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Gold(I)-catalyzed double migration cascades toward (1*E*,3*E*)-dienes and naphthalenes

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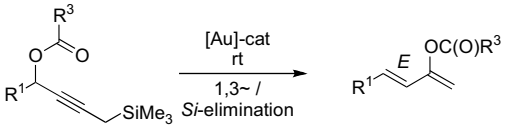
ABSTRACT

A novel gold(I)-catalyzed cascade cycloisomerization of a variety of propargylic esters leading to unsymmetrically substituted naphthalenes has been developed. This domino process involves an unprecedented tandem sequence of 1,3- and 1,2-migrations of two substantially different migrating groups. It is believed that this transformation proceeds via formation of 1,3-diene intermediate or its equivalent, which, upon carbocyclization and aromatization steps, transforms into the naphthalene skeleton. In addition, it was also demonstrated that a variety of 1,3-dienes can be accessed stereoselectively via the 1,3-migration–proton transfer cascade.

1. Introduction

In recent years, gold catalysis received much attention.[1] Particularly, increasing employment of gold catalysis in the cascade transformations of propargylic esters[2] led to the development of diverse and versatile synthetic methods. Remarkable propensity of propargylic esters to undergo formal 1,3-acyl migration[1,2] through the formation of activated allene equivalent allowed for efficient and expeditious assembly of various acyclic unsaturated synthons[3] and complex carbo-[4] and heterocycles.[5] Recently, two stereoselective Au(I)-catalyzed cascade isomerizations of propargylic esters into 1,3-dienes,[6] proceeding via a 1,3-migration–silicon elimination[7] (Eq. 1) or double 1,2-migration[8] (Eq. 2) tandems, have been reported. In addition, several protocols utilizing gold-catalyzed transformations of propargylic[9] (Eq. 3) or related allenyl-[10] and homopropargylic[11] systems (Eqs. 4 and 5) toward assembly of polysubstituted benzene ring have been developed. Generally, these benzannulation cascades proceed via initial carbocyclization followed by elimination step.



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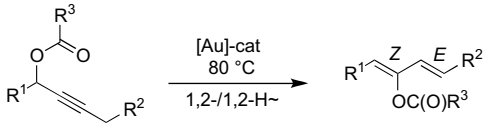

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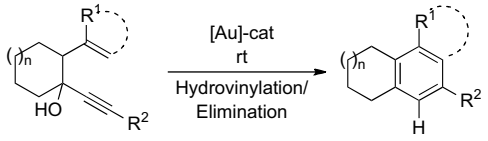

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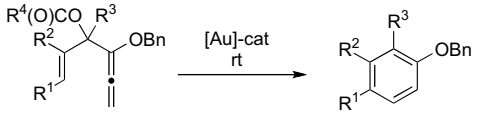

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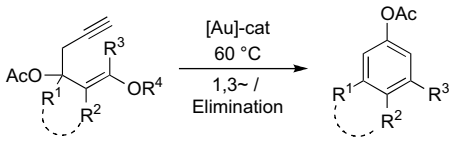

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In line of our continuing effort on the development of novel transition metal-catalyzed protocols toward carbo- and heterocycles involving 1,3- or 1,2-migration steps,[5d,e,12] we aimed at the

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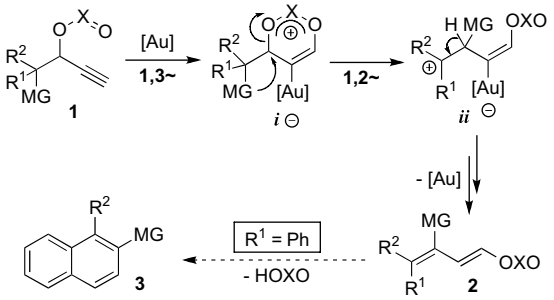


Scheme 1. Proposed Au-catalyzed double migration cascade.

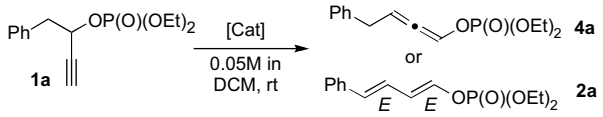
designing a cascade transformation of propargylic systems proceeding via tandem 1,3- and 1,2-migration processes of two different migrating groups. Thus, we have developed two novel gold(I)-catalyzed protocols for the expeditious assembly of multisubstituted napthalenes[13] and stereoselective synthesis of (1*E*,3*E*)-dienes.[14] Depending on the substitution pattern, propargylic esters underwent 1,3-/1,2-migration-benzannulation cascade into naphthalenes[13] or 1,3-migration/proton transfer tandem toward 1,3-dienes. Herein, we summarize our recent developments in this area, and provide more detailed discussion on the scope and mechanisms of these novel cascade transformations.

2. Results and discussion

2.1. Mild and stereoselective synthesis of 1,3-dienes

We anticipated that upon coordination of a cationic gold(I) complex to the triple bond of propargylic ester **1**, the latter would undergo a formal 1,3-acyloxy- or phosphatyloxy-group migration through the cyclic intermediate ***i*** (Scheme 1). Considering electrophilic nature of the sp^3-center[2b] in intermediate ***i***, we envisioned that incorporation of a suitable 1,2-migrating group (MG) in ***i*** would provoke a subsequent 1,2-shift[15,16] to give ***ii*** which, upon proton transfer via proton loss–protiodeauration sequence, would afford 1,3-diene **2**. It was reasonable to propose that the latter may undergo 6π-electrocyclization–elimination cascade into naphthalene[17,18] **2**, analogously to the known carbocyclization of oxy-1,3,5-trienes[19] (Scheme 1). To this end, a possible isomerization of propargyl phosphate **1a**, possessing β-hydrogen atom as the 1,2-migrating group, has been examined in the presence of different catalysts (Table 1). It was found that employment of Ag triflate led to the formation of expected allene **4a** in 73% yield (entry 1). Remarkably, more electrophilic Au(I) triflate afforded target 1,3-diene **2a**, a product of two formal 1,3-migrations, in 86% yield as a sole (1*E*,3*E*)-isomer (entry 2). However, employment of Au(III) complexes (entries 3 and 4), Au(I) halides (entries 5 and 6), Cu(I) and Cu(II) triflates, as well as Brønsted or Lewis acids, resulted in no reaction.

Table 1
Optimization of reaction conditions



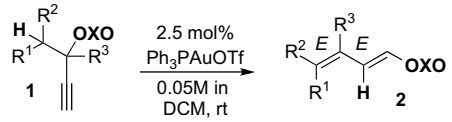
Entry	Catalyst	Time, h	Yield **4a**,[a] %	Yield **2a**,[a] %
1	10% AgOTf	12	73	0
2	5% Ph_3PAuCl, 5% AgOTf	1	0	86
3	5% $AuCl_3$	24	0	0
4	5% $AuCl_3$, 15% AgOTf	24	0	0
5	5% AuI	24	0	0
6	5% R_3PAuCl (R=Et, Ph)	24	0	0
7	10% $[CuOTf]_2 \cdot PhH$	24	0	0
8	10% $Cu(OTf)_2$	24	0	0
9	20% TMSOTf[b]	24	0	0
10	20% TfOH[b]	24	0	0

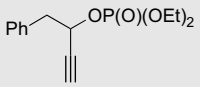
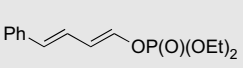
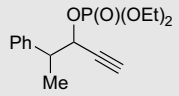
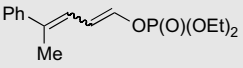
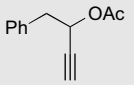
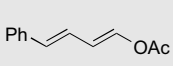
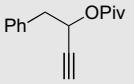
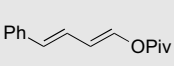
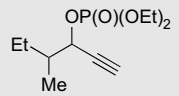
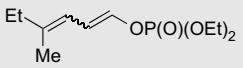
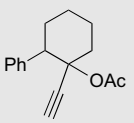
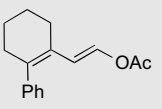
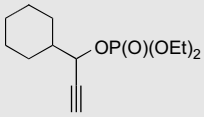
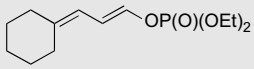
[a] Isolated yield of product for reaction performed on 0.1–0.2 mmol scale.
[b] Compound **1a** decomposes at elevated temperatures in the presence of catalyst.

Next, isomerization of differently substituted propargylic esters **1a**–**g** was examined under optimized conditions (Table 2). Thus, the cascade transformation of propargylic esters **1a**, **1c**, and **1d** possessing various 1,3-migrating groups, such as phosphatyloxy- (entry 1), acetyloxy- (entry 3), and pivaloxy- (entry 4), occurred highly stereoselectively, affording the corresponding (1*E*,3*E*)-dienes **2a**, **2c**, and **2d** in good to high yields. It was found that isomerization of β-dialkyl- (entries 5 and 7), alkyl-aryl (entries 2 and 6), as well as β-diaryl- and α-alkyl- (entry 6) substituted substrates proceeded nearly equally efficient, providing the corresponding 1,3-dienes **2b**, **2e**, **2f**, and **2g** in good to high yields. However, isomerization of phosphates **1b** and **1e**, unsymmetrically substituted at the β-position, proceeded with diminished stereoselectivity (entries 2 and 5).

It should be noted that the analogous isomerization of propargylic acetates **1** into 1,3-dienes **2** in the presence of cationic Ag catalysts at elevated temperatures has been reported[20] (Eq. 6). Although, this cascade reaction was proposed to proceed via allene intermediate **4**, the entire mechanism of this transformation

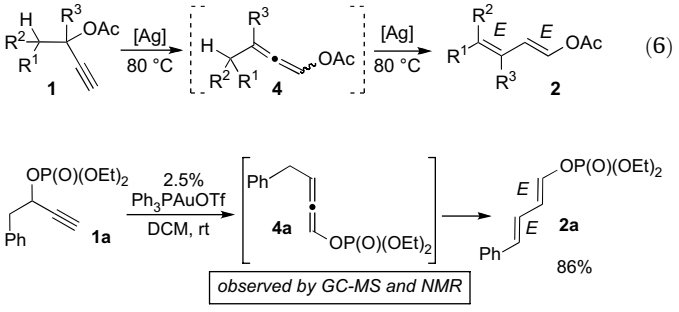
Table 2
Gold(I)-catalyzed synthesis of 1,3-dienes



Entry	Substrate	Product	Yield,[a] %
1	 **1a**	 **2a**	83
2	 **1b**	 **2b**	69[b,c]
3	 **1c**	 **2c**	79
4	 **1d**	 **2d**	86
5	 **1e**	 **2e**	75[b,d]
6	 **1f**	 **2f**	70
7	 **1g**	 **2g**	82[e]

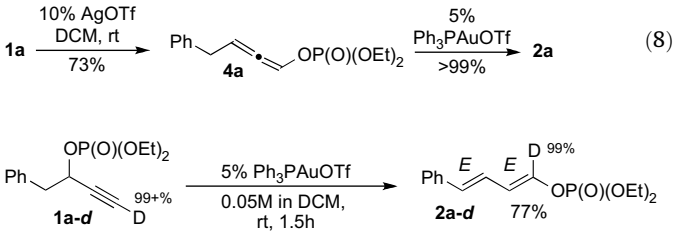
[a] Isolated yield; 0.5 mmol scale.
[b] Au catalyst (5 mol %) was used.
[c] Mixture of 4.3:1 (1*E*,3*E*)/(1*E*,3*Z*)-dienes.
[d] Mixture of 1.3:1 (1*E*,3*E*)/(1*E*,3*Z*)-dienes.
[e] Au catalyst (7.5 mol %) was used.

remained unclear. In order to elucidate the mechanism of this transformation under Au(I)-catalysis, we first examined whether the Au(I)-catalyzed cascade isomerization of phosphatyloxy-substituted substrate **1a** (MG=H) involved formation of the allene intermediate. Careful ^{1}H NMR and GC–MS monitoring of the reaction course at early stages revealed that the corresponding allene intermediate **4a** was initially formed and then completely isomerized into (1*E*,3*E*)-diene **2a** (Eq. 7). In addition, independently prepared phosphatyloxyallene **4a** was quantitatively transformed into 1,3-diene **2a** in the presence of Au(I) triflate (Eq. 8). Finally, our D-labeling studies on the isomerization of propargylic phosphate **1a**-*d* ruled out possible involvement of alkyne–vinylidene isomerization,[21] thus, strongly supporting 1,3-migration path[22] (Eq. 9).



(6)

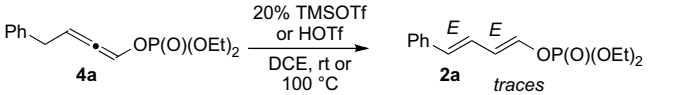
(7)



(8)

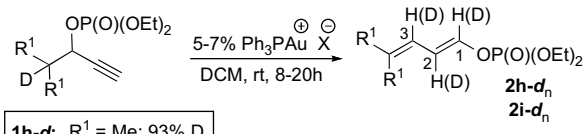
(9)

In light of the recent observations that eventual Brønsted acids are the true catalysts in some transition metal-catalyzed transformations,[23] we investigated what role, if any, Brønsted or Lewis acids may play in the herein described isomerization reaction. Accordingly, our optimization studies (Table 1, entries 9 and 10) revealed that isomerization of propargyl phosphate **1a** in the presence of TfOH or TMSOTf provided no 1,3-diene **2a**. In addition, it was found that isomerization of allene **4a** in the presence of Brønsted or Lewis acids even at elevated temperatures provided trace amounts of **2a** only (Eq. 10).



(10)

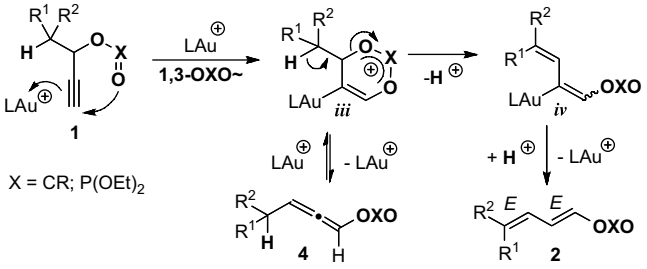
Aiming at distinguishing the nature of elementary processes in the second step, isomerization of D-labeled phosphates **1h**-*d* and **1i**-*d* was investigated in the presence of different cationic Au(I) catalysts. It was found that, along with significant loss of deuterium label,[24] the latter was scrambled between C-1 and C-2 in the corresponding 1,3-dienes **2h**-d_n and **2i**-d_n (Eq. 11).[25] In addition, the nature of the counteranion at Au(I) complex did not significantly affect distribution of D-label in 1,3-diene products.[26] Most importantly, absence of a deuterium label at C-3 strongly indicated exclusive involvement of the proton elimination at the second step.



X	d_1-%	d_2-%	d_3-%	Yield	
OTf	27	21	<2	65%	**2h**-d_n
	10	33	0	64%	**2i**-d_n
SbF_6	29	16	<3	40%	**2h**-d_n
	13	25	0	89%	**2i**-d_n
BF_4	-	-	-	-	**2h**-d_n
	17	28	0	88%	**2i**-d_n

(11)

We propose the following mechanism for the cascade transformation of propargylic esters **1** into 1,3-dienes **2** (Scheme 2). First, propargyl ester **1** undergoes Au(I)-catalyzed 1,3-migration[27] of

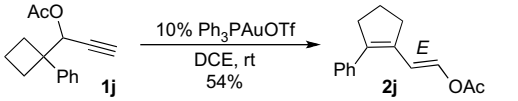


Scheme 2. Mechanistic rationale for Au(I)-catalyzed synthesis of 1,3-dienes.

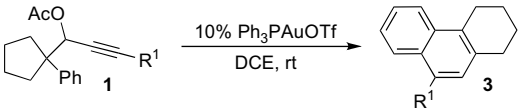
acyloxy- or phosphatyloxy-group to give cyclic intermediate ***iii*** which, upon elimination of Au(I) catalyst, produces allene intermediate **3**. A direct elimination of the β-proton from ***iii*** produces a vinyl gold intermediate ***iv***, which upon protiodeauration furnishes 1,3-diene **2** and regenerates the Au(I) catalyst (Scheme 2).

2.2. Synthesis of naphthalenes

Targeting at the development of 1,3-/1,2-double migration tandem, we hypothesized that successful incorporation of a 1,2-shift into this cascade can only be achieved when a 1,2-migrating group resides at a 'proton-free' quaternary C-4 center.[16] Accordingly, isomerization of acetate **1j**, possessing strained cyclobutane ring, was examined. Gratifyingly, a tandem 1,3-migration and the ring expansion via a 1,2-alkyl shift occurred furnishing 1,3-diene **2j** in 54% yield (Eq. 12). Moreover, cyclopentyl-substituted analogs **1k** and **1l** underwent further cycloisomerization with ring expansion to give the benzannulation products, naphthalenes **3k** and **3l**, respectively (Eq. 13), thus providing a proof of concept for this cascade transformation.[28]



(12)

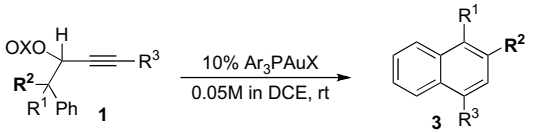


(13)

Product	R^1	Isolated yield, %
3k	H	36
3l	*n*-Hex	30

Next, the scope of this cascade transformation was examined (Table 3). It was found that propargylic esters **1m**–**p** and **1r**–**u** smoothly underwent a tandem acyloxy- or phosphatyloxy- and Ph-group migration/benzannulation cascade to provide naphthalenes **3m**–**p** and **3r**–**u** in good to excellent yields (entries 1–4 and 6–9). Terminal, as well as alkyl- and aryl-substituted propargylic substrates were nearly equally efficient in this cascade transformation (entry 1 vs entries 2 and 4). However, isomerization of nonterminal phosphate **1o** was less facile than that of analogous acetate **1n**, likely due to the increased steric hindrance (entry 3 vs 2). Notably, a variety of substituents, such as methoxy (entry 6), trifluoromethyl (entry 7), and 2-furyl (entry 8), were perfectly tolerated under the reaction conditions. Unexpectedly, cycloizomerization of dimethylphenyl-substituted acetate **1q** proceeded via exclusive 1,2-Me- over 1,2-Ph-group migration to give naphthalene **3q** in 73% yield (entry 5). In contrast, diphenylmethyl-substituted propargylic ester

Table 3
Gold(I)-catalyzed synthesis of naphthalenes



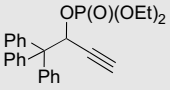
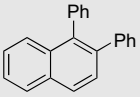
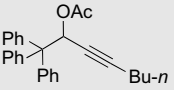
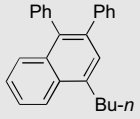
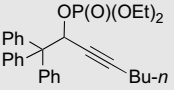
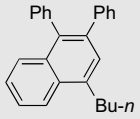
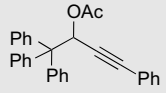
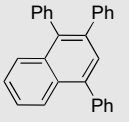
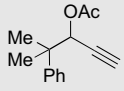
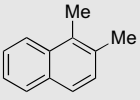
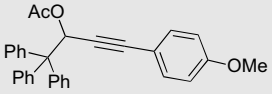
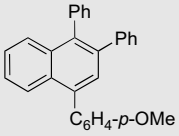
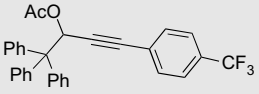
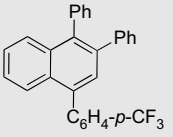
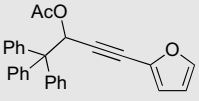
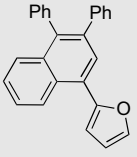
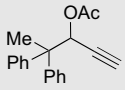
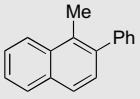
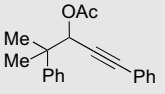
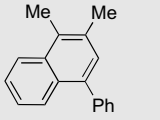
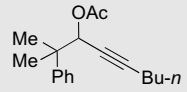
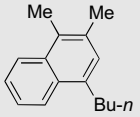
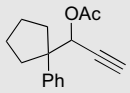
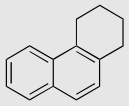
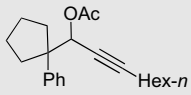
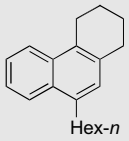
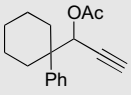
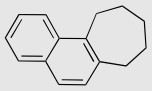
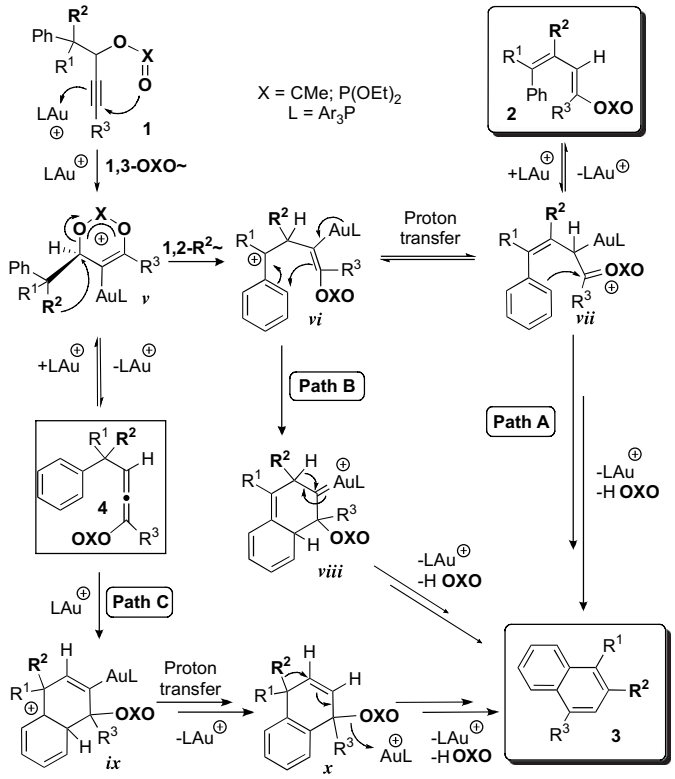
Entry	Substrate	Catalyst[a]	Product		Yield,[b,c] %
1		A		**3m**	86[d]
2		A		**3n**	94
3		A		**3n**	50
4		A		**3p**	75
5		A		**3q**	73
6		A		**3r**	90
7		A		**3s**	84
8		A		**3t**	94
9		A		**3u**	51
10		B		**3v**	57

Table 3 (*continued*)

Entry	Substrate	Catalyst[a]	Product		Yield,[b,c] %
11		B		**3w**	77
12		B		**3k**	96
13		B		**3l**	75
14		B		**3x**	74

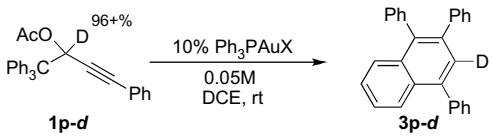
[a] Catalyst A=$Ph_3PAuOTf$; catalyst B=$(F_5C_6)_3PAuSbF_6$.
[b] Isolated yield.
[c] Reactions were performed on 0.5 mmol scale.
[d] Au catalyst (5%) was used.

1u exhibited normal Ph- versus Me-group migratory aptitude upon gold catalysis, providing 1-methyl-2-phenylnaphthalene **3u** as a sole regiosomer via exclusive 1,2-Ph-group migration (entry 9). Moreover, the scope of 1,2-migrating groups was further extended with the employment of a truly cationic $(F_5C_6)_3PAuSbF_6$ catalyst. Thus, a variety of alkyl- and cycloalkyl-substituted substrates **1k**, **1l**, and **1v**–**x** possessing terminal, as well as internal alkyne moiety, readily underwent migrative benzannulation cascade to give the corresponding polysubstituted naphthalenes in good to excellent yields (entries 10–14).



Scheme 3. Mechanistic rationale for Au(I)-catalyzed synthesis of naphthalenes.

We propose the following plausible mechanisms for this cascade cycloisomerization (Scheme 3). The Au(I)-catalyzed 1,3-acyloxy- or 1,3-phosphatyloxy-group migration transforms propargylic ester **1** via cyclic intermediate[2b,3c,5b] ***v*** into allenyl intermediate **4**. According to the path **A**, intermediate ***v*** undergoes a 1,2-alkyl migration[29] to give benzylic cation ***vi***. The latter, upon proton transfer produces oxonium intermediate ***vii***, which upon reversible elimination of Au(I) catalyst furnishes 1,3-diene intermediate **2**. The direct Friedel–Crafts alkylation in ***vii***, followed by the aromatization and loss of Au(I) catalyst, affords naphthalene **3**.[30] In another scenario (path **B**), a direct nucleophilic attack of nucleophilic vinyl–Au moiety at the delocalized benzyl cation in ***vi***[31] produces Au–carbenoid intermediate ***viii***, which upon 1,2-hydride shift[32] and aromatization steps gives naphthalene **3**. Alternatively, a direct intramolecular hydroarylation of allenyl intermediate **4**, followed by 1,2-shift induced by Au(I) catalyst and proton loss in ***x***, produces **3** (path **C**). Path **B** involving carbocyclization of [1,6]-Au-dipole[11] with concomitant 1,2-hydride shift to Au–carbenoid center was not supported by the observed significant loss of D-label during the cycloisomerization of a labeled acetate **1p**-*d* (Eq. 14). In addition, employment of more cationic Au(I) catalyst with noncoordinating hexafluoroantimonate counteranion led to even more pronounced loss of deuterium label in **4p**-*d* compared to that for triflate (Eq. 14).

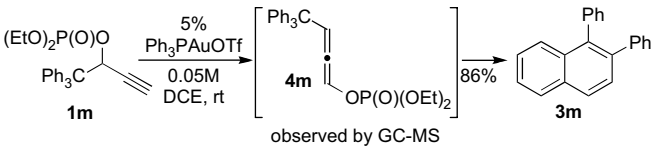


X	D-inc,%	Yield
OTf	33	78%
SbF_6	20	94%

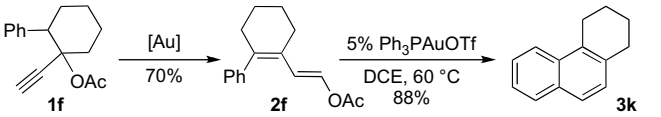
(14)

In order to get an additional support for the involvement of proposed allene **4** and 1,3-diene **2** intermediates in this cascade

process, we performed several mechanistic studies on cycloisomerization of propargylic phosphates and acetates. Our careful GC–MS monitoring of the reaction course at initial stages revealed that propargylic phosphate **1m** underwent facile 1,3-phosphatyloxy group migration to give the corresponding allene intermediate **4m**, which then was completely cycloisomerized into naphthalene **3m** (Eq. 15). In addition, independently prepared phosphatyloxyallene **4m** can be cycloisomerized into naphthalene **3m** with the same efficiency in the presence of Au(I) triflate. Furthermore, successful cycloisomerization of 1,3-diene **2f**, obtained via a 1,3-migration/proton transfer tandem, into naphthalene **3k** provided an additional support for possible intermediacy of 1,3-dienes in this transformation (Eq. 16).[33]

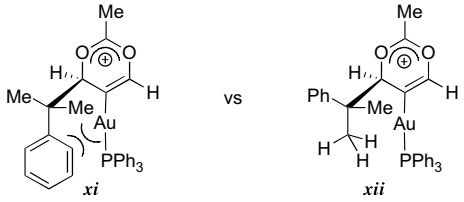


(15)



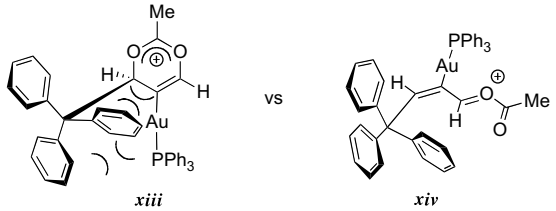
(16)

Unexpected *exclusive Me- over Ph-migration* in dimethylphenyl-substituted acetate **1q** is reasonably rationalized by stereoelectronic effect, according to which Ph-group cannot accommodate requisite antiperiplanar orientation with the leaving group in ***xi*** (Scheme 4).[34] Therefore, migration of a methyl group is strongly favored to



Scheme 4. Stereoelectronic models for cycloisomerization of **1q**.

proceed via a conformationally more stable intermediate ***xii*** (Scheme 4). The same trend is observed for cycloisomerization of cycloalkylphenyl-substituted substrates where the migratory aptitudes are controlled by the stereoelectronic requirements in a cyclic-type intermediate ***v*** (Scheme 3). It is believed that in case of bulkier diphenylmethyl- and triphenyl-substituted propargylic esters, required antiperiplanar orientation cannot be adopted by any of migrating groups due to repulsion of phenyl rings with the 1,3-dioxenium core (***xiii***). Accordingly, 1,2-migration in these cases most likely proceeds through the less stable open enonium intermediate ***xiv*** where steric interactions are insignificant and, thus, 'normal



Scheme 5. 1,2-Migration models for trityl-substituted propargylic esters.

migratory aptitudes' are exhibited (Scheme 5). On the other hand, reversible 1,2-migration leading to the more stable intermediate benzylic carbocation under the thermodynamic control can also account for the observed chemoselectivity.

Alternatively, exclusive Me- versus Ph-migration in dimethylphenyl-substituted propargylic acetate **1q**, as well as Ph- over Me-migration in case of diphenylmethyl-substituted **1u**, can also be explained via path **C**, according to which 1,2-migration occurs after cyclization step. Although path **C** cannot be completely ruled out at this point, it is considered to be less likely since it cannot fully account for the reactivities observed during cycloisomerization of cyclobutyl-substituted propargylic ester **1j** and benzannulation of 1,3-diene **2f**.

3. Conclusions

Two novel Au(I)-catalyzed cascade processes for the synthesis of multisubstituted 1,3-dienes and naphthalenes have been developed. It was demonstrated that β-unsubstituted propargylic phosphates, acetates, and pivalates can undergo an exceptionally mild and stereoselective Au(I)-catalyzed isomerization proceeding via 1,3-migration/proton transfer cascade into the corresponding 1-oxy-1,3-diene esters. Alternatively, a variety of densely substituted naphthalenes can be accessed through the Au(I)-catalyzed cascade cycloisomerization of β-quaternary propargylic phosphates and acetates. This domino transformation involves an unprecedented 1,3-/1,2-migration cascade of two different migrating groups followed by the benzannulation step. In addition, this mild protocol allows for selective and highly efficient assembly of naphthalenes, not available via existing methodologies.

4. Experimental

4.1. General

NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) and DPX-400 (400 MHz) instruments. GC–MS analyses were performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m×0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Silicycle silica gel (43–60 μm). HRMS (EI) analysis was performed on a JEOL GCmate II instrument. All manipulations with transition metal catalysts were conducted under inert atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous toluene, tetrahydrofuran, dichloromethane, and 1,2-dichloroethane purchased from Aldrich were additionally purified on PureSolv PS-400-4 by Innovative Technology, Inc. purification system. All other chemicals and solvents were purchased from Aldrich, Fisher, Acros Organics, TCI, and Alfa Aesar and used without additional purification.

4.2. General procedures for the synthesis of propargyl acetates and phosphates

4.2.1. Procedure A

Neat carbonyl compound (or its solution in 15 ml of anhydrous THF) (33 mmol) was added dropwise to an ice cooled flask containing 60 ml of 0.55 M solution of ethynylmagnesium bromide in THF (33 mmol) while stirring. After addition the reaction mixture was allowed to warm to room temperature and stirred for an additional 1 h. Reaction mixture was placed then in the ice-water bath and 39.6 mmol of neat diethylchlorophosphate (5.69 ml) or acetic anhydride (3.74 ml) was added dropwise. Reaction mixture was allowed to warm to room temperature and was stirred until judged complete by TLC and GC analyses. After completion, reaction mixture was poured into 250 ml of saturated ammonium chloride solution and extracted three times with ethyl acetate (150 ml).

Combined organic extracts were dried over anhydrous sodium sulfate. Solvents were removed under reduced pressure and the residue was purified by column chromatography (EtOAc/Hex) to give the corresponding propargyl acetate or phosphate.

4.2.2. Procedure B

To the cooled −78 °C flask containing 25 ml of anhydrous THF was added 15 mmol of neat terminal acetylene, followed by dropwise addition of 5.8 ml of 2.61 M solution of *n*-BuLi in hexanes (15 mmol). The reaction mixture was allowed to warm to room temperature allowing for formation of ca. 0.5 M solution of corresponding alkynyllithium in THF. After cooling to −78 °C, 15 mmol of carbonyl compound was added dropwise. Reaction mixture was allowed to warm to room temperature and cooled back to −78 °C; 18 mmol of neat diethylchlorophosphate (2.6 ml) or acetic anhydride (1.7 ml) was added to the reaction mixture dropwise. After warming up, reaction mixture was stirred at room temperature until judged complete by TLC and GC analyses. Reaction mixture was poured into 250 ml of saturated ammonium chloride solution and extracted three times with ethyl acetate (150 ml). Combined organic extracts were dried over anhydrous sodium sulfate. Solvents were removed under reduced pressure and the residue was purified by column chromatography (EtOAc/Hex) to give the corresponding propargyl acetate or phosphate.

4.2.3. Procedure C

To a solution of 8.6 mmol of triphenylacetaldehyde in 10 mL anhydrous THF was added 26 mL of a 0.5 M solution of ethynylmagnesium bromide in THF (13 mmol) while stirring. After addition the reaction mixture was allowed to warm to room temperature and stirred for an additional 1 h. The reaction mixture was poured into 50 mL of 2 M HCl(aq) and extracted three times with ethyl acetate. The combined organic phases were dried over anhydrous magnesium sulfate, filtered, and concentrated. The material was filtered through silica (2:1 hexanes/ethyl acetate as eluent) to give 2.57 g (quant.) of material of >98% purity (as judged by NMR analysis). To a 5 ml Wheaton V-vial charged with 3 mol % $PdCl_2(PPh_3)_2$ and 5 mol % CuI, under N_2 atmosphere, was added 1 mmol of the propargyl alcohol. The vial was equipped with a Teflon septa and cap and 2 mL of anhydrous triethylamine was added. The appropriate aryl bromide was added and the reaction mixture heated to 80 °C for several hours, until TLC analysis showed consumption of the starting material. The reaction mixture was filtered through a short silica plug with ethyl acetate and concentrated. The crude material was redissolved in 2 mL anhydrous pyridine and 2 mmol dimethylaminopyridine was added at once. Acetyl chloride (2 mmol) was then added dropwise and the reaction mixture was stirred for several hours. When TLC analysis showed the reaction had completed, the reaction mixture was poured into 20 mL of 2 M HCl(aq) and extracted three times with ethyl acetate. The combined organic phases were dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was purified by column chromatography (silica, 3:1 hexanes/ethyl acetate).

*4.2.3.1. Diethyl 1-phenylbut-3-yn-2-yl phosphate (**1a**).* Yield 45% (procedure A). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19–7.37 (m, 5H), 5.15 (dq, *J*=7.20, 6.97, 2.11 Hz, 1H), 3.98–4.14 (m, 2H), 3.82–3.98 (m, 2H), 3.09–3.19 (m, 2H), 2.58 (d, *J*=2.02 Hz, 1H), 1.29 (td, *J*=7.11, 1.01 Hz, 3H), 1.23 (td, *J*=7.11, 1.01 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.4, 129.8, 128.4, 127.1, 80.7, 75.5, 68.1 (d, J_{CP}=5.5 Hz), 63.93 (d, J_{CP}=5.5 Hz), 63.78 (d, J_{CP}=5.5 Hz), 42.8 (d, J_{CP}=6.5 Hz), 16.0 (2C, d, J_{CP}=5.5 Hz).

*4.2.3.2. Diethyl 1-(1-phenylethyl)prop-2-yn-1-yl phosphate (**1b**).* Yield 55% (procedure A). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18–7.33 (m, 5H), 5.02–5.08 (m, 1H), 3.91–4.10 (m, 4H), 3.14–3.22 (m, 1H), 2.52 (d, *J*=2.20 Hz, 1H), 1.43 (d, *J*=7.15 Hz, 3H), 1.22–1.29 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.93, 128.31, 128.19, 127.09, 80.02, 75.95, 71.81, 71.76, 63.91, 63.86, 63.81, 63.76, 44.89, 44.84, 16.04.

*4.2.3.3. 1-Benzylprop-2-yn-1-yl acetate (**1c**).* Yield 67% (procedure A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.36 (m, 5H), 5.54 (dt, *J*=6.83, 2.12 Hz, 1H), 3.09 (dd, *J*=6.87, 3.07 Hz, 2H), 2.47 (d, *J*=2.19 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.75, 135.64, 129.65, 128.38, 127.08, 80.70, 74.38, 64.30, 40.95, 20.93.

*4.2.3.4. 1-Benzylprop-2-yn-1-yl pivalate (**1d**).* Yield 58% (procedure A). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22–7.33 (m, 5H), 5.51 (dt, *J*=6.88, 2.20 Hz, 1H), 3.10 (d, *J*=6.97 Hz, 2H), 2.44 (d, *J*=2.02 Hz, 1H), 1.15 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.14, 135.83, 129.65, 128.27, 126.97, 80.98, 73.90, 63.99, 40.98, 38.65, 26.95.

*4.2.3.5. Diethyl 1-ethynyl-2-methylbutyl phosphate (**1e**).* Yield 59% (procedure A). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86–4.93 (m, *J*=12.33, 7.34, 5.09, 2.20 Hz, 1H), 4.07–4.18 (m, 4H), 2.53 (dd, *J*=3.30, 2.20 Hz, 1H), 1.72–1.86 (m, 1H), 1.48–1.70 (m, 1H), 1.31–1.36 (m, 6H), 1.21–1.31 (m, 1H), 1.02 (dd, *J*=6.79, 5.69 Hz, 3H), 0.92 (td, *J*=7.47, 4.13 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 80.23, 79.54, 75.39, 75.09, 71.73, 71.69, 71.59, 71.54, 63.93, 63.88, 63.82, 63.78, 40.49, 40.45, 40.12, 40.08, 25.07, 24.39, 16.05, 14.42, 13.85, 11.44, 11.32.

*4.2.3.6. 1-Ethynyl-2-phenylcyclohexyl acetate (**1f**).* Yield 71% (procedure A). Isolated as a 1.3:1 mixture of diastereomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.40 (m, 2H), 7.23–7.34 (m, 3H), 3.07–3.13 (m, 0.58H), 3.05 (dd, *J*=13.0, 3.1 Hz, 0.48H), 2.84–2.90 (m, 0.45H), 2.76 (dd, *J*=12.8, 3.7 Hz, 0.59H), 2.68 (s, 0.35H), 2.45 (s, 0.46H), 2.02–2.23 (m, 1H), 2.09 (s, 1.73H), 1.91 (s, 1.25H), 1.59–1.90 (m, 5H), 1.34–1.54 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 168.9, 141.3, 140.5, 129.6, 129.5, 127.5, 127.4, 126.9, 83.2, 80.5, 79.8, 77.7, 75.7, 74.9, 53.5, 51.7, 35.4, 29.6, 27.9, 25.8, 25.6, 23.6, 21.9, 21.7, 20.7.

*4.2.3.7. 1-Cyclohexylprop-2-yn-1-yl diethyl phosphate (**1g**).* Yield 70% (procedure A). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.70–4.76 (m, 1H), 4.03–4.14 (m, 4H), 2.52 (dd, *J*=2.20, 0.92 Hz, 1H), 1.60–1.85 (m, 6H), 1.26–1.32 (m, 6H), 1.03–1.24 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 80.06, 80.04, 75.31, 72.00, 71.95, 63.88, 63.84, 63.80, 63.76, 43.04, 43.00, 28.09, 27.58, 26.10, 25.60, 25.56, 16.08, 16.03, 15.98.

*4.2.3.8. 1-(1-Phenylcyclobutyl)prop-2-ynyl acetate (**1j**).* Yield 86% (procedure A). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.36 (m, 2H), 7.23–7.28 (m, 3H), 5.66 (d, *J*=2.0 Hz, 1H), 2.42–2.51 (m, 4H), 2.38 (d, *J*=2.0 Hz, 1H), 2.10–2.20 (m, 1H), 2.06 (s, 3H), 1.84–1.95 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 144.8, 127.6, 127.3, 126.3, 79.3, 74.4, 69.5, 48.9, 30.1, 30.0, 20.8, 15.6.

*4.2.3.9. 1-(1-Phenylcyclopentyl)prop-2-ynyl acetate (**1k**).* Yield 96% (procedure A). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.43 (m, 2H), 7.30–7.34 (m, 2H), 7.22–7.27 (m, 1H), 5.55 (d, *J*=2.2 Hz, 1H), 2.36 (d, *J*=2.2 Hz, 1H), 2.18–2.26 (m, 1H), 2.09–2.18 (m, 2H), 2.03–2.08 (m, 1H), 2.02 (s, 3H), 1.74–1.84 (m, 2H), 1.62–1.73 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 143.6, 128.1, 127.7, 126.5, 79.9, 74.4, 69.3, 54.5, 34.8, 34.6, 23.8, 23.5, 20.8.

*4.2.3.10. 1-(1-Phenylcyclopentyl)non-2-ynyl acetate (**1l**).* Yield 78% (procedure B). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.43 (m, 2H), 7.31 (t, *J*=7.6 Hz, 2H), 7.23 (tt, *J*=7.3, 1.1 Hz, 1H), 5.55 (t, *J*=2.0 Hz, 1H), 2.18–2.27 (m, 1H), 2.15 (td, *J*=7.1, 2.0 Hz, 2H), 2.01–2.13 (m, 1H), 2.00 (s, 3H), 1.72–1.87 (m, 2H), 1.56–1.73 (m, 2H), 1.40–1.52 (m, 2H), 1.22–1.38 (m, 6H), 0.91 (t, *J*=7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 70.0, 144.3, 128.1, 127.5, 126.2, 87.1,

76.3, 70.1, 54.9, 34.9, 34.7, 31.3, 28.5, 28.4, 23.9, 23.6, 22.5, 20.9, 18.7, 14.0.

*4.2.3.11. Diethyl 1,1,1-triphenylbut-3-yn-2-yl phosphate (**1g**).* Yield 76%, (procedure A). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.36 (m, 6H), 7.25–7.31 (m, 6H), 7.20–7.25 (m, 3H), 6.39 (dd, J=6.6, 2.2 Hz, 1H), 3.93–4.01 (quin d, J=7.2, 0.9 Hz, 2H), 3.57–3.67 (quin, J=7.2, 1H), 3.46–3.56 (m, 1H), 2.53 (d, J=2.2 Hz, 1H), 1.22 (td, J=7.1, 1.0 Hz, 3H), 1.04 (td, J=7.1, 1.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 130.0, 127.6, 126.6, 80.3, 78.9, 72.4 (d, J_{CP}=6.5 Hz), 64.0 (d, J_{CP}=6.5 Hz), 63.6 (d, J_{CP}=5.5 Hz), 61.9 (d, J_{CP}=7.4 Hz), 15.9 (d, J_{CP}=6.5 Hz).

*4.2.3.12. Diethyl 1,1,1-triphenyloct-3-yn-2-yl phosphate (**1n**).* Yield 82% (procedure B). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J=7.5 Hz, 6H), 7.23–7.30 (m, 6H), 7.16–7.23 (m, 3H), 6.35 (dt, J=6.1, 2.0 Hz, 1H), 3.87–4.01 (m, 2H), 3.54–3.64 (m, 1H), 3.43–3.52 (m, 1H), 1.96–2.09 (m, 2H), 1.21 (td, J=7.1, 0.9 Hz, 3H), 1.15–1.23 (m, 2H), 1.04–1.13 (m, 2H), 1.02 (td, J=7.1, 1.1 Hz, 3H), 0.75 (t, J=7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 130.1, 127.4, 126.4, 91.6, 73.1 (d, J_{CP}=6.5 Hz), 63.7 (d, J_{CP}=5.5 Hz), 63.3 (d, J_{CP}=5.5 Hz), 62.3 (d, J_{CP}=9.2 Hz), 30.0, 21.5, 18.4, 15.8 (d, J_{CP}=5.5 Hz), 15.9 (d, J_{CP}=5.5 Hz), 13.4.

*4.2.3.13. 1,1,1-Triphenyloct-3-yn-2-yl acetate (**1o**).* Yield 82% (procedure B). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18–7.33 (m, 15H), 6.74 (t, J=2.0 Hz, 1H), 1.99–2.05 (m, 2H), 1.85 (s, 3H), 1.17–1.25 (m, 2H), 1.05–1.14 (m, 2H), 0.76 (t, J=7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 144.2, 129.9, 127.5, 126.4, 89.9, 69.3, 61.5, 30.0, 21.5, 20.9, 18.3, 13.5.

*4.2.3.14. 1,1,1,4-Tetraphenylbut-3-yn-2-yl acetate (**1p**).* Yield 74% (procedure B). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.37 (m, 6H), 7.30 (t, J=7.4 Hz, 6H), 7.23–7.28 (m, 4H), 7.18–7.23 (m, 2H), 7.10–7.13 (m, 2H), 6.96 (s, 1H), 1.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 144.0, 131.8, 129.9, 128.5, 128.0, 127.6, 126.6, 122.2, 88.8, 86.2, 69.4, 61.8, 20.9.

*4.2.3.15. 4-Methyl-4-phenylpent-1-yn-3-yl acetate (**1q**).* Yield 78% (procedure A). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.45 (m, 2H), 7.34 (t, J=7.7 Hz, 2H), 7.25 (tt, J=7.2, 1.3 Hz, 1H), 5.58 (d, J=2.2 Hz, 1H), 2.39 (d, J=2.0 Hz, 1H), 1.99 (s, 3H), 1.49 (d, J=2.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7, 144.5, 128.0, 126.5, 126.4, 79.6, 74.4, 71.0, 41.7, 24.8, 23.7, 20.7.

*4.2.3.16. 4-(4-Methoxyphenyl)-1,1,1-triphenylbut-3-yn-2-yl acetate (**1r**).* Yield 57% (procedure C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J=7.7 Hz, 6H), 7.33 (t, J=7.5 Hz, 6H), 7.27 (t, J=6.9 Hz, 3H), 7.09 (d, J=9.0 Hz, 2H), 7.02 (s, 1H), 6.76 (d, J=8.8 Hz, 2H), 3.76 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7, 159.7, 144.0, 133.2, 129.8, 127.5, 126.5, 114.2, 113.6, 88.8, 84.8, 69.5, 61.8, 55.1, 20.8.

*4.2.3.17. 1,1,1-Triphenyl-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-yl acetate (**1s**).* Yield 85%, (procedure C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J=8.1 Hz, 2H), 7.23–7.37 (m, 15H), 7.20 (d, J=7.9 Hz, 2H), 6.97 (s, 1H), 1.91 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 143.9, 132.0, 130.3 (q, J_{CF}=32.4 Hz), 129.8, 127.8, 126.7, 126.0, 125.0 (q, J_{CF}=3.7 Hz), 123.8 (q, J_{CF}=272.0 Hz), 88.8, 87.4, 69.3, 61.8, 20.9.

*4.2.3.18. 4-(Furan-2-yl)-1,1,1-triphenylbut-3-yn-2-yl acetate (**1t**).* Yield 64% (procedure C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22–7.37 (m, 16H), 7.00 (s, 1H), 6.34 (d, J=3.3 Hz, 1H), 6.29 (dd, J=3.2, 2.1 Hz, 1H), 1.88 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7, 143.7, 143.6, 136.1, 129.8, 127.9, 127.7, 126.6, 116.3, 110.7, 90.4, 79.2, 69.2, 61.6, 20.8.

*4.2.3.19. 1-(1,1-Diphenylethyl)prop-2-yn-1-yl acetate (**1u**).* Yield 95% (procedure A). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.31 (m, 8H), 7.20–7.25 (m, 2H), 6.12 (d, J=2.20 Hz, 1H), 2.41 (d, J=2.20 Hz, 1H), 1.95 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.65, 145.26, 144.65, 128.12, 127.99, 127.86, 127.78, 126.50, 79.73, 75.74, 69.14, 50.54, 24.42, 20.76.

*4.2.3.20. 1-(1-Methyl-1-phenylethyl)-3-phenylprop-2-yn-1-yl acetate (**1v**).* Yield 75% (procedure B). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.51 (m, 2H), 7.22–7.41 (m, 8H), 5.80 (s, 1H), 2.01 (s, 3H), 1.56 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.89, 144.88, 131.84, 128.53, 128.22, 128.04, 126.64, 126.55, 122.39, 86.11, 85.34, 71.83, 42.34, 25.10, 23.98, 20.86.

*4.2.3.21. 1-(1-Methyl-1-phenylethyl)hept-2-yn-1-yl acetate (**1w**).* Yield 65% (procedure B). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.44 (m, 2H), 7.27–7.33 (m, 2H), 7.18–7.24 (m, 1H), 5.56 (t, J=2.02 Hz, 1H), 2.16 (dt, J=7.02, 1.93 Hz, 2H), 1.95 (s, 3H), 1.39–1.50 (ov. m, 8H), 1.29–1.37 (m, 2H), 0.88 (t, J=7.34 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.90, 145.17, 127.92, 126.54, 126.32, 87.05, 76.05, 71.79, 42.07, 30.51, 25.05, 23.84, 21.84, 20.85, 18.37, 13.58.

*4.2.3.22. 1-(1-Phenylcyclohexyl)prop-2-yn-1-yl acetate (**1x**).* Yield 97% (procedure A). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.45 (m, 2H), 7.31–7.38 (m, 2H), 7.22–7.26 (m, 1H), 5.36 (d, J=2.20 Hz, 1H), 2.39 (d, J=2.20 Hz, 1H), 2.31–2.43 (m, 2H), 1.97 (s, 3H), 1.70–1.81 (m, 2H), 1.52–1.64 (m, 3H), 1.24–1.37 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.64, 140.18, 128.42, 128.01, 126.46, 79.37, 74.98, 71.64, 45.56, 31.70, 31.00, 26.31, 21.79, 21.72, 20.73.

*4.2.3.23. 1-Benzylprop-2-yn-1-yl diethyl phosphate-d_1 (**1a**-d).* To the cooled −78 °C flask containing 3.5 ml of anhydrous THF was added 288.3 mg (1 mmol) of neat acetylene **1a**, followed by dropwise addition of 384 μl of 2.61 M solution of *n*-BuLi in hexanes (1 mmol). The reaction mixture was stirred at −78 °C allowing for formation of ca. 0.3 M solution of corresponding alkynyllithium in THF. After 1.5 h, 270 μl (15 mmol) of neat D_2O (99.99% D) was added dropwise. Reaction mixture was allowed to warm to room temperature. After warming up, reaction mixture was stirred at room temperature for 20 min. Reaction mixture was filtered through a layer of flash Silica (EtOAc—eluent). Solvents were removed under reduced pressure and the residue was purified by column chromatography (EtOAc/Hex) to give 93.1 mg (32% yield) of the corresponding deuterated propargyl phosphate **1a**-*d* possessing 99+% D-incorporation according to the integration of the residual proton signals in ^{1}H NMR.

Compound **1a**-*d*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21–7.35 (m, 5H), 5.11–5.19 (m, 1H), 3.98–4.14 (m, 2H), 3.82–3.98 (m, 2H), 3.09–3.19 (m, 2H), 2.58 (d, J=2.20 Hz, <0.01H), 1.29 (td, J=7.06, 0.92 Hz, 3H), 1.23 (td, J=7.06, 1.10 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.4, 129.8, 128.4, 127.1, 80.3, 75.2 (t, J_{CD}=38.1 Hz), 68.1 (d, J_{CP}=5.5 Hz), 63.9 (d, J_{CP}=5.5 Hz), 63.8 (d, J_{CP}=5.5 Hz), 42.8 (d, J_{CP}=6.5 Hz), 16.0 (d, J_{CP}=6.5 Hz); ^{2}H NMR (76.8 MHz, $CDCl_3$) δ 2.58.

*4.2.3.24. Diethyl 1-isopropylprop-2-yn-1-yl phosphate-d_1 (**1h**-d).* Compound **1h**-*d* was prepared according to the general procedure A from the known 2-methylpropanal-d_1 in 56% yield. Integration of the residual proton signals in ^{1}H NMR indicated 93+% D-incorporation.

Compound **1h**-*d*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.80 (dd, J=7.61, 2.11 Hz, 1H), 4.08–4.20 (m, 4H), 2.54 (d, J=2.20 Hz, 1H), 2.01–2.09 (m, 0.07H), 1.31–1.38 (m, J=7.11, 7.11, 3.03, 0.92 Hz, 5H), 1.04 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 79.7, 75.2, 72.6 (d, J_{CP}=5.5 Hz), 63.9 (d, J_{CP}=6.5 Hz), 63.8 (d, J_{CP}=6.5 Hz), 32.9–33.6 (m), 17.7, 16.9, 16.0 (d, J_{CP}=2.8 Hz), 16.1 (d, J_{CP}=3.7 Hz); ^{2}H NMR (76.8 MHz, $CDCl_3$) δ 2.05 (m).

*4.2.3.25. 1-(Diphenylmethyl)prop-2-yn-1-yl diethyl phosphate-d_1 (**1i**-d).* Known [(2,2-diphenylvinyl)oxy](trimethyl)silane (2.80 g,

10.44 mmol) was dissolved in 50 ml of anhydrous THF. Solution of 3.17 g of anhydrous CsF (20.88 mmol) in D_2O (99.99% D) was added and reaction mixture was vigorously stirred for 30 min. Formed 2,2-diphenylacetaldehyde-d_1 was extracted with anhydrous hexanes. Combined organic extracts were dried over anhydrous sodium sulfate. Solvents were removed under reduced pressure and the residue was used without purification in the next step.

Following procedure A, 1-(diphenylmethyl)prop-2-yn-1-yl diethyl phosphate-d_1 (**1i**-*d*) was synthesized from a crude 2,2-diphenylacetaldehyde-d_1 in 39% overall yield. Integration of the residual proton signals in ^{1}H NMR indicated 77% D-incorporation.

Compound **1i**-*d*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.42 (m, 2H), 7.36 (dd, J=8.16, 1.01 Hz, 2H), 7.27–7.33 (m, 4H), 7.19–7.25 (m, 2H), 5.65–5.72 (m, 1H), 4.39 (d, J=9.17 Hz, 1H), 3.96–4.12 (m, 2H), 3.59–3.69 (m, 1H), 3.45–3.55 (m, 1H), 2.51 (d, J=2.20 Hz, 1H), 1.28 (td, J=7.11, 1.01 Hz, 3H), 1.05 (td, J=7.06, 1.10 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0–140.5, 128.7, 128.5, 128.5, 127.1, 127.0, 80.3, 76.6, 69.5–69.9 (m), 64.0 (d, J_{CP}=6.5 Hz), 63.6 (d, J_{CP}=5.5 Hz), 57.0 (d, J_{CP}=7.4 Hz), 56.3–56.8 (m), 16.0 (d, J_{CP}=6.5 Hz), 15.9 (d, J_{CP}=7.4 Hz); ^{2}H NMR (76.8 MHz, $CDCl_3$) δ 4.39.

*4.2.3.26. 1-(Triphenylmethyl)-3-phenylprop-2-yn-1-yl acetate-d_1 (**1p**-d_1).* Triphenylacetic acid (4.3 g, 15 mmol), bromoethane (1.3 mL, 18 mmol), and a solution of tetrabutylammonium fluoride in THF (1.0 M, 18 mL, 18 mmol) were added successively to a 50 mL flask. The reaction mixture was stirred for 15 h and TLC analysis judged the reaction complete. The reaction mixture was poured into 50 mL 2 M HCl(aq) and extracted three times with 25 mL of ethyl ether. The organic phases were combined, dried over anhydrous magnesium sulfate, filtered, and concentrated to give 4.74 g (99%) of ethyl triphenylacetate, which required no additional purification.

Ethyl triphenylacetate (2.665 g, 8.4 mmol) was dissolved in anhydrous THF (25 mL) and the solution was cooled to 0 °C. $LiAlD_4$ (177 mg, 4.2 mmol) was added as solid portions and the reaction mixture was kept at 0 °C for an additional hour after complete addition. The reaction mixture was stirred for another 24 h at room temperature before being poured into 100 mL of 2 M H_2SO_4(aq). The aqueous layer was extracted five times with 25 mL ethyl ether, the organic extracts were combined, dried over anhydrous magnesium sulfate, filtered, and concentrated to give 1.96 g (84%) of 2,2,2-triphenylethanol-d_2.

To a 200 mL flask equipped with a stirbar was added anhydrous dichloromethane (50 mL) and the flask was cooled to −78 °C. Oxalyl chloride (720 μL, 8.5 mmol) was added via syringe, followed by the dropwise addition of dimethylsulfoxide (1 mL, 14.2 mmol). The solution was allowed to stir at −78 °C for 30 min before a solution of 2,2,2-triphenylethanol-d_2 (1.96 g, 7.1 mmol) dissolved in anhydrous dichloromethane (20 mL) was added slowly via cannula. The reaction mixture was stirred for another 30 min before triethylamine (4 mL, 28.4 mmol) was added. The reaction mixture was stirred a further 30 min before being brought to room temperature. After several hours, the reaction mixture was poured into 100 mL 2 M HCl(aq) and extracted three times with 25 mL dichloromethane. The organic phases were combined, dried with anhydrous magnesium sulfate, filtered, and concentrated. Purification by column chromatography gave 1.64 g (85%) of triphenylacetaldehyde-d_1.

Phenylacetylene (660 μL, 6 mmol) was dissolved in 5 mL anhydrous THF and the solution was cooled to −78 °C. A solution of butyllithium in hexanes (2.5 M, 2.1 mL, 5.5 mmol) was added dropwise and the reaction mixture was stirred at −78 °C for 1 h. Meanwhile, triphenylacetaldehyde-d_1 (1.37 g, 5 mmol) was dissolved in anhydrous THF (5 mL) and the solution was added via cannula to the lithium acetylide at −78 °C. The reaction mixture was stirred for 30 min before being warmed to 0 °C. After 10 min, acetic anhydride (1 mL, 10 mmol) was added and the reaction mixture was stirred for several hours. The solution was poured into 50 mL 2 M HCl(aq) and extracted three times with 50 mL of ethyl acetate. The combined organic phases were dried with anhydrous magnesium sulfate, filtered, and concentrated. Purification by column chromatography gave 1.47 g (70%) of 1-(triphenylmethyl)-3-phenylprop-2-yn-1-yl acetate-d_1. Integration of the residual proton signals in ^{1}H NMR indicated >96% D-incorporation.

Compound **1p**-d_1: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.37 (m, 6H), 7.30 (t, J=7.4 Hz, 6H), 7.23–7.28 (m, 4H), 7.18–7.23 (m, 2H), 7.10–7.13 (m, 2H), 6.94 (m, 0.04H), 1.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 144.0, 131.8, 129.9, 128.5, 128.0, 127.6, 126.6, 122.2, 88.8, 86.2, 69.3 (br m), 61.8, 20.9; ^{2}H NMR (76.8 MHz, $CDCl_3$) δ 6.94.

4.3. Optimization of reaction conditions: test and mechanistic experiments

To a foiled 3–5 ml Wheaton V-vial charged with catalyst and 2 ml of anhydrous dichloromethane or 1,2-dichloroethane was added propargyl acetate or phosphate (0.1 mmol) under N_2 or argon atmosphere and the reaction mixture was stirred at room temperature until judged complete by TLC and GC–MS analysis. The reaction mixture was filtered through a layer of flash Silica (EtOAc—eluent), the solvents were removed in vacuo, and the residue was analyzed by ^{1}H NMR using dibromomethane as an internal standard.

4.4. General procedure for the synthesis of 1,3-dienes and naphthalenes

A foiled 25 ml flask with septa was charged with a catalytic amount of 1:1 mixture of $Au(PPh_3)Cl$ and AgOTf specified below and 10 ml of anhydrous dichloromethane or 1,2-dichloroethane. After stirring of the reaction mixture for 15 min, propargyl acetate or phosphate (0.5 mmol) was added under argon atmosphere and stirring was continued at room temperature until the reaction was judged complete. The reaction mixture was then filtered through a layer of flash Silica (EtOAc—eluent), the solvents were removed in vacuo, and the residue was purified by column chromatography (EtOAc/Hex: for 1,3-dienes, PhH/Hex: for naphthalenes).

*4.4.1. Diethyl (1E,3E)-4-phenylbuta-1,3-dienyl phosphate (**2a**)*

Yield 83%, 2.5 mol % *Au*, 0.5 mmol scale, 1 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (s, 2H), 7.28–7.33 (m, 2H), 7.19–7.24 (m, 1H), 6.83 (dd, J=11.92, 6.42 Hz, 1H), 6.64 (dd, J=15.77, 11.00 Hz, 1H), 6.52 (d, J=15.77 Hz, 1H), 6.21 (t, J=11.46 Hz, 1H), 4.15–4.24 (m, 4H), 1.37 (td, J=7.11, 1.01 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.7 (d, J_{CP}=5.5 Hz), 137.1, 132.0, 128.6, 127.5, 126.1, 122.9, 118.0 (d, J_{CP}=11.1 Hz), 64.6 (d, J_{CP}=5.5 Hz), 16.1 (d, J_{CP}=5.5 Hz); HRMS (EI) calcd for $C_{14}H_{19}O_4P$: 282.10210, found: 282.10225.

*4.4.2. Diethyl (1E,3E)-4-phenylpenta-1,3-dien-1-yl phosphate (**2b**)*

Yield 69%, 5 mol % *Au*, 0.5 mmol scale, 1 h (4.3:1 (1*E*,3*E*)/(1*E*,3*Z*)). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17–7.44 (m, 5H), 6.82 (dd, J=11.46, 6.14 Hz, 0.2H), 6.71 (dd, J=11.65, 5.78 Hz, 0.8H), 6.43 (t, J=11.65 Hz, 0.2H), 6.32 (d, J=11.55 Hz, 0.2H), 6.09 (t, J=11.65 Hz, 0.8H), 5.99 (d, J=11.55 Hz, 0.8H), 4.03–4.26 (m, 4H), 2.09–2.15 (two ov. s, 3H), 1.29–1.42 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.16, 138.91, 138.66, 138.61, 128.32, 128.20, 128.08, 127.11, 127.06, 125.50, 120.57, 115.59, 115.51, 64.56, 64.52, 64.43, 64.38, 25.46, 16.09, 16.04; HRMS (EI) calcd for $C_{15}H_{21}O_4P$: 296.11775, found: 296.1182.

*4.4.3. (1E,3E)-4-Phenylbuta-1,3-dien-1-yl acetate (**2c**)*

Yield 79%, 2.5 mol % *Au*, 0.5 mmol scale, 2 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J=12.29 Hz, 1H), 7.29–7.41 (m, 4H), 7.20–7.25 (m, 1H), 6.71 (dd, J=15.50, 11.28 Hz, 1H), 6.55 (d, J=15.59 Hz, 1H), 6.21

(m, 1H), 2.18 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.70, 138.73, 137.15, 132.30, 128.63, 127.50, 126.15, 123.64, 115.88, 20.68; HRMS (EI) calcd for $C_{12}H_{12}O_2$: 188.0837, found: 188.0836.

*4.4.4. (1E,3E)-4-Phenylbuta-1,3-dien-1-yl pivalate (**2d**)*

Yield 86%, 2.5 mol % *Au*, 0.5 mmol scale, 4 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J*=12.29 Hz, 1H), 7.29–7.42 (m, 4H), 7.20–7.25 (m, 1H), 6.73 (dd, *J*=15.68, 11.10 Hz, 1H), 6.54 (d, *J*=15.77 Hz, 1H), 6.24 (t, *J*=11.65 Hz, 1H), 1.28 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.26, 139.23, 137.24, 131.95, 128.62, 127.43, 126.14, 123.83, 115.68, 38.77, 26.94; HRMS (EI) calcd for $C_{15}H_{18}O_2$: 230.1307, found: 230.1308.

*4.4.5. Diethyl (1E,3E)-4-Methylhexa-1,3-dien-1-yl phosphate (**2e**)*

Yield 75%, 5 mol % *Au*, 0.5 mmol scale, 4 h (1.3:1 (1*E*,3*E*)/(1*E*,3*Z*)). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.55–6.64 (m, 1H), 6.18–6.28 (m, 1H), 5.60–5.70 (m, 1H), 4.11–4.21 (m, 4H), 2.10 (q, *J*=7.64 Hz, 1H), 2.05 (q, *J*=7.40 Hz, 1H), 1.75 (s, 1.5H), 1.69 (s, 1.5H), 1.34 (tt, *J*=7.06, 1.19 Hz, 6H), 1.00 (t, *J*=7.52 Hz, 1.5H), 0.98 (t, *J*=7.61 Hz, 1.5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.14, 140.83, 137.48, 137.44, 117.63, 116.59, 114.79, 114.71, 114.37, 114.29, 64.37, 64.32, 32.48, 25.30, 23.19, 16.51, 16.09, 16.04, 12.75, 12.39.

*4.4.6. (E)-2-(2-Phenylcyclohex-1-enyl)vinyl acetate (**2f**)*

Yield 70%, 2.5 mol % *Au*, 0.5 mmol scale, 5 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.37 (m, 2H), 7.32 (d, *J*=6.6 Hz, 1H), 7.24–7.28 (m, 1H), 7.13–7.16 (m, 2H), 6.12 (d, *J*=12.7 Hz, 1H), 2.25–2.41 (m, 4H), 2.07 (s, 3H), 1.72–1.81 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 143.1, 138.9, 134.4, 128.6, 128.1, 126.8, 126.5, 116.0, 32.9, 25.5, 23.0, 22.4, 20.7; HRMS (EI) calcd for $C_{16}H_{18}O_2$: 242.1307, found: 242.1303.

*4.4.7. (1E)-3-Cyclohexylideneprop-1-en-1-yl diethyl phosphate (**2g**)*

Yield 82%, 7.5 mol % *Au*, 0.5 mmol scale, 4 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.59 (dd, *J*=11.74, 5.87 Hz, 1H), 6.25 (t, *J*=11.65 Hz, 1H), 5.59 (d, *J*=11.55 Hz, 1H), 4.09–4.19 (m, 4H), 2.04–2.23 (m, 4H), 1.45–1.56 (m, 6H), 1.33 (t, *J*=7.15 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.56, 137.62, 137.58, 114.98, 114.02, 113.94, 64.36, 64.31, 37.23, 29.18, 28.40, 27.61, 26.66, 16.09, 16.04.

*4.4.8. (E)-2-(2-Phenylcyclopent-1-enyl)vinyl acetate (**2j**)*

Yield 54%, 10 mol % *Au*, 0.2 mmol scale, 12 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dt, *J*=12.5, 1.1 Hz, 1H), 7.36–7.40 (m, 2H), 7.29–7.33 (m, 2H), 7.26–7.28 (m, 1H), 6.51 (d, *J*=12.5 Hz, 1H), 2.84 (t, *J*=7.4 Hz, 2H), 2.67 (t, *J*=7.4 Hz, 2H), 2.16 (s, 3H), 1.98–2.06 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 141.4, 137.9, 137.7, 131.8, 128.2, 127.9, 126.9, 111.5, 37.8, 33.9, 21.9, 20.7.

*4.4.9. 1,2,3,4-Tetrahydrophenanthrene (**3k**)*

Yield 36%, 10 mol % *$Ph_3PAuOTf$*, 0.5 mmol scale, 16 h; 96%, 10 mol % *$(F_5C_6)_3PAuSbF_6$*, 0.5 mmol scale, 2.5 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J*=8.44 Hz, 1H), 7.81 (d, *J*=8.07 Hz, 1H), 7.63 (d, *J*=8.44 Hz, 1H), 7.51 (ddd, *J*=8.39, 6.83, 1.47 Hz, 1H), 7.41–7.47 (m, 1H), 7.22 (d, *J*=8.44 Hz, 1H), 3.14 (t, *J*=6.33 Hz, 2H), 2.93 (t, *J*=6.14 Hz, 2H), 1.95–2.04 (m, 2H), 1.85–1.94 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.35, 132.56, 132.07, 131.52, 128.39, 128.30, 125.78, 125.62, 124.69, 122.80, 30.49, 25.71, 23.28, 22.99.

*4.4.10. 9-Hexyl-1,2,3,4-tetrahydrophenanthrene (**3l**)*

Yield 30%, 10 mol % *$Ph_3PAuOTf$*, 0.5 mmol scale, 20 h; 75%, 10 mol % *$(F_5C_6)_3PAuSbF_6$*, 0.5 mmol scale, 2.5 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98–8.06 (m, 2H), 7.45–7.53 (m, 2H), 7.07 (s, 1H), 3.11 (t, *J*=6.33 Hz, 2H), 2.98–3.06 (m, 2H), 2.90 (t, *J*=6.14 Hz, 2H), 1.94–2.02 (m, 2H), 1.85–1.92 (m, 2H), 1.71–1.80 (m, 2H), 1.44–1.52 (m, 2H), 1.32–1.41 (m, 4H), 0.90–0.97 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.34, 133.93, 132.99, 130.59, 129.61, 128.23, 125.30, 124.46, 124.30, 123.42, 33.04, 31.82, 31.07, 30.45, 29.66, 25.63, 23.43, 23.04, 22.71, 14.16.

*4.4.11. 1,2-Diphenylnaphthalene (**3m**)*

Yield 86%, 5 mol % *$Ph_3PAuOTf$*, 0.5 mmol scale, 1 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J*=8.25, 4.95 Hz, 2H), 7.69 (d, *J*=8.44 Hz, 1H), 7.60 (d, *J*=8.62 Hz, 1H), 7.48–7.53 (m, 1H), 7.42 (dt, *J*=8.44, 6.97, 1.28 Hz, 1H), 7.27–7.35 (m, 3H), 7.14–7.24 (m, 7H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.01, 139.02, 138.35, 137.64, 132.79, 132.68, 131.46, 130.14, 128.30, 127.89, 127.81, 127.60, 126.84, 126.73, 126.23, 126.20, 125.69.

*4.4.12. 4-Butyl-1,2-diphenylnaphthalene (**3n**)*

Yield 94%, 10 mol % *$Ph_3PAuOTf$*, 2 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J*=8.4 Hz, 1H), 7.72 (d, *J*=8.4 Hz, 1H), 7.54 (ddd, *J*=8.3, 6.9, 1.3 Hz, 1H), 7.47 (s, 1H), 7.41 (ddd, *J*=8.4, 6.9, 1.2 Hz, 1H), 7.27–7.34 (m, 3H), 7.13–7.24 (m, 7H), 3.15–3.21 (m, 2H), 1.82–1.90 (m, 2H), 1.51–1.61 (m, 2H), 1.03 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3, 139.3, 138.4, 137.9, 135.9, 133.1, 131.7, 131.2, 130.1, 128.3, 127.8, 127.6, 127.6, 126.6, 126.1, 125.7, 125.4, 123.8, 33.0, 33.0, 23.1, 14.1; HRMS (EI) calcd for $C_{26}H_{24}$: 336.1878, found: 336.1880.

*4.4.13. 1,2,4-Triphenylnaphthalene (**3p**)*

Yield 75%, 10 mol % *$Ph_3PAuOTf$*, 12 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99–8.06 (m, 1H), 7.76–7.80 (m, 1H), 7.60–7.65 (m, 2H), 7.59 (s, 1H), 7.51–7.56 (m, 2H), 7.41–7.50 (m, 3H), 7.27–7.38 (m, 5H), 7.14–7.25 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.86, 140.64, 139.81, 139.09, 137.92, 137.17, 133.10, 131.58, 130.98, 130.21, 130.16, 129.39, 128.34, 127.88, 127.62, 127.37, 127.21, 126.79, 126.26, 126.06, 125.76.

*4.4.14. 1,2-Dimethylnaphthalene (**3q**)*

Yield 73%, 10 mol % *$Ph_3PAuOTf$*, 1 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J*=8.44 Hz, 1H), 7.81 (d, *J*=8.07 Hz, 1H), 7.63 (d, *J*=8.25 Hz, 1H), 7.46–7.53 (m, 1H), 7.42 (t, *J*=7.24 Hz, 1H), 7.31 (d, *J*=8.25 Hz, 1H), 2.62 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.12, 132.82, 132.24, 131.12, 129.00, 128.40, 125.70, 125.67, 124.45, 123.70, 20.78, 14.51.

*4.4.15. 4-(4-Methoxyphenyl)-1,2-diphenylnaphthalene (**3r**)*

Yield 90%, 10 mol % *$Ph_3PAuOTf$*, 2 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J*=7.9 Hz, 1H), 7.80 (dd, *J*=8.2, 1.2 Hz, 1H), 7.60 (s, 1H), 7.57 (d, *J*=8.6 Hz, 2H), 7.43–7.50 (m, 2H), 7.28–7.39 (m, 5H), 7.17–7.27 (m, 5H), 7.10 (d, *J*=8.6 Hz, 2H), 3.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 141.9, 139.4, 139.1, 137.9, 136.8, 133.1, 132.9, 131.5, 131.2, 131.1, 130.1, 129.3, 127.8, 127.6, 127.1, 126.7, 126.2, 126.0, 126.0, 125.6, 113.8, 55.3; HRMS (EI) calcd for $C_{29}H_{22}O$: 386.1671, found: 386.1670.

*4.4.16. 1,2-Diphenyl-4-(4-(trifluoromethyl)phenyl)-naphthalene (**3s**)*

Yield 84%, 10 mol % *$Ph_3PAuOTf$*, 2 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.93 (m, 1H), 7.69–7.82 (m, 5H), 7.55 (s, 1H), 7.42–7.50 (m, 2H), 7.30–7.38 (m, 3H), 7.23–7.27 (m, 2H), 7.13–7.22 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 141.5, 138.7, 138.2, 137.9, 133.1, 131.4, 130.6, 130.5, 130.1, 129.7, 129.4, 127.9, 127.7, 127.4, 126.9, 126.4, 126.3, 126.1, 125.5, 125.3 (q, J_{CF}=3.7 Hz), 125.1 (q, J_{CF}=272.0 Hz); HRMS (EI) calcd for $C_{29}H_{19}F_3$: 424.1439, found: 424.1440.

*4.4.17. 2-(3,4-Diphenylnaphthalen-1-yl)furan (**3t**)*

Yield 94%, 10 mol % *$Ph_3PAuOTf$*, 2 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J*=8.4 Hz, 1H), 7.94 (s, 1H), 7.82 (d, *J*=8.6 Hz, 1H), 7.73 (dd, *J*=1.7, 0.7 Hz, 1H), 7.63 (ddd, *J*=8.5, 6.9, 1.3 Hz, 1H), 7.52 (ddd, *J*=8.4, 6.9, 1.2 Hz, 1H), 7.34–7.43 (m, 4H), 7.27–7.33 (m, 4H), 7.21–7.27 (m, 2H), 6.87 (dd, *J*=3.3, 0.6 Hz, 1H), 6.69 (dd, *J*=3.3, 1.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3, 142.5, 141.6, 138.9, 138.0, 138.0, 133.3, 131.4, 130.0, 129.8, 128.6, 128.2, 127.8, 127.6 127.4, 126.8,

126.3, 126.2, 126.2, 125.5, 111.4, 109.5; HRMS (EI) calcd for $C_{26}H_{18}O$: 346.1358, found: 346.1357.

*4.4.18. 1-Methyl-2-phenylnaphthalene (**3u**)*

Yield 51%, 10 mol% *$Ph_3PAuOTf$*, 7 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11–8.14 (m, 1H), 7.90 (dt, J=8.07, 0.73 Hz, 1H), 7.77 (d, J=8.44 Hz, 1H), 7.57–7.61 (m, 1H), 7.51–7.55 (m, 1H), 7.45–7.50 (m, 2H), 7.38–7.44 (m, 4H), 2.63 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.73, 139.06, 132.95, 132.73, 130.81, 129.81, 128.47, 128.31, 128.08, 126.76, 126.20, 125.84, 125.47, 124.57, 16.29.

*4.4.19. 1,2-Dimethyl-4-phenylnaphthalene (**3v**)*

Yield 57%, 10 mol% *$(F_5C_6)_3PAuSbF_6$*, 0.5 mmol scale, 2.5 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, J=8.62 Hz, 1H), 7.88 (d, J=8.44 Hz, 1H), 7.35–7.55 (m, 7H), 7.29 (s, 1H), 2.67 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.04, 137.93, 133.10, 132.64, 130.73, 130.38, 130.17, 130.12, 128.16, 127.00, 126.50, 125.64, 124.57, 123.96, 20.75, 14.63.

*4.4.20. 4-Butyl-1,2-dimethylnaphthalene (**3w**)*

Yield 77%, 10 mol% *$(F_5C_6)_3PAuSbF_6$*, 0.5 mmol scale, 2.5 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (ddd, J=15.68, 8.25, 1.19 Hz, 2H), 7.43–7.53 (m, J=21.85, 8.28, 6.74, 1.47 Hz, 2H), 7.17 (s, 1H), 3.00–3.07 (m, 2H), 2.59 (s, 3H), 2.48 (s, 3H), 1.70–1.78 (m, 2H), 1.43–1.53 (m, 2H), 0.99 (t, J=7.34 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.33, 133.26, 132.65, 130.62, 129.23, 129.12, 125.22, 124.39, 124.30, 124.20, 33.28, 32.73, 22.98, 20.76, 14.46, 14.04.

*4.4.21. 8,9,10,11-Tetrahydro-7H-cyclohepta[a]naphthalene (**3x**)*

Yield 74%, 10 mol% *$(F_5C_6)_3PAuSbF_6$*, 0.5 mmol scale, 2.5 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12–8.16 (m, 1H), 7.83 (dt, J=8.07, 0.73 Hz, 1H), 7.63 (d, J=8.25 Hz, 1H), 7.46–7.52 (m, 1H), 7.39–7.43 (m, 1H), 7.30 (d, J=8.25 Hz, 1H), 3.25–3.31 (m, 2H), 2.99–3.04 (m, 2H), 1.90–1.96 (m, 2H), 1.67–1.75 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.92, 138.55, 132.60, 131.67, 128.62, 128.37, 125.85, 125.67, 124.33, 123.34, 36.64, 32.45, 28.06, 27.65, 26.88.

*4.4.22. Diethyl (1E,3E)-4-phenylbuta-1,3-dien-1-yl phosphate-d_1 (**2a**-d)*

Yield 77%, 5 mol% *$Ph_3PAuOTf$*, 0.1 mmol scale, 1.5 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.39 (m, 2H), 7.28–7.34 (m, 2H), 7.19–7.24 (m, 1H), 6.83 (m, <0.02H), 6.60–6.70 (m, 1H), 6.47–6.55 (m, 1H), 6.20 (d, J=10.82 Hz, 1H), 4.16–4.23 (m, 4H), 1.37 (td, J=7.11, 1.01 Hz, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1–139.7 (m), 137.1, 132.0, 128.6, 127.5, 126.1, 122.9, 117.9 (d, J_{CP}=10.2 Hz), 64.5 (d, J_{CP}=5.5 Hz), 16.1 (d, J_{CP}=6.5 Hz); ^{2}H NMR (76.8 MHz, $CDCl_3$) δ 6.85.

*4.4.23. Diethyl (1E)-4-methylpenta-1,3-dien-1-yl phosphate-d_n (**2h**-d_n)*

Yield 65%, 7 mol% *$Ph_3PAuOTf$*, 0.5 mmol scale, 20 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.59 (dd, J=11.65, 5.78 Hz, 0.73H), 6.22 (t, J=11.55 Hz, 0.79H), 5.63–5.71 (m, 0.98H), 4.10–4.22 (m, 4H), 1.77 (s, 3H), 1.70 (s, 3H), 1.35 (td, J=7.06, 0.92 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.3 (d, J_{CP}=5.5 Hz), 135.4, 118.2, 114.7 (d, J_{CP}=11.1 Hz), 64.4 (d, J_{CP}=5.5 Hz), 26.0, 18.2, 16.1 (d, J_{CP}=6.5 Hz); ^{2}H NMR (76.8 MHz, $CDCl_3$) δ 6.61, 6.25, 5.68.

*4.4.24. (1E)-4,4-Diphenylbuta-1,3-dien-1-yl diethyl phosphate (**2i**-d_n)*

Yield 64%, 5 mol% *$Ph_3PAuOTf$*, 0.5 mmol scale, 8 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.42 (m, 2H), 7.32–7.37 (m, 1H), 7.17–7.31 (m, 7H), 6.90 (dd, J=11.92, 6.05 Hz, 0.9H), 6.54–6.62 (m, 1H), 6.13 (td, J=11.74, 1.10 Hz, 0.67H), 4.11–4.20 (m, 4H), 1.34 (td, J=7.11, 1.01 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 142.0, 140.6 (d, J_{CP}=5.5 Hz), 139.4, 130.3, 128.3 (d, J_{CP}=5.5 Hz), 127.4 (d, J_{CP}=3.7 Hz), 127.4, 121.4–121.9 (ov. s), 116.1 (d, J_{CP}=11.1 Hz), 64.5 (d, J_{CP}=5.5 Hz), 16.1 (d, J_{CP}=6.5 Hz); ^{2}H NMR (76.8 MHz, $CDCl_3$) δ 6.94, 6.17.

*4.4.25. 1,2,4-Triphenylnaphthalene-d_n (**3p**-d_n)*

Yield 78%, 10 mol% *$Ph_3PAuOTf$*, 0.2 mmol, 3 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J=8.3 Hz, 1H), 7.78–7.82 (m, 1H), 7.62–7.66 (m, 2H), 7.61 (s, 0.67H), 7.55 (t, J=7.4 Hz, 2H), 7.42–7.51 (m, 3H), 7.28–7.40 (m, 5H), 7.13–7.26 (m, 5H). *Note*: no loss of D-label in **3p**-d_n in the presence of 10 mol% of *$Ph_3PAuOTf$* catalyst and 1 equiv of AcOH was observed within 12 h.

*4.4.26. Diethyl 4-phenylbuta-1,2-dien-1-yl phosphate (**4a**)*

To a foiled 10 ml flask with septa charged with 10 mol% of AgOTf and 6 ml of anhydrous 1,2-dichloroethane was added propargyl phosphate **1a** (0.3 mmol) under argon atmosphere and the reaction mixture was stirred at room temperature overnight. The reaction mixture was then filtered through a layer of flash Silica (EtOAc—eluent), the solvents were removed in vacuo, and the residue was purified by column chromatography (EtOAc/hexanes) to give 73% of allene **4a** (5:1 mixture together with unreacted **1a**).

Compound **4a**: ^{1}H NMR (400 MHz, CD_3CN) δ 7.32 (t, J=7.3 Hz, 2H), 7.20–7.28 (m, 3H), 6.70–6.76 (m, J=7.8, 5.7, 1.9, 1.9 Hz, 1H), 6.04–6.12 (m, J=7.1, 7.1, 5.6, 2.9 Hz, 1H), 4.02–4.13 (m, 4H), 3.46 (dd, J=7.0, 1.8 Hz, 2H), 1.28 (t, J=7.0 Hz, 6H); ^{13}C NMR (101 MHz, CD_3CN) δ 196.7 (d, J_{CP}=10.2 Hz), 139.9, 129.7, 129.5, 127.5, 113.5 (d, J_{CP}=5.9 Hz), 107.0, 65.3 (d, J_{CP}=5.9 Hz), 37.3, 16.5 (d, J_{CP}=6.6 Hz).

Compound **4a** underwent quantitative transformation into **2a** in the presence of 5 mol% of 1:1 mixture of Ph_3PAuCl/AgOTf catalyst under standard conditions (0.1 mmol scale).

4.5. Monitoring Au-catalyzed transformation of 1a into 2a

An NMR tube, fitted with a rubber septa, was evacuated and backfilled with argon. A solution of 14 mg **1a** dissolved in 600 μL anhydrous $CDCl_3$ was injected into the tube and a ^{1}H spectrum was recorded. The sample was removed and 50 μL of a solution of 2.4 mg Ph_3PAuCl and 1.2 mg AgOTf in 100 μL anhydrous $CDCl_3$ was injected. The tube was quickly shaken and after 1 min the ^{1}H spectrum was recorded. Spectra were obtained at t=0, 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, and 40 min (at which time no starting material or allene was present). Analysis of the spectra concluded that the allene and diene were the sole components observable under the reaction conditions and no other diene isomers formed in detectable quantities.

Allene intermediate **4a** was also observed during GC–MS monitoring of **1a** isomerization reaction course.

4.6. Monitoring Au-catalyzed transformation of 1m into 3m

*4.6.1. Diethyl 4,4,4-triphenylbuta-1,2-dien-1-yl phosphate (**4m**)*

To a foiled 10 ml flask with septa charged with 10 mol% of AgOTf and 6 ml of anhydrous 1,2-dichloroethane was added propargyl phosphate **1m** (0.3 mmol) under argon atmosphere and the reaction mixture was stirred at room temperature overnight. The reaction mixture was then filtered through a layer of flash Silica (EtOAc—eluent), the solvents were removed in vacuo, and the residue was purified by column chromatography (EtOAc/Hexanes) to give 99+% of allene **4m** (2:1 mixture together with unreacted **1m**).

Compound **4m**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19–7.39 (m), 7.05–7.15 (m), 6.89 (dd, J=5.50, 2.38 Hz), 6.73–6.77 (m), 6.39 (dd, J=6.51, 2.11 Hz), 3.91–4.16 (m), 3.46–3.69 (m), 2.53 (d, J=2.02 Hz), 1.18–1.32 (m), 1.04 (td, J=7.06, 1.10 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.6 (d, J_{CP}=11.1 Hz), 145.1, 130.1, 129.9, 127.8, 127.6, 126.7, 115.5 (d, J_{CP}=5.5 Hz), 114.9, 80.3, 79.0, 72.4 (d, J_{CP}=6.5 Hz), 64.2 (t, J=6.9 Hz), 64.0 (d, J_{CP}=6.5 Hz), 63.6 (d, J_{CP}=5.5 Hz), 62.0 (d, J_{CP}=8.3 Hz), 16.0 (d, J_{CP}=6.5 Hz), 15.9 (d, J_{CP}=6.5 Hz).

Allene **4m** was observed as a sole intermediate during GC–MS monitoring of **1m** cycloisomerization reaction course.

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