*: 3019, 1723, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{25}O_2$ (M$^+$+H): 441.1855, found: 441.1841.

3-phenyl-6-vinyl-2,4a-dihydro-1H-fluoren-4-yl benzoate (110j)



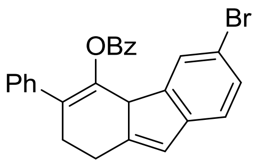
Reaction time 8h, yield 47%; pale-yellow oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.62-2.72 (m, 1H), 2.83 (dd, 1H, *J* = 16.8, 6.4 Hz), 2.90-3.03 (m, 2H), 4.63 (s, 1H), 4.92 (d, 1H, *J* = 10.9 Hz), 5.20 (d, 1H, *J* = 17.6 Hz), 6.48-6.56 (m, 2H), 7.11-7.26 (m, 7H), 7.34 (s, 1H), 7.44 (t, 2H, *J* = 7.8 Hz), 7.58 (t, 1H, *J* = 7.4 Hz), 8.03 (d, 2H, *J* = 7.3 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 26.1, 34.4, 50.5, 112.0, 120.4, 121.7, 123.7, 126.3, 127.1, 127.4, 127.8, 128.1, 128.6, 129.5, 130.1, 133.5, 133.6, 137.0, 138.2, 140.7, 142.5, 145.1, 149.9, 164.9; IR (NaCl, neat) *v*: 3019, 2399, 1722, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{23}O_2$ (M^++H): 391.1698, found: 391.1694.

6-fluoro-3-phenyl-2,4a-dihydro-1H-fluoren-4-yl benzoate (110k)



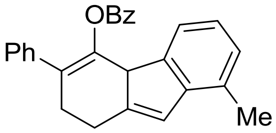
Reaction time 15h, yield 64%; pale-yellow oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.61-2.72 (m, 1H), 2.82 (dd, 1H, *J* = 16.7, 6.0 Hz), 2.88-3.00 (m, 2H), 4.61 (s, 1H), 6.53 (s, 1H), 6.92-6.97 (m, 2H), 7.11-7.24 (m, 6H), 7.42 (t, 2H, *J* = 7.6 Hz), 7.57 (t, 1H, *J* = 7.4 Hz), 7.97 (d, 2H, *J* = 7.8 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 25.9, 34.4, 51.0, 112.4 (1C, d, $J_{C\text{-}F}$ = 23.7), 113.8 (1C, d, $J_{C\text{-}F}$ = 22.5), 120.9 (1C, d, $J_{C\text{-}F}$ = 8.3), 123.1, 127.2, 127.8, 127.9, 128.1, 128.7, 129.2, 130.0, 133.6, 138.1, 140.4, 141.1, 144.1 (1C, d, $J_{C\text{-}F}$ = 8.1), 149.1, 160.8 (1C, d, $J_{C\text{-}F}$ = 240.9), 164.9; IR (NaCl, neat) *v*: 3019, 1723, 1259, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{20}O_2F$ (M^++H): 383.1447, found: 383.1456.

6-bromo-3-phenyl-2,4a-dihydro-1H-fluoren-4-yl benzoate (110l)



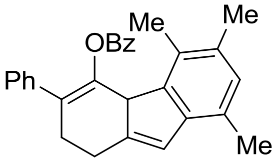
Reaction time 15h, yield 55%; yellow oil;^{1}H NMR (CDCl$_3$, 400MHz): δ 2.62-2.71 (m, 1H), 2.84 (dd, 1H, *J* = 16.7, 6.0 Hz), 2.90-3.01 (m, 2H), 4.60 (s, 1H), 6.54 (s, 1H), 7.12-7.23 (m, 6H), 7.37-7.39 (m, 2H), 7.45 (t, 2H, *J* = 7.6 Hz), 7.59 (t, 1H, *J* = 7.4 Hz), 8.00 (d, 2H, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 25.9, 34.4, 51.0, 118.1, 121.7, 123.3, 127.2, 127.8, 127.9, 128.1, 128.6, 129.2, 130.0, 130.1, 133.6, 138.0, 140.2, 144.1, 144.1, 150.0, 164.9; IR (NaCl, neat) *v*: 3019, 1723, 1450, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{20}O_2Br$ (M^++H): 443.0647, found: 443.0638.

8-methyl-3-phenyl-2,4a-dihydro-1H-fluoren-4-yl benzoate (110m)



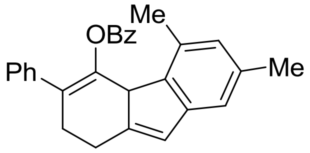
Reaction time 2h, yield 80%; pale-yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.46 (s, 3H), 2.64-2.74 (m, 1H), 2.83 (dd, 1H, *J* = 16.8, 6.4 Hz), 2.94-3.07 (m, 2H), 4.68 (s, 1H), 6.71 (s, 1H), 6.94 (t, 1H, *J* = 7.5 Hz), 7.06-7.27 (m, 7H), 7.44 (t, 2H, *J* = 7.8 Hz), 7.57-7.61 (m, 1H), 8.00-8.02 (m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz): 18.6, 26.1, 34.6, 51.0, 122.0, 122.1, 124.3, 127.0, 127.3, 127.8, 128.1, 128.2, 128.6, 129.5, 130.1, 133.4, 138.3, 141.2, 142.0, 144.0, 148.8, 165.0; IR (NaCl, neat) *v*: 3017, 1721, 1601, 1450, 1261 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{23}O_2$ (M^++H): 379.1698, found: 379.1698.

5,6,8-trimethyl-3-phenyl-2,4a-dihydro-1H-fluoren-4-yl benzoate (110n)



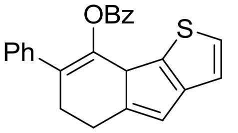
Reaction time 2h, yield 77%; yellow solid, mp = 164-165 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.04 (s, 3H), 2.15 (s, 3H), 2.40 (s, 3H), 2.67 (bs, 1H), 2.84-2.88 (m, 1H), 2.92-3.01 (m, 2H), 4.60 (s, 1H), 6.68 (s, 1H), 6.93 (s, 1H), 7.05-7.22 (m, 5H), 7.32-7.36 (m, 2H), 7.48-7.52 (m, 1H), 7.79 (d, 2H, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 17.8, 18.2, 19.8, 26.2, 35.1, 51.7, 122.6, 126.8, 126.9, 128.2, 128.9, 130.0, 130.3, 131.2, 133.0, 133.4, 138.8, 141.2, 142.2, 142.4, 147.6; IR (NaCl, neat) *v*: 3019, 1725, 1450, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{27}O_2$ (M^++H): 407.2011, found: 407.2003.

5,7-dimethyl-3-phenyl-2,4a-dihydro-1H-fluoren-4-yl benzoate (110o)



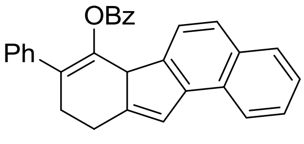
Reaction time 2h, yield 83%; yellow solid, mp = 62-63 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.15 (s, 3H), 2.34 (s, 3H), 2.63 (bs, 1H), 2.82-2.86 (m, 1H), 2.91-3.03 (m, 2H), 4.58 (s, 1H), 6.56 (s, 1H), 6.72 (s, 1H), 7.02 (s, 1H), 7.05-7.09 (m, 1H), 7.15-7.22 (m, 4H), 7.32-7.36 (m, 2H), 7.48-7.52 (m, 1H), 7.80 (d, 2H, *J* = 7.8 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 20.9, 21.2, 26.3, 35.1, 51.2, 119.1, 124.5, 126.9, 127.6, 128.0, 128.2, 128.8, 129.8, 129.9, 133.0, 137.2, 138.0, 138.7, 142.6, 146.2; IR (NaCl, neat) *v*: 3019, 1723, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{25}O_2$ (M$^+$+H): 393.1855, found: 393.1859.

7-phenyl-6,8a-dihydro-5H-indeno[1,2-b]thiophen-8-yl benzoate (110p)



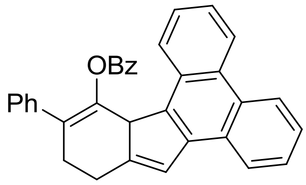
Reaction time 15h, yield 72%; brown oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.71-2.86 (m, 2H), 2.92-3.05 (m, 2H), 4.73 (d, 1H, *J* = 3.8 Hz), 6.53 (d, 1H, *J* = 1.5 Hz), 6.97 (d, 1H, *J* = 4.9 Hz), 7.15-7.29 (m, 6H), 7.42-7.46 (m, 2H), 7.56-7.60 (m, 1H), 8.02 (d, 1H, *J* = 1.4 Hz), 8.05 (d, 1H, *J* = 0.9 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 26.3, 34.8, 49.5, 119.0, 119.8, 127.2, 127.8, 128.1, 128.1, 128.5, 129.4, 130.1, 133.4, 138.1, 139.6, 139.8, 149.5, 151.0, 164.8; IR (NaCl, neat) *v*: 3019, 1734, 1450, 1266 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{18}O_2S$ (M$^+$+H): 371.1106, found: 371.1106.

8-phenyl-9,10-dihydro-6bH-benzo[a]fluoren-7-yl benzoate (110q)



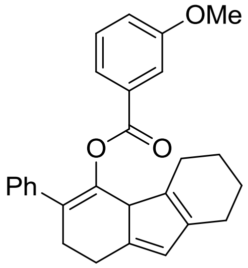
Reaction time 1h, yield 77%; yellow solid, mp = 102-104 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.66-2.76 (m, 1H), 2.87 (dd, 1H, *J* = 16.8, 6.2 Hz), 3.01-3.13 (m, 2H), 4.80 (s, 1H), 7.09-7.12 (m, 1H), 7.16-7.24 (m, 5H), 7.40-7.58 (m, 7H), 7.81 (d, 1H, *J* = 8.0 Hz), 8.00 (d, 2H, *J* = 7.4 Hz), 8.08 (d, 1H, *J* = 8.2 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 26.3, 35.0, 52.0, 121.5, 122.9, 124.1, 124.3, 125.3, 125.6, 127.1, 127.6, 127.6, 127.9, 128.1, 128.4, 128.6, 129.5, 130.1, 133.1, 133.5, 138.2, 139.4, 141.1, 141.6, 150.1, 165.1; IR (NaCl, neat) *v*: 3019, 1722, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{30}H_{23}O_2$ (M$^+$+H): 415.1698, found: 415.1694.

10-phenyl-11,12-dihydro-8cH-indeno[1,2-l]phenanthren-9-yl benzoate (110r)



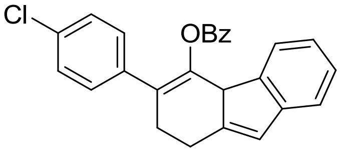
Reaction time 1h, yield 71%; yellow solid, mp = 115-117 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.71-2.93 (m, 2H), 3.14 (s, 2H), 5.06 (s, 1H), 6.87-6.91 (m, 1H), 7.08 (t, 1H, *J* = 7.2 Hz), 7.15-7.31 (m, 8H), 7.47 (t, 1H, *J* = 7.2 Hz), 7.66-7.68 (m, 4H), 7.67-7.89 (m, 1H), 8.19-8.22 (m, 1H), 8.63 (d, 1H, *J* = 7.5 Hz), 8.72 (s, 1H); ^{13}C NMR (CDCl$_3$, 100MHz): 26.3, 35.2, 52.9, 122.1, 123.0, 123.2, 124.5, 124.7, 126.0, 126.1, 126.2, 126.4, 127.0, 127.6, 127.9, 128.0, 128.0, 128.8, 129.9, 130.8, 132.9, 136.6, 138.6, 140.8; IR (NaCl, neat) *v*: 3018, 1734, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{34}H_{25}O_2$ (M$^+$+H): 465.1855, found: 465.1857.

3-phenyl-2,4a,5,6,7,8-hexahydro-1H-fluoren-4-yl 3-methoxybenzoate (110s)



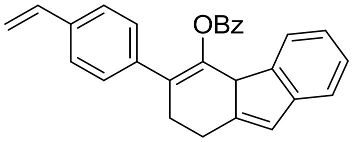
Reaction time 1h, yield 57%; yellow oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.93-1.02 (m, 1H), 1.08-1.38 (m, 2H), 1.88-1.91 (m, 1H), 2.20-2.28 (m, 2H), 2.63-2.69 (m, 2H), 2.76-2.89 (m, 2H), 2.91-2.96 (m, 2H), 3.81 (s, 1H), 3.83 (s, sH), 5.98 (s, 1H), 7.10-7.12 (m, 1H), 7.19-7.26 (m, 3H), 7.35-7.39 (m, 3H), 7.55 (s, 1H), 7.66-7.64 (d, 1H, *J* = 7.7 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 23.1, 25.2, 28.5, 29.2, 30.3, 31.9, 50.6, 55.4, 114.4, 118.5, 119.8, 122.5, 123.4, 126.3, 127.4, 128.0, 129.5, 131.0, 137.1, 138.8, 141.5, 142.9, 153.5, 159.6, 164.8; IR (NaCl, neat) *v*: 3019, 1725, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{27}O_3$ (M$^+$+H): 399.1960, found: 399.1955.

3-(4-chlorophenyl)-2,4a-dihydro-1H-fluoren-4-yl benzoate (110t)



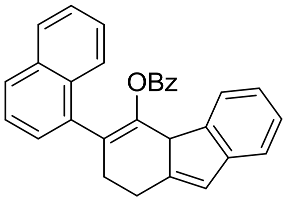
Reaction time 2h, yield 76%; yellow oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.57-2.67 (m, 1H), 2.77 (dd, 1H, *J* = 16.8, 6.0 Hz), 2.89-3.01 (m, 2H), 4.62 (s, 3H), 6.58 (s, 1H), 7.00 (t, 1H, *J* = 7.4 Hz), 7.14-7.24 (m, 6H), 7.31 (d, 1H, *J* = 7.6 Hz), 7.45 (t, 2H, *J* = 7.7 Hz), 7.59 (t, 1H, *J* = 7.4 Hz), 8.00 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 25.9, 34.4, 50.7, 120.7, 124.1, 124.2, 124.5, 126.3, 127.2, 128.3, 128.7, 129.2, 130.1, 132.9, 133.6, 136.7, 141.6, 141.9, 145.2, 149.0, 164.8; IR (NaCl, neat) *v*: 3019, 2926, 1725, 1601, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{20}O_2Cl$ (M$^+$+H): 399.1152, found: 399.1150.

3-(4-vinylphenyl)-2,4a-dihydro-1H-fluoren-4-yl benzoate (110u)



Reaction time 8h, yield 60%; yellow solid, mp = 65-66 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.63-2.71 (m, 1H), 2.77 (dd, 1H, *J* = 16.6, 6.0 Hz), 2.91-3.03 (m, 2H), 4.66 (s, 1H), 5.16 (d, 1H, *J* = 10.9 Hz), 5.65 (d, 1H, *J* = 17.6 Hz), 6.57-6.64 (m, 2H), 7.01 (t, 1H, *J* = 7.4 Hz), 7.20-7.27 (m, 5H), 7.33 (d, 1H, *J* = 7.3 Hz), 7.45 (t, 2H, *J* = 7.6 Hz), 7.59 (t, 1H, *J* = 7.3 Hz), 8.02 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 26.0, 34.3, 50.8, 113.7, 120.6, 123.9, 124.2, 124.5, 126.0, 127.2, 128.0, 128.6, 129.4, 130.1, 133.5, 136.3, 136.5, 137.8, 141.1, 142.1, 145.2, 149.3, 164.9; IR (NaCl, neat) *v*: 3019, 1723 , 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{23}O_2$ (M$^+$+H): 391.1698, found: 391.1689.

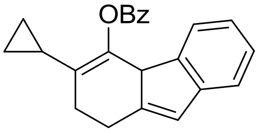
3-(naphthalen-1-yl)-2,4a-dihydro-1H-fluoren-4-yl benzoate (110v)



dr = 1.1:1

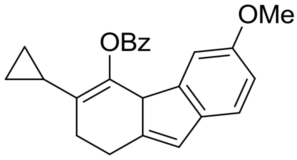
Reaction time 2h, yield 53%; yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.54-2.62 (m, 1H), 2.72-2.82 (m, 3H), 2.92-2.97 (m, 2H), 3.01-3.11 (m, 2H), 4.70 (s, 1H), 4.83 (s, 1H), 6.60 (s, 1H), 6.62 (s, 1H), 6.94-6.98 (m, 2H), 7.13-7.47 (m, 22H), 7.53-7.71 (m, 10H), 8.02 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 26.1, 26.2, 35.0, 35.3, 50.8, 50.9, 120.6, 120.7, 124.1, 124.2, 124.4, 124.6, 125.1, 125.3, 125.4, 125.5, 125.6, 125.7, 125.9, 126.0, 126.8, 127.1, 127.1, 127.4, 127.4, 128.1, 128.2, 128.3, 129.1, 129.4, 129.7, 129.8, 130.8, 133.1, 133.2, 133.4, 133.7, 135.8, 136.4, 142.1, 142.2, 142.4, 142.9, 145.2, 164.7, 165.0; IR (NaCl, neat) *v*: 3019, 1725, 1451, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{30}H_{23}O_2$ (M^++H): 415.1698, found: 415.1704.

3-cyclopropyl-2,4a-dihydro-1H-fluoren-4-yl benzoate (110w)



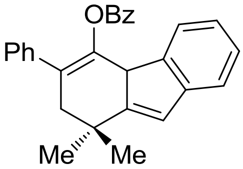
Reaction time 1h, yield 47%; pale-yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.47-0.59 (m, 4H), 1.57-1.62 (m, 1H), 1.99-2.07 (m, 1H), 2.15 (dd, 1H, J = 16.3, 6.3 Hz), 2.70-2.82 (m, 2H), 4.46 (s, 1H), 6.49 (s, 1H), 7.00 (t, 1H, J = 7.2 Hz), 7.19-7.30 (m, 3H), 7.52-7.56 (m, 2H), 7.64-7.68 (m, 1H), 8.24-8.26 (m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz): 3.6, 4.2, 10.7, 25.4, 28.1, 51.0, 120.5, 123.5, 124.0, 124.4, 125.8, 127.0, 128.8, 129.7, 130.2, 133.5, 140.9, 142.5, 145.1, 149.8, 164.8; IR (NaCl, neat) *v*: 3019, 1722, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{23}H_{21}O_2$ (M^++H): 329.1542, found: 329.1545.

3-cyclopropyl-6-methoxy-2,4a-dihydro-1H-fluoren-4-yl benzoate (110x)



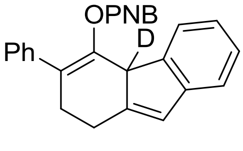
Reaction time 20h, yield 44%; yellow oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 0.51-0.61 (m, 4H), 1.60-1.65 (m, 1H), 2.03-2.16 (m, 2H), 2.68-2.80 (m, 2H), 3.52 (s, 3H), 4.43 (s, 1H), 6.43 (s, 1H), 6.78 (dd, 1H, J = 8.2, 2.2 Hz), 6.91 (s, 1H), 7.16 (d, 1H, J = 8.2 Hz), 7.54 (t, 2H, J = 7.6 Hz), 7.66 (t, 1H, J = 7.2 Hz), 8.29 (d, 2H, J = 7.6 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 3.6, 4.2, 10.8, 25.3, 28.0, 50.9, 55.2, 110.7, 113.2, 120.7, 122.9, 126.1, 128.8, 129.7, 130.2, 133.6, 138.1, 140.7, 144.1, 147.4, 157.2, 164.7; IR (NaCl, neat) v: 3019, 1722, 1601, 1277 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{23}O_3$ (M$^+$+H): 359.1647, found: 359.1642.

1,1-dimethyl-3-phenyl-2,4a-dihydro-1H-fluoren-4-yl benzoate (110y)



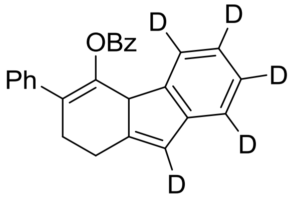
Reaction time 1h, yield 93%; colorless oil; ^{1}H NMR (CDCl$_3$, 400MHz): δ 1.47 (s, 3H), 1.63 (s, 3H), 2.48-2.61 (m, 2H), 4.72 (s, 1H), 6.55 (s, 1H), 7.01-7.07 (m, 1H), 7.12-7.17 (m, 1H), 7.20-7.36 (m, 7H), 7.46 (t, 2H, J = 7.8 Hz), 7.60 (t, 1H, J = 7.4 Hz), 8.03 (d, 2H, J = 7.6 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 26.3, 27.9, 34.6, 49.4, 49.6, 120.7, 121.4, 124.2, 124.4, 126.5, 127.0, 127.2, 127.8, 128.1, 128.6, 129.5, 130.0, 133.4, 138.3, 140.5, 142.4, 144.9, 157.4, 165.1; IR (NaCl, neat) v: 3018, 1734, 1601, 1216 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{25}O_2$ (M$^+$+H): 393.1855, found: 393.1859.

Deuterio-3-phenyl-2,4a-dihydro-1H-fluoren-4-yl 4-nitrobenzoate (d_1-110a)



Reaction time 6h, yield 75%; yellow solid, mp = 71-72 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.63-2.75 (m, 1H), 2.81 (dd, 1H, J = 16.8, 5.8 Hz), 2.92-3.02 (m, 2H), 6.59 (s, 1H), 6.99 (t, 1H, J = 7.4 Hz), 7.13-7.37 (m, 8H), 8.10 (d, 2H, J = 8.8 Hz), 8.25 (d, 2H, J = 8.8 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 25.9, 34.5, 120.9, 123.8, 124.2, 124.2, 124.3, 127.4, 127.4, 127.7, 128.2, 131.1, 134.7, 140.9, 141.8, 145.3, 148.9, 150.8, 163.1; IR (NaCl, neat) *v*: 3019, 2399, 1722, 1528, 1215 cm^{-1}; HRMS (ESI) calcd. For $C_{26}H_{19}D_1NO_4$ (M^++H): 411.1455, found: 411.1457.

Deuterio-3-phenyl-2,4a-dihydro-1H-fluoren-4-yl benzoate (*d*$_5$-110b)

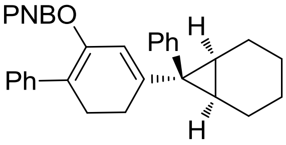


Reaction time 2h, yield 75%; pale-yellow solid, mp = 100-102 °C; ^{1}H NMR (CDCl$_3$, 400MHz): δ 2.66-2.76 (m, 1H), 2.87 (dd, 1H, *J* = 16.8, 6.4 Hz), 2.95-3.08 (m, 2H), 4.70 (s, 1H), 7.14-7.28 (m, 5H), 7.47 (t, 2H, *J* = 7.7 Hz), 7.59-7.63 (m, 1H), 8.03 (d, 2H, *J* = 7.9 Hz); ^{13}C NMR (CDCl$_3$, 100MHz): 26.0, 34.5, 50.7, 123.8, 127.1, 127.3, 127.8, 128.1, 128.6, 129.5, 130.1, 133.4, 138.3, 141.1, 142.1, 145.1, 149.2, 165.0; IR (NaCl, neat) *v*: 3019, 2278, 1726, 1601, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{16}D_5O_2$ (M^++H): 370.1855, found: 370.1848.

General Procedure for the Control Experiment of 106a with cyclohexene and diphenylsulfoxide Catalyzed by Gold Complexes G

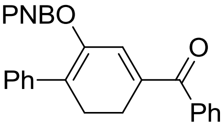
To a solution gold(I) complex **G** (10 μmol), cyclohexene (10 mmol) or diphenylsulfoxide (1 mmol) in anhydrous CH_2Cl_2 (2 mL) was added a solution of **106a** (0.2 mmol) in CH_2Cl_2 (3 mL) under an argon atmosphere. The reaction mixture compl was stirred at room temperature for 6 h when TLC indicated that the reaction was ete. The solution was concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*hexane:EtOAc:DCM = 50:1:1) to give the product **115** or **116** in 71% and 80% yield respectively.

4-((1*R**,6*S**,7*S**)-7-phenylbicyclo[4.1.0]heptan-7-yl)-5,6-dihydro-[1,1'-biphenyl]-2-yl 4-nitrobenzoate (115)



Reaction time 6h, yield 71%; yellow solid, mp = 163-164 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.58-0.64 (m, 2H), 0.97-1.04 (m, 2H), 1.51-1.52 (m, 2H), 1.66-1.71 (m, 2H), 1.89-1.94 (m, 2H), 2.26 (t, 2H, *J* = 9.2 Hz), 2.61 (t, 2H, *J* = 8.8 Hz), 5.48 (s, 1H), 7.07 (t, 1H, *J* = 7.2 Hz), 7.14-7.32 (m, 9H), 8.08 (d, 2H, *J* = 8.7 Hz), 8.20 (d, 2H, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 21.0, 21.0, 21.3, 25.4, 29.0, 37.0, 117.3, 120.2, 123.6, 126.4, 126.9, 127.3, 128.1, 128.4, 131.1, 132.1, 135.1, 137.9, 138.2, 141.9, 149.9, 150.7, 163.0; IR (NaCl, neat) *v*: 3019, 1734, 1528, 1273, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{32}H_{30}NO_4$ (M^++H): 492.2175, found: 492.2179.

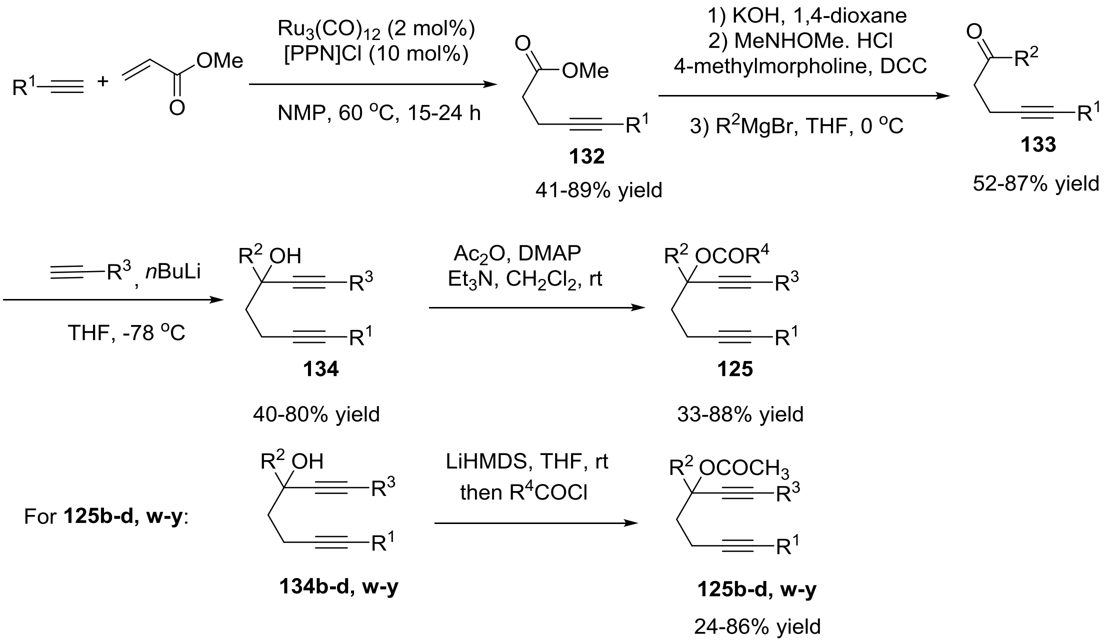
4-benzoyl-5,6-dihydro-[1,1'-biphenyl]-2-yl 4-nitrobenzoate (116)



Reaction time 6h, yield 80%; yellow solid, mp = 120-122 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ 2.81-2.93 (m, 4H), 6.57 (s, 1H), 7.19-7.29 (m, 3H), 7.35-7.48 (m, 5H), 7.70 (d, 2H, *J* = 7.4 Hz), 8.08 (d, 2H, *J* = 8.7 Hz), 8.20 (d, 2H, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 100MHz): 22.1, 28.7, 123.7, 127.5, 128.4, 128.4, 129.2, 131.2, 131.3, 131.9, 134.3, 135.5, 136.5, 136.6, 137.9, 140.7, 150.9, 163.0, 195.9; IR (NaCl, neat) *v*: 3019, 2399, 1734, 1634, 1528, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{20}NO_5$ (M^++H): 426.1341, found: 426.1341.

5.3 Gold-Catalyzed Cycloisomerization of 1,6-Diyne Esters to 1*H*-Cyclopenta[*b*]naphthalenes, Bicyclo[3.2.0]hepta-1,5-dienes and Cyclopenten-2-yl *δ*-Diketones

General Procedures for the Preparation of 1,6-Diyne Esters 125



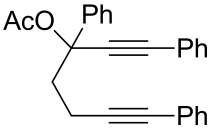
Method A:

To a solution of **134b-d, w-y** (1 mmol) in anhydrous THF (8 mL) was added LiHMDS (1.5 mL, 1.5 mmol, 1.0M in THF) under an argon atmosphere at room temperature, The reaction solution was stirred for a further 20 min at room temperature, then R^3COCl (1.5 mmol) was added and the reaction mixture was stirred at room temperature for 30 min. Upon completion (indicated by TLC), water was added (10 mL), and the solution was extracted with EtOAc (3x 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*hexane:EtOAc:DCM = 50:1:1) to yield the desired product **125b-d, w-y** (24-86% yield).

Method B:

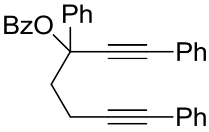
To a solution of **134** and DMAP (0.2 mmol) in CH_2Cl_2 (15 mL) was added Et_3N (0.557 mL, 4 mmol), then acetic anhydride (0.378 mL, 4 mmol). The reaction mixture was stirred at room temperature for 15-24 hours. Upon completion (indicated by TLC), the reaction mixture was quenched by addition of saturated $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (2x 20 mL). The combined organic layers were washed with brine (15 mL), dried over $MgSO_4$, concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*hexane:EtOAc:DCM = 100:3:5) to yield the desired product **125** in 33-88% yield.

1,3,7-triphenylhepta-1,6-diyn-3-yl acetate (125a)



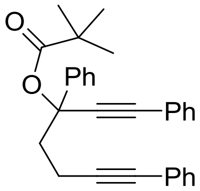
Yield 80%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.15 (s, 3H), 2.40-2.46 (m, 1H), 2.62-2.70 (m, 2H), 2.79-2.85 (m, 1H), 7.30-7.32 (m, 3H), 7.34-7.46 (m, 8H), 7.60-7.63 (m, 2H), 7.67-7.70 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.4, 21.8, 43.7, 78.5, 81.0, 86.6, 89.0, 89.0, 122.3, 123.8, 125.3, 127.8, 128.2, 128.3, 128.4, 128.6, 128.9, 131.6, 132.1, 141.1, 168.4; IR (NaCl, neat) ν: 3017, 2230, 1748, 1489, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{23}O_2$ (M^+ + H): 379.1698, found: 379.1701.

1,3,7-triphenylhepta-1,6-diyn-3-yl benzoate (125b)



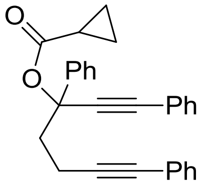
Yield 74%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.53-2.59 (m, 1H), 2.75-2.83 (m, 2H), 2.92-2.99 (m, 1H), 7.29-7.48 (m, 13H), 7.58-7.63 (m, 3H), 7.74-7.76 (m, 2H), 8.14-8.17 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.6, 44.0, 79.1, 81.1, 86.5, 89.2, 89.2, 122.3, 123.8, 125.3, 127.8, 128.2, 128.3, 128.4, 128.5, 128.6, 128.9, 129.8, 130.6, 131.6, 132.1, 133.1, 141.2, 163.9; IR (NaCl, neat) ν: 3019, 2234, 1732, 1491, 1269 cm^{-1}; HRMS (ESI) calcd. for $C_{30}H_{29}O_2$ (M^+ + H): 421.2168, found: 421.2174.

1,3,7-triphenylhepta-1,6-diyn-3-yl pivalate (125c)



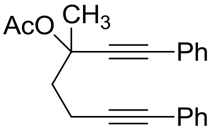
Yield 85%; yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.14 (s, 9H), 2.21-2.30 (m, 1H), 2.46-2.56 (m, 2H),), 2.62-2.70 (m, 1H), 7.12-7.15 (m, 3H), 7.16-7.22 (m, 4H), 7.24-7.28 (m, 4H), 7.42-7.44 (m, 2H), 7.50 (d, 2H, J = 7.4 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 15.5, 27.1, 39.2, 43.9, 78.1, 81.0, 86.6, 88.7, 89.2, 122.4, 123.8, 125.2, 127.8, 128.1, 128.3, 128.4, 128.5, 128.8, 131.6, 132.1, 141.1, 175.3; IR (NaCl, neat) ν: 3019, 2399, 1740, 1491, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{32}H_{25}O_2$ (M$^+$ + H): 441.1855, found: 441.1862.

1,3,7-triphenylhepta-1,6-diyn-3-yl cyclopropanecarboxylate (125d)



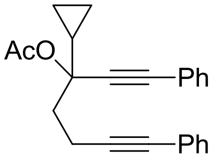
Yield 86%; yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.88-0.93 (m, 2H), 0.97-1.02 (m, 1H), 1.07-1.12 (m, 1H), 1.70-1.77 (m, 1H), 2.39-2.45 (m, 1H), 2.60-2.70 (m, 2H), 2.76-2.88 (m, 1H), 7.29-7.33 (m, 3H), 7.35-7.45 (m, 8H), 7.58-7.61 (m, 2H), 7.66-7.68 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 8.4, 8.6, 13.6, 15.5, 43.8, 78.4, 81.0, 86.7, 88.9, 89.1, 122.4, 123.8, 125.2, 127.7, 128.1, 128.3, 128.4, 128.5, 128.8, 131.6, 132.1, 141.2, 172.0; IR (NaCl, neat) ν: 3017, 2232, 1736, 1491, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{25}O_2$ (M$^+$ + H): 405.1855, found: 405.1865.

3-methyl-1,7-diphenylhepta-1,6-diyn-3-yl acetate (125e)



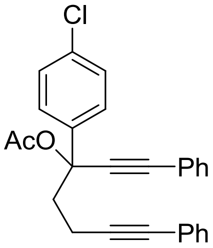
Yield 88%; yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.84 (s, 3H), 2.07 (s, 3H), 2.20-2.27 (m, 1H), 2.36-2.44 (m, 1H), 2.71-2.75 (m, 2H), 7.27-7.33 (m, 6H), 7.40-7.42 (m, 2H), 7.45-7.48 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 15.1, 22.0, 26.6, 40.8, 74.8, 80.8, 85.8, 88.3, 89.3, 122.4, 123.8, 127.7, 128.2, 128.3, 128.5, 131.6, 131.9, 169.3; IR (NaCl, neat) ν: 3017, 2234, 1740, 1489, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{21}O_2$ ($M^+ + H$): 317.1542, found: 317.1547.

3-cyclopropyl-1,7-diphenylhepta-1,6-diyn-3-yl acetate (125f)



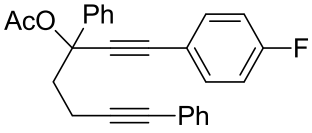
Yield 35%; yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.52-0.57 (m, 3H), 0.83-0.87 (m, 1H), 1.40-1.47 (m, 1H), 1.99 (s, 3H), 2.29-2.36 (m, 1H), 2.53-2.68 (m, 3H), 7.17-7.24 (m, 6H), 7.30-7.36 (m, 4H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 3.3, 3.3, 15.3, 17.9, 22.1, 39.3, 80.7, 81.6, 84.3, 87.3, 89.4, 122.1, 123.9, 127.6, 128.2, 128.3, 128.7, 131.5, 131.9, 169.3; IR (NaCl, neat) ν: 3017, 2234, 1732, 1489, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{23}O_2$ ($M^+ + H$): 343.1698, found: 343.1705.

3-(4-chlorophenyl)-1,7-diphenylhepta-1,6-diyn-3-yl acetate (125g)



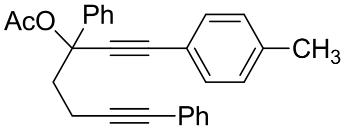
Yield 74%; white solid; mp = 99-100 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.97 (s, 3H), 2.18-2.27 (m, 1H), 2.41-2.51 (m, 2H),), 2.59-2.68 (m, 1H), 7.13-7.16 (m, 3H), 7.20-7.25 (m, 7H), 7.42-7.46 (m, 4H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 15.4, 21.7, 43.4, 78.0, 81.1, 86.0, 88.7, 89.3, 122.0, 123.7, 126.9, 127.8, 128.3, 128.4, 128.7, 129.1, 131.6, 132.1, 134.0, 139.7, 168.3; IR (NaCl, neat) ν: 3019, 2232, 1749, 1489, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{21}O_2ClNa$ ($M^+ + Na$): 435.1128, found: 435.1129.

1-(4-fluorophenyl)-3,7-diphenylhepta-1,6-diyn-3-yl acetate (125h)



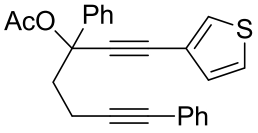
Yield 65%; yellow solid; mp = 96-97 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.09 (s, 3H), 2.32-2.38 (m, 1H), 2.53-2.58 (m, 2H), 2.68-2.73 (m, 1H), 6.70-7.04 (m, 2H), 7.23-7.25 (m, 3H), 7.28-7.39 (m, 5H), 7.50-7.54 (m, 2H), 7.58-7.60 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.4, 21.7, 43.5,78.4, 81.0, 86.3, 87.9, 88.9, 115.5 (1C, d, J $_{C\text{-}F}$ = 22.0), 115.8, 118.3 (1C, d, J $_{C\text{-}F}$ = 4.0), 123.7, 125.2, 127.7, 128.2, 128.2, 128.5, 131.5, 134.0, 134.1, 140.9, 162.9 (1C, d, J $_{C\text{-}F}$ = 249.0), 168.4; IR (NaCl, neat) ν: 3019, 2230, 1748, 1506, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{22}O_2F$ (M^+ + H): 397.1604, found: 397.1605.

3,7-diphenyl-1-(p-tolyl)hepta-1,6-diyn-3-yl acetate (125i)



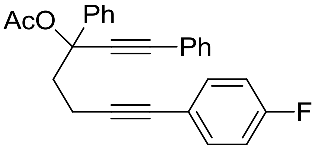
Yield 33%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.09 (s, 3H), 2.31-2.36 (m, 4H), 2.53-2.58 (m, 2H), 2.70-2.77 (m, 1H), 7.14 (d, 2H, J = 7.9 Hz), 7.24-7.26 (m, 3H), 7.28-7.39 (m, 5H), 7.44 (d, 2H, J = 8.1 Hz), 7.60-7.62 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.4, 21.5, 21.8, 43.6, 78.5, 80.8, 85.7, 89.0, 89.1, 119.2, 123.8, 125.3, 127.6, 128.0, 128.2, 128.5, 129.1, 131.5, 132.0, 139.0, 141.1, 168.3; IR (NaCl, neat) ν: 3028, 2228, 1752, 1491, 1225 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{25}O_2$ (M^+ + H): 393.1855, found: 393.1864.

3,7-diphenyl-1-(thiophen-3-yl)hepta-1,6-diyn-3-yl acetate (125j)



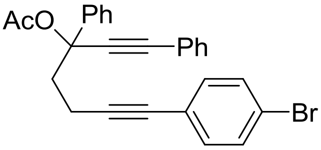
Yield 60%; brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.05 (s, 3H), 2.31-2.36 (m, 1H), 2.52-2.57 (m, 2H), 2.69-2.75 (m, 1H), 7.16-7.17 (m, 1H), 7.21-7.29 (m, 5H), 7.33-7.37 (m, 4H), 7.51-7.52 (m, 1H), 7.58 (d, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.5, 21.8, 43.7, 78.6, 81.1, 84.2, 86.2, 89.1, 121.3, 123.8, 125.4, 125.6, 127.8, 128.2, 128.4, 128.6, 130.0, 130.2, 131.6, 141.1, 168.4; IR (NaCl, neat) ν: 3107, 1748, 1491, 1221 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{21}O_2S$ (M^+ + H): 385.1262, found: 385.1259.

7-(4-fluorophenyl)-1,3-diphenylhepta-1,6-diyn-3-yl acetate (125m)



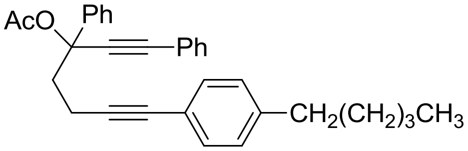
Yield 87%; yellow solid; mp = 75-76 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.15 (s, 3H), 2.39-2.45 (m, 1H), 2.58-2.69 (m, 2H), 2.77-2.83 (m, 1H), 6.98-7.02 (m, 2H), 7.34-7.40 (m, 6H), 7.42-7.46 (m, 2H), 7.60-7.63 (m, 2H), 7.68-7.70 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.4, 21.8, 43.6, 78.5, 80.0, 86.5, 88.7, 89.0, 115.4 (1C, d, J $_{C-F}$ = 22.0), 115.6, 119.9 (1C, d, J $_{C-F}$ = 4.0), 122.3, 125.3, 128.2, 128.4, 128.6, 128.9, 132.1, 133.4, 133.4, 141.1, 162.2 (1C, d, J $_{C-F}$ = 246.0), 168.3; IR (NaCl, neat) ν: 3061, 2230, 1755, 1506, 1225 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{22}O_2$ F(M^+ + H): 397.1604, found: 397.1605.

7-(4-bromophenyl)-1,3-diphenylhepta-1,6-diyn-3-yl acetate (125n)



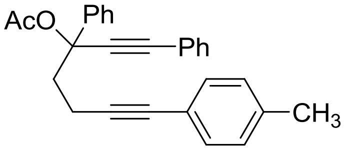
Yield 70%; yellow solid; mp = 100-101 °C; ^{1}H NMR ($CDCl_3$, 400 MHz):): δ 2.08 (s, 3H), 2.31-2.37 (m, 1H), 2.50-2.60 (m, 2H), 2.68-2.75 (m, 1H), 7.16-7.20 (m, 2H), 7.27-7.32 (m, 4H), 7.35-7.38 (m, 4H), 7.52-7.55 (m, 2H), 7.60 (d, 2H, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.5, 21.8, 43.4, 78.5, 80.0, 86.5, 89.0, 90.4, 121.8, 122.2, 122.8, 125.3, 128.2, 128.4, 128.6, 128.9, 131.5, 132.1, 133.1, 141.0, 168.3; IR (NaCl, neat) ν: 3061, 2230, 1748, 1487, 1225 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{18}Br$ (M+ - OAc): 397.0592, found: 397.0581.

7-(4-pentylphenyl)-1,3-diphenylhepta-1,6-diyn-3-yl acetate (125o)



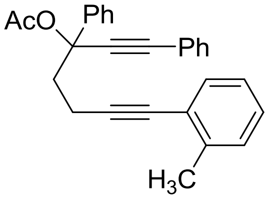
Yield 54%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.76 (t, 3H, J = 6.8 Hz), 1.14-1.23 (m, 4H), 1.41-1.49 (m, 2H), 1.95 (s, 3H), 2.21-2.27 (m, 1H), 2.41-2.48 (m, 4H), 2.60-2.66 (m, 1H), 6.94 (d, 2H, J = 8.1 Hz), 7.15-7.20 (m, 6H), 7.23-7.27 (m, 2H), 7.41-7.44 (m, 2H), 7.48-7.51 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 15.5, 21.8, 22.6, 31.0, 31.5, 35.9, 43.8, 78.5, 81.1, 86.6, 88.2, 89.0, 121.0, 122.3, 125.4, 128.2, 128.4, 128.6, 128.9, 131.5, 132.1, 141.2, 142.8, 168.3; IR (NaCl, neat) ν: 2230, 1755, 1491, 1225 cm^{-1}; HRMS (ESI) calcd. for $C_{32}H_{32}O_2Na$ (M^+ + Na): 471.2300, found: 471.2296.

1,3-diphenyl-7-(p-tolyl)hepta-1,6-diyn-3-yl acetate (125p)



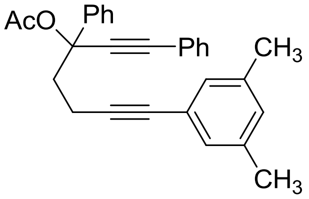
Yield 56%; yellow solid; mp = 108-109 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.16 (s, 3H), 2.38 (s, 3H), 2.42-2.47 (m, 1H), 2.61-2.71 (m, 2H), 2.80-2.87 (m, 1H), 7.14 (d, 2H, J = 8.0 Hz), 7.33-7.47 (m, 8H), 7.62-7.64 (m, 2H), 7.69-7.71 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.5, 21.5, 21.8, 43.8, 78.5, 81.1, 86.6, 88.2, 89.0, 120.8, 122.3, 125.4, 128.2, 128.6, 128.9, 129.1, 131.5, 132.1, 137.7, 141.1, 168.4; IR (NaCl, neat) ν: 3017, 2230, 1749, 1491, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{25}O_2$ (M^+ + H): 393.1855, found: 393.1850.

1,3-diphenyl-7-o-tolylhepta-1,6-diyn-3-yl acetate (125q)



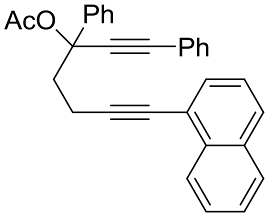
Yield 72%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.06 (s, 3H), 2.33-2.43 (m, 4H), 2.55-2.65 (m, 2H),), 2.74-2.82 (m, 1H), 7.03-7.08 (m, 1H), 7.10-7.14 (m, 2H), 7.28-7.38 (m, 7H), 7.52-7.54 (m, 2H), 7.61 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.7, 20.9, 21.8, 43.9, 78.6, 80.0, 86.6, 89.0, 93.0, 122.3, 123.6, 125.4, 125.6, 127.8, 128.2, 128.4, 128.6, 128.9, 129.4, 131.9, 132.1, 140.0, 141.2, 168.4; IR (NaCl, neat) ν: 3022, 2230, 1748, 1489, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{25}O_2$ (M^+ + H): 393.1855, found: 393.1850.

7-(3,5-dimethylphenyl)-1,3-diphenylhepta-1,6-diyn-3-yl acetate (125r)



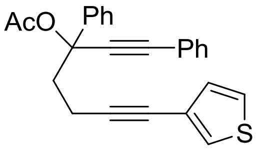
Yield 77%; yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.13 (s, 3H), 2.27 (s, 6H), 2.34-2.40 (m, 1H), 2.53-2.64 (m, 2H), 2.72-2.81 (m, 1H), 6.92 (s, 1H), 7.01 (s, 2H), 7.31-7.42 (m, 6H), 7.57-7.59 (m, 2H), 7.63-7.65 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 15.4, 21.1, 21.8, 43.7, 78.5, 81.2, 86.5, 88.2, 88.9, 122.3, 123.3, 125.3, 128.1, 128.3, 128.5, 128.8, 129.3, 129.6, 132.1, 137.7, 141.1, 168.3; IR (NaCl, neat) ν: 3028, 2230, 1755, 1489, 1223 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{27}O_2$ (M^+ + H): 407.2011, found: 407.2008.

7-(naphthalen-1-yl)-1,3-diphenylhepta-1,6-diyn-3-yl acetate (125s)



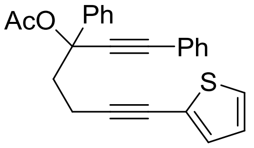
Yield 53%; yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.15 (s, 3H), 2.49-2.54 (m, 1H), 2.74-2.80 (m, 2H), 2.95-3.01 (m, 1H), 7.35-7.47 (m, 7H), 7.51-7.64 (m, 5H), 7.69-7.72 (m, 2H), 7.80 (d, 2H, J = 8.2 Hz), 7.85 (d, 2H, J = 7.7 Hz), 8.36 (d, 1H, J = 8.2 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 15.8, 21.8, 43.8, 78.6, 79.0, 86.5, 89.1, 94.0, 121.5, 122.3, 125.3, 125.3, 126.3, 126.3, 126.6, 128.2, 128.2, 128.3, 128.4, 128.6, 128.9, 130.1, 132.1, 133.2, 133.5, 141.1, 168.4; IR (NaCl, neat) ν: 3057, 2230, 1751, 1491, 1227 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{21}$ (M^+ - OAc): 369.1643, found: 369.1638.

1,3-diphenyl-7-(thiophen-3-yl)hepta-1,6-diyn-3-yl acetate (125t)



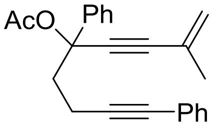
Yield 77%; yellow solid; mp = 80-81 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.05 (s, 3H), 2.30-2.36 (m, 1H), 2.52-2.57 (m, 2H), 2.68-2.73 (m, 1H), 6.99-7.01 (m, 1H), 7.13-7.16 (m, 1H), 7.25-7.31 (m, 5H), 7.33-7.37 (m, 2H), 7.50-7.53 (m, 2H), 7.58-7.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.4, 21.8, 43.6, 76.2, 78.5, 86.6, 88.6, 89.0, 122.3, 122.8, 125.2, 125.4, 127.9, 128.2, 128.6, 129.0, 130.0, 132.1, 141.1, 168.4; IR (NaCl, neat) ν: 3017, 2230, 1751, 1489, 1223 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{21}O_2S$ (M^+ + H): 385.1262, found: 385.1261.

1,3-diphenyl-7-(thiophen-2-yl)hepta-1,6-diyn-3-yl acetate (125u)



Yield 76%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.14 (s, 3H), 2.40-2.46 (m, 1H), 2.63-2.74 (m, 2H), 2.83-2.92 (m, 1H), 7.16-7.23 (m, 2H), 7.37-7.40 (m, 4H), 7.42-7.45 (m, 3H), 7.59-7.62 (m, 2H), 7.67-7.69 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.7, 21.8, 43.5, 77.9, 78.5, 86.5, 89.0, 94.7, 122.2, 123.6, 125.3, 126.4, 128.2, 128.4, 128.6, 128.8, 128.9, 129.2, 132.1, 133.4, 135.7, 141.0, 168.3; IR (NaCl, neat) ν: 3022, 2232, 1748, 1489, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{21}O_2S$ (M^+ + H): 385.1262, found: 385.1257.

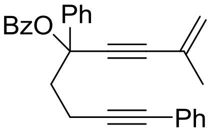
2-methyl-5,9-diphenylnona-1-en-3,8-diyn-5-yl acetate (125v)



Yield 81%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.96 (s, 3H), 2.05 (s, 3H), 2.24-2.30 (m, 1H), 2.42-2.53 (m, 2H), 2.63-2.69 (m, 1H), 5.30 (t, 1H, J = 1.6 Hz), 5.42 (d, 1H, J = 0.8 Hz), 7.21-7.29 (m, 4H), 7.32-7.36 (m, 4H), 7.52-7.54 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.9, 21.6, 24.9, 38.9, 87.0, 112.9, 125.1, 126.8, 126.9, 127.7, 127.8, 128.2, 128.5, 133.3, 134.9, 136.8, 141.8, 147.1, 162.9, 168.6 ; IR

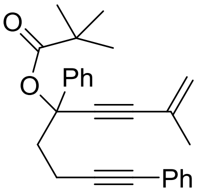
(NaCl, neat) ν: 3019, 2222, 1748, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{23}O_2$ (M^+ + H): 343.1698, found: 343.1703.

2-methyl-5,9-diphenylnona-1-en-3,8-diyn-5-yl benzoate (125w)



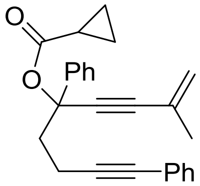
Yield 60%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.90 (s, 3H), 2.31-2.37 (m, 1H), 2.52-2.62 (m, 2H), 2.70-2.74 (m, 1H), 5.24 (t, 1H, J = 1.6 Hz), 5.37 (d, 1H, J = 0.8 Hz), 7.17-7.22 (m, 3H), 7.27-7.36 (m, 6H), 7.42-7.49 (m, 2H), 7.53-7.55 (m, 2H), 7.99-8.01 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.0, 25.1, 38.9, 87.4, 113.2, 125.2, 126.8, 126.8, 127.5, 127.8, 128.3, 128.3, 128.6, 129.8, 130.9, 132.8, 133.4, 134.9, 136.9, 142.1, 147.4, 162.8, 164.1; IR (NaCl, neat) ν: 3019, 2224, 1730, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{25}O_2$ (M^+ + H): 405.1855, found: 405.1843.

2-methyl-5,9-diphenylnona-1-en-3,8-diyn-5-yl pivalate (125x)



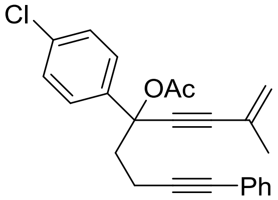
Yield 50%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.22 (s, 9H), 1.96 (s, 3H), 2.24-2.29 (m, 1H), 2.47-2.56 (m, 2H), 2.67-2.72 (m, 1H), 5.30 (t, 1H, J = 1.4 Hz), 5.40 (d, 1H, J = 0.6 Hz), 7.25-7.30 (m, 5H), 7.33-7.37 (m, 4H), 7.52 (d, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.3, 23.4, 27.0, 39.1, 43.8, 77.9, 80.8, 85.5, 89.1, 89.8, 122.8, 123.7, 125.0, 126.1, 127.7, 127.9, 128.2, 128.4, 131.5, 141.4, 175.2; IR (NaCl, neat) ν: 3019, 1740, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{29}O_2$ (M^+ + H): 385.2168, found: 385.2176.

2-methyl-5,9-diphenylnona-1-en-3,8-diyn-5-yl cyclopropanecarboxylate (125y)



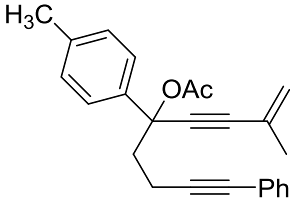
Yield 51%; yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.74-0.77 (m, 2H), 0.82-0.86 (m, 1H), 0.92-0.96 (m, 1H), 1.56-1.60 (m, 1H), 1.88 (s, 3H), 2.17-2.23 (m, 1H), 2.40-2.44 (m, 2H), 2.57-2.63 (m, 1H), 5.23 (d, 1H, *J* = 1.4 Hz), 5.34 (s, 1H), 7.16-7.21 (m, 4H), 7.26-7.29 (m, 4H), 7.44-7.46 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 8.3, 8.4, 9.4, 13.5, 15.3, 23.4, 43.7, 78.2, 80.8, 85.6, 89.1, 90.0, 122.9, 123.8, 125.2, 126.1, 127.7, 127.9, 128.2, 128.4, 131.5, 141.2, 171.8; IR (NaCl, neat) ν: 3019, 2222, 1740, 1159 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{25}O_2$ (M^+ + H): 369.1855, found: 369.1853.

5-(4-chlorophenyl)-2-methyl-9-phenylnona-1-en-3,8-diyn-5-yl acetate (125z)



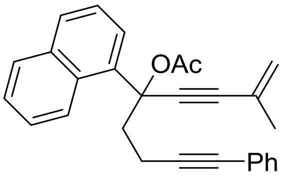
Yield 61%; yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.96 (s, 3H), 2.06 (s, 3H), 2.21-2.29 (m, 1H), 2.42-2.51 (m, 2H), 2.60-2.72 (m, 1H), 5.32 (t, 1H, *J* = 1.4 Hz), 5.42 (s, 1H), 7.25-7.26 (m, 3H), 7.31-7.35 (m, 4H), 7.48 (d, 2H, *J* = 8.6 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 15.2, 21.7, 23.3, 43.3, 77.8, 81.0, 84.8, 88.6, 90.4, 123.3, 123.6, 125.8, 126.8, 127.7, 128.2, 128.6, 131.5, 133.9, 139.7, 168.2; IR (NaCl, neat) ν: 3019, 2224, 1749, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{22}O_2Cl$ (M^+ + H): 377.1308, found: 377.1312.

2-methyl-9-phenyl-5-p-tolylnona-1-en-3,8-diyn-5-yl acetate (125α)



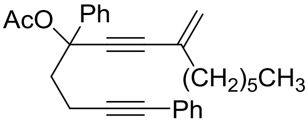
Yield 77%; yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.02 (s, 3H), 2.10 (s, 3H), 2.30-2.39 (m, 4H), 2.48-2.62 (m, 2H), 2.68-2.75 (m, 1H), 5.35-5.37 (m, 1H), 5.48 (t, 1H, *J* = 0.8 Hz), 7.21 (d, 2H, *J* = 8.0 Hz), 7.29-7.31 (m, 3H), 7.39-7.41 (m, 2H), 7.48 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 15.3, 21.1, 21.8, 23.4, 43.5, 78.3, 80.9, 85.7, 89.1, 90.0, 123.0, 123.8, 125.3, 126.1, 127.7, 128.3, 129.2, 131.6, 137.8, 138.1, 168.3; IR (NaCl, neat) ν: 3019, 2224, 1748, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{25}O_2$ (M$^+$ + H): 357.1855, found: 357.1865.

2-methyl-5-(naphthalen-1-yl)-9-phenylnona-1-en-3,8-diyn-5-yl acetate (125β)



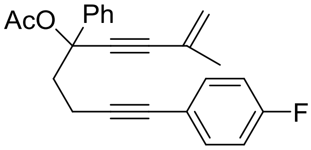
Yield 60%; yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.99 (s, 3H), 2.05 (s, 3H), 2.51-2.55 (m, 1H), 2.59-2.66 (m, 1H), 2.76-2.82 (m, 1H), 2.92-2.96 (m, 1H), 5.33 (t, 1H, *J* = 1.6 Hz), 5.45 (d, 1H, *J* = 0.8 Hz), 7.21-7.23 (m, 3H), 7.28-7.31 (m, 2H), 7.43-7.51 (m, 3H), 7.79 (d, 1H, *J* = 8.2 Hz), 7.84-7.86 (m, 1H), 8.02-8.04 (m, 4H), 8.54 (d, 1H, *J* = 8.5 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 15.6, 21.4, 23.4, 40.8, 80.7, 80.9, 86.5, 89.1, 90.4, 123.1, 123.7, 124.8, 125.0, 125.4, 126.1, 126.1, 126.4, 127.7, 128.2, 129.4, 129.6, 129.7, 131.5, 134.9, 135.2, 168.1; IR (NaCl, neat) ν: 3019, 2224, 1748, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{25}O_2$ (M$^+$ + H): 393.1855, found: 393.1838.

8-methylene-1,5-diphenyltetradeca-1,6-diyn-5-yl acetate (125δ)



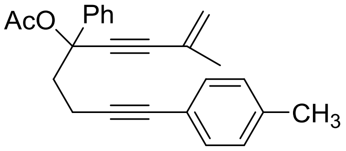
Yield 77%; yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.79-0.83 (m, 3H), 1.21-1.28 (m, 6H), 1.48-1.51 (m, 2H), 1.99 (s, 3H), 2.13-2.23 (m, 3H), 2.38-2.44 (m, 2H), 2.56-2.60 (m, 1H), 5.23 (d, 1H, *J* = 1.6 Hz), 5.36 (d, 1H, *J* = 1.8 Hz), 7.16-7.18 (m, 3H), 7.20-7.22 (m, 1H), 7.25-7.29 (m, 4H), 7.45-7.47 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 14.1, 15.3, 21.7, 22.6, 28.0, 28.6, 31.7, 37.1, 43.6, 78.4, 80.8, 86.1, 89.0, 89.4, 122.1, 123.8, 125.3, 127.6, 128.0, 128.2, 128.4, 131.1, 131.5, 141.1, 168.1; IR (NaCl, neat) ν: 3019, 2222, 1751, 1219 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{33}O_2$ (M$^+$ + H): 413.2481, found: 413.2484.

9-(4-fluorophenyl)-2-methyl-5-phenylnona-1-en-3,8-diyn-5-yl acetate (125ζ)



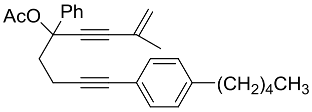
Yield 83%; white solid; mp = 83-84 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.00 (s, 3H), 2.09 (s, 3H), 2.27-2.33 (m, 1H), 2.45-2.57 (m, 2H), 2.65-2.71 (m, 1H), 5.35 (t, 1H, *J* = 1.6 Hz), 5.46 (d, 1H, *J* = 0.7 Hz), 6.95-7.00 (m, 2H), 7.29-7.41 (m, 5H), 7.56-7.58 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.2, 21.6, 23.4, 43.5, 78.3, 79.8, 85.6, 88.6, 90.1, 115.3 (1C, d, $J_{C\text{-}F}$ = 22.0), 119.8 (1C, d, $J_{C\text{-}F}$ = 3.0), 123.0, 125.2, 126.0, 128.0, 128.4, 133.2, 133.3, 141.0, 162.1 (1C, d, $J_{C\text{-}F}$ = 247.0), 168.7 ; IR (NaCl, neat) ν: 3019, 1748, 1506, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{22}O_2F$ (M^+ + H): 361.1604, found: 361.1612.

2-methyl-5-phenyl-9-p-tolylnona-1-en-3,8-diyn-5-yl acetate (125η)



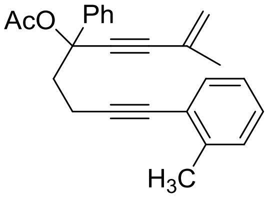
Yield 82%; yellow solid; mp = 113-114 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.96 (s, 3H), 2.06 (s, 3H), 2.22-2.30 (m, 4H), 2.41-2.53 (m, 2H), 2.62-2.71 (m, 1H), 5.31 (d, 1H, *J* = 1.4 Hz), 5.42 (s, 1H), 7.05 (d, 2H, *J* = 8.0 Hz), 7.22-7.29 (m, 3H), 7.33-7.37 (m, 2H), 7.53 (d, 2H, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.3, 21.4, 21.7, 23.4, 43.7, 78.4, 80.9, 85.4, 88.2, 90.1, 120.7, 123.0, 125.2, 126.1, 128.0, 128.5, 129.0, 131.4, 137.7, 141.1, 168.2; IR (NaCl, neat) ν: 3019, 2226, 1748, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{25}O_2$ (M^+ + H): 357.1855, found: 357.1862. θ

2-methyl-9-(4-pentylphenyl)-5-phenylnona-1-en-3,8-diyn-5-yl acetate (125θ)



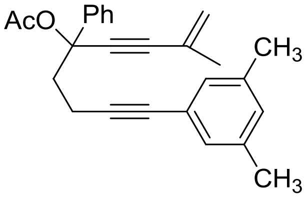
Yield 74%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.79-0.82 (t, 3H, *J* = 6.8 Hz), 1.19-1.27 (m, 5H), 1.49-1.54 (m, 3H), 1.90 (s, 3H), 2.00 (s, 3H), 2.16-2.22 (m, 1H), 2.34-2.43 (m, 2H), 2.46-2.51 (m, 2H), 2.55-2.61 (m, 1H), 5.24 (s, 1H), 5.35 (s, 1H), 6.99 (d, 2H, *J* = 8.0 Hz), 7.17-7.23 (m, 3H), 7.27-7.30 (m, 2H), 7.46 (d, 2H, *J* = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.0, 15.3, 21.7, 22.5, 23.3, 30.9, 31.4, 35.8, 43.6, 78.4, 80.9, 85.4, 88.1, 90.1, 120.8, 122.9, 125.2, 126.1, 128.0, 128.3, 128.4, 131.4, 141.1, 142.7, 168.2; IR (NaCl, neat) ν: 3019, 2224, 1748, 1213 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{33}O_2$ (M^+ + H): 413.2481, found: 413.2485.

2-methyl-5-phenyl-9-o-tolylnona-1-en-3,8-diyn-5-yl acetate (125ι)



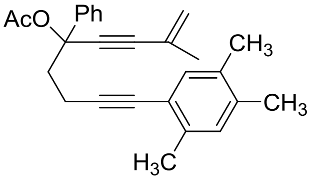
Yield 69%; yellow solid; mp = 60-61 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.98 (s, 3H), 2.09 (s, 3H), 2.26-2.31 (m, 1H), 2.38 (s, 3H), 2.47-2.56 (m, 2H), 2.66-2.77 (m, 1H), 5.32 (s, 1H), 5.44 (s, 1H), 7.06-7.12 (m, 1H), 7.15-7.19 (m, 2H), 7.28-7.33 (m, 2H), 7.35-7.39 (m, 2H), 7.55 (d, 2H, *J* = 7.3 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 15.4, 20.7, 21.7, 23.4, 43.8, 78.3, 79.7, 85.4, 90.1, 92.9, 123.0, 123.5, 125.2, 125.4, 126.0, 127.6, 128.0, 128.5, 129.3, 131.8, 139.9, 141.1, 168.2; IR (NaCl, neat) ν: 3019, 2224, 1748, 1219 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{25}O_2$ (M^+ + H): 357.1855, found: 357.1855.

9-(3,5-dimethylphenyl)-2-methyl-5-phenylnona-1-en-3,8-diyn-5-yl acetate (125κ)



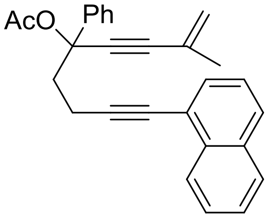
Yield 76%; yellow solid; mp = 82-83 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.05 (s, 3H), 2.13 (s, 3H), 2.32-2.39 (m, 7H), 2.50-2.62 (m, 2H), 2.71-2.78 (m, 1H), 5.39 (t, 1H, *J* = 1.6 Hz), 5.51 (d, 1H, *J* = 0.7 Hz), 6.96 (s, 1H), 7.07 (s, 2H), 7.33-7.37 (m, 1H), 7.41-7.45 (m, 2H), 7.61-7.63 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 15.3, 21.1, 21.7, 23.4, 43.7, 77.6, 78.4, 81.2, 85.6, 88.2, 90.1, 123.1, 123.5, 125.3, 126.1, 128.1, 128.5, 129.3, 129.6, 137.7, 141.1, 168.2; IR (NaCl, neat) ν: 2928, 2224, 1749, 1219 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{27}O_2$ (M^+ + H): 371.2011, found: 371.2013.

2-methyl-5-phenyl-9-(2,4,5-trimethylphenyl)nona-1-en-3,8-diyn-5-yl acetate (125λ)



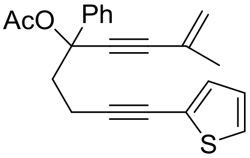
Yield 74%; yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.04 (s, 3H), 2.13 (s, 3H), 2.22 (s, 3H), 2.25 (s, 3H), 2.33-2.38 (m, 4H), 2.53-2.62 (m, 2H), 2.71-2.83 (m, 1H), 5.38 (t, 1H, J = 1.6 Hz), 5.50 (d, 1H, J = 0.8 Hz), 6.98 (s, 1H), 7.17 (s, 1H), 7.33-7.36 (m, 1H), 7.40-7.44 (m, 2H), 7.60-7.62 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 15.5, 19.1, 19.6, 20.1, 21.7, 23.4, 44.0, 78.4, 80.0, 85.6, 90.1, 91.6, 120.7, 123.0, 125.3, 126.1, 128.0, 128.5, 130.8, 132.9, 133.5, 136.3, 137.1, 141.2, 168.2; IR (NaCl, neat) ν: 3017, 2224, 1748, 1219 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{29}O_2$ (M^+ + H): 385.2168, found: 385.2166.

2-methyl-9-(naphthalen-1-yl)-5-phenylnona-1-en-3,8-diyn-5-yl acetate (125μ)



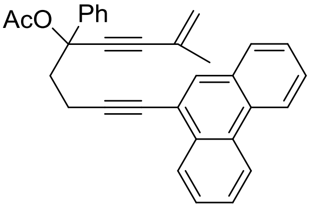
Yield 62%; yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.92 (s, 3H), 2.02 (s, 3H), 2.27-2.36 (m, 1H), 2.50-2.58 (m, 2H), 2.71-2.79 (m, 1H), 5.26 (t, 1H, J = 1.5 Hz), 5.38 (s, 1H), 7.18 (s, 1H), 7.21-7.25 (m, 1H), 7.28-7.33 (m, 3H), 7.40-7.51 (m, 6H), 7.69 (d, 1H, J = 8.2 Hz), 7.74 (d, 1H, J = 7.7 Hz), 8.21 (d, 1H, J = 8.1 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 15.6, 21.7, 23.4, 43.7, 78.4, 78.9, 85.4, 90.2, 94.0, 121.4, 123.0, 125.2, 125.2, 126.0, 126.2, 126.5, 128.1, 128.2, 128.5, 130.1, 133.2, 133.4, 141.1, 168.3; IR (NaCl, neat) ν: 3019, 2222, 1748 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{25}O_2$ (M^+ + H): 393.1855, found: 393.1850.

2-methyl-5-phenyl-9-(thiophen-2-yl)nona-1-en-3,8-diyn-5-yl acetate (125ν)



Yield 70%; yellow solid; mp = 73-74 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.01 (s, 3H), 2.10 (s, 3H), 2.27-2.32 (m, 1H), 2.49-2.59 (m, 2H), 2.68-2.76 (m, 1H), 5.36 (t, 1H, J = 1.6 Hz), 5.47 (d, 1H, J = 0.8 Hz), 6.93-6.95 (m, 1H), 7.11-7.12 (m, 1H), 7.17-7.18 (m, 1H), 7.30-7.34 (m, 1H), 7.38-7.41 (m, 2H), 7.56-7.59 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 15.6, 21.7, 23.4, 43.3, 74.1, 78.3, 85.4, 90.2, 93.1, 123.1, 123.9, 125.2, 126.0, 126.2, 126.8, 128.1, 128.5, 131.1, 141.0, 168.2; IR (NaCl, neat) ν: 3017, 2222, 1749, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{21}O_2S$ (M^+ + H): 349.1262, found: 349.1257.

2-methyl-9-(phenanthren-9-yl)-5-phenylnona-1-en-3,8-diyn-5-yl acetate (125ξ)

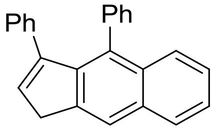


Yield 87%; yellow solid; mp = 111-112 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.05 (s, 3H), 2.14 (s, 3H), 2.35-2.41 (m, 1H), 2.55-2.65 (m, 2H), 2.75-2.82 (m, 1H), 5.39 (t, 1H, J = 1.6 Hz), 5.52 (d, 1H, J = 0.6 Hz), 7.34-7.39 (m, 1H), 7.41-7.46 (m, 3H), 7.48-7.51 (m, 3H), 7.57 (d, 2H, J = 8.3 Hz), 7.63 (d, 4H, J = 7.4 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 15.5, 21.8, 23.5, 43.6, 77.5, 78.4, 80.8, 85.5, 89.8, 90.2, 122.8, 123.2, 125.3, 126.1, 127.0, 127.0, 127.6, 128.1, 128.5, 128.9, 132.0, 140.5, 141.1, 168.3; IR (NaCl, neat) ν: 3019, 2224, 1748, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{32}H_{27}O_2$ (M^+ + H): 443.2011, found: 443.2006.

Representative Experimental Procedure for Gold Complexes C Catalyzed Cycloisomerization of 1,6-Diyne Esters 125a-u

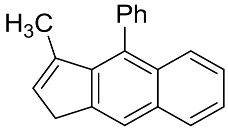
To a solution of 1,6-Diyne Esters **125** (0.2 mmol) in anhydrous CH_2Cl_2 (4 mL) was added gold(I) complex **C** (10 μmol) under an argon atmosphere. The reaction mixture was stirred at rt for 10 min-42 h when TLC indicated that the reaction was complete. The solution was concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*hexane: EtOAc: DCM = 50:1:1) to give the product **129** up to 90% yield.

3,4-diphenyl-1H-cyclopenta[b]naphthalene (129a)



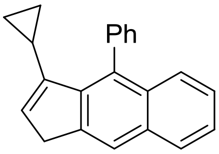
Yield 69%; yellow solid, mp = 218-219 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.69 (d, 2H, *J* = 1.2 Hz), 6.51 (t, 1H, *J* = 2.2 Hz), 6.84-6.86 (m, 2H), 6.90-6.94 (m, 2H), 6.98-7.09 (m, 6H), 7.31-7.35 (m, 1H), 7.43-7.47 (m, 1H), 7.66 (d, 1H, *J* = 7.9 Hz), 7.90 (d, 1H, *J* = 8.1 Hz), 7.98 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 37.0, 122.2, 125.0, 125.1, 125.8, 126.4, 126.5, 127.0, 127.2, 127.7, 128.1, 131.2, 131.9, 132.2, 132.3, 135.5, 137.2, 137.7, 139.9, 142.4, 147.3; HRMS (ESI) calcd. for $C_{25}H_{19}$ (M$^+$ + H): 319.1487, found: 319.1495.

3-methyl-4-phenyl-1H-cyclopenta[b]naphthalene (129e)



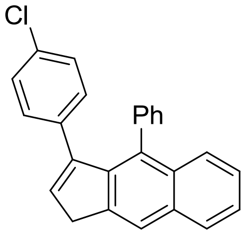
Yield 67%; yellow solid, mp = 157-158 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.54 (t, 3H, *J* = 4.4 Hz), 3.47 (d, 2H, *J* = 0.8 Hz), 6.25 (d, 1H, *J* = 1.5 Hz), 7.29-7.33 (m, 1H), 7.37-7.41 (m, 3H), 7.43-7.48 (m, 4H), 7.85-7.88 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 16.5, 36.3, 121.8, 124.7, 124.9, 126.3, 127.2, 127.6, 131.1, 131.5, 132.5, 139.1, 141.5, 142.6; HRMS (ESI) calcd. for $C_{20}H_{17}$(M$^+$ + H): 257.1330, found: 257.1326.

3-cyclopropyl-4-phenyl-1H-cyclopenta[b]naphthalene (129f)



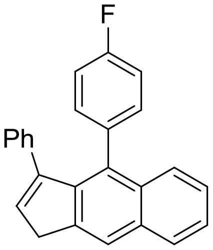
Yield 60%; yellow solid, mp = 134-135 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.26-0.31 (m, 2H), 0.38-0.42 (m, 2H), 0.87-0.90 (m, 1H), 3.46 (s, 2H), 6.13 (d, 1H, J = 1.4 Hz), 7.31-7.34 (m, 1H), 7.41-7.49 (m, 7H), 7.87 (d, 2H, J = 9.6 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 7.6, 11.5, 36.1, 121.8, 124.7, 124.9, 126.5, 127.0, 127.5, 127.5, 128.9, 131.1, 131.6, 131.7, 132.8, 139.5, 141.3, 142.8, 147.8; HRMS (ESI) calcd. for $C_{22}H_{19}$ (M^+ + H): 283.1487, found: 283.1497.

3-(4-chlorophenyl)-4-phenyl-1H-cyclopenta[b]naphthalene (129g)



Yield 71%; yellow solid, mp = 168-169 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.68 (d, 2H, J = 1.1 Hz), 6.50 (t, 1H, J = 2.3 Hz), 6.76-6.78 (m, 2H), 6.87-6.90 (m, 2H), 7.00-7.02 (m, 2H), 7.05-7.08 (m, 2H), 7.14-7.18 (m, 1H), 7.33-7.37 (m, 1H), 7.44-7.48 (m, 1H), 7.67 (d, 1H, J = 8.6 Hz), 7.91 (d, 1H, J = 8.1 Hz), 7.98 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 37.1, 122.3, 125.1, 125.2, 126.4, 126.6, 127.2, 127.3, 127.7, 129.4, 131.3, 131.7, 132.0, 132.2, 135.7, 136.2, 137.2, 139.8, 142.1, 146.2; HRMS (ESI) calcd. for $C_{25}H_{17}ClNa$(M^+ + Na): 375.0916, found: 375.0913.

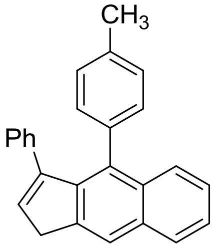
4-(4-fluorophenyl)-3-phenyl-1H-cyclopenta[b]naphthalene (129h)



Yield 86%; yellow solid, mp = 222-223 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.68 (d, 2H, J = 1.2 Hz), 6.52 (t, 1H, J = 2.3 Hz), 6.68-6.72 (m, 2H), 6.83-6.85 (m, 2H), 6.94-7.00 (m, 4H), 7.05-7.09 (m, 1H), 7.33-7.37 (m, 1H), 7.44-7.48 (m, 1H), 7.62 (d, 1H, J

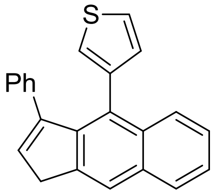
= 8.5 Hz), 7.91 (d, 1H, *J* = 8.1 Hz), 7.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.0, 113.9, 114.1, 122.3, 125.1, 125.2, 126.0, 126.1, 127.2, 127.8, 128.2, 131.9, 132.3, 132.6, 132.7, 135.6, 137.6, 140.4, 142.3, 147.1; HRMS (ESI) calcd. for $C_{25}H_{18}F$ (M^+ + H): 337.1393, found: 337.1401.

1,3,7-triphenylhepta-1,6-diyn-3-yl benzoate (129i)



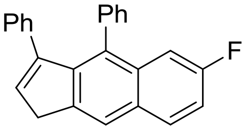
Yield 41%; yellow solid, mp = 182-183 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.24 (s, 3H), 3.66 (d, 2H, *J* = 1.2 Hz), 6.49 (t, 1H, *J* = 2.3 Hz), 6.77- 6.83 (m, 4H), 6.86-6.92 (m, 4H), 6.98-7.02 (m, 1H), 7.30-7.34 (m, 1H), 7.41-7.45 (m, 1H), 7.71 (d, 1H, *J* = 8.4 Hz), 7.88 (d, 1H, *J* = 8.1 Hz), 7.95 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.1, 37.0, 122.0, 124.9, 125.0, 125.3, 126.5, 127.6, 127.8, 128.2, 131.0, 131.9, 132.3, 134.2, 135.3, 136.0, 137.8, 142.3, 147.4; HRMS (ESI) calcd. for $C_{26}H_{21}$ (M^+ + H): 333.1643, found: 333.1641.

3-(3-phenyl-1H-cyclopenta[b]naphthalen-4-yl)thiophene (129j)



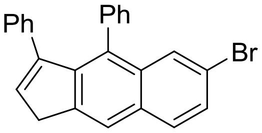
Yield 59%; yellow solid, mp = 219-220 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.67 (d, 2H, *J* = 1.0 Hz), 6.53 (t, 1H, *J* = 2.2Hz), 6.76-6.77 (m, 1H), 6.81-6.83 (m, 1H), 6.93-6.96 (m, 2H), 7.01-7.12 (m, 4H), 7.35-7.39 (m, 1H), 7.44-7.48 (m, 1H), 7.75 (d, 1H, *J* = 8.5 Hz), 7.89 (d, 1H, *J* = 8.0 Hz), 7.97 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.0, 122.3, 123.9, 125.0 ,125.1, 125.2, 125.9, 126.2, 126.9, 127.3, 127.7, 130.4, 131.9, 132.8, 135.8, 137.2, 137.7, 140.6, 142.3, 147.3; HRMS (ESI) calcd. for $C_{23}H_{17}S$ (M^+ + H): 325.1051, found: 325.1047.

6-fluoro-3,4-diphenyl-1H-cyclopenta[b]naphthalene (129m)



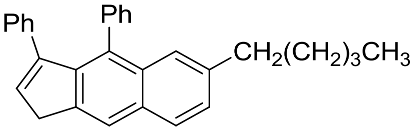
Yield 65%; orange solid, mp = 130-131 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.65(d, 2H, *J* = 1.3 Hz), 6.52 (t, 1H, *J* = 4.6 Hz), 6.81-6.84 (m, 2H), 6.89-6.92 (m, 2H), 6.96-7.06 (m, 6H), 7.18-7.28 (m, 2H), 7.84-7.87 (m, 1H), 7.94 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 36.9, 109.8, 110.0, 115.0, 115.2, 122.0, 125.9, 126.8, 127.1, 127.4, 128.1, 129.7, 129.8, 131.1, 136.2, 136.8, 137.4, 141.7, 147.2; HRMS (ESI) calcd. for $C_{25}H_{18}F(M^+ + H)$: 337.1393, found: 337.1402.

6-bromo-3,4-diphenyl-1H-cyclopenta[b]naphthalene (129n)



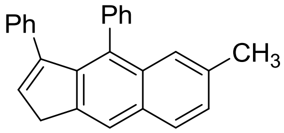
Yield 81%; yellow solid, mp = 176-177 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.66 (d, 2H, *J* = 1.2 Hz), 6.54 (t, 1H, *J* = 2.2 Hz), 6.82-6.84 (m, 2H), 6.90-7.10 (m, 8H), 7.50-7.53 (m, 1H), 7.75-7.80 (m, 2H), 7.93 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.0, 119.4, 122.0, 125.9, 126.9, 127.1, 127.4, 128.1, 128.3, 128.5, 129.3, 130.3, 131.1, 131.5, 133.7, 136.3, 136.4, 137.3, 140.8, 142.9, 147.2; HRMS (ESI) calcd. for $C_{25}H_{18}Br\,(M^+ + H)$: 397.0592, found: 397.0583.

6-pentyl-3,4-diphenyl-1H-cyclopenta[b]naphthalene (129o)



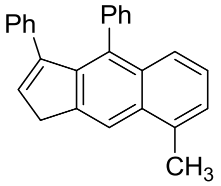
Yield 57%; yellow solid, mp = 83-84 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.76 (t, 3H, *J* = 6.8 Hz), 1.16-1.18 (m, 4H), 1.44-1.52 (m, 2H), 2.52 (t, 2H, *J* = 7.6 Hz), 3.55 (d, 2H, *J* = 1.2 Hz), 6.38 (t, 1H, *J* = 2.2 Hz), 6.73-6.75 (m, 2H), 6.80-6.83 (m, 2H), 6.87-6.98 (m, 6H), 7.20-7.22 (m, 1H), 7.32 (s, 1H), 7.72 (d, 1H, *J* = 8.3 Hz), 7.83 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.1, 22.5, 31.2, 31.5, 36.3, 36.9, 121.9, 124.9, 125.7, 126.5, 127.0, 127.1, 127.6, 127.8, 127.9, 128.1, 128.4, 130.4, 131.3, 131.8, 132.4, 135.4, 137.4, 137.8, 139.7, 139.9, 141.5, 147.4; HRMS (ESI) calcd. for $C_{30}H_{29}\,(M^+ + H)$: 389.2269, found: 389.2265.

6-methyl-3,4-diphenyl-1H-cyclopenta[b]naphthalene (129p)



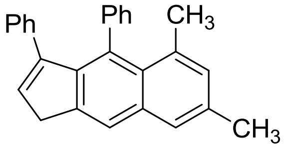
Yield 68%; yellow solid, mp = 151-152 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.39 (s, 3H), 3.67 (d, 2H, J = 1.2 Hz), 6.49 (t, 1H, J = 2.3 Hz), 6.84-6.86 (m, 2H), 6.91-6.94 (m, 2H), 6.98-7.09 (m, 6H), 7.28-7.31 (m, 1H), 7.42 (d, 1H, J = 0.5 Hz), 7.81 (d, 1H, J = 8.3 Hz), 7.94 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 22.0, 36.9, 121.9, 125.3, 125.7, 126.5, 127.0, 127.2, 127.2, 127.6, 128.1, 130.2, 131.3, 131.7, 132.4, 134.6, 135.5, 137.4, 137.8, 140.0, 141.4, 147.4; HRMS (ESI) calcd. for $C_{26}H_{21}$ (M^+ + H): 333.1643, found: 333.1645.

8-methyl-3,4-diphenyl-1H-cyclopenta[b]naphthalene (129q)



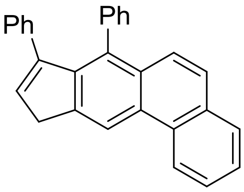
Yield 81%; yellow solid, mp = 207-208 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.78 (s, 3H), 3.70 (d, 2H, J = 1.2 Hz), 6.49 (t, 1H, J = 2.3 Hz), 6.82-6.84 (m, 2H), 6.89-6.92 (m, 2H), 6.95-7.03 (m, 6H), 7.19-7.24 (m, 1H), 7.28 (d, 1H, J = 6.8 Hz), 7.51 (d, 1H, J = 8.5 Hz), 8.16 (d, 1H, J = 0.7 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 20.0, 37.3, 118.4, 124.6, 125.0, 125.8, 125.9, 126.5, 127.0, 127.1, 128.1, 130.9, 131.3, 132.4, 132.7, 133.7, 135.4, 137.6, 137.7, 139.5, 142.3, 147.3; HRMS (ESI) calcd. for $C_{26}H_{21}$ (M^+ + H): 333.1643, found: 333.1638.

5,7-dimethyl-3,4-diphenyl-1H-cyclopenta[b]naphthalene (129r)



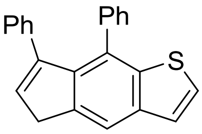
Yield 53%; yellow solid, mp = 166-167 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.79 (s, 3H), 2.46 (s, 3H), 3.61 (d, 2H, J = 1.2 Hz), 6.37 (t, 1H, J = 2.3 Hz), 6.74-6.76 (m, 2H), 6.85-6.93 (m, 4H), 6.97-6.99 (m, 5H), 7.54 (s, 1H), 7.88 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 21.1, 25.1, 36.5, 122.9, 125.3, 126.2, 126.5, 126.5, 127.0, 128.4, 129.4, 131.6, 132.0, 132.8, 133.6, 134.2, 135.4, 136.0, 138.8, 140.2, 140.8, 141.2, 148.0; HRMS (ESI) calcd. for $C_{27}H_{23}$ ($M^+ + H$): 347.1800, found: 347.1792.

7,8-diphenyl-10H-cyclopenta[b]phenanthrene (129s)



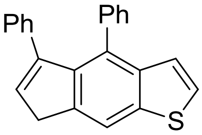
Yield 57%; yellow solid, mp = 196-207 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.78 (s, 2H), 6.56 (t, 1H, J = 2.0 Hz), 6.86-7.11 (m, 10H), 7.57-7.64 (m, 3H), 7.67-7.70 (m, 1H), 7.87 (d, 1H, J = 7.8 Hz), 8.81 (d, 1H, J = 8.4 Hz), 8.91 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.7, 117.3, 122.9, 125.2, 125.8, 125.8, 126.2, 126.4, 126.6, 127.1, 127.2, 128.1, 128.3, 128.4, 130.2, 130.4, 131.3, 131.6, 133.3, 135.3, 137.5, 137.6, 140.5, 143.2, 147.4; HRMS (ESI) calcd. for $C_{29}H_{21}$ (M^+ + H): 369.1643, found: 369.1639.

7,8-diphenyl-5H-indeno[5,6-b]thiophene (129t)



Yield 10%; yellow solid, mp = 201-202 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.62 (d, 2H, J = 1.4 Hz), 6.50 (t, 1H, J = 2.2 Hz), 6.88-6.93 (m, 4H), 6.96-7.07 (m, 4H), 7.11-7.13 (m, 2H), 7.37-7.40 (m, 2H), 7.94 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.2, 117.9, 123.9, 126.0, 126.5, 127.0, 127.1, 127.5, 128.0, 129.6, 130.1, 134.3, 137.4, 137.4, 142.7; HRMS (ESI) calcd. for $C_{23}H_{17}S$ (M^+ + H): 325.1051, found: 325.1060.

4,5-diphenyl-7H-indeno[5,6-b]thiophene (129u)

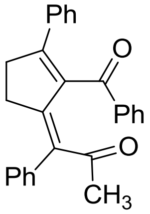


Yield 52%; yellow solid, mp = 182-183 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.72 (d, 2H, J = 1.1 Hz), 6.55 (t, 1H, J = 2.3 Hz), 6.81-6.83 (m, 2H), 6.89-6.93 (m, 2H), 6.96-7.02 (m, 5H), 7.18-7.22 (m, 1H), 7.52-7.57 (m, 2H), 8.45 (d, 1H, J = 0.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.3, 118.6, 124.6, 125.3, 125.7, 125.9, 126.8, 127.1, 127.2, 128.1, 129.1, 131.2, 131.7, 132.5, 133.8, 136.4, 136.9, 137.3, 140.6, 143.7, 147.1; HRMS (ESI) calcd. for $C_{23}H_{17}S$ ($M^+ + H$): 325.1051, found: 325.1058.

Representative Experimental Procedure for Gold Complexes F Catalyzed Cycloisomerization of 1,6-Diyne Esters 125a-u

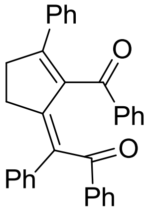
To a solution of 1,6-Diyne Esters **125** (0.2 mmol) in anhydrous CH_2Cl_2 (4 mL) was added gold(III) complex **F** (10 μmol) under an argon atmosphere. The reaction mixture was stirred at rt for 10 min-42 h when TLC indicated that the reaction was complete. The solution was concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*hexane: EtOAc: DCM = 50:1:1) to give the product **130** up to 83% yield.

(Z)-1-(2-benzoyl-3-phenylcyclopent-2-en-1-ylidene)-1-phenylpropan-2-one (130a)



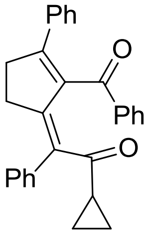
Yield 83%; brown solid, mp = 139-140 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.83 (s, 3H), 2.78-2.80 (m, 2H), 2.97-3.00 (m, 2H), 7.11-7.13 (m, 3H), 7.17-7.19 (m, 2H), 7.25-7.29 (m, 4H), 7.34-7.37 (m, 2H), 7.40-7.44 (m, 2H), 7.82-7.84 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 29.5, 33.4, 34.9, 127.6, 127.8, 128.0, 128.1, 128.8, 129.0, 129.2, 129.2, 132.6, 135.8, 137.5, 139.0, 152.2, 195.3, 201.1; IR (NaCl, neat) ν:3015, 1668, 1653, 1580, 1356, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{23}O_2$ ($M^+ + H$): 379.1698, found: 379.1703.

(Z)-2-(2-benzoyl-3-phenylcyclopent-2-en-1-ylidene)-1,2-diphenylethanone (130b)



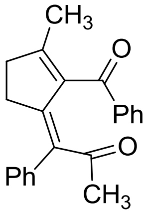
Yield 68%; yellow solid, mp = 173-174 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.08-3.10 (m, 2H), 3.13-3.16 (m, 2H), 7.08-7.09 (m, 3H), 7.13-7.20 (m, 7H), 7.25-7.32 (m, 6H), 7.63-7.69 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 32.9, 35.0, 127.3, 127.8, 127.9, 128.0, 128.6, 128.7, 128.9, 129.5, 129.9, 132.3, 132.8, 133.3, 135.8, 136.9, 137.4, 138.4, 138.6, 150.8, 155.7, 196.1, 196.5; IR (NaCl, neat) ν: 3017, 1655, 1597, 1580, 1449, 1219 cm^{-1}; HRMS (ESI) calcd. for $C_{32}H_{25}O_2$ (M^+ + H): 441.1855, found: 441.1846.

(Z)-2-(2-benzoyl-3-phenylcyclopent-2-en-1-ylidene)-1-cyclopropyl-2-phenylethanone (130d)



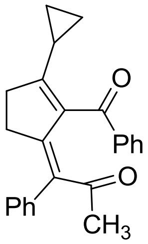
Yield 67%; yellow solid, mp = 109-110 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.57-0.61 (m, 2H), 0.80-0.84 (m, 2H), 1.60-1.66 (m, 1H), 2.88-2.91 (m, 2H), 2.97-3.01 (m, 2H), 7.09-7.15 (m, 5H), 7.25-7.27 (m, 2H), 7.32-7.41(m, 6H), 7.80-7.83 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.7, 21.0, 33.5, 35.0, 127.5, 127.8, 128.0, 128.7, 128.7, 129.1, 129.6, 132.5, 134.3, 136.0, 137.5, 138.6, 138.9, 151.2, 157.5, 194.7, 203.1; IR (NaCl, neat) ν: 3017, 1659, 1597, 1582, 1379, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{25}O_2$ (M^+ + H): 405.1855, found: 405.1858.

(Z)-1-(2-benzoyl-3-methylcyclopent-2-en-1-ylidene)-1-phenylpropan-2-one (130e)



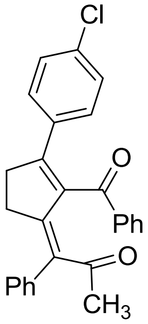
Yield 23%; brown solid, mp = 144-145 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.65 (s, 3H), 1.83 (s, 3H), 2.54-2.55 (m, 2H), 2.58-2.60 (m, 2H), 7.20-7.22 (m, 2H), 7.30-7.33 (m, 1H), 7.38-7.41 (m, 2H), 7.45-7.49 (m, 2H), 7.51-7.55 (m, 1H), 7.92-7.94 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 17.4, 29.4, 32.8, 36.4, 127.4, 128.4, 128.9, 129.0, 129.3, 131.2, 132.6, 138.5, 138.9, 139.5, 154.3, 162.3, 193.7, 200.1; IR (NaCl, neat) ν: 3013, 1670, 1597, 1580, 1356, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{21}O_2$ ($M^+ + H$): 317.1542, found: 317.1534.

(Z)-1-(2-benzoyl-3-cyclopropylcyclopent-2-enylidene)-1-phenylpropan-2-one (130f)



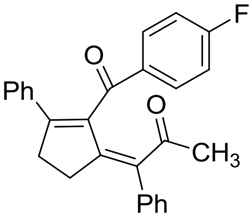
Yield 50%; yellow solid, mp = 142-143 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.77 (d, 4H, J = 6.6 Hz), 1.65 (s, 3H), 1.72-1.76 (m, 1H), 2.19-2.22 (m, 2H), 2.52-2.54 (m, 2H), 7.19-7.21 (m, 2H), 7.28-7.33 (m, 1H), 7.37-7.40 (m, 2H), 7.45-7.55 (m, 3H), 7.99-8.02 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 8.2, 13.7, 28.8, 29.4, 32.2, 127.3, 128.4, 128.9, 129.1, 129.4, 130.1, 132.5, 138.4, 138.6, 139.8, 154.5, 167.5, 193.8, 199.8; IR (NaCl, neat) ν: 3013, 1670, 1647, 1597, 1541, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{23}O_2$ ($M^+ + H$): 343.1698, found: 343.1693.

(Z)-1-(2-benzoyl-3-(4-chlorophenyl)cyclopent-2-enylidene)-1-phenylpropan-2-one (130g)



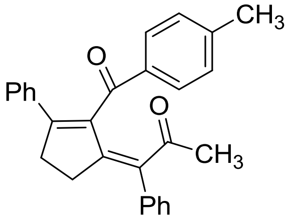
Yield 50%; brown solid, mp = 165-166 °C; ^{1}H NMR ($CDCl_3$, 400 MHz):): δ 1.81 (s, 3H), 2.77-2.80 (m, 2H), 2.94-2.96 (m, 2H), 7.08-7.14 (m, 4H), 7.26-7.36 (m, 5H), 7.40-7.44 (m, 3H), 7.83 (d, 2H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 29.5, 33.2, 34.8, 127.7, 128.2, 128.3, 129.0, 129.1, 129.1, 129.2, 132.8, 134.2, 134.7, 137.4, 138.9, 139.2, 151.9, 156.9, 195.0, 200.9; IR (NaCl, neat) ν: 3019, 1663, 1597, 1580, 1354, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{22}O_2Cl$ (M^+ + H): 413.1308, found: 413.1300.

(Z)-1-(2-(4-fluorobenzoyl)-3-phenylcyclopent-2-en-1-ylidene)-1-phenylpropan-2-one (130h)



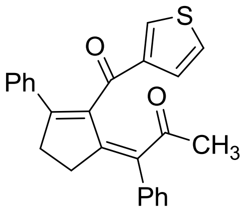
Yield 78%; brown solid, mp = 153-154 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.88 (s, 3H), 2.77-2.80 (m, 2H), 2.97-3.00 (m, 2H), 6.92 (t, 2H, J = 8.7 Hz), 7.10-7.17 (m, 5H), 7.26-7.29 (m, 2H), 7.32-7.36 (m, 1H), 7.40-7.44 (m, 2H), 7.82-7.86 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 29.6, 33.5, 34.8, 115.1 (1C, d, J_{C-F} = 22.0), 127.7,127.8, 128.1, 129.0, 129.0, 129.1, 131.7, 131.8, 133.7, 134.0, 134.1, 135.7, 138.4, 138.9, 152.1, 158.6, 165.3 (1C, d, J_{C-F} = 252.0), 193.9, 201.1; IR (NaCl, neat) ν: 3015, 1663, 1653, 1595, 1219 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{22}O_2F$ (M^+ + H): 397.1604, found: 397.1607.

(Z)-1-(2-(4-methylbenzoyl)-3-phenylcyclopent-2-en-1-ylidene)-1-phenylpropan-2-one (130i)



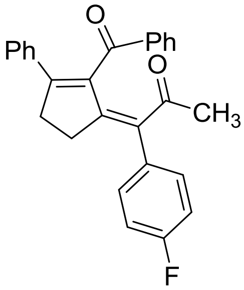
Yield 71%; yellow solid, mp = 148-149 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.83 (s, 3H), 2.29 (s, 3H), 2.77-2.80 (m, 2H), 2.97-2.99 (m, 2H), 7.07 (d, 2H, J = 7.9 Hz), 7.12-7.14 (m, 3H), 7.19-7.21 (m, 2H), 7.26-7.34 (m, 4H), 7.39-7.42 (m, 2H), 7.73 (d, 2H, J = 8.1 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 21.7, 29.5, 33.3, 34.8, 127.6, 127.9, 128.0, 128.8, 128.9, 128.9, 129.1, 129.3, 133.8, 135.1, 135.9, 138.7, 139.0, 143.3, 152.0, 157.9, 195.1, 201.1; IR (NaCl, neat) ν: 1655, 1603, 1572, 1491, 1354, 1265cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{25}O_2$ (M^+ + H): 393.1855, found: 393.1847.

(Z)-1-phenyl-1-(3-phenyl-2-(thiophene-3-carbonyl)cyclopent-2-en-1-ylidene)propan-2-one (130j)



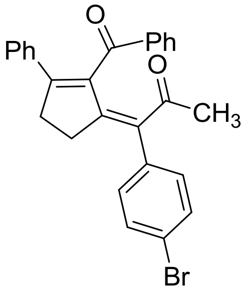
Yield 59%; brown solid, mp = 128-129 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.90 (s, 3H), 2.77-2.79 (m, 2H), 2.96-2.99 (m, 2H), 7.10-7.12 (m, 1H), 7.16-7.23 (m, 5H), 7.25-7.30 (m, 2H), 7.31-7.35 (m, 1H), 7.39-7.43 (m, 3H), 7.79-7.80 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 29.6, 33.3, 34.9, 125.6, 127.5, 127.7, 127.8, 127.8, 128.1, 128.9, 129.0, 129.1, 133.5, 134.0, 135.9, 138.8, 139.4, 142.8, 151.3, 157.9, 189.1, 201.5; IR (NaCl, neat) ν: 1647, 1636 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{17}O_2$ (M^+ + H): 385.1229, found: 385.1260.

7-(4-pentylphenyl)-1,3-diphenylhepta-1,6-diyn-3-yl acetate (130m)



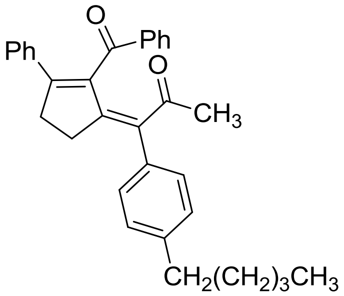
Yield 68%; yellow solid, mp = 129-130 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.83 (s, 3H), 2.75-2.78 (m, 2H), 2.98-3.01 (m, 2H), 7.08-7.14 (m, 5H), 7.15-7.19 (m, 2H), 7.23-7.28 (m, 4H), 7.34-7.39 (m, 1H), 7.81-7.83 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 29.5, 33.4, 34.8, 115.9 (1C, d, J $_{C\text{-}F}$ = 21.0), 127.8, 128.0, 128.1, 128.9, 129.2, 130.9, 130.9, 132.6, 132.6, 134.9, 134.9, 135.7, 137.5, 138.5, 152.7, 158.9, 162.2 (1C, d, J $_{C\text{-}F}$ = 246.0), 195.2, 200.7; IR (NaCl, neat) ν: 1653, 1647 cm^{-1}; HRMS (ESI) calcd. for $C_{30}H_{21}O$ (M^+ + H): 397.1592, found: 397.1607.

(Z)-1-(2-benzoyl-3-phenylcyclopent-2-enylidene)-1-(4-bromophenyl)propan-2-one (130n)



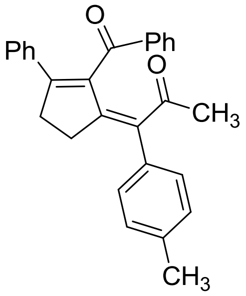
Yield 81%; yellow solid, mp = 153-154 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.84 (s, 3H), 2.75-2.78 (m, 2H), 2.98-3.01 (m, 2H), 7.09-7.12 (m, 3H), 7.15-7.18 (m, 4H), 7.24-7.28 (m, 2H), 7.35-7.38 (m, 1H), 7.54-7.56 (m, 2H), 7.80-7.82 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 29.5, 33.4, 34.9, 121.8, 127.8, 128.1, 128.1, 129.0, 129.2, 130.9, 132.2, 132.4, 132.7, 135.6, 137.4, 137.9, 138.5, 152.8, 159.2, 195.2, 200.4; IR (NaCl, neat) ν: 3015, 1667, 1549, 1356, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{22}O_2$ Br(M^+ + H): 457.0803, found: 457.0813.

(Z)-1-(2-benzoyl-3-phenylcyclopent-2-en-1-ylidene)-1-(4-pentylphenyl)propan-2-one (130o)



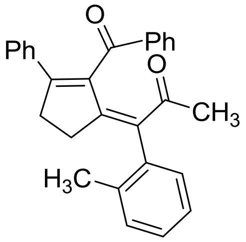
Yield 78%; yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.91 (t, 3H, J = 7.0 Hz), 1.33-1.39 (m, 4H), 1.61-1.68 (m, 2H), 1.83 (s, 3H), 2.63 (t, 2H, J = 7.6 Hz), 2.79-2.82 (m, 2H), 2.96-2.99 (m, 2H), 7.09-7.12 (m, 3H), 7.15-7.27 (m, 8H), 7.33-7.37 (m, 1H), 7.82-7.84 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 14.1, 22.6, 29.5, 31.0, 31.6, 33.4, 34.9, 35.7, 127.8, 128.0, 128.0, 128.7, 128.9, 129.0, 129.2, 132.6, 133.9, 135.9, 136.0, 137.6, 138.7, 142.5, 151.7, 158.1, 195.4, 201.5; IR (NaCl, neat) ν: 3017, 1667, 1582, 1449, 1356, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{32}H_{33}O_2$ (M$^+$ + H): 449.2481, found: 449.2486.

1,3-diphenyl-7-(p-tolyl)hepta-1,6-diyn-3-yl acetate (130p)



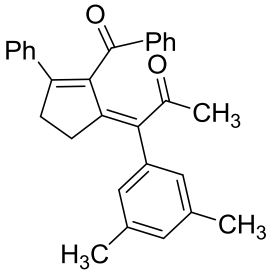
Yield 78%; brown solid, mp = 123-124 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.83 (s, 3H), 2.38 (s, 3H), 2.79-2.81 (m, 2H), 2.96-2.99 (m, 2H), 7.10-7.12 (m, 3H), 7.15-7.18 (m, 4H), 7.21-7.28 (m, 4H), 7.34-7.38 (m, 1H), 7.82-7.84 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 21.3, 29.5, 33.4, 34.9, 127.8, 128.0, 128.0, 128.7, 129.0, 129.2, 129.6, 132.6, 133.8, 135.9, 135.9, 137.4, 137.5, 138.7, 151.8, 158.3, 195.4, 201.5; IR (NaCl, neat) ν: 3017, 1672, 1651, 1580, 1557, 1356, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{25}O_2$ (M$^+$ + H): 393.1855, found: 393.1855.

(Z)-1-(2-benzoyl-3-phenylcyclopent-2-enylidene)-1-o-tolylpropan-2-one (130q)



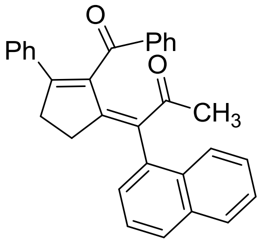
Yield 54%; yellow solid, mp = 187-188 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.69 (s, 3H), 2.26 (m, 3H), 2.40-2.47 (m, 1H), 2.62-2.69 (m, 1H), 2.89-3.03 (m, 2H), 7.13-7.15 (m, 3H), 7.20-7.32 (m, 8H), 7.37-7.40 (m, 1H), 7.85-7.87 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 19.7, 29.0, 33.2, 34.7, 126.7, 127.9, 128.0, 128.1, 128.8, 129.1, 129.5, 130.7, 132.1, 132.4, 135.8, 136.4, 138.0, 139.0, 139.0, 159.8, 194.4, 199.0; IR (NaCl, neat) ν: 3019, 1667, 1356, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{25}O_2$ (M^+ + H): 393.1855, found: 393.1855.

(Z)-1-(2-benzoyl-3-phenylcyclopent-2-enylidene)-1-(3,5-dimethylphenyl)propan-2-one (130r)



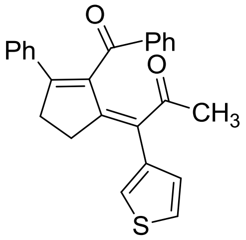
Yield 70%; yellow solid, mp = 161-162 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.83 (s, 3H), 2.33 (s, 6H), 2.78-2.81 (m, 2H), 2.96-2.99 (m, 2H), 6.89 (s, 2H), 6.97 (s, 1H), 7.10-7.13 (m, 3H), 7.15-7.18 (m, 2H), 7.24-7.28 (m, 2H), 7.34-7.39 (m, 1H), 7.81-7.84 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 21.3, 29.5, 33.3, 34.9, 126.8, 127.7, 127.8, 128.0, 128.0, 128.3, 128.7, 129.0, 129.2, 132.5, 134.1, 135.9, 137.6, 138.4, 138.7, 138.8, 151.6, 158.2, 195.3, 201.4; IR (NaCl, neat) ν: 3017, 1667, 1599, 1582, 1356, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{27}O_2$ (M^+ + H): 407.2011, found: 407.2002.

(Z)-1-(2-benzoyl-3-phenylcyclopent-2-enylidene)-1-(naphthalen-1-yl)propan-2-one (130s)



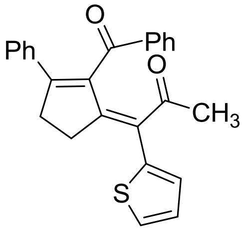
Yield 45%; yellow solid, mp = 144-145 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.68 (s, 3H), 2.41-2.44 (m, 1H), 2.61-2.68 (m, 1H), 2.90-2.93 (m, 2H), 7.12-7.15 (m, 3H), 7.21-7.25 (m, 2H), 7.31-7.35 (m, 2H), 7.39-7.46 (m, 2H), 7.51-7.55 (m, 3H), 7.86-7.97 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 29.0, 33.1, 34.8, 125.0, 126.0, 126.3, 126.9, 127.2, 127.9, 128.0, 128.1, 128.3, 128.7, 128.9, 129.2, 130.8, 131.6, 132.5, 134.1, 135.7, 137.0, 137.9, 138.9, 155.3, 160.0, 194.7, 199.5; IR (NaCl, neat) ν: 3017, 1663, 1655, 1358, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{31}H_{25}O_2$ (M^+ + H): 429.1855, found: 429.1863.

(Z)-1-(2-benzoyl-3-phenylcyclopent-2-enylidene)-1-(thiophen-3-yl)propan-2-one (130t)



Yield 74%; brown solid, mp = 136-137 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.91 (s, 3H), 2.88-2.90 (m, 2H), 3.00-3.03 (m, 2H), 7.02-7.03 (m, 1H), 7.09-7.12 (m, 3H), 7.14-7.20 (m, 3H), 7.23-7.27 (m, 2H), 7.34-7.39 (m, 2H), 7.80-7.82 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 29.4, 33.5, 34.9, 123.9, 126.0, 127.8, 128.0, 128.1, 128.2, 128.7, 128.8, 129.2, 132.7, 135.7, 137.4, 138.5, 138.6, 152.2, 158.3, 195.6, 201.4; IR (NaCl, neat) ν: 3017, 1667, 1661, 1580, 1356, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{21}O_2S$ (M^+ + H): 385.1262, found: 385.1270.

(E)-1-(2-benzoyl-3-phenylcyclopent-2-enylidene)-1-(thiophen-2-yl)propan-2-one (130u)

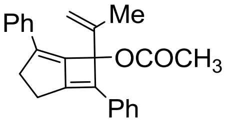


Yield 71%; pink solid, mp = 185-186 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.71 (s, 3H), 2.60-2.63 (m, 2H), 2.89-2.96 (m, 1H), 2.30-3.07 (m, 1H), 7.13-7.15 (m, 3H), 7.21-7.25 (m, 2H), 7.29-7.34 (m, 4H), 7.37-7.41 (m, 1H), 7.49-7.51 (m, 1H), 7.87-7.89 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.8, 33.2, 34.8, 127.6, 127.9, 128.1, 128.1, 129.0, 129.1, 129.4, 129.7, 130.1, 131.3, 132.4, 134.1, 135.6, 138.0, 138.4, 138.9, 156.2, 161.4, 193.8, 197.3; IR (NaCl, neat) ν: 3017, 1676, 1670, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{20}O_2SNa$ (M^+ + Na): 407.1082, found: 407.1075.

Representative Experimental Procedure for Gold Complexes A Catalyzed Cycloisomerization of 1,6-Diyne Esters 125v-ξ

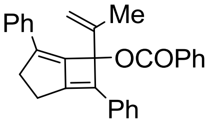
To a solution of 1,6-Diyne Esters **125** (0.2 mmol) in anhydrous pentane (6 mL) was added gold(I) complex **A** (10 μmol) and 4A MS (200 mg) under an argon atmosphere. The reaction mixture was stirred at rt for 12-30 h when TLC indicated that the reaction was complete. The solution was filtrated through celite and then concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*hexane: EtOAc: DCM = 50:1:1) to give the product **131** up to 78% yield.

4,7-diphenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl acetate (131v)



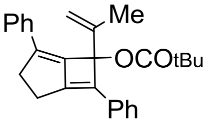
Yield 88%; yellow solid, mp = 87-88 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.72 (s, 3H), 2.10 (s, 3H), 2.83-3.01 (m, 2H), 3.25-3.32 (m, 1H), 3.42-3.49 (m, 1H), 5.19-5.20 (t, 1H, *J* = 1.4 Hz), 5.46 (d, 1H, *J* = 0.4 Hz), 7.16-7.22 (m, 2H), 7.30-7.42 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.9, 21.6, 24.9, 38.9, 87.0, 112.9, 125.1, 126.8, 126.9, 127.7, 127.8, 128.2, 128.5, 133.3, 134.9, 136.8, 14 1.8, 147.1, 162.9, 168.6; IR (NaCl, neat) ν: 3019, 1738, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_2O_2$ (M^+ + H): 343.1698, found: 343.1708.

4,7-diphenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl benzoate (131w)



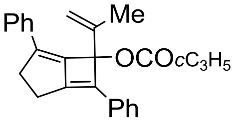
Yield 48%; yellow solid, mp = 122-123 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.80 (s, 3H), 2.89-3.06 (m, 2H), 3.32-3.38 (m, 1H), 3.45-3.52 (m, 1H), 5.26 (t, 1H, *J* = 1.3 Hz), 5.65 (s, 1H), 7.16-7.20 (m, 2H), 7.29-7.34 (m, 4H), 7.40-7.45 (m, 6H), 7.51-7.55 (m, 1H), 8.07-8.09 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.0, 25.1, 38.9, 87.4, 113.2, 125.2, 126.8, 126.8, 127.5, 127.8, 128.3, 128.3, 128.6, 129.8, 130.9, 132.8, 133.4, 134.9, 136.9, 142.1, 147.4, 162.8, 164.1; IR (NaCl, neat) ν: 3019, 1728, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{25}O_2$(M^+ + H): 405.1855, found: 405.1850.

4,7-diphenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl pivalate (131x)



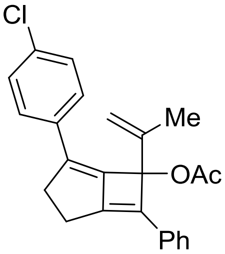
Yield 24%; yellow solid, mp = 117-118 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.22 (s, 9H), 1.71 (s, 3H), 2.84-3.02 (m, 2H), 3.29-3.43 (m, 2H), 5.15 (t, 1H, *J* = 1.5 Hz), 5.60 (d, 1H, *J* = 0.8 Hz), 7.14-7.19 (m, 2H), 7.28-7.35 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 1.0, 19.0, 25.2, 27.4, 38.6, 39.7, 85.9, 112.8, 125.0, 126.6, 126.7, 127.1, 127.3, 128.3, 128.5, 133.4, 135.0, 136.8, 142.6, 148.1, 161.6, 175.7; IR (NaCl, neat) ν: 3019, 1736, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{29}O_2$(M^+ + H): 385.2168, found: 385.2177.

4,7-diphenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl cyclopropanecarboxylate (131y)



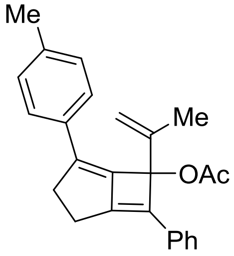
Yield 31%; yellow solid, mp = 119-120 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.78-0.82 (m, 2H), 0.94-0.96 (m, 2H), 1.65-1.70 (m, 4H), 2.83-2.98 (m, 2H), 3.26-3.33 (m, 1H), 3.38-3.45 (m, 1H), 5.17 (s, 1H), 5.50 (s, 1H), 7.15-7.20 (m, 2H), 7.30-7.33 (m, 4H), 7.36-7.39 (m, 4H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 8.3, 8.5, 13.6, 19.0, 25.1, 38.9, 86.8, 113.0, 125.2, 126.8, 127.5, 128.3, 128.6, 133.5, 135.0, 137.0, 142.2, 147.6, 162.6, 172.3; IR (NaCl, neat) ν: 3019, 1734, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{19}(M^+ + H)$: 283.1487, found: 283.1479.

4-(4-chlorophenyl)-7-phenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl acetate (131z)



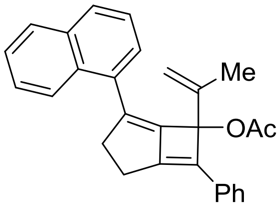
Yield 34%; yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.63 (s, 3H), 2.02 (s, 3H), 2.76-2.90 (m, 2H), 3.13-3.19 (m, 1H), 3.32-3.39 (m, 1H), 5.13 (s, 1H), 5.34 (s, 1H), 7.10-7.14 (m, 1H), 7.18-7.30 (m, 8H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 18.8, 21.6, 24.9, 39.1, 87.1, 113.1, 125.2, 126.6, 127.0, 128.3, 128.6, 128.9, 132.5, 133.1, 133.3, 137.2, 137.9, 141.5, 147.6, 162.8, 168.8; IR (NaCl, neat) ν: 3019, 1744, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{22}O_2Cl\,(M^+ + H)$: 377.1308, found: 377.1317.

7-phenyl-6-(prop-1-en-2-yl)-4-p-tolylbicyclo[3.2.0]hepta-1(7),4-dien-6-yl acetate (131α)



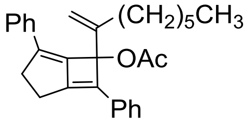
Yield 63%; yellow solid, mp = 77-78 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.73 (s, 3H), 2.10 (s, 3H), 2.35 (s, 3H), 2.83-2.98 (m, 2H), 3.23-3.30 (m, 1H), 3.42-3.48 (m, 1H), 5.20 (s, 1H), 5.44 (s, 1H), 7.14-7.20 (m, 3H), 7.31-7.39 (m, 6H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 18.9, 21.3, 21.6, 24.9, 39.0, 87.2, 112.8, 125.0, 126.6, 127.7, 127.9, 128.5, 128.9, 132.1, 133.5, 136.3, 136.8, 141.9, 146.2, 163.1, 168.6; IR (NaCl, neat) ν: 3019, 1742, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{25}O_2$ ($M^+ + H$): 357.1855, found: 357.1858.

4-(naphthalen-1-yl)-7-phenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl acetate (131β)



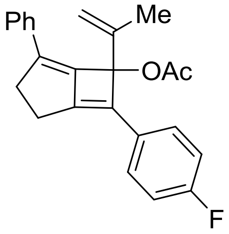
Yield 26%; yellow solid, mp = 78-79 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.62 (s, 3H), 2.04 (s, 3H), 2.90-3.06 (m, 2H), 3.53-3.55 (m, 2H), 5.01 (t, 1H, J = 1.4 Hz), 5.31 (d, 1H, J = 0.4 Hz), 7.18-7.22 (m, 1H), 7.32-7.36 (m, 2H), 7.42-7.49 (m, 6H), 7.74 (d, 1H, J = 7.6 Hz), 7.82-7.85 (m, 1H), 8.20-8.22 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 19.0, 21.6, 24.9, 43.4, 87.9, 113.1, 125.3, 125.4, 125.4, 125.6, 126.1, 126.3, 126.8, 127.6, 128.3, 128.5, 131.4, 133.2, 133.7, 133.9, 136.5, 141.8, 149.0, 162.6, 168.5; IR (NaCl, neat) ν: 3017, 1744, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{25}O_2$ ($M^+ + H$): 393.1855, found: 393.1848.

6-(oct-1-en-2-yl)-4,7-diphenylbicyclo[3.2.0]hepta-1(7),4-dien-6-yl acetate (131δ)



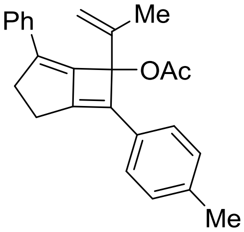
Yield 68%; yellow solid, mp = 67-68 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.77 (t, 3H, J = 6.7 Hz), 1.05-1.17 (m, 6H), 1.33-1.43 (m, 2H), 1.94-2.05 (m, 2H), 2.10 (s, 3H), 2.84-2.99 (m, 2H), 3.26-3.33 (m, 1H), 3.42-3.49 (m, 1H), 5.22 (d, 1H, J = 1.0 Hz), 5.57 (s, 1H), 7.16-7.22 (m, 2H), 7.30-7.43 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.0, 21.7, 22.5, 24.9, 27.9, 29.0, 30.7, 31.6, 38.9, 87.4, 111.2, 125.2, 126.7, 126.8, 127.5, 127.7, 128.1, 128.5, 133.4, 134.9, 137.0, 145.9, 147.4, 163.1, 168.6; IR (NaCl, neat) ν: 3017, 1746, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{33}O_2$ (M^+ + H): 413.2481, found: 413.2475.

7-(4-fluorophenyl)-4-phenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl acetate (131ζ)



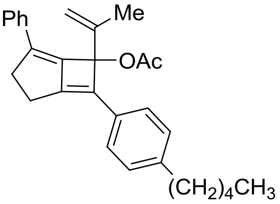
Yield 68%; yellow solid, mp = 92-93 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.71 (s, 3H), 2.10 (s, 3H), 2.81-2.97 (m, 2H), 3.25-3.32 (m, 1H), 3.41-3.48 (m, 1H), 5.20 (s, 1H), 5.46 (s, 1H), 7.00-7.04 (m, 2H), 7.18-7.22 (m, 1H), 7.30-7.36 (m, 4H), 7.40 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.8, 21.6, 24.8, 38.9, 87.0, 113.1, 115.6 (1C, d, $J_{C\text{-}F}$ = 22.0), 126.7, 126.8, 126.9, 127.6, 128.2, 129.8, 134.8, 135.8, 141.6, 146.9, 162.2, 162.9 (1C, d, $J_{C\text{-}F}$ = 246.0), 168.6; IR (NaCl, neat) ν: 3017, 1748, 1219 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{22}O_2F$ (M^+ + H): 361.1604, found: 361.1596.

4-phenyl-6-(prop-1-en-2-yl)-7-p-tolylbicyclo[3.2.0]hepta-1(7),4-dien-6-yl acetate (131η)



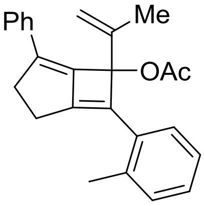
Yield 69%; yellow solid, mp = 144-145 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.71 (s, 3H), 2.08 (s, 3H), 2.33 (s, 3H), 2.81-2.96 (m, 2H), 3.23-3.30 (m, 1H), 3.40-3.47 (m, 1H), 5.17 (t, 1H, J = 1.4 Hz), 5.44 (d, 1H, J = 0.6 Hz), 7.12-7.20 (m, 3H), 7.26-7.33 (m, 4H), 7.39-7.41 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.0, 21.5, 21.7, 24.9, 38.9, 87.1, 112.9, 125.2, 126.8, 127.1, 127.6, 128.2, 129.4, 130.7, 135.0, 136.8, 137.0, 141.9, 161.9, 168.7; IR (NaCl, neat) ν: 3019, 1746, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{25}O_2$(M^+ + H): 357.1855, found: 357.1858.

7-(4-pentylphenyl)-4-phenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl acetate (131θ)



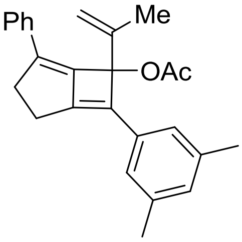
Yield 60%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88-0.93 (m, 3H), 1.32-1.35 (m, 6H), 1.59-1.63 (m, 2H), 2.09 (s, 3H), 2.81-2.99 (m, 2H), 3.24-3.30 (m, 1H), 3.41-3.48 (m, 1H), 5.18 (s, 1H), 5.44 (s, 1H), 7.14 (d, 1H, J = 8.1 Hz), 7.17-7.20 (m, 1H), 7.28-7.33 (m, 4H), 7.40 (d, 2H, J = 7.3 Hz);^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.1, 18.9, 21.6, 22.6, 24.9, 31.1, 31.5, 35.9, 38.9, 87.1, 112.8, 125.1, 126.7, 127.1, 127.6, 128.1, 128.7, 130.8, 135.0, 137.0, 141.8, 141.9, 147.3, 161.8, 168.7; IR (NaCl, neat) ν: 3019, 1717, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{33}O_2$ (M^+ + H): 413.2481, found: 413.2482.

4-phenyl-6-(prop-1-en-2-yl)-7-o-tolylbicyclo[3.2.0]hepta-1(7),4-dien-6-yl acetate (131ι)



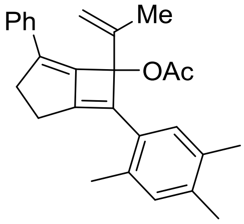
Yield 75%; yellow solid, mp = 91-92 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.72 (s, 3H), 2.10 (s, 3H), 2.50 (s, 3H), 2.93-3.08 (m, 2H), 3.24-3.30 (m, 1H), 3.40-3.46 (m, 1H), 5.22 (d, 1H, J = 1.2 Hz), 5.58 (s, 1H), 7.10-7.23 (m, 4H), 7.31-7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.8, 21.6, 21.7, 28.0, 38.3, 86.7, 113.1, 125.8, 125.9, 126.8, 127.2, 127.5, 127.9, 128.2, 130.6, 132.2, 135.0, 135.1, 136.9, 142.2, 147.6, 163.4, 168.4; IR (NaCl, neat) ν: 3019, 2399, 1746, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{25}O_2$ (M^+ + H): 357.1855, found: 357.1858.

7-(3,5-dimethylphenyl)-4-phenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl acetate (131κ)



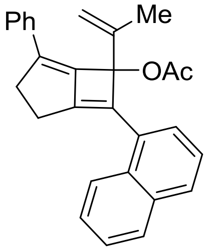
Yield 60%; yellow solid, mp = 129-130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.73 (s, 3H), 2.11 (s, 3H), 2.32 (s, 6H), 2.84-2.99 (m, 2H), 3.25-3.32 (m, 1H), 3.42-3.49 (m, 1H), 5.20 (s, 1H), 5.48 (s, 1H), 6.85 (s, 1H), 7.00 (s, 2H), 7.20 (t, 1H, J = 7.3 Hz), 7.31-7.35 (m, 2H), 7.42 (d, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.9, 21.4, 21.7, 25.0, 38.9, 87.0, 112.8, 122.9, 126.7, 127.3, 127.6, 128.1, 128.8, 133.3, 135.0, 137.1, 138.0, 141.9, 147.3, 162.5, 168.7; IR (NaCl, neat) ν: 3019, 1744, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{27}O_2$ (M^+ + H): 371.2011, found: 371.2010.

4-phenyl-6-(prop-1-en-2-yl)-7-(2,4,5-trimethylphenyl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl acetate (131λ)



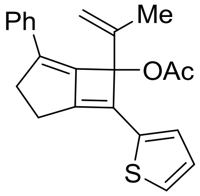
Yield 72%; yellow solid, mp = 158-159 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.72 (s, 3H), 2.10 (s, 3H), 2.22 (s, 3H), 2.23 (s, 3H), 2.43 (s, 3H), 2.90-3.05 (m, 2H), 3.21-3.28 (m, 1H), 3.38-3.44 (m, 1H), 5.22 (t, 1H, J = 1.4 Hz), 5.56 (d, 1H, J = 0.6 Hz), 6.94 (s, 1H), 7.18-7.21 (m, 2H), 7.31-7.39 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.9, 19.4, 19.5, 21.0, 21.8, 27.8, 38.3, 86.7, 112.9, 126.6, 127.0, 127.1, 127.4, 128.2, 129.9, 132.2, 132.6, 133.6, 135.1, 135.8, 137.0, 142.4, 147.8, 162.3, 168.4; IR (NaCl, neat) ν: 3019, 1746, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{29}O_2$ (M^+ + H): 385.2168, found: 385.2177.

7-(naphthalen-1-yl)-4-phenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl acetate (131μ)



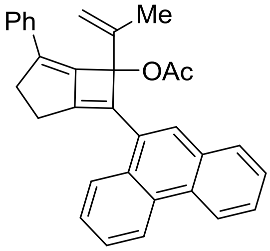
Yield 78%; yellow solid, mp = 126-127 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.74 (s, 3H), 2.11 (s, 3H), 3.10-3.26 (m, 2H), 3.33-3.40 (m, 1H), 3.48-3.55 (m, 1H), 5.25 (t, 1H, J = 1.4 Hz), 5.63 (d, 1H, J = 0.6 Hz), 7.20-7.24 (m, 1H), 7.33-7.37 (m, 2H), 7.41-7.44 (m, 3H), 7.48-7.60 (m, 3H), 7.72 (d, 1H, J = 8.1 Hz), 7.84-7.86 (m, 1H), 8.40 (d, 1H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.0, 21.9, 28.4, 38.7, 87.2, 113.4, 124.2, 124.9, 125.8, 126.0, 126.3, 127.1, 127.7, 128.0, 128.5, 128.6, 129.0, 142.5, 163.9, 168.6; IR (NaCl, neat) ν: 3019, 2399, 1744, 1215 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{25}O_2$ (M^+ + H): 393.1855, found: 393.1858.

4-phenyl-6-(prop-1-en-2-yl)-7-(thiophen-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl acetate (131ν)



Yield 69%; yellow solid, mp = 89-90 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.68 (s, 3H), 2.02 (s, 3H), 2.67-2.81 (m, 2H), 3.15-3.22 (m, 1H), 3.30-3.37 (m, 1H), 5.10 (t, 1H, *J* = 1.4 Hz), 5.33 (s, 1H), 6.90-6.92 (m, 1H), 6.98 (d, 1H, *J* = 3.4 Hz), 7.09-7.16 (m, 2H), 7.22-7.26 (m, 2H), 7.32-7.35 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.0, 21.6, 24.7, 38.8, 87.6, 113.3, 123.6, 125.0, 126.9, 127.6, 127.7, 127.8, 128.2, 131.6, 134.8, 136.4, 141.3, 146.9, 160.8, 168.7; IR (NaCl, neat) ν: 3019, 2359, 1748, 1219 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{21}O_2S$(M^+ + H): 349.1262, found: 349.1257.

7-(phenanthren-9-yl)-4-phenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl acetate (131ξ)



Yield 65%; yellow solid, mp = 89-90 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.77 (s, 3H), 2.13 (s, 3H), 2.88-3.03 (m, 2H), 3.29-3.35 (m, 1H), 3.45-3.52 (m, 1H), 5.24 (t, 1H, *J* = 1.4 Hz), 5.52 (d, 1H, *J* = 0.4 Hz), 7.21-7.24 (m, 1H), 7.33-7.37 (m, 3H), 7.43-7.48 (m, 6H), 7.58-7.63 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.9, 21.7, 25.0, 38.9, 87.1, 113.0, 125.6, 126.9, 127.3, 127.3, 127.7, 128.0, 128.2, 128.8, 132.4, 134.9, 136.6, 139.4, 140.8, 141.8, 147.3, 163.1, 168.7; IR (NaCl, neat) ν:3015, 1668, 1653, 1580, 1356, 1215 cm^{-1}; IR (NaCl, neat) ν: 3017, 1746, 1217 cm^{-1}; HRMS (ESI) calcd. for $C_{32}H_{27}O_2$ (M^+ + H): 443.2011, found: 443.2003.

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