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Gold(I)-Catalysed Tandem Cyclisation of Propargyl Acetals and Vinyl Esters

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The results of our previous comparative study of chemoselective gold(I)-catalysed alkene cycloadditions of propargyl substrates demonstrated that propargyl acetals react by different cyclisation pathways from the corresponding esters, and that they also have significantly higher reactivities. To increase understanding of the chemistry of propargyl acetals and to explore the possibilities of generating new compounds through gold(I)-catalysed reactions, a range of reactions of propargyl acetals with vinyl esters have been carried out. A new type of cyclopropyl–cyclopentenyl products, (1,3-dimethoxy-4,5-diphenylcyclopent-2-en-1-yl)-cyclopropyl ester derivatives, was obtained. A plausible mechanism, including sequential [1+2] and [2+3] cycloadditions, is proposed for these highly regio- and stereoselective gold(I)-catalysed reactions. The cyclopentenylation took place stereoselectively, whereas *cis*/*trans* mixtures of diastereoisomers were formed in the cyclopropanation step, with the selectivity being controlled by the bulkier vinylic substituent. The tandem reaction allows the construction of polysubstituted and highly functionalised bicyclic compounds.

Introduction

Gold(I) complexes are known to be efficient catalysts for the activation of C–C multiple bonds towards nucleophilic attack.[1–4] Propargylic esters and acetals have been shown to undergo triple-bond activation, followed by, respectively, 1,2-acyloxy and 1,5-alkoxy migrations. Subsequent nucleophilic attack generates a variety of complex small molecules with one or more chiral centres.[5–7] The structures of the products depend on the nature of both the propargyl moiety and the nucleophile.

The Fiksdahl group has previously reported a comparative study of the reactivity of chemoselective gold(I)-catalysed cycloadditions of propargyl esters and acetals with vinyl derivatives (Scheme 1a and b), and has shown how the regioselectivity of the cycloadditions is controlled by the electronic nature of the substrates.[8,9] Such propargyl derivatives are known to undergo gold(I)-catalysed migration–fragmentations to give gold carbenoid intermediates (**I**, **II**), which can be trapped with different reagents, typically alkenes, to give adducts **I′** and **II′**. We have studied such reactions with olefins directly connected to a heteroatom.

Cyclopropanation by a [1+2] cycloaddition reaction pathway is typical for the reactions of terminal *propargyl esters* with vinyl esters or amides (Scheme 1a, product **III**).[8] Changing from propargylic esters to acetals, the reaction pathway switches. The gold(I)-catalysed cyclisation reactions of *propargyl acetals* with vinyl amides or vinyl ethers are characterised by two important features. Firstly, in contrast to the usual olefin cyclopropanation that normally takes place with propargyl esters, an atypical cyclopentenylation by a [2+3] cycloaddition mechanism is the favoured reaction pathway for the corresponding acetals,[9] leading to *trans*-configured cyclopentenyl products (Scheme 1b, product **IV**). This reaction proceeds by a "C-3–C-1" reaction sequence, due to the presence of an alkoxy group in adduct **II′**, which activates it for C-1 cyclisation. Secondly, propargyl acetals show a significantly higher reactivity than the corresponding esters,[9,10] which is consistent with the assumption that the alkoxy substituent may activate the intermediate gold–propargyl-acetal complex **II**. Our recent studies have shown that propargyl acetals also undergo a gold-catalysed [2+5] cycloaddition with benzaldimines to give benz[*c*]azepine products (Scheme 1c, compound **V**).[10]

However, by replacing the vinyl amides or vinyl ethers (Scheme 1, b) with vinyl esters, the reaction outcome was altered. Propargyl acetals and vinyl esters were found to undergo a gold(I)-catalysed tandem cyclisation reaction involving two propargyl–gold units **II**, generated from propargyl acetals, to give rise to cyclopropyl–cyclopentenyl products **VI** (Scheme 1, d).

We wanted to further investigate the ability of the highly reactive gold(I) vinylcarbenoid complexes **II** to promote chemoselective cyclisations, and we chose to study the po-

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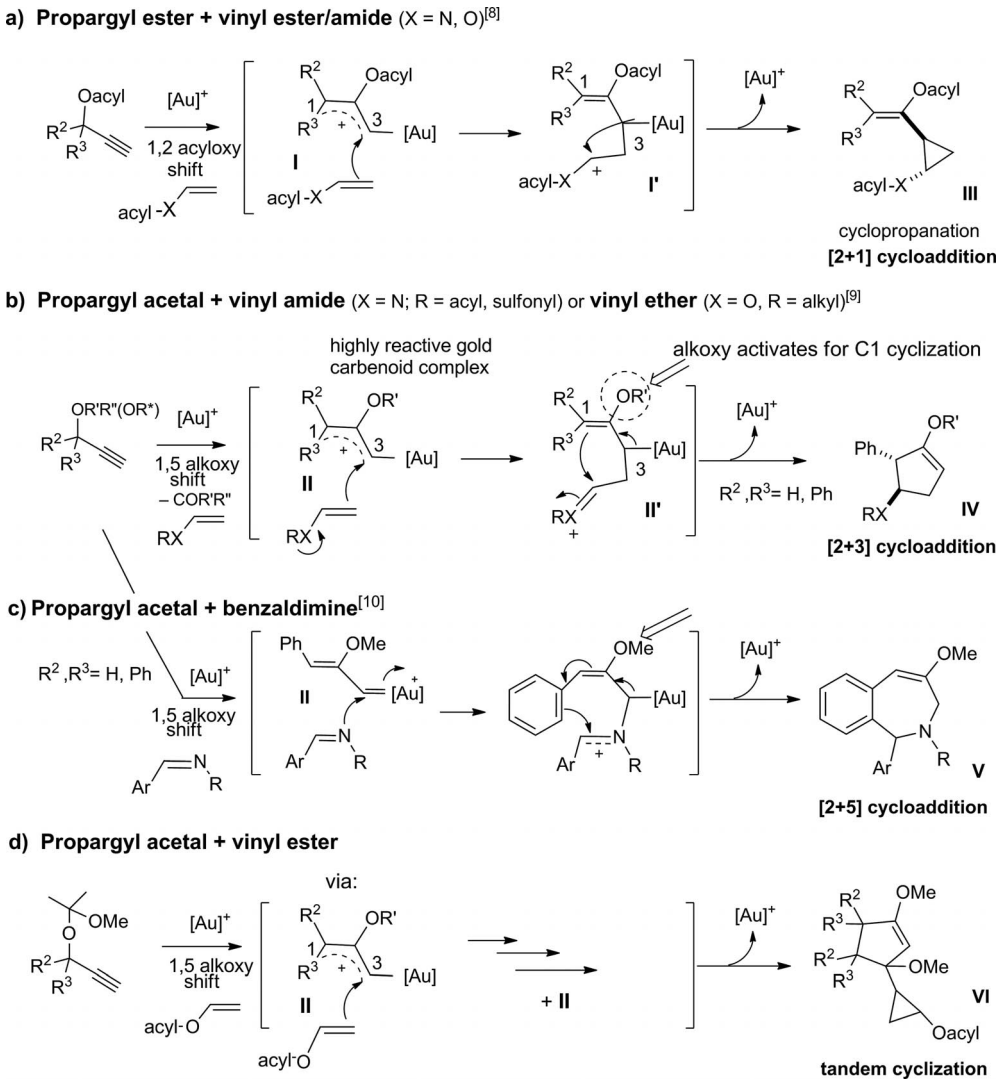


Scheme 1. Gold(I)-catalysed cycloaddition reactions of propargyl substrates.[8–10]

tential for propargyl acetals to give tandem products with vinyl esters by a double cycloaddition process. In this paper, we report the results of our studies on the new gold(I)-catalysed tandem reaction.

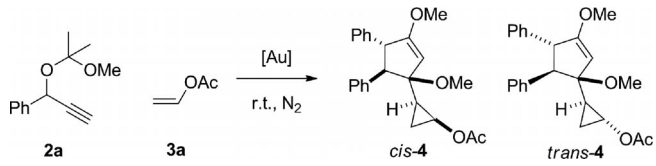
Results and Discussion

Introductory studies into the reaction of propargyl acetal **2a** and vinyl acetate (**3a**; 3 equiv. based on the propargyl substrate) in the presence of a gold(I) catalyst were carried out under reaction conditions previously used for propargyl acetal cycloadditions.[9] Structural studies (NMR spectroscopy) showed that the tandem cyclisation product could be identified as 2-(1,3-dimethoxy-4,5-diphenylcyclopent-2-enyl)cyclopropyl acetate, formed as a mixture of diastereomers (*cis*-/*trans*-**4a**).

Optimisation Studies

Optimisation studies showed that substrates **2a** and **3a** readily gave a 54% yield of products **4** after 15 min in the presence of [Au{P(*t*Bu)$_2$(*o*-biphenyl)CH$_3$CN}]SbF$_6$ (5 mol-%) in dichloromethane (Table 1, entry 1). These reaction conditions were used in further studies, as they gave the highest reactivity towards tandem cyclisation. The use of acetonitrile as a solvent resulted in a lower yield, and required a longer reaction time (48%, 60 min; Table 1, entry 2). Tetrahydrofuran seemed to undergo polymerisation, so it was deemed to be an unsuitable solvent for these reactions (Table 1, entry 3). A similar gold(I) catalytic complex lacking the acetonitrile ligand gave lower yields (31%; Table 1, entry 4). As previously observed,[9] no reaction took place when [Au{P(*t*Bu)$_2$(*o*-biphenyl)}]Cl was used, and it was important to generate the active gold(I) species by exchange of the chloride counterion with SbF$_6^-$ (Table 1,

Table 1. Optimisation studies of gold(I)-catalysed tandem cyclisation reactions.[a]



2a 3a cis-4 trans-4

Entry	Gold catalyst	Solvent (time)	Yield [%] (*cis*/*trans*)
1	{Au[P(*t*Bu)$_2$(*o*-biphenyl)CH$_3$CN]}SbF$_6$	CH_2Cl_2 (15 min)	54 (60:40)
2	{Au[P(*t*Bu)$_2$(*o*-biphenyl)CH$_3$CN]}SbF$_6$	CH_3CN (60 min)	48 (60:40)
3	{Au[P(*t*Bu)$_2$(*o*-biphenyl)CH$_3$CN]}SbF$_6$	THF (60 min)	n.d.[b]
4	{Au[P(*t*Bu)$_2$(*o*-biphenyl)]}Cl + AgSbF$_6$	CH_2Cl_2 (15 min)	31 (65:35)
5	{Au[P(*t*Bu)$_2$(*o*-biphenyl)]}Cl	CH_2Cl_2 (19 h)	n.d.
6	Au(PPh$_3$)Cl + AgSbF$_6$	CH_2Cl_2 (15 min)	n.d.[c]
7	$AuCl_3$	CH_2Cl_2 (15 min)	n.d.[c]
8	$PicAuCl_2$	CH_2Cl_2 (19 h)	**1a**/**2a**; 3:2[c]

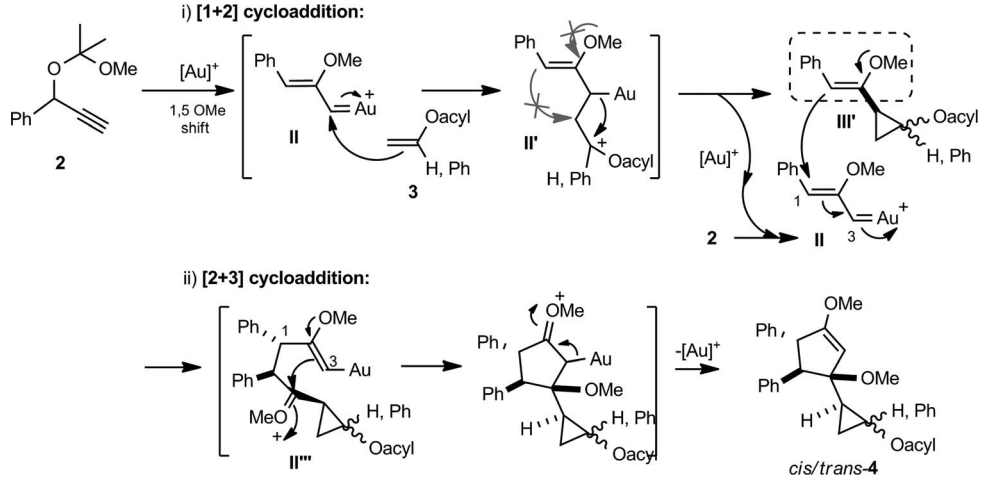
[a] The reactions were performed with **2a** (1 equiv.) and **3a** (3 equiv.) in solvent (approx. c = 90 mM) together with 5 mol-% gold catalyst at room temp. [b] Target molecules not detected (n.d.); polymerisation of THF at room temp.; no conversion at –78 °C. [c] Target molecules not detected (n.d.); hydrolysis into 1-phenylprop-2-yn-1-ol **1a** was observed by GC.

entry 5). A triphenylphosphane-based gold(I) catalyst (Table 1, entry 6) and gold(III) salts (Table 1, entries 7 and 8) resulted in full or partial hydrolysis into to the propargyl alcohol.

Proposed Mechanism

Based on our previous studies of regioselective cycloadditions of propargyl substrates,[8,9] the formation of tandem product **4** is proposed to take place by a two-step reaction. The general mechanism is shown for propargyl acetal **2** and vinyl ester **3** in Scheme 2.

Propargyl acetal **2** and vinyl ester **3** undergo an initial gold(I)-catalysed [1+2] cycloaddition reaction to give the cyclopropanation product (i.e., **III′**) by nucleophilic attack of the vinyl species on the gold carbenoid intermediate (i.e., **II**). The observed cyclopropyl products correspond to products formed in reactions of propargyl esters with vinyl esters or sulfonamides (Scheme 1, a).[8] The results of our previous studies indicate that propargyl acetals may be expected to undergo [2+3] cycloadditions with vinylic substrates (Scheme 1, b).[9] Nevertheless, we have also seen that the electronic nature of the vinylic reactants connected to a heteroatom may affect the reactivity and alter the reaction pathway and the outcome of propargyl cycloaddition reactions.[8–10] The unexpected cyclopropanation reaction that was found to be the favoured pathway for the reaction of propargyl acetals and vinyl esters may be a result of the presence of the electron-withdrawing ester moiety in adduct **II′** (Scheme 2). This is in contrast to the situation with vinylic compounds attached to an electron-releasing nitrogen or oxygen atom, which would enable stabilisation of an ammonium or oxonium cation intermediate **II′** (Scheme 1, b). Hence, electron-deficient vinylic compounds such as vinyl



Scheme 2. Proposed mechanism for gold(I)-catalysed tandem cyclisation reaction of propargyl acetals and vinyl esters.

esters may reduce the electron-releasing effect of the vinylic alkoxy group[9] in adduct **II′**. This would then decrease the tendency for the alkoxy group to promote a C-1 cyclisation that would result in pentaannulation. This electronic effect appears to make it more favourable for intermediate adduct **II′** to undergo cyclopropyl ring formation.

In contrast to the cyclopropyl products **III** previously obtained from propargyl esters (Scheme 1, a), product **III′** contains an activated vinyl ether moiety. Thus, intermediate **III′** may give rise to the new tandem reaction pathway by a subsequent cycloaddition reaction with gold carbenoid intermediates **II**, generated from a second unit of propargyl acetal **2**. However, in contrast to the "C-3–C-1" reaction sequence previously reported for the [2+3] cycloadditions of monosubstituted vinylic reactants (Scheme 1, b),[9] the opposite regioselectivity (i.e., a "C-1–C-3" reaction order) was observed, since the vinyl nucleophile (i.e., **III′**) attacks at the electrophilic allylic C-1 position of the second gold carbenoid complex (i.e., **II**) to give adduct **II′′′**. This change in regioselectivity may be due to the bulk of the 3-substituted vinyl ether **III′**. A similar "C-1–C-3" reaction order has been reported for [2+3] cycloaddition reactions of non-terminal propargyl acetals connected to an electron-withdrawing group, with aldehydes.[4]

The fact that a cyclopropyl intermediate **III′** (i.e., **3e**) was actually isolated from the reaction of the deactivated *p*-nitrophenylpropargyl acetal **2d** (see below; Table 2, entry 12) supports the proposed tandem mechanism.

Despite the formation of five stereogenic centres in product **4**, only one pair of *cis*/*trans* cyclopropyl diastereomers could be observed (Table 1), as the cyclopentenyl ring was formed in a diastereoselective 4,5-*trans* (Ph–Ph)/1,5-*cis* (OMe-Ph) /it>/*trans*-cyclopropanation[8] and stereoselective pentaannulation[9] reactions.

The overall outcome of the reaction is therefore the formation of tandem products *cis*/*trans*-**4** by two sequential cycloaddition reactions, involving two units of propargyl acetal **2** and one unit of vinyl ester **3**.

Reactivity

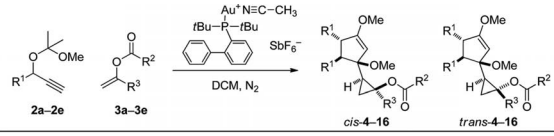
The tandem transformation was further studied by modifying the substrates and the reaction conditions. The results from the reactions of propargyl acetals **2a**–**2e** with vinylic esters **3a**–**3d** in the presence of $\{Au[P(tBu)_2(o\text{-biphenyl})CH_3CN]\}SbF_6$ in CH_2Cl_2 are presented in Table 2. The propargyl acetals gave the expected tandem cyclisation products (i.e., **4**–**16**), but the yields varied depending on the substituents on the propargyl acetal and the vinylic reactant. Additionally, the stability of the tandem products at room temperature appeared to vary, which could account for a reduction in the isolated yields. Temperature optimisation (room temp. to –78 °C) was carried out for each reaction, as complex mixtures of products were most often obtained at room temperature. The optimised reactions reached completion quickly (15–20 min), and moderate to high yields (39–77%; Table 2, entries 1, 2, 4, 5, 7, and 8) were generally obtained at –40 to –78 °C. This clearly demonstrates the ability of these highly reactive substrates to undergo tandem reactions. The corresponding tandem reactions with vinylsulfonamides were not as promising. With vinyltosylate (vinyl-OTs), propargyl substrates **2a** and **2c** gave two major products (as judged by TLC), but these were unstable, and they decomposed during work-up. Only low yields (up to 15%) of the unstable *cis* tandem products were obtained.

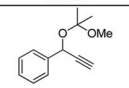
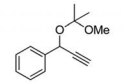
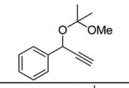
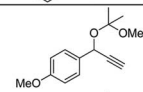
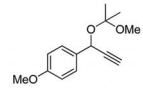
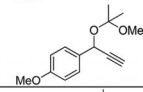
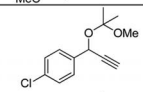
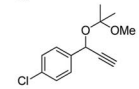
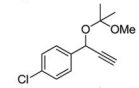
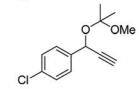
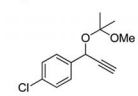
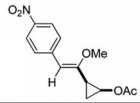
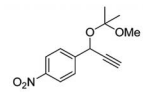
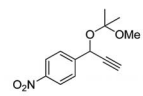
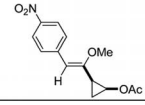
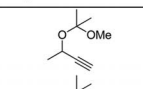
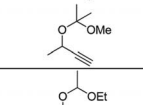
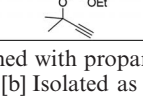
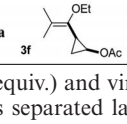
Aromatic propargyl acetals (**2a**–**2d**, up to 77% yields, Table 2, entries 1, 2, 5, 7, 8, 9, and 11) generally performed better than alkyl propargyl acetal **2e** (up to 15% yield, Table 2, entries 14 and 15). This demonstrates that benzylic stabilisation of the cationic gold intermediate is beneficial, but that it is not a requirement for the tandem cycloaddition. Bulky dimethyl propargyl substrate **2f** (Table 2, entry 16) failed to undergo the tandem cyclisation with vinyl acetate (**3a**), and only a minor compound (approx. 5%), which, by NMR spectroscopy, seemed to be cyclopropyl intermediate **3f**, was obtained. The difference in reactivity observed between dimethylpropargyl acetal **2f** and monomethyl substrate **2e** (Table 2, entry 14) may be explained by steric effects. Tandem cyclisations were also disfavoured by increasing the bulk of the vinyl ester substrates, as the reactivity dropped and the yields were reduced when further substituents were introduced onto the vinyl moiety (Me/**3c**; Ph/**3d**; Table 2, entries 3, 6, 9, and 10).

The presence of a *para* substituent on the aromatic propargyl acetals affected the reactivity and the outcome of the tandem reactions. Unsubstituted phenyl propargyl acetal **2a** gave good yields of the respective tandem products **4** and **5** (65–69%; Table 2, entries 1 and 2) in reactions with vinyl acetate (**3a**) and vinyl benzoate (**3b**) at –78 °C. Test reactions with the bulkier, but analogous ethyl acetal, PhCH(CCH)OCHMe(OEt), and vinyl benzoate (**3b**) indicated a slower reaction, but similar yields of the corresponding tandem product seemed to be formed.

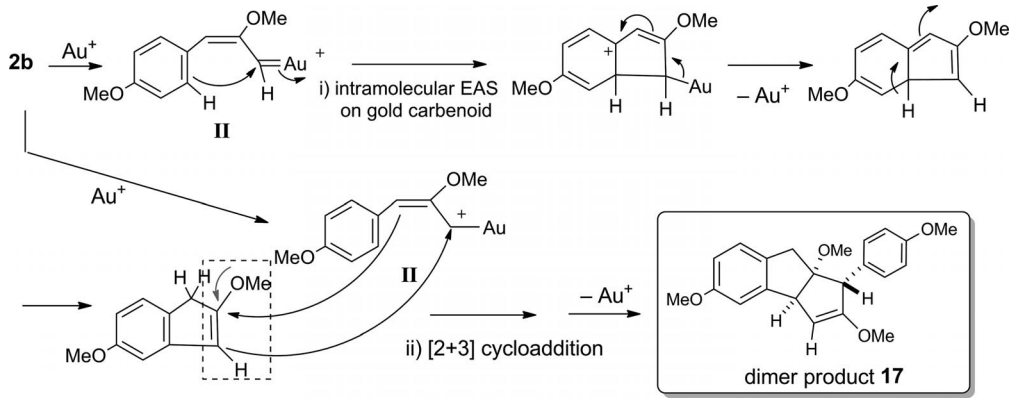
The presence of an electron-donating group in the propargyl substrate, such as the methoxy functionality in **2b**, would make it less electrophilic, and so make the nucleophilic attack of the vinyl species on the gold carbenoid intermediates **II** in both steps of the tandem cyclisation less favourable (Scheme 2). Consistent with this hypothesis, we observed decreased yields of tandem products **6** and **7** (39–49%; Table 2, entries 4 and 5) from *p*-OMe-phenylpropargyl acetal **2b** and vinyl esters **3a** and **3b**. Furthermore, a propargyl acetal dimer **17** was formed in the reactions carried out at room temperature (Table 2, entries 4 and 5; footnote [h]). Significant amounts of the dimer were formed (GLC, TLC), but it was unstable both during flash chromatography and in deuterated solvents. Attempts to prepare larger amounts of dimer **17** by separate dimerisation of propargyl acetal **2b** resulted in the formation of only small amounts of **17** (< 5%), which could be used for characterisation and structural elucidation. A possible tandem dimerisation reaction pathway, based on an intramolecular electrophilic aromatic substitution promoted by the

Table 2. Gold(I)-catalysed tandem cyclisation reactions of propargyl acetals and vinyl esters.[a]



Entry	Acetal		Alkene		Product	*T* [°C]	*t* [min]	Ratio *cis*/*trans*	Yield [%]
1		**2a**		**3a**	**4**	20	15	60:40	54
						0	15	62:38	45
						–40	15	50:50	54
						–78	**15**	**50:50**	**69**[b]
2		**2a**		**3b**	**5**	20	25	–	0
						0	25	31:69	29
						–30	25	63:27	38
						–40	25	45:55	62
						–78	**20**	**48:52**	**65**
3		**2a**		**3d**	_[c]	–40 to 0	45	17:83	<18[c]
4		**2b**		**3a**	**6**	20	15	85:15	29[b,h]
						–40	**30**	**87:13**	**39**[b]
						–78	120	83:17	36[b]
5		**2b**		**3b**	**7**	20	15	67:33	45[c,h]
						–40	**30**	**67:33**	**49**[b]
						–78	120	67:33	53[b]
6		**2b**		**3d**	**8**	–40 to 0	45	25:75	19[b,c]
7		**2c**		**3a**	**9**	20	9	73:27	56
						–40	**15**	**58:42**	**77**
						–78	30	57:43	46
8		**2c**		**3b**	**10**	20	18	64:36	44
						–40	**15**	**54:46**	**72**[b]
						–78	120	48:52	61
9		**2c**		**3c**	**11**	**20**	**15**	**75:25**	**<53**[b,c]
10		**2c**		**3d**	**12**	–40 to 0	45	44:55	17[c]
11		**2c**		**3e**	**13**	**–40**	**30**	**58:42**	**77**[d]
12		**2d**		**3a**	**14** + **3e**	**20**	**120**	**58:42**	**14** (62)[b,e]
						–40	15	68:32 100:0	**14** (58)[a] **3e** (20)
						–40	15	44:56 100:0	**14** (43) **3e** (40)[f]
						–78	15	100:0	**14** (0) **3e** (16)
13		**2d**		**3e**	**14**	–40 to r.t.	**120**	**52:48**	**65**[g]
14		**2e**		**3a**	**15**	20	15	67:33	<15[c]
						0	15	78:22	14
						–40 to 0	120	60:40	15[b]
15		**2e**		**3b**	**16**	0–20	30	100:0	5
16		**2f**		**3a**	 **3f**	20	15	100:0	5

[a] The reactions were performed with propargyl acetals **2a**–**2d** (1 equiv.) and vinyl esters **3a**–**3d** (3 equiv.) in CH_2Cl_2 ($c \approx 90$ mM) together with gold catalyst (5 mol-%). [b] Isolated as a mixture, which was separated later for full characterisation of the diastereomers, or as a combination of pure products and mixtures. [c] Purification and characterisation was not possible for all or some of the products; *cis*/*trans* ratio was calculated from the ^{1}H NMR spectrum of the crude product mixture based on a comparison of chemical shift values of similar products. [d] A 10% excess of acetal **2c** relative to intermediate **3e** was used; see the Exp. Sect. for details. [e] Ratio of acetal **2d**/alkene **3a** = 2:1; see the Exp. Sect. for details. [f] Ratio of acetal **2d**/alkene **3a** = 1:10; see the Exp. Sect. for details. [g] The preparation of product **14** could alternatively be carried out separately from acetal **2d** and intermediate **3e** (10% excess); see the Exp. Sect. for details. [h] Dimer **17** (2–4%) was isolated.



Scheme 3. Possible mechanism for tandem dimerisation of *p*-methoxyphenylpropargyl acetal **2b** (EAS = electrophilic aromatic substitution).

p-OMe substituent of the phenyl group, followed by [2+3] cycloaddition activated by the vinyl ether moiety of the intermediate, is shown in Scheme 3. The final [2+3] cycloaddition took place in a stereoselective manner, as shown by the relative stereochemistry (NOESY NMR spectra) of dimer **17**, which is consistent with previous observations.[9] The *cis* relationship of the OMe and Ph substituents on the pentenyl ring of dimer **17**, which is established in the final [2+3] cycloaddition, is also consistent with the corresponding 1,5-*cis* OMe/Ph configuration of tandem products **4**–**14**. The lower yields of tandem products **6** and **7** seem to be caused by the competing formation of dimer **17**, indicating that the nucleophilicity of vinyl esters **3a** and **3b** is insufficient to favour attack on the less electrophilic gold intermediate **II** (Scheme 2) and lead to the formation of tandem compounds **6** and **7** as the major products.

An electron-withdrawing chloride substituent (as in **2c**) should increase the electrophilicity of gold intermediate **II**. The higher yields obtained of the corresponding tandem products **9** and **10** (77–72%; Table 2, entries 7 and 8) demonstrate that an electron-withdrawing group on the phenyl ring does tend to favour the tandem cycloaddition reaction pathway. The electron-withdrawing chloride substituent allows an easier nucleophilic attack on the gold(I) carbenoid complex **II** by vinyl esters **3a** and **3b**, as well as by vinyl ether intermediates **III′** in both the cycloaddition steps (Scheme 2).

We thought that an electron-withdrawing *p*-nitro substituent could assist in activating the gold intermediate in the same way, and so allow easy nucleophilic attack of the vinyl species. On the other hand, the second [2+3] cycloaddition step might be hampered, since the cyclopropyl vinyl ether intermediate **III′** (Scheme 2) would be deactivated by the *p*-nitrophenyl moiety, and its nucleophilicity would be strongly decreased. The most successful reaction conditions discussed above were tested for the reactions of nitro derivative **2d** and vinyl acetate (**3a**). Both tandem product **14** (58%) and intermediate **3e** (20%) were produced at –40 °C (Table 2, entry 12, line 2). At –78 °C, the reaction failed to give any of the tandem product, and only intermediate **3e** (16%, Table 2, entry line 4) could be isolated. Addition of further amounts of **2d** (**2d**/**3a** = 2:1; standard ratio = 1:3) to a reaction carried out at room temperature resulted in the consumption of intermediate **3e**, but only a slight increase in the yields of tandem product **14** was observed (62%, Table 2, entry 12, line 1). By using a large excess of the vinyl reactant (**2d**/**3a** = 1:10, –40 °C, Table 2, entry 12, line 3), a 40% yield of intermediate **3e** was isolated, which could be used in a separate new reaction with acetal **2d** (Table 2, entry 13) or with a different propargyl reactant in the second step of the tandem reaction. Thus, the reaction of intermediate **3e** with *p*-Cl-phenyl propargyl acetal **2c** (10 mol-% excess of **2c**) gave a high yield of mixed *p*-NO_2/*p*-Cl tandem product **13** (76%; Table 2, entry 11). This demonstrates how the different effects of the electron-withdrawing nitro group, i.e., activating for nucleophilic attack but deactivating for the second step in the tandem cyclisation, can be used strategically to lead to a selective cyclopropanation, and so provide the possibility of introducing two different *para* phenyl substituents in mixed tandem products.

Tandem products **4**–**16** were formed as mixtures of two diastereomers (Table 1) in the *cis*/*trans*-cyclopropanation[8] and stereoselective pentaannulation[9] reactions. Due to challenging chromatographic separations, the isolation of each diastereomer was sometimes demanding. A slight preference for the formation of the *cis* isomer was observed, as had previously been seen for the cyclopropylations of propargyl substrates,[8] and consistent with the assumption that the cyclopropanation is controlled by the bulkier vinylic substituent.[5] However, varying the vinyl ester (OAc, OBz) gave no significant difference in the isomeric ratios of the products. In general, diastereomeric ratios were fairly low (*dr* approx. 20–50), being lower when reactivity and yields were higher. The only reaction that gave a significantly higher diastereoselectivity was the reaction between deactivated methoxypropargyl substrate **2b** and vinyl acetate (**3a**). The tandem product (i.e., **6**; up to 39%) was formed with a consistent diastereoselectivity (*dr* approx. 70; Table 2, entry 4) over all temperatures.

Conclusions

To contribute to a better understanding of the chemistry of propargyl acetals in the presence of gold(I), we have studied chemoselective gold(I)-catalysed cycloadditions of propargyl acetals **2a**–**2e** and vinyl esters **3a**–**3e**. We have found that that such substrates follow a new tandem cyclisation pathway.

Although the propargyl acetals were expected to undergo a gold(I)-catalysed [2+3] cycloaddition with vinyl substrates,[9] the propargyl acetals and vinyl acetates studied here were found to undergo an initial [1+2] cycloaddition reaction to give *cis*-/*trans*-cyclopropanation intermediates **III** by nucleophilic attack of the vinyl species at propargyl-generated gold(I) carbenoid intermediates **II**. This different chemoselectivity may be explained by the relatively electron-poor nature of the vinyl acetates, and this demonstrates how varying the electronic nature of the vinylic reactant can change the outcome of gold(I)-catalysed alkene–propargyl cycloadditions.

With its activated vinyl ether moiety, intermediate **III** may undergo a subsequent [2+3] cycloaddition with gold carbenoid intermediates **II**, in which an additional pentenyl ring is stereoselectively formed by a "C-1–C-3" cyclisation pathway. The standard "C-3–C-1" would be the expected reaction order,[9] and the observed "C-1–C-3"regioselectivity may be explained by the bulk of vinyl intermediate **III**.

The overall outcome of the reactions was therefore the formation of *cis*/*trans*-cyclopropyl–cyclopentenyl tandem products **4**–**16** by two sequential cycloaddition reactions, involving two units of propargyl acetals **2a**–**2e** and one unit of vinyl esters **3a**–**3e**. The highest tandem reactivity was observed for propargyl substrates with a moderately electron-withdrawing group (Cl) or with no substituent at the *para* position of the phenyl moiety. Strongly electron-withdrawing groups, or electron-donating groups, such as nitro and methoxy groups, hamper selective parts of the tandem process, resulting in a lower overall tandem reactivity.

The vinylic alkoxy group in cyclopropane intermediate **III**, which activates it for the final cycloaddition with a second unit of gold(I) carbenoid intermediate **II**, is the key prerequisite of this tandem reaction, which enables the construction of polysubstituted and highly functionalised bicyclic compounds.

Experimental Section

General Methods: All reactions were performed under a nitrogen atmosphere. Commercial grade reagents were used as received. 1-Phenylvinyl acetate was synthesised following a literature procedure.[11] Dry solvents were collected from a solvent-purification system. All reactions were monitored by GC and by thin-layer chromatography (TLC) using silica gel 60 F254 plates (0.25 mm thickness). Flash chromatography was carried out using silica gel 60 (0.040–0.063 mm). High-Throughput Flash Purification (HPFP) was carried out using pre-packed cartridges. ^{1}H and ^{13}C NMR spectra were recorded using 300 or 400 MHz spectrometers. Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane, which was used as an internal standard. Coupling constants (J) are reported in Hertz (Hz). The assignments of the chemical shifts were determined using COSY, HMQC, HMBC, and NOESY experiments. Melting points (m.p.) were determined using a Stuart apparatus. Accurate mass determination in either positive or negative mode was performed with a "Synapt G2-S" Q-TOF instrument from Waters. Samples were ionised with an ASAP probe, and no chromatographic separation was used before the mass analysis. IR spectra were obtained using a Smart Endurance reflection cell.

Preparation of the Propargyl Acetals: Propargyl acetals were synthesised following a modified procedure starting from the appropriate aldehyde or propargyl alcohol (compounds **1**).[4,12] Propargyl acetal **2f** was synthesised following a literature procedure.[9]

{1-[(2-Methoxypropan-2-yl)oxy]prop-2-yn-1-yl}benzene (2a): A mixture of 1-phenylprop-2-yn-1-ol (213.5 mg, 1.615 mmol) and 2-methoxypropene (10.0 mL, 104 mmol) was cooled to 0 °C, then pyridinium *p*-toluenesulfonate (catalytic amount) was added. The cooling bath was removed, and the mixture was stirred at room temperature for 4 h. The mixture was diluted with CH_2Cl_2 (20 mL), washed with water (3 × 20 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (1:50 EtOAc/pentane) to give **2a** (266.0 mg, 81%) as a colourless oil. R_f = 0.78 (1:10 EtOAc/pentane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.47 (m, 2 H, H_{arom}), 7.38–7.7.26 (m, 3 H, H_{arom}), 5.42 (d, J = 2.2 Hz, 1 H, CHC≡), 3.18 (s, 3 H, OCH_3), 2.53 (d, J = 2.3 Hz, 1 H, C≡CH), 1.54 (s, 3 H, CCH_3) 1.33 (s, 3 H, CCH_3) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 140.3 (1 C, C_{arom}), 128.5 (2 C, CH_{arom}), 128.0 (1 C, CH_{arom}), 126.9 (2 C, CH_{arom}), 101.9 (1 C, $OCOCH_3$), 84.5 (1 C, CHC≡), 73.7 (1 C, ≡CH), 62.6 (1 C, CHC≡) 49.5 (1 C, OCH_3), 25.4 (1 C, CCH_3), 24.9 (1 C, CCH_3) ppm. ^{1}H and ^{13}C NMR spectroscopic data are consistent with literature data.[9]

1-(4-Methoxyphenyl)prop-2-yn-1-ol (1b): A solution of ethynylmagnesium bromide (0.50 M in THF; 19.0 mL, 9.5 mmol) was cooled to –20 °C. A solution of 4-methoxybenzaldehyde (1.0336 g, 7.5916 mmol) in dry THF (1.5 mL) was added, and the flask was washed out with further THF (0.5 mL), which was added to the reaction mixture. The cooling bath was removed, and the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched by the addition of saturated aqueous ammonium chloride (10 mL), and the mixture was extracted with Et_2O (2 × 20 mL). The combined organic layers were dried with Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (1:3 EtOAc/pentane) to give **1b** (1.113 g, 90%) as a pale yellow oil. R_f = 0.31 (1:3 EtOAc/pentane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.46 (m, 2 H, H_{arom}), 6.93–6.90 (m, 2 H, H_{arom}), 5.43 (dd, J = 6.2, 2.1 Hz, CHC≡), 3.82 (s, 3 H, OCH_3), 2.66 (d, J = 2.2 Hz, ≡CH), 2.10 (d, 6.2 Hz, OH) ppm. ^{1}H NMR spectroscopic data are consistent with literature data.[13]

1-Methoxy-4-{1-[(2-methoxypropan-2-yl)oxy]prop-2-yn-1-yl}benzene (2b): A mixture of **1b** (1.113 g, 6.862 mmol) and 2-methoxypropene (25.0 mL, 261 mmol) was cooled to 0 °C, then pyridinium *p*-toluenesulfonate (catalytic amount) was added. The cooling bath was removed, and the mixture was stirred at room temperature for 90 min. The mixture was diluted with dichloromethane (100 mL), washed with water (3 × 100 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (gradient 1:50 to 1:20 EtOAc/pentane) to give **2b** (1.217 g, 76%) as a colourless oil. R_f = 0.57 (1:5 EtOAc/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.7 Hz, 2 H, H_{arom}), 6.89 (d, J = 8.8 Hz, 2 H, H_{arom}), 5.37 (d, J = 2.2 Hz, 1

H, C*H*C≡), 3.80 (s, 3 H, PhOCH_3), 3.18 (s, 3 H, COCH_3), 2.54 (d, *J* = 2.2 Hz, 1 H, C≡C*H*) 1.53 (s, 3 H, CCH_3), 1.33 (s, 3 H, CCH_3) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 159.4 (1 C, C_{arom}), 132.5 (1 C, C_{arom}), 128.3 (2 C, CH_{arom}), 113.9 (2 C, CH_{arom}), 101.8 (1 C, O*C*OCH$_3$), 84.7 (1 C, CH*C*≡), 73.5 (1 C, ≡*C*H), 62.2 (1 C, *C*HC≡) 55.3 (1 C, PhO*C*H$_3$), 49.5 (1 C, O*C*H$_3$), 25.4 (1 C, C*C*H$_3$), 25.0 (1 C, C*C*H$_3$) ppm. IR (thin film): $\tilde{\nu}$ = 3286, 2991, 1463, 1209, 968, 826, 637 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_{18}O_3$ 234.1250; found 234.1250.

1-(4-Chlorophenyl)prop-2-yn-1-ol (1c): A solution of ethynylmagnesium bromide (0.50 M in THF; 18 mL, 9.0 mmol) was cooled to –20 °C. A solution of 4-chlorobenzaldehyde (1.0105 g, 7.19 mmol) in THF (2.5 mL) was added, and the flask washed out with more THF (0.5 mL), which was then added to the reaction mixture. The cooling bath was removed, and the reaction mixture was stirred at room temperature for 5 min. The reaction was quenched by the addition of saturated aqueous ammonium chloride (10 mL), and the mixture was extracted with Et_2O (2× 20 mL). The combined organic extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (gradient 1:10–1:3 EtOAc/pentane) to give **1c** (1.078 g, 90%) as a pale yellow oil. R_f = 0.47 (1:3 EtOAc/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.48 (m, 2 H, H_{arom}), 7.38–7.35 (m, 2 H, H_{arom}), 5.45 (dd, *J* = 6.1, 2.1 Hz, CHC≡), 2.68 (d, *J* = 2.2 Hz, ≡CH), 2.21 (d, *J* = 6.1 Hz, OH) ppm. ^{1}H NMR spectroscopic data are consistent with literature data.[14]

1-Chloro-4-{1-[(2-methoxypropan-2-yl)oxy]prop-2-yn-1-yl}benzene (2c): A mixture of **1c** (1.078 g, 6.47 mmol) and 2-methoxypropene (20.0 mL, 209 mmol) was cooled to 0 °C, then pyridinium *p*-toluenesulfonate (catalytic amount) was added. The cooling bath was removed, and the mixture was stirred at room temperature for 2 h. The mixture was diluted with dichloromethane (100 mL), washed with water (3× 100 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (1:30 EtOAc/pentane) to give **2c** (1.3234 g, 86%) as a colourless oil. R_f = 0.28 (1:30 EtOAc/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.4 Hz, 2 H, H_{arom}), 7.33 (d, *J* = 8.5 Hz, 2 H, CH_{arom}), 5.39 (d, *J* = 2.2 Hz, 1 H, CHC≡), 3.17 (s, 3 H, OCH$_3$), 2.54 (d, *J* = 2.2 Hz, 1 H, C≡CH), 1.53 (s, 3 H, CCH$_3$), 1.32 (s, 3 H, CCH$_3$) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 138.9 (1 C, C_{arom}), 133.8 (1 C, C_{arom}), 128.7 (2 C, CH_{arom}), 128.2 (2 C, CH_{arom}), 102.0 (1 C, O*C*OCH$_3$), 84.0 (1 C, CH*C*≡), 74.0 (1 C, ≡CH), 61.9 (1 C, *C*HC≡), 49.5 (1 C, OCH$_3$), 25.4, (1 C, C*C*H$_3$), 24.9 (1 C, C*C*H$_3$) ppm. IR (thin film): $\tilde{\nu}$ = 3296, 1210, 1146, 1092, 842, 633 cm^{-1}. HRMS (EI): calcd. for $C_{12}H_{11}OCl$ [M – CH_4O]$^+$ 206.0493; found 206.0490.

1-(4-Nitrophenyl)prop-2-yn-1-ol (1d): A solution of ethynylmagnesium bromide (0.50 M in THF; 16 mL, 8.0 mmol) was cooled to –20 °C. A solution of 4-nitrobenzaldehyde (1.0296 g, 6.8135 mmol) in THF (10 mL) was added, and the flask was washed out with THF (a total of 5 mL), which was then added to the reaction mixture. The cooling bath was removed, and the reaction mixture was stirred at room temperature for 30 min. The reaction was quenched by the addition of saturated aqueous ammonium chloride (10 mL), and the mixture was diluted with Et_2O (50 mL), water (25 mL), and EtOAc (50 mL). The phases were separated, and the aqueous phase was extracted with EtOAc (50 mL). The combined organic extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (1:4 EtOAc/pentane) to give **1d** (1.1091 g, 92%) as a pale yellow oil. R_f = 0.17 (1:4 EtOAc/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27–8.23 (m, 2 H, H_{arom}), 7.75–7.73 (m, 2 H, H_{arom}), 5.58 (dd, *J* = 5.9, 2.2 Hz, CHC≡), 2.74 (d, *J* = 2.2 Hz, ≡CH), 2.43 (d, *J* = 5.8 Hz, OH) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 147.9 (1 C, C_{arom}), 146.6 (1 C, C_{arom}), 127.3 (2 C, CH_{arom}), 123.8 (2 C, CH_{arom}), 82.3 (1 C, C≡), 76.0 (1 C, ≡CH), 63.3 (1 C, C-OH) ppm. ^{1}H and ^{13}C NMR spectroscopic data are consistent with literature data.[15]

1-{1-[(2-Methoxypropan-2-yl)oxy]prop-2-yn-1-yl}-4-nitrobenzene (2d): A mixture of **1d** (1.1091 g, 6.26 mmol) and 2-methoxypropene (20.0 mL, 209 mmol) was cooled to 0 °C, then pyridinium *p*-toluenesulfonate (catalytic amount) was added. The cooling bath was removed, and the mixture was stirred at room temperature for 1 h. The mixture was diluted with dichloromethane (100 mL), washed with water (3× 100 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (1:50 EtOAc/pentane) to give **2d** (1.335 g, 86%) as a colourless oil. R_f = 0.10 (1:50 EtOAc/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24–8.22 (m, 2 H, H_{arom}), 7.69 (m, 2 H, CH_{arom}), 5.52 (d, *J* = 2.2 Hz, 1 H, CHC≡), 3.18 (s, 3 H, OCH$_3$), 2.58 (d, *J* = 2.3 Hz, 1 H, C≡CH), 1.56 (s, 3 H, CCH$_3$), 1.34 (s, 3 H, CCH$_3$) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 147.6 (1 C, C_{arom}-NO_2), 147.3 (1 C, C_{arom}), 127.5 (2 C, CH_{arom}), 123.8 (2 C, CH_{arom}), 102.2 (1 C, O*C*OCH$_3$), 83.1 (1 C, CH*C*≡), 74.7 (1 C, ≡CH), 61.6 (1 C, *C*HC≡), 49.6 (1 C, OCH$_3$), 25.3, (1 C, C*C*H$_3$), 24.8 (1 C, C*C*H$_3$) ppm. IR (thin film): $\tilde{\nu}$ = 3257, 2992, 2940, 2857, 1517, 1343, 1211, 1186, 1145, 1030, 852, 701 cm^{-1}. HRMS (EI): calcd. for [M – CH_3O]$^+$ 218.0817; found 218.0815.

3-[(2-Methoxypropan-2-yl)oxy]but-1-yne (2e): A mixture of 3-butyn-2-ol (513.0 mg, 7.319 mmol) and 2-methoxypropene (10.0 mL, 104 mmol) was cooled to 0 °C, then pyridinium *p*-toluenesulfonate (catalytic amount) was added. The cooling bath was removed, and the mixture was stirred at room temperature for 1 h. The mixture was diluted with diethyl ether (25 mL), washed with water (3× 25 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (1:20 Et_2O/pentane) to give **2e** (668.6 mg, 64%) as a colourless oil. R_f = 0.58 (1:20 Et_2O/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.49 (dq, *J* = 6.7, 2.0 Hz, 1 H, CHC≡), 3.24 (s, 3 H, OCH$_3$), 2.36 (d, *J* = 2.0 Hz, 1 H, ≡CH), 1.45 (s, 3 H, CCH$_3$), 1.43 (d, *J* = 6.7 Hz, 3 H, CH$_3$CC≡), 1.36 (s, 3 H, CCH$_3$) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 101.1 (1 C, O*C*OCH$_3$), 86.1 (1 C, CH*C*≡), 71.3 (1 C, ≡CH), 56.3 (1 C, *C*HC≡), 49.1 (1 C, OCH$_3$), 25.4 (1 C, MeOC*C*H$_3$), 24.6 (1 C, MeOC*C*H$_3$), 23.4 (1 C, CH*C*H$_3$) ppm. ^{1}H and ^{13}C NMR spectroscopic data are consistent with literature data.[9]

Tandem Cyclisation Reactions

General Procedure: The gold catalyst ({Au[P(*t*Bu)$_2$(*o*-biphenyl)-CH$_3$CN]}SbF$_6$, 5 mol-%) was dissolved in dry CH_2Cl_2 (1.5 mL), and the solution was stirred under a nitrogen atmosphere at the required temperature. The appropriate propargyl acetal (compounds **1a**–**1d**) and vinyl ester or alkene (3 equiv.) were dissolved in dry CH_2Cl_2 (1.0 mL), and this solution was added to the solution of the gold catalyst. The flask was washed out with further dry CH_2Cl_2 (2× 0.5 mL), and this was added to the mixture. When the acetal had been consumed, the reaction was quenched with NEt_3 (5 drops), the mixture was filtered through Celite™, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography using an appropriate eluent system to give the desired tandem products.

***cis*-/*trans*-2-(1,3-Dimethoxy-4,5-diphenylcyclopent-2-en-1-yl)cyclopropyl Acetate (*cis*-/*trans*-4):** Compounds ***cis*-4** and ***trans*-4** were synthesised following the general procedure, using gold catalyst (13.0 mg, 16.8 μmol), compound **2a** (73.5 mg, 360 μmol), and vinyl acetate (85.1 mg, 989 μmol), at –78 °C for 15 min. The products

were purified using an eluent system of 1:20 EtOAc/pentane to give a 1:1 mixture of compounds ***cis*-4** and ***trans*-4** (47.2 mg, 69%) as a yellow oil.

Data for ***cis*-4**: R_f = 0.36 (1:10 EtOAc/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.26 (m, 10 H, H_{arom}), 4.85 (dd, J = 2.3, 1.5 Hz, 1 H, C=CH), 4.44 (s, 1 H, C=C*H*CH), 4.06 (d, J = 1.2 Hz, 1 H, C=CHC*H*), 4.00 (dt, J = 7.1, 4.2 Hz, 1 H, C*H*OAc), 3.70 (s, 3 H, C=COCH$_3$), 3.04 (s, 3 H, C=CHCOC*H*$_3$), 2.09 (s, 3 H, COOCH$_3$), 0.91 (ddd, J = 8.2, 6.6, 4.2 Hz, 1 H, AcOCHC*H*$_2$), 0.81 (dt, J = 10.2, 6.8 Hz, 1 H, AcOCHC*H*$_2$), 0.39 (ddd, J = 10.2, 8.2, 7.2 Hz, 1 H, AcOCHC*H*) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 171.2 (1 C, OC=O), 159.7 (1 C, C=*C*OCH$_3$), 141.2 (1 C, *C*$_{arom}$CHCHC=), 137.6 (1 C, *C*$_{arom}$CHC=), 129.7 (2 C, *o*-CH$_{arom}$), 129.4 (2 C, *o*-CH$_{arom}$), 128.0 (2 C, *m*-CH$_{arom}$), 127.8 (2 C, *m*-CH$_{arom}$), 126.9 (1 C, *p*-CH$_{arom}$), 126.4 (1 C, *p*-CH$_{arom}$), 99.7 (1 C, C=*C*H), 86.8 (1 C, C=CH*C*OCH$_3$), 60.3 (1 C, C=CHCH), 56.7 (=CO*C*H$_3$), 53.2 (1 C, *C*HOAc), 53.1 (1 C, C=CH*C*H), 51.8 (1 C, C=CHCO*C*H$_3$), 21.7 (1 C, OOC*C*H$_3$), 21.2 (1 C, *C*HCHOAc), 9.2 (1 C, *C*H$_2$CHOAc) ppm. IR (thin film): $\tilde{\nu}$ = 3034, 2940, 2826, 1742, 1228, 701 cm^{-1}. HRMS (EI): calcd. for $C_{24}H_{26}O_4$ [M]$^+$ 378.1831; found 378.1828.

Data for ***trans*-4**: R_f = 0.32 (1:10 EtOAc/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.37 (m, 2 H, H_{arom}), 7.32–7.20 (m, 8 H, H_{arom}), 4.66 (t, J = 2.0 Hz, 1 H, C=CH), 4.46 (dt, J = 7.4, 4.0 Hz, 1 H, C*H*OAc), 4.17 (br. s, 1 H, C=C*H*CH), 4.01 (br. s, 1 H, C=CHC*H*), 3.60 (s, 3 H, C=COCH$_3$), 2.47 (s, 3 H, C=CHCOC*H*$_3$), 2.10 (s, 3 H, COOCH$_3$), 1.47–1.36 (m, 2 H, AcOCHC*H*$_2$ and AcOCHC*H*), 1.17–1.11 (m, 1 H, AcOCHC*H*$_2$) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 171.6 (1 C, C=O), 159.1 (1 C, *C*=CH), 141.3 (1 C, C=CHCH*C*$_{arom}$), 137.8 (1 C, C=CH*C*$_{arom}$), 130.9 (2 C, C=CHCHC*C*H$_{arom}$), 129.8 (2 C, C=CHC*C*H$_{arom}$), 127.7 (2 C, *m*-CH$_{arom}$), 127.4 (2 C, *m*-CH$_{arom}$), 126.6 (1 C, *p*-CH$_{arom}$), 126.2 (1 C, *p*-CH$_{arom}$), 97.5 (1 C, C=CH), 84.9 (1 C, CH$_3$O*C*H), 58.0 (1 C, Ph*C*H), 57.3 (1 C, Ph*C*H), 56.5 (1 C, *C*H$_3$OC=), 52.3 (1 C, *C*H$_3$OCH), 51.9 (1 C, AcO*C*H), 24.5 (1 C, AcOCH*C*H), 20.8 (1 C, OCO*C*H$_3$), 9.2 (1 C, CH$_2$) ppm. IR (thin film): $\tilde{\nu}$ = 3023, 2935, 2826, 1745, 1227, 1035, 701 cm^{-1}. HRMS (EI): calcd. for $C_{23}H_{23}O_3$ [M – CH$_3$O]$^+$ 347.1647; found 347.1647.

***cis*-/*trans*-2-(1,3-Dimethoxy-4,5-diphenylcyclopent-2-en-1-yl)cyclopropyl Benzoate (*cis*-/*trans*-5):** Compounds ***cis*-5** and ***trans*-5** were synthesised following the general procedure, using gold catalyst (13.2 mg, 16.8 μmol), compound **2a** (68.2 mg, 334 μmol), and vinyl benzoate (152.0 mg, 1.03 mmol), at –78 °C for 20 min. The products were purified using an eluent system of 1:1 CH_2Cl_2/pentane then CH_2Cl_2 to give ***cis*-5** (25.7 mg, 34%) as a colourless solid and ***trans*-5** (23.0 mg, 31%) as a yellow oil.

Data for ***cis*-5**: R_f = 0.57 (CH_2Cl_2), m.p. 154–158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (dd, J = 8.3, 1.3 Hz, 2 H, CH$_{o\text{-OBz}}$), 7.59 (t, J = 7.4 Hz, 1 H, CH$_{p\text{-OBz}}$), 7.46 (t, J = 7.7 Hz, 2 H, CH$_{m\text{-OBz}}$), 7.23–7.35 (m, 10 H, CH$_{arom}$), 4.99 (dd, J = 2.2, 1.3 Hz, 1 H, C=CH), 4.40 (s, 1 H, C=C*H*CH), 4.17 (s, 1 H, C=CHC*H*), 4.08 (dt, J = 7.1, 4.2 Hz, CHOBz), 3.73 (s, 3 H, C=COCH$_3$), 3.16 (s, 3 H, C=CHCOC*H*$_3$), 1.11 (ddd, J = 8.1, 6.4, 4.2 Hz, 1 H, CH$_2$), 0.97 (dt, J = 10.1, 6.7 Hz, 1 H, CH$_2$) 0.58 (ddd, J = 10.1 8.2, 7.1 Hz, 1 H, BzOCHC*H*) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 167.2 (1 C, C=O), 160.2 (1 C, C=*C*OCH$_3$), 140.6 (1 C, *C*$_{arom}$CHCHC=), 137.7 (1 C, *C*$_{arom}$CHC=), 133.1 (1 C, CH$_{p\text{-OBz}}$), 130.3 (1 C, C$_{arom\text{-OBz}}$), 129.6 (2 C, CH$_{o\text{-OBz}}$), 129.5 (1 C, CH$_{arom}$), 129.1 (2 C, CH$_{arom}$), 128.4 (2 C, CH$_{m\text{-OBz}}$), 128.1 (2 C, CH$_{arom}$), 127.7 (2 C, CH$_{arom}$), 127.0 (1 C, C$_{arom}$), 126.4 (2 C, CH$_{arom}$), 99.3 (1 C, C=*C*H), 86.2 (1 C, C=CH*C*OCH$_3$), 59.8 (1 C, C=*C*HCH), 56.8 (=CO*C*H$_3$), 54.5 (1 C, C=CH*C*H), 53.5 (1 C, *C*HOBz), 52.0 (1 C, C=CHCO*C*H$_3$), 22.9 (1 C, *C*HCHOBz), 9.1 (1 C, CH$_2$) ppm. IR (neat): $\tilde{\nu}$ = 2927, 1722, 1644, 1452, 1272, 709 cm^{-1}. HRMS (EI): calcd. for $C_{29}H_{28}O_4$ [M]$^+$ 440.1982; found 440.1979.

Data for ***trans*-5**: R_f = 0.64 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 7.2 Hz, 2 H, CH$_{o\text{-OBz}}$), 7.56 (t, J = 7.4 Hz, 1 H, CH$_{p\text{-OBz}}$), 7.45–7.40 (m, 2 H, CH$_{m\text{-OBz}}$), 7.34–7.23 (m, 10 H, CH$_{arom}$), 4.70 (dt, J = 7.0, 4.6 Hz, 1 H, CHOBz), 4.55 (t, J = 1.9 Hz, 1 H, C=C*H*), 4.34 (s, 1 H, C=C*H*), 4.09 (s, 1 H, C=CHC*H*), 3.23 (s, 3 H, C=COC*H*$_3$), 2.46 (s, 3 H, C=CHCOC*H*$_3$), 1.63 (m, 1 H, BzOCHC*H*$_2$), 1.59 (m, 1 H, BzOCHC*H*), 1.28 (m, 1 H, BzOCHC*H*$_2$) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 167.3 (1 C, O*C*=O), 158.8 (1 C, C=*C*OCH$_3$), 141.4 (1 C, *C*$_{arom}$CHC=), 137.9 (1 C, *C*$_{arom}$CHCHC=), 133.2, (1 C, CH$_{p\text{-OBz}}$), 130.7 (2 C, CH$_{arom}$), 130.0 (1 C, OCO*C*$_{arom\text{-OBz}}$), 129.6 (2 C, CH$_{o\text{-OBz}}$), 129.6 (1 C, CH$_{arom}$), 128.4 (2 C, CH$_{m\text{-OBz}}$), 127.8 (2 C, CH$_{arom}$), 127.4 (2 C, CH$_{arom}$), 126.6 (2 C, CH$_{arom}$), 126.2 (1 C, CH$_{arom}$), 97.6 (1 C, C=*C*H), 84.9 (1 C, C=CH*C*OCH$_3$), 59.3 (1 C, C=CHCH), 56.5 (1 C, C=CH*C*H), 56.2 (1 C, C=CO*C*H$_3$), 52.4 (1 C, CH*C*OCH$_3$), 51.9 (1 C, *C*HOBz), 24.8 (1 C, *C*HCHOBz), 9.8 (1 C, *C*H$_2$) ppm. IR (thin film): $\tilde{\nu}$ = 3012, 2930, 1714, 1662, 1267, 716, 696 cm^{-1}. HRMS (EI): calcd. for $C_{29}H_{28}O_4$ [M]$^+$ 440.1982; found 440.1982.

***cis*-/*trans*-2-[1,3-Dimethoxy-4,5-bis(4-methoxyphenyl)cyclopent-2-en-1-yl]cyclopropyl Acetate (*cis*-/*trans*-6):** Compounds ***cis*-6** and ***trans*-6** were synthesised following the general procedure, using gold catalyst (13.3 mg, 17.2 μmol), compound **2b** (80.7 mg, 344 μmol), and vinyl acetate (89.6 mg, 1.04 mmol), at –40 °C for 30 min. The products were purified using an eluent system of 1:3 Et_2O/pentane to give a 87:13 mixture of compounds ***cis*-6** and ***trans*-6** (29.3 mg, 39%).

Data for ***cis*-6**: R_f = 0.19 (1% THF/CH_2Cl_2). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.23 (m, 2 H, C=CHCC*H*$_{arom}$), 7.18–7.16 (m, 2 H, C=CHCCHCC*H*$_{arom}$), 6.87–6.85 (m, 2 H, C=CHCCHC*H*$_{arom}$), 6.85–6.84 (m, 2 H, C=CHCCHCCH-C*H*$_{arom}$), 4.80–4.79 (m, 1 H, C=CH), 4.37 (br. s, 1 H, C=C*H*), 4.05–4.00 (m, 1 H, C*H*OAc), 3.99 (br. s, C=CHC*H*), 3.80 (s, 3 H, C*H*$_3$O-PhCHC=), 3.78 (s, 3 H, C*H*$_3$O-PhCHCCH=), 3.68 (s, 3 H, C=COCH$_3$), 3.04 (s, 3 H, C=CHCOC*H*$_3$), 2.10 (s, 3 H, OCOCH$_3$), 0.92–0.87 (m, 1 H, CH$_2$), 0.85–0.79 (m, 1 H, CH$_2$), 0.42–0.36 (m, 1 H, C*H*CHOAc) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 171.1 (1 C, OC=O), 159.6 (1 C, C=*C*OCH$_3$), 158.5 (1 C, MeO-C$_{arom}$), 158.1 (1 C, MeO-C$_{arom}$), 133.1 (1 C, C=CHCCHC$_{arom}$), 130.5 (2 C, C=CHCCHCCH$_{arom}$), 130.2 (2 C, C=CHC*C*H$_{arom}$), 129.4 (1 C, C=CH*C*$_{arom}$), 113.4 (2 C, C=CHCCHCCH*C*H$_{arom}$), 113.1 (2 C, C=CHCCH*C*H$_{arom}$), 99.7 (1 C, C=CH), 86.6 (1 C, C=CH*C*H), 59.5 (1 C, C=CH), 56.6 (1 C, C=CO*C*H$_3$), 55.1 (1 C, *C*H$_3$OPh), 55.1 (1 C, *C*H$_3$OPh), 53.2 (1 C, *C*HOAc), 51.9 (1 C, C=CH*C*H), 51.8 (1 C, C=CHCO*C*H$_3$), 21.5 (1 C, *C*HCHOAc), 21.2 (1 C, OCO*C*H$_3$), 9.1 (1 C, CH$_2$) ppm. IR (thin film): $\tilde{\nu}$ = 2934, 1742, 1609, 1509, 1463, 1227, 1175, 830, 729 cm^{-1}. HRMS (EI): calcd. for $C_{26}H_{30}O_6$ [M]$^+$ 438.2042; found 438.2038.

Data for ***trans*-6**: R_f = 0.15 (1% THF/CH_2Cl_2). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29–7.26 (m, 2 H, C=CHCC*H*$_{arom}$), 7.22–7.19 (m, 2 H, C=CHCCHCC*H*$_{arom}$), 6.86–6.85 (m, 2 H, C=CHCCHC*H*$_{arom}$), 6.83–6.82 (m, 2 H, C=CHCCH-CCHC*H*$_{arom}$), 4.61–4.60 (m, 1 H, C=CH), 4.47–4.41 (m, 1 H, C*H*OAc), 4.08 (br. s, 1 H, C=C*H*), 3.95 (br. s, C=CHC*H*), 3.80 (s, 3 H, C*H*$_3$O-Ph), 3.79 (s, 3 H, C*H*$_3$O-Ph), 3.59 (s, 3 H, C=COCH$_3$), 2.52 (s, 3 H, C=CHCOC*H*$_3$), 2.10 (s, 3 H, OCOCH$_3$), 1.41–1.31 (m, 1 H, CH$_2$), 1.41–1.31 (m, 1 H, C*H*CHOAc), 1.16–1.09 (m, 1 H, CH$_2$) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 171.6 (1 C, OC=O), 159.1 (1 C, C=*C*OCH$_3$), 158.3 (1 C, MeO-C$_{arom}$), 158.1 (1 C, MeO-C$_{arom}$), 133.5 (1 C, C=CHCCHC$_{arom}$), 131.5 (2 C,

C=CHCCHCCH$_{arom}$), 130.6 (2 C, C=CHCCH$_{arom}$), 129.9 (1 C, C=CHC$_{arom}$), 113.2 (2 C, MeO-CCH$_{arom}$), 112.9 (2 C, MeO-CCH$_{arom}$), 97.4 (1 C, C=CH), 84.6 (1 C, C=CHCH), 57.0 (1 C, C=CH), 56.6 (1 C, C=COCH$_3$), 56.5 (1 C, C=CHCH), 55.2 (1 C, CH$_3$OPh), 55.1 (1 C, CH$_3$OPh), 52.4 (1 C, C=CHCOCH$_3$), 51.9 (1 C, CHOAc), 24.3 (1 C, CHCHOAc), 20.8 (1 C, OCOCH$_3$), 9.2 (1 C, CH$_2$) ppm. IR (thin film): $\tilde{\nu}$ = 2930, 2826, 1743, 1609, 1511, 1246, 1177, 1034 cm^{-1}. HRMS (EI): calcd. for $C_{26}H_{30}O_6$ [M]$^+$ 438.2042; found 438.2044.

***cis*-/*trans*-2-[1,3-Dimethoxy-4,5-bis(4-methoxyphenyl)cyclopent-2-en-1-yl]cyclopropyl Benzoate (*cis*-/*trans*-7):** Compounds ***cis*-7** and ***trans*-7** were synthesised following the general procedure, using gold catalyst (13.7 mg, 17.7 μmol), compound **2b** (80.7 mg, 344 μmol), and vinyl benzoate (152.6 mg, 1.03 mmol), at –78 °C for 120 min. The products were purified using an eluent system of 1:9 Et$_2$O/pentane to give a 63:37 mixture of compounds ***cis*-7** and ***trans*-7** (49.5 mg, 53%).

Data for ***cis*-7**: R_f = 0.09 [1:4 (1:20 EtOAc/pentane)/CH$_2$Cl$_2$]; yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.04–8.02 (m, 2 H, CH$_{o\text{-OBz}}$), 7.60–7.56 (m, 1 H, CH$_{p\text{-OBz}}$), 7.48–7.44 (m, 2 H, CH$_{m\text{-OBz}}$), 7.24–7.22 (m, 2 H, C=CHCCHCCH$_{arom}$), 7.22–7.19 (m, 2 H, CH=CCHCCH$_{arom}$), 6.86–6.84 (m, 2 H, CH=CCHCCHCH$_{arom}$), 6.80–6.78 (m, 2 H, C=CHCCHCCHCH$_{arom}$), 4.93–4.92 (m, 1 H, C=CH), 4.35 (br. s, 1 H, CH=CCH), 4.15–4.10 (m, 1 H, CHOBz), 4.091–4.088 (m, 1 H, C=CHCCH), 3.79 (s, 3 H, CH$_3$OPh), 3.78 (s, 3 H, CH$_3$OPh), 3.72 (s, 3 H, C=COCH$_3$), 3.15 (s, 3 H, C=COCH$_3$), 1.12–1.07 (m, 1 H, CH$_2$), 0.99–0.93 (m, 1 H, CH$_2$), 0.61–0.54 (m, 1 H, CHCHOAc) ppm. ^{13}C NMR (400 MHz, CDCl$_3$): δ = 167.2 (1 C, C$_{arom\text{-}OBz}$), 160.1 (1 C, C=CH), 158.6 (1 C, CH$_3$OC$_{arom}$), 158.1 (1 C, CH$_3$OC$_{arom}$), 133.0 (1 C, CH$_{p\text{-}OBz}$), 132.6 (1 C, C=CHCCHC$_{arom}$), 130.4 (2 C, CH=CCHCCH$_{arom}$), 130.3 (1 C, C$_{OBz}$), 129.9 (2 C, C=CHCCHCCH$_{arom}$), 129.6 (1 C, CH=CCHC$_{arom}$), 129.5 (2 C, CH$_{o\text{-}OBz}$), 128.4 (2 C, CH$_{m\text{-}OBz}$), 113.6 (2 C, CH=CCHCCHCH$_{arom}$), 113.1 (2 C, C=CHCCHCCHCH$_{arom}$), 99.3 (1 C, C=CH), 86.1 (1 C, C=CHC), 59.0 (1 C, CH=CCH), 56.7 (1 C, =COCH$_3$), 55.2 (1 C, CH$_3$OC$_{arom}$), 55.1 (1 C, CH$_3$OC$_{arom}$), 53.5 (1 C, CHOBz), 53.3 (1 C, C=CHCCH), 51.9 (1 C, C=CHCOCH$_3$), 22.7 (1 C, CHCHOAc), 9.0 (1 C, CH$_2$) ppm. IR (thin film): $\tilde{\nu}$ = 2951, 2930, 2826, 1721, 1510, 1270, 1245, 1175, 1110, 1034, 712 cm^{-1}. HRMS (EI): calcd. for $C_{31}H_{32}O_6$ [M]$^+$ 500.2199; found 500.2199.

Data for ***trans*-7**: R_f = 0.13 [1:4 (1:20 EtOAc/pentane)/CH$_2$Cl$_2$]; yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.03–8.01 (m, 2 H, CH$_{o\text{-}OBz}$), 7.58–7.53 (m, 1 H, CH$_{p\text{-}OBz}$), 7.44–7.39 (m, 2 H, CH$_{m\text{-}OBz}$), 7.28–7.25 (m, 2 H, CH$_3$OCCHCH$_{arom}$), 7.24–7.21 (m, 2 H, CH$_3$OCCHCH$_{arom}$), 6.84–6.81 (m, 4 H, CH$_{arom}$COCH$_3$), 4.71–4.65 (m, 1 H, CHOBz), 4.51–4.49 (m, 1 H, C=CH), 4.25 (br. s, 1 H, CH=CCH), 4.04 (br. s, 1 H, C=CHCCH), 3.79 (s, 3 H, CH$_3$OPh), 3.77 (s, 3 H, CH$_3$OPh), 3.24 (s, 3 H, =COCH$_3$), 2.52 (s, 3 H, =CHCOCH$_3$), 1.62–1.50 (m, 1 H, CH$_2$), 1.62–1.50 (m, 1 H, CHCHOBz), 0.88–0.83 (m, 1 H, CH$_2$) ppm. ^{13}C NMR (400 MHz, CDCl$_3$): δ = 167.2 (1 C, C$_{arom\text{-}OBz}$), 158.7 (1 C, C=CH), 158.3 (1 C, CH$_3$OC$_{arom}$), 158.0 (1 C, CH$_3$OC$_{arom}$), 133.5 (1 C, C=CHCCHC$_{arom}$), 133.1 (1 C, C$_{p\text{-}OBz}$), 131.6 (2 C, CH$_3$OCCHCH$_{arom}$), 130.5 (2 C, CH$_3$OCCHCH$_{arom}$), 129.9 (1 C, CH=CCHC$_{arom}$), 129.6 (2 C, CH$_{o\text{-}OBz}$), 129.5 (1 C, C$_{arom\text{-}OBz}$), 128.4 (2 C, CH$_{m\text{-}OBz}$), 113.2 (2 C, CH$_3$OCCH$_{arom}$), 112.9 (2 C, CH$_3$OCCH$_{arom}$), 97.6 (1 C, C=CH), 84.5 (1 C, C=CHC), 58.3 (1 C, CH=CCH), 56.2 (1 C, =COCH$_3$), 55.6 (1 C, C=CHCCH), 55.13 (1 C, CH$_3$OC$_{arom}$), 55.11 (1 C, CH$_3$OC$_{arom}$), 52.4 (1 C, C=CHCOCH$_3$), 52.0 (1 C, CHOBz), 24.6 (1 C, CHCHOBz), 9.7 (CH$_2$) ppm. IR (thin film): $\tilde{\nu}$ = 2930, 2831, 1722, 1510, 1267, 1246, 1175, 1035, 711 cm^{-1}. HRMS (EI): calcd. for $C_{31}H_{32}O_6$ [M]$^+$ 500.2199; found 500.2196.

***cis*-/*trans*-2-[1,3-Dimethoxy-4,5-bis(4-methoxyphenyl)cyclopent-2-en-1-yl]-1-phenylcyclopropyl Acetate (*cis*-/*trans*-8):** Compounds ***cis*-8** and ***trans*-8** were synthesised following the general procedure, using gold catalyst (10.5 mg, 13.6 μmol), compound **2b** (63.0 mg, 269 μmol), and 1-phenylvinyl acetate (128.0 mg, 0.789 mmol), at –40 °C for 30 min, then 0 °C for 15 min. The products were purified using an eluent system of 1:10 EtOAc/pentane to give a 1:3 mixture of compounds ***cis*-8** and ***trans*-8** (26.0 mg, 19%).

Data for ***cis*-8**: R_f = 0.25 (1% Et$_2$O/CH$_2$Cl$_2$). Yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.33–7.28 (m, 2 H, C=CHCCHCCH$_{arom}$), 7.16–7.08 (m, 2 H, C=CHCCH$_{arom}$), 7.16–7.08 (m, 2 H, CH$_{m\text{-Ph}}$), 7.16–7.08 (m, 2 H, CH$_{p\text{-Ph}}$), 6.89–6.87 (m, 2 H, C=CHCCHCCHCH$_{arom}$), 6.73–6.71 (m, 2 H, CH$_{o\text{-Ph}}$), 6.65–6.63 (m, 2 H, C=CHCCHCH$_{arom}$), 4.90 (br. s, 1 H, C=CH), 4.31 (br. s, 1 H, C=CH), 4.14 (br. s, 1 H, C=CHCCH), 3.82 (s, 3 H, CH$_3$OPh), 3.71 (s, 3 H, CH$_3$OPh), 3.67 (s, 3 H, C=COCH$_3$), 3.15 (s, 3 H, C=CHCOCH$_3$), 1.62–1.60 (m, 2 H, CH$_2$), 2.17 (s, 3 H, OCOCH$_3$), 0.74–0.69 (m, 1 H, CHCOAc) ppm. ^{13}C NMR (400 MHz, CDCl$_3$): δ = 170.1 (1 C, C=O), 160.6 (1 C, MeOC$_{arom}$), 158.4 (1 C, C=), 158.2 (1 C, MeOC$_{arom}$), 141.4 (1 C, C$_{arom}$COAc), 132.5 (1 C, C=CHCCHC$_{arom}$), 130.3 (2 C, C=CHCCH$_{arom}$), 129.9 (2 C, C=CHCCHCCH$_{arom}$), 129.4 (1 C, C=CHC$_{arom}$), 127.9 (2 C, CH$_{m\text{-Ph}}$), 126.1 (1 C, CH$_{p\text{-Ph}}$), 123.4 (2 C, CH$_{o\text{-Ph}}$), 113.6 (2 C, C=CHCCHCH$_{arom}$), 113.3 (2 C, C=CHCCHCCHCH$_{arom}$), 98.7 (1 C, C=CH), 86.6 (1 C, C=CHC), 62.0 (1 C, COAc), 58.2 (1 C, C=CH), 56.8 (1 C, MeOPh), 55.2 (1 C, MeOPh), 55.1 (1 C, C=COCH$_3$), 53.8 (1 C, C=CHCCH), 52.2 (1 C, C=CHCOCH$_3$), 34.9 (1 C, CHCOAc), 21.5 (1 C, OCOCH$_3$), 19.0 (1 C, CH$_2$) ppm. Data for a mixture of ***cis*-8** and ***trans*-8**: IR (thin film): $\tilde{\nu}$ = 2930, 2831, 1751, 1652, 1610, 1510, 1244, 1176, 1034, 731 cm^{-1}. HRMS (EI): calcd. for $C_{32}H_{24}O_6$ [M]$^+$ 514.2355; found 514.2346.

Data for ***trans*-8**: R_f = 0.30 (1% Et$_2$O/CH$_2$Cl$_2$). Yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.46–7.44 (m, 2 H, CH$_{o\text{-Ph}}$), 7.33–7.30 (m, 2 H, CH$_{m\text{-Ph}}$), 7.33–7.30 (m, 2 H, CH$_{p\text{-Ph}}$), 7.26–7.24 (m, 2 H, C=CHCCH$_{arom}$), 6.94–6.92 (m, 2 H, C=CHCCHCH$_{arom}$), 6.67–6.65 (m, 2 H, C=CHCCHCCHCH$_{arom}$), 6.47–6.45 (m, 2 H, C=CHCCHCCH$_{arom}$), 4.60 (br. s, 1 H, C=CH), 4.22 (br. s, 1 H, C=CH), 3.85 (s, 3 H, CH$_3$OPh), 3.75 (s, 3 H, CH$_3$OPh), 3.62 (s, 3 H, C=COCH$_3$), 3.31 (br. s, 1 H, C=CHCCH), 2.99 (s, 3 H, C=CHCOCH$_3$), 1.83–1.80 (m, 1 H, CH$_2$), 1.80 (s, 3 H, OCOCH$_3$), 1.46–1.41 (m, 1 H, CHCOAc), 1.28–1.24 (m, 1 H, CH$_2$) ppm. ^{13}C NMR (400 MHz, CDCl$_3$): δ = 169.9 (1 C, C=O), 160.2 (1 C, C=), 158.5 (1 C, MeOC$_{arom}$), 157.9 (1 C, MeOC$_{arom}$), 136.7 (1 C, C$_{arom}$-COAc), 132.5 (1 C, C=CHCCHC$_{arom}$), 131.4 (2 C, C=CHCCH$_{arom}$), 130.1 (2 C, CH$_{p\text{-Ph}}$), 130.0 (2 C, C=CHCCHCCH$_{arom}$), 129.8 (1 C, C=CHC$_{arom}$), 127.8 (2 C, CH$_{m\text{-Ph}}$), 127.6 (1 C, CH$_{p\text{-Ph}}$), 113.5 (2 C, C=CHCCHCH$_{arom}$), 112.8 (2 C, C=CHCCHCCHCH$_{arom}$), 98.7 (1 C, C=CH), 85.5 (1 C, C=CHC), 63.9 (1 C, COAc), 58.7 (1 C, C=CH), 56.6 (1 C, C=COCH$_3$), 55.3 (1 C, MeOPh), 55.1 (1 C, MeOPh), 52.0 (1 C, C=CHCOCH$_3$), 51.8 (1 C, C=CHCCH), 30.2 (1 C, CHCOAc), 21.5 (1 C, OCOCH$_3$), 15.9 (1 C, CH$_2$) ppm. IR (thin film): $\tilde{\nu}$ = 2997, 2935, 2831, 1750, 1652, 1610, 1510, 1243, 1176, 1034, 731 cm^{-1}. HRMS (EI): calcd. for $C_{32}H_{34}O_6$ [M]$^+$ 514.2355; found 514.2346.

***cis*-/*trans*-2-[4,5-Bis(4-chlorophenyl)-1,3-dimethoxycyclopent-2-en-1-yl]cyclopropyl Acetate (*cis*-/*trans*-9):** Compounds ***cis*-9** and ***trans*-9** were synthesised following the general procedure, using gold catalyst (13.3 mg, 17.2 μmol), compound **2c** (80.8 mg, 338 μmol), and vinyl acetate (93.6 mg, 1.09 mmol), at –40 °C for 15 min. The prod-

ucts were purified using an eluent system of 1:30 EtOAc/pentane to give ***cis*-9** (33.8 mg, 45%) and ***trans*-9** (24.5 mg, 32%) as pale yellow waxes.

Data for ***cis*-9**: R_f = 0.31 (1:10 EtOAc/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.23 (m, 6 H, CH_{arom}), 7.20–7.17 (m, 2 H, CH_{arom}), 4.81–4.80 (m, 1 H, C=CH), 4.38 (br. s, 1 H, C=C*H*), 4.05–4.01 (m, 1 H, CHOAc), 4.02 (br. s, 1 H, C=CHC*H*), 3.69 (s, 3 H, =$COCH_3$), 3.03 (s, 3 H, C=CHCOCH_3), 2.08 (s, 3 H, OC-OCH_3), 0.90–0.79 (m, 2 H, CH_2), 0.39–0.33 (m, 1 H, AcOCHC*H*) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 171.0 (1 C, OC=O), 159.6 (1 C, CH=*C*OCH_3), 139.5 (1 C, C_{arom}CHC=), 135.9 (1 C, C_{arom}CHCHC=), 132.8 (1 C, C_{arom}Cl), 132.2 (1 C, C_{arom}Cl), 130.9 (2 C, CH_{arom}), 130.7 (2 C, CH_{arom}), 128.2 (2 C, CH_{arom}), 127.9 (2 C, CH_{arom}), 99.6 (1 C, C=*C*H), 86.6 (1 C, =CH*C*OCH_3), 59.8 (1 C, C=CHCH), 56.8 (1 C, =CO*C*H_3), 53.1 (1 C, *C*HOAc), 52.5 (1 C, C=CH*C*H), 51.9 (1 C, =CHCO*C*H_3), 21.5 (1 C, *C*HCHOAc), 21.2 (1 C, OCO*C*H_3), 9.1 (1 C, CH_2) ppm. IR (neat): $\tilde{\nu}$ = 2934, 1743, 1652, 1489, 1225, 1090, 1014, 907, 730 cm^{-1}. HRMS (EI): calcd. for $C_{24}H_{24}O_4Cl_2$ $[M]^+$ 446.1046; found 446.1043.

Data for ***trans*-9**: R_f = 0.20 (1:10 EtOAc/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.24 (m, 6 H, CH_{arom}), 7.21–7.19 (m, 2 H, CH_{arom}), 4.61 (t, *J* = 1.8 Hz, 1 H, C=CH), 4.44 (dt, *J* = 7.3, 4.1 Hz, 1 H, CHOAc), 4.12 (d, *J* = 1.0 Hz, 1 H, C=C*H*), 3.96 (br. s, 1 H, C=CHC*H*), 3.59 (s, 3 H, =$COCH_3$), 2.50 (s, 3 H, =CHCOCH_3), 2.09 (s, 3 H, OCOCH_3), 1.39 (m, 1 H, AcOCHC*H*), 1.31 (m, 1 H, AcOCHCH_2), 1.15 (td, *J* = 9.6, 7.3 Hz, 1 H, AcOCHCH_2) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 171.5 (1 C, O*C*=O), 159.1 (1 C, CH=*C*OCH_3), 139.6 (1 C, C_{arom}CHC=), 136.2 (1 C, C_{arom}CHCHC=), 132.6 (1 C, C_{arom}Cl), 132.1 (1 C, C_{arom}Cl), 131.9 (2 C, CH_{arom}), 131.0 (2 C, CH_{arom}), 128.0 (2 C, CH_{arom}), 127.6 (2 C, CH_{arom}), 97.2 (1 C, C=*C*H), 84.8 (1 C, =CH*C*OCH_3), 57.4 (1 C, =C*C*HCH), 56.7 (=CO*C*H_3), 56.6 (1 C, =CCH*C*H), 52.4 (1 C, =CHCO*C*H_3), 51.8 (1 C, *C*HOAc), 24.2 (1 C, *C*HCHOAc), 20.8 (1 C, OCO*C*H_3), 9.3 (1 C, CH_2) ppm. IR (neat): $\tilde{\nu}$ = 2933, 1744, 1662, 1489, 1223, 1090, 1014, 908, 730 cm^{-1}. HRMS (EI): calcd. for $C_{24}H_{24}O_4Cl_2$ $[M]^+$ 446.1046; found 446.1050.

***cis*-/*trans*-2-[4,5-Bis(4-chlorophenyl)-1,3-dimethoxycyclopent-2-en-1-yl]cyclopropyl Benzoate (*cis*-/*trans*-10):** Compounds ***cis*-10** and ***trans*-10** were synthesised following the general procedure, using gold catalyst (13.0 mg, 16.8 μmol), compound **2c** (80.5 mg, 337 μmol), and vinyl benzoate (157.2 mg, 1.06 mmol), at –40 °C for 15 min. The products were purified using an eluent system of 1:50–1:9 Et_2O/pentane, followed by a second purification using 1:10 Et_2O/pentane to give ***cis*-10** (33.1 mg, 39%) as a colourless solid and ***trans*-10** (28.2 mg, 33%) as a pale yellow oil.

Data for ***cis*-10**: R_f = 0.35 (10:2 pentane/diethyl ether), m.p. 174–177 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (m, 2 H, $CH_{o\text{-}OBz}$), 7.62–7.58 (m, 1 H, $CH_{p\text{-}OBz}$), 7.49–7.44 (m, 2 H, $CH_{m\text{-}OBz}$), 7.30–7.20 (m, 8 H, CH_{arom}), 4.91–4.90 (m, 1 H, C=CH), 4.37 (br. s, 1 H, =CC*H*), 4.15 (td, *J* = 7.1, 4.2 Hz, 1 H, CHOBz), 4.09 (d, *J* = 1.3 Hz, 1 H, =CCHC*H*), 3.71 (s, 3 H, =COCH_3), 3.12 (s, 3 H, =CHCOCH_3), 1.09 (ddd, *J* = 8.2, 6.5, 4.3 Hz, 1 H, CH_2), 0.96 (dt, *J* = 9.9, 7.0 Hz, 1 H, CH_2), 0.53 (ddd, *J* = 10.0, 8.2, 7.2 Hz, 1 H, BzOCHC*H*) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 167.1 (1 C, OC=O), 159.9 (1 C, CH=*C*OCH_3), 139.0 (1 C, C_{arom}CHCHC=), 136.0 (1 C, C_{arom}CHC=), 133.2 (1 C, $CH_{p\text{-}OBz}$), 132.9 (1 C, C_{arom}Cl), 132.2 (1 C, C_{arom}Cl), 130.8 (2 C, CH_{arom}), 130.4 (2 C, CH_{arom}), 130.1 (1 C, OCOC_{arom}), 129.5 (2 C, $CH_{o\text{-}OBz}$), 128.5 (2 C, $CH_{m\text{-}OBz}$), 128.4 (2 C, CH_{arom}), 127.9 (2 C, CH_{arom}), 99.3 (1 C, C=*C*H), 86.2 (1 C, =CH*C*OCH_3), 59.4 (1 C, =C*C*HCH), 56.9 (=CO*C*H_3), 53.5 (1 C, *C*HOBz), 53.4 (1 C, =CCH*C*H), 52.0 (1 C, =CHCO*C*H_3), 22.5 (1 C, *C*HCHOBz), 9.04 (1 C, CH_2) ppm. IR (neat): $\tilde{\nu}$ = 2934, 1721, 1651, 1489, 1266, 1090, 1014, 710 cm^{-1}. HRMS (EI): calcd. for $C_{29}H_{26}O_4Cl_2$ $[M]^+$ 508.1203; found 508.1203.

Data for ***trans*-10**: R_f = 0.27 (10:2 pentane/diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 7.2 Hz, 2 H, $CH_{o\text{-}OBz}$), 7.57 (t, *J* = 7.4 Hz, 1 H, $CH_{p\text{-}OBz}$), 7.42 (t, *J* = 7.6 Hz, 2 H, $CH_{m\text{-}OBz}$), 7.27–7.26 (m, 2 H, CH_{arom}), 7.25–7.24 (m, 2 H, CH_{arom}), 7.24–7.23 (m, 2 H, CH_{arom}), 7.22–7.20 (m, 2 H, CH_{arom}), 4.68 (dt, *J* = 7.2, 4.2 Hz, 1 H, CHOBz), 4.49 (t, *J* = 1.9 Hz, 1 H, C=C*H*), 4.29 (d, *J* = 1.2 Hz, 1 H, =CC*H*), 4.03 (s, 1 H, =CCHC*H*), 3.20 (s, 3 H, =COCH_3), 2.50 (s, 3 H, =CHCOCH_3), 1.59–1.55 (m, 1 H, CH_2), 1.55–1.53 (m, 1 H, BzOCHC*H*), 1.32–1.27 (m, 1 H, CH_2) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 167.2 (1 C, OC=O), 158.8 (1 C, CH=*C*OCH_3), 139.7 (1 C, C_{arom}CHC=), 136.3 (1 C, C_{arom}CHCHC=), 133.3 (1 C, $CH_{p\text{-}OBz}$), 132.6 (1 C, C_{arom}Cl), 132.0 (1 C, C_{arom}Cl), 131.9 (2 C, CH_{arom}), 130.9 (2 C, CH_{arom}), 129.6 (2 C, $CH_{o\text{-}OBz}$), 129.4 (1 C, OCOC_{arom}), 128.5 (2 C, $CH_{m\text{-}OBz}$), 128.0 (2 C, CH_{arom}), 127.6 (2 C, CH_{arom}), 97.3 (1 C, C=*C*H), 84.7 (1 C, =CH*C*OCH_3), 58.6 (1 C, =C*C*HCH), 56.2 (1 C, =CO*C*H_3), 55.9 (1 C, =CCH*C*H), 52.5 (1 C, =CHCO*C*H_3), 51.9 (1 C, CHOBz), 24.7 (1 C, *C*HCHOBz), 9.7 (1 C, *C*H_2) ppm. IR (thin film): $\tilde{\nu}$ = 2933, 1722, 1661, 1489, 1264, 1089, 1014, 709 cm^{-1}. HRMS (EI): calcd. for $C_{29}H_{26}O_4Cl_2$ $[M]^+$ 508.1203; found 508.1202.

***cis*-/*trans*-2-[4,5-Bis(4-chlorophenyl)-1,3-dimethoxycyclopent-2-en-1-yl]-1-methylcyclopropyl Acetate (*cis*-/*trans*-11):** Compounds ***cis*-11** and ***trans*-11** were synthesised following the general procedure, using gold catalyst (13.4 mg, 0.02 mmol), compound **2c** (80.0 mg, 0.33 mmol), and isopropenyl acetate (64.8 mg, 0.65 mmol). The reaction mixture was stirred at room temperature for 16 min. An isocratic eluent of 1:30 Et_2O/pentane was used to isolate a mixture of ***cis*-11** and ***trans*-11** (32.5 mg, 42%). A small amount of ***cis*-11** was isolated from the isomeric mixture as a yellow oil (8.1 mg, 11%). Due to the complexity of the ^{1}H and ^{13}C NMR spectra of the isomeric mixture, the chemical shifts of ***trans*-11** could not be assigned (overall *cis*/*trans* ratio 73:27). ***trans*-11**: R_f = 0.32 (10:3 pentane/diethyl ether). Data for ***cis*-11**: R_f = 0.26 (10:3 pentane/diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.30 (m, 2 H, CH_{arom}), 7.27–7.26 (m, 2 H, CH_{arom}), 7.26–7.24 (m, 2 H, CH_{arom}), 7.24–7.22 (m, 2 H, CH_{arom}), 4.88 (dd, *J* = 1.8, 1.1 Hz, 1 H, C=CH), 4.28 (s, 1 H, C=C*H*CH), 4.05 (s, 1 H, C=CHC*H*), 3.70 (s, 3 H, C=COCH_3), 3.11 (s, 3 H, C=CHCOCH_3), 2.03 (s, 3 H, OCOCH_3), 1.14–1.18 (m, 2 H, CH_2), 1.05 (s, 3 H, CHCCH_3), 0.28 (dd, *J* = 10.0, 7.8 Hz, 1 H, AcOCCH) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 170.2 (1 C, OC=O), 160.7 (1 C, CH=*C*OCH_3), 139.0 (1 C, C_{arom}CHCHC=), 136.6 (1 C, C_{arom}CHC=), 132.8 (1 C, C_{arom}Cl), 132.2 (1 C, C_{arom}Cl), 131.0 (2 C, CH_{arom}), 130.2 (2 C, CH_{arom}), 128.4 (2 C, CH_{arom}), 127.9 (2 C, CH_{arom}), 98.5 (1 C, C=*C*H), 86.2 (1 C, C=CH*C*OCH_3), 58.8 (1 C, *C*OAc), 58.3 (1 C, C=CH), 57.0 (1 C, C=CO*C*H_3), 54.6 (1 C, C=CH*C*H), 52.0 (1 C, C=CHCO*C*H_3), 29.4 (1 C, *C*HCOAc), 22.6 (1 C, CHC*C*H_3), 21.6 (1 C, OCO*C*H_3), 16.7 (1 C, CH_2) ppm. Data for a mixture of ***cis*-11** and ***trans*-11**: IR (thin film): $\tilde{\nu}$ = 2935, 1744, 1653, 1489, 1207, 1089, 1014, 908, 729 cm^{-1}. HRMS (EI): calcd. for $C_{25}H_{26}O_4Cl_2$ $[M]^+$ 460.1203; found 460.1205.

***trans*-2-[4,5-Bis(4-chlorophenyl)-1,3-dimethoxycyclopent-2-en-1-yl]-1-methylcyclopropyl Acetate (*trans*-12):** Compound ***trans*-12** was synthesised following the general procedure, using gold catalyst (9.8 mg, 12.7 μmol), compound **2c** (59.8 mg, 251 μmol), and 1-phenylvinyl acetate (130.6 mg, 0.805 mmol), at –40 °C for 30 min, then 0 °C for 15 min. An isocratic eluent of 1:20 EtOAc/pentane was used to isolate compound ***trans*-12** (11.2 mg, 17%), and an impure mixture of ***cis*-12** and compound **1c** that could not be fully

characterised. The amount of the *cis*-isomer was estimated from the NMR spectrum to be 11.8 mg, 18%.

Data for ***trans*-12**: R_f = 0.21 (1:20 EtOAc/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.44 (m, 2 H, CH_{arom} COAc), 7.37–7.35 (m, 2 H, CH=CCHCCHCH_{arom}), 7.33–7.32 (m, 2 H, C$H_{m\text{-Ph}}$), 7.33–7.32 (m, 1 H, C$H_{p\text{-Ph}}$), 7.25–7.24 (m, 2 H, CH=CCHCCH_{arom}), 7.07–7.05 (m, 2 H, C=CHCCHCCHCH_{arom}), 6.40–6.38 (m, 2 H, C=CHCCHCCH_{arom}), 4.60–4.59 (m, 1 H, C=CH), 4.25 (br. s, 1 H, CH=CC*H*), 3.61 (s, 3 H, =COCH_3), 3.29 (br. s, 1 H, CH=CCHC*H*), 3.02 (s, 3 H, C=CHCOCH_3), 1.83–1.79 (m, 1 H, CH_2), 1.82 (s, 3 H, OCOCH_3), 1.39–1.33 (m, 1 H, C*H*COAc), 1.29–1.24 (m, 1 H, CH_2) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 169.8 (1 C, OC=O), 159.9 (1 C, *C*=CH), 138.9 (1 C, C=CHCCH*C*$_{arom}$), 136.33 (1 C, CH=CCH*C*$_{arom}$), 136.31 (1 C, *C*$_{arom}$COAc), 132.8 (1 C, C$_{arom}$Cl), 131.9 (1 C, C$_{arom}$Cl), 131.8 (2 C, CH=CCHC*C*H$_{arom}$), 130.5 (2 C, C=CHCCHC*C*H$_{arom}$), 130.1 (2 C, CH$_{o\text{-Ph}}$), 128.3 (2 C, CH=CCHCCH*C*H$_{arom}$), 128.0 (2 C, CH$_{m\text{-Ph}}$), 127.9 (1 C, CH$_{p\text{-Ph}}$), 127.4 (2 C, C=CHCCHCCH*C*H), 98.7 (1 C, C=*C*H), 85.7 (1 C, C=CH*C*), 63.7 (1 C, *C*OAc), 59.4 (1 C, C=CHC*C*H), 56.7 (1 C, =CO*C*H$_3$), 52.1 (1 C, C=CHCO*C*H$_3$), 51.9 (1 C, C=CHC*C*H), 29.8 (1 C, *C*HCOAc), 21.4 (1 C, OCO*C*H$_3$), 16.0 (1 C, CH$_2$) ppm. IR (thin film): $\tilde{\nu}$ = 2935, 2831, 1753, 1654, 1489, 1232, 1090, 1015, 732, 699 cm^{-1}. HRMS (EI): calcd. for $C_{30}H_{28}O_4Cl_2$ [M]$^+$ 522.1365; found 522.1355.

***cis*-/*trans*-2-[4-(4-Chlorophenyl)-1,3-dimethoxy-5-(4-nitrophenyl)-cyclopent-2-en-1-yl]cyclopropyl Acetate (*cis*-/*trans*-13):** Compounds ***cis*-13** and ***trans*-13** were synthesised following the general procedure, using gold catalyst (10.1 mg, 13.1 μmol), compound **2c** (67.2 mg, 282 μmol), and compound **3e** (see below; 70.3 mg, 254 μmol), at –40 °C for 30 min. The product was purified using an eluent system of CH_2Cl_2 to give compounds ***cis*-13** (51.7 mg, 45%) and ***trans*-13** (37.1 mg, 32%) as pale yellow oil-foams.

Data for ***cis*-13**: R_f = 0.17 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18–8.15 (m, 2 H, CH$_{arom}$CNO$_2$), 7.49–7.47 (m, 2 H, CH_{arom}CHCNO$_2$), 7.31–7.29 (m, 2 H, CH$_{arom}$CCl), 7.21–7.19 (m, 2 H, CH_{arom}CHCCl), 4.84–4.83 (m, 1 H, C=CH), 4.40 (br. s, 1 H, CH=CC*H*), 4.16 (br. s, 1 H, C=CHCC*H*), 4.05–4.00 (m, 1 H, CHOAc), 3.72 (s, 3 H, =COCH_3), 3.07 (s, 3 H, C=CHCOCH_3), 2.09 (s, 3 H, OCOCH_3), 0.88–0.84 (m, 2 H, CH_2), 0.46–0.40 (m, 1 H, C*H*CHOAc) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 170.8 (1 C, OC=O), 160.5 (1 C, *C*=CH), 149.2, 146.7, 135.6, 133.0, 130.8 (2 C, *C*H$_{arom}$CHCCl), 130.1 (2 C, *C*H$_{arom}$CHCNO$_2$), 128.3 (2 C, *C*H$_{arom}$CCl), 122.9 (2 C, *C*H$_{arom}$CNO$_2$), 98.6 (1 C, C=*C*H), 86.7, 59.4 (1 C, CH=C*C*H), 56.9 (1 C, =CO*C*H$_3$), 53.6 (1 C, C=CHC*C*H), 52.8 (1 H, CHOAc), 52.0 (1 C, C=CHCO*C*H$_3$), 21.4 (1 C, C*H*CHOAc), 21.1 (1 C, OCO*C*H$_3$), 9.1 (1 C, CH$_2$) ppm. IR (thin film): $\tilde{\nu}$ = 2932, 2829, 1745, 1653, 1516, 1345, 1229, 1091, 1015, 835, 729 cm^{-1}. HRMS (EI): calcd. for $C_{24}H_{24}NO_6Cl$ [M]$^+$ 457.1292; found 457.1289.

Data for ***trans*-13**: R_f = 0.23 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16–8.14 (m, 2 H, CH$_{arom}$CNO$_2$), 7.51–7.49 (m, 2 H, CH_{arom}CHCNO$_2$), 7.28–7.26 (m, 2 H, CH$_{arom}$CCl), 7.21–7.19 (m, 2 H, CH_{arom}CHCCl), 4.65–4.64 (m, 1 H, C=CH), 4.49–4.44 (m, 1 H, CHOAc), 4.29 (br. s, 1 H, CH=CC*H*), 3.98 (br. s, 1 H, C=CHCC*H*), 3.62 (s, 3 H, =COCH_3), 2.47 (s, 3 H, C=CHCOCH_3), 2.10 (s, 3 H, OCOCH_3), 1.43–1.36 (m, 1 H, CH_2), 1.43–1.36 (m, 1 H, C*H*CHOAc), 1.23–1.18 (m, 1 H, CH_2) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 171.4 (1 C, OC=O), 159.8 (1 C, *C*=CH), 149.3, 146.7, 135.8, 132.8, 131.8 (2 C, *C*H$_{arom}$CHCCl), 130.2 (2 C, *C*H$_{arom}$CHCNO$_2$), 128.0 (2 C, *C*H$_{arom}$CCl), 122.6 (2 C, *C*H$_{arom}$CNO$_2$), 96.2 (1 C, C=*C*H), 85.0 (1 C, C=CH*C*), 58.2 (1 C, CH=C*C*H), 56.8 (1 C, =CO*C*H$_3$), 56.2 (1 C, C=CHC*C*H), 52.5 (1 C, C=CHCO*C*H$_3$), 51.4 (1 C, CHOAc), 24.3 (1 C, C*H*CHOAc), 20.7 (1 C, OCO*C*H$_3$), 9.3 (1 C, CH$_2$) ppm. IR (thin film): $\tilde{\nu}$ = 2940, 2826, 1744, 1515, 1344, 1224, 1090, 1014, 728 cm^{-1}. HRMS (EI): calcd. for $C_{24}H_{24}NO_6Cl$ [M]$^+$ 457.1292; found 457.1290.

***cis*-/*trans*-2-[1,3-Dimethoxy-4,5-bis(4-nitrophenyl)cyclopent-2-en-1-yl]cyclopropyl Acetate (*cis*-/*trans*-14):** Gold catalyst (13.4 mg, 17.4 μmol) was dissolved in dry CH_2Cl_2 (1.5 mL) at room temperature under a nitrogen atmosphere. A solution of compound **2d** (84.9 mg, 341 μmol) and vinyl acetate (89.0 mg, 1.03 mmol) in dry CH_2Cl_2 (1 mL) was added, and the flask was washed out with CH_2Cl_2 (2 × 0.5 mL). At 15, 30, and 60 min, further **2d** (56.7, 56.6, and 315.1 mg, respectively) was added in CH_2Cl_2 (1 mL each time) (total amount of compound **2d** used: 513.2 mg, 2.06 mmol). After 120 min, reaction was quenched with NEt_3 (5 drops), then the mixture was filtered through Celite, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography using an eluent of CH_2Cl_2 to give a 58:42 mixture of compounds ***cis*-14** and ***trans*-14** (343.1 mg, 62%).

Data for ***cis*-14**: R_f = 0.17 (CH_2Cl_2). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.203–8.200 (m, 2 H), 8.19–8.17 (m, 2 H), 7.50–7.48 (m, 2 H), 7.45–7.43 (m, 2 H), 4.89–4.88 (m, 1 H, C=CH), 4.56 (br. s, 1 H, CH=CC*H*), 4.202–4.198 (m, 1 H, CH=CCHC*H*), 4.07–4.02 (m, 1 H, CHOAc), 3.74 (s, 3 H, =COCH_3), 3.05 (s, 3 H, C=CHCOCH_3), 0.94–0.83 (m, 2 H, CH_2), 0.37–0.31 (m, 1 H, C*H*CHOAc) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 170.6 (1 C, OC=O), 159.6 (1 C, *C*=CH), 148.7 (1 C, CH=CCH*C*$_{arom}$), 147.1 (1 C, C$_{arom}$NO$_2$), 146.8 (1 C, C$_{arom}$NO$_2$), 145.1 (1 C, C=CH-CCH*C*$_{arom}$), 130.4 (2 C, *C*H$_{arom}$CNO$_2$), 130.1 (2 C, *C*H$_{arom}$CNO$_2$), 123.2 (2 C, *C*H$_{arom}$CHCNO$_2$), 123.0 (2 C, *C*H$_{arom}$CHCNO$_2$), 99.3 (1 C, C=*C*H), 87.1 (1 C, C=CH*C*), 60.3 (1 C, CH=C*C*H), 57.0 (1 C, =CO*C*H$_3$), 53.2 (1 C, C=CHC*C*H), 52.8 (1 C, CHOBz), 52.1 (1 C, C=CH*C*), 21.3 (1 C, *C*HCHOBz), 21.2 (1 C, OCO*C*H$_3$), 9.1 (1 C, CH$_2$) ppm. IR (thin film): $\tilde{\nu}$ = 2940, 2842, 1740, 1657, 1517, 1344, 1228, 906, 727, 648 cm^{-1}. HRMS (EI): calcd. for $C_{24}H_{24}N_2O_8$ [M]$^+$ 468.1533; found 468.1533.

Data for ***trans*-14**: R_f = 0.21 (CH_2Cl_2). Pale yellow foam-solid, m.p. 214–216 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18–8.17 (m, 2 H, CH_{arom}CNO$_2$), 8.16–8.15 (m, 2 H, CH_{arom}CNO$_2$), 7.52–7.50 (m, 2 H, CH_{arom}CHCNO$_2$), 7.44–7.43 (m, 2 H, CH_{arom}CHCNO$_2$), 4.71–4.70 (m, 1 H, C=CH), 4.52–4.48 (m, 1 H, CHOAc), 4.33 (br. s, 1 H, CH=CC*H*), 4.12 (br. s, 1 H, C=CHCC*H*), 3.63 (s, 3 H, =COCH_3), 2.46 (s, 3 H, C=CHCOCH_3), 2.12 (s, 3 H, OCOCH_3), 1.46–1.42 (m, 1 H, C*H*CHOAc), 1.39–1.33 (m, 1 H, CH_2), 1.28–1.22 (m, 1 H, CH_2) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 171.3 (1 C, OC=O), 159.1 (1 C, *C*=CH), 148.8, 147.0, 146.8, 145.3, 131.3 (2 C, *C*H$_{arom}$CNO$_2$), 130.2 (2 C, *C*H$_{arom}$CNO$_2$), 122.9 (2 C, *C*H$_{arom}$CHCNO$_2$), 122.8 (2 C, *C*H$_{arom}$CHCNO$_2$), 97.0, 85.5 (1 C, C=CH*C*), 58.1 (1 C, CH=C*C*H), 56.87 (1 C, C=CHC*C*H), 56.86 (1 C, =CO*C*H$_3$), 52.5 (1 C, C=CHCO*C*H$_3$), 51.6 (1 C, CHOBz), 24.3 (1 C, *C*HCHOBz), 20.7 (1 C, OCO*C*H$_3$), 9.4 (1 C, CH$_2$) ppm. IR (thin film): $\tilde{\nu}$ = 2940, 2826, 1745, 1663, 1596, 1515, 1343, 1225, 1108, 855, 734 cm^{-1}. HRMS (EI): calcd. for $C_{24}H_{24}N_2O_8$ [M]$^+$ 468.1533; found 468.1528.

Compound **14** could alternatively be prepared from propargyl acetal **2d** and compound **3e** (see below). Gold catalyst (2.6 mg, 3.4 μmol) was dissolved in CH_2Cl_2 (0.5 mL), and the solution was cooled to –40 °C. Compounds **2d** (17.1 mg, 68.6 μmol) and **3e** (17.2 mg, 75.7 μmol) were dissolved in CH_2Cl_2 (1 mL), and this solution was added to the solution of the gold catalyst. The flask was washed out with further CH_2Cl_2 (1 mL). The reaction mixture was stirred at –40 °C for 60 min, then at room temperature for 60 min. The product was purified using an eluent system of 1:2

EtOAc/pentane to give a mixture (52:48) of compounds ***cis*-14** and ***trans*-14** (21.0 mg, 65%) as a pale yellow oil.

The ratio of product **14** to intermediate **3e** could be varied by altering the reaction conditions, depending on which compound was to be obtained. For example, at –40 °C and the standard ratio of compound **2d** to vinyl acetate of 1:3, ***cis*-14** (39%), ***trans*-14** (19%), and **3e** (20%) were formed. When the ratio of compound **2d** to vinyl acetate was increased to 1:10 (see below), a higher yield of **3e** (40%) and lower yields of product **14** (***cis*-14**: 19%, ***trans*-14**: 25%) were obtained. At very low temperatures (–78 °C), only trace amounts of the tandem product were observed (GLC); purification gave compound **3e** (16%).

***cis*-2-[(*Z*)-1-Methoxy-2-(4-nitrophenyl)vinyl]cyclopropyl Acetate (3e):** Compound **3e** was synthesised following the general procedure, using gold catalyst (13.1 mg, 17.0 μmol), compound **2d** (84.6 mg, 340 μmol), and vinyl acetate (295.3 mg, 3.43 mmol), at –40 °C for 15 min. The product was purified using an eluent system of CH_2Cl_2 to give compound **3e** (37.6 mg, 40%) as a bright yellow oil, along with ***cis*-14** (15.0 mg, 19%) and ***trans*-14** (19.2 mg, 24%). Data for **3e**: R_f = 0.30 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13–8.11 (m, 2 H, $CH_{arom}CNO_2$), 7.69–7.67 (m, 2 H, $CH_{arom}CC$=), 5.47 (br. s, 1 H, =CH), 4.45–4.40 (m, 1 H, CHOAc), 3.92 (s, 3 H, OCH_3), 2.00 (s, 3 H, $OCOCH_3$), 1.22 (m, 1 H, C*H*CHOAc), 1.38–1.33 (m, 1 H, CH_2), 1.22–1.18 (m, 1 H, CH_2) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 171.5 (1 C, OC=O), 156.4 (1 C, *C*=CH), 144.8 (1 C, $C_{arom}NO_2$), 143.2 (1 C, $C_{arom}CH$=), 128.3 (2 C, $CH_{arom}CCH$=), 123.6 (2 C, $CH_{arom}CNO_2$), 105.7 (1 C, C=*C*H), 55.3 (1 C, OCH_3), 52.6 (1 C, CHOAc), 20.8 (1 C, OC-O*C*H$_3$), 18.8 (1 C, *C*HCHOAc), 11.0 (1 C, CH_2) ppm. IR (thin film): $\tilde{\nu}$ = 2942, 2914, 2852, 1747, 1589, 1509, 1334, 1230, 1109, 1073, 861 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_{16}NO_5$ [M + H]$^+$ 278.1028; found 278.1026.

***cis*-/*trans*-2-(1,3-Dimethoxy-4,5-dimethylcyclopent-2-en-1-yl)cyclopropyl Acetate (*cis*-/*trans*-15):** Compounds ***cis*-15** and ***trans*-15** were synthesised following the general procedure, using gold catalyst (20.2 mg, 26.2 μmol), compound **2e** (76.3 mg, 537 μmol), and vinyl acetate (149.2 mg, 1.73 mmol), at –40 °C for 90 min, then 0 °C for 30 min. The products were purified using an eluent system of 1:1 (1:20 Et_2O/pentane)/CH_2Cl_2 to give compounds ***cis*-15** (3.2 mg, 7%) and ***trans*-15** (1.9 mg, 4%), and a 1:1 mixture of ***cis*-15** and ***trans*-15** (1.9 mg, 4%), all as yellow oils.

Data for ***cis*-15**: R_f = 0.18 [1:1 (1:20 EtOAc/pentane)/CH_2Cl_2]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.30 (br. s, 1 H, C=CH), 4.26–4.21 (m, 1 H, CHOAc), 3.57 (s, 3 H, =$COCH_3$), 3.30 (s, 3 H, CHCOC*H*$_3$), 2.91–2.85 (m, 1 H, CH=CCHC*H*), 2.77–2.72 (m, 1 H, CH=CC*H*), 2.04 (s, 3 H, $OCOCH_3$), 1.09–1.03 (m, 1 H, C*H*CHOAc), 1.14 (d, *J* = 7.4 Hz, 3 H, CH=CCHC*H*$_3$), 0.99–0.94 (m, 2 H, CH_2) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 171.7 (1 C, OC=O), 160.7 (1 C, *C*=CH), 97.2 (1 C, C=*C*H), 84.4 (1 C, C=CH*C*), 56.2 (1 C, =CO*C*H$_3$), 52.2 (1 C, CHOAc), 51.8 (1 C, C=CHCO*C*H$_3$), 45.8 (1 C, CH=C*C*H), 41.6 (1 C, CH=CCH*C*H), 21.1 (1 C, OCO*C*H$_3$), 19.7 (1 C, *C*HCHOAc), 14.7 (1 C, C=CHCCH*C*H$_3$), 13.2 (1 C, CH=CCH*C*H$_3$), 8.01 (1 C, CH_2) ppm. IR (thin film): $\tilde{\nu}$ = 2931, 2834, 1746, 1648, 1228, 1093, 781 cm^{-1}. HRMS (EI): calcd. for $C_{12}H_{19}O_2$ [M – OAc]$^+$ 195.1385; found 195.1384.

Data for ***trans*-15**: R_f = 0.25 [1:1 (1:20 EtOAc/pentane)/CH_2Cl_2]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.31–4.27 (m, 1 H, CHOAc), 4.31–4.27 (m, 1 H, C=CH), 3.56 (s, 3 H, =$COCH_3$), 3.40 (s, 3 H, C=CHCOC*H*$_3$), 2.68–2.62 (m, 1 H, CH=CC*H*), 2.57–2.52 (m, 1 H, CH=CCHC*H*), 2.03 (s, 3 H, $OCOCH_3$), 1.20–1.16 (m, 1 H, C*H*CHOAc), 1.88 (d, *J* = 7.0 Hz, 3 H, CH=CCHC*H*$_3$), 1.03 (d, *J* = 7.0 Hz, 3 H, CH=CCHCHC*H*$_3$), 0.93–0.87 (m, 2 H, CH_2) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 171.6 (1 C, OC=O), 161.3 (1 C, *C*=CH), 96.5 (1 C, C=*C*H), 83.2 (1 C, C=CH*C*), 56.1 (1 C, =CO*C*H$_3$), 52.7 (1 C, C=CHCO*C*H$_3$), 52.3 (1 C, CHOAc), 47.8 (1 C, C=CHC*C*H), 42.5 (1 C, CH=C*C*H), 23.7 (1 C, *C*HCHOAc), 20.8 (1 C, OCO*C*H$_3$), 17.4 (1 C, CH=CCH*C*H$_3$), 14.6 (1 C, C=CHCCH*C*H$_3$), 9.0 (1 C, CH_2) ppm. IR (thin film): $\tilde{\nu}$ = 2931, 2829, 1745, 1228, 1058, 914, 732 cm^{-1}. HRMS (EI): calcd. for $C_{12}H_{19}O_2$ [M – OAc]$^+$ 195.1385; found 195.1383.

***cis*-2-(1,3-Dimethoxy-4,5-dimethylcyclopent-2-en-1-yl)cyclopropyl Benzoate (*cis*-16):** Compound ***cis*-16** was synthesised following the general procedure, using gold catalyst (21.0 mg, 2.72 μmol), compound **3e** (77.3 mg, 0.54 μmol), and vinyl benzoate (142.5 mg, 0.96 mmol), at 0 °C for 15 min, then 20 °C for 15 min. The product was purified using an eluent system of 1:40 Et_2O/pentane to give compound ***cis*-16** (7.8 mg, 5%) as a grey oil. R_f = 0.44 (3:10 Et_2O/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 7.1 Hz, 2 H, $CH_{o\text{-}OBz}$), 7.55 (t, *J* = 7.4 Hz, 1 H, $CH_{p\text{-}OBz}$), 7.43 (t, *J* = 7.5 Hz, 2 H, $CH_{m\text{-}OBz}$), 4.51–4.47 (m, 1 H, CHOBz), 4.33 (d, *J* = 0.8 Hz, 1 H, C=CH), 3.57 (s, 3 H, =$COCH_3$), 3.31 (s, 3 H, =CHCOCH_3), 2.89–2.86 (m, 1 H, BzOCHC*H*), 1.26 (s, 1 H, =CC*H*CH), 1.18 (d, *J* = 7.3 Hz, 3 H, C*H*$_3$CHC=), 1.15–1.13 (m, 1 H, BzOCHC*H*$_2$), 1.11 (s, 1 H, =CCHC*H*), 1.10–1.07 (m, 1 H, BzOCHC*H*$_2$), 1.04 (d, *J* = 7.0 Hz, 3 H, C*H*$_3$CHCHC=) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 167.4 (1 C, O*C*=O), 160.9 (1 C, CH=*C*OCH$_3$), 132.9 (1 C, $CH_{p\text{-}OBz}$), 130.2 (1 C, OCO*C*$_{arom}$), 129.5 (2 C, $CH_{o\text{-}OBz}$), 128.4 (1 C, $CH_{p\text{-}OBz}$), 97.3 (1 C, C=*C*H), 84.3 (1 C, =CH*C*OCH$_3$), 56.3 (1 C, =CO*C*H$_3$), 52.8 (1 C, *C*HOBz), 52.1 (1 C, =CHCO*C*H$_3$), 45.9 (1 C, *C*HCHOBz), 29.7 (1 C, =C*C*HCH), 20.1 (1 C, =CCH*C*H), 14.6 (1 C, *C*H$_3$CHCHC=), 12.9 (1 C, *C*H$_3$CHC=), 8.0 (1 C, *C*H$_2$CHOBz) ppm. IR (thin film): $\tilde{\nu}$ = 2932, 1722, 1646, 1451, 1269, 1090, 731, 710 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{24}NaO_4$ [M + Na]$^+$ 339.1567; found 339.1572.

***cis*-2-(1-Ethoxy-2-methylprop-1-en-1-yl)cyclopropyl Acetate (3f):** Compound **3f** was synthesised following the general procedure, using gold catalyst (16.9 mg, 0.02 mmol), compound **2f**[9] (66.1 mg, 0.43 mmol), and vinyl acetate (74.1 mg, 0.86 mmol). The reaction mixture was stirred at room temperature for 15 min. A gradient eluent of diethyl ether in pentane was used for purification. At the stage of 40:1 pentane/diethyl ether, **3f** (9.3 mg, 6%) was isolated as a colourless oil. R_f = 0.46 (3:10 diethyl ether/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.35 (dt, *J* = 3.9, 6.6 Hz, 1 H, CHOAc), 3.78–3.70 (m, 1 H, C*H*$_2$CH$_3$), 3.58–3.50 (m, 1 H, C*H*$_2$CH$_3$), 1.97 (s, 3 H, CO_2CH_3), 1.67 (m, 1 H, AcOCHC*H*), 1.62 [s, 3 H, C=C(C*H*$_3$)CH$_3$], 1.62 [s, 3 H, C=C(C*H*$_3$)CH$_3$], 1.20 (t, *J* = 7.0 Hz, 3 H, CH$_2$C*H*$_3$), 1.11–1.06 (m, 1 H, AcOCHC*H*$_2$), 1.02–0.98 (m, 1 H, AcOCHC*H*$_2$) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 171.9 (1 C, OC=O), 142.0 [1 C, $(CH_3)_2C$=*C*], 119.4 [1 C, $(CH_3)_2C$=C], 64.9 (1 C, *C*H$_2$CH$_3$), 52.5 (1 C, CHOAc), 20.9 (1 C, CO_2CH_3), 18.6 [1 C, C=C(*C*H$_3$)$_2$] 17.6 [1 C, C=C(*C*H$_3$)$_2$], 16.2 (1 C, *C*HCHOAc), 15.2 (1 C, CH$_2$*C*H$_3$), 9.7 (1 C, *C*H$_2$CHOAc) ppm.

***cis*-(1,8a)-*trans*-(3a,8a)-2,5,8a-Trimethoxy-1-(4-methoxyphenyl)-1,3a,8,8a-tetrahydrocyclopenta[*a*]indene (17):** Gold catalyst (8.4 mg, 11 μmol) was dissolved in dry CH_2Cl_2 (1.5 mL), and the solution was stirred under a nitrogen atmosphere at room temperature. Compound **2b** (50.9 mg, 217 μmol) was dissolved in dry CH_2Cl_2 (1.0 mL), and this solution was added added to the solution of the gold catalyst. The flask was washed out with further dry CH_2Cl_2 (2 × 0.5 mL), and this was added to the mixture. The reaction was quenched with NEt_3 (5 drops), the mixture was filtered through Celite™, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (1:3 Et_2O/pentane) to give

dimer **17** (3.6 mg, 5%) as a yellow oil. R_f = 0.3 (1:3 Et_2O/pentane). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.22 (m, 2 H, CH_{arom}CH-COMe), 7.13 (d, J = 8.2 Hz, 1 H, MeOCCH_{arom}), 6.87 (d, J = 2.4 Hz, 2 H, CH_{arom}COMe), 6.83–6.82 (m, 1 H, CCH_{arom}COMe), 6.75 (dd, J = 2.4, 8.2 Hz, 1 H, CCCH_{arom}CH), 4.63–4.61 (m, 1 H, C=CH), 4.18 (br. s, 1 H=CHCH), 3.81 (s, 3 H, CCHCOCH_3), 3.80 (s, 3 H, p-OCH_3), 3.77 (br. s, 1 H, =CCH), 3.51 (s, 3 H, =$COCH_3$), 3.44 (d, J = 16.6 Hz, 1 H, CH_2), 3.06 (d, J = 16.8 Hz, 1 H, CH_2), 2.86 (s, 3 H, =CCHCOCH_3) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 160.1 (1 C, =C), 159.1 (1 C, C_{arom}OMe), 158.5 (1 C, CCH-C_{arom}OMe), 145.9 (1 C, =CHCHC_{arom}), 133.1 (1 C, CH_2C_{arom}), 130.6 (1 C, =CCHC_{arom}), 130.1 (2 C, CH_{arom}CHCOMe), 125.1 (1 C, CH_2CCH_{arom}), 113.6 (2 C, CH_{arom}COMe), 112.6 [1 C, CH_{arom}C(OMe)CHC], 109.6 (1 C, MeOCH_{arom}C), 96.0 (1 C, =CH), 93.9 (1 C, CH_2COMe), 59.1 (1 C, =CCH), 57.4 (1 C, =CHCH), 56.5 (1 C, =COCH_3), 55.4 (1 C, $C_{arom}OCH_3$), 55.2 (1 C, $C_{arom}OCH_3$), 52.3 (1 C, CH_2COCH_3), 41.5 (1 C, CH_2) ppm. IR (thin film): $\tilde{\nu}$ = 2928, 2829, 1511, 1248, 1177, 1033, 832, 580 cm^{-1}. HRMS (EI): calcd. for $C_{22}H_{24}O_4$ $[M]^+$ 352.1675; found 352.1674.

Supporting Information (see footnote on the first page of this article): Copies of ^1H and ^{13}C NMR spectra.

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[1] N. D. Shapiro, F. D. Toste, *J. Am. Chem. Soc.* **2008**, *130*, 9244.
[2] N. D. Shapiro, Y. Shi, F. D. Toste, *J. Am. Chem. Soc.* **2009**, *131*, 11654.
[3] N. Kim, Y. Kim, W. Park, D. Sung, A. K. Gupta, C. H. Oh, *Org. Lett.* **2005**, *7*, 5289.
[4] G. Zhang, L. Zhang, *J. Am. Chem. Soc.* **2008**, *130*, 12598.
[5] M. J. Johansson, D. J. Gorin, S. T. Staben, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 18002.
[6] K. Fourmy, S. Mallet-Laeira, O. Dechy-Cabaret, *Organometallics* **2013**, *32*, 1571.
[7] a) V. V. Pagar, A. M. Jadhav, R.-S. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 20728; b) Shu, X.-Z. D. Shu, C. M. Schienebeck, W. Tang, *Chem. Soc. Rev.* **2012**, *41*, 7698.
[8] C. A. Sperger, J. E. Tungen, A. Fiksdahl, *Eur. J. Org. Chem.* **2011**, 3719.
[9] N. Iqbal, C. A. Sperger, A. Fiksdahl, *Eur. J. Org. Chem.* **2013**, 907.
[10] N. Iqbal, A. Fiksdahl, *J. Org. Chem.* **2013**, *78*, 7885.
[11] C. Wiles, P. Watts, S. J. Haswell, E. Pombo-Villar, *Tetrahedron Lett.* **2002**, *43*, 2945.
[12] X. Hang, W. Gu, Q. Chen, J. Xiao, *Tetrahedron* **2009**, *65*, 6320.
[13] M. P. Kumar, R.-S. Liu, *J. Org. Chem.* **2006**, *71*, 4951.
[14] M. C. Bagley, C. Glover, *Molecules* **2010**, *15*, 3211.
[15] A. Kolarovic, Z. Faberova, *J. Org. Chem.* **2009**, *74*, 7199.

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