Palladium-Catalyzed Hydrovinylation of Vinyl Triflates with Alkynes An Approach to the Synthesis of 3-Vinylfuran-2(5*H*)-ones

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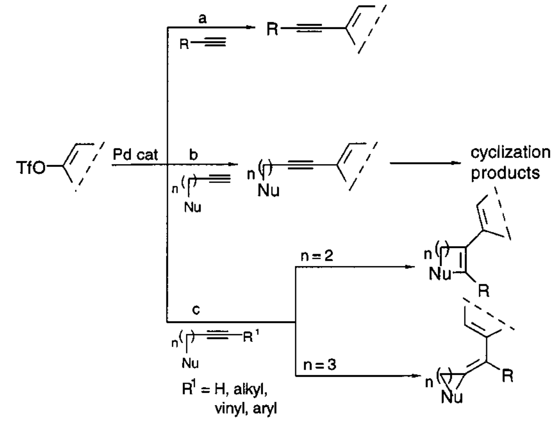
The reaction of alkynes with vinyl triflates in the presence of catalytic amounts of $Pd(OAc)_2$ and HCOOK, omitting phosphane ligands, affords hydrovinylation products usually in good to high yields. The reaction has been employed to develop a regioselective synthesis of 3-vinylfuran-2(5*H*)-ones from methyl 4-hydroxy-2-butynoates.

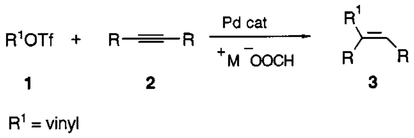
Introduction

The palladium-catalyzed reaction of vinyl triflates with alkynes represents a useful tool in organic synthesis.[1] Depending on the reaction conditions and on the nature of the acetylene building block, it can produce a variety of functionalized derivatives. For example, with terminal alkynes the reaction affords conjugated enynes (Scheme 1, route a). Dienynes related to vitamin D,[2] propargylglycine derivatives,[3] dienediynes related to neocarzinostatin,[4] a potent antitumor agent, and 5-alkynyluracils[5] have been prepared in this manner. In cases where terminal alkynes contain a weak nucleophile close to the carbon−carbon triple bond, the coupling step can be followed by a cyclization reaction[6] (Scheme 1, route b). With terminal and internal alkynes bearing relatively strong, proximate nucleophilic centers, cyclic derivatives can be obtained through carbo-[7] and heteropalladation/reductive elimination tandem reactions[8][9] (Scheme 1, route c).



Scheme 1. Palladium-catalyzed coupling, coupling/cyclization, and carbon-, oxy-, aminopalladation/reductive elimination tandem reaction of vinyl triflates and alkynes

Changing the reaction profile whereby the vinyl triflates and alkynes can be channeled into different products would greatly expand the scope of the methodology and its synthetic flexibility. Our interest in the palladium-catalyzed hydrovinylation of alkynes[10] led us to consider whether such a reaction may be extended to vinyl triflates (Scheme 2). We report the results of this study.



Scheme 2. Palladium-catalyzed hydrovinylation of vinyl triflates with alkynes

Results and Discussion

The main problem we expected to face when we initiated this project was the premature reduction to alkenes[11] of σ-vinylpalladiums formed through the oxidative insertion of palladium into the carbon-oxygen bond of **1**. Excess vinyl donor was used in similar reactions with vinyl halides.[10] However, the present system was limited to 1 equiv. due to the cost of the vinyl triflate. Our investigation with diphenylacetylene and the vinyl triflate **1e** revealed that the olefinic derivative **4m** is generated in significant amount or as the main product in the presence of phosphane ligands (Scheme 3). For example, exposure of **1e** to 1 equiv. of diphenylacetylene in the presence of 5 mol-% $Pd(OAc)_2$, 10 mol-% of PPh_3 and 2 equiv. of HCOOK in DMF at 60°C for 6 h gave **3′m** and **4m** in 12% and 26% yield, respectively. Under the same conditions, with 10 mol-% of $P(o\text{tol})_3$, **3′m** and **4m** were isolated in 38% and 20% yield, respectively. The employment of 5 mol-% of dppp [1,3-bis(diphenylphosphanyl)propane] produced the same products in 19% and 53% yield, respectively. Remarkably, omitting phosphane ligands redirects the reaction to give preferentially the hydrovinylation derivative, albeit in low yield: **3′m** was formed in 34% yield along with trace amounts of **4m** after 7 h (the starting triflate was recovered in 50% yield). Attempts to

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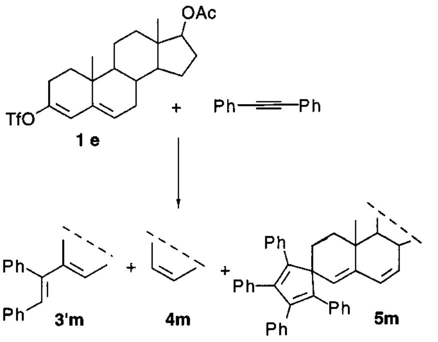
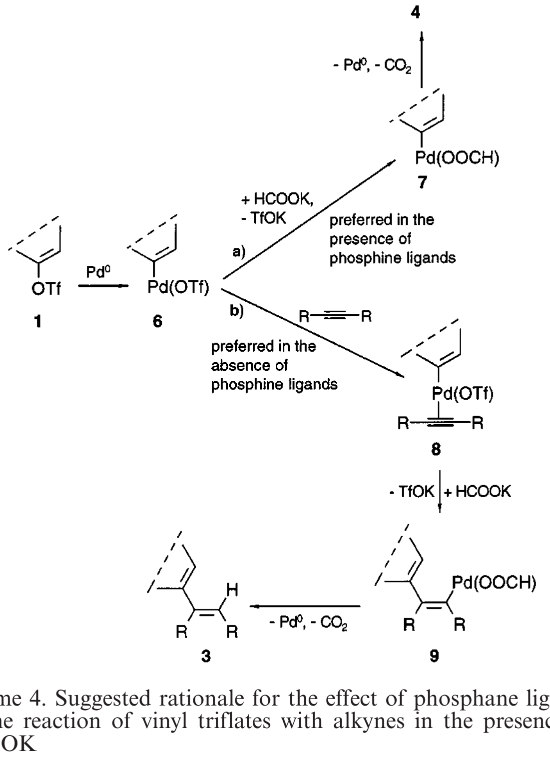
increase the yield of the desired hydrovinylation derivative by using an excess of diphenylacetylene resulted instead in the isolation of the multiinsertion derivative **5m**[12] (formed in minor amounts with a 1:1 alkyne to triflate ratio) as the main by-product. For example, in the presence of 1.5 equiv. of diphenylacetylene, **3′m**, **4m** and **5m** were isolated in 30%, 5% and 30% yield, respectively. The reaction temperature was found to affect the hydrovinylation to reduction ratio. The yield of **3′m** increased up to 50% when **1e** and diphenylacetylene were subjected to Pd(OAc)$_2$ and HCOOK at 40 °C for 24 h (trace amounts, if any, of **4m** were observed and the starting triflate was recovered in 36% yield). A better yield of the hydrovinylation product was obtained with our model system[13] by slow addition of 0.8 equiv. of diphenylacetylene to a mixture of **1e**, 2 equiv. of HCOOK, 0.2 equiv. of diphenylacetylene,[14] and 0.05 equiv. of Pd(OAc)$_2$ at 40 °C over a period of 24 h: under these conditions **3′m** was isolated in 79% yield along with a 15% yield of **4m**.



Scheme 3. Palladium-catalyzed hydrovinylation of **1e** with diphenylacetylene



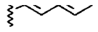
Scheme 4. Suggested rationale for the effect of phosphane ligands on the reaction of vinyl triflates with alkynes in the presence of HCOOK

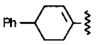
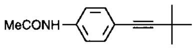
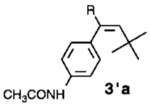
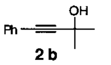
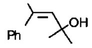
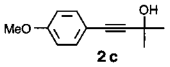
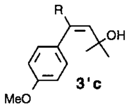
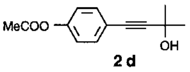
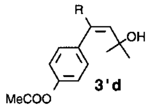
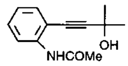
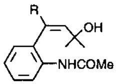
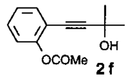
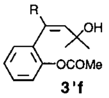
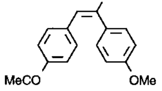
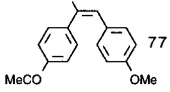
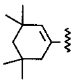
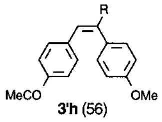
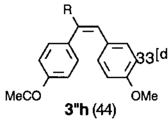
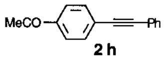
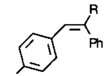
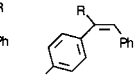
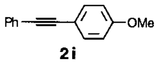
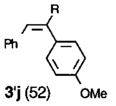
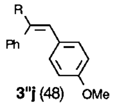
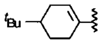
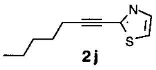
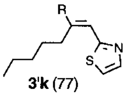
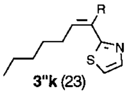
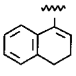
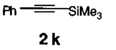
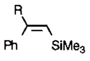
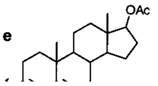
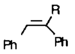
In all probability, phosphane ligands hamper the coordination of the alkyne to palladium and the σ-vinylpalladium complex **6** may undergo (preferentially or to a significant extent) the substitution of the formate anion for the poorly-ligated triflate anion (Scheme 4, route a). Subsequently, the resulting σ-vinylpalladium formate complex **7** generates the alkene **4** through decarboxylation and reductive elimination steps. Omitting phosphane ligands might favor the coordination of the alkyne to the σ-vinylpalladium complex **6**, the η^2-alkyne-σ-vinylpalladium complex **8** is formed preferentially and the reaction affords the desired hydrovinylation product through the intermediacy of the carbopalladation adduct **9** (Scheme 4, route b).

Having established the feasibility of the hydrovinylation reaction, we applied the best conditions found with our model system to other alkynes, in particular to unsymmetrical acetylenic systems. The regiochemistry, assigned by NOE experiments (apart from **3′k** and **3′′k**), was found to be controlled primarily by steric and coordinating effects and to follow the pattern established in our previous studies on this type of alkyne additions.[10][15] Steric effects act so as to favor the addition of the organic framework to the less hindered end of the alkyne and that of the palladium moiety (the hydrogen atom in the hydrovinylation product) to the more hindered end (Table 1, entry 1, 12). With *tert*-propargyl alcohols, hydroxyl coordination[16] to palladium most probably reinforces steric effects in directing the addition of σ-vinylpalladium intermediates to the carbon−carbon triple bond (Table 1, entries 2−6). Electronic effects appear to be less important.[10b−c,17] Evidence of this is found in the results obtained in the reaction of vinyl triflates with unsymmetrical diaryl acetylenes such as (*p*-acetylphenyl)-(*p*-methoxyphenyl)acetylene (Table 1, entries 7 and 8), (*p*-acetylphenyl)-phenylacetylene (Table 1, entry 9) and (*p*-methoxyphenyl)-phenylacetylene (Table 1, entry 10), where the acetylenic carbons should be differentiated only by the electron-withdrawing and electron-donating effects of the substituents. These reactions displayed only modest to low regioselectivities.

Compounds **3** have been isolated as single stereoisomers. The stereochemistry of **3′a**, **3′f**, **3′g/3′′g**, **3′h/3′′h**, **3′i/3′′i** and **3′j/3′′j** has been assigned by NOE experiments. That of the other hydrovinylation derivatives has been assigned based on these data and on all our previous work on hydroarylation and hydrovinylation reactions in which the *cis* adduct has usually been the main product.[10,15b,15d] The NMR spectra of hydrovinylation products **3′e** and **3′f** could suggest the presence of (*E*)/(*Z*) isomers. For example, the vinylic and methyl hydrogens, as well as the hydrogens linked to the nitrogen and oxygen atoms of **3′e**, appear as two close singlets at 25 °C in [D$_6$]DMSO. However, when its [D$_6$]DMSO solution (10 mg in 0.7 mL) is warmed, coalescence of all these signals occurs at 100 °C and the two singlets are regenerated for each type of hydrogen on cooling to 25 °C. Such a behavior argues in favor of the existence of diastereomeric conformers and rules out that of stereoisomers. These diastereomeric conformers might result from the presence of a configurational stereogenic center on the

Table 1. Palladium-catalyzed hydrovinylation of unsymmetrical alkynes[a]



					(%)
1	**1a** 	 **2a**	6	 **3'a**	94
2	**1a**	 **2b**	6	 **3'b**	69
3	**1a**	 **2c**	7	 **3'c**	70
4	**1a**	 **2d**	7	 **3'd**	80
5	**1a**	 **2e**	2	 **3'e**	74
6	**1a**	 **2f**	20	 **3'f**	60
7	**1a**	 **2g**	20	 **3'g** (65)  **3"g** (35)	77
8	**1b** 	**2g**	20	 **3'h** (56)  **3"h** (44)	33[d]
9	**1a**	 **2h**	20	 **3'i** (66)  **3"i** (33)	80
10	**1a**	 **2i**	76	 **3'j** (52)  **3"j** (48)	58
11	**1c** 	 **2j**	4	 **3'k** (77)  **3"k** (23)	51[e]
12	**1d** 	 **2k**	6.5	 **3'l**	45
13	**1e** 	 **2l**	24	 **3'm**	79[f]

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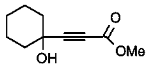
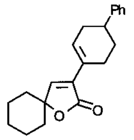
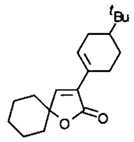
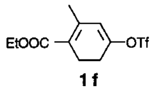
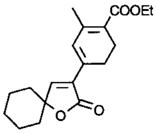
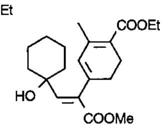
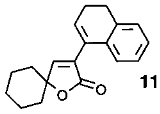
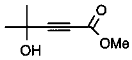
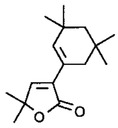
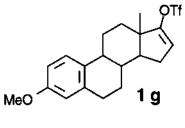
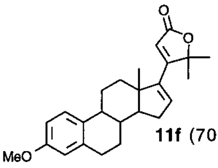
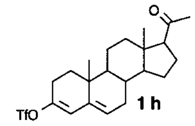
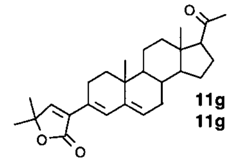
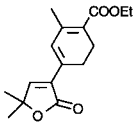
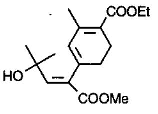
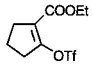
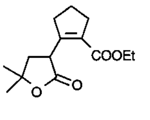
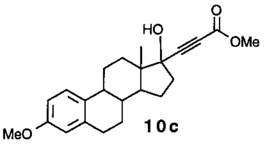
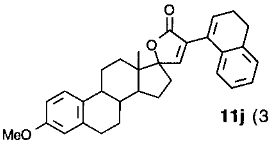
[a] Unless otherwise stated, reactions have been carried out in DMF at 40°C using the following molar ratios: **1**:**2**:HCOOK:Pd(OAc)$_2$ = 1:1.2:2:0.05. – [b] Yields are given for isolated products and refer to single runs. – [c] Regioisomeric ratios were calculated by NMR analysis. – [d] The starting triflate and alkyne were recovered in 28 and 43% yield, respectively. – [e] At 80°C. – [f] 0.8 equiv. of diphenylacetylene were added to a mixture of **1e**, 2 equiv. of HCOOK, 0.2 equiv. of diphenylacetylene, and 0.05 equiv. of Pd(OAc)$_2$ at 40°C over a period of 24 h.

Table 2. Synthesis of 2-vinylfuran-2(5*H*)-ones (**11**) from methyl 4-hydroxy-2-butenoates (**10**)[a]

entry	vinyl triflate **1**	methyl 4-hydroxy-2-butenoate **10**	time (h)	yield % of **11**[b]
1	**1a**	 **10a**	7	 **11a** (74)
2	**1c**	**10a**	7	 **11b** (80)
3	 **1f**	**10a**	2.5	 **11c** (37)  **12c** (35)
4	**1d**	**10a**	2	 **11d** (68)
5	**1b**	 **10b**	7	 **11e** (71)
6	 **1g**	**10b**	6	 **11f** (70)
7	 **1h**	**10b**	7	 **11g** (48)[d]
8		**10b**	7	**11g** (91)[e]
9	**1f**	**10b**	1	 **11h** (42)  **12h** (35)
10	 **1i**	**10b**	1	 **11i** (82)
11	**1d**	 **10c**	2.5	 **11j** (30)

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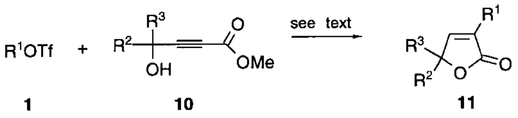
[a] Unless otherwise stated, reactions have been carried out in DMF at 40°C using the following molar ratios: **1**:**2**:HCOOK:Pd(OAc)$_2$ = 1:1.2:2:0.05. – [b] Yields are given for pure, isolated products and refer to single runs. – [c] The starting trilfate was recovered in 44% yield. – [d] Vinyl triflate:alkyne = 1:2.

added vinyl unit, in addition to a conformational stereogenic axis.[18] The latter is most probably due to *ortho* substituents large enough to inhibit free rotation at 25°C about the bond joining the aryl group to the vinyl carbon. Work is in progress to clarify this point.

Since the *cis* stereochemistry of the hydrovinylation pushes the substituents joined to the acetylenic carbons onto the same side of the olefin product, in the presence of suitable functionalities intramolecular cyclization can follow the addition step, and the procedure can provide a new route for appending heterocyclic moieties to vinyl triflates. Therefore, bearing in mind the widespread occurrence of oxygen heterocycles in natural and unnatural biologically active compounds, we explored the development of a furan-2(5*H*)-one synthesis from vinyl triflates based on the concept of sequential hydrovinylation/cyclization of methyl 4-hydroxy-2-butynoates **10**. We were pleased to find that subjection of **10** to our standard hydrovinylation conditions produced regioselectively 3-vinylfuran-2(5*H*)-ones (Scheme 5) in good to high yield, nicely complementing our synthesis of 4-vinylfuran-2(5*H*)-ones based on the palladium-catalyzed vinylic substitution/cyclization of vinyl triflates and methyl 4-hydroxy-2-butenoate.[19] Even in this case the regiochemistry of the carbopalladation step is governed by the strong directing effect of the tertiary alcohol group, which apparently exerts more influence on the direction of the addition than the ester group does.



Scheme 5. Preparation of 3-vinylfuran-2(5*H*)-ones **11** from vinyl triflates **1** and methyl 4-hydroxy-2-butynoates **10**

Only the reaction of the triflate **1f** with the alkynoates **10a** and **10b** gave the expected furan-2(5*H*)-ones, **11c** and **11h**, along with significant amounts of the overall *trans* hydrovinylation products **12c** and **12h**[20] (Table 2, entries 3 and 9). The formation of the latter could be dependent on the combined electron-withdrawing effect of the ester groups, which might favor the isomerization of the σ-vinylpalladium adduct resulting from the carbopalladation step.[21][22]

In conclusion, we have shown that the palladium-catalyzed hydrovinylation of vinyl triflates with internal alkynes can be achieved. The results obtained with a variety of vinyl triflates and internal alkynes demonstrate that the reaction is quite general. Its high stereo- and regioselectivity, which allowed the development of a new and convenient route to 3-vinylfuran-2(5*H*)-ones, makes this hydrovinylation an attractive synthetic protocol.

Experimental Section

Melting points were determined with a Büchi apparatus and are uncorrected. − Methyl 4-hydroxy-2-butynoates **10a**, **10b** and **10c**[14d] were prepared according to ref.[23]. Vinyl triflates **1** were prepared according to ref.[24] and were purified by chromatography on silica gel, eluted with *n*-hexane/EtOAc mixtures. Alkynes **2** were prepared by coupling reactions of aryl iodides with 1-alkynes according to the procedure given in ref.[25]. All the other reagents and the catalyst are commercially available and were used as purchased, without further purification. Reaction products were purified on axially-compressed columns, packed with SiO_2 25−40 μm (Macherey−Nagel), connected to a Gilson solvent delivery system and to a Gilson refractive index detector, and eluted with *n*-hexane/ethyl acetate mixtures. − ^{1}H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra ($CDCl_3$, unless otherwise stated; TMS as internal standard) were recorded with a Bruker AM 200 spectrometer. − IR spectra were recorded with a Nicolet 5DX FT/IR spectrometer. − MS spectra were recorded with a Hewelett−Packard HP 5980A spectrometer equipped with a Data System 5934A.

(*E*)-17-β-Acetoxy-3-[1,2-diphenylethenyl]androsta-3,5-diene (3′m): M.p. 155°C (dec.). − IR (KBr): ṽ = 1729 cm^{-1}, 1253, 773, 760, 703, 691. − ^{1}H NMR: δ = 7,43−7,25 (m, 3 H), 7,22−6,85 (m, 4 H), 6.80−6.60 (m, 2 H), 6.67 (s, 1 H), 5.65 (s, 1 H), 5.31 (s, 1 H), 4.61 (t, *J* = 7.1 Hz, 1 H), 2.01 (s, 3 H), 0.98 (s, 3 H), 0.82 (s, 3 H). − ^{13}C NMR: δ = 171.4, 143.7, 142.4, 139.9, 137.6, 136.1, 130.5, 130.2, 129.4, 128.6, 127.9, 127.0, 126.2, 125.6, 125.2, 82.8, 51.3, 48.3, 42.6, 36.8, 34.9, 34.2, 31.7, 31.6, 27.6, 23.7, 23.5, 21.3, 20.7, 19.2, 12.2. − MS; *m/z* (%): 492 (100) [M^+], 217 (11). − $C_{35}H_{40}O_2$: calcd. C 85.31, H 8.19; found C 85.47, H, 8.12.

17-β-Acetoxyandrosta-3,5-diene (4m): M.p. 61−63°C. − IR (KBr): ṽ = 1737 cm^{-1}, 1253, 1056 − ^{1}H NMR: δ = 5.93 (d, J = 9,8 Hz, 1 H), 5.70−5.51 (m, 1 H), 5.43−5.31 (m, 1 H), 4.61 (t, *J* = 8.1 Hz, 1 H), 2.05 (s, 3 H), 0.96 (s, 3 H), 0.83 (s, 3 H). − ^{13}C NMR: δ = 171.4, 141.6, 128.3, 125.2, 122.7, 82.9, 51.3, 48.4, 42.6, 36.8, 35.3, 33.8, 31.6, 31.3, 27.6, 23.5, 23.0, 21.3, 20.9, 20.5, 19.3, 18.9, 12.1. − $C_{21}H_{30}O_2$: calcd. C 80.20, H 9.62; found: C 80.10, H 9.50.

Spiro Compound 5m: M.p. 160°C (dec.). − IR (KBr): ṽ = 1734 cm^{-1}, 1247, 1028, 760, 696. − ^{1}H NMR: δ = 7.31−6,75 (m, 20 H), 6.16 (d, *J* = 9.6 Hz, 1 H), 5.54 (d, *J* = 9.6, 1 H), 5. 31 (s, 1 H), 4.56 (t, *J* = 7.2 Hz, 1 H), 1.99 (s, 3 H), 0.74 (s, 3 H), 0.65 (s, 3 H). − ^{13}C NMR: δ = 171.3, 151.1, 150.2, 146.9, 145.8, 142.3, 141.4, 137.6, 136.8, 136.0, 135.7, 130.9, 130.2, 130.1, 130.0, 129.1, 129.2, 127.6, 127.4, 127.2, 126.7, 126.6, 126.3, 126.2, 123.6, 77.3, 62.4, 50.8, 48.9, 43.3, 42.5, 36.8, 35.8, 33.8, 29.7, 29.4, 27.5, 21.2, 17.2, 14.2, 12.1. − MS; *m/z* (%): 668, (72) [M^+], 382 (15), 105 (87), 91 (100). − $C_{49}H_{48}O_2$: calcd. C 87.98, H 7.24; found C 87.90, H 7.26.

1-(*p*-Acetamidophenyl)-3,3-dimethyl-1-butyne (2a): M.p. 171−172°C. − IR (KBr): ṽ = 3244 cm^{-1}, 1667, 835. − ^{1}H NMR δ = 7.85 (br. s, 1 H), 7.43 (d, *J* = 8.6 Hz, 2 H), 7.30 (d, *J* = 8.6 Hz, 2 H), 2.13 (s, 3 H), 1.31 (s, 9 H). − ^{13}C NMR: δ = 168.1, 137.5, 132.2, 119.8, 119.5, 98.0, 78.3, 31.1, 27.4, 26.1. − MS; *m/z* (%): 215 (60) [M^+], 200 (48), 158 (100). − $C_{14}H_{17}NO$: calcd. C 78.09, H 7.96, N 6.51; found C 78.25, H 7.90, N 6.76.

2-Methyl-4-phenyl-3-butyn-2-ol (2b): Oil. − IR (KBr): ṽ = 3400 cm^{-1}, 2205, 760. − ^{1}H NMR: δ = 7.55−7.40 (m, 2 H), 7.38−7.20 (m, 3 H), 3.05 (br. s, 1 H), 1.75 (s, 6 H). − ^{13}C NMR: δ = 132.3, 128.9, 123.4, 117.8, 94.6, 82.8, 66.6, 32.1; MS (CI); *m/z* (%): 161 (16) [M^+ + 1], 143 (100). − $C_{11}H_{12}O$: calcd. C 82.45, H 7.55; found C 82.55, H 7.52.

4-(*p*-Methoxyphenyl)-2-methyl-3-butyn-2-ol (2c): M.p. 33−35°C. − IR (KBr): ṽ = 3500 cm^{-1}, 2223, 770. − ^{1}H NMR: δ = 7.36 (dd, *J* = 6.0 Hz, *J* = 1.4 Hz, 1 H), 7.26 (dt, *J* = 6.0 Hz, *J* = 1.4 Hz, 1 H), 6.90−6.75 (m, 2 H), 3.85 (s, 3 H), 3.05 (br. s, 1 H), 1.63 (s, 6 H). − ^{13}C NMR: δ = 159.7, 133.5, 129.6, 120.3, 111.6, 110.6, 98.1, 78.2, 65.5, 55.7, 31.4. − MS; *m/z* (%): 190 (65) [M^+], 175 (100). − $C_{12}H_{14}O_2$: calcd. C 75.75, H 7.42; found C, 75.84; H, 7.40.

4-(*p*-Acetoxyphenyl)-2-methyl-3-butyn-2-ol (2d): M.p. 59−60°C. − IR (KBr): $\tilde{\nu}$ = 3397 cm^{-1}, 2221, 1762, 785. − ^{1}H NMR: δ = 7.41 (d, *J* = 8.4 Hz, 2 H), 7.03 (d, *J* = 8.4 Hz, 2 H), 2.65 (br. s, 1 H), 2.29 (s, 3 H), 1.60 (s, 6 H). − ^{13}C NMR: δ = 169.2, 150.4, 132.8, 121.6, 120.4, 93.9, 81.6, 65.5, 31.4, 21.1. − MS; *m/z* (%): 218 (5) [M^{+}], 161 (94), 118 (100). − $C_{13}H_{14}O_3$: calcd. C 71.53, H 6.47; found C 71.54, H, 6.39.

4-(*o*-Acetamidophenyl)-2-methyl-3-butyn-2-ol (2e): M.p. 95−97°C. − IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1}, 1673, 759. − ^{1}H NMR: δ = 8.35 (d, *J* = 8.0 Hz, 1 H), 8.01 (d, *J* = 7.2 Hz, 1 H), 7.43−7.20 (m, 2 H), 7.01 (t, *J* = 7.2 Hz, 1 H), 3.30 (br. s, 1 H), 2.21 (s, 3 H), 1.68 (s, 6 H). − ^{13}C NMR: δ = 168.5, 138.9, 131.5, 129.6, 123.4, 119.6, 111.6, 101.6, 77.3, 65.6, 31.5, 24.7. − MS; *m/z* (%): 217 (1) [M^{+}], 117 (100). − $C_{13}H_{15}NO_2$: calcd. C 71.85, H, 6.96; found C 71.80, H 6.87.

4-(*o*-Acetoxyphenyl)-2-methyl-3-butyn-2-ol (2f): Oil. − IR (KBr): $\tilde{\nu}$ = 3415 cm^{-1}, 1765, 760. − ^{1}H NMR: δ = 7.44 (dd, *J* = 8.1 Hz, *J* = 1.4 Hz, 1 H), 7.32 (td, *J* = 7.8 Hz, *J* = 1.8 Hz, 1 H), 7.17 (td, *J* = 7.5 Hz, *J* = 1.3 Hz, 1 H), 7.06 (dd, *J* = 8.0 Hz, *J* = 1.0 Hz, 1 H), 3.11 (br. s, 1 H), 2.32 (s, 3 H), 1.58 (s, 6 H). − ^{13}C NMR: δ = 169.7, 152.2, 133.6, 130.1, 126.5, 122.7, 117.5, 99.6, 76.9, 66.1, 31.9, 21.5. − MS; *m/z* (%):218 (1) [M^{+}], 158 (100). − $C_{13}H_{14}O_3$: calcd. C 71.53, H 6.47; found C 71.36, H 6.66.

1-(*p*-Acetylphenyl)-2-(p-methoxyphenyl)acetylene (2g): M.p. 120−122°C. − IR (KBr): $\tilde{\nu}$ = 2233 cm^{-1}, 1671, 820. − ^{1}H NMR: δ = 7.91 (d, *J* = 8.6 Hz, 2 H), 7.57 (d, *J* = 8.6 Hz, 2 H), 7.48 (d, *J* = 8.8 Hz, 2 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 3.82 (s, 3 H), 2.59 (s, 3 H). − ^{13}C NMR: δ = 197.4, 160.1, 135.8, 133.3, 131.5, 128.6, 128.3, 114.7, 114.1, 93.0, 87.6, 55.3, 26.6. − MS; *m/z* (%): 250 (97) [M^{+}], 235 (100). − $C_{17}H_{14}O_2$: calcd. C 81.57, H 5.64; found C 81.35, H 5.79.

2-(*p*-Acetylphenyl)-1-phenylacetylene (2h): M.p. 94−96°C. − IR (KBr): $\tilde{\nu}$ = 2205 cm^{-1}, 1680, 834, 761. − ^{1}H NMR: δ = 7.89 (d, *J* = 8.2 Hz, 2 H), 7.60−7.45 (m, 4 H), 7.40−7.25 (m, 3 H), 2.55 (s, 3 H). − ^{13}C NMR: δ = 197.2, 136.2, 131.8, 131.7, 128.8, 128.5, 128.3, 128.1, 122.8, 92.7, 88.7, 26.6. − MS; *m/z* (%): 220 (100) [M^{+}], 205 (100), 176 (51). − $C_{16}H_{12}O$: calcd. C 87.24, H 5.50; found C 87.33, H 5.45.

2-(*p*-Methoxyphenyl)-1-phenylacetylene (2i): M.p. 50−51°C. − IR (KBr): $\tilde{\nu}$ = 2221 cm^{-1}, 834, 753, 710. − ^{1}H NMR: δ = 7.60−7.42 (m, 4 H), 7.41−7.35 (m, 3 H), 7.86 (d, *J* = 7.0 Hz, 2 H), 3.79 (s, 3 H). − ^{13}C NMR: δ = 159.6, 133.1, 131.5, 128.3, 128.0, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3. − MS; *m/z* (%): 208 (100) [M^{+}], 193 (56), 165 (50). − $C_{15}H_{12}O$: calcd. C 86.50, H 5.81; found C 86.60, H 5.85.

Methyl 3-(1-Hydroxycyclohexyl)-2-propynoate (10a): M.p. 55−57°C. − IR (KBr): $\tilde{\nu}$ = 3279 cm^{-1}, 2237, 1712. − ^{1}H NMR: δ = 3.75 (s, 3 H), 2.70 (br. s, 1 H), 2.10−1.85 (m, 2 H), 1.80−1.40 (m, 8 H). − ^{13}C NMR: δ = 160.1, 97.0, 81.5, 58.8, 45.1, 30.9, 28.9. − MS (CI); *m/z* (%): 183 (2) [M^{+} + 1], 165 (100). − $C_{10}H_{14}O_3$: calcd. C 65.90, H 7.75; found C 65.81, H 7.86.

Methyl 4-Hydroxy-4-methyl-2-butynoate (10b): Oil. − IR (KBr): $\tilde{\nu}$ = 3250 cm^{-1}, 2230, 1715. − ^{1}H NMR: δ = 3.78 (s, 3 H), 3.55 (br. s, 1 H), 1.58 (s, 6 H). − ^{13}C NMR: δ = 154.7, 92.4, 74.1, 65.3, 53.4, 31.0. − MS; *m/z* (%): 142 (10) [M^{+}], 125 (100). − $C_7H_{10}O_3$: calcd. C 59.13, H 7.09; found C 59.19, H 7.01.

1-(2-Thiazolyl)-1-heptyne (2j): Oil. − IR (KBr): $\tilde{\nu}$ = 2229 cm^{-1}, 1482, 1132. − ^{1}H NMR: δ = 7.75 (d, *J* = 3.4 Hz, 1 H), 7.27 (d, *J* = 3.4 Hz, 1 H), 2.45 (t, *J* = 7.0 Hz, 2 H), 1.63 (q, *J* = 7.0 Hz, 2 H), 1.53−1.21 (m, 4 H), 0.91 (t, *J* = 7.3 Hz, 3 H). − ^{13}C NMR: δ = 149.4, 142.9, 119.7, 96.3, 74.0, 31.0, 27.6, 22.1, 19.4, 13.9. − MS; *m/z* (%): 179 (25) [M^{+}], 136 (100). − $C_{10}H_{13}NS$: calcd. C 67.01, H 7.32, N 7.82; found C 67.12, H 7.26, N 7.99.

Typical Procedure for the Palladium-Catalyzed Hydrovinylation of Alkynes. − Preparation of 3-(4-Phenylcyclohex-1-enyl)-1-oxaspiro[4.5]dec-3-en-2-one (11a): See also Table 2, entry 1. To a stirred solution of **1a** (0.150 g, 0.49 mmol) and **10a** (0.107 g, 0.59 mmol) in DMF (2 mL), were added HCOOK (0.082 g, 0.98 mmol) and $Pd(OAc)_2$ (0.005 g, 0.024 mmol) under argon. The mixture was stirred at 40°C for 7 h. It was then cooled at room temperature, diluted with ethyl acetate, and washed with water. The organic layer was dried (Na_2SO_4) and evaporated under vacuum and the residue was purified by chromatography on silica gel, eluted with a *n*-hexane/EtOAc, 90:10 (v/v) mixture to afford 0.112 g of **11a** (74% yield) as a white solid: m.p. 139−141°C. − IR(KBr): $\tilde{\nu}$ = 1737 cm^{-1}, 834, 760, 695. − ^{1}H NMR: δ = 7.40−7.12 (m, 6 H), 7.10 (s, 1 H), 2.70−2.45 (m, 1 H), 2.6−1.2 (m, 16 H). − ^{13}C NMR: δ = 171.72, 149.86, 148.85, 130.57, 130.46, 128.97, 127.55, 127.34, 126.72, 85.2, 39.90, 35.58, 34.24, 29.96, 27.53, 25.20, 23.08. − (MS); *m/z* (%): 308 (100) [M^{+}], 290 (25), 263 (30), 204 (58), 185 (96). − $C_{21}H_{24}O_2$: calcd. C 81.77, H 7.85; found C 81.86, H 7.81.

(*Z*)-1-(*p*-Acetamidophenyl)-3,3-dimethyl-1-(4-phenylcyclohex-1-enyl)-1-butene (3′a): M.p. 115−117°C. − IR: $\tilde{\nu}$ = 3297 cm^{-1}, 1678, 814, 760, 700. − ^{1}H NMR: δ = 8.13 (s, 1 H), 7.51 (d, *J* = 8.3 Hz, 2 H), 7.31−7.18 (m, 4 H), 7.05 (d, *J* = 8.3 Hz, 2 H), 5.71 (s, 1 H), 5.19 (br. s, 1 H), 2.90−2.70 (m, 1 H), 2.18 (s, 3 H), 2.60−1.60 (m, 6 H), 0.87 (s, 9 H). − ^{13}C NMR: δ = 168.9, 147.1, 139.8, 139.3, 136.6, 136.5, 136.3, 131.0, 128.4, 126.9, 126.8, 126.1, 118.9, 40.1, 34.5, 33.5, 31.7, 30.3, 27.0, 24.6. − MS; *m/z* (%): 373 (97) [M^{+}], 235 (100), 193 (76). − $C_{26}H_{31}NO$: calcd. C 83.59, H 8.37, N 3.75; found C 83.50, H 8.31, N, 3.83.

(*Z*)-3-Methyl-1-phenyl-1-(4-phenylcyclohex-1-enyl)-1-buten-3-ol (3′b): M.p. 110−112°C. − IR (KBr): $\tilde{\nu}$ = 3486 cm^{-1}, 814, 756, 705. − ^{1}H NMR: δ = 7.57 (m, 10 H), 5.75 (s, 1 H), 5.23 (br. s, 1 H), 2.90−2.70 (m, 1 H), 2.70−1.50 (m, 7 H), 1.18 (s, 6 H). − ^{13}C NMR: δ = 146.7, 140.6, 139.3, 138.3, 132.7, 131.6, 129.9, 128.4, 128.2, 127.1, 126.7, 126.0, 71.7, 39.8, 34.3, 31.6, 30.1, 26.7. − MS; *m/z* (%): 318 (1) [M^{+}], 300 (32), 182 (100). − $C_{23}H_{26}O$: calcd. C 86.74, H 8.23; found C 86.61, H 8.27.

(*Z*)-1-(*p*-Methoxyphenyl)-3-methyl-1-(4-phenylcyclohex-1-enyl)-1-buten-3-ol (3′c): M.p. 74−76°C. − IR (KBr): $\tilde{\nu}$ = 3456 cm^{-1}, 750, 707. − ^{1}H NMR: δ = 7.40−7.11 (m, 6 H), 7.10−6.81 (m, 3 H), 5.93 (s, 1 H), 5.28 (br. s, 1 H), 3.82 (s, 3 H), 2.90−2.71 (m, 1 H), 2.60−1.64 (m, 7 H), 1.25 (s, 6 H). − ^{13}C NMR: δ = 156.6, 146.9, 137.5, 137.4, 132.9, 131.5, 128.7, 128.3, 126.8, 126.0, 120.4, 111.0, 70.9, 55.6, 39.8, 34.2, 31.4, 30.1, 21.0. − MS; *m/z* (%): 348 (2) [M^{+}], 330 (51), 175 (100). − $C_{24}H_{28}O_2$: calcd. C 82.71, H 8.10; found C 82.83, H 8.02.

(*Z*)-1-(*p*-Acetoxyphenyl)-3-methyl-1-(4-phenylcyclohex-1-enyl)-1-buten-3-ol (3′d): M.p. 102−104°C. − IR(KBr): $\tilde{\nu}$ = 3463 cm^{-1}, 1752, 821, 745, 698. − ^{1}H NMR: δ = 7.50−7.00 (m, 9 H), 5.88 (s, 1 H), 5.27 (br. s, 1 H), 2.80−2.61 (m, 1 H), 2.48−1.51 (m, 7 H), 2.21 (s, 3 H), 1.21 (s, 6 H). − ^{13}C NMR: δ = 169.2, 149.6, 146.6, 139.8, 138.3, 136.8, 133.3, 132.7, 130.9, 128.4, 126.7, 126.0, 120.9, 71.6, 39.8, 34.2, 31.5, 30.0, 26.7, 21.0. − MS; *m/z* (%): 376 (1) [M^{+}], 357 (29), 314 (100). − $C_{25}H_{28}O_3$: calcd. C 79.74, H 7.50; found C 79.62, H 7.60.

(*Z*)-1-(*o*-Acetamidophenyl)-3-methyl-1-(4-phenylcyclohex-1-enyl)-1-buten-3-ol (3′e): M.p. 128−130°C. − IR (KBr): $\tilde{\nu}$ = 3402 cm^{-1}, 1687, 819, 760, 700. − ^{1}H NMR: δ = 8.00 (m, 1 H), 7.57 (br. s, 0.5 H), 7.50 (br. s, 0.5 H), 7.45−7.01 (m, 8 H), 5.99 (s, 0.5 H), 5.94

(s, 0.5 H), 5.28 (br. s, 1 H), 3.00−2.71 (m, 2 H), 2.50−1.81 (m, 6 H), 2.09 (s, 1.5 H), 2.03 (s, 1.5 H), 1.25 (s, 3 H), 1.18 (s, 3 H). − ^{13}C NMR (selected signals): δ = 168.6, 146.3 and 146.2, 122.3 and 122.1, 71.2, 39.7 and 39.3. − MS; *m/z* (%): 375 (2) [M$^+$], 203 (50), 161 (100). − $C_{25}H_{29}NO_2$: calcd. C 79.95, H 7.79, N 3.73; found C 79.83, H 7.75, N 3.81.

(*Z*)-1-(*o*-Acetoxyphenyl)-3-methyl-1-(4-phenylcyclohex-1-enyl)-1-buten-3-ol (3′f): M.p. 79−81°C. − IR (KBr): ṽ = 3505 cm^{-1}, 1734, 826, 754, 701. − ^{1}H NMR: δ = 7.35−7.04 (m, 8 H), 7.01 (d, *J* = 5.8 Hz, 1 H), 5.80 (s, 0.5 H), 5.77 (s, 0.5 H), 5.48−5.26 (m, 1 H), 2.90−2.61 (m, 1 H), 2.50−1.71 (m, 7 H), 2.21 (s, 1.5 H), 2.19 (s, 1.5 H), 1.25 (s, 3 H), 1.23 (s, 3 H). − ^{13}C NMR (selected signals): δ = 170.00, 146.6 and 146.5, 133.2 and 133.1, 71.3, 39.7 and 39.6. − MS; *m/z* (%): 376 (3) [M$^+$], 358 (80), 301 (100). − $C_{25}H_{28}O_3$: calcd. C 79.74, H 7.50; found C 79.63, H 7.45.

(*Z*)-1-(*p*-Acetylphenyl)-2-(*p*-methoxyphenyl)-2-(4-phenylcyclohex-1-enyl)ethene (3′g) and (*Z*)-1-(*p*-Acetylphenyl)-2-(*p*-methoxyphenyl)-1-(4-phenylcyclohex-1-enyl)ethene (3′′g): Obtained as a 65:35 regioisomeric mixture. − IR: ṽ = 1682 cm^{-1}, 833, 750, 698. − ^{1}H NMR: δ = 7.96 (d, *J* = 8.0 Hz, 0.7 H), 7.67 (d, *J* = 8.4 Hz, 1.3 H), 7.37−7.20 (m, 6.05 H), 7.04 (d, *J* = 10.0 Hz, 1.3 H), 6.97−6.86 (m, 2.6 H), 6.75 (d, *J* = 8.8 Hz, 0.7 H), 6.63−6.58 (m, 1.35 H), 5.67 (br. s, 0.65 H), 5.43 (br. s, 0.35 H), 3.85 (s, 1.95 H), 3.72 (s, 1.05 H), 2.83−2.77 (m, 1 H), 2.64−1.60 (m, 6 H), 2.64 (s, 1.05 H), 2.57 (s, 1.95 H). − ^{13}C NMR (selected signals): δ = 198.0 (**3′g**), 197.7 (**3′′g**), 158.9 (**3′′g**), 158.3 (**3′g**), 114.1 (**3′′g**), 113.3 (**3′g**), 55.3 (**3′′g**), 55.2 (**3′g**). − MS; *m/z* (%): 408 (100) [M$^+$], 289 (56).

(*Z*)-1-(*p*-Acetylphenyl)-2-(*p*-methoxyphenyl)-2-(3,3,5,5-tetramethylcyclohex-1-enyl)ethene (3′h) and (*Z*)-1-(*p*-Acetylphenyl)-2-(*p*-methoxyphenyl)-1-(3,3,5,5-tetramethylcyclohex-1-enyl)ethene (3′′h): Obtained as a 56:44 regioisomeric mixture. − IR: ṽ = 1680 cm^{-1}, 833, 750, 691. − ^{1}H NMR: δ = 7.92 (d, *J* = 8.3 Hz, 0.88 H), 7.67 (d, *J* = 8.4 Hz, 1.12 H), 7.24 (d, *J* = 8.3 Hz, 0.88 H), 7.03−6.54 (m, 6.12 H), 5.35 (br. s, 0.56 H), 5.13 (br. s, 0.44 H), 3.84 (s, 1.68 H), 3.71 (s, 1.32 H), 2.63 (s, 1.68 H), 2.51 (s, 1.32 H), 2.05−2.02 (m, 2 H), 1.38−1.35 (m, 2 H), 1.03 (s, 3.36 H), 1.02 (s, 2.64 H), 0.98 (s, 3.36 H), 0.96 (s, 2.64 H). − ^{13}C NMR (selected signals): δ = 197.8 (**3′′h**) and 193.3 (**3′h**), 154.5 (**3′h**) and 153.8 (**3′′h**), 109.6 (**3′h**) and 109.0 (**3′′h**), 50.8 (**3′h**) and 50.7 (**3′′h**). − MS; *m/z* (%): 388 (100) [M$^+$], 373 (78).

(*Z*)-1-(*p*-Acetylphenyl)-2-phenyl-2-(4-phenylcyclohex-1-enyl)ethene (3′i) and (*Z*)-1-(*p*-Acetylphenyl)-2-phenyl-1-(4-phenylcyclohex-1-enyl)ethene (3′′i): Obtained as a 65:35 regioisomeric mixture. − IR (KBr): ṽ = 1675 cm^{-1}, 831, 756, 699, 696. − ^{1}H NMR: δ = 8.02 (d, *J* = 8.0 Hz, 0.7 H), 7.65 (d, *J* = 8.0 Hz, 1.3 H), 7.41−6.85 (m, 12 H), 6.71 (s, 0.35 H), 6.66 (s, 0.65 H), 5.78 (br. s, 0.65 H), 5.59 (br. s, 0.35 H), 3.05−2.88 (m, 1 H), 2.70 (s, 1.05 H), 2.56 (s, 1.95 H), 2.81−1.79 (m, 6 H). − ^{13}C NMR (selected signals): δ = 197.9 (**3′′i**) and 197.5 (**3′i**), 142.8 (**3′′i**) and 142.7 (**3′i**), 30.1 (**3′i**) and 29.7 (**3′′i**). − MS; *m/z* (%): 378 (100) [M$^+$], 231 (61).

(*Z*)-1-(*p*-Methoxyphenyl)-2-phenyl-1-(4-phenylcyclohex-1-enyl)ethene (3′j) and (*Z*)-1-(*p*-Methoxyphenyl)-2-phenyl-2-(4-phenylcyclohex-1-enyl)ethene (3′′j): Obtained as an unseparable mixture with the starting 1-(*p*-methoxyphenyl)-2-phenylacetylene and the yields were calculated by ^{1}H NMR analysis. Selected ^{1}H NMR signals for the regioisomeric mixture are: δ = 5.60 (br. s, 0.52 H), 5.50 (br. s, 0.48 H), 3.78 (s, 1.56 H), 3.65 (s, 1.44 H).

(*E*)-2-(4-*tert*-Butylcyclohex-1-enyl)-1-(2-thiazolyl)-1-heptene (3′k) and (*E*)-1-(4-*tert*-Butylcyclohex-1-enyl)-1-(2-thiazolyl)-1-heptene (3′′k): Obtained as a 77:23 regioisomeric mixture. − IR (KBr): ṽ = 1591 cm^{-1}, 820, 798, 718. − ^{1}H NMR: δ = 7.79 (d, *J* = 4.1 Hz, 0.23 H), 7.75 (d, *J* = 4.0 Hz, 0.77 H), 7.34 (d, *J* = 4.1 Hz, 0.23 H), 7.23 (d, *J* = 4.0 Hz, 0.77 H), 6.75 (s, 0.77 H), 6.19−6.10 (m, 0.77 H), 5.83 (t, *J* = 7.4 Hz, 0.23 H), 5.42−5.31 (m, 0.23 H), 2.90−2.61 (m, 2 H), 2.51−1.23 (m, 16 H), 0.98 (s, 6.93 H), 0.90 (s, 2.07 H). − ^{13}C NMR: δ = 166.6, 165.9, 147.9, 142.7, 142.5, 137.2, 136.5, 135.7, 131.6, 128.0, 127.8, 119.3, 118.0, 116.9, 43.8, 43.7, 32.3, 32.2, 31.4, 29.5, 29.3, 29.2, 28.7, 28.0, 27.7, 27.4, 27.2, 24.4, 22.5, 14.1, 14.0. − MS; *m/z* (%): 317 (25) [M$^+$], 260 (100), 246 (61).

(*Z*)-1-(3,4-Dihydronapthyl)-1-phenyl-2-(trimethylsilyl)ethene (3′l): M.p. 58−60°C. − IR (KBr): ṽ = 1673 cm^{-1}, 834. − ^{1}H NMR: δ = 7.35−7.30 (m, 6 H), 7.20−7.14 (m, 2 H), 6.00 (s, 1 H), 5.97 (t, *J* = 6.2 Hz, 1 H), 2.81 (t, *J* = 8.0 Hz, 2 H), 2.41−2.28 (m, 2 H), −0.01 (s, 9 H). − ^{13}C NMR: δ = 143.5, 143.0, 137.0, 134.6, 131.6, 128.9, 128.4, 127.9, 127.8, 127.5, 127.4, 126.7, 126.2, 125.8, 30.4, 28.4, 0.3. − MS; *m/z* (%): 304 (29) [M$^+$], 231 (98), 230 (100). − $C_{21}H_{24}Si$: calcd. C 82.85, H 7.95; found C 82.72, H 8.01.

3-(4-*tert*-Butylcyclohex-1-enyl)-1-oxaspiro[4.5]dec-3-en-2-one (11b): M.p. 121−122°C. − IR (KBr): ṽ = 1737 cm^{-1}, 1647, 991. − ^{1}H NMR: δ = 7.11 (t, *J* = 2.5 Hz, 1 H), 7.04 (s, 1 H), 0.88 (s, 9 H). − ^{13}C NMR: δ = 171.2, 148.7, 130.8, 130.0, 126.9, 84.5, 43.4, 35.0, 32.0, 27.8, 27.1, 27.0, 24.6, 23.6, 22.5. − MS; *m/z* (%): 288 (28) [M$^+$], 231 (46), 190 (30), 145 (10). − $C_{19}H_{28}O_2$: calcd. C 79.11, H 9.79; found C 79.20, H 9.72.

3-(4-Ethoxycarbonyl-3-methyl-1,3-cyclohexadienyl)-1-oxaspiro[4.5]dec-3-en-2-one (11c): Oil. − IR (KBr): ṽ = 1745 cm^{-1}, 1704. − ^{1}H NMR: δ = 7.29 (s, 1 H), 7.22 (s, 1 H), 4.25 (q, *J* = 7.7 Hz, 2 H), 2.65−2.50 (m, 2 H), 2.45−2.25 (m, 2 H), 2.20 (s, 3 H), 1.80−1.50 (m, 4 H), 1.35 (t, *J* = 7.7 Hz, 3 H). − ^{13}C NMR: δ = 170.2, 168.1, 152.0, 142.6, 130.9, 130.8, 129.3, 129.0, 122.9, 85.0, 60.0, 34.9, 24.6, 24.5, 23.7, 22.4, 20.6, 14.2. − MS; *m/z* (%): 316 (59) [M$^+$], 271 (51), 243 (50), 197 (100), 189 (90), 188 (95). − $C_{19}H_{24}O_4$: calcd. C 72.11, H 7.65; found C 72.22, H 7.68.

Methyl (*E*)-2-(4-Ethoxycarbonyl-3-methyl-1,3-cyclohexadienyl)-3-(1-hydroxycyclohexyl)-2-propenoate (12c): Oil. − IR (liquid film): ṽ = 3517 cm^{-1}, 1696, 1253, 736. − ^{1}H NMR: δ = 6.88 (s, 1 H), 5.77 (s, 1 H), 4.21 (q, *J* = 7.3 Hz, 2 H), 3.73 (s, 3 H), 2.74−2.46 (m, 2 H), 2.43−2.26 (m, 2 H), 2.16 (t, *J* = 1.5 Hz, 3 H), 2.11 (br. s, 1 H), 1.77−1.43 (m, 10 H), 1.30 (t, *J* = 7.3 Hz, 3 H). − ^{13}C NMR: δ = 168.3, 167.2, 149.4, 141.7, 141.5, 131.6, 130.1, 121.9, 72.7, 60.1, 52.3, 38.5, 28.7, 25.2, 24.1, 21.5, 20.5, 14.4. − MS; *m/z* (%): 348 (4) [M$^+$], 298 (35), 225 (48), 197 (100). − $C_{20}H_{28}O_5$: calcd. C 68.93, H 8.10; found C 68.84, H 8.19.

3-(3,4-Dihydronaphtyl)-1-oxaspiro[4.5]dec-3-en-2-one (11d): M.p. 128−130°C. − IR (KBr): ṽ = 1737 cm^{-1}, 769. − ^{1}H NMR: δ = 7.35 (s, 1 H), 7.18−7.11 (m, 4 H), 6.68 (t, *J* = 4.8 Hz, 1 H), 2.77 (t, *J* = 7.5 Hz, 2 H), 2.42−2.35 (m, 2 H), 1.83−1.65 (m, 10 H). − ^{13}C NMR: δ = 171.8, 154.7, 136.8, 133.1, 131.7, 129.4, 128.5, 127.9, 127.4, 126.3, 124.0, 85.5, 35.1, 27.7, 24.7, 23.1, 22.6. − MS; *m/z* (%): 280 (97) [M$^+$], 235 (100), 193 (76). − $C_{19}H_{20}O_2$: calcd. C 81.39, H 7.19; found C 81.28, H 7.21.

5,5-Dimethyl-3-(3,3,5,5-tetramethylcyclohex-1-enyl)furan-2(5*H*)-one (11e): M.p. 90−92°C. − IR (KBr): ṽ = 1745 cm^{-1}, 1646, 966, 859. − ^{1}H NMR: δ = 7.02 (s, 1 H), 6.85 (s, 1 H), 1.92 (s, 2 H), 1.48 (s, 6 H), 1.35 (s, 2 H), 1.10 (s, 6 H), 0.98 (s, 6 H). − ^{13}C NMR: δ = 171.0, 150.0, 138.7, 130.3, 123.2, 82.6, 49.1, 39.9, 33.0, 31.2, 30.2, 29.6, 25.8. − MS; *m/z* (%): 248 (74) [M$^+$], 233 (100), 205 (70), 187 (89). − $C_{16}H_{24}O_2$: calcd. C 77.36, H 9.75; found C 77.44, H 9.80.

3-[3-Methoxy-1,3,5(10),16-estratetraen-17-yl]-5,5-dimethylfuran-2(5*H*)-one (11f): M.p. 136−138°C. − IR (KBr): ṽ = 1745 cm^{-1}, 1605. − ^{1}H NMR: δ = 7.20 (d, *J* = 8.3 Hz, 1 H), 7.16 (s, 1 H), 6.88 (t, J = 1.9 Hz, 1 H), 6.74−6.64 (m, 2 H), 3.78 (s, 3 H), 3.00−2.80 (m, 2 H), 1.50 (s, 6 H), 0.93 (s, 3 H). − ^{13}C NMR: δ = 171.9, 157.4, 148.8, 143.1, 137.9, 133.7, 132.4, 125.9, 125.0, 113.7, 111.4, 83.3, 55.5, 55.1, 47.6, 44.0, 37.0, 35.2, 31.6, 29.6, 27.6, 26.5, 25.8, 15.9. − MS; m/z (%): 378 (100) [M$^+$], 363 (35), 227 (27), 173 (69). − $C_{25}H_{30}O_3$: calcd. C 79.32, H 7.99; found C 79.41, H 7.84.

3-(17-β-Acetylandrosta-3,5-dien-3-yl)-5,5-dimethylfuran-2(5*H*)-one (11g): M.p. 225−227°C. − IR (KBr): ṽ = 1745 cm^{-1}, 1704, 1097. − ^{1}H NMR: δ = 7.32 (s, 1 H), 7.03 (s, 1 H), 5.72 (br. s, 1 H), 2.54 (t, J = 9.8 Hz, 1 H), 2.11 (s, 3 H), 1.50 (s, 6 H), 0.97 (s, 3 H), 0.68 (s, 3 H). − ^{13}C NMR: δ = 170.8, 149.7, 141.2, 130.5, 129.8, 128.1, 126.6, 82.7, 63.5, 56.9, 48.0, 31.5, 31.4, 25.8, 19.0, 13.2. − MS; m/z (%): 408 (100) [M$^+$], 393 (17), 218 (36). − $C_{27}H_{36}O_3$: calcd. C 79.36, H 8.89; found C 79.44, H 8.80.

3-(4-Ethoxycarbonyl-3-methyl-1,3-cyclohexadienyl)-5,5-dimethylfuran-2(5*H*)-one (11h): Oil. − IR (KBr): ṽ = 1745 cm^{-1}, 1704. − ^{1}H NMR: δ = 7.24 (s, 1 H), 7.22 (s, 1 H), 4.22 (q, J = 7.1 Hz, 2 H), 2.65−2.50 (m, 2 H), 2.56−2.51 (m, 2 H), 2.38−2.29 (m, 2 H), 2.21 (d, J = 1.6 Hz, 3 H), 1.51 (s, 6 H), 1.30 (t, J = 7.1 Hz, 3 H). − ^{13}C NMR: δ = 170.3, 168.2, 152.9, 142.7, 131.1, 130.7, 128.8, 123.0, 83.3, 60.2, 25.8, 24.7, 23.8, 20.7, 14.3. − MS; m/z (%): 276 (5) [M$^+$], 274 (46), 231 (49), 203 (100). − $C_{16}H_{20}O_4$: calcd. C 69.53, H 7.30; found C 69.46, H 7.36.

Methyl 4-Hydroxy-2-(4-ethoxycarbonyl-3-methyl-1,3-cyclohexadien-1-yl)-4-methyl-(*E*)-2-butenoate (12h): Oil. − IR (KBr): ṽ = 3484 cm^{-1}, 1716, 1695, 1256. − ^{1}H NMR: δ = 6.91 (s, 1 H), 5.79 (s, 1 H), 4.23 (q, J = 7.8 Hz, 2 H), 3.75 (s, 3 H), 2.71−2.29 (m, 4 H), 2.17 (s, 3 H), 1.65 (br. s, 1 H), 1.39 (s, 6 H), 1.28 (t, J = 7.8 Hz, 3 H). − ^{13}C NMR: δ = 168.3, 167.1, 149.4, 141.5, 141.1, 131.1, 130.1, 121.9, 71.7, 60.1, 52.3, 30.7, 28.5, 24.0, 20.5, 14.3. − MS; m/z (%): 308 (2) [M$^+$], 290 (10), 258 (24), 157 (100). − $C_{17}H_{24}O_5$: calcd. C 66.20, H 7.85; found C 66.31, H 7.87.

3-[2-(Ethoxycarbonyl)cyclopent-1-enyl]-5,5-dimethylfuran-2(5*H*)-one (11i): M.p. 65−66°C. − IR (KBr): ṽ = 1750 cm^{-1}, 1704, 1373. − ^{1}H NMR: δ = 7.37 (s, 1 H), 4.11 (q, J = 7.1 Hz, 2 H), 2.74 (t, J = 7.2 Hz, 4 H), 1.91 (quint., J = 7.2 Hz, 2 H), 1.48 (s, 6 H), 1.21 (t, J = 7.1 Hz, 3 H). − ^{13}C NMR: δ = 170.3, 165.3, 156.2, 140.9, 134.6, 127.9, 84.2, 60.2, 38.0, 34.5, 25.4, 21.7, 14.0. − MS; m/z (%): 250 (2) [M$^+$], 204 (100), 158 (84). − $C_{14}H_{18}O_4$: calcd. C 67.17, H 7.25; found C 67.10, H 7.23.

Lactone 11j: Oil. − IR (KBr): ṽ = 1769 cm^{-1}, 736. − ^{1}H NMR: δ = 7.41 (s, 1 H), 7.25−7.12 (m, 5 H), 6.74−6.63 (m, 3 H), 3.77 (s, 3 H), 2.89−2.74 (m, 4 H), 1.12 (s, 3 H). − ^{13}C NMR: δ = 171.9, 157.5, 152.9, 137.7, 136.8, 133.1, 131.8, 131.6, 128.5, 127.7, 127.3, 126.9, 126.4, 123.9, 113.8, 111.5, 95.9, 55.1, 50.4, 47.3, 43.6, 38.9, 33.6, 31.9, 29.6, 27.7, 27.3, 26.0, 23.4, 23.1, 14.9, 14.1. − MS; m/z (%): 466 (70) [M$^+$], 267 (34), 227 (100). − $C_{32}H_{34}O_3$: calcd. C 82.36, H 7.35; found C 82.46, H 7.38.

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[13] Only our model system required the slow addition of the alkyne component to achieve the best results. With all the other vinyl triflates, the reaction produced hydrovinylation derivatives or furan-2(5*H*)-ones according to the general procedure reported in the experimental section.

[14] The presence of a small amount (0.2 equiv.) of diphenylacetylene in the solution containing **1e**, HCOOK and Pd(OAc)$_2$ was found necessary to prevent (possibly by coordination to pal-

ladium) early precipitation of the catalyst, which was observed when diphenylacetylene was added slowly to a solution of **1e**, HCOOK and $Pd(OAc)_2$. The idea that the alkyne has a stabilizing effect on the catalyst under these phosphane-free conditions is further supported by the almost quantitative recovery of **1e** when it was subjected to HCOOK in the presence of $Pd(OAc)_2$. Premature precipitation of palladium occurred and no olefin derivative was formed.[11]

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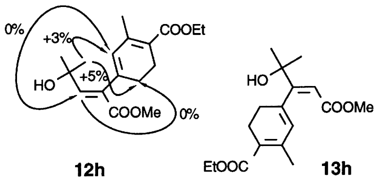
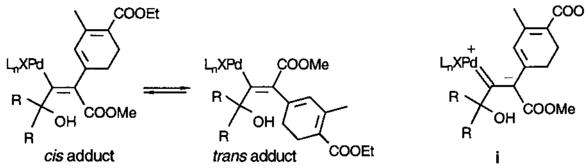
[20] The stereochemistry of the *trans* hydrovinylation products **12c** and **12h** has been assigned on the basis of NOE experiments. As an example, the relevant NOE effects for the determination of the stereochemistry of **12h**, presented by arrows, are as shown.



Scheme 6. Relevant NOE effects for the determination of the stereochemistry of **12h** and the stereoisomer **13h**

The regiochemistry of **12h** (compared to **13h**; the stereoisomer of **13h** would be expected to cyclize and none of the corresponding furan-2(5*H*)-one derivative was observed), has been assigned on the basis of NMR simulation, which gave the singlet of the vinyl proton β to the carbomethoxy group at $\delta = 6.94$ (in good agreement with the experimental value $\delta = 6.91$), and on the basis of all our previous work on this type of addition to propargylic alcohols in which the organic fragment has always added preferentially away from the tertiary alcoholic group.[14]

[21] A possible rationale for the appearance of the *trans* addition products **12c** and **12h** considers the *cis-trans* isomerization of carbopalladation intermediates through contributions from zwitterionic resonance forms of type **i**.



Scheme 7. *cis-trans* Isomerization of carbopalladation adducts **12c**, **12h** and resonance form **i**

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