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Gold(I)-Catalyzed [4+2] Annelation/Nucleophilic Addition Sequence: Stereoselective Synthesis of Functionalized Bicyclo[4.3.0]nonenes

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This work is dedicated to Professor Daniel Uguen at the occasion of his 65th birthday.

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Abstract: The gold(I)-catalyzed isomerization of readily available 1,8-dien-4-ynes allows the rapid construction of a variety of synthetically useful bicyclo[4.3.0]nonenes by a stereoselective sequence involving a [4+2] annelation/nucleophilic addition process.

Keywords: cycloaddition; 1,5-enynes; gold; homogeneous catalysis; polycycles

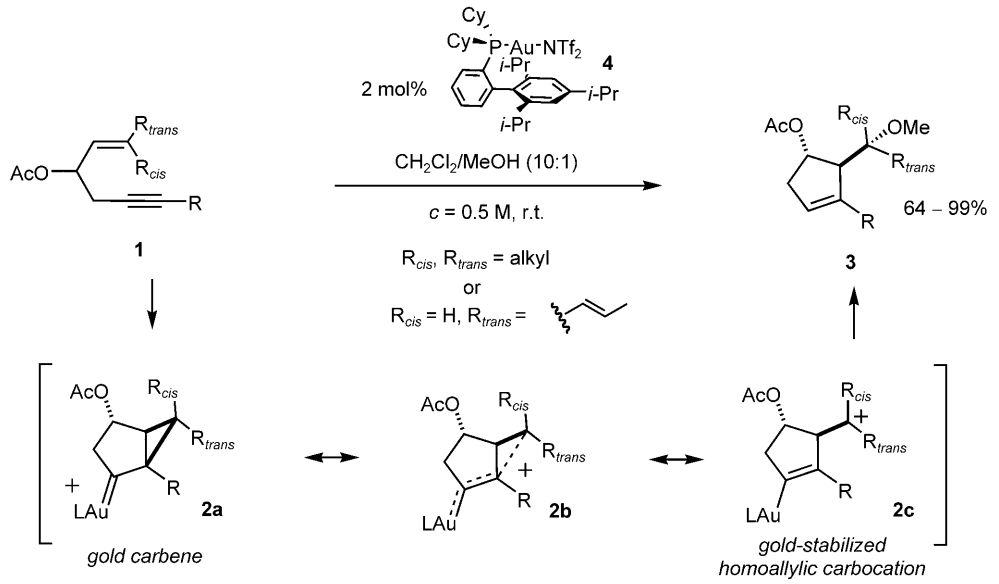
Introduction

The bicyclo[4.3.0]nonane framework is a structural unit that is frequently found in a wide range of natural products such as steroids, terpenoids or even alkaloids. Among the variety of known strategies leading to this common bicyclic structure, those related to the use of [4+2] annelations are especially attractive since they are generally selective and allow the rapid and efficient creation of new C–C bonds.[1] In the past few years, homogeneous gold and platinum catalysis[2] have emerged as powerful synthetic tools to generate molecular diversity and structural complexity. Several recent reports have shown, for instance, that the activation of either an alkyne or an allene by gold- or platinum-based catalysts can lead to intermediates that can participate in various [4+2],[3] 1,3-dipolar[4] or [4+3] cycloadditions.[5] As part of a program directed towards the development of new gold-catalyzed reactions,[6] we discovered and report herein that 1,8-dien-4-ynes can be transformed into functionalized bicyclo[4.3.0]nonenes by a new gold(I)-catalyzed sequence of [4+2] annelation/nucleophilic addition.

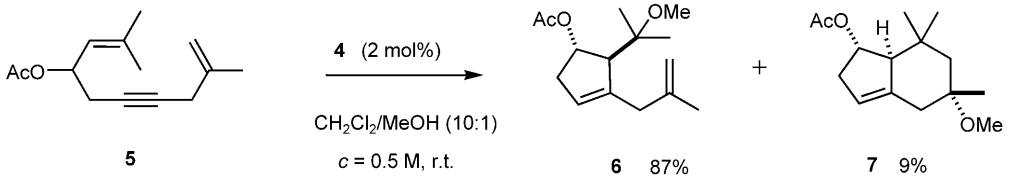
Results and Discussion

We recently reported that functionalized cyclopentenes **3** could be efficiently synthesized by a gold(I)-catalyzed 5-*endo*-methoxycyclization of 1,5-enynes **1** (Scheme 1).[6f,7] To account for the observed regio- and stereoselectivity, gold carbene **2a** was initially proposed as the key intermediate. However, similar studies on the cycloisomerization of 1,6-enynes[7c–l] and recent investigations by Fürstner and Morency[8] suggest that an intermediate possessing a pronounced carbocationic character might play a significant role in this transformation. Even if formulae **2a–c** are mesomeric forms of the same intermediate, the presence of stabilizing groups on the alkene moiety would electronically favour an intermediate of type **2c** compared to **2a**. This stabilized carbocationic form is indeed in good agreement with our reported results since 1,5-enynes possessing cation-stabilizing subtituents on the alkene moiety (trisubstituted alkenes or 1,3-dienes) proved to be excellent substrates for this transformation.

During the course of the study, we also noticed that substrate **5** furnished two structurally different products under the same reaction conditions [2 mol% of gold(I) complex **4**[9] in a 10:1 CH_2Cl_2/MeOH mixture at $c=0.5$ M] (Scheme 2). While the expected cyclopentene **6** was mainly produced, a very small amount (9%) of an unidentified product was also isolated.[10]



Scheme 1. Methoxycyclization of 1,5-enynes.



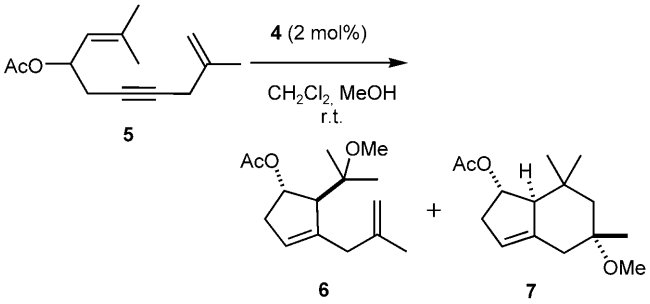
Scheme 2. First experimental observation of [4+2] annelation.

This transformation was repeated on a larger scale and spectroscopic studies showed that this by-product was bicyclo[4.3.0]nonene **7**, derived from a formal sequence of [4+2] annelation/nucleophilic addition.

Even though low yielding, the formation of **7** was remarkable since two cycles, three new bonds and two quaternary centres were created in a stereospecific manner. Given the synthetic potential of this new and unexpected transformation, we decided to improve the yield of **7**. Assuming that the *intramolecular* [4+2] annelation was a competitive process to the *intermolecular* nucleophilic addition of methanol leading to cyclopentene **6**, we decided to study the effects of the concentration and the quantity of methanol used on the course of the reaction. The results, compiled in Table 1, clearly indicate that the direct intermolecular nucleophilic addition of methanol is a more favoured process than the intramolecular [4+2] annelation. Even if diluting the reaction medium from 0.5 M to 0.025 M and lowering the quantity of methanol gradually improved the formation of bicyclic compound **7**, it was not possible to suppress the formation of cyclopentene **6**. A limit was reached at a 0.05 M concentration, using a slight excess of methanol (entry 4). Bicyclo[4.3.0]nonene **7** was formed in 48% yield under these conditions.

We next focused our attention onto the variation of the nucleophile, presuming that the nature of this latter species should influence the course of the reac-

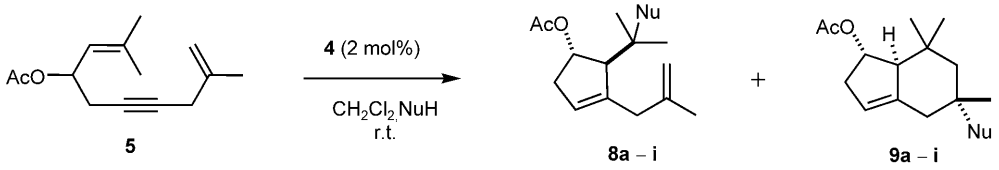
Table 1. Optimization of the reaction conditions.



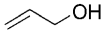
Entry	MeOH (equiv.)	[*c*] (M)	*t* [h]	**6** [%][a]	**7** [%][a]
1	5	0.5	5	72	15
2	1.5	0.5	4	61	17
3	5	0.05	6	52	30
4	1.5	0.05	20	40	48
5	5	0.025	5	43	41
6	1.5	0.025	18	38	49

[a] NMR spectroscopic yields with respect to 1,3,5-trimethoxybenzene.

Table 2. Effect of the nucleophile on the formation of the bicyclo[4.3.0]nonene.



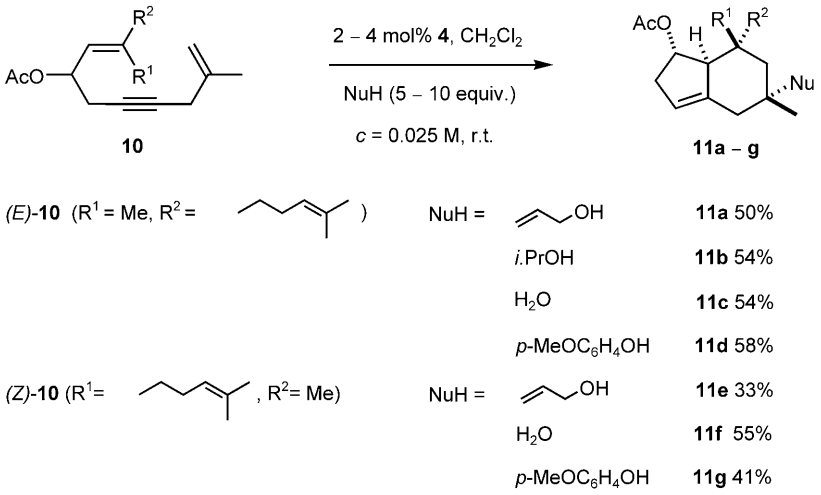
5 8a – i 9a – i

Entry	Nucleophile	(equiv.)	[*c*] (M)	*t* [h]	**8a–i**	[%][a]	**9a–i**	[%][a]
1		1.5	0.025	12	**8a**	20	**9a**	62
2	BnOH	1.5	0.025	12	**8b**	7	**9b**	53
3	*i*-PrOH	1.5	0.025	24	**8c**	10	**9c**	65
4	H_2O[b]	1.5	0.025	20	**8d**	<5[c]	**9d**	65
5	*p*-MeO-C_6H_4OH	5	0.025	19	**8e**	traces	**9e**	70[d]
6	*p*-Cl-C_6H_4OH	5	0.25	15	**8f**	traces	**9f**	40
7	$Ph(CH_2)_2COOH$	5	0.25	12	**8g**	traces	**9g**	56
8[e]	$BocNH_2$	5	0.25	70	**8h**	7	**9h**	37[f]
9	$CBzNH_2$	5	0.25	12	**8i**	7[c]	**9i**	36

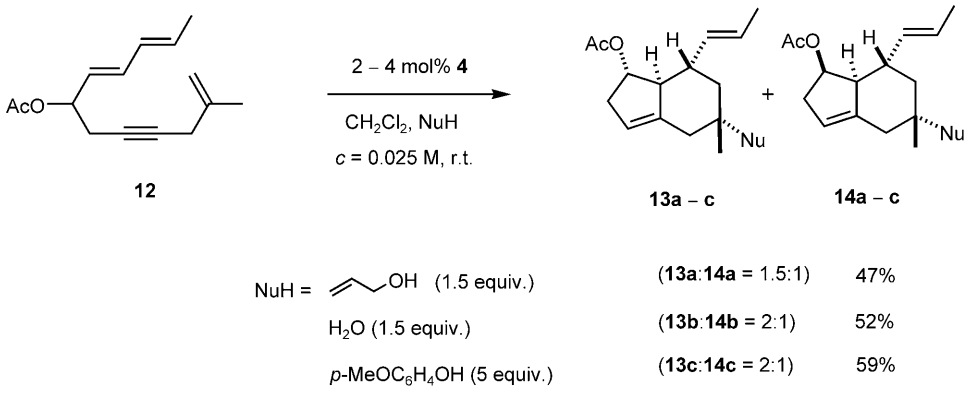
[a] Isolated yields.
[b] Acetone was used as a cosolvent.
[c] NMR spectroscopic yield.
[d] Isolated in 40% yield with 1.5 equiv. of *p*-$MeOC_6H_4OH$.
[e] 4 mol% of **4**/conversion of **5**: 76%.
[f] Isolated in mixture with **8h**.

tion. The use of a weaker nucleophile was supposed to slow down the direct trapping leading to the monocyclized product, thus favoring the [4+2] annelation process. The results of this study are compiled in Table 2.

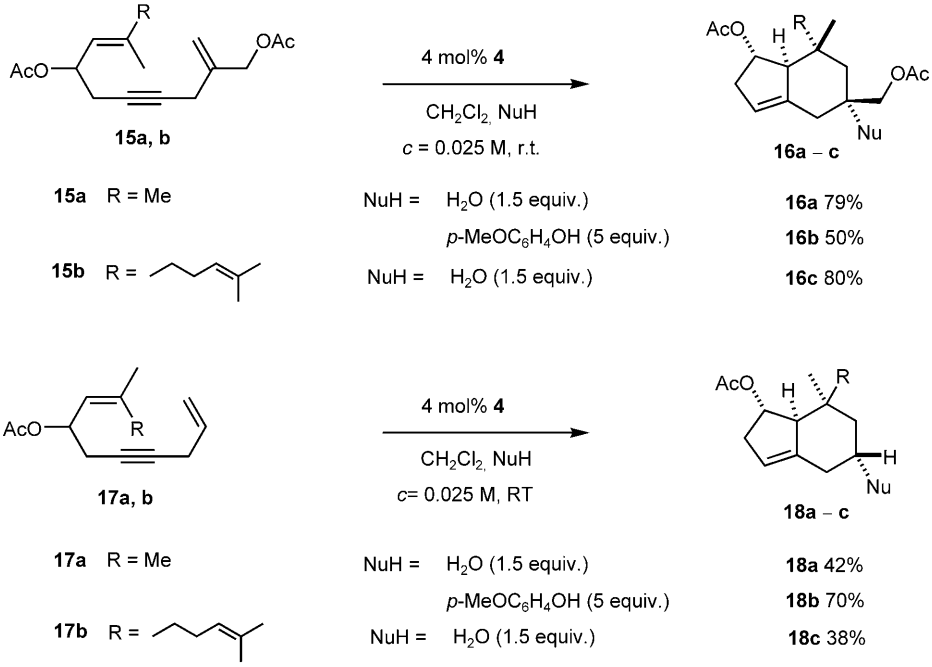
The reaction proved to be quite general and dienyne **5** reacted with various nucleophiles to furnish compounds **9a–i** in yields ranging from 36–70%. It is noteworthy that bicyclo[4.3.0]nonenes **9a–i** were isolated as single isomers, thus attesting of the general stereospecificity of the transformation. Working with 1.5 equiv. of another primary or secondary alcohol (allyl, benzyl or isopropyl alcohol) at a 0.025 M overall concentration only slightly improved the [4+2] annelation process, while the amount of cyclopentene **8** produced was noticeably reduced (entries 1–3). In these cases, bicyclo[4.3.0]nonenes **9a–c** were isolated in yields ranging from 53–65%. Water was also successfully used as a nucleophile allowing the formation of tertiary alcohol **9d** which was isolated in 65% yield (entry 4). For more acidic species (phenol, carboxylic acid), a higher overall concentration and/or a greater amount of the nucleophile were required for the efficient formation of the bicyclic product (entries 5–7). Bicyclo[4.3.0]nonenes **9e–g** were isolated in yields ranging from 40–70% and only low amounts or traces



Scheme 3. Au(I)-catalyzed transformation of (*E*)-**10** and (*Z*)-**10**



Scheme 4. Au(I)-catalyzed transformation of **12**.



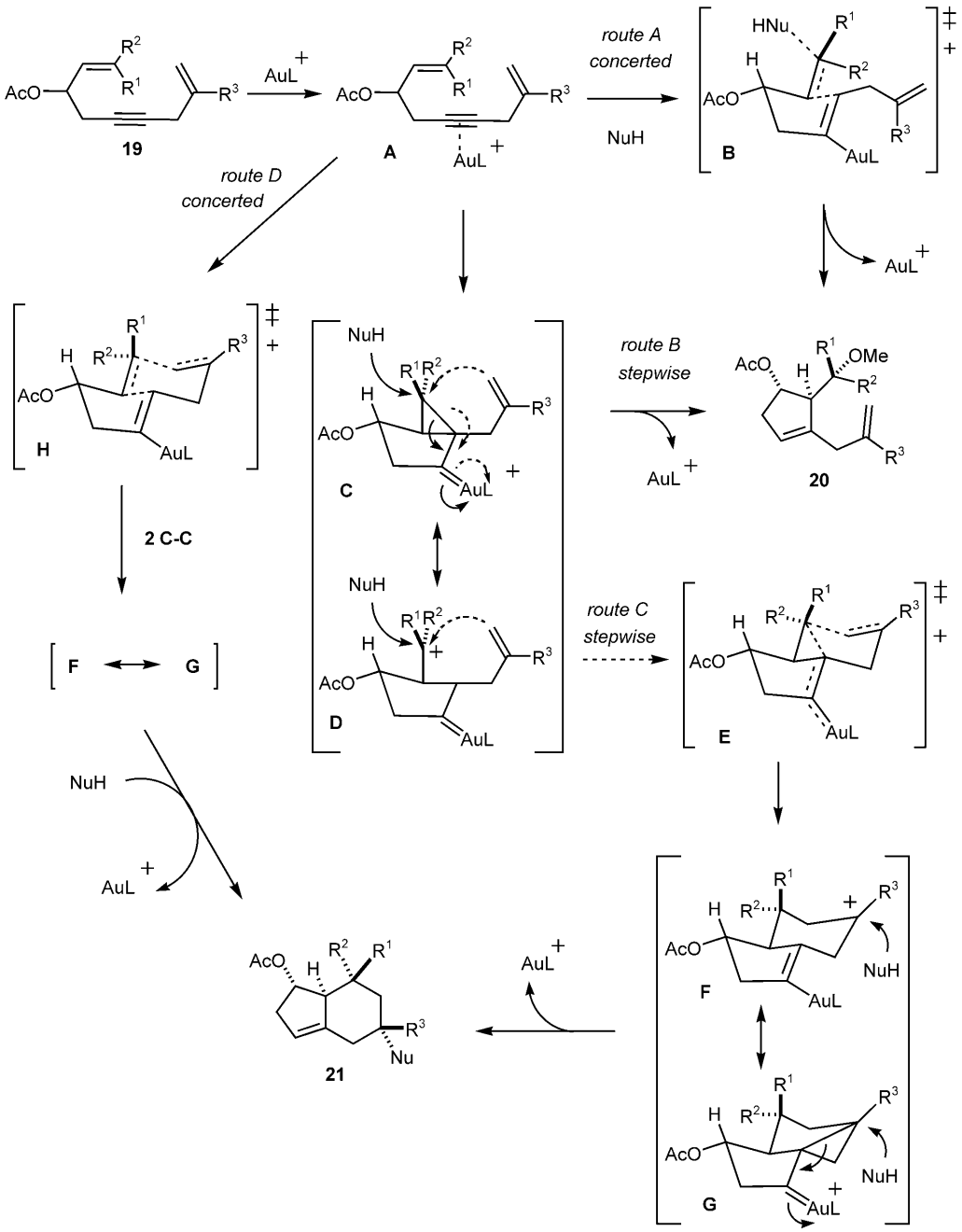
Scheme 5. Au(I)-catalyzed transformation of **15a** and **b** and **17a** and **b**.

of cyclopentene by-products **8e–g** could be observed. Interestingly, primary benzyloxy- and *tert*-butyloxycarbamates were also compatible nucleophiles, even if the reaction proved to be more sluggish in these cases (entries 8 and 9).[11]

The stereospecificity of the reaction was further highlighted by the conversion of substrate (*E*)-**10** and (*Z*)-**10** into the corresponding bicyclo[4.3.0]nonenes **11a–d** and **11e–g** (Scheme 3). The stereoinformation from the *cis*- or *trans*-substituted alkenes was completely transferred to the final bicyclo[4.3.0]nonenes with the formation of two new quaternary asymmetric centres. It is also interesting to note that (*Z*)-**10** was the less reactive substrate. A higher loading of catalyst **4** (4 mol%) and a lower amount of nucleophile (5 equiv.) were required in this case.[12]

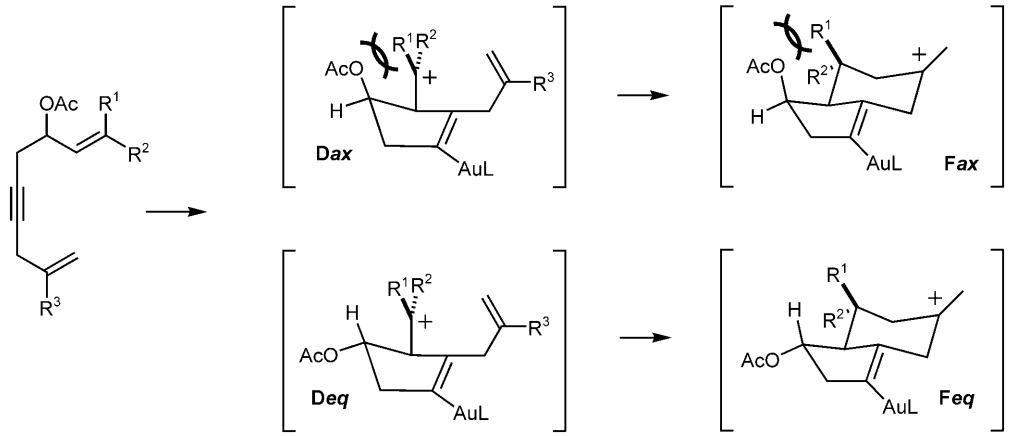
Substrate **12**, derived from sorbal and possessing cation-stabilizing subtituents on the alkene moiety, also reacted with a series of nucleophiles in the presence of catalyst **4** (2–4 mol%) (Scheme 4). However, the reaction was surprisingly not selective and led to diastereoisomeric mixtures of bicyclo[4.3.0]nonenes **13a–c** and **14a–c**.

Finally, the transformation was also effective with substrates bearing other allylic substituents at the alkyne terminus (Scheme 5). Substrates **15a** and **b** reacted, for instance with water, in the presence of catalyst **4** (4 mol%) to furnish bicyclo[4.3.0]nonenes **16a** and **16c** in respectively 79% and 80% yields. A simple, less nucleophilic allyl group, could also be used as attested by the stereoselective conversion of **17a** and **b** into **18a–c**.



Scheme 6. Mechanistic proposal.

To account for these observations, a divergent mechanism leading to cyclopentene **20** and bicyclo-[4.3.0]nonene **21** is presented in Scheme 6. Complexation of the cationic gold species to the alkyne function of 1,8-dien-4-yne **19** furnishes intermediate **A**. The formation of cyclopentene **20** may then proceed *via* a concerted diastereoselective cyclization/nucleophilic addition sequence through a possible transition state of type **B** (route A).[13] Even if such a mechanism cannot be completely ruled out, it is rather unlikely. In the related case of 1,6-enynes, the carbocyclization can indeed occur in the absence of an internal or external nucleophile as previously reported by Chung and co-workers.[14] The formation of cyclopentene **20** may alternatively proceed *via* a stepwise mechanism. The gold(I) activation of the triple bond may promote the 5-*endo* nucleophilic addition of the pendant olefin which leads to the formation of intermediate **C**, as proposed in numerous gold-catalyzed cycloisomerizations of enynes.[7] This intermediate should possess a very distorted cyclopropyl-carbene structure[15] and should actually be better depicted as a gold(I)-stabilized homoallylic carbocation[8] (canonical form **D**) due to the presence of stabilizing groups on the



Scheme 7. Source of stereoselectivity.

alkene moiety (trisubstituted alkenes or 1,3-dienes).[16]

Following route B, a nucleophilic *intermolecular* attack of the nucleophile, furnishes cyclopentene **20** after a final protodemetallation step. Alternatively, the *intramolecular* nucleophilic attack of the allyl moiety (route C), through a chair-like transition state of type **E**, completes the [4+2] annelation process and leads to the formation of the gold(I)-stabilized homoallylic carbocation **F**, which could have some carbene character (canonical form **G**). A final intermolecular and regioselective nucleophilic attack of the nucleophile onto this configurationally stable intermediate stereoselectively furnishes bicyclo-[4.3.0]nonene **21**.[17]

This mechanism accounts for the observed effects of the dilution and the nature of the nucleophile on the relative formation of **20** and **21** (see Table 1 and Table 2). One may assume that using a lower quantity of the nucleophile in combination with a more diluted reaction medium or using a weaker nucleophile would kinetically disfavour route B thus allowing the addition of the less nucleophilic allyl moiety on the activated intermediate **D**. The stereoselective functionalization by the nucleophile could be explained by the formation of the configurationally stable gold-stabilized homoallylic cation **F**.[8] To the best of our knowledge, no example of translocation of such a stabilized intermediate (from **C**↔**D** to **F**↔**G**) during a gold-stabilized process has been reported in the literature.

An alternative mechanism for the formation of bicyclo[4.3.0]nonene **21** is also presented in Scheme 6. On the basis of the recent report by Fürstner and Morency,[8] a more concerted [4+2] annelation process, involving a "*highly ordered, chair-like and charge-delocalized*" transition state of type **H**, could also be envisaged. Even if such a concerted mechanism was effective, it cannot be presented as the only one leading to the formation of **21**, since it does not account for all the experimental observations. This concerted mechanism does not explain the formation of cyclopentene **20**, which should therefore be produced by the initially proposed mechanism (route B). Consequently, if route B and route D were the only two competing pathways leading respectively to **20** and **21**, one would not expect a variation of the **20**:**21** ratio when diluting the reaction medium and/or lowering the quantity of the nucleophile (see Table 1). It seems therefore more likely that bicyclo[4.3.0]nonene **21** is produced from key intermediate **D** following a stepwise mechanism (route C). However, a concerted mechanism cannot be completely ruled out and could be involved to some extent in the formation of **21**.

While the reaction proved to be generally stereospecific, the reaction of substrate **12** furnished a mixture of diastereoisomers **13a–c** and **14a–c** (Scheme 4). This loss of stereoselectivity might be explained by examining the possible intermediates involved in the synthesis of the bicyclo[4.3.0]nonenes (Scheme 7). In the case of a substrate possessing a trisubstituted alkene (R^1, $R^2 \neq H$), a pseudo-1,3-diaxial interaction strongly disfavours the formation of intermediates **D*ax*** and **F*ax***. The stereoselective synthesis of the products results from the exclusive formation of intermediates **D*eq*** and **F*eq*** in which the acetoxy group occupies a pseudo-equatorial position. The lack of a similar 1,3-diaxal interaction in the case of substrate **12** ($R^1 = H$), leads to the competitive formation of intermediates **D*ax*** and **D*eq*** from which are respectively produced **14** and **13**. A preference is however noted for **13**, due to the more favoured pseudo-equatorial position of the acetoxy moiety.

Conclusions

In summary, it was found that 1,8-dien-4-ynes could be transformed into functionalized bicyclo-[4.3.0]nonenes by a gold(I)-catalyzed sequence of [4+

2] annelation/nucleophilic addition. Even if the previously reported process of 5-*endo* cyclization/nucleophilic trapping strongly competes with this new transformation, a proper choice of the nucleophile and the reaction conditions allows the relatively efficient synthesis of a variety of bicyclo[4.3.0]nonenes. This two-component reaction, which is proposed to proceed *via* a stereospecific two-step [4+2] annelation, allows a rapid increase of structural complexity since two new cycles and up to three asymmetric centres can be generated in a single transformation from readily available linear substrates. Further studies, including the development of an asymmetric version of this gold(I)-catalyzed process, are underway and will be reported in due course.

Experimental Section

General Procedures for the Au(I)-Catalyzed Cyclization of 1,8-dien-4-ynes

Procedure A (NuH = alcohol, phenol, carbamate, acid): The 1,8-dien-4-yne (1.0 equiv.) and the nucleophile were dissolved in CH_2Cl_2. To this solution catalyst **4** (0.02 equiv.) was added. The mixture was stirred at room temperature and periodically monitored by TLC. Upon completion of the reaction, the mixture was evaporated and purified by flash column chromatography (SiO_2, PE/Et_2O).

Procedure B (NuH = H_2O): The 1,8-dien-4-yne (1.0 equiv.) was dissolved in CH_2Cl_2. To this solution wet acetone (approximately 1.5 equiv. H_2O) or a particular amount of H_2O with acetone as a cosolvent and catalyst **4** (0.02 equiv.) were added. The mixture was stirred at room temperature and was periodically monitored by TLC. Upon completion of the reaction, the mixture was evaporated and purified by flash column chromatography (SiO_2, PE/Et_2O).

rac-(1*S*,2*S*)-2-(2-Methoxypropan-2-yl)-3-(2-methylallyl)cyclopent-3-enyl Acetate (6)

According to procedure A using compound **5** (55.1 mg, 0.25 mmol) and MeOH (50 μL, 1.25 mmol) in CH_2Cl_2 (0.450 mL) afforded compound **6** as a yellowish oil after 5 h; yield: 38.6 mg (61%); R_f (PE/Et_2O 8:2); 0.39; ^{1}H NMR (400.2 MHz, $CDCl_3$): δ = 5.49 (br. s, 1H), 5.20 (d, J = 6.4 Hz, 1H), 4.81 (s, 1H), 4.73 (s, 1H), 3.18 (s, 3H), 2.92 (q, J = 15.8 Hz, 2H), 2.82 (s, 1H), 2.77–2.68 (m, 1H), 2.14 (d, J = 17.9 Hz, 1H), 2.02 (s, 3H), 1.71 (s, 3H), 1.18 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.2 (C), 143.9 (C), 141.8 (C), 126.6 (CH), 111.7 (CH_2), 78.0 (CH), 76.9 (C), 60.2 (CH), 49.0 (CH_3), 39.8 (CH_2), 39.3 (CH_2), 23.4 (CH_3), 22.8 (CH_3), 22.5 (CH_3), 21.4 (CH_3); IR (CCl_4): ν = 3075 (w), 2976 (s), 2935 (s), 2831 (m), 1736 (s), 1647 (w), 1441 (m), 1372 (m), 1243 (s), 1182 (m), 1143 (m), 1077 (m), 1026 cm^{-1} (m); MS (CI, NH_3): m/z = 253 (MH^+), 238, 229, 221; HR-MS-EI: m/z = 252.1726 (calcd. for $C_{15}H_{24}O_3$: 252.1726).

rac-(1*S*,5*S*,7a*S*)-5-Methoxy-5,7,7-trimethyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (7)

According to procedure using compound **5** (55.1 mg, 0.25 mmol) and MeOH (50 μL, 1.25 mmol) in CH_2Cl_2 (0.450 mL) afforded compound **7** as a yellowish ouil after 5 h; yield: 10.6 mg (17%); R_f (PE/Et_2O 8:2): 0.33; ^{1}H NMR (400.2 MHz, $CDCl_3$): δ = 5.39–5.35 (m, 1H), 5.18 (d, J = 6.9 Hz, 1H), 3.22 (s, 3H), 2.75–2.66 (m, 1H), 2.46 (dd, J = 12.6 Hz, J = 1.7 Hz, 1H), 2.32–2.24 (m, 2H), 2.21–2.14 (m, 1H), 2.04 (s, 3H), 1.63 (dd, J = 13.5 Hz, J = 1.9 Hz, 1H), 1.56 (d, J = 13.6 Hz, 1H), 1.18 (s, 3H), 1.06 (s, 3H), 0.76 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.7 (C), 140.6 (C), 121.3 (CH), 75.6 (C), 74.8 (CH), 62.8 (CH), 51.4 (CH_2), 48.8 (CH_3), 41.1 (CH_2), 40.6 (CH_2), 34.2 (C), 31.7 (CH_3), 23.5 (CH_3), 22.0 (CH_3), 21.5 (CH_3); IR (CCl_4): ν = 3049 (w), 2935 (s), 2848 (m), 2360 (w), 1737 (s), 1666 (w), 1639 (w), 1591 (w), 1460 (m), 1436 (m), 1372 (m), 1245 (s), 1112 (m), 1072 (m), 1028 cm^{-1} (m); MS (CI, NH_3): m/z = 270 (MNH_4^+), 253 (MH^+), 238, 221; HR-MS EI: m/z = 252.1718 (calcd. for $C_{15}H_{24}O_3$: 252.1726).

rac-(1*S*,2*S*)-2-[2-(Allyloxy)propan-2-yl]-3-(2-methylallyl)cyclopent-3-enyl Acetate (8a)

According to procedure A using compound **5** (55.1 mg, 0.25 mmol) and allylic alcohol (26 μL, 0.375 mmol) in CH_2Cl_2 (10 mL) afforded compound **8a** as a yellowish oil after 12 h; yield: 14.0 mg (20%); R_f (PE/Et_2O 9:1): 0.63; ^{1}H NMR (400.2 MHz, $CDCl_3$): δ = 5.89 (ddt, J = 17.3 Hz, J = 10.6 Hz, J = 5.3 Hz, 1H), 5.50 (br. s, 1H), 5.25 (ddd, J = 17.2 Hz, J = 3.4 Hz, J = 1.7 Hz, 1H), 5.25 (d, J = 6.3 Hz, 1H), 5.10 (ddd, J = 10.3 Hz, J = 2.9 Hz, J = 1.5 Hz, 1H), 4.81 (s, 1H), 4.74 (s, 1H), 3.92 (dt, J = 5.0 Hz, J = 1.3 Hz, 2H), 2.97 (d, J = 16.2 Hz, 1H), 2.90 (d, J = 16.4 Hz, 1H), 2.85 (s, 1H), 2.79–2.70 (m, 1H), 2.19–2.11 (m, 1H), 2.02 (s, 3H), 1.71 (s, 3H), 1.33 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.7 (C), 144.0 (C), 141.8 (C), 135.9 (CH), 126.7 (CH), 115.5 (CH_2), 111.7 (CH_2), 78.0 (CH), 77.2 (C), 62.5 (CH_2), 61.0 (CH), 39.8 (CH_2), 39.3 (CH_2), 24.0 (CH_3), 23.1 (CH_3), 22.5 (CH_3), 21.4 (CH_3); IR (CCl_4): ν = 3077 (m), 2976 (s), 2930 (s), 2858 (s), 1737 (s), 1647 (m), 1436 (m), 1372 (s), 1243 (s), 1142 (s), 1026 cm^{-1} (s); MS (CI, NH_3): m/z = 279 (MH^+), 238, 221; HR-MS-EI: m/z = 278.1886 (calcd. for $C_{17}H_{26}O_3$: 278.1882).

rac-(1*S*,5*S*,7a*S*)-5-(Allyloxy)-5,7,7-trimethyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (9a)

According to procedure A using compound **5** (55.1 mg, 0.25 mmol) and allylic alcohol (26 μL, 0.375 mmol) in CH_2Cl_2 (10 mL) afforded compound **9a** as a yellowish oil after 12 h; yield: 43.1 mg (62%); R_f (PE/Et_2O 8:2): 0.57; ^{1}H NMR (400.2 MHz, $CDCl_3$): δ = 5.91 (ddt, J = 17.2 Hz, J = 10.3 Hz, J = 5.5 Hz, 1H), 5.39–5.36 (m, 1H), 5.27 (ddd, J = 17.2 Hz, J = 3.4 Hz, J = 1.7 Hz, 1H), 5.18 (d, J = 7.0 Hz, 1H), 5.12 (ddd, J = 10.3 Hz, J = 3.1 Hz, J = 1.4 Hz, 1H), 3.95 (ddt, J = 7.0 Hz, J = 5.5 Hz, J = 1.5 Hz, 2H), 2.76–2.66 (m, 1H), 2.50 (d, J = 12.4 Hz, 1H), 2.32–2.20 (m, 3H), 2.04 (s, 3H), 1.65 (s, 2H), 1.23 (s, 3H), 1.07 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.7 (C), 140.6 (C), 136.1 (CH), 121.3 (CH), 116.0 (CH_2), 76.0 (C), 74.8 (CH), 62.8 (CH), 62.4 (CH_2), 51.9 (CH_2), 41.1 (CH_2), 41.0 (CH_2),

34.2 (C), 31.7 (CH_3), 24.3 (CH_3), 22.0 (CH_3), 21.5 (CH_3); IR (CCl_4): $\nu = 3051$ (m), 2954 (s), 2924 (s), 2870 (s), 1736 (s), 1648 (m), 1458 (s), 1437 (s), 1372 (s), 1239 (s), 1111 (s), 1062 (s), 1025 cm^{-1} (s); MS (CI, NH_3): $m/z = 296$ (MNH_4^+), 279 (MH^+), 238, 221; HR-MS-EI: $m/z = 278.1872$ (calcd. for $C_{17}H_{26}O_3$: 278.1882).

rac-(1*S*,2*S*)-2-(2-(Benzyloxy)propan-2-yl)-3-(2-methylallyl)cyclopent-3-enyl Acetate (8b)

According to procedure A using compound **5** (55.1 mg, 0.25 mmol) and BnOH (39 μL, 0.375 mmol) in CH_2Cl_2 (10 mL) afforded compound **8b** as a yellowish oil after 12 h; yield: 5.9 mg (7%); R_f (PE/Et_2O 9:1): 0.40; ^1H NMR (400.2 MHz, $CDCl_3$): $\delta = 7.32$ (d, $J = 4.4$ Hz, 4H), 7.27–7.22 (m, 1H), 5.52 (br. s, 1H), 5.31 (d, $J = 6.4$ Hz, 1H), 4.78 (s, 1H), 4.67 (s, 1H), 4.46 (s, 2H), 2.96–2.91 (m, 3H), 2.81–2.72 (m, 1H), 2.20–2.13 (m, 1H), 2.00 (s, 3H), 1.64 (s, 3H), 1.30 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta =$ 170.8 (C), 144.0 (C), 141.8 (C), 139.6 (C), 128.3 (CH), 127.3 (CH), 127.1 (CH), 126.9 (CH), 111.7 (CH_2), 78.1 (CH), 77.5 (C), 63.5 (CH_2), 61.3 (CH), 39.8 (CH_2), 39.4 (CH_2), 24.1 (CH_3), 23.2 (CH_3), 22.4 (CH_3), 21.4 (CH_3); IR (CCl_4): $\nu =$ 3069 (w), 3033 (w), 2974 (m), 2929 (m), 1737 (s), 1647 (w), 1451 (m), 1372 (m), 1243 (s), 1141 (m), 1050 (m), 1027 cm^{-1} (m); MS (CI, NH_3): $m/z = 346$ (MNH_4^+), 329 (MH^+), 293, 238; HR-MS-EI: $m/z = 328.2041$ (calcd. for $C_{21}H_{28}O_3$: 328.2039).

rac-(1*S*,5*S*,7a*S*)-5-(Benzyloxy)-5,7,7-trimethyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (9b)

According to procedure A using compound **5** (55.1 mg, 0.25 mmol) and BnOH (39 μL, 0.375 mmol) in CH_2Cl_2 (10 mL) afforded compound **9b** as a yellowish oil after 12 h; yield: 43.6 mg (53%); R_f (PE/Et_2O 9:1): 0.35; ^1H NMR (400.2 MHz, $CDCl_3$): $\delta = 7.37$–7.30 (m, 4H), 7.28–7.22 (m, 1H), 5.40 (br. s, 1H), 5.21 (d, $J = 6.9$ Hz, 1H), 4.51 (d, $J =$ 20.4 Hz, 1H), 4.48 (d, $J = 20.4$ Hz, 1H), 2.78–2.67 (m, 1H), 2.58 (d, $J = 12.7$ Hz, 1H), 2.36–2.26 (m, 3H), 2.04 (s, 3H), 1.74 (s, 2H), 1.32 (s, 3H), 1.09 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 170.7$ (C), 140.6 (C), 139.6 (C), 128.4 (CH), 127.5 (CH), 127.3 (CH), 121.4 (CH), 76.3 (C), 74.9 (CH), 63.4 (CH_2), 62.9 (CH), 52.0 (CH_2), 41.1 (CH_2), 41.0 (CH_2), 34.3 (C), 31.8 (CH_3), 24.4 (CH_3), 22.1 (CH_3), 21.5 (CH_3); IR (CCl_4): $\nu = 3031$ (w), 2975 (s), 2929 (s), 2866 (s), 1737 (s), 1663 (w), 1606 (w), 1452 (m), 1375 (s), 1244 (s), 1115 cm^{-1} (s); MS (CI, NH_3): $m/z = 346$ (MNH_4^+), 300, 293; HR-MS-EI: $m/z = 328.2032$ (calcd. for $C_{21}H_{28}O_3$: 328.2039).

rac-(1*S*,2*S*)-2-(2-Isopropoxypropan-2-yl)-3-(2-methylallyl)cyclopent-3-enyl Acetate (8c)

According to procedure A using compound **5** (55.1 mg, 0.25 mmol) and *i*-PrOH (29 μL, 0.375 mmol) in CH_2Cl_2 (10 mL) afforded compound **8c** as a yellowish oil after 24 h; yield: 7.0 mg (10%); R_f (PE/Et_2O 9:1): 0.40; ^1H NMR (400.2 MHz, $CDCl_3$): $\delta = 5.48$ (br. s, 1H), 5.22 (d, $J = 6.3$ Hz, 1H), 4.81 (s, 1H), 4.76 (s, 1H), 3.81 (sept., $J = 6.1$ Hz, 1H), 2.98 (s, 2H), 2.76–2.66 (m, 2H), 2.17–2.09 (m, 1H), 2.01 (s, 3H), 1.71 (s, 3H), 1.17 (s, 3H), 1.12–1.07 (m, 9H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 170.9$ (C), 144.2 (C), 142.4 (C), 126.4 (CH), 111.9 (CH_2), 78.2 (CH), 77.5 (C), 63.2 (CH), 63.0 (CH), 40.3 (CH_2), 39.4 (CH_2), 25.3 (CH_3), 25.1 (CH_3), 24.5 (CH_3), 22.9 (CH_3), 22.5 (CH_3), 21.5 (CH_3); IR (CCl_4): $\nu = 3075$ (w), 3045 (w), 2974 (s), 2360 (w), 2336 (w), 1736 (s), 1647 (w), 1458 (w), 1372 (m), 1243 (s), 1173 (w), 1116 cm^{-1} (m); MS (CI, NH_3): $m/z = 298$ (MNH_4^+), 281 (MH^+), 238, 221; HR-MS-EI: $m/z = 280.2026$ (calcd. for $C_{17}H_{28}O_3$: 280.2038).

rac-(1*S*,5*S*,7a*S*)-5-Isopropoxy-5,7,7-trimethyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (9c)

According to procedure A using compound **5** (55.1 mg, 0.25 mmol) and *i*-PrOH (29 μL, 0.375 mmol) in CH_2Cl_2 (10 mL) afforded compound **9c** as a yellowish oil after 24 h; yield: 45.5 mg (65%); R_f (PE/Et_2O 9:1): 0.23; ^1H NMR (400.2 MHz, $CDCl_3$): $\delta = 5.36$ (br. s, 1H), 5.18 (d, $J = 6.9$ Hz, 1H), 3.87 (sept., $J = 6.2$ Hz, 1H), 2.74–2.64 (m, 1H), 2.47 (dd, $J = 12.4$ Hz, $J = 1.5$ Hz, 1H), 2.31–2.24 (m, 2H), 2.24–2.17 (m, 1H), 2.03 (s, 3H), 1.63 (d, $J = 13.5$ Hz, 1H), 1.58 (dd, $J = 13.5$ Hz, $J = 1.8$ Hz, 1H), 1.19 (s, 3H), 1.12 (d, $J =$ 6.1 Hz, 3H), 1.12 (d, $J = 6.1$ Hz, 3H), 1.06 (s, 3H), 0.76 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 170.7$ (C), 140.8 (C), 121.1 (CH), 76.3 (C), 74.9 (CH), 63.0 (CH), 62.9 (CH), 52.7 (CH_2), 41.2 (CH_2), 41.1 (CH_2), 34.2 (C), 31.9 (CH_3), 25.4 (2 x CH_3), 25.2 (CH_3), 22.1 (CH_3), 21.5 (CH_3); IR (CCl_4): $\nu = 3049$ (w), 2971 (s), 2926 (s), 2874 (m), 2360 (w), 1736 (s), 1459 (w), 1437 (w), 1372 (m), 1245 (s), 1109 cm^{-1} (m); MS (CI, NH_3): $m/z = 298$ (MNH_4^+), 238, 221; HR-MS-EI: $m/z = 280.2042$ (calcd. for $C_{17}H_{28}O_3$: 280.2038).

rac-(1*S*,2*S*)-2-(2-Hydroxypropan-2-yl)-3-(2-methylallyl)cyclopent-3-enyl Acetate (8d)

According to procedure B using compound **5** (55.1 mg, 0.25 mmol), H_2O (7 μL, 0.375 mmol) and acetone (0.1 mL) in CH_2Cl_2 (9.9 mL) afforded compound **8d** as a yellowish oil after 12 h; yield: 11.5 mg (19%); R_f (PE/Et_2O 8:2): 0.15; ^1H NMR (400.2 MHz, $CDCl_3$): $\delta = 5.58$ (br. s, 1H), 5.25 (d, $J = 6.3$ Hz, 1H), 4.82 (s, 1H), 4.75 (s, 1H), 2.94 (s, 2H), 2.77–2.67 (m, 1H), 2.59 (s, 1H), 2.36 (br. s, 1H), 2.24 (br. d, $J = 19.4$ Hz, 1H), 2.02 (s, 3H), 1.68 (s, 3H), 1.20 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 171.4$ (C), 143.6 (C), 141.3 (C), 127.5 (CH), 112.3 (CH_2), 78.3 (CH), 72.8 (C), 64.6 (CH), 40.2 (CH_2), 38.7 (CH_2), 27.9 (2 x CH_3), 22.2 (CH_3), 21.4 (CH_3); IR (CCl_4): $\nu = 3513$ (m), 3075 (w), 3048 (w), 2974 (s), 2931 (s), 1733 (s), 1646 (w), 1439 (m), 1372 (s), 1247 (s), 1181 (m), 1115 (w), 1026 cm^{-1} (m); MS (CI, NH_3): $m/z = 256$ (MNH_4^+), 239 (MH^+), 221, 161; HR-MS-EI: $m/z = 238.1568$ (calcd. for $C_{14}H_{22}O_3$: 238.1569).

rac-(1*S*,5*S*,7a*S*)-5-Hydroxy-5,7,7-trimethyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (9d)

According to procedure B using compound **5** (55.1 mg, 0.25 mmol) and wet acetone (0.5 mL) in CH_2Cl_2 (9.5 mL) afforded compound **9d** as a colourless solid after 20 h; yield: 38.5 mg (65%); R_f (PE/Et_2O 8:2): 0.05; mp 94–96 °C (PE/Et_2O); ^1H NMR (400.2 MHz, $CDCl_3$): $\delta = 5.38$ (br. s, 1H), 5.17 (d, $J = 6.9$ Hz, 1H), 2.76–2.66 (m, 1H), 2.50 (dd, $J =$ 12.7 Hz, $J = 1.6$ Hz, 1H), 2.33–2.25 (m, 2H), 2.17 (br. d, $J =$ 13.0 Hz, 1H), 2.05 (s, 3H), 1.66 (br. s, 1H), 1.62 (d, $J =$ 13.5 Hz, 1H), 1.56 (dd, $J = 13.5$ Hz, $J = 1.8$ Hz, 1H), 1.24 (s,

3H), 1.06 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=170.7 (C), 140.6 (C), 121.3 (CH), 74.7 (CH), 71.9 (C), 62.7 (CH), 55.4 (CH_2), 43.8 (CH_2), 41.1 (CH_2), 34.4 (C), 31.6 (CH_3), 28.8 (CH_3), 21.7 (CH_3), 21.5 (CH_3); IR (CCl_4): ν=3609 (m), 3050 (w), 2957 (s), 2926 (s), 2872 (m), 1737 (s), 1437 (w), 1372 (m), 1244 (s), 1156 (w), 1028 cm^{-1} (m); MS (CI, NH_3): *m/z*=256 (MNH_4^+), 239 (MH^+), 221; HR-MS-EI: *m/z*=238.1568 (calcd. for $C_{14}H_{22}O_3$: 238.1569).

rac-(1*S*,5*S*,7a*S*)-5-(4-Methoxyphenoxy)-5,7,7-trimethyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (9e)

According to procedure A using compound **5** (55.1 mg, 0.25 mmol) and 4-methoxyphenol (155.1 mg, 1.25 mmol) in CH_2Cl_2 (10 mL) afforded compound **9e** as a yellowish solid after 19 h; yield: 60.4 mg (70%); R_f (PE/Et_2O 9:1): 0.30; mp 70–72 °C (PE/Et_2O); ^{1}H NMR (400.2 MHz, $CDCl_3$): δ= 6.95–6.89 (m, 2H), 6.83–6.78 (m, 2H), 5.39 (br. s, 1H), 5.19 (d, *J*=6.9 Hz, 1H), 3.79 (s, 3H), 2.76–2.66 (m, 1H), 2.55 (dd, *J*=12.6 Hz, *J*=1.8 Hz, 1H), 2.47 (br. d, *J*=13.4 Hz, 1H), 2.34–2.25 (m, 2H), 2.05 (s, 3H), 1.88 (d, *J*=13.5 Hz, 1H), 1.68 (dd, *J*=13.5 Hz, *J*=2.0 Hz, 1H), 1.26 (s, 3H), 1.09 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ= 170.7 (C), 156.0 (C), 147.9 (C), 140.4 (C), 125.5 (CH), 121.6 (CH), 113.9 (CH), 80.8 (C), 74.7 (CH), 62.7 (CH), 55.5 (CH_3), 52.7 (CH_2), 41.6 (CH_2), 41.2 (CH_2), 34.5 (C), 31.8 (CH_3), 25.8 (CH_3), 22.0 (CH_3), 21.5 (CH_3); IR (CCl_4): ν= 3049 (w), 2952 (s), 2843 (m), 1737 (s), 1662 (w), 1607 (w), 1505 (s), 1462 (m), 1440 (m), 1373 (m), 1335 (w), 1292 (w), 1243 (s), 1220 (s), 1179 (w), 1152 (w), 1102 (m), 1043 cm^{-1} (s); MS (CI, NH_3): *m/z*=362 (MNH_4^+), 344; HR-MS-EI: *m/z*=344.1975 (calcd. for $C_{21}H_{28}O_4$: 344.1988).

rac-(1*S*,5*S*,7a*S*)-5-(4-Chlorophenoxy)-5,7,7-trimethyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (9f)

According to procedure A using compound **5** (55.1 mg, 0.25 mmol) and 4-chlorophenol (160.7 mg, 1.25 mmol) in CH_2Cl_2 (1 mL) afforded compound **9f** as a yellowish solid after 15 h; yield: 34.5 mg (40%); R_f (PE/Et_2O 8:2): 0.44; mp 72–74 °C (PE/Et_2O); ^{1}H NMR (400.2 MHz, $CDCl_3$): δ= 7.25–7.20 (m, 2H), 6.93–6.88 (m, 2H), 5.40 (br. s, 1H), 5.18 (d, *J*=7.0 Hz, 1H), 2.76–2.66 (m, 1H), 2.57 (dd, *J*=12.6 Hz, *J*=2.0 Hz, 1H), 2.46 (br. d, *J*=12.4 Hz, 1H), 2.35–2.26 (m, 2H), 2.05 (s, 3H), 1.86 (d, *J*=13.4 Hz, 1H), 1.70 (dd, *J*= 13.5 Hz, *J*=2.0 Hz, 1H), 1.29 (s, 3H), 1.09 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=170.7 (C), 153.3 (C), 140.0 (C), 129.0 (CH), 128.7 (C), 125.4 (CH), 122.0 (CH), 81.6 (C), 74.6 (CH), 62.6 (CH), 52.7 (CH_2), 41.7 (CH_2), 41.1 (CH_2), 34.5 (C), 31.7 (CH_3), 25.8 (CH_3), 22.0 (CH_3), 21.5 (CH_3); IR (CCl_4): ν=3049 (w), 2955 (s), 2874 (s), 2255 (w), 1887 (w), 1736 (s), 1663 (m), 1587 (m), 1486 (s), 1437 (s), 1374 (s), 1247 (s), 1154 (s), 1097 (s), 1048 (s), 1031 cm^{-1} (s); MS (CI, NH_3): *m/z*=366 (MNH_4^+), 332, 321, 305; HR-MS-EI: *m/z*=348.1506 (calcd. for $C_{20}H_{25}ClO_3$: 348.1492).

rac-(1*S*,5*S*)-1-Acetoxy-5,7,7-trimethyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-5-yl 3-Phenylpropanoate (9g)

According to procedure A using compound **5** (55.1 mg, 0.25 mmol) and hydrocinnamic acid (187.7 mg, 1.25 mmol) in CH_2Cl_2 (1 mL) afforded compound **9g** as a yellowish oil after 12 h; yield: 51.4 mg (56%); R_f (PE/Et_2O 8:2): 0.54; ^{1}H NMR (400.2 MHz, $CDCl_3$): δ=7.32–7.25 (m, 2H), 7.22–7.17 (m, 3H), 5.42 (br. s, 1H), 5.17 (d, *J*=7.0 Hz, 1H), 2.90 (t, *J*=7.8 Hz, 2H), 2.81 (dd, *J*=12.7 Hz, *J*=1.4 Hz, 1H), 2.75–2.65 (m, 1H), 2.54 (t, *J*=7.8 Hz, 2H), 2.37–2.23 (m, 3H), 2.09 (dd, *J*=13.7 Hz, *J*=1.9 Hz, 1H), 2.04 (s, 3H), 1.62 (d, *J*=14.0 Hz, 1H), 1.47 (s, 3H), 1.05 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $<\iota\tau>\delta</\iota\tau>$=172.0 (C), 170.7 (C), 140.7 (C), 139.3 (C), 128.5 (CH), 128.4 (CH), 126.2 (CH), 122.4 (CH), 83.4 (C), 74.7 (CH), 62.6 (CH), 50.9 (CH_2), 41.0 (CH_2), 41.0 (CH_2), 37.1 (CH_2), 34.4 (C), 31.4 (CH_3), 31.2 (CH_2), 25.2 (CH_3), 21.8 (CH_3), 21.5 (CH_3); IR (CCl_4): ν=3059 (w), 3028 (m), 2955 (s), 2928 (s), 2870 (s), 1736 (s), 1641 (m), 1604 (w), 1496 (w), 1450 (m), 1372 (s), 1234 (s), 1183 (s), 1149 (s), 1104 (s) 1053 (m), 1029 cm^{-1} (m); MS (CI, NH_3): *m/z*=388 (MNH_4^+), 353, 341, 311; HR-MS-EI: *m/z*=370.2126 (calcd. for $C_{23}H_{30}O_4$: 370.2144).

rac-(1*S*,5*S*,7a*S*)-5-(*tert*-Butoxycarbonylamino)-5,7,7-trimethyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (9h)

According to procedure A (0.04 equiv. catalyst **4** added) using compound **5** (55.1 mg, 0.25 mmol) and *tert*-butyl carbamate (146.4 mg, 1.25 mmol) in CH_2Cl_2 (1 mL) afforded compound **9h** as a yellowish oil (isolated in mixture with **8h**) after 20 h; yield: 37%. Careful separation led to the isolation of pure **9h**; yield: 18.1 mg (21%); R_f (PE/Et_2O 8:2): 0.33; ^{1}H NMR (400.2 MHz, $CDCl_3$): δ=5.39 (br. s, 1H), 5.19 (d, *J*=6.8 Hz, 1H), 4.51 (br. s, 1H), 2.76–2.66 (m, 1H), 2.57 (dd, *J*=12.8 Hz, *J*=1.4 Hz, 1H), 2.47 (br. d, *J*= 12.3 Hz, 1H), 2.32–2.24 (m, 2H), 2.03 (s, 3H), 1.70–1.61 (m, 2H), 1.44 (s, 9H), 1.29 (s, 3H), 1.06 (s, 3H), 0.79 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=170.7 (C), 154.2 (C), 140.1 (C), 121.6 (CH), 74.8 (CH), 65.9 (C), 62.7 (CH), 54.1 (C), 51.4 (CH_2), 41.0 (CH_2), 40.0 (CH_2), 34.4 (C), 31.6 (CH_3), 28.5 ($3\times CH_3$), 26.4 (CH_3), 22.2 (CH_3), 21.5 (CH_3); IR (CCl_4): ν=3445 (m), 2976 (s), 2932 (s), 2864 (s), 2805 (s), 2779 (s), 2740 (m), 2247 (m), 1958 (w), 1725 (s), 1492 (s), 1447 (s), 1378 (s), 1247 (s), 1157 (s), 1117 (s), 1076 (s), 1049 cm^{-1} (s); MS (CI, NH_3): *m/z*=355 (MNH_4^+), 338 (MH^+), 299, 282; HR-MS-EI: *m/z*=337.2265 (calcd. for $C_{19}H_{31}NO_4$: 337.2253).

rac-(1*S*,5*S*)-5-(Benzyloxycarbonylamino)-5,7,7-trimethyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (9i)

According to procedure A using compound **5** (55.1 mg, 0.25 mmol) and benzyl carbamate (189.0 mg, 1.25 mmol) in CH_2Cl_2 (1 mL) afforded compound **9i** as a yellowish oil after 12 h; yield: 33.7 mg (36%); R_f (PE/Et_2O 8:2): 0.15; ^{1}H NMR (400.2 MHz, $CDCl_3$): δ=7.41–7.28 (m, 5H), 5.41 (br. s, 1H), 5.19 (d, *J*=6.8 Hz, 1H), 5.04 (s, 2H), 4.75 (br. s, 1H), 2.76–2.65 (m, 1H), 2.61 (dd, *J*=12.8 Hz, *J*=1.3 Hz, 1H), 2.48 (br. d, *J*=13.1 Hz, 1H), 2.35–2.24 (m, 2H), 2.03 (s, 3H), 1.85 (d, *J*=13.3 Hz, 1H), 1.68 (dd, *J*=13.7 Hz, *J*= 1.8 Hz, 1H), 1.32 (s, 3H), 1.05 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=170.7 (C), 154.3 (C), 139.9 (C), 136.7 (C), 128.6 (CH), 128.2 (CH), 128.1 (CH), 121.9 (CH), 74.8 (CH), 66.2 (CH_2), 62.7 (CH), 54.4 (C), 51.4

(CH_2), 41.0 (CH_2), 39.9 (CH_2), 34.5 (C), 31.8 (CH_3), 26.3 (CH_3), 22.2 (CH_3), 21.5 (CH_3); IR (CCl_4): $\tilde{\nu}$3442 (w), 3034 (w), 2958 (m), 2868 (m), 1733 (s), 1501 (s), 1456 (w), 1374 (m), 1246 (s), 1211 (m), 1119 (w), 1088 (w), 1055 (m), 1028 cm^{-1} (w); MS (CI, NH_3): m/z = 389 (MNH_4^+), 372 (MH^+), 343, 312, 310, 281, 251; HR-MS-EI: m/z = 371.2083 (calcd. for $C_{22}H_{29}NO_4$: 371.2097).

rac-(1*S*,5*S*,7*R*,7a*S*)-5-(Allyloxy)-5,7-dimethyl-7-(4-methylpent-3-enyl)-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (11a)

According to procedure A using compound (*E*)-**10** (72.1 mg, 0.25 mmol) and allylic alcohol (170 μL, 2.50 mmol) in CH_2Cl_2 (10 mL) afforded compound **11a** as a yellowish oil after 26 h; yield: 43.4 mg (50%); R_f (PE/Et_2O 8:2): 0.50; ^{1}H NMR (400.2 MHz, $CDCl_3$): δ = 5.91 (ddt, J = 17.0 Hz, J = 10.7 Hz, J = 5.5 Hz, 1H), 5.38 (br. s, 1H), 5.27 (ddd, J = 17.2 Hz, J = 3.4 Hz, J = 1.6 Hz, 1H), 5.16 (d, J = 7.0 Hz, 1H), 5.12 (ddd, J = 10.3 Hz, J = 3.0 Hz, J = 1.4 Hz, 1H), 5.08 (t, J = 10.3 Hz, 1H), 4.01–3.90 (m, 2H), 2.77–2.67 (m, 1H), 2.51 (dd, J = 12.5 Hz, J = 1.5 Hz, 1H), 2.39 (s, 1H), 2.29–2.17 (m, 2H), 2.02 (s, 3H), 2.00–1.85 (m, 2H), 1.75 (dd, J = 13.4 Hz, J = 1.9 Hz, 1H), 1.67 (s, 3H), 1.61 (br. d, J = 13.4 Hz, 1H), 1.59 (s, 3H), 1.48 (dt, J = 13.4 Hz, J = 4.9 Hz, 1H), 1.30–1.22 (m, 1H), 1.21 (s, 3H), 0.76 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.7 (C), 140.3 (C), 136.1 (CH), 131.3 (C), 124.7 (CH), 121.5 (CH), 116.0 (CH_2), 76.2 (C), 74.9 (CH), 62.4 (CH_2), 61.5 (CH), 48.6 (CH_2), 44.6 (CH_2), 41.4 (CH_2), 40.9 (CH_2), 36.7 (C), 25.7 (CH_3), 24.4 (CH_3), 22.2 (CH_2), 21.5 (CH_3), 20.3 (CH_3), 17.6 (CH_3); IR (CCl_4): ν = 2976 (s), 2930 (s), 2863 (s), 2805 (m), 1736 (s), 1445 (m), 1378 (s), 1245 (s), 1119 (s), 1072 cm^{-1} (s); MS (CI, NH_3): m/z = 364 (MNH_4^+), 306, 289, 229; HR-MS-EI: m/z = 346.2515 (calcd. for $C_{22}H_{34}O_3$: 346.2508).

rac-(1*S*,5*S*,7*R*,7a*S*)-5-Isopropoxy-5,7-dimethyl-7-(4-methylpent-3-enyl)-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (11b)

According to procedure A using compound (*E*)-**10** (72.1 mg, 0.25 mmol) and *i*-PrOH (191 μL, 2.50 mmol) in CH_2Cl_2 (10 mL) afforded compound **11b** as a yellowish oil after 22 h; yield: 47.0 mg (54%); R_f (PE/Et_2O 8:2): 0.59; ^{1}H NMR (400.2 MHz, $CDCl_3$): δ = 5.36 (br. s, 1H), 5.15 (d, J = 6.9 Hz, 1H), 5.08 (tt, J = 7.1 Hz, J = 1.2 Hz, 1H), 3.87 (sept., J = 6.2 Hz, 1H), 2.75–2.65 (m, 1H), 2.47 (dd, J = 12.4 Hz, J = 1.3 Hz, 1H), 2.36 (s, 1H), 2.28–2.16 (m, 2H), 2.01 (s, 3H), 2.00–1.84 (m, 2H), 1.67 (s, 3H), 1.72–1.66 (m, 1H), 1.62–1.55 (m, 1H), 1.58 (s, 3H), 1.53–1.40 (m, 1H), 1.30–1.20 (m, 1H), 1.18 (s, 3H), 1.12 (d, J = 6.1 Hz, 6H), 0.75 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.7 (C), 140.6 (C), 131.2 (C), 124.8 (CH), 121.3 (CH), 76.4 (C), 74.9 (CH), 63.0 (CH), 61.7 (CH), 49.4 (CH_2), 44.8 (CH_2), 41.4 (CH_2), 41.2 (CH_2), 36.7 (C), 25.7 (CH_3), 25.4 (CH_3), 25.4 (CH_3), 25.3 (CH_3), 22.3 (CH_2), 21.5 (CH_3), 20.3 (CH_3), 17.6 (CH_3); IR (CCl_4): ν = 3048 (w), 2972 (s), 2926 (s), 2855 (m), 1736 (s), 1446 (m), 1374 (s), 1245 (s), 1172 (w), 1109 (m), 1053 (m), 1025 cm^{-1} (m); MS (CI, NH_3): m/z = 366 (MNH_4^+), 306, 289, 229; HR-MS-EI: m/z = 348.2650 (calcd. for $C_{22}H_{36}O_3$: 348.2664).

rac-(1*S*,5*S*,7*R*,7a*S*)-5-Hydroxy-5,7-dimethyl-7-(4-methylpent-3-enyl)-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (11c)

According to procedure B (0.04 equiv. catalyst **4** added) using compound (*E*)-**10** (72.1 mg, 0.25 mmol), H_2O (45 μL, 2.50 mmol) and acetone (1 mL) in CH_2Cl_2 (9 mL) afforded compound **11c** as a yellowish oil after 30 h; yield: 54.1 mg (54%); R_f (PE/Et_2O 8:2): 0.14; ^{1}H NMR (400.2 MHz, $CDCl_3$): δ = 5.37 (br. s, 1H), 5.15 (d, J = 7.0 Hz, 1H), 5.08 (t, J = 6.9 Hz, 1H), 2.76–2.66 (m, 1H), 2.50 (dd, J = 1.4 Hz, J = 12.6 Hz, 1H), 2.37 (s, 1H), 2.24 (dd, J = 17.8 Hz, J = 1.7 Hz, 1H), 2.17 (br. d, J = 14.1 Hz, 1H), 2.02 (s, 3H), 2.01–1.84 (m, 2H), 1.72–1.66 (m, 1H), 1.67 (s, 3H), 1.64–1.55 (m, 2H), 1.58 (s, 3H), 1.52–1.42 (m, 1H), 1.29–1.16 (m, 1H), 1.23 (s, 3H), 0.76 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.7 (C), 140.4 (C), 131.4 (C), 124.6 (CH), 121.4 (CH), 74.8 (CH), 71.9 (C), 61.4 (CH), 51.9 (CH_2), 44.5 (CH_2), 43.8 (CH_2), 41.4 (CH_2), 36.9 (C), 29.0 (CH_3), 25.7 (CH_3), 22.2 (CH_2), 21.5 (CH_3), 20.0 (CH_3), 17.6 (CH_3). IR (CCl_4): ν = 3609 (m), 2968 (s), 2921 (s), 2854 (s), 1737 (s), 1440 (m), 1375 (s), 1245 (s), 1159 (m), 1093 (m), 1026 cm^{-1} (m); MS (CI, NH_3): m/z = 324 (MNH_4^+), 307 (MH^+), 306, 289, 229; HR-MS-EI: m/z = 306.2191 (calcd. for $C_{19}H_{30}O_3$: 306.2195).

rac-(1*S*,5*S*,7*R*,7a*S*)-5-(4-Methoxyphenoxy)-5,7-dimethyl-7-(4-methylpent-3-enyl)-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (11d)

Following method A using compound (*E*)-**10** (72.1 mg, 0.25 mmol) and 4-methoxyphenol (155.1 mg, 1.25 mmol) in CH_2Cl_2 (10 mL) compound **11d** as a yellowish oil after 22 h; yield: 60.2 mg (58%); R_f (PE/Et_2O 8:2): 0.43; ^{1}H NMR (400.2 MHz, $CDCl_3$): δ = 6.94–6.86 (m, 2H), 6.83–6.76 (m, 2H), 5.38 (br. s, 1H), 5.16 (d, J = 7.0 Hz, 1H), 5.10 (tt, J = 7.1 Hz, J = 1.3 Hz, 1H), 3.77 (s, 3H), 2.77–2.67 (m, 1H), 2.53 (dd, J = 12.6 Hz, J = 1.2 Hz, 1H), 2.46 (br. d, J = 13.5 Hz, 1H), 2.41 (s, 1H), 2.25 (br. d, J = 17.9 Hz, 1H), 2.03 (s, 3H), 2.00–1.91 (m, 2H), 1.86 (d, J = 13.4 Hz, 1H), 1.78 (dd, J = 13.4 Hz, J = 1.7 Hz, 1H), 1.69 (s, 3H), 1.60 (s, 3H), 1.57–1.45 (m, 1H), 1.33–1.23 (m, 1H), 1.24 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.7 (C), 156.0 (C), 147.8 (C), 140.2 (C), 131.4 (C), 125.5 (CH), 124.7 (CH), 121.8 (CH), 113.9 (CH), 81.0 (C), 74.8 (CH), 61.4 (CH), 55.5 (CH_3), 49.5 (CH_2), 44.7 (CH_2), 41.6 (CH_2), 41.5 (CH_2), 36.9 (C), 25.9 (CH_3), 25.8 (CH_3), 22.3 (CH_2), 21.5 (CH_3), 20.3 (CH_3), 17.6 (CH_3); IR (CCl_4): ν = 3048 (w), 2971 (s), 2929 (s), 2857 (s), 1737 (s), 1505 (s), 1443 (m), 1376 (s), 1244 (s), 1219 (s), 1102 (m), 1041 cm^{-1} (m); MS (CI, NH_3): m/z = 430 (MNH_4^+), 366, 352, 308, 229; HR-MS-EI: m/z = 412.2613 (calcd. for $C_{26}H_{36}O_4$: 412.2614).

rac-(1*S*,5*S*,7*S*,7a*S*)-5-(Allyloxy)-5,7-dimethyl-7-(4-methylpent-3-enyl)-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (11e)

According to procedure A (0.04 equiv. catalyst **4** added) using compound (*Z*)-**10** (72.1 mg, 0.25 mmol) and allylic alcohol (85 μL, 1.25 mmol) in CH_2Cl_2 (10 mL) afforded compound **11e** as a yellowish oil after 22 h; yield: 29.0 mg (33%); R_f (PE/Et_2O 9:1): 0.29; ^{1}H NMR (400.2 MHz, $CDCl_3$): δ = 5.91 (ddt, J = 17.0 Hz, J = 10.7 Hz, J = 5.5 Hz,

1H), 5.36 (s, 1H), 5.32–5.24 (m, 2H), 5.12 (dd, $J=10.3$ Hz, $J=1.2$ Hz, 1H), 5.00 (t, $J=7.1$ Hz, 1H), 4.03–3.90 (m, 2H), 2.73–2.63 (m, 1H), 2.50 (d, $J=12.3$ Hz, 1H), 2.33 (s, 1H), 2.30–2.21 (m, 2H), 2.03 (s, 3H), 1.96 (dd, $J=14.0$ Hz, $J=1.4$ Hz, 1H), 1.95–1.84 (m, 2H), 1.66 (s, 3H), 1.58 (s, 3H), 1.41 (d, $J=15.2$ Hz, 1H), 1.24–1.16 (m, 1H), 1.25 (s, 3H), 1.06 (s, 3H), 1.02–0.90 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=170.7$ (C), 140.1 (C), 136.0 (CH), 131.3 (C), 124.5 (CH), 121.1 (CH), 116.0 (CH_2), 76.1 (C), 74.4 (CH), 64.8 (CH), 62.4 (CH_2), 45.5 (CH_2), 41.2 (CH_2), 41.0 (CH_2), 37.3 (C), 32.6 (CH_2), 28.6 (CH_3), 25.8 (CH_3), 23.6 (CH_3), 22.8 (CH_2), 21.5 (CH_3), 17.7 (CH_3); IR (CCl_4): $\nu=2974$ (s), 2930 (s), 2865 (s), 1736 (s), 1441 (m), 1376 (s), 1245 (s), 1153 (m), 1118 (s), 1064 (m), 1024 cm^{-1} (s); MS (CI, NH_3): $m/z=$ 364 (MNH_4^+), 347 (MH^+), 346, 306, 289, 229; HR-MS-EI: $m/z=346.2511$ (calcd. for $C_{22}H_{34}O_3$: 346.2508).

rac-(1*S*,5*S*,7*S*,7a*S*)-5-Hydroxy-5,7-dimethyl-7-(4-methylpent-3-enyl)-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (11f)

According to procedure B (0.04 equiv. catalyst **4** added) using compound (*Z*)-**10** (72.1 mg, 0.25 mmol) and wet acetone (0.5 mL) in CH_2Cl_2 (9.5 mL) afforded compound **11f** as a yellowish oil after 20 h; yield: 42.5 mg (55%); R_f (PE/Et_2O 6:4): 0.20; ^{1}H NMR (400.2 MHz, $CDCl_3$): $\delta=5.37$ (br. s, 1H), 5.28 (d, $J=6.5$ Hz, 1H), 5.00 (tt, $J=7.1$ Hz, $J=1.3$ Hz, 1H), 2.74–2.64 (m, 1H), 2.51 (dd, $J=12.6$ Hz, $J=1.8$ Hz, 1H), 2.31 (s, 1H), 2.27 (br. d, $J=18.1$ Hz, 1H), 2.20 (br. d, $J=13.1$ Hz, 1H), 2.03 (s, 3H), 1.96–1.86 (m, 3H), 1.66 (s, 3H), 1.58 (s, 3H), 1.50 (br. s, 1H), 1.38 (br. s, $J=14.0$ Hz, 1H), 1.27 (s, 3H), 1.26–1.19 (m, 1H), 1.06 (s, 3H), 1.01–0.92 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=170.7$ (C), 140.1 (C), 131.3 (C), 124.5 (CH), 121.0 (CH), 74.3 (CH), 71.9 (C), 64.7 (CH), 49.1 (CH_2), 44.1 (CH_2), 41.3 (CH_2), 37.5 (C), 32.4 (CH_2), 28.5 (CH_3), 28.3 (CH_3), 25.8 (CH_3), 22.8 (CH_2), 21.5 (CH_3), 17.7 (CH_3); IR (CCl_4): $\nu=$ 3609 (m), 2962 (s), 2928 (s), 2873 (s), 1736 (s), 1439 (m), 1374 (s), 1245 (s), 1158 (m), 1098 (m), 1024 cm^{-1} (m); MS (CI, NH_3): $m/z=324$ (MNH_4^+), 307 (MH^+), 306, 289, 247, 229; HR-MS-EI: $m/z=306.2196$ (calcd. for $C_{19}H_{30}O_3$: 306.2195).

rac-(1*S*,5*S*,7*S*,7a*S*)-5-(4-Methoxyphenoxy)-5,7-dimethyl-7-(4-methylpent-3-enyl)-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (11g)

According to procedure A (0.04 equiv. catalyst **4** added) using compound (*Z*)-**10** (72.1 mg, 0.25 mmol) and 4-methoxyphenol (155.1 mg, 1.25 mmol) in CH_2Cl_2 (10 mL) afforded compound **11g** as a yellowish oil after 70 h; yield: 42.2 mg (41%); R_f (PE/Et_2O 8:2): 0.35; ^{1}H NMR (400.2 MHz, $CDCl_3$): $\delta=6.94$–6.89 (m, 2H), 6.82–6.77 (m, 2H), 5.36 (br. s, 1H), 5.28 (d, $J=6.6$ Hz, 1H), 4.22 (t, $J=7.2$ Hz, 1H), 3.78 (s, 3H), 2.74–2.63 (m, 1H), 2.50 (br. s, 2H), 2.34 (s, 1H), 2.27 (d, $J=18.0$ Hz, 1H), 2.03 (s, 3H), 1.99 (d, $J=13.8$ Hz, 1H), 1.95–1.79 (m, 2H), 1.65 (s, 3H), 1.15 (d, $J=14.3$ Hz, 1H), 1.56 (s, 3H), 1.28 (s, 3H), 1.26–1.18 (m, 1H), 1.08 (s, 3H), 2.02–1.92 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=$ 170.7 (C), 156.0 (C), 147.8 (C), 139.9 (C), 131.3 (C), 125.5 (CH), 124.5 (CH), 121.4 (CH), 114.0 (CH), 80.9 (C), 74.3 (CH), 64.6 (CH), 55.5 (CH_3), 46.3 (CH_2), 41.7 (CH_2), 41.3 (CH_2), 37.5 (C), 32.7 (CH_2), 28.7 (CH_3), 25.8 (CH_3), 25.3 (CH_3), 22.8 (CH_2), 21.5 (CH_3), 17.7 (CH_3); IR (CCl_4): $\nu=$ 2973 (s), 2932 (s), 2866 (s), 1735 (s), 1504 (s), 1460 (s), 1443 (s), 1376 (s), 1244 (s), 1220 (s), 1177 (s), 1154 (s), 1116 (s), 1043 cm^{-1} (s); MS (CI, NH_3): $m/z=430$ (MNH_4^+), 366, 338, 306, 289, 229; HR-MS-EI: $m/z=412.2615$ (Calcd. for $C_{26}H_{36}O_4$: 412.2614).

rac-(1*S*,5*S*,7*S*,7a*S*)-5-(Allyloxy)-5-methyl-7-((*E*)-prop-1-enyl)-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (13a)

According to procedure A using compound **12** (58.1 mg, 0.25 mmol) and allylic alcohol (26 μL, 0.375 mmol) in CH_2Cl_2 (10 mL) afforded compounds **13a** and **14a** (*dr*= 1.5:1) as a yellowish oil (isolated from a mixture of the two diastereomers with total yield 47%) after 21 h; yield: 18.1 mg (25%); R_f (PE/Et_2O 8:2): 0.54; ^{1}H NMR (400.2 MHz, $CDCl_3$): $\delta=5.91$ (ddt, $J=17.0$ Hz, $J=10.6$ Hz, $J=5.4$ Hz, 1H), 5.46 (dq, $J=15.1$ Hz, $J=6.3$ Hz, 1H), 5.32–5.23 (m, 2H), 5.12 (ddd, $J=10.4$ Hz, $J=2.9$ Hz, $J=1.3$ Hz, 1H), 5.05 (dt, $J=8.1$ Hz, $J=4.1$ Hz, 1H), 4.01–3.92 (m, 2H), 2.90–2.79 (m, 1H), 2.45 (dd, $J=12.6$ Hz, $J=2.0$ Hz, 1H), 2.34–2.14 (m, 3H), 2.01 (s, 3H), 1.82–1.73 (m, 3H), 1.64 (dd, $J=6.3$ Hz, $J=1.4$ Hz, 3H), 1.56–1.46 (m, 1H), 1.13 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.7 (C), 140.9 (C), 136.0 (CH), 133.4 (CH), 125.3 (CH), 121.0 (CH), 116.0 (CH_2), 78.3 (CH), 75.9 (C), 62.6 (CH_2), 56.0 (CH), 43.6 (CH_2), 43.5 (CH), 40.6 (CH_2), 39.5 (CH_2), 22.1 (CH_3), 21.3 (CH_3), 18.0 (CH_3); IR (CCl_4): $\nu=2969$ (s), 2932 (s), 2855 (s), 1738 (s), 1649 (m), 1437 (m), 1372 (s), 1247 (s), 1178 (m), 1135 (s), 1114 (s), 1080 (s), 1036 cm^{-1} (s); MS (CI, NH_3): $m/z=308$ (MNH_4^+), 291 (MH^+), 250, 233, 173; HR-MS-EI: $m/z=$ 290.1882 (calcd. for $C_{18}H_{26}O_3$: 290.1882).

rac-(5*S*,7*S*,7a*S*)-5-Hydroxy-5-methyl-7-[(*E*)-prop-1-enyl]-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (13b/14b)

According to procedure B (0.04 equiv. catalyst **4** added) using compound **12** (58.1 mg, 0.25 mmol) and wet acetone (0.5 mL) in CH_2Cl_2 (9.5 mL) afforded compounds **13b** and **14b** (*dr*=2:1) as a yellowish oil after 15 h; yield: 32.6 mg (52%); R_f (PE/Et_2O 6:4): 0.12; ^{1}H NMR (400.2 MHz, $CDCl_3$, unambiguously assignable peaks): $\delta=5.04$ (dt, $J=$ 8.1 Hz, $J=4.1$ Hz, 1H, *major*), 2.90–2.78 (m, 1H, *major*), 2.73–2.63 (m, 1H, *minor*), 2.49 (dd, $J=13.6$ Hz, $J=2.2$ Hz, 1H, *minor*), 2.42 (dd, $J=12.8$ Hz, $J=2.0$ Hz, 1H, *major*), 1.14 (s, 3H, *major*); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=$ 170.7 (C, *major*), 170.5 (C, *minor*), 141.1 (C, *minor*), 140.9 (C, *major*), 134.3 (CH, *minor*), 133.1 (CH, *major*), 125.3 (CH, *major*), 124.2 (CH, *minor*), 121.0 (CH, *minor*), 120.8 (CH, *major*), 78.2 (CH, *major*), 73.3 (CH, *minor*), 71.5 (C, *major*), 71.4 (C, *minor*), 55.6 (CH, *major*), 52.4 (CH, *minor*), 47.0 (CH_2, *major*), 46.5 (CH_2, *minor*), 44.0 (CH, *major*), 43.5 (CH_2, *major*), 43.1 (CH_2, *minor*), 40.2 (CH_2, *minor*), 39.5 (CH_2, *major*), 36.8 (CH, *minor*), 26.4 (CH_3, *major*), 26.2 (CH_3, *minor*), 21.3 (CH_3, *minor*), 21.2 (CH_3, *major*), 18.1 (CH_3, *minor*), 17.9 (CH_3, *major*); IR (CCl_4, mixture): $\nu=$ 3609 (w), 2966 (s), 2928 (s), 2853 (s), 1738 (s), 1439 (m), 1373 (s), 1245 (s), 1178 (s), 1138 (s), 1107 (s), 1033 cm^{-1} (s); MS (CI, NH_3): $m/z=268$ (MNH_4^+), 251 (MH^+), 233, 191,

173; HR-MS-EI: $m/z = 250.1580$ (calcd. for $C_{15}H_{22}O_3$: 250.1569).

rac-(1*S*,5*S*,7*S*,7a*S*)-5-(4-Methoxyphenoxy)-5-methyl-7-[(*E*)-prop-1-enyl]-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (13c)

According to procedure A using compound **12** (58.1 mg, 0.25 mmol) and 4-methoxyphenol (155.1 mg, 1.25 mmol) in CH_2Cl_2 (10 mL) afforded compounds **13c** and **14c** ($dr = 2:1$) as a yellowish oil (isolated from a mixture of the two diastereomers with total yield 59%); yield: 29.6 mg (33%); R_f (PE/Et_2O 8:2): 0.27; ^{1}H NMR (400.2 MHz, $CDCl_3$): $\delta =$ 6.95–6.88 (m, 2H), 6.82–6.76 (m, 2H), 5.45 (dq, $J = 15.1$ Hz, $J = 6.5$ Hz, 1H), 5.32–5.21 (m, 2H), 5.05 (dt, $J = 8.0$ Hz, $J =$ 4.2 Hz, 1H), 3.78 (s, 3H), 2.89–2.78 (m, 1H), 2.49 (dd, $J =$ 12.7 Hz, $J = 2.0$ Hz, 1H), 2.38 (d, $J = 13.8$ Hz, 1H), 2.33–2.17 (m, 2H), 2.00 (s, 3H), 1.86–1.75 (m, 2H), 1.70 (d, $J =$ 13.3 Hz, 1H), 1.64 (dd, $J = 6.3$ Hz, $J = 1.5$ Hz, 3H), 1.18 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 170.7$ (C), 156.0 (C), 147.7 (C), 140.7 (C), 133.2 (CH), 125.6 (CH), 125.5 (CH), 121.3 (CH), 113.9 (CH), 80.4 (C), 78.2 (CH), 55.8 (CH_3), 55.5 (CH), 44.3 (CH_2), 43.9 (CH), 41.3 (CH_2), 39.5 (CH_2), 23.6 (CH_3), 21.2 (CH_3), 17.9 (CH_3); IR (CCl_4): $\nu =$ 2937 (m), 2853 (m), 1739 (s), 1505 (s), 1442 (m), 1373 (m), 1244 (s), 1219 (s), 1101 (w), 1039 cm^{-1} (m); MS (CI, NH_3): $m/z = 374$ (MNH_4^+), 332, 315, 295, 250, 233; HR-MS-EI: $m/z = 356.1985$ (calcd. for $C_{22}H_{28}O_4$: 356.1988).

rac-[(1*S*,5*S*,7a*S*)-1-Acetoxy-5-hydroxy-7,7-dimethyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-5-yl]methyl Acetate (16a)

According to procedure B using compound **15a** (55.7 mg, 0.20 mmol) and wet acetone (0.5 mL) in CH_2Cl_2 (7.5 mL) afforded compound **16a** as a yellowish oil after 14 h; yield: 46.9 mg (79%); R_f (PE/Et_2O 1:1): 0.11; ^{1}H NMR (400.2 MHz, $CDCl_3$): $\delta = 5.41$ (br. s, 1H), 5.18 (d, $J = 6.9$ Hz, 1H), 4.10 (d, $J = 11.7$ Hz, 1H), 3.96 (d, $J = 11.7$ Hz, 1H), 2.74–2.64 (m, 1H), 2.61 (dd, $J = 13.4$ Hz, $J = 1.7$ Hz, 1H), 2.41 (br. s, 1H), 2.34 (s, 1H), 2.32–2.24 (m, 1H), 2.18 (d, $J =$ 12.2 Hz, 1H), 2.12 (s, 3H), 2.04 (s, 3H), 1.78 (dd, $J =$ 14.0 Hz, $J = 1.9$ Hz, 1H), 1.58 (d, $J = 14.0$ Hz, 1H), 1.09 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 171.2$ (C), 170.7 (C), 139.3 (C), 122.3 (CH), 74.4 (CH), 72.2 (C), 69.8 (CH_2), 62.8 (CH), 49.8 (CH_2), 41.0 (CH_2), 38.5 (CH_2), 34.2 (C), 31.4 (CH_3), 21.5 (CH_3), 21.5 (CH_3), 20.9 (CH_3); IR (CCl_4): $\nu =$ 3600 (w), 2954 (m), 2927 (m), 2875 (w), 1740 (s), 1436 (m), 1371 (m), 1237 (s), 1168 (w), 1032 cm^{-1} (m); MS (CI, NH_3): $m/z = 314$ (MNH_4^+), 297 (MH^+), 279, 219, 159; HR-MS-EI: $m/z = 296.1634$ (calcd. for $C_{16}H_{24}O_5$: 296.1624).

rac-[(1*S*,5*S*,7a*S*)-1-Acetoxy-5-(4-methoxyphenoxy)-7,7-dimethyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-5-yl]methyl Acetate (16b)

According to procedure A using compound **15a** (55.7 mg, 0.20 mmol) and 4-methoxyphenol (124.1 mg, 1.00 mmol) in CH_2Cl_2 (8 mL) afforded compound **16b** as a colouirless oil after 16.5 h; yield: 40.3 mg (50%); R_f (PE/Et_2O 8:2): 0.10; mp 105–107 °C (PE/Et_2O); ^{1}H NMR (400.2 MHz, $CDCl_3$): $\delta =$ 6.92–6.85 (m, 2H), 6.83–6.75 (m, 2H), 5.38 (br. s, 1H), 5.17 (d, $J = 6.9$ Hz, 1H), 4.16 (d, $J = 12.8$ Hz, 1H), 3.99 (d, $J = 12.8$ Hz, 1H), 3.77 (s, 3H), 2.74–2.63 (m, 1H), 2.53 (dd, $J = 13.2$ Hz, $J = 1.4$ Hz, 1H), 2.40 (d, $J = 13.5$ Hz, 1H), 2.32 (s, 1H), 2.27 (d, $J = 18.2$ Hz, 1H), 2.10 (s, 3H), 2.05–1.97 (m, 1H), 2.02 (s, 3H), 1.73 (d, $J = 14.0$ Hz, 1H), 1.11 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 170.7$ (C), 170.5 (C), 156.3 (C), 146.7 (C), 139.0 (C), 125.4 (CH), 122.7 (CH), 114.1 (CH), 80.5 (C), 74.3 (CH), 65.9 (CH_2), 62.7 (CH), 55.5 (CH_3), 46.7 (CH_2), 41.0 (CH_2), 36.5 (CH_2), 34.3 (C), 31.7 (CH_3), 21.4 (CH_3), 21.3 (CH_3), 20.9 (CH_3); IR (CCl_4): $\nu =$ 3050 (m), 2954 (m), 1741 (s), 1608 (w), 1505 (s), 1461 (m), 1441 (m), 1370 (m), 1240 (s), 1042 cm^{-1} (s); MS (CI, NH_3): $m/z = 403$ (MH^+); HR-MS-EI: $m/z = 402.2042$ (calcd. for $C_{23}H_{30}O_6$: 402.2042).

rac-[(1*S*,5*S*,7*R*,7a*S*)-1-Acetoxy-5-hydroxy-7-methyl-7-(4-methylpent-3-enyl)-2,4,5,6,7,7a-hexahydro-1*H*-inden-5-yl]methyl Acetate (16c)

According to procedure B using compound **15b** (48.5 mg, 0.14 mmol) and wet acetone (0.5 mL) in CH_2Cl_2 (5 mL) afforded compound **16c** as a yellowish after 18.5 h; yield: 40.9 mg (80%); R_f (PE/Et_2O 1:1): 0.25; ^{1}H NMR (400.2 MHz, $CDCl_3$): $\delta = 5.41$ (s, 1H), 5.16 (d, $J = 7.0$ Hz, 1H), 5.08 (t, $J = 7.0$ Hz, 1H), 4.11 (d, $J = 11.4$ Hz, 1H), 3.93 (d, $J = 11.6$ Hz, 1H), 2.76–2.66 (m, 1H), 2.61 (dd, $J =$ 13.3 Hz, $J = 1.7$ Hz, 1H), 2.44 (s, 1H), 2.40–2.14 (m, 2H), 2.11 (s, 3H), 2.02 (s, 3H), 2.02–1.90 (m, 2H), 1.86 (dd, $J =$ 13.9 Hz, $J = 1.5$ Hz, 1H), 1.67 (s, 3H), 1.59 (s, 3H), 1.59–1.53 (m, 1H), 1.49 (dt, $J = 13.9$ Hz, $J = 5.8$ Hz, 1H), 1.34–1.23 (m, 2H), 0.73 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 171.2$ (C), 170.7 (C), 139.1 (C), 131.5 (C), 124.5 (CH), 122.5 (CH), 74.5 (CH), 72.3 (C), 69.9 (CH_2), 61.3 (CH), 46.5 (CH_2), 44.2 (CH_2), 41.4 (CH_2), 38.5 (CH_2), 36.7 (C), 25.7 (CH_3), 22.2 (CH_2), 21.4 (CH_3), 20.9 (CH_3), 19.9 (CH_3), 17.6 (CH_3); IR (CCl_4): $\nu =$ 3599 (m), 2965 (s), 2922 (s), 2854 (s), 1738 (s), 1441 (s), 1375 (s), 1331 (s), 1235 (s), 1170 (m), 1033 cm^{-1} (s); MS (CI, NH_3): $m/z = 382$ (MNH_4^+), 365 (MH^+), 305, 287, 227; HR-MS-EI: $m/z = 364.2238$ (calcd. for $C_{21}H_{32}O_5$: 364.2250).

rac-(1*S*,5*S*,7a*S*)-5-Hydroxy-7,7-dimethyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (18a)

According to procedure method B (0.04 equiv. catalyst **4** added) using compound **17a** (51.6 mg, 0.25 mmol) and wet acetone (0.5 mL) in CH_2Cl_2 (9.5 mL) afforded compound **18a** as a yellowish oil after 13.5 h; yield: 23.6 mg (42%); R_f (PE/Et_2O 1:1): 0.20; ^{1}H NMR (400.2 MHz, $CDCl_3$): $\delta = 5.35$ (t, $J = 8.9$ Hz, 1H), 5.16 (dt, $J = 7.2$ Hz, $J = 2.0$ Hz, 1H), 3.76–3.67 (m, 1H), 2.80 (dd, $J = 5.2$ Hz, $J = 1.7$ Hz, 1H), 2.74–2.64 (m, 1H), 2.29 (s, 1H), 2.27–2.19 (m, 1H), 2.03 (s, 3H), 1.97–1.86 (m, 1H), 1.76–1.62 (m, 2H), 1.32 (t, $J =$ 12.4 Hz, 1H), 1.04 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 170.8$ (C), 139.3 (C), 121.1 (CH), 74.7 (CH), 67.5 (CH), 62.0 (CH), 50.2 (CH_2), 40.8 (CH_2), 38.3 (CH_2), 34.4 (C), 29.8 (CH_3), 21.5 (CH_3), 20.6 (CH_3); IR (CCl_4): $\nu =$ 3463 (br. m), 2956 (s), 2927 (s), 2870 (s), 1735 (s), 1667 (m), 1459 (s), 1437 (s), 1371 (s), 1245 (s), 1165 (s), 1118 (s), 1035 cm^{-1} (s); MS (CI, NH_3): $m/z = 242$ (MNH_4^+), 225 (MH^+), 165, 159, 147; HR-MS-EI: $m/z = 224.1413$ (calcd. for $C_{13}H_{20}O_3$: 224.1412).

rac-(1*S*,5*S*,7a*S*)-5-(4-Methoxyphenoxy)-7,7-dimethyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (18b)

According to procedure A (0.04 equiv. catalyst **4** added) using compound **17a** (51.6 mg, 0.25 mmol) and 4-methoxyphenol (155.1 mg, 1.25 mmol) in CH_2Cl_2 (10 mL) afforded compound **1b** as a yellowish oil (isolated as a mixture of bicyclic product **18b** with corrected yield 70% and the corresponding monocyclic product; only the major isomer **18b** is described below) after 16 h; yield: 66.3 mg (80%); R_f (PE/Et_2O 7:3): 0.51; ^{1}H NMR (400.2 MHz, $CDCl_3$): $\delta = 6.90$–6.82 (m, 4H), 5.44 (t, $J = 1.8$ Hz, 1H), 5.25 (dt, $J = 7.2$ Hz, $J = 2.1$ Hz, 1H), 4.26–4.15 (m, 1H), 3.81 (s, 3H), 2.99 (ddd, $J = 12.7$ Hz, $J = 5.1$ Hz, $J = 1.6$ Hz, 1H), 2.83–2.73 (m, 1H), 2.42 (s, 1H), 2.35–2.25 (m, 1H), 2.18–2.11 (m, 1H), 2.09 (s, 3H), 1.98–1.91 (m, 1H), 1.52 (t, $J = 12.2$ Hz, 1H), 1.12 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 170.7$ (C), 154.2 (C), 151.7 (C), 139.5 (C), 121.7 (CH), 117.6 (CH), 114.7 (CH), 74.7 (CH), 74.3 (CH), 62.2 (CH), 55.7 (CH_3), 46.6 (CH_2), 40.8 (CH_2), 35.2 (CH_2), 34.3 (C), 29.7 (CH_3), 21.4 (CH_3), 20.6 (CH_3). IR (CCl_4): $\nu = 3050$ (m), 2952 (s), 2871 (s), 1737 (s), 1506 (s), 1462 (s), 1441 (s), 1371 (s), 1291 (s), 1250 (s), 1234 (s), 1177 (s), 1034 cm^{-1} (s); MS (CI, NH_3): $m/z = 348$ (MNH_4^+), 331, 330, 271, 207, 147; HR-MS-EI: $m/z = 330.1821$ (calcd. for $C_{20}H_{26}O_4$: 330.1831).

rac-(1*S*,5*S*,7*S*,7a*S*)-5-Hydroxy-7-methyl-7-(4-methylpent-3-enyl)-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl Acetate (18c)

According to procedure B using compound **17b** (41.2 mg, 0.15 mmol) and wet acetone (0.5 mL) in CH_2Cl_2 (5.5 mL) afforded compound **18c** as a colourless oil after 20 h; yield: 16.2 mg (38%); R_f (PE/Et_2O 1:1): 0.19; ^{1}H NMR (400.2 MHz, $CDCl_3$): $\delta = 5.36$ (s, 1H), 5.25 (d, $J = 7.2$ Hz, 1H), 5.03 (t, $J = 6.7$ Hz, 1H), 3.72–3.62 (m, 1H), 2.81 (dd, $J = 12.6$ Hz, $J = 4.3$ Hz, 1H), 2.74–2.64 (m, 1H), 2.33 (s, 1H), 2.23 (d, $J = 18.1$ Hz, 1H), 2.03 (s, 3H), 2.00–1.78 (m, 4H), 1.66 (s, 3H), 1.59 (s, 3H), 1.23–1.07 (m, 2H), 1.03 (s, 3H), 0.98–0.87 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 170.7$ (C), 139.5 (C), 131.5 (C), 124.5 (CH), 121.5 (CH), 74.1 (CH), 67.2 (CH), 63.8 (CH), 45.2 (CH_2), 41.0 (CH_2), 38.4 (CH_2), 36.8 (C), 31.6 (CH_2), 26.3 (CH_3), 25.7 (CH_3), 21.9 (CH_2), 21.4 (CH_3), 17.7 (CH_3); IR (CCl_4): $\nu = 3620$ (w), 2958 (s), 2926 (s), 2863 (s), 1737 (s), 1455 (m), 1375 (s), 1245 (s), 1160 (m), 1118 (m), 1033 cm$^{<-1>1}$ (s); MS (CI, NH_3): $m/z = 310$ (MNH_4^+), 293 (MH^+), 233, 215; HR-MS-EI: $m/z = 292.2029$ (calcd. for $C_{18}H_{28}O_3$: 292.2038).

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[11] Numerous by-products were formed during the reactions, including bicyclo[4.3.0]nonadienes derived from intermediate **F** (see Scheme 6) by a proton loss instead of a nucleophilic trapping.

[12] The lower reactivity of isomer (*Z*)-10 might be explained by a possible stronger pseudo 1,3-diaxal steric interaction between R^1 and R^3 in a transition state of type **E** (cf Scheme 6) which should kinetically disfavour the [4+2] annelation process.

[13] Such a concerted mechanism has been previously proposed for the cycloisomerization of related 1,6-enynes; see, for instance, refs.[7j,l]

[14] Chung and co-workers have shown that related 1,6-enynes could be cycloisomerized into 1,4-dienes in the presence of a gold catalyst. The formation of the second alkene is proposed to occur after the loss of a proton on a cyclopropyl gold carbene intermediate; see: S. I. Lee, S. M. Kim, S. Y. Kim, Y. K. Chung *Synlett* **2006**, 2256–2260.

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