CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200901614

# Gold-Catalyzed Intermolecular Addition of Carbonyl Compounds to 1,6-Enynes: Reactivity, Scope, and Mechanistic Aspects

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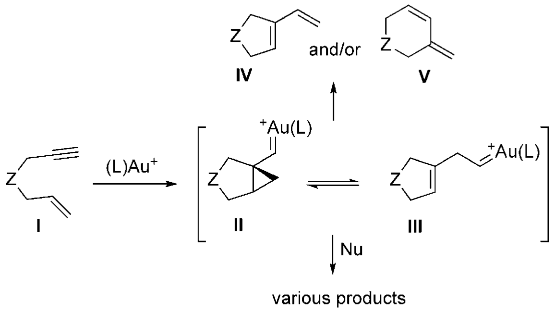
**Abstract:** A full account of a recently discovered gold(I)-catalyzed reaction, a cycloaddition of carbonyl compounds to enynes yielding 2-oxabicyclo[3.1.0]hexanes with four stereogenic centers, is presented. The reaction proceeds with very high diastereoselectivity. The scope of the reaction has been investigated. In addition, experiments and DFT calculations concerning mechanistic aspects were carried out. The reaction course varies with the substitution pattern of the alkene moiety of the starting enyne. Branched olefins led to 2-oxabicyclo[3.1.0]hexanes; terminally substituted olefins proceeded with the incorporation of two carbonyl components to give hexahydrocyclopenta[*d*][1,3]dioxines.

**Keywords:** aldehydes • cyclization • enynes • gold • homogeneous catalysis • ketones

## Introduction

In recent years, gold complexes have found increasing use as homogeneous catalysts for the activation of alkynes, and numerous novel reaction pathways have been discovered.[1,2] Among them are isomerization reactions of 1,6-enynes. These can be induced by many transition-metal catalysts.[3] Gold-catalyzed processes are distinguished by an unusually large spectrum of new reaction modes.[4] The fundamental Au-catalyzed isomerizations are described in Scheme 1.



Scheme 1. Isomerization reactions of 1,6-enynes.

Typically, Au-catalyzed isomerization reactions of 1,6-enynes of type **I** yield the dienes **IV** and/or **V**. The ratio of these reaction products depends on the connector Z and the substituents at the enyne moiety.[5] Crucial intermediates are the carbene complexes **II** and **III**. Evidence for their involvement was provided by DFT calculations.[2d,6,7c] The carbenoid character of **II** and **III** was illustrated by cyclopropanation of alkenes.[1b,7] Fürstner and others have pointed out that the nature of these complexes may be better described as gold-stabilized carbocations.[1b,2e,8] A 6-*endo-dig* pathway has been proposed for the formation of products **V**;[2d] however, recent research suggests that both **IV** and **V** are formed by 5-*exo-dig* cyclizations through carbene intermediates **II** and **III**.[9]

Furthermore, the intermediates of type **II** and **III** undergo a variety of addition reactions with nucleophiles (arenes[10] and alcohols or water[5]). In a communication, we have recently shown that oxabicyclo[3.1.0]hexanes of type **VI** can be obtained by an Au-catalyzed reaction of 1,6-enynes with carbonyl compounds (Scheme 2).[11] Echavarren et al.[12] had previously described a different reaction mode, an intramolecular gold-catalyzed reaction of en-yn-ones, which proceeds through a Prins-type reaction and gives rise to other types of products.

After publication, we extended our investigation. In particular, we have investigated the scope and mechanism of the formation of products **VI**. In the course of this work a

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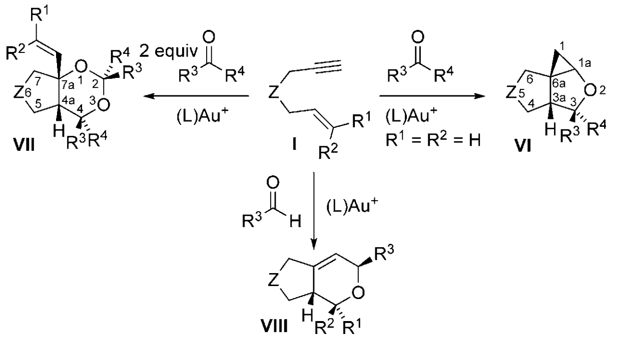
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901614.



Scheme 2. Addition of carbonyl compounds to 1,6-enynes.

new reaction mode was discovered: twofold addition of the carbonyl component to give 1,3-dioxolanes **VII**, which is observed with terminally substituted olefins as substrates (Scheme 2). A further reaction mode that leads to products of type **VIII** was very recently reported by Echavarren et al., who employed gold complexes with ligands L other than PPh$_3$ as catalysts.[13]

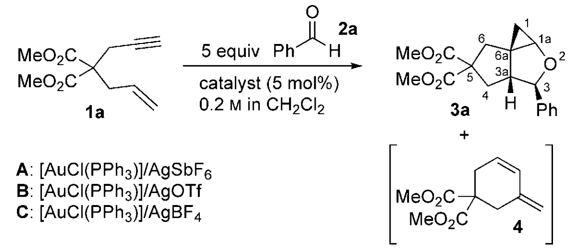
## Results and Discussion

The reaction conditions of the conversion **I**→**VI** were optimized by varying the catalyst, the temperature, and the ratio of the carbonyl component and enyne. The reaction of the enyne **1a** with benzaldehyde (**2a**) was used as a probe (Table 1). The best yields were obtained at a reaction temperature of −45 °C with an excess of benzaldehyde (Table 1, entries 3, 4, and 8). The cationic catalysts [AuCl(PPh$_3$)]/AgSbF$_6$ (**A**) and [Au(NTf$_2$)(PPh$_3$)] (Tf = trifluoromethylsulfonyl) showed high activity,[14] whereas AuCl, AuCl$_3$, CuOTf, ZnOTf, PtCl$_2$, and AgSbF$_6$ as well as [AuCl(PPh$_3$)], without added silver salt, or BF$_3$·Et$_2$O, were not catalytically active (entries 9–12, and experiments that are not listed). Among the weakly coordinating anions that were tested, SbF$_6^-$ proved best suited (entries 1–5). Success with [Au(NTf$_2$)(PPh$_3$)] as homogeneous catalyst (entry 8)[15] shows that insoluble silver salts, formed in conjunction with most of the catalysts, do not exert a significant effect on the reaction.

In the absence of an aldehyde, enyne **1a** expectedly[5] gave product **4** at a low temperature (Table 1, entry 1). This compound was also detected (GC–MS) in the reaction mixture containing only one equivalent of benzaldehyde (entry 2) and in reactions run at temperatures ≥ −20 °C (entries 4 and 5). With the exception of a run according to entry 1, the compound was not isolated; in the presence of catalyst **A**, diene **4** was unstable at room temperature and gave rise to side products, which were not identified. The diene **4** was not formed upon use of the optimal reaction conditions (entry 3).

To gain more insight into the competing reaction pathways, the reaction was monitored by NMR spectroscopy at −20 °C. Results for the reaction of enyne **1a** in the presence of catalyst **A** are displayed in Figure 1. The isomeric dienes **4** and **5** were formed after approximately 30 min in a ratio **4**/**5** = 11:1. Echavarren et al. reported a ratio **4**/**5** = 7:1 for the reaction at 0 °C.[5]

Table 1. Results for the reaction of **1a** with benzaldehyde (**2a**).



| Entry | Catalyst | Conditions | Yield of **3a** [%] |
|---|---|---|---|
| 1[a] | A | 1.5 h −45 °C | –[b] |
| 2[c] | A | 6 h −45 °C, then → RT (16 h) | 38 |
| 3 | A | 6 h −45 °C, then → RT (16 h) | 68 |
| 4 | A | 4 h −20 °C | 66 |
| 5 | A | 1.5 h RT | 42 |
| 6 | B | 6 h −45 °C, then → RT (12 h) | –[d] |
| 7 | C | 6 h −45 °C, then → RT (14 h) | 59 |
| 8 | [Au(NTf$_2$)(PPh$_3$)] (2 mol %) | 6 h −45 °C, then → RT (22 h) | 68 |
| 9 | [AuCl(PPh$_3$)] | 6 h −45 °C, then → RT (13 h) | n.r.[e] |
| 10 | AgSbF$_6$ | 6 h −45 °C, then → RT (15 h) | n.r.[e] |
| 11 | AuCl | 6 h −45 °C, then → RT (12 h) | n.r.[e] |
| 12 | CuOTf | 6 h −45 °C, then → RT (18 h) | n.r.[e] |

[a] No benzaldehyde (**2a**) was added. [b] Yield of **4**: 49 %. [c] One equivalent of benzaldehyde (**2a**) was added. [d] Conversion to **3a** < 50 % after 18 h (GC–MS). [e] No reaction.

Conversion versus time for the reaction of enyne **1a** in the presence of catalyst **A** and two equivalents of benzaldehyde is described in Figure 2. The amount of the products of the enyne isomerization was significantly reduced, that is, at −20 °C, the oxabicyclo[3.1.0]hexane **3a** was formed as the main product and diene **4** as a side product. Diene **5** was not detected under these conditions.

These experiments show that there are several competing reaction pathways. An excess of benzaldehyde favors the formation of the oxabicyclo[3.1.0]hexane **3a** at the expense of the enyne isomerization. Furthermore, the addition of only 0.2 equiv benzaldehyde leads to a significant decrease in the reaction rate. Thus, it is likely that **3a** is formed from one of the species in the isomerization manifold.

Investigation of the scope of the reaction with respect to the carbonyl component gave the following results (Scheme 3). Isobutyraldehyde (**2c**) and *o*-nitrobenzaldehyde (**2b**) reacted at about the same rate as benzaldehyde **2a**. The reactions of acetone (**2d**) and cyclohexanone (**2e**) were comparatively slow; reaction temperatures above 0 °C were

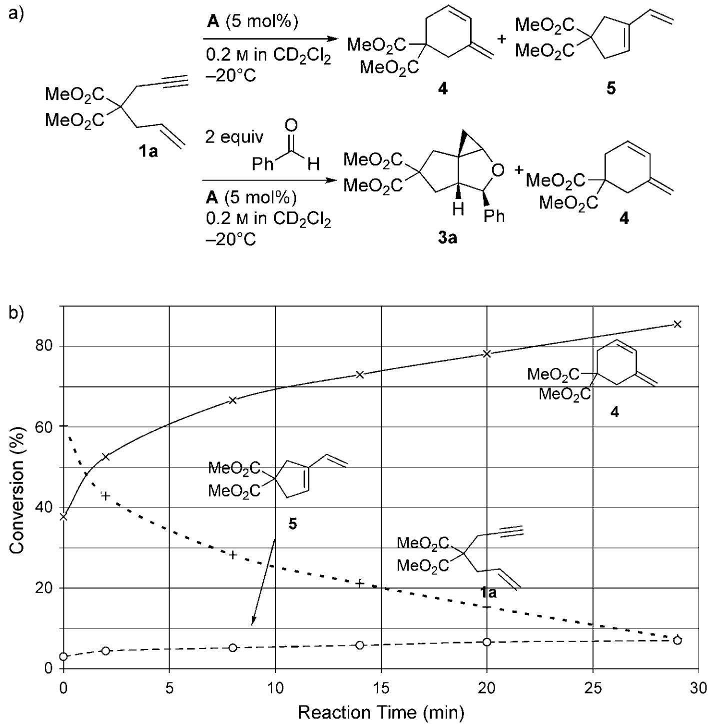


Figure 1. Conversion of **1a** to **4** and **5** versus reaction time; conditions: −20 °C, $CD_2Cl_2$ ($c$(**1a**) = 0.17 M), 5 mol% of **A** (cf. Table 1, entry 1).

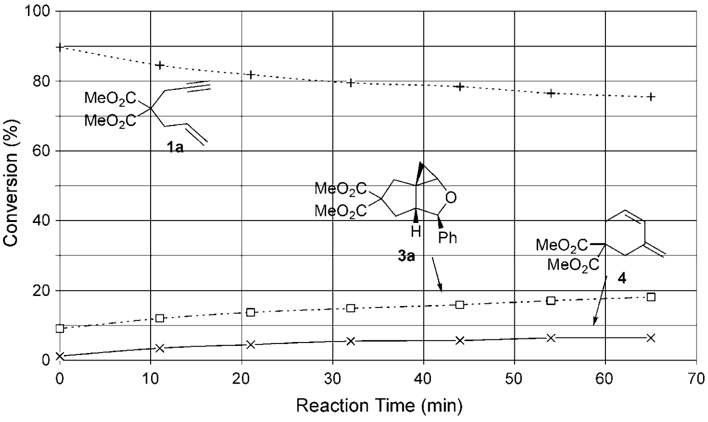
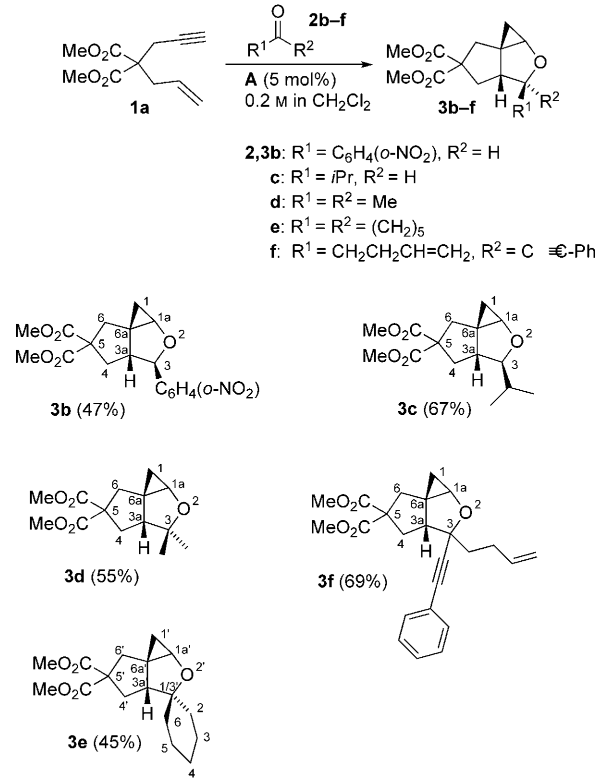


Figure 2. Conversion of **1a** to **3a** and **4** in the presence of 2 equiv benzaldehyde; conditions: −20 °C, $CD_2Cl_2$ ($c$(**1a**) = 0.17 M), 5 mol% of **A**.



Scheme 3. Products of the intermolecular addition of different aldehydes and ketones to **1a**.

required. Surprisingly, the addition of ketone **2f**[16] to **1a** gave the adduct **3f**, an oil, as a single diastereoisomer. This experiment was conducted with the idea of probing the interception of an intermediate of the addition reaction.

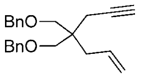
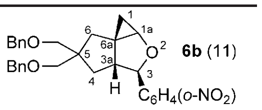
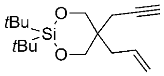
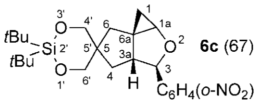
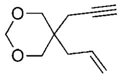
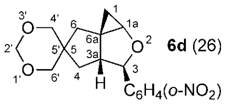
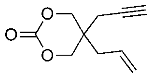
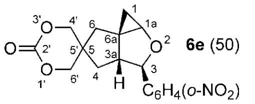
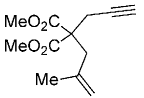
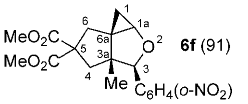
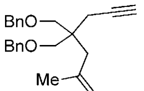
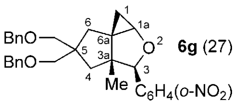
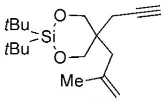
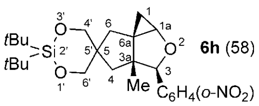
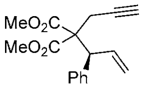
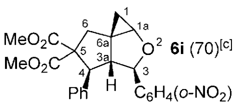
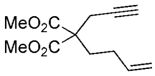
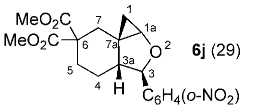
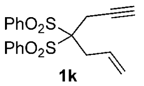
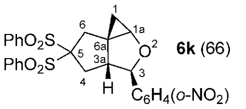
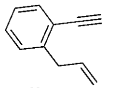
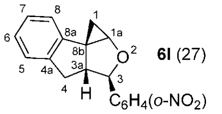
The scope of the reaction was further explored with 1,6-enynes and the 1,7-enyne **1j** (Table 2). The products **3b**, **6d**, **6e**, **6f**, **6i**, **6j**, and **6l** were characterized by X-ray crystal structure analysis (see Table 4 in the Experimental Section). In all cases, the reaction proceeded with complete diastereoselectivity with respect to the stereogenic centers C-1a, C-3, C-3a, and C-6a. Despite the formation of two quaternary centers in vicinal positions,[17] the substrate **1f** (Table 2, entry 5), which incorporated a 1-methylvinyl group, reacted significantly faster than compound **1a**. The reaction of substrate **1i** with a stereogenic center led exclusively to the diastereomer represented in entry 8.[18] The influence of the backbone was assessed with the substrates **1k** and **1l**. Whereas the bis-sulfonyl derivative **1k** (entry 10) reacted with a yield comparable to that of the malonic esters, a lower yield was obtained with **1l**, which contained an *ortho*-phenylene moiety as backbone (entry 11).

Limits became apparent upon further varying the backbone of the enyne. With Z = NTs (Ts = tosylyl) or O (cf. Scheme 2), selective formation of the oxabicyclo[3.1.0]hexanes of type **VI** was not accomplished. Compounds with Z = NTs yielded complex product mixtures, and those with Z = O did not react. This could be due to coordination effects of the heteroatoms or lack of a *gem*-disubstitution effect.[19]

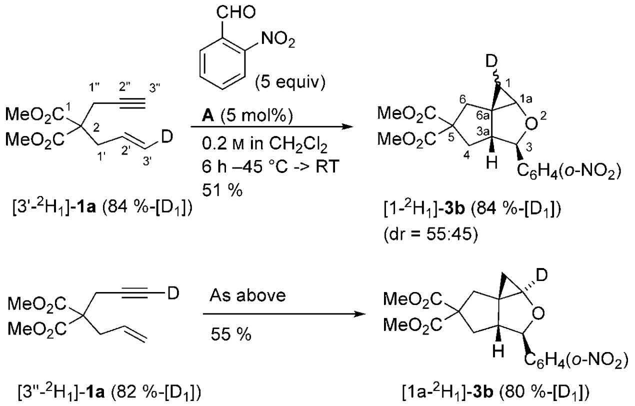
For exploration of the steric course of the reaction, deuterated substrates were subjected to the optimal reaction conditions. The enyne [3′-$^2H_1$]-**1a** with a *trans* configuration of the double bond furnished product [1-$^2H_1$]-**3b** as a 1:1 mixture of epimers with respect to C-1 (Scheme 4), and its isotopomer [3″-$^2H_1$]-**1a** gave [1a-$^2H_1$]-**3b** as product.

**Mechanistic proposal and computational investigation**: Our initial proposal for the mechanism of the new reaction is displayed in Scheme 5. The mechanism is supported by DFT calculations described below.

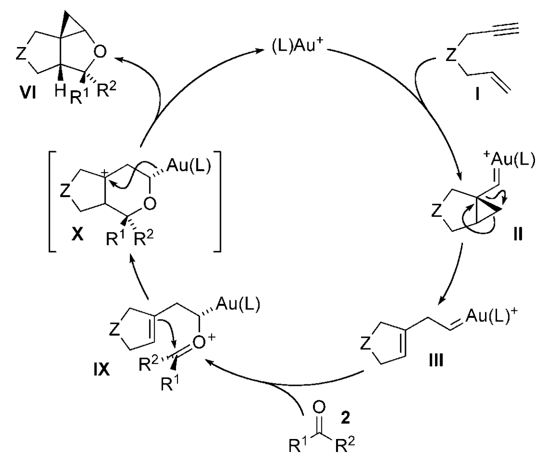
Table 2. Addition of *ortho*-nitrobenzaldehyde (**2b**) to various enynes.[a]

| Entry | Enyne | $t$ [h] | Product (Yield [%]) |
|---|---|---|---|
| 1 |  **1b** | 3[b] |  **6b** (11) |
| 2 |  **1c** | 1[b] |  **6c** (67) |
| 3 |  **1d** | 4[b] |  **6d** (26) |
| 4 |  **1e** | 7 |  **6e** (50) |
| 5 |  **1f** | 4[b] |  **6f** (91) |
| 6 |  **1g** | 16 |  **6g** (27) |
| 7 |  **1h** | 18 |  **6h** (58) |
| 8 |  **1i** | 21 |  **6i** (70)[c] |
| 9 |  **1j** | 43 |  **6j** (29) |
| 10 |  **1k** | 16 |  **6k** (66) |
| 11 |  **1l** | 22 |  **6l** (27) |

[a] Reaction conditions: 0.2 M enyne in $CH_2Cl_2$, 5 equiv *o*-nitrobenzaldehyde (**2b**), catalyst: 5 mol% **A**, 6 h −45 °C, then →RT. [b] Complete conversion after the time indicated at −45 °C; for details see the Experimental Section. [c] The reaction proceeded without racemization.



Scheme 4. Addition of carbonyl compounds to deuterated enynes [3′-$^2H_1$]-**1a** and [3″-$^2H_1$]-**1a**.



Scheme 5. Mechanistic working hypothesis concerning the formation of the products **VI**.

The eastern part of the catalytic cycle, leading to the intermediate **III**, is adopted from previous work of the Echavarren group.[6,7b] The subsequent addition of the carbonyl compound and the following cyclization was assumed to proceed by means of a stepwise cationic mechanism including the six-membered ring intermediate **X**. Alternatively, a 1,3-dipolar cycloaddition as typical for addition reactions of rhodium carbene complexes[20] was suggested because of the observed high diastereoselectivity.

For a DFT study, the unsubstituted 1,6-enyne and benzaldehyde were chosen as model substrates. The catalyst was represented by the cationic complex $[Au(PMe_3)]^+$. The methods used in the computational investigation are outlined in the computational details part of the Experimental Section (below). The rearrangement of the unsubstituted 1,6-enyne has previously been theoretically investigated with respect to the formation of dienes of type **V**.[9] The established reaction pathway leading to the dienes of type **IV**,[2d,6,7c] which constitutes the first part of our mechanistic proposal for the addition reaction depicted in Scheme 5, has only been calculated with enynes substituted at the alkene moiety. Results of our investigation of the corresponding pathway of the rearrangement of the unsubstituted 1,6-enyne and the subsequent reaction with benzaldehyde are described in Figure 3.

Consistent with the findings of the Echavarren group for substituted enynes, the initial enyne gold complex **A** reacts through two steps to give intermediate **E**, which contains a partially opened cyclopropyl moiety with a C−C distance of about 1.8 Å (drawn with a dashed line in Figure 3). This intermediate has previously been presented as achiral gold carbene **III** (cf. Scheme 5). However, **E** possesses character-

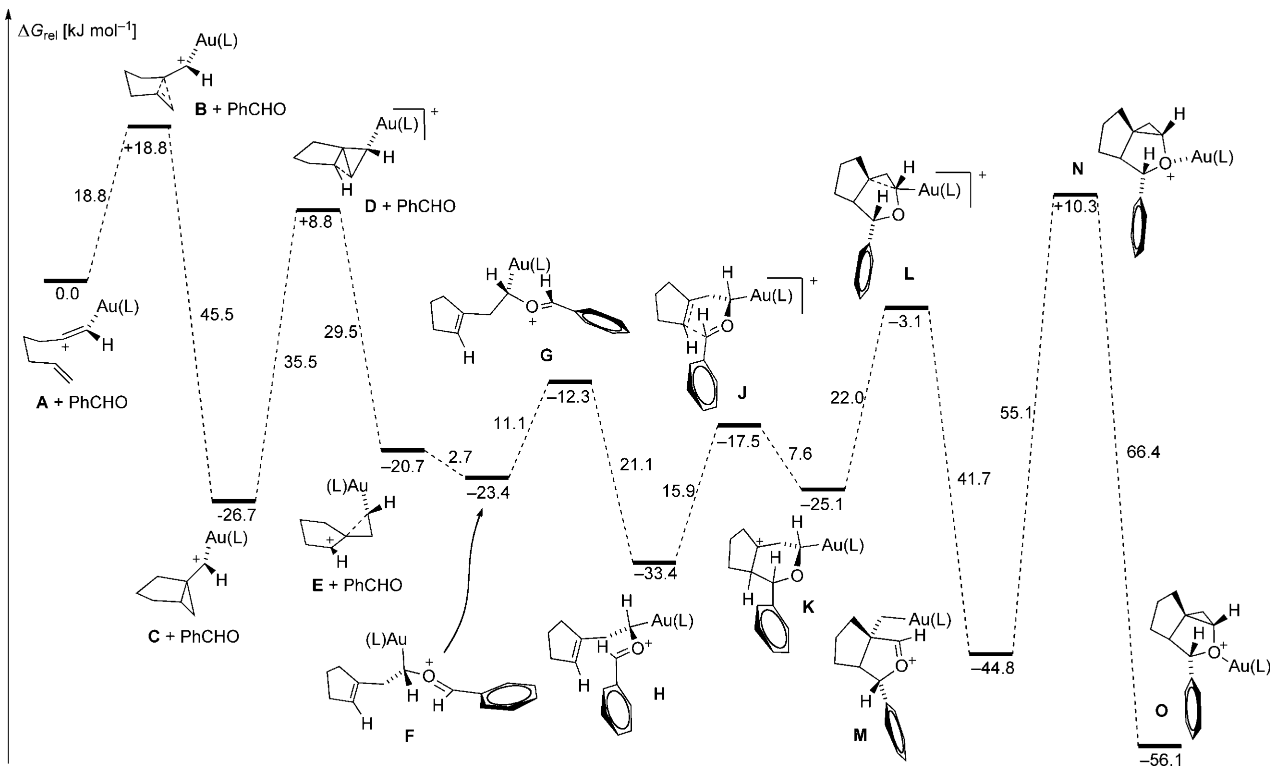


Figure 3. Formation of products **VI** according to DFT calculations.

istics of a homoallyl cation as well as of a cyclopropyl methyl cation and displays a low barrier to racemization; this is consistent with the observed lack of stereoselectivity in the reaction of the deuterated substrate $[3'\text{-}^{2}H_{1}]$-**1a** (Scheme 4). The highly cationic character of gold carbene complexes has recently been demonstrated experimentally by Fürstner et al.[8a]

Examples of intermolecular additions of nucleophiles to gold complexes of type **II** and **III** have been described by Echavarren et al.[21] Furthermore, Hashmi et al.[21] proposed an intramolecular addition of a carbonyl oxygen to a carbenoid gold complex. Toste et al.[22] have described oxidations of intermediary carbenoid gold complexes with sulfoxides. According to the DFT calculations, the reaction of **E** with benzaldehyde to give **F** proceeds with a low activation barrier. No transition state was found for this step; this was sought by stepwise variation of the C–O bond length. The reactive conformer **H** was found by C–C bond rotation.

Two steps rather than a concerted pathway were identified for the cyclization of **H**. The first step, in which the diastereoselectivity with respect to C-3 is determined, leads to the six-membered-ring intermediate **K** with the phenyl ring and the catalyst in equatorial positions. The cyclization of **K** furnishes the intermediate **M** with an opened cyclopropyl moiety, in which the positive charge is delocalized at the newly formed C–O bond. **M** is finally transformed to the gold complex **O** of the final product through a relatively high reaction barrier of about 55 $kJ\,mol^{-1}$. The final two steps are possibly not traversed in solution in which a variety of possibilities for the coordination of the gold species exist.

Overall, our proposal for the western part of the catalytic cycle as described in Scheme 5 is strongly supported by the DFT calculations.

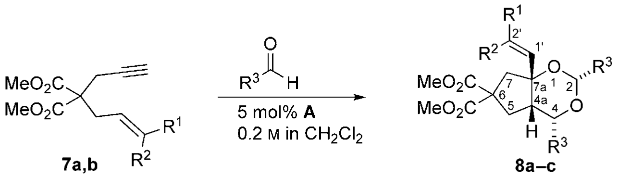
**Twofold addition of aldehydes to substituted enynes**: Further investigation of the scope of the addition reaction revealed another reaction mode in which 1,6-enynes with a terminal substituent at the alkene moiety led to dioxolanes of type **8** (Table 3) rather than to products of type **3**. The dioxolanes **8a**, **8b**, and **8c** were obtained as single diastereoisomers. The relative configurations of **8a** and **8b** were determined by X-ray crystal structure analysis.

The reaction to give dioxolanes **8** does not proceed by means of an enyne isomerization to give a diene of type **IV** followed by a Prins-type reaction of two aldehydes and a diene, a reaction known to occur upon acid catalysis.[23] This was established by a control experiment with the diene **9**, which did not form a product of type **8** under the stated reaction conditions (Scheme 6). The diene **9** was prepared from **7b** by $PtCl_2$-catalyzed rearrangement.[24]

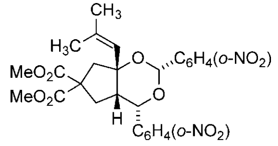
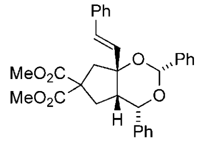
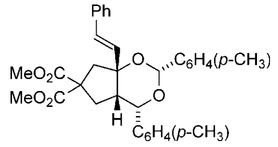
## Conclusion

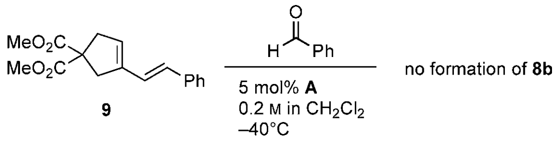
A gold(I)-catalyzed cycloaddition of carbonyl compounds to enynes yielding 2-oxabicyclo[3.1.0]hexanes with four stereogenic centers has been found and mechanistically character-

Table 3. Intermolecular additions of aldehydes to enynes **7** and **7b**.



**7,8a**: $R^1 = CH_3$, $R^2 = CH_3$, $R^3 = C_6H_4(o\text{-}NO_2)$
**b**: $R^1 = Ph$, $R^2 = H$, $R^3 = Ph$
**c**: $R^1 = Ph$, $R^2 = H$, $R^3 = C_6H_4(p\text{-}CH_3)$

| Entry | Enyne | *t* [h] | Product (Yield [%]) |
|---|---|---|---|
| 1 | **7a** | 1 h at −40° | <br>**8a** (36) |
| 2 | **7b** | 5 h at −40 °C | <br>**8b** (75) |
| 3 | **7b** | 2 h at −40 °C | <br>**8c** (62) |



Scheme 6. Control experiment concerning the formation of the products of type **8**.

ized. The reaction proceeds with a very high level of diastereoselectivity. The scope of the reaction has been investigated. Additionally, DFT calculations concerning mechanistic aspects were carried out. The reaction course varies with the substitution pattern of the alkene moiety of the enyne. Whereas branched olefins led to 2-oxabicyclo[3.1.0]hexanes, terminally substituted olefins proceeded with the incorporation of two carbonyl components to give hexahydrocyclopenta[*d*][1,3]dioxines. A third reaction mode has been recently described by Echavarren et al.

## Experimental Section

**Computational details**: The geometries of all structures described here were optimized using the Jaguar 6.5 quantum chemistry program package at the BP86/LACVP* level of theory.[25,26,27] Stationary points were characterized as equilibrium structures (number of imaginary frequencies (NIMAG) = 0) or transition states (NIMAG = 1) using the Gaussian 03 program package[28] at the BP86 level of theory[26] with the 6-31G* basis set on C, H, O, and P[29] and the LANL2DZ effective core potential and basis set on Au.[27] Single-point energy calculations were performed using the LACV3P++** basis set. For all Gibbs free energies stated, the single-point energies were combined with the Gibbs correction data for 298.15 K and 1 atm obtained from the frequency analyses. The energies and geometries of all calculated compounds are presented in the Supporting Information.

**General**: Unless stated otherwise, reactions were carried out under argon using anhydrous conditions. $^1H$ NMR spectra were recorded at RT using the following spectrometers: Bruker AC-300 (300 MHz), Bruker Avance 500 (500 MHz). Chemical shifts are reported in $\delta$ units relative to $CHCl_3$ ($\delta_H = 7.26$). $^{13}C$ NMR spectra were recorded using the following spectrometers: Bruker AC-300 (75 MHz), Bruker Avance 500 (125 MHz). Chemical shifts are reported in $\delta$ units relative to $CHCl_3$ ($\delta_C = 77.16$ {central line of the triplet}). The following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The assignments of signals for compounds **1**–**8** were confirmed by H,H COSY, H,C COSY, HMBC, and DEPT spectra. Atom numbers are specified in the formulas. $^1H$ NMR spectra of all newly described compounds are presented in the Supporting Information. Optical rotations were measured using a Perkin–Elmer 341 polarimeter in a 1 dm curvette with a thermostat using a mercury lamp. Concentration *c* is given in g per 100 mL. High resolution mass spectra (HRMS) were recorded using a JEOL JMS-700 instrument. Elemental analyses were carried out at the Organisch-Chemisches Institut, Universität Heidelberg. Enantiomeric excesses were determined by chiral HPLC using an HP 1100 instrument; column: Chiralpak AD-H (Daicel, 250 × 4.6 mm, 5 µm) with guard cartridge AD-H (Daicel, 10 × 4 mm, 5 µm). For preparative HPLC, the following system was used: a Gilson-305 pump coupled with a Knauer UV detector 2600; column: silica gel (Latek, 5 µ, 21 × 250 mm and/or Prontosil 120-10-SI, 10 µ, 20 × 250 mm). X-ray data were collected using a Bruker Smart CCD (**6d**, **6j**, **6l**) or a Bruker APEX (**3b**, **6e**, **6f**, **6i**, **8a**, **8b**) diffractometer equipped with a $Mo_{K\alpha}$ radiation source ($\lambda = 0.71073$ Å) and a graphite monochromator. Intensities were corrected for Lorentz and polarization effects; an empirical absorption correction was applied using SADABS.[30] All structures were solved by direct methods and refined against $F^2$ using the SHELXTL-PLUS software package.[31] The corresponding crystallographic data are displayed in Table 4. CCDC-641967 (**3b**), 696063 (**6d**), 696064 (**6e**), 641968 (**6f**), 641969 (**6i**), 641970 (**6j**), 641971 (**6l**), 696065 (**8a**), and 696066 (**8b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Syntheses and spectroscopic data of the following compounds have been published previously: **1a**,[32a,b] **1f**,[33] **1j**,[34] **1k**,[35a,b] **4**,[36] **5**,[37] **7a**,[38] **7b**,[32a] and **9**.[39] Syntheses of enynes [3′-$^2H_1$]-**1a**, [3″-$^2H_1$]-**1a**, **1b**, **1c**, **1d**, **1e**, **1g**, **1h**, **1i**, **1l**, and **2f** are described in the Supporting Information.

**General procedure for the reaction of enynes with carbonyl compounds (GP)**: In a flame-dried Schlenk flask under an argon atmosphere, a stirred solution of the enyne **1** (1 equiv), the carbonyl compound **2**, and $AgSbF_6$ (0.05 equiv) in anhydrous $CH_2Cl_2$ (5 mL) was treated with $[AuCl(PPh_3)]$ (0.05 equiv) at the temperature indicated. The mixture was stirred for the time and at the temperature indicated, filtered through Celite, and washed with $CH_2Cl_2$. The solvent was removed under reduced pressure and the residue subjected to flash column chromatography.

**(±)-Dimethyl (1a*R*,3*R*,3a*R*,6a*R*)-3-phenyltetrahydro-3*H*-cyclopenta[*c*]-cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (3a)**: According to GP, a mixture of benzaldehyde (530 mg, 5.0 mmol), enyne **1a** (210 mg, 1.0 mmol), and $AgSbF_6$ (17 mg, 50 µmol) in anhydrous $CH_2Cl_2$ (5 mL) was cooled to −45 °C and treated with $[AuCl(PPh_3)]$ (24.7 mg, 50 µmol). The mixture turned orange and was kept at −45 °C for 6 h. The cooling device was switched off, which initiated slow warming to RT. After an overall reaction time of 22 h, a black precipitate had formed and GC–MS indicated complete consumption of the substrate. Workup according to GP and flash column chromatography on silica (25 g, petroleum ether/ethyl acetate 10:1) yielded 2-oxabicyclo[3.1.0]hexane **3a** (216 mg, 68 %) as a colorless oil. $R_f = 0.31$ (petroleum ether/ethyl acetate 3:1); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.98$ (dd, $J = 6.2$, 5.1 Hz, 1H; 1-$H_a$), 1.14

Table 4. Data of the crystal structure analysis of several products.

| | **3b** | **6d** | **6e** | **6f** | **6i** |
|---|---|---|---|---|---|
| formula | $C_{18}H_{19}NO_7$ | $C_{17}H_{19}NO_5$ | $C_{17}H_{17}NO_6$ | $C_{19}H_{21}NO_7$ | $C_{24}H_{23}NO_7$ |
| $M_r$ | 361.34 | 317.33 | 331.32 | 375.37 | 437.43 |
| crystal size [mm$^3$] | 0.47×0.39×0.20 | 0.47×0.24×0.10 | 0.20×0.13×0.11 | 0.39×0.24×0.13 | 1.10×0.14×0.12 |
| crystal system | orthorhombic | orthorhombic | monoclinic | monoclinic | triclinic |
| space group | $P2_12_12_1$ | $Pbca$ | $P2_1/c$ | $P2_1$ | $P1$ |
| $a$ [Å] | 9.3604(15) | 9.1698(2) | 24.968(5) | 8.1973(6) | 8.5155(12) |
| $b$ [Å] | 9.9285(16) | 15.1226(3) | 5.8198(12) | 14.1531(10) | 9.7995(13) |
| $c$ [Å] | 17.935(3) | 21.0707(4) | 21.670(4) | 15.6051(11) | 13.5216(19) |
| $\alpha$ [°] | 90 | 90 | 90 | 90 | 87.912(3) |
| $\beta$ [°] | 90 | 90 | 110.040(6) | 98.515(2) | 79.187(3) |
| $\gamma$ [°] | 90 | 90 | 90 | 90 | 87.987(3) |
| $V$ [Å$^3$] | 1666.8(5) | 2921.90(10) | 2958.2(10) | 1790.5(2) | 1107.1(3) |
| $Z$ | 4 | 8 | 8 | 4 | 2 |
| $\rho_{calcd}$ [Mgm$^{-3}$] | 1.440 | 1.44 | 1.49 | 1.392 | 1.312 |
| $\mu$ [mm$^{-1}$] | 0.11 | 0.11 | 0.11 | 0.107 | 0.097 |
| $T_{max}$, $T_{min}$ | 0.98, 0.95 | 0.99, 0.95 | 0.99, 0.98 | 0.99, 0.96 | 0.99, 0.90 |
| index ranges $hkl$ | −12 to 12,<br>−13 to 13,<br>−23 to 23 | −11 to 11,<br>−19 to 19,<br>−27 to 27 | −32 to 32,<br>−7 to 7,<br>−27 to 27 | −10 to 10,<br>−18 to 18,<br>−20 to 20 | −11 to 11,<br>−13 to 13,<br>−18 to 18 |
| $\theta$ [°] | 2.27 to 28.33 | 1.9 to 27.5 | 1.7 to 27.1 | 2.51 to 28.39 | 2.08 to 28.37 |
| $T$ [K] | 200(2) | 200(2) | 200(2) | 200(2) | 200(2) |
| reflns collected | 16742 | 28198 | 27167 | 18982 | 11221 |
| independent reflns ($R_{int}$) | 4145 (0.0320) | 3345 (0.0911) | 6518 (0.0625) | 8797 (0.0255) | 9876 (0.0273) |
| observed reflns ($I>2\sigma(I)$) | 3813 | 2506 | 5016 | 8239 | 8659 |
| data/restraints/params | 4145/0/273 | 3345/0/208 | 6518/0/433 | 8797/1/541 | 9876/3/645 |
| GOF on $F^2$ | 1.09 | 1.03 | 1.21 | 1.08 | 1.03 |
| final $R$ indices ($I>2\sigma(I)$) $R_1$, $wR_2$ | 0.047, 0.117 | 0.041, 0.098 | 0.083, 0.144 | 0.045, 0.112 | 0.047, 0.119 |
| absolute structural params | 0.3(9) | – | – | 0.0(6) | −0.2(6) |
| residual electron density [eÅ$^{-3}$] | 0.40 and −0.28 | 0.24 and −0.22 | 0.31 and −0.25 | 0.27 and −0.21 | 0.31 and −0.21 |

| | **6j** | **6l** | **8a** | **8b** |
|---|---|---|---|---|
| formula | $C_{19}H_{21}NO_7$ | $C_{18}H_{15}NO_3$ | $C_{27}H_{28}N_2O_{10}$ | $C_{31}H_{30}O_6$ |
| $M_r$ | 375.37 | 293.31 | 540.51 | 498.55 |
| crystal size [mm$^3$] | 0.26×0.14×0.12 | 0.55×0.27×0.04 | 0.42×0.12×0.05 | 0.60×0.20×0.17 |
| crystal system | triclinic | monoclinic | triclinic | monoclinic |
| space group | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ | $P2_1/c$ |
| $a$ [Å] | 9.0680(1) | 8.1289(1) | 7.7398(9) | 9.5686(16) |
| $b$ [Å] | 9.8733(2) | 20.4867(4) | 9.7750(11) | 12.954(2) |
| $c$ [Å] | 10.5679(2) | 8.4067(2) | 18.297(2) | 20.972(3) |
| $\alpha$ [°] | 81.437(1) | 90 | 100.934(2) | 90 |
| $\beta$ [°] | 73.921(1) | 94.858(1) | 100.087(2) | 97.172(3) |
| $\gamma$ [°] | 77.761(1) | 90 | 103.236(2) | 90 |
| $V$ [Å$^3$] | 884.82(3) | 1394.97(5) | 1288.0(3) | 2579.2(7) |
| $Z$ | 2 | 4 | 2 | 4 |
| $\rho_{calcd}$ [Mgm$^{-3}$] | 1.409 | 1.397 | 1.39 | 1.28 |
| $\mu$ [mm$^{-1}$] | 0.108 | 0.096 | 0.11 | 0.09 |
| $T_{max}$, $T_{min}$ | 0.99, 0.97 | 1.00, 0.95 | 0.99, 0.96 | 0.99, 0.95 |
| index ranges $hkl$ | −11 to 11,<br>−12 to 12,<br>−13 to 13 | −10 to 10,<br>−26 to 26,<br>−10 to 10 | −10 to 10,<br>−12 to 13,<br>−24 to 24 | −12 to 12,<br>−17 to 17,<br>−27 to 27 |
| $\theta$ [°] | 2.01 to 27.45 | 1.99 to 27.52 | 2.2 to 28.4 | 1.9 to 28.3 |
| $T$ [K] | 200(2) | 200(2) | 200(2) | 200(2) |
| reflns collected | 8993 | 13739 | 13392 | 26573 |
| independent reflns ($R_{int}$) | 4017 (0.0721) | 3202 (0.0581) | 6334 (0.0278) | 6418 (0.0297) |
| obsd reflns ($I>2\sigma(I)$) | 2599 | 2323 | 4858 | 5495 |
| data/restraints/params | 4017/0/246 | 3202/0/200 | 6334/0/356 | 6418/0/336 |
| GOF on $F^2$ | 1.01 | 1.04 | 1.10 | 1.03 |
| final $R$ indices ($I>2\sigma(I)$) $R_1$, $wR_2$ | 0.059, 0.136 | 0.049, 0.109 | 0.063, 0.135 | 0.046, 0.118 |
| residual electron density [eÅ$^{-3}$] | 0.27 and −0.25 | 0.26 and −0.17 | 0.43 and −0.29 | 0.35 and −0.22 |

(dd, $J$=6.3, 1.8 Hz, 1H; 1-H$_b$), 2.38 (s, 2H; 6-H), 2.47–2.62 (m, 3H; 3a-H, 4-H), 3.75 (s, 3H; OCH$_3$), 3.84 (s, 3H; OCH$_3$), 3.87 (dd, $J$=5.1, 1.7 Hz, 1H; 1a-H), 5.09 (dt, $J$=7.5, 3.7 Hz, 1H; 3-H), 7.22–7.35 ppm (m, 5H; Ph); $^{13}$C NMR (75 MHz, CDCl$_3$, 25°C, DEPT, HMBC): $\delta$=23.08 (t; C-1), 36.50 (s; C-6a), 37.98, 38.33 (2 t; C-4, C-6), 53.05 (q; 2OCH$_3$), 55.13 (d; C-3a), 61.56 (s; C-5), 65.57 (d; C-1a), 95.70 (d; C-3), 125.74 (d; Ph), 127.68 (d; Ph), 128.54 (d; Ph), 141.63 (s; Ph), 171.94 (s; $CO_2CH_3$), 172.27 ppm (s; $CO_2CH_3$); HRMS (EI): $m/z$: calcd for $C_{18}H_{20}O_5$: 316.1311; found: 316.1324 [$M^+$]; elemental analysis calcd (%) for $C_{18}H_{20}O_5$ (316.4): C 68.34, H 6.37; found: C 68.32, H 6.33.

**(±)-Dimethyl (1a*R*,3*R*,3a*R*,6a*R*)-3-(2-nitrophenyl)tetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (3b)**: According to GP, a solution of enyne **1a** (210 mg, 1.0 mmol), 2-nitrobenzaldehyde (**2b**) (756 mg, 5.0 mmol), and $AgSbF_6$ (17 mg, 50 μmol) in anhydrous $CH_2Cl_2$ (5 mL) was cooled to −50 °C and treated with $[AuCl(PPh_3)]$ (24.7 mg, 50 μmol). The temperature was allowed to rise to −25 °C over a period of 5 h when GC monitoring indicated complete conversion. Workup and flash column chromatography on silica (35 g, petroleum ether/ethyl acetate 10:1) afforded **3b** (168 mg, 47 %) as a yellow solid. Crystallization from methanol at RT gave colorless crystals, suitable for X-ray crystal structure analysis; for data, see Table 4. $R_f=0.37$ (petroleum ether/ethyl acetate 3:1); m.p. 98–100 °C; $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=0.83$ (dd, $J=6.1$, 6.1 Hz, 1H; 1-H), 1.01 (dd, $J=6.8$, 1.1 Hz, 1H; 1-H), 2.30 (d, $J=13.6$ Hz, 1H; 6-H), 2.43 (d, $J=13.6$ Hz, 1H; 6-H), 2.50 (dt, $J=7.8$, 5.9 Hz, 1H; 3a-H), 2.65–2.81 (m, 2H; 4-H), 3.73 (d, $J=0.9$ Hz, 3H; $OCH_3$), 3.81 (d, $J=0.9$ Hz, 3H; $OCH_3$), 3.88 (dd, $J=5.1$, 1.3 Hz, 1H; 1a-H), 5.80 (d, $J=4.9$ Hz, 1H; 3-H), 7.38 (dd, $J=7.6$, 7.6 Hz, 1H; Ar), 7.58 (dd, $J=7.4$, 7.4 Hz, 1H; Ar), 7.71 (d, $J=7.7$ Hz, 1H; Ar), 7.94 ppm (d, $J=8.1$ Hz, 1H; Ar); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, DEPT, HMBC): $\delta=19.26$ (t; C-1), 35.43 (s; C-6a), 38.15 (t; C-6), 40.26 (t; C-4), 53.00 (q; $OCH_3$), 54.80 (d; C-3a), 61.01 (s; C-5), 66.32 (d; C-1a), 88.70 (d; C-3), 124.79 (d; Ar), 128.06 (d; Ar), 128.17 (d; Ar), 133.45 (d; Ar), 139.42 (s; Ar), 147.32 (s; Ar), 172.09 (s; C=O), 172.15 ppm (s; C=O); IR (KBr): $\tilde{\nu}=$ 729, 791, 1077, 1120, 1165, 1202, 1242, 1277, 1349, 1433, 1528, 1735 (C=O), 2953, 3436 $cm^{-1}$; HRMS (FAB): *m*/*z*: calcd for $C_{18}H_{20}NO_7$: 362.1240; found: 362.1267 $[M+H^+]$; elemental analysis calcd (%) for $C_{18}H_{19}NO_7$ (361.3): C 59.83, H 5.30, N 3.88; found: C 59.73, H 5.28, N 3.85.

**(±)-[1-$^2H_1$]-Dimethyl (1a*R*,3*R*,3a*R*,6a*R*)-3-phenyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate ([1-$^2H_1$]-3b)**: According to GP, a mixture of 2-nitrobenzaldehyde (755 mg, 5.0 mmol), enyne [3′-$^2H_1$]-**1a** (84 % [$^2H_1$], 211 mg, 1.0 mmol), and $AgSbF_6$ (17 mg, 50 μmol) in anhydrous $CH_2Cl_2$ (5 mL) was cooled to −45 °C and treated with $[AuCl(PPh_3)]$ (24.7 mg, 50 μmol). The mixture turned orange and was kept at −45 °C for 6 h. The cooling device was switched off, which initiated slow warming to RT. After an overall reaction time of 18 h, TLC control indicated complete consumption of the substrate. Workup according to GP and flash column chromatography on silica (40 g, petroleum ether/ethyl acetate 10:1) yielded [1-$^2H_1$]-**3b** (84 % [$^2H_1$], 185 mg, 51 %) as a slightly yellow crystalline solid. The product was a 55:45 mixture of the epimers with respect to C-1 according to $^1H$ NMR spectroscopy. $R_f=0.36$ (petroleum ether/ethyl acetate 3:1); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C; the epimers are designated by A and B, A/B = 55:45): $\delta=0.79$ (d, $J=5.5$ Hz, 1H; epimer A, 1-H), 0.98 (d, $J=2.1$ Hz, 1H; epimer B, 1-H), 2.27 (d, $J=13.6$ Hz, 1H, A and B; 6-$H_a$), 2.40 (d, $J=13.6$ Hz, 1H, A and B; 6-$H_b$), 2.47 (ddd, $J=8.2$, 5.9, 5.3 Hz, 1H; A and B, 3a-H), 2.67 (dd, $J=14.0$, 8.4 Hz, 1H; A and B, 4-$H_a$), 2.75 (dd, $J=14.1$, 6.2 Hz, 1H; A and B, 4-$H_b$), 3.70 (s, 3H; A and B, $OCH_3$), 3.78 (s, 3H; A and B, $OCH_3$), 3.83–3.87 (m, 1H; A and B, 1a-H), 5.80 (d, $J=4.9$ Hz, 1H; A and B, 3-H), 7.33–7.39 (m, 1H; A and B, Ar), 7.56 (td, $J=7.6$, 1.2 Hz, 1H; A and B, Ar), 7.69 (d, $J=7.7$ Hz, 1H; A and B, Ar), 7.91 ppm (dd, $J=8.2$, 1.2 Hz, 1H; A and B, Ar); $^{13}C$ NMR (125 MHz, $CDCl_3$, 25 °C, DEPT, HMBC): $\delta=18.81$ (dt, $J(^{13}C\text{-}D)=24.5$ Hz; A or B, C-1), 18.90 (dt, $J(^{13}C\text{-}D)=24.0$ Hz; A or B, C-1), [19.18 (t; C-1, nondeuterated)], 35.23, 35.25 (s; A and B, C-6a), 38.04 (t; A and B, C-6), 40.16 (t; A and B, C-4), 52.91 (q; A and B, $OCH_3$), 54.68, 54.69 (d; A and B, C-3a), 61.91 (s; A and B, *C*-$(CO_2Me)_2$), 66.15, 66.17 (d; A and B, C-1a), 88.60, 88.63 (d; A and B, C-3), 124.69 (d; A and B, Ar), 127.96, 127.98 (d; A and B, Ar), 128.12 (d; A and B, Ar), 133.38 (d; A and B, Ar), 139.30 (s; A and B, Ar), 147.24 (s; A and B, Ar), 172.00 (s; A and B, C=O), 172.06 ppm (s; A and B, C=O); HRMS (FAB): *m*/*z*: calcd for $C_{18}H_{19}DNO_7$: 363.1303; found: 363.1328 $[M+H^+]$.

**(±)-[1a-$^2H_1$]-Dimethyl (1a*R*,3*R*,3a*R*,6a*R*)-phenyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate ([1a-$^2H_1$]-3b)**: According to GP, a mixture of 2-nitrobenzaldehyde (770 mg, 5.0 mmol), enyne [3″-$^2H_1$]-**1a** (82 % [$^2H_1$], 211 mg, 1.0 mmol), and $AgSbF_6$ (17 mg, 50 μmol) in anhydrous $CH_2Cl_2$ (5 mL) was cooled to −45 °C and treated with $[AuCl(PPh_3)]$ (25 mg, 50 μmol). The mixture turned orange and was kept at −45 °C for 6 h. The cooling device was switched off, which initiated slow warming to RT. After an overall reaction time of 18 h, workup was carried out according to GP. Flash column chromatography on silica (80 g, petroleum ether/ethyl acetate 10:1) furnished [1a-$^2H_1$]-**3b** (80 % [$^2H_1$], 200 mg, 55 %) as a slightly yellow crystalline solid. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=0.82$ (d, $J=6.9$ Hz, 1H; 1-$H_a$), 1.00 (d, $J=6.9$ Hz, 1H; 1-$H_b$), 2.30 (d, $J=13.6$ Hz, 1H; 6-$H_a$), 2.43 (d, $J=13.6$ Hz, 1H; 6-$H_b$), 2.50 (ddd, $J=8.1$, 6.2, 5.3 Hz, 1H; 3a-H), 2.70 (dd, $J=14.2$, 8.4 Hz, 1H; 4-$H_a$), 2.77 (dd, $J=14.2$, 6.6 Hz, 1H; 4-$H_b$), 3.72 (s, 3H; $OCH_3$), 3.80 (s, 3H; $OCH_3$), 5.81 (d, $J=4.8$ Hz, 1H; 3-H), 7.35–7.41 (m, 1H; Ar), 7.58 (td, $J=7.6$, 1.0 Hz, 1H; Ar), 7.72 (d, $J=7.8$ Hz, 1H; Ar), 7.94 ppm (dd, $J=8.1$, 1.1 Hz, 1H; Ar); $^{13}C$ NMR (125 MHz, $CDCl_3$, 25 °C, DEPT, HMBC): $\delta=19.08$ (t; C-1), 35.29 (s; C-6a), 38.11 (t; C-6), 40.29 (t; C-4), 53.00 (q; $OCH_3$), 54.80 (d; C-3a), 61.00 (s; *C*$(CO_2Me)_2$), 65.96 (t, $J(^{13}C\text{-}D)=29.8$ Hz; C-1a), [66.32 (d; C-1a, non-deuterated)], 88.67 (d; C-3), 124.80 (d; Ar), 128.05 (d; Ar), 128.17 (d; Ar), 133.45 (d; Ar), 139.46 (s; Ar), 147.31 (s; Ar), 172.10 (s; C=O), 172.16 ppm (s; C=O); HRMS (FAB): *m*/*z*: calcd for $C_{18}H_{19}DNO_7$: 363.1303; found: 363.1327 $[M+H^+]$.

**(±)-Dimethyl (1a*R*,3*S*,3a*R*,6a*R*)-3-isopropyltetrahydro-3*H*-cyclopenta[*c*]-cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (3c)**: According to GP, a solution of enyne **1a** (210 mg, 1.0 mmol), 2-methylpropanal (**2c**) (1.44 g, 20 mmol), and $AgSbF_6$ (17 mg, 50 μmol) in anhydrous $CH_2Cl_2$ (5 mL) was cooled to −45 °C and treated with $[AuCl(PPh_3)]$ (24.7 mg, 50 μmol). After 6 h, the cooling device was switched off, which initiated slow warming to RT. GC monitoring indicated complete conversion after an overall reaction time of 14.5 h. Workup according to GP and flash column chromatography on silica (20 g, petroleum ether/ethyl acetate 10:1) afforded **3c** (189 mg, 67 %) as a colorless oil. $R_f=0.50$ (petroleum ether/ethyl acetate 3:1); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=0.78$–0.89 (m, 2H; 1-H), 0.80 (d, $J=6.8$ Hz, 3H; $CH_3$), 0.86 (d, $J=6.4$ Hz, 3H; $CH_3$), 1.45–1.62 (m, 1H; $CH(CH_3)_2$), 2.24 (dd, $J=8.8$, 3.4 Hz, 1H; 3a-H), 2.27–2.30 (m, 2H; 6-H), 2.36 (dd, $J=13.8$, 3.1 Hz, 1H; 4-H), 2.48 (dd, $J=13.8$, 9.1 Hz, 1H; 4-H), 3.66 (dd, $J=4.4$, 2.4 Hz, 1H; 1a-H), 3.72 (s, 3H; $OCH_3$), 3.77 (s, 3H; $OCH_3$), 3.80 ppm, (dd, $J=7.8$, 7.8 Hz, 1H; 3-H); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, DEPT, HMBC): $\delta=18.49$ (q; $CH_3$), 19.36 (q; $CH_3$), 23.27 (t; C-1), 33.47 (d; $CH(CH_3)_2$), 36.47 (s; C-6a), 38.40 (t; C-6), 38.97 (t; C-4), 49.69 (d; C-3a), 52.91 (q; $OCH_3$), 52.97 (q; $OCH_3$), 61.81 (s; C-5), 64.90 (d; C-1a), 100.94 (d; C-3), 172.06 (s; C=O), 172.15 ppm (s; C=O); IR (film): $\tilde{\nu}=795$, 815, 840, 879, 939, 978, 1014, 1043, 1074, 1111, 1205, 1223, 1270, 1324, 1366, 1388, 1436, 1736 (C=O), 2876, 2957 $cm^{-1}$; HRMS (EI): *m*/*z*: calcd for $C_{15}H_{22}O_5$: 282.1467; found: 282.1464 $[M^+]$; elemental analysis calcd (%) for $C_{15}H_{22}O_5$ (282.3): C 63.81, H 7.85; found: C 63.65, H 7.83.

**(±)-Dimethyl (1a*R*,3a*R*,6a*R*)-3,3-dimethyltetrahydro-3*H*-cyclopenta[*c*]-cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (3d)**: According to GP, a solution of enyne **1a** (210 mg, 1.0 mmol), acetone (**2d**) (1.16 g, 20 mmol), and $AgSbF_6$ (17 mg, 50 μmol) in anhydrous $CH_2Cl_2$ (5 mL) was cooled to −5 °C and treated with $[AuCl(PPh_3)]$ (24.7 mg, 50 μmol). The solution was kept at −5 °C for 8.5 h until GC monitoring indicated complete conversion. Workup according to GP and flash column chromatography on silica (20 g, petroleum ether/ethyl acetate 10:1) afforded **3d** (148 mg, 55 %) as a colorless oil. $R_f=0.41$ (petroleum ether/ethyl acetate 3:1); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=0.78$ (dd, $J=6.0$, 5.7 Hz, 1H; 1-H), 0.96 (dd, $J=6.4$, 1.8 Hz, 1H; 1-H), 1.15 (s, 3H; $CH_3$), 1.18 (s, 3H; $CH_3$), 2.19 (dd, $J=11.6$, 7.6 Hz, 1H; 4-H), 2.29–2.48 (m, 4H; 3a-H, 4-H, 6-H), 3.59 (dd, $J=5.3$, 1.8 Hz, 1H; 1a-H), 3.73 (s, 3H; $OCH_3$), 3.75 ppm (s, 3H; $OCH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, DEPT, HMBC): $\delta=23.26$ (t; C-1), 25.63 (q; $CH_3$), 31.28 (q; $CH_3$), 36.24 (s; C-6a), 36.38 (t; C-4), 38.54 (t; C-6), 52.85 (q; $OCH_3$), 52.99 (q; $OCH_3$), 55.76 (d; C-3a), 62.64 (s; C-5), 62.98 (d; C-1a), 89.18 (s; C-3), 171.90 (s; C=O), 172.45 ppm (s, C=O); IR (film): $\tilde{\nu}=889$, 1077, 1124, 1175, 1202, 1228, 1252, 1277, 1367, 1384, 1436, 1736 (C=O), 2972 $cm^{-1}$; HRMS (EI): *m*/*z*: calcd for $C_{14}H_{20}O_5$: 268.1311; found: 268.1290 $[M^+]$; elemental analysis calcd (%) for $C_{14}H_{20}O_5$ (268.3): C 62.67, H 7.51; found: C 62.54, H 7.42.

**(±)-Dimethyl (1a′*R*,3a′*R*,6a′*R*)-tetrahydrospiro(cyclohexane-1,3′-cyclopenta[*c*]cyclopropa[*b*]furan)-5′,5′(6′*H*)-dicarboxylate (3e)**: According to GP, a solution of enyne **1a** (210 mg, 1.0 mmol), cyclohexanone (**2e**) (1.96 g, 20 mmol), and $AgSbF_6$ (17 mg, 50 μmol) in anhydrous $CH_2Cl_2$ (5 mL) was cooled to 5 °C and treated with $[AuCl(PPh_3)]$ (24.7 mg, 50 µmol). After 16 h, the cooling device was switched off, which initiated slow warming to RT. GC monitoring indicated complete conversion after an overall reaction time of 17 h. Workup according to GP and flash column chromatography on silica (20 g, petroleum ether/ethyl acetate 10:1) afforded **3e** (139 mg, 45 %) as a slightly yellow oil. $R_f = 0.64$ (petroleum ether/ethyl acetate 3:1); $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 0.74$ (dd, $J = 5.9$, 5.8 Hz, 1 H; 1′-H), 0.92 (dd, $J = 6.4$, 1.7 Hz, 1 H; 1′-H), 1.15–1.68 (m, 10 H; 5 CH$_2$), 2.24–2.47 (m, 5 H; 3a′-H, 4′-H, 6′-H), 3.58 (dd, $J = 5.3$, 1.7 Hz, 1 H; 1a′-H), 3.73 (s, 3 H; OCH$_3$), 3.76 ppm (s, 3 H; OCH$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C, DEPT, HMBC): $\delta = 22.48$ (t; C-1′), 23.33 (t; CH$_2$), 23.36 (t; CH$_2$), 25.50 (t; CH$_2$), 34.42 (t; CH$_2$), 35.48 (s; C-6a′), 35.67, 38.42 (2 t; C-4′, C-6′), 41.05 (t; CH$_2$), 52.85 (q; OCH$_3$), 52.98 (q; OCH$_3$), 54.57 (d; C-3a′), 62.28 (s; C-5′), 62.90 (d; C-1a′), 90.33 (s; C-3′), 171.99 (s; C=O), 172.54 ppm (s; C=O); IR (film): $\tilde{\nu} = 703$, 819, 882, 921, 992, 1071, 1125, 1169, 1201, 1271, 1373, 1437, 1735 (C=O), 2858, 2934 cm$^{-1}$; HRMS (EI): $m/z$: calcd for $C_{17}H_{24}O_5$: 308.1624; found: 308.1628 [$M^+$]; elemental analysis calcd (%) for $C_{17}H_{24}O_5$ (308.4): C 66.21, H 7.84; found: C 66.37, H 7.81.

**(±)-Dimethyl (1a*R*,3a*R*,6a*R*)-3-but-3-en-1-yl-3-(phenylethynyl)tetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (3f)**: According to GP, a mixture of AgSbF$_6$ (17 mg, 50 µmol), enyne **1a** (210 mg, 1.0 mmol), and enyne **2f** (921 mg, 5.0 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was cooled to −45 °C and treated with [AuCl(PPh$_3$)] (25 mg, 50 µmol). The mixture turned orange and was kept at −45 °C for 2 h. The cooling device was switched off, which initiated slow warming to −5 °C. After an overall reaction time of 6 h, the solution had turned brown and GC monitoring indicated complete conversion. Workup according to GP and flash column chromatography on silica (25 g, petroleum ether/ethyl acetate 15:1) afforded **3f** (271 mg, 69 %) as a pale yellow oil. $R_f = 0.12$ (petroleum ether/ethyl acetate 10:1); $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 0.95$ (dd, $J = 5.8$, 5.6 Hz, 1 H; 1-H$_a$), 1.06 (dd, $J = 6.2$, 1.7 Hz, 1 H; 1-H$_b$), 1.70 (ddd, $J = 13.1$, 11.6, 5.3 Hz, 1 H; C$H_a$H$_b$CH$_2$CH=CH$_2$), 1.83 (ddd, $J = 13.1$, 11.2, 5.4 Hz, 1 H; CH$_a$$H_b$CH$_2$CH=CH$_2$), 2.12–2.35 (m, 2 H; CH$_a$H$_b$C$H_2$CH=CH$_2$), 2.20 (d, $J = 13.2$ Hz, 1 H; 6-H$_a$), 2.55 (dd, $J = 8.1$, 8.1 Hz, 1 H; 3a-H), 2.63 (d, $J = 13.2$ Hz, 1 H; 6-H$_b$), 2.67–2.75 (m, 2 H; 4-H), 3.64 (s, 3 H; OCH$_3$), 3.77 (s, 3 H; OCH$_3$), 3.88 (dd, $J = 5.0$, 1.8 Hz, 1 H; 1a-H), 4.95 (ddd, $J = 10.2$, 2.5, 0.9 Hz, 1 H; =CH$_2$), 5.02 (ddd, $J = 17.1$, 3.4, 1.7 Hz, 1 H; =CH$_2$), 5.82 (dddd, $J = 17.0$, 10.3, 6.8, 5.2 Hz, 1 H; C$H$=CH$_2$), 7.29–7.34 (m, 3 H; Ph), 7.45–7.50 ppm (m, 2 H; Ph); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C, DEPT, HMBC): $\delta = 22.47$ (t; C-1), 29.51 (t; CH$_2$$C$H$_2$CH=CH$_2$), 37.40 (t; C-4), 37.51 (s; C-6a), 38.42 (t; C-6), 41.60 (t; $C$H$_2$CH$_2$CH=CH$_2$), 52.85 (q; OCH$_3$), 53.01 (q; OCH$_3$), 57.96 (d; C-3a), 63.56 (d; C-1a), 64.01 (s; C-5), 88.61, 89.37 (2 s; C≡C), 93.26 (s; C-3), 114.79 (t; CH=$C$H$_2$), 122.73 (s; Ph), 128.38 (d; Ph), 128.56 (d; Ph), 131.90, (d; Ph), 138.00 (d; $C$H=CH$_2$), 171.48 (s; C=O), 172.49 ppm (s; C=O); IR (film): $\tilde{\nu} = 693$, 733, 759, 913, 1008, 1072, 1227, 1273, 1436, 1491, 1641, 1735, 2225, 2251, 2341, 2358, 2846, 2952, 2988, 3067 cm$^{-1}$; HRMS (FAB): $m/z$: calcd for $C_{24}H_{27}O_5$: 395.1859; found 395.1848 [$M$+$H$]$^+$; elemental analysis calcd (%) for $C_{24}H_{26}O_5$ (394.5): C 73.08, H 6.64; found: C 72.91, H 6.56.

**(±)-(1a*R*,3*R*,3a*R*,6a*R*)-5,5-Bis[(benzyloxy)methyl]-3-(2-nitrophenyl)hexahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan (6b)**: According to GP, a solution of enyne **1b** (335 mg, 1.0 mmol), 2-nitrobenzaldehyde (**2b**) (756 mg, 5.0 mmol), and AgSbF$_6$ (17 mg, 50 µmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was cooled to −40 °C and treated with [AuCl(PPh$_3$)] (24.7 mg, 50 µmol). After stirring for 3 h at this temperature, GC monitoring indicated complete conversion, and the cooling device was switched off, which initiated slow warming to RT. The reaction mixture was then filtered through Celite and concentrated in vacuo. The residual oil was subjected to flash column chromatography on silica (100 g, petroleum ether/ethyl acetate 3:1). Fractions not containing 2-nitrobenzaldehyde were collected and subjected to preparative HPLC on silica gel (column: Latek, 5 µ, 21 × 250 mm; petroleum ether/ethyl acetate 10:1; 22 mL min$^{-1}$, 50 bar) to yield **6b** (52 mg, 11 %) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 0.65$ (dd, $J = 6.1$, 5.8 Hz, 1 H; 1-H), 0.85 (dd, $J = 6.7$, 1.8 Hz, 1 H; 1-H), 1.67 (d, $J = 13.6$ Hz, 1 H; 6-H), 1.79 (d, $J = 13.4$ Hz, 1 H; 6-H), 1.92 (dd, $J = 13.6$, 7.7 Hz, 1 H; 4-H), 2.29 (dd, $J = 13.6$, 8.7 Hz, 1 H; 4-H), 2.43 (td, $J = 8.1$, 4.1 Hz, 1 H; 3a-H), 3.44 (s, 2 H; BnOC$H_2$), 3.57 (s, 2 H; BnOC$H_2$), 3.80 (dd, $J = 5.3$, 1.7 Hz, 1 H; 1a-H), 4.51–4.63 (m, 4 H; PhC$H_2$), 5.80 (d, $J = 4.0$ Hz, 1 H; 3-H), 7.20–7.43 (m, 11 H; Ph, Ar), 7.58 (td, $J = 7.6$, 0.9 Hz, 1 H; Ar), 7.76 (d, $J = 7.9$ Hz, 1 H; Ar), 7.97 ppm (dd, $J = 8.1$, 1.1 Hz, 1 H; Ar); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C, DEPT, H,C-COSY): $\delta = 18.31$ (t; C-1), 35.40 (s; C-6a), 36.71 (t; C-6), 40.05 (t; C-4), 49.93 (s; C-5), 55.02 (d; C-3a), 66.74 (d; C-1a), 73.33 (t; Ph$C$H$_2$), 73.33 (t; Ph$C$H$_2$), 74.03 (t; BnO$C$H$_2$), 74.30 (t; BnO$C$H$_2$), 88.48 (d; C-3), 124.81, 127.45, 127.52, 127.53, 127.62, 127.83, 127.95, 128.38, 128.41, 133.26 (10 d; Ar, Ph), 138.89, 138.90 (2 s; Ph), 140.48, 147.16 ppm (2 s; Ar); HRMS (FAB): $m/z$: calcd for $C_{30}H_{32}NO_5$: 486.2280; found: 486.2336 [$M$+H$^+$]; elemental analysis calcd (%) for $C_{30}H_{31}NO_5$ (485.6): C 74.21, H 6.43, N 2.88; found: C 74.03, H 6.58, N 2.74.

**(±)-(1a*R*,3*R*,3a*R*,6a*R*)-2′,2′-Di-*tert*-butyl-3-(2-nitrophenyl)tetrahydro-3*H*-spiro(cyclopenta[*c*]cyclopropa[*b*]furan-5,5′-[1,3,2]dioxasilinane) (6c)**: According to GP, a solution of enyne **1c** (295 mg, 1.0 mmol), 2-nitrobenzaldehyde (**2b**) (756 mg, 5.0 mmol), and AgSbF$_6$ (17 mg, 50 µmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was cooled to −40 °C and treated with [AuCl(PPh$_3$)] (24.7 mg, 50 µmol). After stirring for 1 h at this temperature, TLC monitoring showed no further conversion. Workup and flash column chromatography on silica (50 g, petroleum ether/ethyl acetate 10:1) afforded **6c** (178 mg; 40 %, corr. 67 %) as adhesive needles. $R_f = 0.24$ (petroleum ether/ethyl acetate 10:1); m.p. 100 °C; $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 0.69$ (dd, $J = 5.9$, 5.9 Hz, 1 H; 1-H), 0.84–0.90 (m, 1 H; 1-H), 1.03 (s, 9 H; SiC(C$H$)$_3$), 1.10 (s, 9 H; SiC(C$H$)$_3$), 1.78 (dd, $J = 14.0$, 8.6 Hz, 1 H; 4-H), 1.80 (d, $J = 13.6$ Hz, 1 H; 6-H), 1.92 (d, $J = 13.8$ Hz, 1 H; 6-H), 2.12 (dd, $J = 13.9$, 8.7 Hz, 1 H; 4-H), 2.41 (td, $J = 8.3$, 3.7 Hz, 1 H; 3a-H), 3.82–4.16 (m, 5 H; SiOC$H_2$, 1a-H), 5.80 (d, $J = 3.6$ Hz, 1 H; 3-H), 7.39 (t, $J = 7.4$ Hz, 1 H; Ar), 7.60 (t, $J = 7.6$ Hz, 1 H; Ar), 7.77 (d, $J = 7.9$ Hz, 1 H; Ar), 8.00 ppm (d, $J = 7.9$ Hz, 1 H; Ar); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C, DEPT, H,C-COSY): $\delta = 17.65$ (t; C-1), 21.49 (s; Si$C$(CH$_3$)$_3$), 22.82 (s; Si$C$(CH$_3$)$_3$), 27.87 (q; SiC($C$H$_3$)$_3$), 28.34 (q; SiC($C$H$_3$)$_3$), 35.12 (s; C-6a), 38.71 (t; C-6), 41.18 (t; C-4), 48.67 (s; C-5), 54.23 (d; C-3a), 66.80 (d; C-1a), 73.50 (t; SiO$C$H$_2$), 73.66 (t; SiO$C$H$_2$), 88.30 (d; C-3), 125.08, 127.95, 128.03, 133.55 (4 d; Ar), 140.59, 146.91 ppm (s; Ar); HRMS (FAB): $m/z$: calcd for $C_{24}H_{35}NO_5Si$: 446.2363; found: 446.2325 [$M$+H$^+$]; elemental analysis calcd (%) for $C_{24}H_{35}NO_5Si$ (445.6): C 64.69, H 7.92, N 3.14; found: C 64.46, H 7.95, N 3.03.

**(±)-(1a*R*,3*R*,3a*R*,6a*R*)-3-(2-Nitrophenyl)tetrahydro-3*H*-spiro(cyclopenta[*c*]cyclopropa[*b*]furan-5,5′-[1,3]dioxane) (6d)**: According to GP, a solution of enyne **1d** (166 mg, 1.0 mmol), 2-nitrobenzaldehyde (**2b**) (756 mg, 5.0 mmol), and AgSbF$_6$ (17 mg, 50 µmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was cooled to −40 °C and treated with [AuCl(PPh$_3$)] (24.7 mg, 50 µmol). Stirring was continued at this temperature for 4 h until TLC monitoring showed complete conversion. Workup according to GP and flash column chromatography on silica (120 g, petroleum ether/ethyl acetate 3:1) afforded **6d** (82 mg, 26 %) as a white solid. Crystallization from methanol at 0 °C gave colorless polyhedral crystals, suitable for X-ray crystal structure analysis; for data, see Table 4. $R_f = 0.14$ (petroleum ether/ethyl acetate 5:1); m.p. 147 °C; $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 0.74$ (dd, $J = 6.7$, 5.7 Hz, 1 H; 1-H), 0.91 (dd, $J = 6.8$, 2.1 Hz, 1 H; 1-H), 1.81 (dd, $J = 14.0$, 7.4 Hz, 1 H; 6-H), 1.83 (d, $J = 13.8$ Hz, 1 H; 4-H), 1.89 (d, $J = 13.8$ Hz, 1 H; 4-H), 2.07 (dd, $J = 14.0$, 8.8 Hz, 1 H; 6-H), 2.41 (ddd, $J = 8.3$, 7.6, 4.4 Hz, 1 H; 3a-H), 3.59–3.76 (m, 2 H; OCH$_2$OC$H_2$), 3.88–3.97 (m, 3 H; OCH$_2$OC$H_2$, 1a-H), 4.76 (d, $J = 6.0$ Hz, 1 H; OC$H_2$O), 4.91 (d, $J = 6.0$ Hz, 1 H; OC$H_2$O), 5.79 (d, $J = 4.1$ Hz, 1 H; 3-H), 7.39 (td, $J = 7.7$, 1.1 Hz, 1 H; Ar), 7.60 (td, $J = 7.6$, 1.1 Hz, 1 H; Ar), 7.76 (d, $J = 7.9$ Hz, 1 H; Ar), 7.98 ppm (dd, $J = 8.2$, 1.1 Hz, 1 H; Ar); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C, DEPT, H,C-COSY): $\delta = 18.45$ (t; C-1), 35.02 (s; C-6a), 38.39 (t; C-6), 40.11 (t; C-4), 44.67 (s; C-5), 54.54 (d; C-3a), 66.67 (d; C-1a), 75.66 (t; OCH$_2$O$C$H$_2$), 75.75 (t; OCH$_2$O$C$H$_2$), 88.72 (d; C-3), 94.19 (t; O$C$H$_2$O), 124.94, 127.95, 128.07, 133.53 (4 d; Ar), 140.12, 147.03 ppm (2 s; Ar); HRMS (FAB): $m/z$: calcd for $C_{17}H_{20}NO_5$: 318.1341; found: 318.1392 [$M$+H$^+$]; elemental analysis calcd (%) for $C_{17}H_{19}NO_5$ (317.3): C 64.34, H 6.03, N 4.41; found: C 64.33, H 6.05, N 4.30.

**(±)-(1a*R*,3*R*,3a*R*,6a*R*)-3-(2-Nitrophenyl)tetrahydro-3*H*-spiro(cyclopenta[*c*]cyclopropa[*b*]furan-5,5′-[1,3]dioxan)-2′-one (6e)**: According to GP, a solution of enyne **1e** (180 mg, 1.0 mmol), 2-nitrobenzaldehyde (**2b**) (756 mg, 5.0 mmol), and AgSbF$_6$ (17 mg, 50 µmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was cooled to −40 °C and treated with [AuCl(PPh$_3$)] (24.7 mg, 50 μmol). After stirring for 7 h at this temperature, TLC monitoring showed complete conversion. The reaction mixture was filtered through Celite and the filtrate concentrated in vacuo. The residual oil was subjected to flash column chromatography on silica (100 g, petroleum ether/ethyl acetate 3:1). Fractions not containing 2-nitrobenzaldehyde were collected and subjected to preparative HPLC on silica gel (columns: Latek, 5 μ, 21×250 mm and Prontosil 120-10-SI, 10 μ, 20×250 mm; petroleum ether/ethyl acetate 10:1, 22 mL min$^{-1}$, 50 bar) to yield **6e** (173 mg, 52%) as colorless needles, suitable for X-ray crystal structure analysis; for data, see Table 4. $R_f = 0.36$ (petroleum ether/ethyl acetate 1:1); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.81$ (dd, $J = 7.0$, 5.6 Hz, 1H; 1-H), 1.00 (dd, $J = 7.0$, 2.0 Hz, 1H; 1-H), 1.85 (d, $J = 13.7$ Hz, 1H; 6-H), 1.99 (d, $J = 13.7$ Hz, 1H; 6-H), 2.03 (dd, $J = 14.1$, 7.1 Hz, 1H; 4-H), 2.25 (dd, $J = 14.1$, 8.8 Hz, 1H; 4-H), 2.51 (ddd, $J = 8.7$, 7.3, 4.2 Hz, 1H; 3a-H), 4.00 (dd, $J = 5.5$, 2.0 Hz, 1H; 1a-H), 4.15–4.47 (m, 4H, O=C-O$CH_2$), 5.82 (d, $J = 4.1$ Hz, 1H; 3-H), 7.42 (td, $J = 7.7$, 0.9 Hz, 1H; Ar), 7.63 (td, $J = 7.6$, 1.1 Hz, 1H; Ar), 7.73–7.80 (m, 1H; Ar), 8.02 ppm (dd, $J = 8.1$, 1.3 Hz, 1H; Ar); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, DEPT, H,C-COSY): $\delta = 18.15$ (t; C-1), 34.60 (s; C-6a), 36.94 (t; C-6), 38.89 (t; C-4), 41.44 (s; C-5), 54.15 (d; C-3a), 66.50 (d; C-1a), 75.93 (t; O=C-O$CH_2$), 76.12 (t; O=C-O$CH_2$), 88.65 (d; C-3), 125.19 (d; Ar), 127.90 (d; Ar), 128.42 (d; Ar), 133.85 (d; Ar), 146.83 (s; Ar), 148.10 (s; Ar), 148.32 ppm (s; C=O); HRMS (FAB): $m/z$: calcd for $C_{17}H_{18}NO_6$: 332.1134; found: 332.1102 $[M+H^+]$.

**(±)-Dimethyl (1a*R*,3*R*,3a*R*,6a*R*)-3a-methyl-3-(2-nitrophenyl)tetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (6f)**: According to GP, a mixture of 2-nitrobenzaldehyde (756 mg, 5.0 mmol), enyne **1f** (224 mg, 1.0 mmol), and $AgSbF_6$ (17 mg, 50 μmol) in anhydrous $CH_2Cl_2$ (5 mL) was cooled to −45 °C and treated with $[AuCl(PPh_3)]$ (24.7 mg, 50 μmol). The mixture turned yellow and was kept at −45 °C for 4 h until TLC control ($R_f$(**1f**) = 0.43, petroleum ether/ethyl acetate 3:1) indicated complete consumption of the substrate. Workup according to GP and flash column chromatography on silica (40 g, petroleum ether/ethyl acetate 10:1 to 5:1) yielded **6f** (342 mg, 91%) as a colorless oil. This was dissolved in *n*-hexane/ethyl acetate 6:1 and the solution kept at 5 °C to give colorless plates. The relative configuration of 2-oxabicyclo[3.1.0]hexane **6f** was verified by X-ray crystal structure analysis; for data, see Table 4. $R_f = 0.22$ (petroleum ether/ethyl acetate 3:1); m.p. 81–83 °C; $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.67$ (s, 3H; $CH_3$), 0.81 (dd, $J = 6.8$, 5.0 Hz, 1H; 1-$H_a$), 1.07 (dd, $J = 6.8$, 1.8 Hz, 1H; 1-$H_b$), 2.20 (dd, $J = 13.5$, 1.2 Hz, 1H; 4-$H_a$), 2.29 (d, $J = 14.6$ Hz, 1H; 6-$H_a$), 2.51 (d, $J = 13.5$ Hz, 1H; 6-$H_b$), 3.24 (dd, $J = 14.6$, 1.2 Hz, 1H; 4-$H_b$), 3.74, 3.84 (2s, 6H; $OCH_3$), 3.82–3.87 (m, 1H; 1a-H), 5.96 (s, 1H; 3-H), 7.39 (td, $J = 7.7$, 1.3 Hz, 1H; Ar), 7.57 (td, $J = 7.6$, 1.0 Hz, 1H; Ar), 7.69 (dd, $J = 8.1$, 1.3 Hz, 1H; Ar), 7.88 ppm (dd, $J = 8.1$, 1.2 Hz, 1H; Ar); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, DEPT, H,C-COSY): $\delta = 18.26$ (t; C-1), 21.99 (q; $CH_3$), 38.00 (t; C-6), 41.07 (s; C-6a), 48.49 (t; C-4), 53.03, 53.08 (2 q; $OCH_3$), 53.80 (s; C-3a), 60.00 (s; C-5), 65.03 (d; C-1a), 93.42 (d; C-3), 124.38, 128.27, 128.94, 132.99 (4d; Ar), 136.27, 147.95 (2s; Ar), 172.05, 172.46 ppm (2s; $CO_2CH_3$); IR (KBr): $\tilde{\nu} = 726$, 856, 970, 1014, 1067, 1083, 1113, 1142, 1175, 1199, 1235, 1261, 1278, 1357, 1434, 1529, 1734 (C=O), 2958, 3447 cm$^{-1}$); HRMS (FAB): $m/z$: calcd for $C_{19}H_{22}NO_7$: 376.1396; found: 376.1360 $[M+H^+]$; elemental analysis calcd (%) for $C_{19}H_{21}NO_7$ (375.4): C 60.79, H 5.64, N 3.73; found: C 60.82, H 5.64, N 3.68.

**(±)-(1a*R*,3*R*,3a*R*,6a*R*)-5,5-Bis[(benzyloxy)methyl]-3a-methyl-3-(2-nitrophenyl)hexahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan (6g)**: According to GP, a mixture of 2-nitrobenzaldehyde (756 mg, 5.0 mmol), enyne **1g** (349 mg, 1.0 mmol), and $AgSbF_6$ (17 mg, 50 μmol) in anhydrous $CH_2Cl_2$ (5 mL) was cooled to −45 °C and treated with $[AuCl(PPh_3)]$ (24.7 mg, 50 μmol). The mixture turned yellow and was kept at −45 °C for 6 h. The cooling device was switched off, which initiated slow warming to RT. After an overall reaction time of 16 h, TLC control ($R_f$(**1g**) = 0.62, petroleum ether/ethyl acetate 3:1) indicated complete consumption of the substrate. Workup according to GP and flash column chromatography on silica (30 g, petroleum ether/ethyl acetate 15:1) yielded 2-oxabicyclo[3.1.0]hexane **6g** (135 mg, 27%) as a slightly yellow oil. $R_f = 0.46$ (petroleum ether/ethyl acetate 3:1); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.60$ (dd, $J = 6.6$, 5.1 Hz, 1H; 1-$H_a$), 0.64 (s, 3H; $CH_3$), 0.92 (dd, $J = 6.6$, 1.7 Hz, 1H; 1-$H_b$), 1.56 (d, $J = 13.4$ Hz, 1H; 6-$H_a$), 1.93 (d, $J = 13.6$ Hz, 1H; 6-$H_b$), 1.94 (d, $J = 14.7$ Hz, 1H; 4-$H_a$), 2.31 (d, $J = 14.7$ Hz, 1H; 4-$H_b$), 3.46 (s, 2H; $OCH_2$), 3.60 (d, $J = 8.7$ Hz, 1H; $OCH_2$), 3.68 (d, $J = 8.9$ Hz, 1H; $OCH_2$), 3.71–3.74 (m, 1H; 1a-H), 4.52 (s, 2H; $OCH_2$), 4.53 (d, $J = 12.1$ Hz, 1H; $OCH_2$), 4.61 (d, $J = 12.1$ Hz, 1H; $OCH_2$), 5.91 (s, 1H; 3-H), 7.24–7.41 (m, 11H; Ar), 7.57 (td, $J = 7.6$, 1.2 Hz, 1H; Ar), 7.70 (dd, $J = 8.0$, 1.2 Hz, 1H; Ar), 7.92 ppm (d, $J = 8.1$, 1.3 Hz, 1H; Ar); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, DEPT, H,C-COSY): $\delta = 16.79$ (t; C-1), 22.31 (q; $CH_3$), 36.14 (t; C-6), 41.13 (s; C-6a), 48.64 (s; C-3a), 49.02 (t; C-4), 54.34 (s; C-5), 66.05 (d; C-1a), 73.33, 73.36, 73.70, 75.05 (4t; $PhCH_2OCH_2$), 94.53 (d; C-3), 124.46, 127.46, 127.50, 127.62, 127.81, 127.99, 128.39, 128.44, 128.69, 133.07 (10d; Ar), 137.69, 138.86, 139.00, 147.88 ppm (4s; Ar); IR (film): $\tilde{\nu} = 699$, 731, 857, 1028, 1111, 1204, 1357, 1452, 1527, 1608, 2855, 2931, 3030, 3063 cm$^{-1}$; HRMS (FAB): $m/z$: calcd for $C_{31}H_{34}NO_5$: 500.2437; found: 500.2434 $[M+H^+]$; elemental analysis calcd (%) for $C_{31}H_{33}NO_5$ (499.6): C 74.63, H 6.66, N 2.80; found: C 74.26, H 6.88, N 2.47.

**(±)-(1a*R*,3*R*,3a*R*,6a*R*)-2′,2′-Di-*tert*-butyl-3a-methyl-3-(2-nitrophenyl)tetrahydro-3*H*-spiro(cyclopenta[*c*]cyclopropa[*b*]furan-5,5′-[1,3,2]dioxasilinane) (6h)**: According to GP, a mixture of 2-nitrobenzaldehyde (761 mg, 5.0 mmol), enyne **1h** (310 mg, 1.0 mmol), and $AgSbF_6$ (17 mg, 50 μmol) in anhydrous $CH_2Cl_2$ (5 mL) was cooled to −45 °C and treated with $[AuCl(PPh_3)]$ (25 mg, 50 μmol). The reaction mixture was kept at −45 °C for 6 h. The cooling device was switched off, which initiated slow warming to RT. After an overall reaction time of 18 h, the mixture turned brown and TLC control ($R_f$(**1h**) = 0.75, petroleum ether/ethyl acetate 4:1) indicated complete consumption of the substrate. Workup according to GP and flash column chromatography on silica (30 g, petroleum ether/ethyl acetate 9:1) yielded 2-oxabicyclo[3.1.0]hexane **6h** (267 mg, 58%) as a slightly yellow oil. $R_f = 0.33$ (petroleum ether/ethyl acetate 4:1); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.65$ (s, 3H; $CH_3$), 0.67 (dd, $J = 6.6$, 5.0 Hz, 1H; 1-$H_a$), 0.97 (dd, $J = 6.7$, 1.6 Hz, 1H; 1-$H_b$), 1.04, 1.11 (2 s, 18H; $C(CH_3)_3$), 1.72 (d, $J = 14.7$ Hz, 1H; 4-$H_a$), 1.91 (s, 2H; 6-H), 2.22 (d, $J = 14.7$ Hz, 1H; 4-$H_b$), 3.87 (dd, $J = 10.9$, 1.3 Hz, 1H; $CH_2O$), 3.96–3.99 (m, 1H; 1a-H), 4.06 (d, $J = 11.1$ Hz, 1H; $CH_2O$), 4.13–4.23 (m, 2H; $CH_2O$), 5.93 (s, 1H; 3-H), 7.36–7.42 (m, 1H; Ar), 7.59 (td, $J = 7.6$, 1.0 Hz, 1H; Ar), 7.70–7.73 (m, 1H; Ar), 7.96 ppm (dd, $J = 8.2$, 1.2 Hz, 1H; Ar); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, DEPT, H,C-COSY): $\delta = 16.54$ (t; C-1), 21.34 (s; $C(CH_3)_3$), 22.11 (q; $CH_3$), 22.90 (s; $C(CH_3)_3$), 27.86, 28.38 (2 q; $C(CH_3)_3$), 38.42 (t; C-6), 41.06 (s; C-6a), 47.62 (s; C-3a), 50.41 (t; C-4), 53.99 (s; C-5), 65.92 (d; C-1a), 73.17, 75.00 (2t; $OCH_2$), 94.25 (d; C-3), 124.65, 128.14, 128.63, 133.35 (4d; Ar), 137.72, 147.73 ppm (2s; Ar); IR (film): $\tilde{\nu} = 651$, 726, 769, 785, 827, 1010, 1052, 1118, 1183, 1354, 1443, 1472, 1528, 2859, 2934, 2969 cm$^{-1}$; HRMS (FAB): $m/z$: calcd for $C_{25}H_{38}NO_5Si$: 460.2519; found: 460.2529 $[M+H^+]$; elemental analysis calcd (%) for $C_{25}H_{37}NO_5Si$ (459.7): C 65.33, H 8.11, N 3.05; found: C 65.66, H 8.40, N 2.86.

**(−)-Dimethyl (1a*R*,3*R*,3a*R*,4*S*,6a*R*)-3-(2-nitrophenyl)-4-phenyltetrahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan-5,5(6*H*)-dicarboxylate (6i)**: According to GP, a mixture of 2-nitrobenzaldehyde (756 mg, 5.0 mmol), enyne (+)-(*S*)-**1i** (98.5% *ee*, 286 mg, 1.0 mmol), and $AgSbF_6$ (17 mg, 50 μmol) in anhydrous $CH_2Cl_2$ (5 mL) was cooled to −45 °C and treated with $[AuCl(PPh_3)]$ (24.7 mg, 50 μmol). The mixture turned orange and was kept at −45 °C for 6 h. The cooling device was switched off, which initiated slow warming to RT. After an overall reaction time of 15 h, TLC control ($R_f$(**1i**) = 0.38, petroleum ether/ethyl acetate 3:1) indicated complete consumption of the substrate. Workup according to GP and flash column chromatography on silica (30 g, petroleum ether/ethyl acetate 5:1) yielded the product as slightly yellow oil. The compound was crystallized from hot ethanol to yield (−)-**6i** (307 mg, 70%) as colorless rod-shaped crystals. The relative configuration of (−)-**6i** was verified by X-ray crystal structure analysis; for data, see Table 4. $R_f = 0.21$ (petroleum ether/ethyl acetate 3:1); m.p. 127–128 °C; optical rotation: $[\alpha]^{20}_D = -109$ ($c = 0.42$ in MeOH, >99% *ee* according to HPLC); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.03$ (dd, $J = 6.6$, 5.4 Hz, 1H; 1-$H_a$), 1.24 (dd, $J = 6.7$, 1.9 Hz, 1H; 1-$H_b$), 2.10 (d, $J = 14.1$ Hz, 1H; 6-$H_a$), 2.78 (dd, $J = 5.6$, 3.0 Hz, 1H; 3a-H), 3.09 (d, $J = 14.0$ Hz, 1H; 6-$H_b$), 3.29, 3.87 (2s, 6H; $OCH_3$), 3.84 (dd, $J = 5.2$, 1.8 Hz, 1H; 1a-H), 4.65 (d, $J = 2.7$ Hz, 1H; 4-H), 6.28 (d, $J = 5.6$ Hz, 1H; 3-H), 7.17–7.28 (m, 5H; Ph), 7.30–7.36 (m, 1H; Ar), 7.55 (td, $J = 7.7$, 1.1 Hz, 1H; Ar), 7.69 (d, $J = 7.8$ Hz, 1H; Ar), 7.77 ppm (dd, $J=8.1$, 1.2 Hz, 1H; Ar); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C, DEPT, H,C-COSY): $\delta=19.26$ (t; C-1), 34.88 (s; C-6a), 37.31 (t; C-6), 52.17, 53.20 (2 q; OCH$_3$), 56.03 (d; C-4), 63.03 (d; C-3a), 66.55 (s; C-5), 66.76 (d; C-1a), 90.72 (d; C-3), 124.53, 127.26, 127.97, 128.10, 128.14, 128.99, 133.21 (7d; Ar), 139.17, 141.14, 147.83 (3s; Ar), 169.09, 172.25 ppm (2s; $CO_2CH_3$); IR (KBr): $\tilde{\nu}=704$, 746, 1156, 1219, 1274, 1352, 1435, 1455, 1528, 1736, 2954, 3445 cm$^{-1}$; HRMS (EI): $m/z$: calcd for $C_{24}H_{23}NO_7$: 437.1475; found: 437.1487 [$M^+$]; elemental analysis calcd (%) for $C_{24}H_{23}NO_7$ (459.7): C 65.90, H 5.30, N 3.20; found: C 65.73, H 5.37, N 3.18; HPLC (Daicel Chiralpak AD-H, *n*-hexane/isopropanol 95:5, 20 °C, 210 nm): $t_R((-)$-**6i**$)=62.4$ min, $t_R((+)$-**6i**$)=73.9$ min, >99% *ee*.

**(±)-Dimethyl (1a*R*,3*R*,3a*R*,7a*R*)-3-(2-nitrophenyl)hexahydrobenzo[*c*]cyclopropa[*b*]furan-6,6(7*H*)-dicarboxylate (6j)**: According to GP, a solution of enyne **1j** (224 mg, 1.0 mmol), 2-nitrobenzaldehyde (756 mg, 5.0 mmol), and AgSbF$_6$ (17 mg, 50 µmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was cooled to −45 °C and treated with [AuCl(PPh$_3$)] (24.7 mg, 50 µmol). After 6 h the cooling device was switched off, which initiated slow warming to RT. TLC monitoring indicated complete conversion after an overall reaction time of 43 h. Workup according to GP, flash column chromatography on silica (30 g, petroleum ether/ethyl acetate 10:1), and further purification by HPLC on silica (columns: Latek, 5 µ, 21×250 mm and Prontosil 120-10-SI, 10 µ, 20×250 mm; petroleum ether/ethyl acetate 10:1, 13 mL min$^{-1}$, 46 bar) afforded **6j** (108 mg, 29%) as a slightly yellow solid. Crystallization from methanol at −5 °C gave colorless polyhedral crystals, suitable for X-ray crystal structure analysis; for data, see Table 4. $R_f=0.47$ (petroleum ether/ethyl acetate 3:1); m.p. 93–95 °C; $^1$H NMR (500 MHz, CDCl$_3$, 25 °C): $\delta=0.08$ (dd, $J=6.2$, 5.9 Hz, 1H; 1-H), 0.61 (dd, $J=7.0$, 1.7 Hz, 1H; 1-H), 1.49–1.59 (m, 1H; 4-H), 1.76–1.83 (m, 1H; 5-H), 1.89 (dd, $J=14.3$, 2.2 Hz, 1H; 7-H), 1.96–1.01 (m, 1H; 3a-H), 2.16 (d, $J=14.4$ Hz, 1H; 7-H), 2.22–2.28 (m, 1H; 4-H), 2.41–2.46 (m, 1H; 5-H), 3.69 (s, 3H; OCH$_3$), 3.81 (s, 3H; OCH$_3$), 4.06 (dd, $J=5.3$, 1.3 Hz, 1H; 1a-H), 5.47 (s, 1H; 3-H), 7.37 (dd, $J=7.8$, 7.6 Hz, 1H; Ar), 7.58 (dd, $J=7.9$, 7.4 Hz, 1H; Ar), 7.81 (d, $J=8.0$ Hz, 1H; Ar), 7.92 ppm (d, $J=8.1$ Hz, 1H; Ar); $^{13}$C NMR (125 MHz, CDCl$_3$, 25 °C, DEPT, H,C-COSY): $\delta=15.89$ (t; C-1), 25.05 (s; C-7a), 29.10 (t; C-4), 29.78 (t; C-5), 34.57 (t; C-7), 47.39 (d; C-3a), 52.76, 52.89 (2q; OCH$_3$), 54.67 (s; C-6), 64.99 (d; C-1a), 83.36 (d; C-3), 125.08, 127.90, 128.48, 133.20 (4d; Ar), 141.02, 146.87 (2s; Ar), 171.28, 172.34 ppm (2s; C=O); IR (KBr): $\tilde{\nu}=728$, 790, 826, 959, 1006, 1080, 1104, 1122, 1171, 1260, 1352, 1436, 1451, 1526, 1610, 1631, 1734 (C=O), 2954, 3438 cm$^{-1}$; HRMS (FAB): $m/z$: calcd for $C_{19}H_{22}NO_7$: 376.1396; found: 376.1370 [$M$+H$^+$]; elemental analysis calcd (%) for $C_{19}H_{21}NO_7$ (375.4): C 60.79, H 5.64, N 3.73; found: C 60.83, H 5.73, N 3.68.

**(±)-(1a*R*,3*R*,3a*R*,6a*S*)-3-(2-Nitrophenyl)-5,5-bis(phenylsulfonyl)hexahydro-3*H*-cyclopenta[*c*]cyclopropa[*b*]furan (6k)**: According to GP, a solution of 2-nitrobenzaldehyde (756 mg, 5.0 mmol), enyne **1k** (375 mg, 1.0 mmol), and AgSbF$_6$ (17 mg, 50 µmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was cooled to −45 °C and treated with [AuCl(PPh$_3$)] (24.7 mg, 50 µmol). The mixture turned orange and was kept at −45 °C for 6 h. The cooling device was switched off, which initiated slow warming to RT. After an overall reaction time of 16 h, TLC control ($R_f$(1k)=0.24, petroleum ether/ethyl acetate 3:1) indicated complete consumption of the substrate. Workup according to GP, washing with CH$_2$Cl$_2$ (100 mL), and flash column chromatography on silica (15 g, petroleum ether/ethyl acetate 5:1 to 2:1) yielded 2-oxabicyclo[3.1.0]hexane **6k** (345 mg, 66%) as a slightly gray solid. The melting point could not be determined because of decomposition beginning at 220 °C. $R_f=0.06$ (petroleum ether/ethyl acetate 3:1); $^1$H NMR (300 MHz, D$_6$-DMSO, 25 °C): $\delta=0.68$ (dd, $J=6.9$, 2.0 Hz, 1H; 1-H$_a$), 0.77 (dd, $J=6.7$, 5.8 Hz, 1H; 1-H$_b$), 2.23 (ddd, $J=8.5$, 8.5, 2.4 Hz, 1H; 3a-H), 2.64 (d, $J=16.4$ Hz, 1H; 6-H$_a$), 2.75 (d, $J=16.4$ Hz, 1H; 6-H$_b$), 2.88 (d, $J=8.7$ Hz, 2H; 4-H), 3.64 (dd, $J=5.1$, 1.7 Hz, 1H; 1a-H), 5.76 (d, $J=2.1$ Hz, 1H; 3-H), 7.52–8.15 ppm (m, 14H; Ar); $^{13}$C NMR (75 MHz, D$_6$-DMSO, 25 °C, DEPT, H,C-COSY): $\delta=15.75$ (t; C-1), 33.98 (t; C-6), 34.30 (s; C-6a), 38.91 (t; C-4), 53.46 (d; C-3a), 65.00 (d; C-1a), 85.06 (d; C-3), 92.72 (s; C-5), 125.24, 127.27, 128.73, 129.24, 121.00, 131.11, 134.03, 135.10, 135.14 (9d; Ar), 135.42, 136.09, 138.93, 146.04 ppm (4s; Ar); IR (KBr): $\tilde{\nu}=664$, 689, 727, 756, 1079, 1124, 1148, 1312, 1331, 1447, 1522, 3432 cm$^{-1}$; HRMS (FAB): $m/z$: calcd for $C_{26}H_{24}NO_7S_2$: 526.0994; found: 526.0989 [$M$+H$^+$]; elemental analysis calcd (%) for $C_{26}H_{23}NO_7S_2$ (525.6): C 59.41, H 4.41, N 2.66, S 12.20; found: C 59.15, H 4.39, N 2.61, S 12.11.

**(±)-(1a*R*,3*R*,3a*R*,8b*R*)-3-(2-Nitrophenyl)-1,1a,3a,4-tetrahydro-3*H*-cyclopropa[*b*]indeno[1,2-*c*]furan (6l)**: According to GP, a solution of enyne **1l** (142 mg, 1.0 mmol), 2-nitrobenzaldehyde (**2b**) (756 mg, 5 mmol), and AgSbF$_6$ (17 mg, 50 µmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was cooled to −45 °C and treated with [AuCl(PPh$_3$)] (24.7 mg, 50 µmol). After 6 h the cooling device was switched off, which initiated slow warming to RT. GC monitoring indicated complete conversion after an overall reaction time of 22 h. Workup according to GP and flash column chromatography on silica (40 g, petroleum ether/ethyl acetate 20:1) afforded **6l** (79 mg, 27%) as a yellow solid. Crystallization from diethyl ether at −5 °C gave colorless polyhedral crystals, suitable for X-ray crystal structure analysis; for data, see Table 4. $R_f=0.72$ (petroleum ether/ethyl acetate 3:1); m.p. 97–98 °C; $^1$H NMR (500 MHz, CDCl$_3$, 25 °C): $\delta=1.42$ (dd, $J=6.9$, 2.4 Hz, 1H; 1-H), 1.51 (dd, $J=6.8$, 5.3 Hz, 1H; 1-H), 3.03 (ddd, $J=9.2$, 6.7, 6.3 Hz, 1H; 3a-H), 3.36–3.47 (m, 2H; 4-H), 4.07 (dd, $J=5.3$, 2.4 Hz, 1H; 1a-H), 5.94 (d, $J=6.1$ Hz, 1H; 3-H), 6.75 (d, $J=7.1$ Hz, 1H; Ph), 7.14–7.25 (m, 3H; Ph), 7.44 (dd, $J=8.1$, 7.3 Hz, 1H; Ar), 7.65 (dd, $J=7.9$, 7.3 Hz, 1H; Ar), 7.84 (d, $J=7.9$ Hz, 1H; Ar), 7.96 ppm (d, $J=8.1$ Hz, 1H; Ar); $^{13}$C NMR (125 MHz, CDCl$_3$, 25 °C, DEPT, HMBC): $\delta=22.66$ (t; C-1), 37.38 (t; C-4), 42.99 (s; C-8b), 57.30 (d; C-3a), 67.34 (d; C-1a), 90.64 (d; C-3), 118.98, 124.73, 124.84, 126.86, 126.89, 128.27, 128.35, 133.47 (8d; Ph, Ar), 138.64, 142.06, 143.34, 147.76 ppm (4s; Ph, Ar); IR (KBr): $\tilde{\nu}=712$, 740, 753, 788, 810, 859, 948, 1007, 1090, 1103, 1125, 1301, 1318, 1350, 1439, 1461, 1484, 1524, 1579, 1609, 3852, 2934, 3023, 3046, 3067, 3438 cm$^{-1}$; HRMS (FAB): $m/z$: calcd for $C_{18}H_{16}NO_3$: 294.1130; found: 294.1134 [$M$+H$^+$].

**(±)-Dimethyl (2*R*,4*S*,4a*S*,7a*R*)-7a-(2-methylprop-1-en-1-yl)-2,4-bis(2-nitrophenyl)tetrahydrocyclopenta[*d*][1,3]dioxine-6,6(4*H*)-dicarboxylate (8a)**: According to GP, a mixture of 2-nitrobenzaldehyde (756 mg, 5.0 mmol), enyne **7a** (238 mg, 1.0 mmol), and AgSbF$_6$ (17 mg, 50 µmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was cooled to −45 °C and treated with [AuCl(PPh$_3$)] (24.7 mg, 50 µmol). After 1 h of stirring at this temperature, TLC control ($R_f$(**7a**)=0.36, petroleum ether/ethyl acetate 5:1) indicated complete consumption of the substrate. Workup according to GP of the reaction mixture according to the general procedure and flash column chromatography on silica (100 g, petroleum ether/ethyl acetate 5:1) yielded dioxane **8a** (192 mg, 36%) as a colorless solid. The product was dissolved in warm methanol/CH$_2$Cl$_2$ 1:1 (2 mL). Evaporation of the solvent gave colorless needles. The relative configuration of **8a** was verified by X-ray crystal structure analysis; for data, see Table 4. $R_f=0.09$ (petroleum ether/ethyl acetate 5:1); m.p. 195–197 °C; $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta=1.64$ (dd, $J=13.6$, 8.3 Hz, 1H; 5-H$_a$), 1.79 (d, $J=0.9$ Hz, 3H; 3′$_E$-H), 1.88 (d, $J=1.1$ Hz, 3H; 3′$_Z$-H), 2.46 (d, $J=14.7$, 1H; 7-H$_a$), 2.57 (ddd, $J=11.1$, 8.5, 2.3 Hz, 1H; 4a-H), 2.87 (dd, $J=13.7$, 11.4 Hz, 1H; 5-H$_b$), 3.08 (d, $J=14.7$ Hz, 1H; 7-H$_b$), 3.63, 3.68 (2s, 6H; OCH$_3$), 5.61 (s, 1H; 1′-H), 5.84 (d, $J=1.9$ Hz, 1H; 4-H), 6.40 (s, 1H; 2-H), 7.39–7.46 (m, 1H; Ar), 7.50 (td, $J=7.8$, 1.4 Hz, 1H; Ar), 7.61 (td, $J=7.6$, 1.2 Hz, 1H; Ar), 7.67 (td, $J=7.7$, 1.2 Hz, 1H; Ar), 7.75 (dd, $J=7.9$, 0.9 Hz, 1H; Ar), 7.80 (dd, $J=8.1$, 1.3 Hz, 1H; Ar), 7.94 (dd, $J=7.9$, 1.1 Hz, 1H; Ar), 8.07 ppm (dd, $J=8.3$, 1.3 Hz, 1H; Ar); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C, DEPT, H,C-COSY, HMBC): $\delta=19.64$ (q; C-3′$_Z$), 27.03 (q; C-3′$_E$), 31.36 (t; C-5), 46.82 (d; C-4a), 46.87 (t; C-7), 52.92, 53.09 (2q; OCH$_3$), 58.00 (s; C-6), 72.15 (d; C-4), 85.17 (s; C-7a), 92.44 (d; C-2), 121.90 (d; C-1′), 123.98, 125.13, 128.33, 128.42, 128.43, 129.63, 132.86, 134.09 (8d; Ar), 132.51, 135.80 (2s; Ar), 142.14 (s; C-2′), 146.42, 148.60 (2s; Ar), 172.28, 173.07 ppm (2s; C=O); HRMS (FAB): $m/z$: calcd for $C_{27}H_{29}N_2O_{10}$: 541.1822; found: 541.1827 [$M$+H$^+$]; elemental analysis calcd (%) for $C_{27}H_{28}N_2O_{10}$ (540.5): C 60.00, H 5.22, N 5.18; found: C 59.98, H 5.22, N 5.14.

**(±)-Dimethyl (2*R*,4*S*,4a*S*,7a*R*)-2,4-diphenyl-7a-[(*E*)-2-phenylethenyl]tetrahydrocyclopenta[*d*][1,3]dioxine-6,6(4*H*)-dicarboxylate (8b)**: According to GP, a solution of enyne **7b** (286 mg, 1 mmol), benzaldehyde (531 mg, 5.0 mmol), and AgSbF$_6$ (17 mg, 50 µmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was cooled to −40 °C and treated with [AuCl(PPh$_3$)] (24.7 mg, 50 µmol). After stirring for 5 h at this temperature, GC monitoring indicated complete conversion. Workup according to GP and flash column chromatography on silica (25 g, petroleum ether/ethyl acetate 10:1) afforded **8b** (375 mg, 75 %) as a white solid. Crystallization from methanol at 0 °C gave colorless polyhedral crystals, suitable for X-ray crystal structure analysis; for data, see Table 4. $R_f=0.35$ (petroleum ether/ethyl acetate 3:1); m.p. 118 °C; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=1.89$ (dd, $J=14.1$, 8.6 Hz, 1H; $CH_2CH$), 2.62 (d, $J=14.7$ Hz, 1H; $CH_2qCO$), 2.64 (dt, $J=10.6$, 2.2 Hz, 1H; $CH_2CH$), 2.87 (d, $J=14.5$ Hz, 1H; $CH_2qCO$), 3.17 (dd, $J=14.0$, 10.8 Hz, 1H; $CH_2CH$), 3.68 (s, 3H; $OCH_3$), 3.69 (s, 3H; $OCH_3$), 5.19 (d, $J=2.2$ Hz, 1H; CHC*H*O), 5.84 (s, 1H; OC*H*O), 6.42 (d, $J=16.4$ Hz, 1H; C*H*=CHPh), 6.84 (d, $J=16.5$ Hz, 1H; CH=C*H*Ph), 7.23–7.64 ppm (m, 15H; Ph); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, DEPT, H,C-COSY, HMBC): $\delta=32.49$ (t; $CH_2CH$), 47.18 (d; $CH_2CH$), 49.28 (t; $CH_2qCO$), 52.92 (q; $OCH_3$), 53.11 (q; $OCH_3$), 57.70 (s; $C(CO_2Me)_2$), 75.15 (d; CHCHO), 85.15 (s; $CH_2qCO$), 97.51 (d; OCHO), 125.25, 126.65, 126.83, 127.39, 128.25, 128.39, 128.48, 128.61, 128.88, 129.12, 133.84 (11 d; Ph), 130.31 (d; CH=CHPh), 132.37 (d; CH=CHPh), 136.34, 138.68, 140.29 (3s; Ph), 172.04, 173.57 ppm (2s; C=O); HRMS (FAB): $m/z$: calcd for $C_{31}H_{30}O_6$: 498.2042; found: 498.2031 [$M^+$]; elemental analysis calcd (%) for $C_{31}H_{30}O_6$ (498.6): C 74.68, H 6.07; found: C 74.26, H 5.99.

**(±)-Dimethyl (2*R*,4*S*,4a*S*,7a*R*)-2,4-bis(4-methylphenyl)-7a-[(*E*)-2-phenylethenyl]tetrahydrocyclopenta[*d*][1,3]dioxine-6,6(4*H*)-dicarboxylate (8c)**: According to GP, a solution of enyne **7b** (286 mg, 1 mmol), 4-methylbenzaldehyde (601 mg, 5.0 mmol), and $AgSbF_6$ (17 mg, 50 μmol) in anhydrous $CH_2Cl_2$ (5 mL) was cooled to −40 °C and treated with [AuCl($PPh_3$)] (24.7 mg, 50 μmol). After stirring for 2 h at this temperature, GC monitoring indicated complete conversion. Workup according to GP and flash column chromatography on silica (70 g, petroleum ether/ethyl acetate 10:1) afforded **8c** (327 mg, 62 %) as a colorless oil. $R_f=0.11$ (petroleum ether/ethyl acetate 10:1); $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=1.86$ (dd, $J=14.1$, 8.7 Hz, 1H; $CH_2CH$), 2.38 (s, 6H; $PhCH_3$), 2.59 (d, $J=14.5$ Hz, 1H; $CH_2qCO$), 2.60 (dt, $J=10.7$, 2.3 Hz, 1H; $CH_2CH$), 2.84 (d, $J=14.5$ Hz, 1H; $CH_2qCO$), 3.15 (dd, $J=14.0$, 10.8 Hz, 1H; $CH_2CH$), 3.67 (s, 3H; $OCH_3$), 3.70 (s, 3H; $OCH_3$), 5.17 (d, $J=2.2$ Hz, 1H; CHC*H*O), 5.86 (s, 1H; OC*H*O), 6.34 (d, $J=16.4$ Hz, 1H; C*H*=CHPh), 6.78 (d, $J=16.4$ Hz, 1H; CH=C*H*Ph), 7.15–7.52 ppm (m, 13H; Ar, Ph); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, DEPT, H,C-COSY, HMBC): $\delta=21.37$ (q; $ArCH_3$), 21.45 (q; $ArCH_3$), 32.50 (t; $CH_2CH$), 47.15 (d; $CH_2CH$), 49.33 (t; $CH_2qCO$), 52.93 (q; $OCH_3$), 53.09 (q; $OCH_3$), 57.69 (s; $C(CO_2Me)_2$), 75.08 (d; CHCHO), 85.12 (s; $CH_2qCO$), 97.48 (d; OCHO), 125.28, 126.56, 126.76, 127.33, 127.89, 128.45 129.57 (7d; Ar, Ph), 129.04 (d; CH=CHPh), 132.16 (d; CH=CHPh), 133.62, 135.95, 138.16, 138.88, 140.44 (5s; Ar, Ph), 172.08, 173.64 ppm (2s; C=O); HRMS (FAB): $m/z$: calcd for $C_{33}H_{34}O_6$: 526.2355; found: 526.2360 [$M^+$].

## Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 623), the Studienstiftung des deutschen Volkes (scholarship to M.S.), and the Fonds der Chemischen Industrie. We thank Prof. B. F. Straub for useful discussions and advice concerning the DFT calculations and Prof. G. Hilt for an interesting mechanistic proposal concerning the formation of the addition products **8**. Furthermore, we thank O. Tverskoy and M. Krauter for experimental assistance.

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Received: June 13, 2009