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Gold(I)-catalysed tandem cyclization of propargyl acetals and alkynes

Huey-San Melanie Siah, Morten Christian Hogsnes, Naseem Iqbal, Anne Fiksdahl *

Department of Chemistry, Norwegian University of Science and Technology, Høgskoleringen 5, NO-7491 Trondheim, Norway

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ABSTRACT

To expand the understanding of the chemistry of propargyl acetals, their gold(I) catalysed cycloaddition reactions with alkynes have been investigated. We hereby report a novel tandem reaction that allows the construction of a new type of polysubstituted and highly functionalised bicyclic pentalene compounds, 2,6a-dimethoxy-3a-methyl-1,4,5-triphenyl-1,3a,4,6a-tetrahydropentalenes, with four stereogenic centres.

Pure diastereomers were successfully isolated in up to 51% yield from mixtures of diastereomeric products (up to 60% total yield) and characterized individually by NMR spectroscopy. A plausible mechanism for the formation of these novel tandem products, based on subsequent [2+2] and [2+3] cycloadditions, is proposed for this gold(I) catalysed reaction.

1. Introduction

Gold-catalysed reactions of propargyl esters are widely reported in the literature and their ability to undergo very different reaction pathways has been systematically studied and reviewed.[1a–d] The gold catalysed activation process of propargyl esters by 1,2-acyloxy migration has, in particular, been shown to be a versatile strategy for the generation of vinyl gold carbene species (Scheme 1a).[3,4c,i,v] Hence, the propargyl-gold approach represents an important supplement to the conventional vinyl-metal carbenoids, generated in situ by metal-catalysed diazo decomposition, for the preparation of effective vinyl-carbene all-carbon 1,3-dipolar reactants. The efficiency of propargyl esters as safe surrogates of diazo compounds for gold catalysed cyclopropanation has been thoroughly studied.[4a–w] Some applications of propargyl esters in [2+2],[5a–b] [3+2],[6a–d] [4+2],[7] [4+3][8a–d] and [3+3][9] cycloaddition reactions have also been reported.

In contrast to propargyl esters, studies on gold(I)-catalysed reactions of corresponding propargyl acetals are scarce. Gold(I)-catalysed [3+2] cycloaddition of propargyl acetals and aldehydes is reported to afford 2,5-dihydrofurans,[10] recently also in an enantioselective manner.[11] However, it was emphasized that a terminal carboxylate EWG was essential for the reaction to take place.

The Fiksdahl group has shown that propargyl acetals show significantly higher reactivity than the corresponding esters (Scheme 1a).[2] Additionally, cycloaddition reactions of propargyl acetals provide access to a rich chemistry, as the choice of reactants gives rise to a diverse range of products. Hence, the propargyl acetals follow different cyclization pathways in gold(I) catalysed cycloadditions (Scheme 1a–d).[2,12–14] Terminal propargyl acetals were studied, demonstrating that the presence of terminal EWGs[10,11] are not required for such substrates.

Propargyl esters and acetals have been shown to undergo Au(I) triple-bond activation and, respectively, 1,2-acyloxy and 1,5-alkoxy migrations (Scheme 1a,b). The migration-fragmentation processes afford, respectively, the gold-allyl-cation/gold-carbenoid species **I** (Scheme 1a) and the respective highly reactive complex **II** (Scheme 1b).[3]

These intermediates can be trapped with different reagents, typically alkenes. We have shown how the chemoselectivity of the cycloadditions and, hence, the structures of the resulting products are controlled by the nature of the substrates. By changing from propargylic esters to acetals, the reaction pathway switches from cyclopropanation[2] (Scheme 1a) to [2+3] cycloaddition (Scheme 1b),[12] while a study on gold(I) catalysed cycloadditions of propargyl acetals with vinyl acetates, showed that such substrates follow a new tandem cyclization pathway (Scheme 1c).[13] The total outcome of the latter reactions was the formation of the cyclopropyl-cyclopentenyl tandem products **V** by two subsequent cycloaddition reactions. Phenylpropargyl acetals were also shown to undergo intermolecular [5+2] cycloaddition with benzaldimine

* Corresponding author. Fax: +47 735 50 877; e-mail address: anne.fiksdahl@chem.ntnu.no (A. Fiksdahl).

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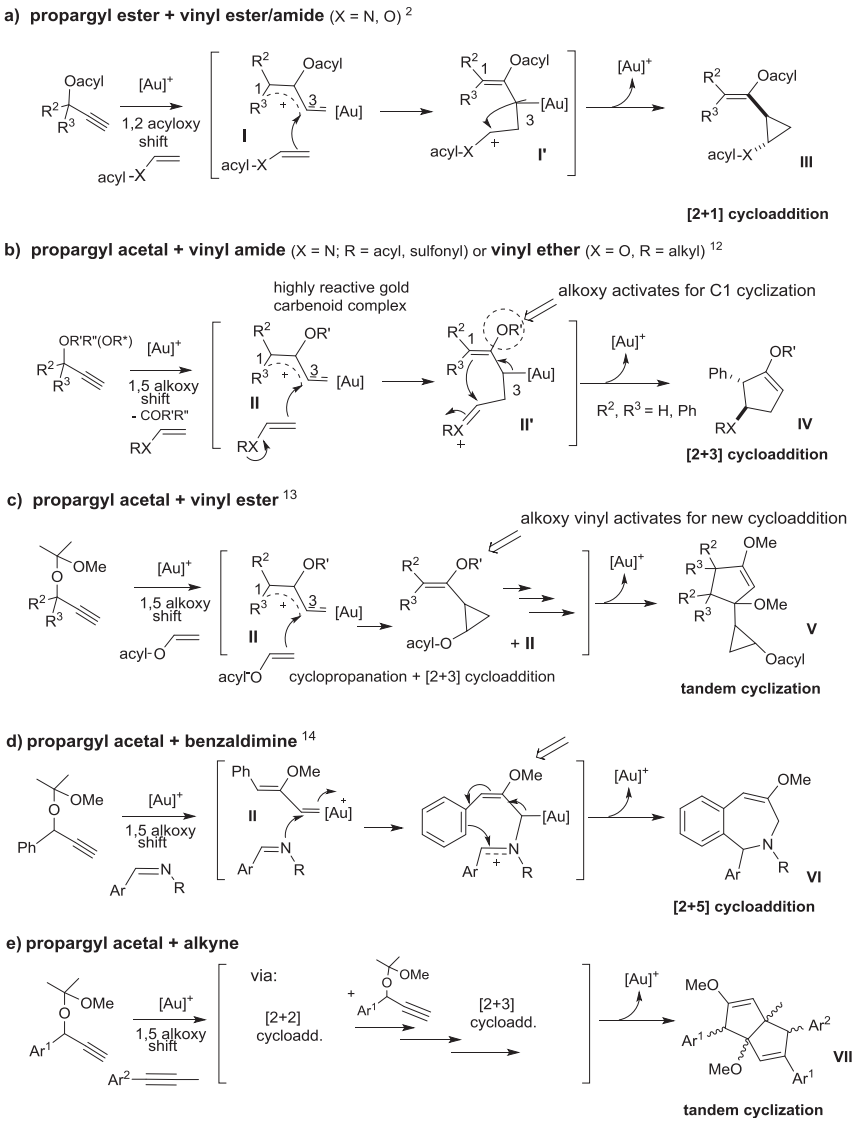


Scheme 1. Proposed mechanisms of gold(I)-catalysed propargyl cycloadditions.[2,12–14].

substrates in the presence of a gold(I) catalyst to afford benzo[c] azepin-4-ol derivatives **VI** (Scheme 1d).[14] As shown in Scheme 1b–d, the alkyl vinyl ether groups, originating from the propargyl acetal substrates, are incorporated in central intermediates. The proposed mechanisms indicate how the activating and directing effect of these structure moieties are essential for the different chemoselective outcomes of these reactions of propargyl acetals.

The previous results demonstrate that gold-catalysed cycloadditions of propargyl acetals are attractive and valuable synthetic tools. To expand the knowledge of the highly reactive propargyl acetals, it was decided to investigate the potential of other multiple bond substrates, such as alkynes, to undergo chemoselective cycloaddition reactions (Scheme 1e). We herein report the results from our study of gold(I)-catalysed cyclization reactions of propargyl acetals and different alkynes to give rise to highly functionalised pentalene tandem products through double cycloaddition.

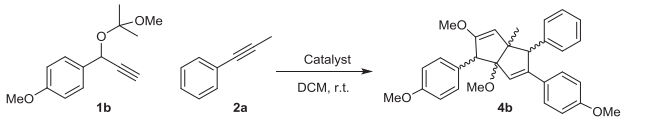
2. Results and discussion

2.1. Optimization studies

Results from a brief screening of reaction conditions are summarised in Table 1. The initial reaction conditions were chosen from prior experience and optimization of gold catalysed propargyl acetal cycloadditions.[2–4] The introductory studies of the reaction of propargyl acetal **1b** (1 equiv) and phenylpropyne **2a** (3 equiv) in dichloromethane readily gave complete conversion into a mixture of products after 15 min at room temperature in the presence of 5 mol-% of gold(I) catalyst [Au{P(*t*-Bu)$_2$(*o*-biphenyl)CH$_3$CN}]-SbF$_6$ (Table 1, entry 1). Structural studies utilising NMR spectroscopy and MS spectrometry identified the major product of the reaction as the tandem bicyclic 2,6a-dimethoxy-1,5-bis[4-methoxyphenyl]-3a-methyl-4-phenyl-1,3a,4,6a-tetrahydropentalene compound **4b**, formed in a mixture of diastereomers, due to the formation of four stereogenic centres. Since the bicyclic product **4b** is constructed of two acetal units and one alkyne unit (see *Proposed mechanism* and Scheme 2 below), it would be relevant to test whether a decrease in the amount of alkyne **2a** (from originally 3 equiv above) would favour the tandem reaction. However, reduction to 1 equiv of alkyne **2a** only caused a decrease in isolated total yields of formed diastereomers, dropping from 51% to 42% (Table 1, entry 1, footnotes [c], [d]), indicating that a large excess of alkyne is necessary for the formation of these particular products.

A few other gold catalysts were additionally screened using GLC analysis to ascertain if a change in catalyst affected the outcome of the reaction. Related gold(I) catalytic systems to that used in entry

Table 1
Optimization studies of gold(I)-catalysed tandem cyclization reactions[a]



Entry	Gold catalyst	Time	Conversion [%][b]
1	[Au[I]{P(*t*-Bu)$_2$(*o*-biphenyl)CH$_3$CN}]SbF$_6$	15 min	**95** (51% isol. yield)[c] (42% isol. yield)[d]
2	[Au[I]{P(*t*-Bu)$_2$(*o*-biphenyl)}]Cl+AgSbF$_6$	60 min	80
3	[Au[I]{P(*t*-Bu)$_2$(*o*-biphenyl)}]Cl+AgNTf$_2$	15 min	66
4	[Au[I]{P(*t*-Bu)$_2$(*o*-biphenyl)}]Cl	24 h	nc
5	Au[I](PPh$_3$)Cl+AgSbF$_6$	15 min	nd[e]
6	Au[I](PPh$_3$)Cl	24 h	nc
7	PicAu[III]Cl$_2$	15 min	17
8	AgSbF$_6$	15 min	nd[f]
9	AgNTf$_2$	15 min	nd[f]

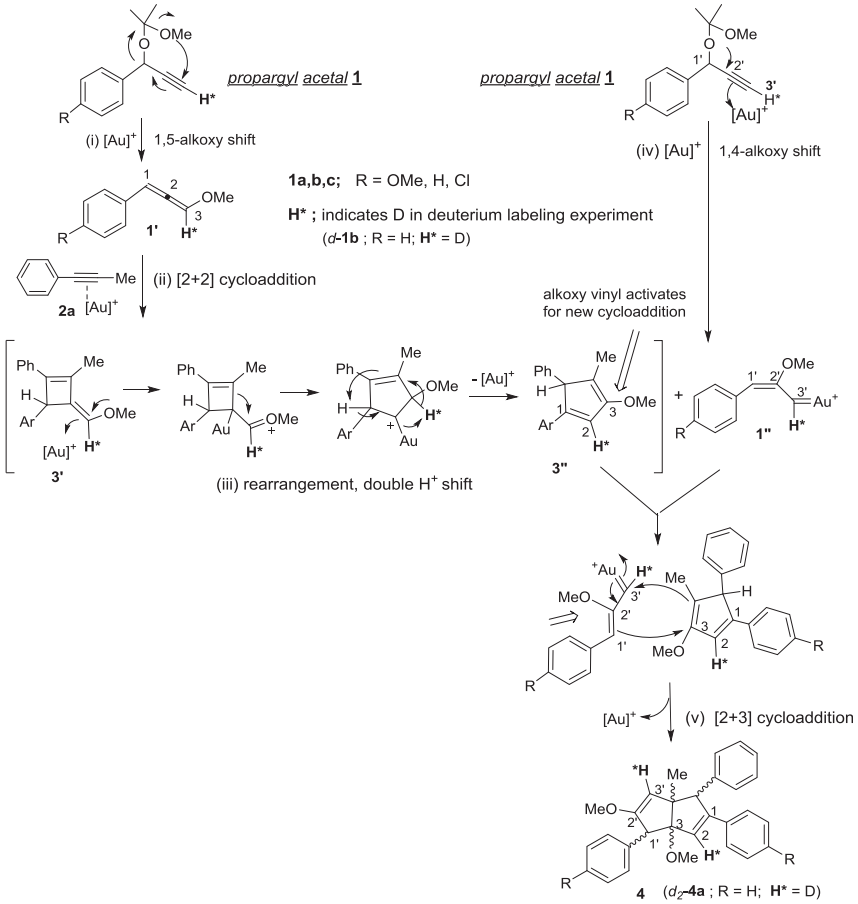
[a] The reactions were performed with **1b** (1 equiv) and **2a** (3 equiv) in DCM (approx. *c*=150 mM) together with 5 mol-% catalyst at rt. The reactions were allowed to stir for the required time before being quenched with NEt$_3$.
[b] The reactions were analysed by GLC. The target compound **4b** was the main product.
[c] Isolated total yield by reaction of **1b** (1 equiv) and **2a** (3 equiv).
[d] Isolated total yield by reaction of **1b** (1 equiv) and **2a** (1 equiv).
[e] Full conversion, but target product **4b** was not detected.
[f] Full conversion, but target product **4b** was not detected; 1-methoxy-4-(1-methoxyprop-2-yn-1-yl)benzene was observed as the main product.

1, but lacking the acetonitrile ligand, were prepared in situ by counterion exchange of the respective gold chloride salt (entries 2, 3). These gave a decrease in conversion at the same or lower rate, but the target diastereomeric compounds **4b** were always the dominating products. As chloride counterion exchange with e.g., SbF_6^- or NTf_2^- is supposed to be crucial for the activity of the gold(I) catalyst,[12–14] no reaction took place with the gold(I) chloride salt, as expected (entry 4). The less bulky triphenylphosphane-based gold(I) catalysts (entries 5, 6) gave no conversion into the desired product **4b**. Consistent with earlier observations, the gold(III) salt,[12–14] PicAu[III]Cl$_2$ (entry 7), gave poor conversion to the desired products. No cycloaddition took place in the presence of the silver salts AgSbF$_6$ or AgNTf$_2$, ruling out a possible silver salt catalysed reaction (entries 8, 9).[12,15]

The original reactions conditions (entry 1) were used in further studies. However, reduced reaction temperature was later shown to increase the reaction effectivity, as discussed below (Table 2, entries 6,7).

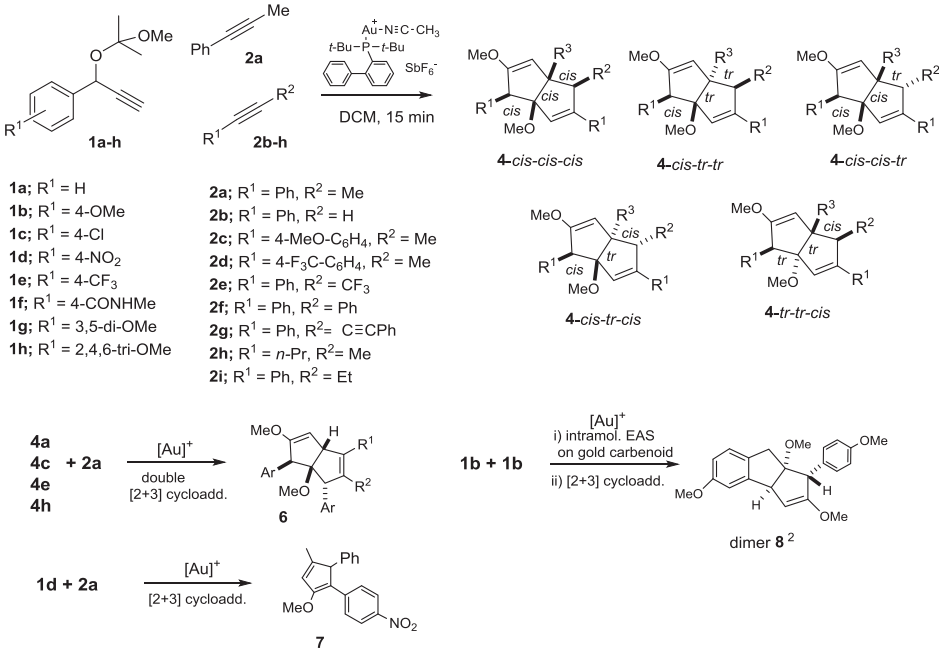
2.2. Proposed mechanism

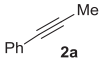
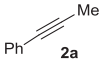
Based on our previous studies on regioselective cycloadditions of propargyl substrates, the formation of tandem product **4** is proposed to take place via two cycloaddition reactions. The general mechanism is shown for propargyl acetal **1** and alkyne **2a** in Scheme 2. Propargyl acetal **1** can both undergo a 1,5- and a 1,4-alkoxy shift to generate intermediate gold(I) species **1′** and **1″**. It has previously been demonstrated that gold(I)-activated propargyl



Scheme 2. Proposed mechanism for gold(I)-catalysed tandem cyclization reaction of propargyl acetals **1** and alkyne **2a** to afford the pentalene products **4**.

Table 2
Gold(I)-catalysed tandem cyclization reactions of propargyl acetals **1** and alkynes **2**[a]



Entry	Acetal	Alkyne	Temp	Product, yield[b]					
				4 [total yield][c]	4-*cis-cis-cis*	4-*cis-tr-tr*	4-*cis-cis-tr*	4-*cis-tr-cis*	4-*tr-tr-cis*
1	**1a**		rt.	**4a** (60)[c]	22	14	6	5	<5
2	**1b**		rt.	**4b** (51)	44	5	<1	<1	—
3	**1c**		rt.	**4c** (29)[c]	—	12	6	4	—
4	**1d**[d]		rt.	n.c.[d]	—	—	—	—	—
5	**1e,f,g,h**		rt.	**4e**, **f**, **g**, **h**[c] (10–30)[e]	10–24[e]	—	—	—	—
6	**1b**		0 °C	**4b** (57)	51	6	—	—	—
7	**1b**		−40 °C	**4b** (57)	51	6	—	—	—
8	**1b**		−78 °C (3 h)	**4b** (14)	14	—	—	—	—
9	**1b**	**2b**	0 °C	**4i**[f]	14	—	—	<2	
10	**1b**	**2c**	0 °C	**4j** (52)	15	—	19	—	18
11	**1b**	**2d**, **e**, **f**, **g**	0 °C	n.c.[g]					
12	**1b**	**2h**	0 °C	n.c.[h]					
13	**1b**	**2i**	0 °C	**4k** (32)	32	—	—	—	

[a] The reactions were performed at rt with propargyl acetal **1** (1 equiv) and alkyne **2** (3 equiv) in DCM (approx. *c*=150 mM) together with 5 mol-% of gold catalyst. The reactions were allowed to stir for 15 min. before being quenched with NEt_3. Diastereomers were isolated by flash chromatography.

[b] Isolated yields refer to chromatographically purified compounds from complex mixtures of diastereomers. These numbers represent the maximum possible yield as the products may contain minor amounts of other diastereoisomers or impurities. However, where necessary, the yields have been adjusted for solvent content. See spectra in the Supplementary data for more information.

[c] Product **6** was isolated in up to 10% yield from reactions with substrates **1a**, **1c**, **1e** and **1h**.

[d] **1d** afforded [2+3] cycloaddition product **7** (15%).

[e] The *cis-cis-cis* isomers of **4f** (24%) and **4g** (10%) were isolated as well as minor amounts of other diastereomers of **4f**–**g**.

[f] The isolated products were impure and the suggested stereochemistry is based on ^{1}H NMR. Several additional diastereomers and regioisomers seem to be produced.

[g] Full conversion of acetal **1b** in 1–24 h, mainly into propargyl alcohol (up to 10%) and dimer **8** (up to 15%). The alkynes **2d**–**g** were recovered and products **4** were not observed.

[h] The product was impure; several other formed products decomposed over time, even at low temperatures.

substrates exist in rapid equilibrium with gold complexes, such as **1′** and **1″**, which can lead irreversibly to a range of stable products.[3,12]

In this case, alkyne **2a** is believed initially to undergo a gold(I)-catalysed [2+2] cycloaddition[5a,b] reaction (ii) with one unit of propargyl acetal **1** in the allenic form **1′**, generated by a 1,5-methoxy migration (i). The reaction would give rise to a cyclobutylidene intermediate **3′**. We have previously identified[12] similar cyclobutylidene products from [2+2] cycloaddition reactions of propargyl acetal. Subsequent intramolecular rearrangement and double proton shift (iii) are proposed to take place via the oxonium ion to afford the less strained pentadienyl intermediate **3″**. Due to the presence of an activating vinyl ether moiety in **3″**, an additional [2+3] cycloaddition (v) with the active gold(I)-carbenoid species **1″** may take place. In this case, **1″** is generated by a 1,4-alkoxy shift of a second unit of propargyl acetal (iv). As observed in our former

tandem reaction of propargyl acetals (Scheme 1c),[13] the vinylic alkoxy group, which activates for the second cycloaddition, is the key prerequisite of both steps in the present new tandem reaction, as well.

A deuterium-labelling experiment with propargyl acetal, *d*-**1a**, deuterated in the terminal position, afforded the tandem product d_2-**4a** with full incorporation of two deuterium atoms. The ^{1}H NMR spectrum showed the absence of the signals for the two affected vinylic protons. As shown in Scheme 2, where **H*** indicates the specific incorporation of deuterium, the results of the experiment were consistent with the proposed mechanism for the formation of the tandem products by subsequent (ii) [2+2] and (iv) [2+3] cycloadditions including (iii) rearrangement and proton shifts.

The reaction takes place with one unit of an alkyne substrate (**2a**) and two units of propargyl acetals (**1**). Since the two propargyl substrates undergo an initial gold(I) catalysed 1,5- and a 1,4-alkoxy shift, respectively, both the allene derivative (**1′**) and the allylic/carbenoid gold(I) complex (**1″**) are reactive intermediates in this tandem cycloaddition reaction.

2.3. Reactivity

Applying the optimized reaction conditions (Table 1, entry 1), the novel tandem transformation was further studied by modifying the substrate(s), starting with the aryl propargyl moiety. The results of the Au(I) catalysed reactions of propargyl acetals **1a**–**d** with phenylpropyne **2a** are presented in Table 2. All reactions were allowed to stir for 15 min at room temperature before quenching with triethylamine. TLC analysis showed full conversion after this time and the propargyl acetals **1a**–**c** gave the expected tandem cyclization products **4a**–**c**, obtained as diastereomeric mixtures (Table 2, entries 1–3). As discussed below, NOESY ^{1}H NMR experiments were mainly used to propose the relative stereochemistry of the diastereomers. The presence of a *para*-substituent on the aromatic propargyl acetals proved to affect both the reactivity and the outcome of the tandem reactions. Unsubstituted phenyl propargyl acetal **1a** and alkyne **2a** gave mostly the **4a**-*cis-cis-cis* diastereomer (22%) in addition to several other diastereomers (60% total yield, entry 1). The presence of a strong electron-donating group (OMe) in the *para*-phenyl position (**1b**) improved the selectivity in the tandem reaction, as 44% out of the total yield of 51% represented the **4b**-*cis-cis-cis* diastereomer (entry 2). In contrast, a halogen (Cl, **1c**, entry 3), gave reduced yield (29%) and selectivity. The nitro-substituted phenylpropargyl substrate **1d** failed to undergo tandem reaction (entry 4). Due to the electron-deficient nature of the substrate acetal **1d**, the reaction with alkyne **2a** afforded a different, single ring structure **7** (15%), analogous to the [2+3] cycloaddition products obtained from propargyl acetals with vinyl compounds (Scheme 1b).[12] This was attributed to the strongly withdrawing nature of the nitro group that favours an unusual [2+3] alkyne cycloaddition with the electrophilic gold carbenoid **II** (Scheme 2b). The less selective substrates (**4a**, **4c**, **4e**, **4g**, entries 1,3,5; footnote [c]) also promoted a second reaction pathway giving the different tandem product **6**. This product appeared to be the result of two [2+3] cycloaddition reactions, proceeding through an intermediate corresponding to product **7** below (entry 4, footnote [d]).

A series of reactions at varying temperature were carried out on the most promising substrate **1b** (entries 6–8). At 0 °C and −40 °C, both the selectivity (51% *cis-cis-cis* isomer) and the total yield of product **4b** increased (57%, entries 6,7). The reaction rate slowed down significantly at −78 °C, as only 14% conversion of **1b** was observed by GLC after 3 h (entry 8). It was decided to carry out the further experiments with propargyl acetal at 0 °C.

With these results in hand, variation of the alkyne (**2b**–**i**, entries 9–13) was carried out. The reaction with the terminal alkyne **2b** with acetal **1b** afforded product **4i**-*cis-cis-cis* (14%, entry 9), but also seemed to produce a mixture of several diastereomers and regioisomers, showing that removal of the methyl group appears to lower the selectivity of this reaction substantially, allowing for many other pathways to be accessed. The 4-OMe-phenylalkyne substrate **2c** afforded similar total yield to the non-substituted **2a**, but poor selectivity was obtained (entry 10). The more electron-deficient alkynes **(2d,e,f,g** entry 11) were unable to undergo a tandem reactions. Products **4** were not observed, while the alkynes **2d**–**g** were recovered. However, full conversion of acetal **1b** took place in 1–24 h, mainly into propargyl alcohol, but also the propargyl acetal tricyclic dimer **8** was generated. This is in accordance with our previous[3] observations for the electron-rich *p*-OMe-phenylpropargyl acetal **1b** in other cycloaddition reactions. The formation of dimer **8** has previously been proposed to take place by a tandem dimerization reaction pathway, based on an intramolecular electrophilic aromatic substitution, activated by the *p*-OMe-phenyl group, and a subsequent [2+3] cycloaddition, activated by the vinyl ether moiety of the intermediate.[3] Hence, the competing formation of dimer **8**, could be explained by insufficient nucleophilicity of the second reactant, in the present case the alkynes **2d**–**g** (entry 11), to afford the desired tandem reaction. The dialkylalkyne **2h** (entry 12) showed poor ability to undergo tandem reaction, while the ethyl-phenylalkyne **2i** (entry 13) gave selectively the **4k** *cis-cis-cis* diastereomer (32%).

^{1}H NMR spectra for each individual diastereomer of product **4** appeared to be quite characteristic. In particular, the distinguishing

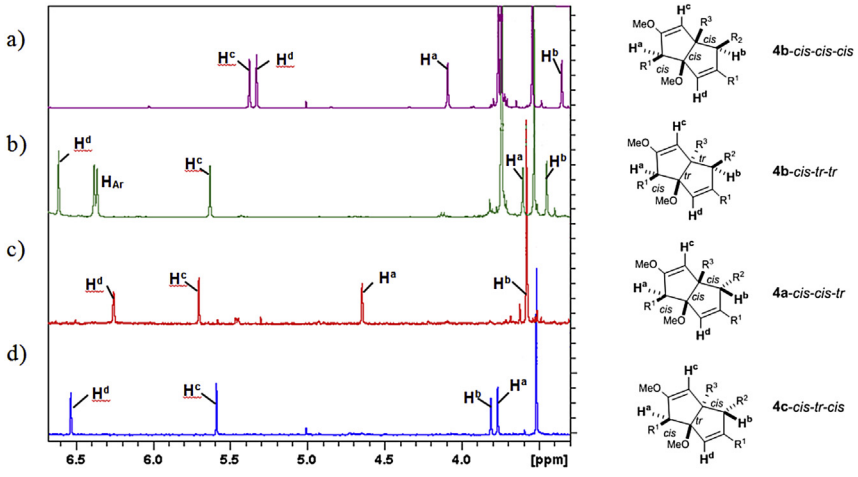


Fig. 1. ^{1}H NMR spectra for individual diastereomers of product **4,** demonstrating the distinguishing shift value patterns for the CH^{a-d} protons.

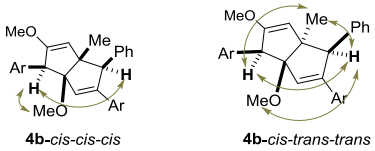
shift value patterns for the CH^a and CH^b methines and the=CH^c and=CH^d vinylic protons, shown in Fig. 1a–d, represented general recognisable features for all the analogous *cis-cis-cis*, *cis-trans-trans, cis-cis-trans* and *cis-trans-cis* diastereomers of products **4**. As demonstrated, quite large differences in shift values may be observed for some proton-signals (e.g., $\Delta\delta>1$ ppm for CH^a and CH^d).

The identification and characterization of the different diastereomers of products **4** as well as for products **6** and **7** were based on 2D NMR (HMBC/COSY, HSQC, NOESY). In particular, NOESY ^{1}H NMR experiments were essential in order to suggest the relative stereochemistry of the four stereogenic centres in tandem product **4**. Designation of the stereochemistry was based on a thorough comparative study of the observed NOESY correlations with the groups of diastereomeric structures (based on ^{1}H NMR patterns above, Fig. 1a–d). The conformational complexity and size of the products allow a range of NOESY correlations to be obtained, also between *trans* groups, as shown by models. Based on a variety of combinations of NOESY correlations between the CH^a and CH^b methines, the Me- and OMe-groups connected to the quaternary carbons, we have proposed relative stereochemistry of the four chiral centres in four isolated diastereomers (Fig. 1a–d). Examples of how the observed NOESY correlations indicated the designated stereochemistry are shown in Fig. 2.

The generally low isolated yields can be explained by the close chromatographic elution of the several produced diastereomers, which gave overlapping zones both on TLC and flash chromatography. This can be illustrated by e.g., the respective R_f values 0.19/0.23/0.29 (1:10 EtOAc:pentane) of the three main isolated diastereomers of tandem product **4c.** Due to challenging chromatographic separation, the isolation of each diastereomer to the level required for NMR characterization and identification of the particular diastereomers was demanding and loss of material during purification was unavoidable. In addition, the stability of these products was questionable. Thus, the real total amount of tandem products formed in the most successful reactions could be more than 60% of products **4a** and **4b**.

3. Conclusions

In order to contribute to a better understanding of the chemistry of propargyl acetals in the presence of gold(I), we have performed a study on chemoselective gold(I)-catalysed cycloadditions of propargyl acetals **1** with alkynes **2**. We have shown that such substrates undergo a new tandem cyclization pathway to readily afford highly functionalised pentalene tandem products **4**, obtained as diastereomeric mixtures, from one unit of an alkyne substrate (**2**) and two units of propargyl acetal (**1**). The proposed mechanism involves a gold(I)-catalysed [2+2] cycloaddition reaction with an allene derivative. A subsequent rearrangement and a [2+3] cycloaddition with an allylic gold(I) complex afford the tandem products **4**. The allene and allyl intermediates are formed by respectively 1,5- and 1,4-alkoxy shift of two propargyl substrates. Highest yield and stereoselectivity was obtained with phenyl or 4-OMe-phenyl propargyl acetal (**1a** or **1b**) and phenylpropyne **2a** at 0 °C, affording up to 51% yield of the pure **4**-*cis-cis-cis* diastereomer.



4b-*cis-cis-cis* **4b**-*cis-trans-trans*

Fig. 2. Examples of NOESY correlations used to suggest stereochemistry of diastereomers.

4. Experimental

4.1. General

All reactions were performed under nitrogen atmosphere. Commercial grade reagents were used as received. Dry solvents were collected from a solvent purification system. All reactions were monitored by GLC and thin-layer chromatography (TLC) using silica gel 60 F254 (0.25 mm thickness). Flash chromatography was carried out using silica gel 60 (0.040–0.063 mm). High Throughput Flash Purification (HPFP) was performed on pre-packed cartridges. ^{1}H and ^{13}C NMR spectra were recorded using a 300, 400 or 600 MHz spectrometer. Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane (TMS) as internal standard. Coupling constants (J) are reported in Hertz (Hz). The attributions of the chemical shifts were determined by means of COSY, HMQC, HMBC and NOESY experiments. Melting points (mp) were determined using a Stuart apparatus and are uncorrected. Accurate mass determination was performed on a 'Synapt G2-S' Q-TOF instrument from Waters. Samples were ionized with the use of ASAP probe, no chromatography separation was used before the mass analysis. IR spectra were obtained using a Smart Endurance reflection cell.

4.2. Preparation of the propargyl acetals

Propargyl acetals **1a–d** were generated as previously described.[3] ^{1}H and ^{13}C NMR shifts were consistent with those in the literature. Propargyl acetals **1e–h** were generated following a similar procedure:

*4.2.1. 1-(1-((2-Methoxypropan-2-yl)oxy)prop-2-yn-1-yl)-4-(trifluoromethyl)benzene (**1e**). 1-(4-(Trifluoromethyl)phenyl)prop-2-yn-1-ol:* A solution of ethynylmagnesium bromide (7.5 mL, 0.50 M in THF, 3.8 mmol) was cooled to 0 °C and a solution of 4-(trifluoromethyl)benzaldehyde (0.40 mL, 2.9 mmol) in dry THF (3 mL) was added slowly. The reaction mixture was stirred for 5 min at that temperature, then the cooling bath was removed and the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched by addition of 10 mL saturated aqueous ammonium chloride and extracted with DCM (3×20 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash chromatography (1:30 EtOAc:pentane) to yield 1-(4-(trifluoromethyl) phenyl)prop-2-yn-1-ol as a bright yellow oil (451.3 mg, 77%). R_f=0.21 (1:30 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.69–7.64 (m, 4H), 5.54 (d, J=2.4 Hz, 1H), 2.71(s, 1H), 2.32 (dd, J=2.4, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 143.7, 130.7 (q, J=32.4 Hz), 126.8, 125.6 (q, J=3.8 Hz), 124.0 (q, J=270.4 Hz), 82.7, 75.5, 63.7; HRMS (EI) calcd for $C_{10}H_6F_3$ $[M-OH]^+$ 183.0422, obsd 183.0425.

A mixture of 1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol (449.0 mg, 2.243 mmol) and 2-methoxypropene (5.0 mL, 52 mmol) was cooled to 0 °C, then pyridinium *p*-toluenesulfonate (PPTS, catalytic amount, <5 mg) was added. The cooling bath was removed and the mixture stirred at room temperature for 1 h. The mixture was diluted with DCM (50 mL), washed with water (3×50 mL), then dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash chromatography (1:50 EtOAc:pentane) to yield 1-(1-((2-methoxypropan-2-yl) oxy)prop-2-yn-1-yl)-4-(trifluoromethyl)benzene (**1e**) as a pale yellow oil (520.1 mg, 85%). R_f=0.31 (1:30 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.62 (s, 4H, H), 5.48 (s, 1H, OCH), 3.18 (s, 3H, OCH_3), 2.56 (s, 1H, ≡CH), 1.55 (s, 3H, CH_3), 1.33 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 144.1, 130.2 (q, J=32.1 Hz), 127.1, 125.5 (q, J=3.72 Hz), 124.0 (q, J=270.4 Hz), 102.1, 83.7, 74.2, 61.9, 49.6, 25.3, 24.9; ^{13}C NMR (376 MHz, $CDCl_3$, C_6F_6 used as reference) δ ppm

264.1; IR (neat, cm^{-1}) 3300, 2993, 2938, 2828, 1616, 1323, 1123, 1066, 1015, 848, 826; HRMS (EI) calcd for $C_{14}H_{15}O_2F_3$ $[M]^+$ 272.1024, obsd 272.1019.

*4.2.2. 4-(1-((2-Methoxypropan-2-yl)oxy)prop-2-yn-1-yl)-N-methylbenzamide (**1f**). 4-(1-Hydroxyprop-2-yn-1-yl)-N-methylbenzamide:* A solution of ethynylmagnesium bromide (8.0 mL, 0.50 M in THF, 4.0 mmol) was cooled to 0 °C and 4-formyl-*N*-methylbenzamide (517.0 mg, 3.168 mmol) in dry THF (50 mL) was added slowly. The reaction mixture was stirred for 5 min at that temperature, then the cooling bath was removed and the reaction mixture was stirred at room temperature for 2 h. Additional ethynylmagnesium bromide (6.0 mL, 0.50 M in THF, 3.0 mmol) was added and the mixture stirred for a further 30 min. Additional ethynylmagnesium bromide (3.0 mL, 0.50 M in THF, 1.5 mmol) was added and the mixture stirred for a further 30 min. Complete conversion was not obtained. The reaction was quenched by addition of saturated aqueous ammonium chloride (20 mL) and solvents were evaporated. The residue was dissolved in DCM (100 mL) and water (50 mL) added. The phases were separated and the water phase extracted with DCM (2×50 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash chromatography (1:1 EtOAc:pentane) to yield 4-(1-hydroxyprop-2-yn-1-yl)-*N*-methylbenzamide as a colourless oil (263.7 mg, 44%). R_f=0.13 (1:1 EtOAc:pentane). The product was used directly without further analysis.

A mixture of 4-(1-hydroxyprop-2-yn-1-yl)-*N*-methylbenzamide (263.7 mg, 1.394 mmol) and 2-methoxyprop-1-ene (5.0 mL, 52 mmol) were stirred at 0 °C. PPTS (catalytic, <5 mg) was added and the mixture stirred for 5 min. The mixture was allowed to come to ambient temperature and stirred for 1 h. The mixture was diluted with DCM (50 mL), washed with water (3×50 mL), the combined water phase extracted with DCM (3×50 mL), then the combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by recrystallization (DCM/pentane) to yield 4-(1-((2-methoxypropan-2-yl)oxy)prop-2-yn-1-yl)-*N*-methylbenzamide (**1f**) as a colourless powder (136.7 mg, 38%). Mp 127–129 °C; R_f=0.25 (1:1 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.51–7.49 (m, 2H), 7.46–7.44 (m, 2H), 7.20 (br s, NH), 5.39 (s, 1H, OCH), 3.18 (s, 3H, OCH_3), 2.54 (s, 1H, ≡CH), 2.18 (s, 3H, NCH_3), 1.54 (s, 3H, CH_3), 1.32 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 168.2, 137.6, 136.2, 127.6, 119.8, 101.8, 84.3, 73.7, 62.1, 49.5, 25.4, 24.9, 24.6; IR (neat, cm^{-1}) 3299, 3184, 2987, 1668, 1608, 1549, 1319, 1014, 858, 668; HRMS (EI) calcd for $C_{15}H_{20}NO_3$ $[M+H]^+$ 262.1443, obsd 262.1440.

*4.2.3. 1,3-Dimethoxy-5-(1-((2-methoxypropan-2-yl)oxy)prop-2-yn-1-yl)benzene (**1g**). 1-(3,5-Dimethoxyphenyl)prop-2-yn-1-ol:* A solution of ethynylmagnesium bromide (8.0 mL, 0.50 M in THF, 4.0 mmol) was cooled to 0 °C. 3,5-Dimethoxybenzaldehyde (521.6 mg, 3.139 mmol) in dry THF (10 mL) was added slowly. The reaction mixture was stirred for 5 min at that temperature, then the cooling bath was removed and the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched by addition of saturated aqueous ammonium chloride (10 mL), the phases separated and the water phase extracted with DCM (3×50 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product of 1-(3,5-dimethoxyphenyl)prop-2-yn-1-ol (557.1 mg) was reacted directly without further purification. R_f=0.23 (1:4 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.72 (d, J=2.1 Hz, 2H), 6.43 (t, J=2.3 Hz, 1H), 5.40 (dd, J=6.3, 2.2 Hz, 1H), 3.81 (s, 6H), 2.66 (d, J=2.24 Hz, 1H), 2.18 (d, J=6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 161.0, 142.3, 104.5, 100.6, 83.3, 74.8, 64.4, 55.4.

A mixture of the crude product of 1-(3,5-dimethoxyphenyl) prop-2-yn-1-ol and 2-methoxyprop-1-ene (5.0 mL, 52 mmol) was stirred at 0 °C. PPTS (catalytic, <5 mg) was added and the mixture stirred for 5 min. The mixture was allowed to come to ambient temperature and stirred for 1 h. The mixture was diluted with DCM (100 mL), washed with water (3×50 mL), the combined water phase extracted with DCM (100 mL), then the combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash chromatography (1:10 EtOAc:pentane) to yield 1,3-dimethoxy-5-(1-((2-methoxypropan-2-yl)oxy)prop-2-yn-1-yl)benzene (**1g**) as a colourless oil (640.4 mg, 84% over two steps). R_f=0.09 (1:30 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.66 (d, J=2.2 Hz, 2H), 6.40 (t, J=2.3 Hz, 1H), 5.36 (d, J=2.2 Hz, OCH), 3.80 (s, 6H, 2×$ArOCH_3$), 3.21 (s, 3H, OCH_3), 2.53 (d, J=2.2 Hz, 1H, ≡CH), 1.53 (s, 3H, CH_3), 1.33 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 160.8, 142.5, 104.8, 101.9, 99.9, 84.2, 73.6, 62.5, 55.4, 49.5, 25.3, 24.9; IR (neat, cm^{-1}) 3268, 2982, 2940, 2831, 1609, 1319, 1151, 1023, 864, 646; HRMS (EI) calcd for $C_{15}H_{20}O_4$ $[M+H]^+$ 264.1362, obsd 264.1358.

*4.2.4. 1,3,5-Trimethoxy-2-(1-((2-methoxypropan-2-yl)oxy)prop-2-yn-1-yl)benzene (**1h**). 1-(2,4,6-Trimethoxyphenyl)prop-2-yn-1-ol:* A solution of ethynylmagnesium bromide (6.5 mL, 0.50 M in THF, 3.3 mmol) was cooled to 0 °C. 2,4,6-Trimethoxybenzaldehyde (505.3 mg, 2.575 mmol) in dry THF (15 mL) was added slowly. The reaction mixture was stirred for 5 min at that temperature, then the cooling bath was removed and the reaction mixture was stirred at room temperature for 30 min. The reaction was quenched by addition of saturated aqueous ammonium chloride (20 mL), the phases separated and the water phase extracted with DCM (3×20 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product of 1-(2,4,6-trimethoxyphenyl)prop-2-yn-1-ol (554.4 mg) was reacted directly without further purification. R_f=0.15 (1:4 EtOAc:pentane).

A mixture of the crude product of 1-(2,4,6-trimethoxyphenyl) prop-2-yn-1-ol and 2-methoxyprop-1-ene (10.0 mL, 104 mmol) were stirred at 0 °C. PPTS (catalytic, <5 mg) was added and the mixture stirred for 5 min. The mixture was allowed to come to ambient temperature and stirred for 1 h. The mixture was diluted with DCM (50 mL), washed with water (3×50 mL), the combined water phase extracted with DCM (100 mL), then the combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash chromatography (1:4 EtOAc:pentane) to yield 1,3,5-trimethoxy-2-(1-((2-methoxypropan-2-yl)oxy)prop-2-yn-1-yl)benzene (**1h**) as a colourless oil (696.9 mg, 95% over two steps). R_f=0.29 (1:4 EtOAc:pentane); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 6.13 (s, 2H), 6.05 (d, J=2.4 Hz, 1H, OCH), 3.86 (s, 6H, 2×$ArOCH_3$), 3.81 (s, 3H, $ArOCH_3$), 3.14 (s, 3H, OCH_3), 2.36 (dd, J=2.4, 0.66 Hz, 1H, ≡CH), 1.48 (s, 3H, CH_3), 1.26 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 161.2, 110.1, 101.4, 91.3, 84.8, 70.1, 56.1, 55.3, 53.4, 49.0, 25.1, 24.8; IR (neat, cm^{-1}) 3268, 3231, 2982, 2940, 1589, 1413, 1194, 1107, 967, 815; HRMS (EI) calcd for $C_{16}H_{22}O_5$ $[M]^+$ 294.1467, obsd 294.1470.

4.3. Preparation of alkynes

Alkynes **2a, 2b, 2f** and **2h** were purchased from Sigma Aldrich and used as received. Alkynes **2c** and **2d** were synthesised through base-induced methylation of their relevant terminal alkynes. Alkyne **2e** was synthesised through copper-catalysed trifluoromethylation of phenylacetylene. The dimeric alkyne **2g** was synthesised through Sonogashia self-cross-coupling of phenylacetylene.

*4.3.1. 1-Methoxy-4-(prop-1-yn-1-yl)benzene (**2c**).* To a flame-dried round-bottom flask under nitrogen was added 1-ethynyl-4-methoxybenzene (520.9 mg, 3.941 mmol) in THF (20 mL). The

flask was placed in an ice-water/salt bath and allowed to cool. *n*-Butyllithium (5.0 mL, 8.0 mmol) was added slowly and the reaction was allowed to stir for 1 h. Iodomethane (0.50 mL, 8.0 mmol) was added at that temperature and the reaction was stirred at room temperature for 1 h. The reaction was quenched with saturated solution of ammonium chloride (20 mL) and extracted with dichloromethane. The organic phases were dried over $MgSO_4$ and the solvent removed in vacuo. The residue was purified by flash chromatography (100% pentane—2% EtOAc/pentane) to give 1-methoxy-4-(prop-1-yn-1-yl)benzene (**2c**) as a colourless oil (194.5 mg, 34%). R_f=0.16 (1:100 EtOAc:pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.34–7.31 (m, 2H), 6.82–6.79 (m, 2H), 3.80 (s, 3H), 2.03 (s, 3H). ^{1}H NMR shifts were consistent with those in the literature.[16]

*4.3.2. 1-(Prop-1-yn-1-yl)-4-(trifluoromethyl)benzene (**2d**).* Product **2d** was generated using a similar procedure as that used for product **2c**. ^{1}H and ^{13}C NMR shifts were consistent with those in the literature.[17]

*4.3.3. (3,3,3-Trifluoroprop-1-yn-1-yl)benzene (**2e**).* Under dry conditions, copper(I) iodide (58.7 mg, 0.308 mmol), 1,10-phenanthroline (108.7 mg, 0.6032 mmol) and potassium bicarbonate (295.4 mg, 2.951 mmol) were weighed into a Schlenk flask and Togni's reagent 1 (3,3-dimethyl-1-(trifluoromethyl)-1,2-benziodoxole, 501.4 mg, 1.519 mmol) was added. Freshly distilled DCM (5 mL) was added into this tube. Ethynylbenzene (158.1 mg, 1.548 mmol) in DCM (5 mL) was added to the tube over 6 h, using a syringe pump. After addition, the reaction mixture was stirred for another 18 h at room temperature. The reaction was quenched with NH_4Cl (10 mL) and water (10 mL) added. The aqueous phase was extracted with DCM (3×20 mL) and the combined organic phases were dried over anhydrous Na_2SO_4 and concentrated in vacuo (moderate vacuum, approx. 500 mbar at rt, was used to avoid product evaporation). The product was purified by flash chromatography (pentane) to give (3,3,3-trifluoroprop-1-yn-1-yl)benzene (**2e**) (92.5 mg, 35%) as a colourless oil. R_f=0.67 (pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.54–7.49 (m, 2H), 7.48–7.46 (m, 1H), 7.41–7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 132.4 (d, J=1.2 Hz), 130.9, 128.6, 118.5 (q, J=1.9 Hz), 114.9 (q, J=256.6 Hz), 86.5 (q, J=6.4 Hz), 75.7 (q, J=53.0 Hz). ^{1}H and ^{13}C NMR shifts were consistent with those in the literature.[18]

*4.3.4. 1,4-Diphenylbuta-1,3-diyne (**2g**).* In an open flask, copper(I) iodide (77.0 mg, 0.404 mmol), potassium bicarbonate (410.4 mg, 4.099 mmol) were stirred in DCM (2 mL). Ethynylbenzene (204.7 mg, 2.004 mmol) was dissolved in DCM (1 mL) and added to the reaction mixture, then 1,10-phenanthroline (145.4 mg, 0.8069 mmol) and the reaction mixture was stirred for 24 h. Water (25 mL) was added and the mixture was extracted with DCM (3×25 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash chromatography (pentane) to give 1,4-diphenylbuta-1,3-diyne (**2g**) (92.2 mg, 46%) as a white crystalline solid. R_f=0.30 (pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.56–7.54 (m, 2H), 7.40–7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 132.5, 129.2, 128.4, 121.7, 81.5, 73.9. ^{1}H and ^{13}C NMR shifts were consistent with those in the literature.[19]

4.4. General procedure for gold-catalysed reactions

The relevant propargyl acetal **1a**–**h** (1 equiv) and alkyne **2a**–**h** (3 equiv) were dissolved in dichloromethane (2–3.4 mL) and added to a solution of the gold catalyst, Au[P(*t*-Bu)$_2$(*o*-biphenyl)]SbF$_6$ (5 mol-%), in dichloromethane (1.7–3 mL). The reaction was stirred for 15 min at the required temperature. The reaction mixture was filtered through Celite and concentrated in vacuo. The products **4, 6, 7** and **8**[3] were isolated by flash chromatography using an appropriate eluent system.

*4.4.1. 2,6a-Dimethoxy-3a-methyl-1,4,5-triphenyl-1,3a,4,6a-tetrahydropentalene (**4a**) and 5,6a-dimethoxy-2-methyl-1,3,6-triphenyl-1,3a,6,6a-tetrahydropentalene (**6a**).* Compounds **4a** and **6a** were synthesised according to the General Procedure at rt, using propargylic acetal **1a** (149.8 mg, 0.7334 mmol) and alkyne **2a** (261.4 mg, 2.250 mmol). Flash chromatography (1:50 EtOAc:pentane) gave products **4a** and **6a** as off-white or pale yellow oils.

4a-*cis-cis-cis* (33.0 mg, 22%, mixture with two unknown isomers, yield calculated from ^{1}H NMR): R_f=0.44 (1:10 EtOAc:pentane); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.15–7.02 (m, 15H), 5.40 (d, J=1.0 Hz, 1H, H^c), 5.34 (s, 1H, H^d), 4.15 (s, 1H, H^a), 3.54 (s, 3H,=$COCH_3$), 3.42 (s, 1H, H^b), 3.01 (s, 3H, -$COCH_3$), 1.03 (s, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 128.1, 152.6, 138.5, 138.2, 136.3, 136.2, 129.4, 128.4, 128.2, 127.9, 127.6, 127.3, 127.0, 126.7, 109.6, 90.2, 69.9, 54.6, 51.2, 50.8, 49.4, 20.5; IR (thin film, cm^{-1}) 3018, 2925, 2821, 1644, 1492, 1453, 1096, 753, 701, 699; HRMS (EI) calcd for $C_{29}H_{28}O_2$ [M]$^+$ 408.2089, obsd 408.2085.

4a-*cis-tr-tr* (21.3 mg, 14%): R_f=0.29 (1:10 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.61–7.13 (m, 10H), 6.98 (t, 1H, J=7.2 Hz), 6.90 (t, 2H, J=8.0 Hz), 6.64 (s, 1H, H^d), 6.31 (d, 2H, J=7.2 Hz), 5.66 (s, 1H, H^c), 3.66 (s, 1H, H^a), 3.53 (s, 3H,=$COCH_3$), 3.52 (s, 1H, H^b), 3.16 (s, 3H,-$COCH_3$), 0.99 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 156.8, 142.0, 138.7, 138.1, 138.0, 136.1, 132.0, 128.2, 128.1, 127.8, 127.6, 127.4, 127.0, 126.7, 126.5, 105.3, 86.1, 72.3, 57.5, 57.2, 54.5, 51.2, 20.8; IR (thin film, cm^{-1}) 3012, 2952, 2925, 1646, 1490, 1453, 1231, 1096, 1032, 751; HRMS (EI) calcd for $C_{29}H_{28}O_2$ [M]$^+$ 408.2089, obsd 408.2087.

4a-*cis-cis-tr* (6%): R_f=0.33 (1:10 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.09–6.95 (m, 15H), 6.26–6.25 (m, 1H, H^d), 5.72 (s, 1H, H^c), 4.70 (s, 1H, H^a), 3.62 (s, 1H, H^b), 3.59 (s, 3H,=$COCH_3$), 3.08 (s, 3H, −$COCH_3$), 1.05 (d, 3H, J=1.4 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 156.6, 139.7, 138.8, 138.3, 137.8, 135.4, 129.6, 128.8, 127.6, 127.2, 126.5, 125.9, 125.7, 106.3, 86.4, 71.5, 66.6, 54.4, 51.4, 51.3, 16.7; IR (thin film, cm^{-1}) 2987, 2955, 2925, 2587, 1490, 1454, 1376, 1183, 1147, 1068, 1013, 872; HRMS (EI) calcd for $C_{29}H_{28}O_2$ [M]$^+$ 408.2089, obsd 408.2090.

4a-*cis-tr-cis* (5%): R_f=0.33 (1:10 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.68–6.84 (m, 15H), 6.53 (m, 1H, H^d), 5.59 (s, 1H, H^c), 3.81 (s, 1H, H^b), 3.77 (s, 1H, H^a), 3.51 (s, 3H,=$COCH_3$), 3.21 (s, 3H, −$COCH_3$), 0.49 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 156.6, 142.1, 140.5, 139.5, 137.6, 128.2, 127.9, 127.6, 127.1, 127.0, 126.4, 106.2, 100.0, 87.1, 61.1, 54.8, 54.6, 54.6, 51.7, 20.8 (not possible to assign all ^{13}C shifts); IR (thin film, cm^{-1}) 2954, 2924, 2869, 2853, 1492, 1453, 1230, 1097, 699, 581, 570; HRMS (EI) calcd for $C_{29}H_{28}O_2$ [M]$^+$ 408.2089, obsd 408.2086.

6a (10.4 mg, 7%): R_f=0.51 (1:10 EtOAc:pentane); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.44–7.39 (m, 4H), 7.31–7.19 (m, 11H), 4.78 (dd, J=2.1, 1.5 Hz, 1H), 4.34–4.34 (m, 1H), 4.09 (br s, 1H), 4.070–4.066 (m, 1H), 3.58 (s, 3H), 2.52 (s, 3H), 1.70 (d, J=1.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 159.8, 138.9, 137.9, 137.7, 137.5, 135.7, 130.2, 129.5, 128.23, 128.21, 127.9, 126.7, 126.6, 126.5, 95.9, 93.6, 66.6, 60.1, 57.1, 56.5, 54.7, 14.5; IR (thin film, cm^{-1}) 3049, 3023, 2925, 1695, 1494, 1452, 1104, 758, 731, 698; HRMS (EI) calcd for $C_{29}H_{28}O_2$ [M]$^+$ 408.2089, obsd 408.2082.

*4.4.2. 2,6a-Dimethoxy-1,5-bis(4-methoxyphenyl)-3a-methyl-4-phenyl-1,3a,4,6a-tetrahydropentalene (**4b**).* Compounds **4b** were synthesized according to the General Procedure at 0 °C, using propargylic acetal **1b** (153.3 mg, 0.6543 mmol) and alkyne **2a** (223.0 mg, 2.250 mmol). Flash chromatography (1:20 EtOAc:pentane) gave products **4b** as pale yellow or yellow oils.

4b-*cis-cis-cis* (77.7 mg, 51%): R_f=0.24 (1:10 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.56–7.51 (m, 1H), 7.35–7.26 (m, 5H),

7.16–7.04 (m, 1H), 6.94 (d, 2H, J=8.5 Hz), 6.77 (d, 4H, J=8.7 Hz), 5.37 (s, 1H, H^c), 5.33 (s, 1H, H^d), 4.09 (s, 1H, H^a), 3.77 (s, 3H), 3.75 (s, 3H), 3.54 (s, 3H,=$COCH_3$), 3.35 (s, 1H, H^b), 3.02 (s, 3H, −$COCH_3$), 1.02 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.3, 158.2, 158.2, 152.6, 136.3, 130.3, 128.4, 128.2, 127.3, 127.0, 126.9, 113.2, 113.1, 109.6, 90.1, 69.0, 55.13, 55.08, 54.6, 51.1, 49.9, 49.4, 25.6, 20.5; IR (film, cm^{-1}) 2919, 2824, 1644, 1610, 1509, 1243, 1177, 1124, 1034, 903, 826, 730, 699; HRMS (EI) calcd for $C_{31}H_{32}O_4$ $[M]^+$ 468.2301, obsd 468.2299.

4b-*cis-tr-tr* (8.6 mg, 6%): R_f=0.14 (1:10 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.53–7.51 (m, 1H), 7.05–6.92 (m, 6H), 6.79–6.72 (m, 4H), 6.61 (s, 1H, H^d), 6.38 (d, 2H, J=7.2 Hz), 5.63 (s, 1H, H^c), 3.74 (s, 3H), 3.74 (s, 3H), 3.60 (s, 1H, H^a), 3.53 (s, 3H,=$COCH_3$), 3.45 (s, 1H, H^b), 3.16 (s, 3H, −$COCH_3$), 0.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.8, 158.3, 156.8, 142.1, 138.0, 136.2, 132.9, 130.9, 130.2, 128.9, 127.6, 127.4, 126.5, 113.2, 105.3, 86.0, 71.4, 57.2, 56.6, 55.4, 55.1, 54.5, 51.2, 20.8; IR (cm-1) 2900, 2240, 1710, 1302, 1223, 905, 734; HRMS (EI) calcd for $C_{31}H_{32}O_4$ $[M]^+$ 468.2301, obsd 468.2299.

4b-*cis-cis-tr* *and* ***4-cis-tr-cis*** were isolated as a mixture (trace): ^{1}H NMR of the mixture is supplied. Identification of the isomers was carried out by comparison with the **4a** analogue. The characteristic ^{1}H NMR signals are given below.

4b-*cis-cis-tr:* ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.22 (s, 1H, H^d), 5.69 (s, 1H, H^c), 4.62 (s, 1H, H^a), 3.58 (s, 3H,=$COCH_3$), 3.55 (s, 1H, H^b), 3.08 (s, 3H, −$COCH_3$), 1.09 (s, 3H, CH_3).

4b-*cis-tr-cis:* ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.50 (s, 1H, H^d), 5.56 (s, 1H, H^c), 3.81 (s, 1H, H^b), 3.72 (s, 1H, H^a), 3.51 (s, 3H,=$COCH_3$), 3.20 (s, 3H, −$COCH_3$), 0.49 (s, 3H, CH_3).

*4.4.3. 1,5-Bis(4-chlorophenyl)-2,6a-dimethoxy-3a-methyl-4-phenyl-1,3a,4,6a-tetrahydropentalene (**4c**) and 1,6-bis(4-chlorophenyl)-5,6a-dimethoxy-2-methyl-3-phenyl-1,3a,6,6a-tetrahydropentalene (**6c**).* Compounds **4c** and **6c** were synthesized according to the General Procedure at rt, using propargylic acetal **1c** (110 mg, 0.461 mmol) and alkyne **2a** (161 mg, 1.38 mmol). Flash chromatography (1:100 EtOAc:pentane) gave the products **4c** and **6c** as off-white oils.

4c-*cis-tr-tr* (12 mg, 12%): R_f=0.19 (1:10 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.55–7.53 (m, 1H), 7.23–7.06 (m, 6H), 7.06–7.03 (m, 2H), 6.98–9.95 (m, 2H), 6.63 (s, 1H, H^d), 6.39–6.37 (m, 2H), 5.64 (d, 1H, J=1.1 Hz, H^c), 3.61 (s, 1H, H^a), 3.52 (s, 3H,=$COCH_3$), 3.47 (s, 1H, H^b), 3.14 (s, 3H, −$COCH_3$), 0.99 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 156.4, 141.5, 138.1, 137.1, 136.4, 135.7, 133.2, 133.0, 132.6, 129.5, 128.2, 128.1, 127.6, 127.4, 126.9, 105.3, 85.9, 71.4, 57.0, 56.8, 54.5, 51.3, 20.9; IR (thin film, cm^{-1}) 2919, 2839, 1639, 1490, 1445, 1226, 1091, 1014, 838, 813, 741, 702; HRMS (EI) calcd for $C_{29}H_{26}O_2{}^{35}Cl_2$ $[M]^+$ 476.1310, obsd 476.1309.

4c-*cis-cis-tr* (6.4 mg, 6%, isolated as a mixture with **4c-*cis-tr-cis*):** R_f=0.23 (1:10 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.51–7.49 (m, 1H), 7.37–7.35 (m, 3H), 7.18–7.16 (m, 1H), 7.06 (d, 4H, J=8.4 Hz), 7.02–7.00 (m, 2H), 6.88 (d, 2H, J=8.6 Hz), 6.26–6.25 (m, 1H, H^d), 5.70 (s, 1H, H^c), 4.64 (s, 1H, H^a), 3.58 (s, 4H,=$COCH_3$ and H^b, overlapping), 3.07 (s, 3H, −$COCH_3$), 1.09 (d, 3H, J=1.3 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 138.6, 106.3, 70.7, 54.5, 51.5, 50.8, 17.0 (not possible to assign all carbon shifts); IR (film, cm^{-1}) 2955, 2923, 2867, 1490, 1257, 1091, 1014, 817, 742, 703, 568; HRMS (EI) calcd for $C_{29}H_{28}O_2{}^{35}Cl_2$ $[M]^+$ 476.1310, obsd 476.1309.

4c-*cis-tr-cis* (3.6 mg, 4%, isolated as a mixture with **4c-*cis-cis-tr***): ^{1}H NMR of the mixture is supplied. Identification of the isomers was carried out by comparison with the **4a** analogue. The characteristic ^{1}H and ^{13}C NMR signals are given below. R_f=0.29 (1:10 THF:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.50 (m, 1H, H^d), 6.58 (s, 1H, H^c), 3.71 (s, 1H, H^b), 3.69 (s, 1H, H^a), 3.51 (s, 3H,=$COCH_3$, overlapping with **4c-*cis-cis-tr***), 3.18 (s, 3H, −$COCH_3$), 0.48 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 156.6, 142.1, 140.5, 139.5, 137.6, 128.2, 127.9, 127.6, 127.1, 127.0, 126.4, 106.2, 100.0, 87.1, 61.1, 54.8, 54.6, 54.6, 51.7, 20.8 (not possible to assign all carbon shifts); IR (film, cm^{-1}) 2955, 2923, 2867, 1490, 1257, 1091, 1014, 817, 742, 703, 568; HRMS (EI) calcd for $C_{29}H_{26}O_2{}^{35}Cl_2$ $[M]^+$ 476.1310, obsd 476.1310.

6c (7 mg, 7%): R_f=0.58 (1:10 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.41 (d, 4H, J=4.3 Hz), 7.32–7.26 (m, 2H), 7.26–7.23 (m, 2H), 7.17–7.11 (m, 5H), 4.78 (s, 1H), 4.32 (s, 1H), 4.03 (s, 1H), 3.99 (s, 1H), 3.58 (s, 3H), 2.64 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 159.3, 138.1, 137.1, 137.1, 136.2, 135.1, 132.5, 131.4, 130.8, 128.3, 128.2, 128.2, 128.1, 127.8, 96.1, 93.1, 66.1, 59.5, 56.6, 56.0, 54.7, 14.4; IR (thin film, cm^{-1}) 2950, 2919, 1646, 1490, 1340, 1225, 1090, 1014, 701; HRMS (EI) calcd for $C_{29}H_{26}{}^{35}Cl_2O_2$ $[M]^+$ 477.1385, obsd 477.1388.

*4.4.4. Products **4e** and **6e** were synthesized according to the General Procedure at rt, using propargylic acetal **1e** (150.3 mg, 0.5520 mmol) and alkyne **2a** (191.9 mg, 1.652 mmol).* Flash chromatography (2:1 EtOAc:pentane) gave products **4e** and **6e** as a mixture of pale yellow oils. This mixture was inseparable by flash chromatography and appeared to contain both compounds of type **4e** and **6e**, but their identity could not be determined conclusively. (^{1}H NMR in Supplementary data).

*4.4.5. 4,4′-(2,6a-Dimethoxy-3a-methyl-4-phenyl-1,3a,4,6a-tetrahydropentalene-1,5-diyl)bis(N-methylbenzamide) (**4f**).* Compounds **4f** were synthesized according to the General Procedure at rt, using propargylic acetal **1f** (136.0 mg, 0.5204 mmol) and alkyne **2a** (181.0 mg, 1.561 mmol). Flash chromatography (2:1 EtOAc:pentane) gave products **4f** as pale yellow or yellow oils.

4f-*cis-cis-cis* (32 mg, 24%): R_f=0.29 (2:1 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.57–7.50 (m, 2H), 7.47–7.43 (m, 2H), 7.39–7.32 (m, 4H), 7.18–7.05 (m, 3H), 6.97–6.95 (m, 2H), 5.37 (s, 1H, H^c), 5.32 (s, 1H, H^d), 4.10 (s, 1H, H^a), 3.52 (s, 3H,=$COCH_3$), 3.36 (s, 1H, H^b), 3.00 (s, 3H, −$COCH_3$), 2.10 (s, 6H), 1.01 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 168.3, 168.2, 157.9, 152.9, 136.6, 136.4, 135.9, 134.0, 132.3, 129.9, 128.2, 127.4, 126.9, 126.5, 119.1, 109.6, 90.2, 69.2, 60.4, 54.6, 51.1, 50.1, 49.4, 24.5, 24.4, 20.5; IR (thin film, cm^{-1}) 3304, 3049, 2925, 1669, 1601, 1533, 1517, 1412, 1317, 768, 699; HRMS (EI) calcd for $C_{33}H_{34}N_2O_4$ $[M]^+$ 522.2519, obsd 522.2518.

4f-*cis-tr-tr* was isolated as a mixture (8 mg, 6%): ^{1}H NMR of the mixture is supplied. Identification of the isomers was carried out by comparison with the **4a** analogue. The characteristic ^{1}H NMR signals are given below.

4f-*cis-tr-tr:* ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.62 (s, 1H, H^d), 5.63 (s, 1H, H^c), 3.62 (s, 1H, H^a), 3.51 (s, 3H,=$COCH_3$), 3.47 (s, 1H, H^b), 3.15 (s, 3H, −$COCH_3$), 0.99 (s, 3H, CH_3).

*4.4.6. 1,5-Bis(3,5-dimethoxyphenyl)-2,6a-dimethoxy-3a-methyl-4-phenyl-1,3a,4,6a-tetrahydropentalene (**4g**).* Compound **4g** was synthesized according to the General Procedure at rt, using propargylic acetal **1f** (153.4 mg, 0.5804 mmol) and alkyne **2a** (206.5 mg, 1.778 mmol). Flash chromatography (1:10 EtOAc:pentane) gave products **4f** as colourless oils.

4g-*cis-cis-cis* (14.8 mg, 10%): R_f=0.22 (1:4 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.32–7.26 (m, 5H), 6.86 (s, 1H), 6.37 (s, 1H), 6.34 (s, 1H), 6.31 (s, 1H), 6.21 (s, 2H), 5.42 (s, 1H, H^c), 5.37 (s, 1H, H^d), 4.07 (s, 1H, H^a), 3.61 (s, 6H), 3.55 (s, 3H,=$COCH_3$), 3.32 (s, 1H, H^b), 3.11 (s, 3H, −$COCH_3$), 1.05 (s, 3H, CH_3); ^{13}C NMR was not obtained due to impurity. Identification of the isomer was carried out by comparison with the **4a** analogue. HRMS (EI) calcd for $C_{33}H_{36}O_6$ $[M]^+$ 528.2512, obsd 528.2511.

*4.4.7. 3a,5-Dimethoxy-2,4-bis(4-methoxyphenyl)-1-phenyl-1,3a,4,6a-tetrahydropentalene (**4i**).* Compounds **4i** were synthesized according to the General Procedure at 0 °C, using propargylic acetal **1b** (152.4 mg, 0.6505 mmol) and alkyne **2b** (197.5 mg, 1.934 mmol). Flash chromatography (1:20 EtOAc:pentane) gave mixtures of products **4i** as pale yellow oils. One compound was identified as the **4i-*cis-cis-cis*** isomer, while another also seemed to be a stereoisomer of **4**, but did not correspond to any of the already identified isomers. The minor amount did not to allow for characterisation. ^{1}H NMR of both compounds is provided.

4i-*cis-cis-cis* (20.5 mg, 14%): Identification of the isomer was carried out by comparison with the **4a** analogue. The characteristic ^{1}H signals are given below. HRMS (EI) calcd for $C_{30}H_{30}O_4$ $[M]^+$ 454.2144, obsd 454.2145.

Not determined isomer of **4**: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.54 (s, 1H, H^c), 5.47 (s, 1H, H^d), 4.14 (s, 1H, H^a), 3.59 (s, 1H, H^b), 3.54 (s, 3H,=$COCH_3$), 2.97 (s, 3H, −$COCH_3$).

*4.4.8. 2,6a-Dimethoxy-1,4,5-tris(4-methoxyphenyl)-3a-methyl-1,3a,4,6a-tetrahydropentalene (**4j**).* Compounds **4j** were synthesized according to the General Procedure at 0 °C, using propargylic acetal **1b** (70.4 mg, 0.300 mmol) and alkyne **2c** (130.4 mg, 0.8920 mmol). Flash chromatography (1:10 EtOAc:pentane) gave products **4j** as yellow oils/waxes.

4j-*cis-cis-cis* (11 mg, 15%, isolated as a mixture with an unknown isomer): Identification of the isomer was carried out by comparison with the **4a** analogue. The characteristic ^{1}H signals are given below. R_f=0.12 (1:10 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.35 (s, 1H, H^d), 5.25 (s, 1H, H^c), 4.08 (s, 1H, H^a), 3.81 (s, 3H), 3.76 (s, 3H), 3.75 (s, 3H), 3.53 (s, 3H,=$COCH_3$), 3.33 (s, 1H, H^b), 3.01 (s, 3H, −$COCH_3$), 1.02 (s, 3H, CH_3).

4j-*cis-cis-tr* (14.0 mg, 19%): R_f=0.10 (1:10 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.93 (d, 2H, J=8.2 Hz), 6.87 (d, 2H, J=8.7 Hz), 6.94–6.85 (m, 2H, overlapping), 6.64 (d, 2H, J=8.6 Hz), 6.59 (d, 2H, J=8.8 Hz), 6.65–6.42 (m, 2H, overlapping), 6.20 (s, 1H, H^d), 5.68 (s, 1H, H^c), 4.53 (s, 1H, H^a), 3.71 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 3.57 (s, 3H,=$COCH_3$), 3.53 (s, 1H, H^b), 3.07 (s, 3H, -$COCH_3$), 1.07 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.2, 157.6, 157.4, 156.7, 138.0, 135.9, 132.1, 130.9, 130.5, 130.2, 129.9, 113.0, 112.6, 112.4, 106.2, 86.3, 70.6, 65.8, 55.1, 55.04, 55.00, 54.4, 51.3, 50.9, 16.8; IR (thin film, cm^{-1}) 2935, 2826, 1609, 1509, 1463, 1245, 1178, 1035, 910, 826, 794, 730; HRMS (EI) calcd for $C_{32}H_{34}O_5$ $[M]^+$ 498.2406, obsd 498.2398.

4j-*tr-tr-cis* (13.2 mg, 18%): R_f=0.15 (1:10 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.94 (d, 2H, J=8.8 Hz), 6.85 (d, 2H, J=8.5 Hz), 6.75 (d, 2H, J=8.8 Hz), 6.62 (d, 2H, J=8.7 Hz), 7.19–6.61 (m, 4H, overlapping), 5.76 (s, 1H, H^c), 5.16 (s, 1H, H^d), 4.13 (s, 1H, H^a), 3.81 (s, 3H), 3.73 (s, 3H), 3.69 (s, 3H), 3.60 (s, 3H,=$COCH_3$), 3.36 (s, 1H, H^b), 3.06 (s, 3H, -$COCH_3$), 1.74 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.7, 158.3, 157.8, 157.6, 146.5, 133.0, 130.2, 130, 129.4, 128.3, 127.1, 113.2, 112.8, 107.1, 89.5, 68.7, 59.1, 55.19, 55.16, 55.0, 54.7, 50.5, 48.7, 13.8; IR (thin film, cm^{-1}) 2930, 2909, 2826, 1610, 1510, 1463, 1246, 1177, 1099, 1036, 824, 732; HRMS (EI) calcd for $C_{32}H_{34}O_5$ $[M]^+$ 498.2406, obsd 498.2402.

*4.4.9. 3a-Ethyl-2,6a-dimethoxy-1,5-bis(4-methoxyphenyl)-4-phenyl-1,3a,4,6a-tetrahydropentalene (**4k**).* The title compound was synthesized according to the General Procedure at 0 °C, using propargylic acetal **1b** (151.1 mg, 0.6449 mmol) and alkyne **2i** (260.0 mg, 1.997 mmol). Flash chromatography (1:20 EtOAc:pentane) gave product **4k** as a pale yellow oil.

4k-*cis-cis-cis* (50.1 mg, 32%): R_f=0.21 (1:10 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60–7.53 (m, 1H), 7.37–7.28 (m, 5H), 7.20–7.14 (m, 1H), 6.94 (d, 2H, J=8.6 Hz), 6.75 (d, 4H, J=8.7 Hz), 5.41 (s, 1H, H^d), 5.29 (s, 1H, H^c), 4.02 (s, 1H, H^a), 3.76 (s, 3H), 3.73 (s, 3H), 3.56 (s, 3H,=$COCH_3$), 3.43 (s, 1H, H^b), 2.90 (s, 3H, -$COCH_3$), 1.82–1.70 (m, 1H, CH_2), 1.45–1.33 (m, 1H, CH_2), 0.75 (t, J=7.3 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.4, 158.3, 158.2, 153.9, 136.5, 130.3, 130.2, 128.4, 128.2, 127.3, 127.2, 126.2, 113.0, 107.3, 90.8, 66.5, 55.1, 55.0, 54.6, 53.3, 51.9, 51.5, 24.5, 8.5; IR (thin film, cm^{-1}) 2962, 2930, 2826, 1704, 1610, 1510, 1244, 178, 1034, 809, 824, 729, 699; HRMS (EI) calcd for $C_{32}H_{34}O_4$ $[M]^+$ 482.2457, obsd 482.2462.

*4.4.10. 5,6a-Dimethoxy-2-methyl-3-phenyl-1,6-bis(2,4,6-trimethoxyphenyl)-1,3a,6,6a-tetrahydropentalene (**6h**).* The title compound was synthesized according to the General Procedure at rt, using propargylic acetal **1h** (151.2 mg, 0.5137 mmol) and alkyne **2a** (184.0 mg, 1.584 mmol). Flash chromatography (1:3 EtOAc:-pentane) gave product **6h** as a pale yellow oil (16.4 mg, 11%): R_f=0.18 (1:3 EtOAc:pentane); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.41–7.39 (m, 2H), 7.37–7.35 (m, 2H), 7.23–7.20 (m, 1H), 6–11 (d, J=2.4 Hz, 1H), 6.10 (d, J=2.4 Hz, 1H), 6.08 (d, J=2.3 Hz, 1H), 6.06 (d, J=2.3 Hz, 1H), 4.92 (s, 1H), 4.84 (t, J=1.5 Hz, 1H), 4.57 (t, J=2.1 Hz), 4.47–4.46 (m, 1H), 3.808 (s, 3H), 3.806 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H), 3.70. (s, 3H), 3.50 (s, 3H), 2.84 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 159.8, 159.7, 159.6, 159.5, 139.2, 135.0, 134.9, 128.2, 127.9, 125.6, 109.5, 108.1, 95.2, 92.9, 91.5, 90.8, 90.8, 90.5, 60.4, 59.5, 56.2, 56.0, 55.9, 55.7, 55.4, 55.2, 55.1, 54.1, 49.4, 14.2; IR (thin film, cm^{-1}) 2935, 2836, 1692, 1590, 1226, 1204, 1127, 812, 732; HRMS (EI) calcd for $C_{35}H_{40}O_8$ $[M]^+$ 588.2723, obsd 588.2719.

*4.4.11. 1-(3-Methoxy-4-methyl-5-phenylcyclopenta-1,3-dien-1-yl)-4-nitrobenzene (**7**).* The title compound was synthesized according to the General Procedure at rt, using propargylic acetal **1d** (202 mg, 0.810 mmol) and alkyne **2a** (284 mg, 2.43 mmol). Flash chromatography (1:60 EtOAc:pentane) gave compound **7** as an orange solid/wax (18 mg, 15%): R_f=0.43 (1:5 EtOAc:pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.97 (d, 2H, J=9.2 Hz), 7.56 (d, 2H, J=9.1 Hz), 7.27–7.08 (m, 5H), 6.34 (s, 1H), 4.27 (s, 1H), 4.04 (s, 3H), 1.86 (d, 3H, J=1.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 162.7, 155.3, 143.3, 141.7, 138.5, 129.0, 127.8, 127.0, 125.2, 123.7, 120.0, 116.5, 58.5, 58.1, 15.5; IR (film, cm^{-1}) 2924, 2841, 1589, 1515, 1331, 1315, 1107, 852, 752, 735, 699; HRMS (EI) calcd for $C_{19}H_{17}NO_3$ $[M]^+$ 308.1287, obsd 308.1287.

*4.4.12. 2,5,8a-Trimethoxy-1-(4-methoxyphenyl)-1,3a,8,8a-tetrahydrocyclopenta[a]indene (**8**).*[3] Propargylic acetal **1b** and alkynes **2e**, **f**, **g**, **h** were mixed according to the General Procedure. Full conversion of acetal **1b** at 0 °C (1–24 h) afforded dimer **8**[13] (up to 15%) and propargyl alcohol (up to 10%), while products **4** could not be detected.

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Supplementary data

Supplementary data (spectroscopic data ^{1}H and ^{13}C NMR) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.12.080.

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