

Stereospecific synthesis of allylic and homoallylic alcohols from functionalized propargylic alcohols

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Dedicated to my good friend Professor Udo H. Binker on the occasion of his 65th birthday

Abstract

1-Substituted 4,4,5,5-tetraethoxy-2-pentyn-1-ols undergo stereospecific reduction to allylic and homoallylic alcohols under the right conditions. Hydrogenation over Lindlar's catalyst gave the corresponding (*Z*)-allylic alcohols in excellent yield *provided potassium carbonate was added*. Reduction was also achieved with lithium aluminum hydride, but the product *appeared to be solvent and temperature dependent*. In THF at -15 °C the corresponding (*E*)-allylic alcohols were formed, in better than 70% yield from secondary propargylic alcohols, but below 60% from tertiary ones; in refluxing diethyl ether the products were the corresponding 1-substituted derivatives of homoallylic alcohol (*E*)-4,5,5-triethoxypent-3-en-1-ol, obtained in 93% yield in the best case.

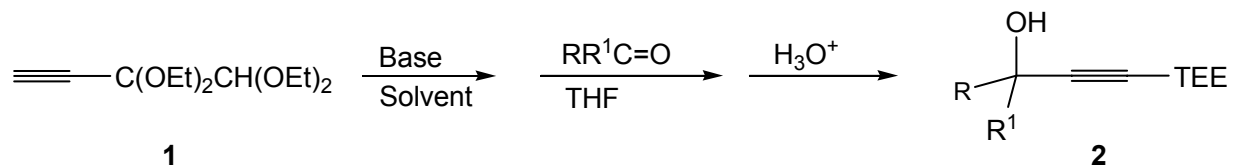
Keywords: Acetylide, propargylic alcohols, Lindlar hydrogenation, LAH reduction, allylic alcohols, homoallylic alcohols

Introduction

Recently we reported a high-yield synthesis of 3,3,4,4-tetraethoxybut-1-yne (**1**), denoted TEB.¹⁻³ In spite of the compound's polar and bulky 1,1,2,2-tetraethoxyethyl group (TEE) the corresponding propargylic alcohols (**2**) are obtained when TEB acetylide is generated with base in the usual way and subsequently treated with an aldehyde or a ketone. Generally the alcohols are formed in good to excellent yields, but there are, as expected,⁴⁻⁶ some exceptions (see experimental).

Alcohols **2** are somewhat special due to the TEE moiety which is sterically demanding, has a large number of oxygen atoms that can engage in complex formation, and contains ethoxy groups that can act as a leaving group under the right reaction conditions. Consequently, it is

quite conceivable that conversion of **2** to the corresponding (*Z*)- and (*E*)-allylic alcohols, by standard hydrogenation over Lindlar's catalyst and by treatment with lithium aluminum hydride, respectively, can be hampered by various effects caused by TEE. As reported here, that appeared indeed to be the case.



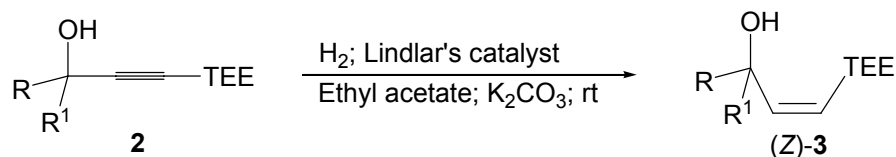
Scheme 1

Results and Discussion

(*Z*)-Allylic alcohols

Although hydrogenation over Lindlar's catalyst is generally a good method for the transformation of propargylic alcohols to the corresponding (*Z*)-allylic alcohols,⁷⁻⁹ the method has its limitations. If there are voluminous substituents close to the triple bond, the reaction rate may drop considerably and in some cases the conversion even fails completely. This is for instance the case with di-*t*-butylacetylene, which does not give the corresponding alkene at all when exposed to hydrogen under standard Lindlar conditions.¹⁰ (If the catalyst is changed to Raney nickel, however, hydrogenation takes place, but the corresponding alkene, 2,2,5,5-tetramethylhex-3-ene, obtained in 49% yield, has the *E* and not the *Z* configuration.¹⁰) Furthermore, if other functional groups are present next to the carbon-carbon multiple bond, most notably hydroxyl groups, halogen atoms, and carbon-sulfur single bonds, hydrogenolysis may occur to such an extent that the method becomes unsuitable.^{11,12}

On this basis it was quite reasonable to expect that propargylic alcohols **2**, with the large TEE group on one side of the triple bond and a 1-hydroxyalkyl group on the other would react sluggishly, and indeed, initially that turned out to be the case. Thus, exploratory experiments with some of the alcohols under normal Lindlar conditions revealed that neither alkene formation nor hydrogenolysis occurred, not even when 4,4,5,5-tetraethoxypent-2-yn-1-ol (**2a**), with the least sterically hindered triple bond in the series, was exposed to hydrogen for more than a week. Variation of the temperature, the solvent (methanol, ethanol, hexane, acetone, and ethyl acetate), concentrations, and the stirring speed had no major impact on the outcome of the reaction, but *when a small amount of potassium carbonate was added*^{12,13} to a stirred suspension of the Lindlar catalyst in a solution of **2a** in ethyl acetate, reduction of the triple bond took place, albeit at a slow rate, and furnished the corresponding allylic alcohol (*Z*)-4,4,5,5-tetraethoxypent-2-en-1-ol ((*Z*)-**3a**). No products due to hydrogenolysis were detected.



Scheme 2

On the basis of these observations the way the hydrogen was added to the suspension was studied. When the gas was introduced into the flask through a glass tube just *above the stirred suspension* (method 1), days were required to achieve complete conversion even of the most reactive alcohols. However, when hydrogen was bubbled directly *into the suspension* just above the stirring bar (method 2), the reaction was much faster and even hindered propargylic alcohols gave the corresponding allylic alcohols.

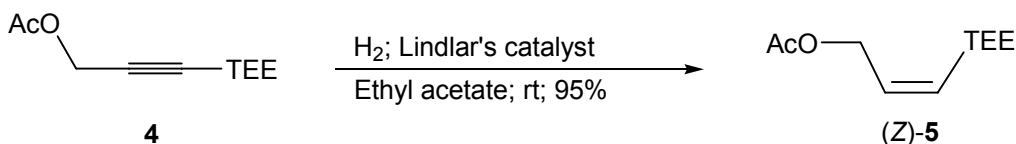
Based on these findings eight propargylic alcohols were hydrogenated using the two methods outlined above (for details, see Experimental). The results, compiled in Table 1, show that all the alcohols were converted to the corresponding (*Z*)-allylic alcohol in almost quantitative yield within a fairly short time (8 hours) when method 2 was applied. However, when hydrogenation was performed according to the less efficient method 1, reactivity differences became apparent. Thus, whereas 5,5,6,6-tetraethoxyhex-3-yn-2-ol (**2b**) was reduced quantitatively in 24 hours, the tertiary analogues (**2g** – **2i**) reacted more reluctantly and required up to three days of hydrogenation to achieve a good yield of the propargylic alcohol (Table 1). Another interesting observation was that the only primary propargylic alcohol investigated, 4,4,5,5-tetraethoxypent-2-yn-1-ol (**2a**), deviated from this trend and turned out to require about the same reaction time as the secondary analogues.

The *Z* configuration of the allylic alcohols was substantiated by inspection of the vicinal coupling constant ($^3J_{\text{HH}}$) across the C=C bond in their ¹H-NMR spectra. In every case this coupling constant was 14.1 Hz or smaller for the allylic alcohols obtained by hydrogenation of **2** over Lindlar's catalyst, and at the same time more than 1.8 Hz smaller than the corresponding 3J in the proton spectra of the corresponding (*E*)-allylic alcohols obtained by LAH reduction of **2** (*vide infra*). Based on the general and well documented observation that $^3J_{\text{trans}} > ^3J_{\text{cis}}$ for $^3J_{\text{HH}}$ across C=C bonds¹⁴ it was concluded that the allylic alcohols afforded by hydrogenation over Lindlar's catalyst exhibit *Z* stereochemistry.

Table 1. Conversion of propargylic alcohols **2** to the corresponding (*Z*)-allylic alcohols ((*Z*)-**3**) by hydrogenation over Lindlar's catalyst in ethyl acetate containing potassium carbonate

2	R, R ¹	Method	Reaction time (h)	Product	Isolated yield (%)
a	R=R ¹ =H	1	48	(Z)-3a	99
		2	3		91
b	R=H, R ¹ =methyl	1	24	(Z)-3b	99
		2	3		94
e	R=H, R ¹ =hexyl	1	24	(Z)-3e	99
		2	14		92
f	R=H, R ¹ =phenyl	1	48	(Z)-3f	99
		2	3		90
g	R=R ¹ =methyl	1	48	(Z)-3g	99
		2	16		91
h	R=R ¹ =ethyl	1	72	(Z)-3h	80
		2	5		90
i	R, R ¹ =(CH ₂) ₅ -	1	72	(Z)-3i	71
		2	4		89
j	R, R ¹ =(CH ₂) ₄ -	2	8	(Z)-3j	88

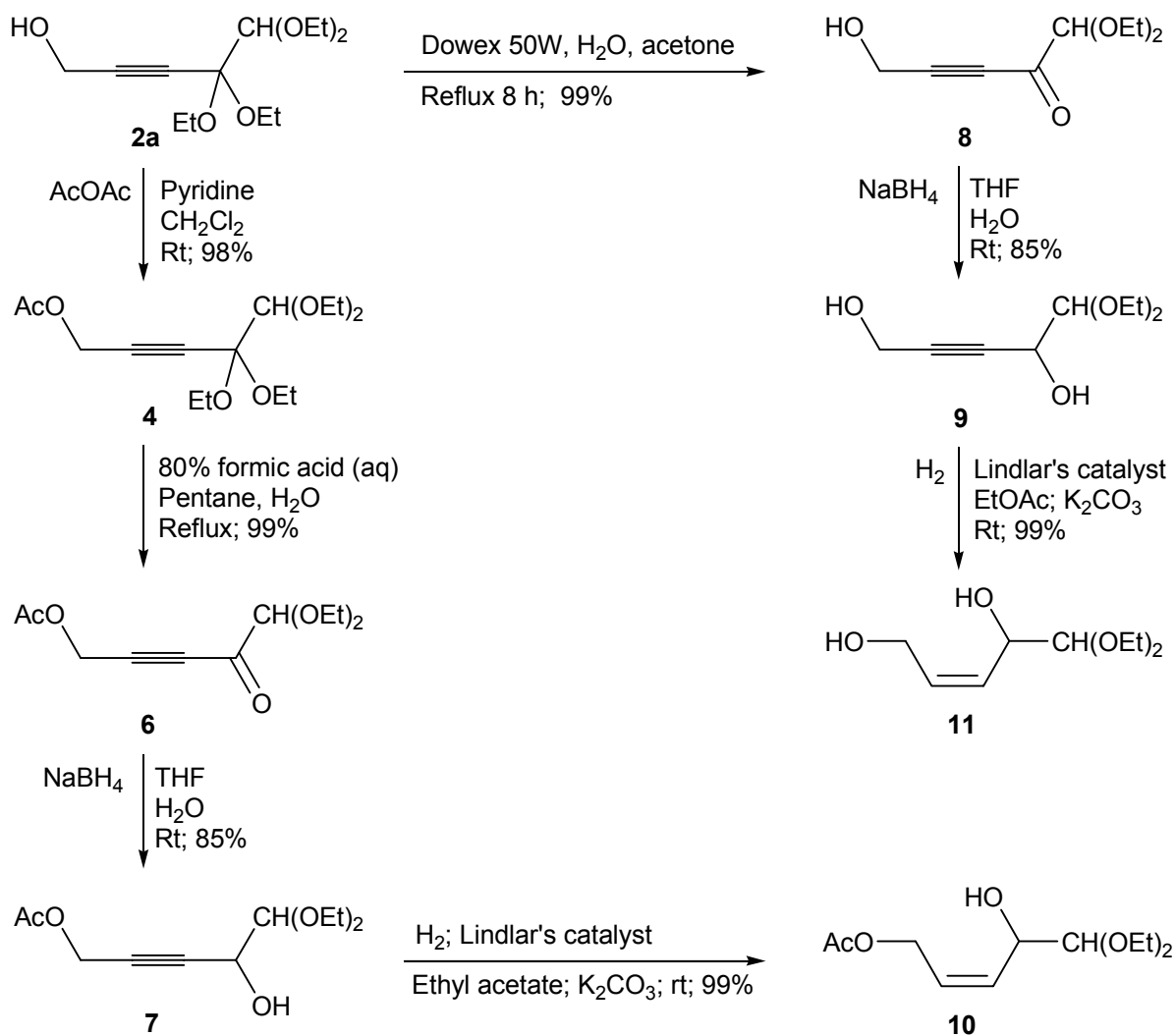
The observation that **2** was not hydrogenated in the absence of potassium carbonate indicates that the reactivity is strongly influenced by the hydroxyl group's ability to engage in hydrogen bonding. In order to test this hypothesis 4,4,5,5-tetraethoxypent-2-yn-1-ol (**2a**) was converted to the corresponding acetate, 4,4,5,5-tetraethoxypent-2-ynyl acetate (**4**), which was exposed to hydrogen in the presence of Lindlar's catalyst, but *in the absence of potassium carbonate* (Scheme 3), *i.e. conditions under which 2a does not react*. To our satisfaction ester **4** was consumed relatively quickly (complete consumption after 15 h) and afforded (*Z*)-4,4,5,5-tetraethoxypent-2-enyl acetate ((*Z*)-**5**) in 95% yield, and this clearly indicates that our line of reasoning is correct. This conclusion was further supported by hydrogenation of a 1:1 mixture of **2a** and **4** over Lindlar's catalyst *in the presence of potassium carbonate*. When the progress of the reaction was monitored by thin-layer chromatography, the acetate (**4**) appeared to react significantly faster than the alcohol, and furthermore, when **4** had been completely consumed and the reaction was quenched and worked up, the corresponding alkenes (*Z*)-**3a** and (*Z*)-**5** were isolated in a 1:5 ratio (see Experimental).



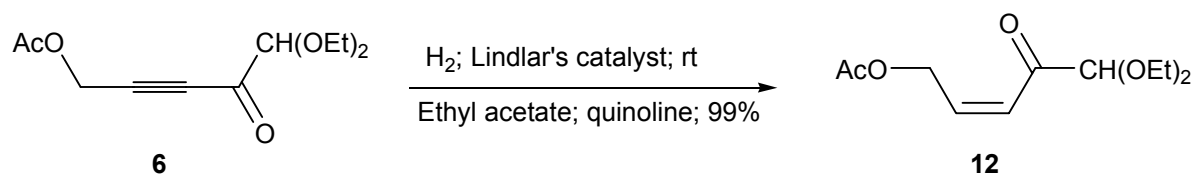
Scheme 3

Primary alcohol **2a** is significantly less sterically crowded around the OH group than the secondary and tertiary analogues (**2b - 2f** and **2g - 2j**, respectively), and the hydrogen-bonding effects should therefore be significantly more pronounced for **2a** than for the other alcohols. If the hydrogen-bonding effects contribute more to retard the hydrogenation than moderate steric effects, the rate of hydrogenation for **2a** should be similar to or smaller than for the secondary analogues. The results for compounds **2b - 2f** in Table 1 are in accordance with this line of thinking, but to test the hypothesis, 5,5-diethoxy-4-hydroxypent-2-ynyl acetate (**7**) and the corresponding “double propargylic” diol, 5,5-diethoxypent-2-yne-1,4-diol (**9**), were prepared as outlined in Scheme 4 and hydrogenated *in the presence of potassium carbonate* (method 2; see Experimental). Both **7** and **9** gave the corresponding (*Z*)-allylic alcohol, (*Z*)-5,5-diethoxy-4-hydroxypent-2-enyl acetate ((*Z*)-**10**) and (*Z*)-5,5-diethoxypent-2-ene-1,4-diol ((*Z*)-**11**), respectively, under these conditions, but the reaction appeared to be significantly slower for **9** than for **7**. In order to compare the relative reactivity more accurately a 1:1 mixture of **7** and **9** was hydrogenated over Lindlar’s catalyst in accordance with method 2. The progress of the reaction was monitored by thin-layer chromatography, and when the more reactive compound, **7**, had been completely consumed and the reaction was quenched and worked up, alkenes (*Z*)-**10** and (*Z*)-**11** were isolated in a 2:1 ratio (see Experimental) (Scheme 4).

The influence of the sterically demanding TEE group on the hydrogenation is difficult to assess from the results presented above, but an impression is obtained by comparing the rate of hydrogenation for acetates **4** and **6**. Both compounds give the corresponding *Z* alkene, (*Z*)-**5** and (*Z*)-5,5-diethoxy-4-oxopent-2-enyl acetate ((*Z*)-**12**) (Scheme 5), respectively, in high yield when hydrogenated in the absence of potassium carbonate, but the reaction appeared to be significantly slower for **4** than for **6**. In order to compare the relative reactivity more accurately a 1:1 mixture of **4** and **6** was hydrogenated over Lindlar’s catalyst in accordance with method 1. The progress was monitored by thin-layer chromatography, and when the more reactive compound, **6**, had been completely consumed and the reaction was quenched and worked up, alkenes (*Z*)-**5** and (*Z*)-**12** were isolated in a 1:8 ratio (see Experimental). Thus, the ketal moiety seems to slow down the reactivity of the triple bond a lot, although some of the difference is probably due to electronic influence of the carbonyl group, which is conjugated to the triple bond in **6**.



Scheme 4

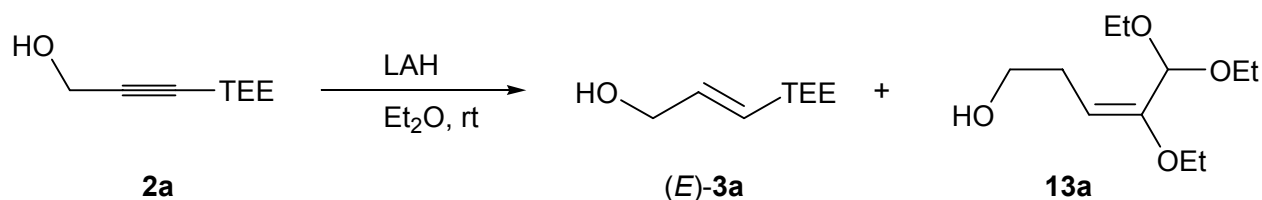


Scheme 5

(E)-Allylic alcohols

In order to convert **2** to the corresponding (*E*)-allylic alcohols **3** a standard procedure with literature precedence, *viz.* treatment with lithium aluminum hydride (LAH) in diethyl ether at room temperature,¹⁵ was applied first. When 4,4,5,5-tetraethoxy-2-yn-1-ol (**1a**) was reacted following this procedure, (*E*)-4,4,5,5-tetraethoxy-2-en-1-ol ((*E*)-**3a**) was obtained, but in

addition a significant amount of a by-product, homoallylic alcohol (*E*)-4,5,5-triethoxypent-3-en-1-ol (**13a**), was formed (Scheme 6). Studies of the literature revealed that formation of (*E*)-allylic alcohol has been favoured by lowering the reaction temperature,^{16,17} and sure enough, when **2a** was reacted with LAH at -15 °C, the yield of (*E*)-**3a** increased whereas the by-product formation dropped considerably. Even better results were obtained when the reaction at low temperature was repeated with THF as solvent;¹⁶ under these conditions **2a** gave (*E*)-**3a** only in almost quantitative yield (Table 3). Five other propargylic alcohols were reduced with LAH under the same conditions and in all cases the corresponding (*E*)-allylic alcohol was the only major product obtained. The secondary alcohols ((*E*)-**3b**, (*E*)-**3e**, and (*E*)-**3f**) were obtained in good to excellent yields, whereas the tertiary analogs ((*E*)-**3g** and (*E*)-**3h**) were obtained in 54% only (Table 2), conceivably reflecting the steric congestion around the hydroxyl group.



Scheme 6

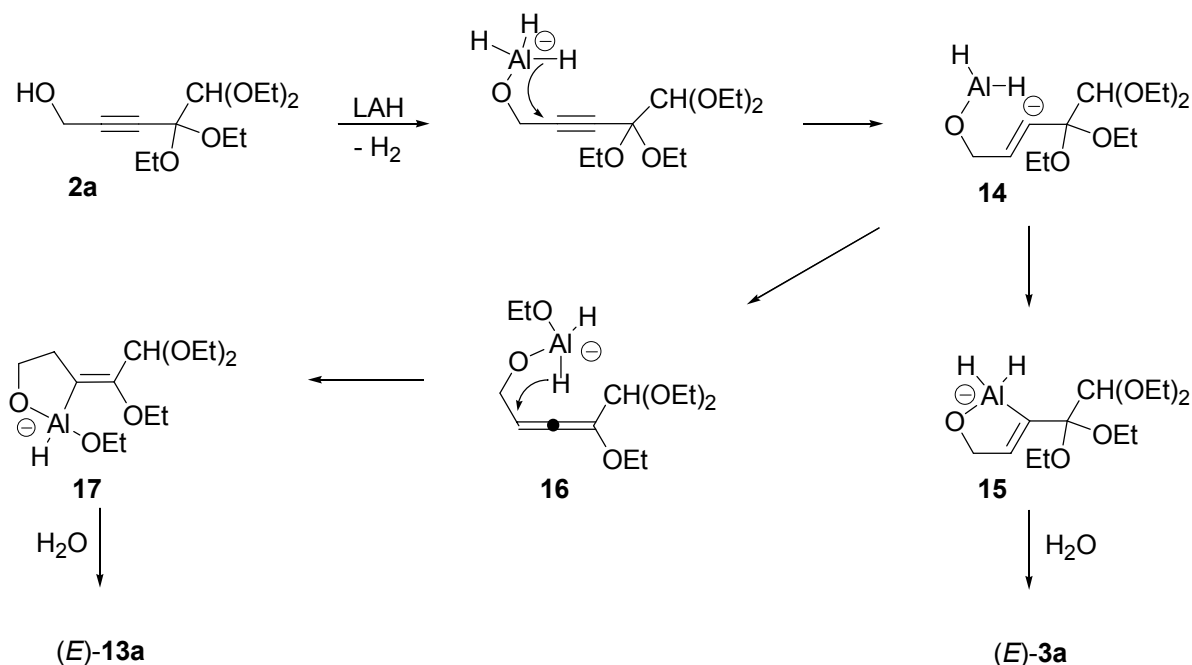
Table 2. Conversion of propargylic alcohols **2** to the corresponding (*E*)-allylic alcohols ((*E*)-**3**) by treatment with LAH in THF at -15 °C

2	R, R ¹	Product	Isolated yield (%)
a	R = R ¹ = H	(<i>E</i>)- 3a	98
b	R = H, R ¹ = methyl	(<i>E</i>)- 3b	93
e	R = H, R ¹ = hexyl	(<i>E</i>)- 3e	81
f	R = H, R ¹ = phenyl	(<i>E</i>)- 3f	72
g	R = R ¹ = methyl	(<i>E</i>)- 3g	54
h	R = R ¹ = ethyl	(<i>E</i>)- 3h	54

As pointed out previously the *E* configuration of the alcohols could in all cases be substantiated by the ¹H-NMR spectroscopy and inspection of the vicinal coupling constant (³J_{HH}) across the C=C bond because this ³J_{HH} was both large (> 15.6 Hz) and at the same time significantly larger than the corresponding coupling constant for the *Z* analogues (in the case of **3f** the difference was as much as 4.1 Hz; see Table 2).¹⁴

The concurrent formation of allylic alcohols (*E*)-**3** and homoallylic alcohols (*E*)-**13** can be accounted for by the mechanism outlined in Scheme 7, using propargylic alcohol **2a** as an example. Hydride attack of the triple bond to give carbanion **14** has solid literature support.¹⁸ This intermediate can undergo two transformations, either ring closure to form metallocycle **15**, as described by Borden and others,¹⁸ or expulsion of one of the ethoxy groups next to the anion

to give allene **16** in accordance with reports by Cowie, Claesson and co-workers.^{17,19} Based on literature precedence²⁰ **16** will undergo hydride transfer and ultimately form metallocycle **17** under the prevailing reaction conditions. Neither **15** nor **17** are stable under aqueous conditions;^{18,20} both are therefore cleaved upon hydrolysis and form (*E*)-**3a** and (*E*)-**13a**, respectively.



Scheme 7

Despite numerous reports of allene formation from propargylic alcohols with a leaving group attached to C-4,²¹ none of our experiments gave any indications of formation of such byproducts. NMR and IR spectroscopic techniques were used extensively to detect signals due to the allene moiety,²² but all attempts were unsuccessful.

Homoallylic alcohols

As reported above LAH reduction of 4,4,5,5-tetraethoxypent-2-yn-1-ol (**2a**) in diethyl ether at room temperature gave two products, mainly (*E*)-4,4,5,5-tetraethoxypent-2-en-1-ol ((*E*)-**3a**), but also some of homoallylic alcohol (*E*)-4,5,5-triethoxypent-3-en-1-ol ((*E*)-**13a**). The amount of the latter product decreased when the reaction temperature was lowered, and this, combined with the fact that (*E*)-**13a** formation is envisaged to go via allene intermediate **16** (Scheme 7) which reacts more effectively at elevated temperature,²⁰ triggered us to believe that homoallylic-alcohol formation could be rendered more favourable by running the LAH reduction in refluxing ether or at higher temperature in a different solvent. Small-scale experiments were performed with **2a** to test this prediction, and to our satisfaction **13a** turned out to be the only major product when the reduction was carried out in refluxing diethyl ether (bp 34 °C). Five propargylic alcohols were

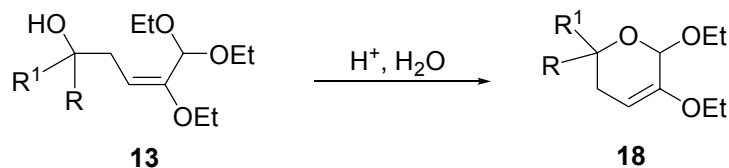
then reacted on a larger scale under the same conditions. All the compounds reacted similar to **2a**; the reaction was over in less than 20 minutes, and as seen from Table 3, the corresponding homoallylic alcohols were obtained in good to excellent yield after isolation by flash chromatography.

A noteworthy feature of the transformation is its stereospecificity, which in all cases led to formation of one isomer only, the *E* stereoisomer. The *E* configuration was substantiated by NOESY experiments, which gave spectra with significant cross peaks between the methine proton in the diethoxymethyl moiety and the protons in the methylene group on the other side of the C=C bond, but no cross peaks between the same methine proton and the olefinic proton.

Table 3. Conversion of propargylic alcohols **2** to the corresponding homoallylic alcohols **13** by LAH in refluxing diethyl ether

2	R, R ¹	Product	Isolated yield (%)
a	R = R ¹ = H	13a	70
b	R = H, R ¹ = methyl	13b	74
e	R = H, R ¹ = hexyl	13e	93
f	R = H, R ¹ = phenyl	13f	72
g	R = R ¹ = methyl	13g	54

A few words regarding the workup of the reaction mixtures are in place since the products contain acid-labile groups, *i.e.* an enol-ether moiety as well as an acetal function. If hydrolysis was carried out with an aqueous acid instead of water so that the hydrolysate remains acidic at the end, partial decomposition of the product takes place. Several products were detected, including dihydropyran **18** (Scheme 8), the formation of which is expected on the basis of the work of Newman.⁹ Similar reactions took place when **13** was purified by column chromatography with certain types of silica gel as the stationary phase (conceivably due to variable density and nature of acidic sites). These transformations are currently under investigation.



Scheme 8

Experimental Section

General Procedures. IR spectra were recorded on a Nicolet Impact 410 infrared spectrophotometer. NMR spectra were run on a Bruker Spectrospin AC 200 F or a Bruker Spectrospin DMX 400. Chemical shifts are reported downfield from TMS and coupling constants are given in Hz. GC analyses were performed on a HP 5890 Gas Chromatograph with a flame ionization detector and a HP Ultra 1 column (100% dimethyl-polysiloxane, 25 m, 0.2 mm i.d., 0.33 μ m). Flash chromatography was performed with Silica gel (230-400 mesh) as the stationary phase and mixtures of hexane and ethyl acetate as the mobile phase. Thin-layer chromatographic (TLC) analyses of the reaction mixtures were carried out with Silica gel (60 F₂₅₄) on aluminium sheets with mixtures of hexane and ethyl acetate as the mobile phase. Mass spectra were obtained on a VG 7070 Micromass spectrometer and an Autospec Ultima instrument, a three-sector instrument with EBE geometry from Micromass, both operated in the EI mode at 70 eV.

Chemicals. 3,3,4,4-Tetraethoxybut-1-yne (TEB) was synthesized from ethyl vinyl ether as described in the literature.² Ethylmagnesium bromide was prepared according to the literature, and the reagent's concentration was determined by titration following literature procedure.²³ All other chemicals and reagents, the syntheses of which are not described or referred to in this section, were commercially available from Aldrich and Fluka (now SigmaAldrich) and were, with the exception of some solvents, used without further purification. Ethanol, hexane, ethyl acetate, tetrahydrofuran (THF), and diethyl ether were dried and purified as described in the literature.²⁴

Synthesis of propargylic alcohols. General procedures

Method A. The reactions carried out with NaNH₂ generated *in situ* were performed following the procedure described by Furniss *et al.*²⁵ TEB (1.0 g, 4.3 mmol) was reacted with sodium amide prepared from Na (0.20 g, 8.7 mmol in all cases except one, the preparation of **2f**) and NH₃ (50 mL), the resulting acetylide was treated with 5.2 mmol of aldehyde or ketone, and the reaction was quenched by adding NH₄Cl (0.9 g, 0.17 mmol). The product was worked up by flash chromatography as specified for each alcohol.

Method B. The reactions performed with commercially available butyllithium as base were carried out following a procedure published by Brandsma.²⁶ The amounts of the reactants and butyllithium are specified for each alcohol.

Method C. The reactions with ethylmagnesium bromide as base were performed as follows: An ether solution of ethylmagnesium bromide (ca 1.2 equiv.) was added dropwise to a stirred solution of 3,3,4,4-tetraethoxybut-1-yne (TEB) (1.0 equiv.) in THF. When the addition was complete, the reaction mixture was stirred at reflux for 80 min and cooled to rt before aldehyde or ketone (ca 1.2 equiv.) was added dropwise. The resulting mixture was stirred at 35 °C for 3 h before it was cooled to rt and quenched by adding a saturated aqueous solution of NH₄Cl

(approximately 0.5 mL/mmol TEB). The mixture was extracted with dichloromethane (3 x 10 mL), and the combined organic phases were dried (MgSO₄), filtered, and concentrated *in vacuo* on a rotary evaporator. Finally, the product was isolated by flash chromatography.

4,4,5,5-Tetraethoxypent-2-yn-1-ol (2a). **Method A.** The TEB acetylide generated with NaNH₂ was reacted with paraformaldehyde (0.20 g, 5.2 mmol). Product isolation by flash chromatography (hexane-ethyl acetate, 70:30) gave **1a** (0.10 g, 7%). **Method B.** BuLi (2.7 mL, 1.6 M, 4.3 mmol), TEB (1.0 g, 4.3 mmol) in a mixture of diethyl ether (50 mL) and THF (25 mL), and paraformaldehyde (0.20 g, 6.6 mmol) were used. Isolation by flash chromatography (hexane-ethyl acetate, 80:20) gave **1a** (0.30 g, 25%). **Method C.** EtMgBr (15.9 mL, 3.0 M, 47.8 mmol), TEB (10.0 g, 43.4 mmol) in THF (80 mL), and paraformaldehyde (1.43 g, 47.8 mmol) were used. Isolation by flash chromatography (hexane-ethyl acetate, 70:30) gave **2a** (9.6 g, 85%) as a clear liquid.

2a. IR (film): ν_{\max} 3442 (s), 2977 (s), 2930 (s), 2893 (s), 2628 (w), 2248 (m), 1935 (w), 1727 (w), 1637 (w), 1446 (w), 1387 (w), 1336 (s), 1294 (m), 1246 (s), 1111 (s), 1076 (s), 981 (m), 919 (m), 879 (w), 806 (w), 751 (m) cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 4.38 (s, 1H), 4.34 (s, 2H), 3.86-3.55 (m, 8H), 2.13 (s, 1H), 1.35-1.18 (m, 12H); ¹³C NMR (50 MHz, CDCl₃): δ 103.4, 98.0, 85.3, 64.0, 58.9, 49.5, 14.4, 14.3; MS (EI): *m/z* 215 (6), 157 (12), 129 (9), 113 (20), 103 (100), 84 (25), 75 (76); HRMS *m/z* calcd for C₁₁H₁₉O₄ [M⁺ - EtO⁻] 215.1283, found 215.1283.

5,5,6,6-Tetraethoxyhex-3-yn-2-ol (2b). **Method C.** EtMgBr (14.5 mL, 1.8 M, 26.1 mmol), TEB (6.00 g, 26.1 mmol) in THF (50 mL), and acetaldehyde (1.26 g, 28.7 mmol) were used. Isolation by flash chromatography (hexane-ethyl acetate, 70:30) gave **2b** (5.9 g, 82%) as a clear liquid.

2b: IR (reflective) : ν_{\max} 3446 (w), 2977 (s), 2932 (m), 2891 (m), 1445 (w), 1389 (w), 1371 (w), 1329 (w), 1247 (w), 1116 (s), 1075 (s), 1017 (m), 953(w), 875 (w), 849 (w) cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 4.61 (q, *J* = 6.6 Hz, 1H), 4.38 (s, 1H), 3.85-3.62 (m, 8H), 1.47 (d, *J* = 6.6 Hz, 3H), 1.28-1.13 (m, 12H); ¹³C NMR (50 MHz, CDCl₃) δ 103.8, 98.6, 88.9, 78.3, 64.8, 64.7, 59.4, 58.0, 23.8, 15.5, 15.2; MS (EI) *m/z* 257 (20), 231 (35), 230 (92), 229 (100), 202 (20), 201 (80), 185 (20), 184 (60), 173 (18), 172 (70), 171 (50), 160 (38), 156 (48), 155 (88), 143 (30), 137 (80), 126 (40), 125 (90), 115 (30), 111 (65), 104 (100), 98 (80), 95 (45), 85 (50), 83 (70), 82 (82), 79 (80); HRMS *m/z* calcd for C₁₁H₁₈O₄ [M⁺ - EtO⁻] 214.1205, found 214.1201.

7,7,8,8-Tetraethoxyoct-5-yn-4-ol (2c). **Method A.** The TEB acetylide generated with NaNH₂ was reacted with butanal (0.40 g, 5.2 mmol). Product isolation by flash chromatography (hexane-ethyl acetate, 80:20) gave **1c** (0.50 g, 38%). **Method C.** EtMgBr (3.5 mL, 3.0 M, 10.5 mmol), TEB (2.3 g, 10.0 mmol) in THF (30 mL) and butanal (0.78 g, 10.5 mmol) in THF (10 mL) were used. Isolation by flash chromatography (hexane-ethyl acetate, 70:30) gave **2c** (2.36 g, 78%) as a clear liquid.

2c. IR (film) : ν_{\max} 3428 (m), 2975 (s), 2931 (s), 2898 (s), 2874 (s), 2240 (w), 1449 (m), 1445 (m), 1389 (m), 1331 (m), 1295 (w), 1245 (m), 1117 (s), 1078 (s), 1020 (s), 940 (w), 920 (w), 877 (w), 804 (w), 738 (w) cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 4.46 (t, *J* = 6.5 Hz, 1H), 4.37 (s, 1H), 3.87-3.61 (m, 8H), 2.51 (bs, 1H), 1.78-1.40 (m, 4H), 1.20-1.10 (m, 12H), 0.94 (t, *J* = 6.0 Hz, 3H); ¹³C NMR (50 MHz, CDCl₃): δ 103.8, 98.5, 88.1, 79.0, 64.6, 61.9, 59.5, 39.4, 18.2, 15.1,

15.0, 13.6; MS (EI): m/z 257 (50), 229 (15), 214 (29), 200 (17), 199 (14), 103 (100), 75 (49); HRMS m/z calcd for $C_{11}H_{18}O_4$ [$M^+ - EtO^-$] 214.1205, found 214.1201; anal: calcd for $C_{16}H_{30}O_5$ C, 62.28; H, 9.99; found: C, 61.99; H, 9.83.

6,6,7,7-Tetraethoxy-2,2-dimethylhept-4-yn-3-ol (2d). **Method A.** The TEB acetylide generated with $NaNH_2$ was reacted with 2,2-dimethylpropanal (0.40 g, 5.2 mmol). Product isolation by flash chromatography (hexane-ethyl acetate, 80:20) gave **2d** (0.50 g, 34%). **Method B.** BuLi (1.4 mL, 1.6 M, 2.2 mmol), TEB (0.50 g, 2.2 mmol) in a mixture of diethyl ether (30 mL) and THF (15 mL), and 2,2-dimethylpropanal (0.30 g, 3.3 mmol) were used. Isolation by flash chromatography (hexane-ethyl acetate, 80:20) gave **2d** (0.53 g, 72%). **Method C.** EtMgBr (4.8 mL, 3.0 M, 14.3 mmol), TEB (1.02 g, 4.4 mmol) in THF (30 mL) and 2,2-dimethylpropanal (0.46 g, 5.3 mmol) in THF (10 mL) were used. Isolation by flash chromatography (hexane-ethyl acetate, 70:30) gave **2d** (0.38 g, 27%) as a clear liquid and 6,6,7,7-tetraethoxy-2,2-dimethylhept-4-yn-3-one as a yellowish liquid (0.39 g, 28%).

2d. IR (film): ν_{max} 3355 (s), 2974 (s), 2933 (s), 2892 (s), 2251 (w), 1638 (w), 1447 (m), 1388 (m), 1365 (m), 1329 (m), 1296 (w), 1241 (m), 1116 (s), 1078 (s), 1020 (s), 930 (w), 876 (m), 821 (w), 763 (m) cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$): δ 4.38 (s, 1H), 4.09 (s, 1H), 3.87-3.61 (m, 8H), 2.37 (bs, 1H), 1.26-1.18 (m, 12H), 1.01 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 103.9, 98.7, 86.9, 80.0, 70.9, 64.4, 59.6, 35.8, 25.1, 15.2, 15.1; MS (EI): m/z 272 (1), 271 (7), 214 (7), 213 (20), 169 (6), 168 (16), 153 (4), 151 (3), 141 (5), 139 (8), 111 (5), 103 (100), 75 (49); HRMS m/z calcd for $C_{15}H_{27}O_4$ [$M^+ - EtO^-$] 271.1909, found 271.1912.

6,6,7,7-Tetraethoxy-2,2-dimethylhept-4-yn-3-one. IR (film): ν_{max} 2976 (s), 2932 (s), 2977 (s), 2873 (m), 2219 (w), 1677 (s), 1479 (m), 1445 (m), 1393 (m), 1391 (m), 1372 (m), 1314 (m), 1230 (m), 1116 (s), 1082 (s), 1019 (s), 936 (w), 895 (w), 844 (w); 1H NMR (200 MHz, $CDCl_3$): δ 4.44 (s, 1H), 3.87-3.65 (m, 8H), 1.39-1.07 (m, 21H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 193.4, 103.6, 98.9, 87.2, 82.5, 64.4, 60.2, 45.0, 25.7, 15.2, 15.1; MS (ESI $^+$): m/z 269 (5), 211 (5), 205 (5), 109 (20), 103 (50), 75 (100), 57 (40); HRMS m/z calcd for $C_{15}H_{25}O_4$ [$M^+ - EtO^-$] 269.1753, found 269.1752

EtMgBr (1.5 mL, 3.0 M, 4.43 mmol), TEB (1.02 g, 4.43 mmol) in THF (10 mL), and pivalaldehyde (0.38 g, 4.43 mmol) in THF (4 mL) were used. After work up and evaporation of solvent the crude product (1.4 g) were dissolved in ethanol (10 mL) and cooled to 0 °C before $NaBH_4$ (0.08 g, 2.2 mmol) was added in one portion. The mixture was stirred at rt for another 15 min. Most of the ethanol was evaporated and the residue was taken up into 0.1 M HCl (10 mL). Water (10 mL) was added and the reaction mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated. Isolation by flash chromatography (80:20, hexane-ethyl acetate) yielded **2d** (0.78 g, 55%) as a clear liquid and neopentyl alcohol (0.09 g, 24%).

1,1,2,2-Tetraethoxyundec-3-yn-5-ol (2e). **Method C.** EtMgBr (2.9 mL, 1.8 M, 5.2 mmol), TEB (1.01 g, 4.4 mmol) in THF (30 mL), and heptaldehyde (0.60 g, 5.3 mmol) were used. Isolation by flash chromatography (hexane-ethyl acetate, 80:20) gave **2e** (1.32 g, 87%) as a yellowish liquid.

2e: IR (film): ν_{\max} 3427 (m), 2975 (s), 2958 (s), 2930 (s), 2872 (s), 2860 (s), 2241 (w), 1736 (w), 1638 (w), 1457 (m), 1445 (m), 1389 (m), 1377 (m), 1332 (m), 1295 (w), 1244 (m), 1117 (s), 1074 (s), 1019 (s), 916 (w), 876 (w), 804 (w), 786 (w), 725 (w) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 4.44 (t, $J = 6.5$ Hz, 1H), 4.37 (s, 1H), 3.84-3.62 (m, 8H), 1.17-1.79 (m, 22H), 0.88 (t, $J = 6.5$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3): δ 103.8, 98.6, 88.3, 78.8, 64.6, 64.5, 62.0, 59.5, 37.3, 31.7, 31.6, 28.8, 24.8, 22.5, 22.3, 15.1, 15.0, 13.8; MS (EI): m/z 327 (9), 299 (18), 241 (33), 214 (15), 103 (100), 75 (43); HRMS m/z calcd for $\text{C}_{17}\text{H}_{31}\text{O}_4$ [$\text{M}^+ - \text{EtO}^-$] 299.2222, found 299.2233.

4,4,5,5-Tetraethoxy-1-phenylpent-2-yn-1-ol (2f). **Method A.** TEB acetylide generated with NaNH_2 (10 times excess) was reacted with benzaldehyde (0.60 g, 5.2 mmol). Product isolation by flash chromatography (hexane-ethyl acetate, 75:25) gave **2f** (0.20 g, 10%). **Method C:** EtMgBr (4.8 mL, 3.0 M, 14.3 mmol), TEB (3.0 g, 13.0 mmol) in THF (30 mL), and benzaldehyde (1.38 g, 13.0 mmol) in THF (10 mL) were used. Isolation by flash chromatography (hexane-ethyl acetate, 80:20, followed by hexane-ethyl acetate, 95:5) gave **2f** (3.06 g, 70%) as a yellowish liquid, and 4,4,5,5-tetraethoxy-1-phenylpent-2-yn-1-one (0.56 g, 13%), also as a yellowish liquid.

1f: IR (film): ν_{\max} 3418 (s), 3062 (m), 3031 (m), 2977 (s), 2930 (s), 2892 (s), 2245 (w), 1945 (w), 1634 (w), 1606 (w), 1485 (m), 1449 (s), 1387 (s), 1333 (s), 1244 (s), 1113 (s), 1074 (s), 918 (m), 880 (m), 817 (m), 750 (m), 702 (s), 646 (m) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 7.59-7.54 (m, 2H), 7.34-7.28 (m, 3H), 5.53 (s, 1H), 4.40 (s, 1H), 3.82-3.63 (m, 8H), 3.20 (bs, 1H), 1.25-1.16 (m, 12H); ^{13}C NMR (50 MHz, CDCl_3): δ 140.2, 128.2, 127.9, 126.6, 103.8, 98.7, 86.8, 81.0, 64.5, 64.1, 59.6, 15.1, 15.0; MS (EI): m/z 292 (13), 233 (15), 182 (3), 166 (2), 159 (7), 143 (9), 131 (6), 115 (20), 105 (7), 104 (6), 103 (100), 77 (7), 75 (51); HRMS m/z calcd for $\text{C}_{17}\text{H}_{23}\text{O}_4$ [$\text{M}^+ - \text{EtO}^-$] 291.1596, found 291.1599.

4,4,5,5-Tetraethoxy-1-phenylpent-2-yn-1-one. IR (film): ν_{\max} 3063 (w), 3030 (w), 2977 (s), 2932 (m), 2892 (m), 2224 (m), 1650 (s), 1598 (m), 1581 (m), 1450 (m), 1391 (m), 1372 (m), 1314 (m), 1263 (s), 1117 (s), 1079 (s), 1020 (s), 909 (w), 878 (w), 795 (w), 704 (s) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 8.25-8.21 (m, 2H), 7.62-7.51 (m, 3H), 4.52 (s, 1H), 3.92-3.67 (m, 8H), 1.32-1.19 (m, 12H); ^{13}C NMR (50 MHz, CDCl_3): δ 177.3, 136.6, 134.1, 129.7, 128.4, 103.8, 99.1, 88.0, 83.1, 64.6, 60.2, 59.5, 15.2; MS (ESI $^+$): m/z 352 (80), 335 (15), 289 (60), 215 (25), 75 (30); HRMS calcd for $\text{C}_{19}\text{H}_{27}\text{O}_5$ [$\text{M}+\text{H}$] $^+$ 335.18585 found 335.18339.

EtMgBr (1.5 mL, 3.0 M, 4.43 mmol), TEB (1.02 g, 4.43 mmol) in THF (10 mL), and benzaldehyde (0.47 g, 4.43 mmol) in THF (4 mL) were used. After work up and evaporation of solvent the crude product (1.54 g) were dissolved in ethanol (10 mL) and cooled to 0 °C before NaBH_4 (0.08 g, 2.2 mmol) was added in one portion. The mixture was stirred at rt for another 15 min. Most of the ethanol was evaporated and the residue was taken up into 0.1 M HCl (10 mL). Water (10 mL) was added and the reaction mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried (MgSO_4), filtered and evaporated. Isolation by flash chromatography (80:20, hexane-ethyl acetate) yielded **2f** (1.20 g, 81%) as a yellowish liquid and benzyl alcohol (0.05 g, 11%)

5,5,6,6-Tetraethoxy-2-methylhex-3-yn-2-ol (2g). **Method A.** TEB acetylide generated with NaNH_2 was reacted with acetone (0.30 g, 5.2 mmol). Product isolation by flash chromatography (hexane-ethyl acetate, 75:25) gave **2g** (0.70 g, 56%). **Method B.** BuLi (2.7 mL, 1.6 M, 4.3 mmol), TEB (1.0 g, 4.3 mmol) in a mixture of diethyl ether (50 mL) and THF (25 mL), and acetone (0.40 g, 6.5 mmol) were used. Isolation by flash chromatography (hexane-ethyl acetate, 75:25) gave **2g** (0.80 g, 65%). **Method C.** EtMgBr (8.0 mL, 3M, 23.9 mmol), TEB (5.00 g, 21.7 mmol) in THF (30 mL), and acetone (1.51 g, 26.1 mmol) were used. Isolation by flash chromatography (hexane-ethyl acetate, 80:20) gave **2g** (5.00 g, 80%) as a clear liquid.

2g. IR (film): ν_{max} 3431 (m), 2978 (s), 2931 (s), 2896 (s), 2244 (w), 1480 (w), 1445 (m), 1388 (m), 1373 (m), 1336 (m), 1243 (m), 1169 (s), 1116 (s), 1017 (m), 969 (m), 933 (m), 879 (w), 808 (w), 760 (w), 736 (w) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 4.38 (s, 1H), 3.88-3.62 (m, 8H), 1.54 (s, 6H), 1.13-1.30 (m, 12H); ^{13}C NMR (50 MHz, CDCl_3): δ 103.6, 98.2, 91.5, 76.3, 64.4, 64.3, 59.2, 30.9, 15.0, 14.9; MS (EI): m/z 243 (9), 215 (2), 185 (21), 169 (5), 141 (4), 139 (4), 123 (6), 111 (9), 104 (4), 103 (100), 95 (19), 83 (5), 75 (59); HRMS m/z calcd for $\text{C}_{13}\text{H}_{23}\text{O}_4$ [$\text{M}^+ - \text{EtO}^-$] 243.1596, found 243.1592.

6,6,7,7-Tetraethoxy-3-ethylhept-4-yn-3-ol (2h). **Method C.** EtMgBr (5.1 mL, 1.0 M, 5.1 mmol), TEB (1.00 g, 4.3 mmol) in THF (30 mL), and pentan-3-one (0.44 g, 5.1 mmol) were used. Isolation by flash chromatography (hexane-ethyl acetate, 80:20) gave **2h** (1.10 g, 81%) as a clear liquid.

2h. IR (film): ν_{max} 3431 (m), 2976 (s), 2934 (s), 2883 (s), 2241 (w), 1480 (w), 1458 (m), 1445 (m), 1389 (m), 1372 (m), 1328 (m), 1295 (m), 1275 (m), 1241 (m), 1117 (s), 1078 (s), 1018 (s), 975 (m), 959 (m), 931 (w), 891 (w), 813 (w), 733 (w) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 4.38 (s, 1H), 3.86-3.61 (m, 8H), 2.64 (bs, 1H), 1.71 (q, $J = 7.5$ Hz, 4H), 1.26-1.17 (m, 12H), 1.05 (t, $J = 7.5$ Hz, 6H); ^{13}C NMR (50 MHz, CDCl_3): δ 103.9, 98.6, 89.6, 78.9, 71.8, 64.2, 59.6, 34.1, 15.2, 15.1, 8.3; MS (EI): m/z 271 (7), 213 (20), 167 (6), 139 (7), 103 (100), 75 (45); HRMS m/z calcd for $\text{C}_{15}\text{H}_{27}\text{O}_4$ [$\text{M}^+ - \text{EtO}^-$] 271.1909, found 271.1906.

1-(3,3,4,4-Tetraethoxybut-1-ynyl)cyclohexanol (2i). **Method C.** EtMgBr (2.9 mL, 1.8 M, 5.2 mmol), TEB (1.00 g, 4.3 mmol) in THF (30 mL), and cyclohexanone (0.51 g, 5.2 mmol) were used. Isolation by flash chromatography (hexane-ethyl acetate, 80:20) gave **2i** (1.17 g, 82%) as a clear liquid.

2i. IR (film): ν_{max} 3418 (m), 2976 (s), 2934 (s), 2898 (m), 2862 (m), 2236 (w), 1481 (w), 1446 (m), 1389 (m), 1371 (m), 1340 (m), 1285 (m), 1260 (m), 1236 (m), 1117 (s), 1078 (s), 1017 (m), 967 (m), 903 (w), 893 (w), 876 (w), 852 (w), 836 (w), 789 (w), 733 (w) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 4.39 (s, 1H), 3.87-3.61 (m, 8H), 2.75 (bs, 1H), 1.98-1.91 (m, 2H), 1.74-1.54 (m, 8H), 1.30-1.18 (m, 12H); ^{13}C NMR (50 MHz, CDCl_3): δ 103.8, 98.5, 90.5, 78.8, 68.3, 64.1, 59.6, 39.6, 25.0, 23.0, 15.2, 15.0; MS (EI): m/z 283 (7), 225 (23), 179 (7), 103 (100), 75 (49); HRMS m/z calcd for $\text{C}_{16}\text{H}_{27}\text{O}_4$ [$\text{M}^+ - \text{EtO}^-$] 283.1909, found 283.1918.

1-(3,3,4,4-Tetraethoxybut-1-ynyl)cyclopentanol (2j). **Method C.** EtMgBr (1.6 mL, 3.05 M, 4.9 mmol, 1.1 eq), TEB (1.02 g, 4.43 mmol) in THF (25 mL), and cyclopentanone (0.43 g, 5.11

mmol) in THF (10 mL) were used. The ketone was added fairly slowly. Isolation by flash chromatography (hexane-ethyl acetate, 80:20) gave **2j** (0.99 g, 71%) as a clear liquid.

2j. IR (film): ν_{\max} 3417 (m), 2974 (s), 2932 (s), 2897 (s), 2243 (w), 1741 (w), 1635 (w), 1480 (w), 1444 (m), 1389 (m), 1372 (m), 1332 (m), 1251 (m), 1174 (s), 1074 (s), 1017 (s), 916 (m), 876 (m), 805 (w), 733 (m) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 4.38 (s, 1H), 3.88-3.62 (m, 8H), 3.07 (bs, 1H), 2.05-1.67 (m, 8H), 1.30-1.17 (m, 12H); ^{13}C NMR (50 MHz, CDCl_3): δ 103.3, 98.0, 90.5, 63.8, 59.0, 41.6, 22.7, 14.7, 14.6; MS (EI): m/z 270 (19), 211 (47), 165 (7), 137 (9), 121 (8), 103 (100), 75 (41); HRMS m/z calcd for $\text{C}_{15}\text{H}_{25}\text{O}_4$ [M^+ - EtO] 269.1753, found 269.1753.

If the ketone was added quickly large amounts of 2-(1-hydroxycyclopentyl)cyclopentanone were formed.^{4,27}

Hydrogenation of 2. General procedures

Method 1. Propargylic alcohol (**2**) (2.00 mmol) was added to a suspension of Lindlar's catalyst (0.08 g) and potassium carbonate (0.08 g) in ethyl acetate (10 mL) which was stirred at room temperature under a hydrogen atmosphere for a variable length of time. H_2 was led into the reaction flask through a glass inlet tube which was kept with the mouth well above the suspension. When the reaction was finished, as evidenced by TLC, the reaction mixture was filtered through a Celite plug, and the solvent was subsequently removed under vacuum without heating on a rotary evaporator. The residue contained the product which was analyzed and further was worked up as required and detailed below. **Method 2.** The propargylic alcohol (4.0-6.0 mmol) was added to a suspension of Lindlar's catalyst (0.04 g) and potassium carbonate (0.02 g) in ethyl acetate (20 mL), which was stirred with a magnetic bar at room temperature. H_2 was lead into the reaction flask through a glass inlet tube which was kept with the mouth in the middle of the suspension, slightly above the stirring bar. The reaction was followed by TLC and stopped when all the starting material was consumed. The reaction mixture was filtered through a Celite plug, and the solvent was subsequently removed under vacuum, leaving a residue from which the products were isolated by flash chromatography on silica gel using hexane/ethyl acetate 80:20 as mobile phase.

(Z)-4,4,5,5-Tetraethoxypent-2-en-1-ol ((Z)-3a). **Method 1.** 4,4,5,5-Tetraethoxypent-2-yn-1-ol (**2a**) (0.52 g) was used, reacted for 48 h, and gave **(Z)-3a** (0.52 g, 99%) without further purification. **Method 2.** **2a** (1.04 g) was used, reacted for 3 h, and afforded **(Z)-3a** (0.95 g, 91%) as a clear liquid.

(Z)-3a. IR (film): ν_{\max} 3462 (m, broad), 2973 (s), 2904 (s), 1449 (m), 1390 (m), 1122 (s), 1078 (s), 878 (m), 807 (m) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 6.00 (dt, $J = 6.9, 12.3$ Hz, 1H), 5.46 (dt, $J = 1.9, 12.3$ Hz, 1H), 4.46 (s, 1H), 4.28 (dd, $J = 1.9, 6.9$ Hz, 2H), 3.85-3.44 (m, 8H), 2.84 (bs, 1H, OH), 1.27-1.17 (m, 12H); ^1H NMR (50 MHz, CDCl_3): δ 134.9, 129.0, 103.6, 102.4, 65.0, 58.4, 56.5, 15.1, 15.0; MS (EI): m/z 244 (1), 231 (1), 216 (1), 199 (1), 187 (1), 171 (1), 159

(23), 142 (8), 125 (7), 113 (16), 103 (100), 97 (14), 85 (60), 75 (57); HRMS m/z calcd for $[M^+ - EtO^-]$ $C_{11}H_{21}O_4$ 217.1440, found 217.1432.

(Z)-5,5,6,6-Tetraethoxyhex-3-en-2-ol ((Z)-3b). **Method 1.** 5,5,6,6-Tetraethoxyhex-3-yn-2-ol (**2b**) (0.55 g) was used, reacted for 48 h, and gave **(Z)-3b** (0.55 g, 99%) without further purification. **Method 2:** **2b** (1.10 g) was used, reacted for 3 h, and gave **(Z)-3b** (1.04 g, 94%) as a clear liquid.

(Z)-3b. IR (reflective): ν_{max} 3433 (w, broad), 3035 (w), 2977 (m), 2931 (w), 2891 (w), 1628 (w), 1479 (w), 1445 (w), 1390 (w), 1371 (w), 1328 (w), 1248 (w), 1160 (s), 1074 (s), 1018 (m), 922 (w), 879 (w), 799 (w), 735 (w) cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$): δ 5.75 (dd, $J = 12.2, 4.5$ Hz, 1H), 5.37 (d, $J = 12.2$ Hz, 1H), 4.94 (p, $J = 6.6$ Hz, 1H), 4.46 (s, 1H), 3.83-3.45 (m, 8H), 3.08 (bs, 1H, OH), 1.14-1.39 (m, 15H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 140.5, 128.0, 103.7, 102.6, 65.3, 65.0, 62.5, 56.7, 56.6, 22.2, 15.3, 15.2, 15.0; MS (EI): m/z 231 (15), 215 (12), 201 (10), 187 (52), 186 (65), 185 (70), 184 (52), 174 (75), 173 (50), 169 (12), 160 (20), 157 (70), 155 (20), 143 (70), 139 (92), 129 (75), 127 (85), 125 (30), 115 (75), 111 (95), 104 (95), 101 (85), 97 (80), 95 (45), 87 (70), 81 (88), 76 (78); HRMS m/z calcd for $C_{12}H_{23}O_4$ $[M^+ - EtO^-]$ 231.1596, found 231.1606.

(Z)-1,1,2,2-Tetraethoxyundec-3-en-5-ol ((Z)-3e). **Method 1.** 1,1,2,2-Tetraethoxyundec-3-yn-5-ol (**2e**) (0.66 g) was used, reacted for 24 h, and gave **(Z)-3e** (0.66 g, 99%) without further purification. **Method 2.** **2e** (1.31 g) was used, reacted for 14 h, and gave **(Z)-3e** (1.22 g, 92%) as a yellowish liquid.

(Z)-3e. IR (film): ν_{max} 3508 (m, broad), 2975 (s), 2929 (s), 2873 (s), 2859 (s), 2242 (w), 1481 (m), 1444 (m), 1437 (m), 1416 (m), 1376 (m), 1389 (m), 1220 (w), 1118 (s), 1074 (s), 1018 (s), 920 (w), 879 (w), 733 (m) cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$): δ 5.74 (dd, $J = 12.3, 4.3$ Hz, 1H), 5.40 (d, $J = 12.3$ Hz, 1H), 4.72 (q, $J = 7.2$ Hz, 1H), 4.45 (s, 1H), 3.83-3.45 (m, 8H), 3.03 (broad s, 1H, OH), 1.54-1.16 (m, 22H), 0.87 (t, $J = 6.2$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 139.6, 128.4, 103.6, 102.6, 66.3, 65.2, 65.0, 56.7, 56.5, 36.5, 31.7, 29.4, 25.4, 22.5, 15.3, 15.2, 15.0, 13.9; MS (EI): m/z 256 (20), 255 (70), 244 (45), 243 (98), 231 (8), 227 (18), 226 (70), 215 (30), 209 (68), 197 (35), 187 (20), 181 (25), 170 (40), 169 (100), 158 (25), 153 (35), 142 (50), 129 (35), 123 (55), 113 (60), 109 (78), 104 (67), 97 (55), 95 (40), 86 (20), 85 (30), 83 (65), 81 (72), 75 (80); HRMS m/z calcd for $C_{17}H_{33}O_4$ $[M^+ - EtO^-]$ 301.2379, found 301.2381.

(Z)-4,4,5,5-Tetraethoxy-1-phenylpent-2-en-1-ol((Z)-3f). **Method 1.** 4,4,5,5-Tetraethoxy-1-phenylpent-2-yn-1-ol (**2f**) (0.67 g) was used, reacted for 48 h, and gave **(Z)-3f** (0.67 g, 99%) without further purification. **Method 2.** 4,4,5,5-Tetraethoxy-1-phenylpent-2-yn-1-ol (**2f**) (1.35 g) was used, reacted for 3 h, and gave **(Z)-3f** (1.22 g, 90%) as a yellowish liquid.

(Z)-3f: IR (reflective): ν_{max} 3442 (w, broad), 3036 (w), 2977 (w), 2939 (w), 1725 (m), 1679 (s), 1597 (w), 1568 (w), 1521 (m), 1474 (m), 1450 (m), 1391 (m), 1370 (w), 1287 (w), 1269 (w), 1256 (m), 1219 (m), 1158 (m), 1065 (m), 1025 (s), 1001 (m), 969 (m), 921 (m), 801 (m), 761 (s), 689 (s) cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$): δ 7.49-7.40 (m, 2H), 7.38-7.16, (m, 3H), 6.01 (d, $J = 8.4$ Hz, 1H), 5.93 (dd, $J = 11.6, 8.4$ Hz, 1H), 5.49 (d, $J = 11.6$ Hz, 1H), 4.52 (s, 1H), 3.90-3.46 (m, 8H), 3.08 (bs, 1H, OH), 1.33-1.16 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 143.7, 139.1,

128.6, 128.0, 126.7, 126.0, 103.7, 102.6, 68.3, 65.3, 65.2, 56.8, 56.6, 15.3, 15.2, 15.1; MS (EI): m/z 247 (15), 235 (18), 218 (14), 201 (20), 189 (7), 173 (5), 161 (35), 133 (14), 115 (27), 103 (100), 91 (7), 75 (56); HRMS m/z calcd for $C_{17}H_{25}O_4$ [$M^+ - EtO^-$] 293.1750, found 293.1744.

(Z)-5,5,6,6-Tetraethoxy-2-methylhex-3-en-2-ol ((Z)-3g). **Method 1.** 5,5,6,6-Tetraethoxy-2-methylhex-3-yn-2-ol (**2g**) (0.58 g) was used, reacted for 48 h, and gave (**Z**)-**3g** (0.58 g, 99%) without further purification. **Method 2.** 5,5,6,6-Tetraethoxy-2-methylhex-3-yn-2-ol (**2g**) (1.15 g) was used, reacted for 16 h, and gave (**Z**)-**3g** (1.06 g, 91%) as a clear liquid.

(**Z**)-**3g**. IR (film): ν_{max} 3454 (m, broad), 3035 (w), 2975 (s), 2930 (m), 2899 (m), 1481 (w), 1445 (w), 1414 (w), 1390 (w), 1374 (w), 1356 (w), 1327 (w), 1295 (w), 1223 (s), 1172 (m), 1118 (s), 1075 (s), 1047 (s), 963 (m), 926 (w), 887 (w), 807 (w), 783 (w) cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$): δ 5.88 (d, $J = 13.8$ Hz, 1H), 5.58 (broad s, 1H, OH), 5.30 (d, $J = 13.8$ Hz, 1H), 4.50 (s, 1H), 3.82-3.56 (m, 8H), 1.36 (s, 6H), 1.23 (t, $J = 7.1$ Hz, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 143.6, 124.6, 103.6, 102.3, 69.2, 64.9, 57.3, 31.0, 15.0, 14.9; MS (EI): m/z 202 (2), 201 (5), 199 (10), 198 (8), 187 (38), 183 (2), 169 (8), 158 (2), 141 (50), 127 (10), 113 (90), 103 (50), 97 (52), 95 (42), 87 (8), 81 (13), 75 (92), 67 (30), 55 (20), 47 (100), 43 (80); HRMS m/z calcd for $C_{10}H_{19}O_2$ [$M^+ - EtOCH^-$] 187.1334 found 187.1330.

(Z)-6,6,7,7-Tetraethoxy-3-ethylhept-4-en-3-ol (Z-3h). **Method 1.** 6,6,7,7-Tetraethoxy-3-ethylhept-4-yn-3-ol (**2h**) (0.63 g) was used, reacted for 72 h, and gave (**Z**)-**3h** (0.51 g, 80%) after isolation by flash chromatography (hexane-ethyl acetate, 80:20). **Method 2.** 6,6,7,7-Tetraethoxy-3-ethylhept-4-yn-3-ol (**2h**) (1.90 g) was used, reacted for 5 h, and gave (**Z**)-**3h** (1.72 g, 90%) as a clear liquid.

(**Z**)-**3h**: IR (film): ν_{max} 3419 (m), 3035 (w), 2976 (s), 2932 (m), 2899 (m), 2878 (m), 2235 (w), 1660 (w), 1456 (w), 1445 (w), 1390 (w), 1327 (w), 1274 (w), 1118 (s), 1075 (s), 1048 (s), 988 (w), 924 (w), 878 (w), 733 (s), 645 (w) cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$): δ 5.73 (s, 1H, OH), 5.63 (d, $J = 14.1$ Hz, 1H), 5.42 (d, $J = 14.1$ Hz, 1H), 4.50 (s, 1H), 3.81-3.57 (m, 8H), 1.55 (m, 4H), 1.22 (t, $J = 6.1$ Hz, 12H), 0.90 (t, $J = 7.3$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 141.6, 125.8, 103.8, 102.2, 74.8, 64.9, 57.4, 33.9, 15.1, 14.9, 8.1; MS (EI): m/z 244 (2), 243 (12), 232 (10), 228 (30), 227 (60), 216 (55), 215 (78), 199 (20), 198 (55), 197 (20), 186 (25), 181 (15), 169 (50), 158 (15), 157 (45), 153 (60), 142 (55), 135 (20), 129 (45), 125 (85), 113 (85), 95 (100), 85 (55), 83 (80), 75 (95), 71 (50); HRMS m/z calcd for $C_{15}H_{25}O_4$ [$M^+ - EtO^-$] 273.2066, found 273.2055.

1-((Z)-3,3,4,4-Tetraethoxybut-1-enyl)cyclohexanol ((Z)-3i). **Method 1.** 1-(3,3,4,4-Tetraethoxybut-1-ynyl)cyclohexanol (**2i**) (0.66 g) was used, reacted for 72 h, and gave (**Z**)-**3i** (0.47 g, 71%) after isolation by flash chromatography (hexane-ethyl acetate, 80:20). **Method 2.** 1-(3,3,4,4-Tetraethoxybut-1-ynyl)cyclohexanol (**2i**) (1.31 g) was used, reacted for 4 h, and gave (**Z**)-**3i** (1.18 g, 89%) as a clear liquid.

(**Z**)-**3i**. IR (film): ν_{max} 3455 (m, broad), 3035 (w), 2976 (s), 2930 (s), 2858 (m), 1446 (w), 1423 (w), 1390 (w), 1375 (w), 1346 (w), 1328 (w), 1295 (w), 1118 (s), 1077 (s), 1047 (s), 989 (w), 725 (w) cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$): δ 5.88 (d, $J = 13.8$ Hz, 1H), 5.34 (d, $J = 13.8$ Hz, 1H), 5.29 (s, 1H, OH), 4.48 (s, 1H), 3.85-3.51 (m, 8H), 1.72-1.29 (m, 10H), 1.29 (t, $J = 7.0$ Hz, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 143.3, 125.3, 103.6, 102.3, 70.0, 69.4, 64.9, 57.3, 38.8,

25.5, 22.1, 15.1, 22.1, 15.1, 15.0; MS (EI): m/z 284 (10), 240 (15), 239 (40), 227 (88), 210 (40), 181 (65), 153 (80), 135 (70), 103 (100), 81 (30), 75 (90); HRMS m/z calcd for $C_{16}H_{28}O_4$ [$M^+ - EtO$] 284.1988, found 284.1985.

1-((Z)-3,3,4,4-Tetraethoxybut-1-enyl)cyclopentanol ((Z)-3j). Method 2. 1-(3,3,4,4-Tetraethoxybut-1-ynyl)cyclopentanol (**2j**) (1.26) was used, reacted for 8 h, and gave (Z)-**3j** (1.11 g, 88%) without further purification as a clear liquid.

(Z)-**3j**. IR (film): ν_{max} 3444 (m, broad), 3035 (w), 2975 (s), 2931 (s), 2900 (s), 2872 (s), 2237 (w), 1651 (w), 1445 (m), 1419 (w), 1390 (w), 1375 (w), 1325 (w), 1300 (m), 1215 (m), 1117 (s), 1075 (s), 1048 (s), 945 (w), 923 (m), 878 (m), 733 (m) cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$): δ 5.96 (d, $J = 13.6$ Hz, 1H), 5.35 (d, $J = 13.6$ Hz, 1H), 5.25 (s, 1H, OH), 4.51 (s, 1H), 3.87-3.51 (m, 8H), 1.98-1.53 (m, 8H), 1.25 (t, $J = 7.1$ Hz, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 142.6, 125.7, 103.7, 102.2, 79.6, 64.9, 57.2, 41.8, 23.5, 15.1, 15.0; MS (EI): m/z 271 (2), 270 (20), 242 (10), 241 (50), 226 (95), 225 (90), 214 (70), 213 (75), 198 (30), 197 (50), 196 (92), 195 (60), 186 (25), 179 (70), 173 (70), 167 (85), 158 (30), 151 (72), 141 (30), 140 (92), 130 (50), 133 (50), 123 (100), 121 (85), 111 (55), 105 (75), 95 (70), 93 (85), 91 (52), 82 (70), 79 (80), 73 (70), 67 (85), 65 (45), 57 (65); HRMS m/z calcd for $C_{16}H_{28}O_4$ [$M^+ - EtO$] 271.1909, found 271.1895

Preparation of derivatives of 2a

4,4,5,5-Tetraethoxypent-2-ynyl acetate (4). 4,4,5,5-Tetraethoxypent-2-yn-1-ol (**2a**) (1.72 g, 6.6 mmol) was added dropwise to a solution of acetic anhydride (1.53 g, 15.0 mmol) and pyridine (1.58 g, 20.0 mmol) in dichloromethane (20 mL). The mixture was stirred at rt for 12 h and then quenched by adding water. The hydrolysate was extracted with dichloromethane (3 x 20 mL), and the combined organic phases were dried ($MgSO_4$), filtered, and concentrated under vacuum on a rotary evaporator. The residue was purified by flash chromatography (hexane-ethyl acetate, 70:30) and gave pure **4** (1.96 g, 98%) as a clear liquid.

4. IR (film): ν_{max} 2980 (s), 2932 (s), 2894 (s), 2221 (w), 1750 (s), 1481 (w), 1443 (m), 1378 (s), 1333 (m), 1225 (s), 1184 (s), 1117 (s), 1078 (s), 1033 (s), 961 (m), 913 (w), 881 (w), 827 (w), 754 (w) cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$): δ 4.76 (s, 2H), 4.39 (s, 1H), 3.84-3.62 (m, 8H), 2.08 (s, 3H), 1.23 (q, $J = 7.0$ Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.9, 103.6, 98.4, 81.1, 80.5, 64.7, 59.4, 52.1, 20.4, 15.0; MS (EI): m/z 260 (8), 259 (30), 258 (80), 257 (85), 229 (40), 212 (45), 200 (55), 199 (65), 187 (35), 172 (85), 171 (20), 170 (35), 169 (75), 155 (85), 143 (15), 142 (48), 141 (65), 140 (80), 129 (55), 126 (70), 125 (40), 124 (35), 114 (45), 112 (80), 111 (75), 104.1 (70), 97 (80), 85 (70), 84 (100), 83 (80), 76 (70); HRMS m/z calcd for $C_{13}H_{21}O_5$ [$M^+ - EtO$] 257.1389, found 257.1384.

5,5-Diethoxy-4-oxopent-2-ynyl acetate (6). 4,4,5,5-Tetraethoxypent-2-ynyl acetate (**4**) (1.02 g, 3.4 mmol) was added to a stirred mixture of pentane (25 mL), water (0.5 mL), and 80% aqueous formic acid (1.0 mL). The resulting mixture was stirred and refluxed for 3 h and was then allowed to cool to rt. Additional water (10 mL) was added and the mixture was extracted with dichloromethane (3 x 15 mL). The combined organic phases were dried ($MgSO_4$), filtered, and

concentrated under vacuum on a rotary evaporator. The residue was **6** (0.76 g, 99%) which was obtained pure without further purification.

6. IR (reflective): ν_{\max} 2980 (m), 2934 (m), 2888 (m), 2220 (m), 1754 (s), 1692 (s), 1560 (m), 1444 (m), 1376 (m), 1319 (w), 1221 (s), 1168 (m), 1117 (s), 1065 (s), 964 (w), 906 (w), 828 (w) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 4.89 (s, 2H), 4.74 (s, 1H), 3.81-3.56 (m, 4H), 2.12 (s, 3H), 1.25 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (50 MHz, CDCl_3): δ 181.9, 169.5, 101.2, 88.9, 83.0, 63.0, 51.2, 20.2, 14.8; MS (EI): m/z 183 (6), 113 (6), 103 (93), 75 (57), 66 (14), 55 (8), 47 (100); HRMS calcd for $\text{C}_9\text{H}_{11}\text{O}_4$ [$\text{M}^+ - \text{EtO}^-$] 183.0660, found 183.0657.

5,5-Diethoxy-4-hydroxypent-2-ynyl acetate (7). 5,5-Diethoxy-4-oxopent-2-ynyl acetate (**6**) (90 mg, 0.040 mmol) was dissolved in a mixture of THF (6 mL) and water (0.2 mL). The reaction mixture was cooled to 0 °C and NaBH_4 (0.008 g, 0.020 mmol) was added in one portion. The reaction was followed by TLC and after 15 min all the starting material was consumed. Only one product was observed, which had an R_f value of 0.12 with 70:30 hexane-ethyl acetate. H_2O (10 mL) was added and the reaction mixture stirred at rt for another 30 min. The reaction mixture was extracted with diethyl ether (3 x 10 mL), the ether extracts were combined, dried over MgSO_4 and concentrated under vacuum. Flash chromatography with 70:30 hexane-ethyl acetate as the mobile phase furnished **7** (0.076 g, 85 %) as a clear liquid.

7. IR (reflective): ν_{\max} 3460 (m), 2978 (s), 2932 (m), 2888 (m), 1747 (s), 1481 (w), 1442 (w), 1378 (s), 1361 (m), 1227 (s), 1123 (s), 1067 (s), 1028 (s), 968 (w), 918 (w), 916 (w), 831 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 4.72 (d, $J = 1.7$ Hz, 2H), 4.48 (d, $J = 5.4$ Hz, 1H), 4.37 (dt, $J = 5.5$ Hz, 1.7 Hz, 1H), 3.90-3.56 (m, 4H), 2.67 (d, $J = 5.4$ Hz, 1H), 2.09 (s, 3H), 1.25 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (50 MHz, CDCl_3): δ 170.0, 103.1, 83.9, 79.4, 64.3, 63.9, 52.1, 20.5, 15.0; MS (EI): m/z 185 (50), 143 (52), 139 (20), 127 (15), 115 (18), 113 (22), 105 (10), 104 (70), 103 (100), 97 (72), 89 (18), 88 (19), 85 (38), 81 (18), 76 (45), 75 (97), 69 (58), 68 (78), 67 (51), 61 (65), 59 (70), 53 (33), 51 (49); HRMS calcd for $\text{C}_9\text{H}_{13}\text{O}_4$ [$\text{M}^+ - \text{EtO}^-$] 185.0814, found 185.0822.

1,1-Diethoxy-5-hydroxypent-3-yn-2-one (8). 4,4,5,5-Tetraethoxypent-2-yn-1-ol (**2a**) (0.50 g, 2.2 mmol) was stirred at reflux in a suspension of Dowex50W (0.50 g) in acetone (20 mL) and water (0.5 mL) for 8 h. The Dowex pellets were filtered off and reaction mixture was then filtered, dried through a plug of silica. Removal of the acetone on a rotary evaporator gave **8** (0.40 g, 99%) as a pure yellowish liquid.

8. IR (film): ν_{\max} 3449 (s), 2980 (s), 2932 (s), 2897 (s), 2211 (s), 1689 (s), 1444 (m), 1395 (m), 1373 (m), 1323 (m), 1250 (s), 1162 (s), 1114 (s), 1063 (s), 909 (w), 832 (w) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 4.74 (s, 1H), 4.48 (s, 1H), 3.82-3.57 (m, 4H), 3.04 (bs, 1H), 1.28 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (50 MHz, CDCl_3): δ 182.2, 101.4, 94.0, 82.4, 63.2, 50.6, 14.9; MS (EI): m/z 141 (25), 113 (20), 103 (53), 83 (18), 75 (100), 53 (17); HRMS m/z calcd for $\text{C}_7\text{H}_9\text{O}_3$ [$\text{M}^+ - \text{EtO}^-$] 141.0552, found 141.0542.

5,5-Diethoxypent-2-yne-1,4-diol (9). 1,1-Diethoxy-5-hydroxypent-3-yn-2-one (**8**) (4.16 g, 22.3 mmol) was dissolved in a solution of THF (180 mL) and water (20 mL). The reaction mixture was cooled to 0 °C and NaBH_4 (0.42 g, 11.2 mmol, 0.5 eq) was added in one portion. The reaction was followed by TLC and after 15 min at 0 °C all the starting substance was consumed.

Most of the solvent was evaporated and the residue was taken up into water (50 mL) and extracted with dichloromethane (3 x 50 mL). The combined extracts were combined, dried over MgSO₄ and concentrated under vacuum. Diol **9** (3.57 g, 85 %) was isolated as a yellowish oil by flash chromatography with 70:30 hexane-ethyl acetate as the mobile phase.

9. IR (reflective): ν_{\max} 3404 (s), 2977, (s), 2930 (s), 2899 (s), 2247 (w), 1707 (w), 1445 (m), 1372 (m), 1351 (m), 1270 (m), 1230 (m), 1124 (s), 1067 (s), 915 (w), 844 (w), 805 (w), 732 (m) cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 4.49-4.30 (m, 2H), 4.30 (d, J = 1.5 Hz, 2H), 3.67-3.60 (m, 6H), 1.21 (t, J = 7.1 Hz, 6H); ¹³C NMR (50 MHz, CDCl₃): δ 103.1, 84.0, 82.4, 63.9, 63.4, 50.2, 14.9, 14.8; MS (EI): m/z 144 (5), 143 (48), 115 (25), 104 (65), 103 (32), 97 (65), 89 (10), 85 (25), 76 (30), 75 (52), 69 (79), 68 (81), 59 (100), 57 (70), 55 (65); HRMS m/z calcd for C₇H₁₁O₃ [M⁺ - EtO⁻] 143.0708, found 143.0711.

Hydrogenation of derivatives of **2a**

Reduction of 4. Formation of (Z)-4,4,5,5-tetraethoxypent-2-enyl acetate ((Z)-5). 4,4,5,5-Tetraethoxypent-2-ynyl acetate (**4**) (0.094 g, 0.31 mmol) was added to a suspension of Lindlar's catalyst (0.02 g) in ethyl acetate (8 mL). H₂ was bubbled through the reaction mixture at room temperature. The reaction time was 5 h, and (Z)-**5** (0.090 g, 95%) was obtained as a clear liquid after purification by flash chromatography (90:10 hexane-ethyl acetate).

(Z)-**5.** IR (film): ν_{\max} 2976 (s), 2931 (m), 2888 (m), 2246 (w), 1740 (s), 1444 (m), 1372 (s), 1340 (w), 1236 (s), 1119 (s), 1076 (s), 1051 (s), 1033 (s), 973 (w), 917 (w), 880 (w), 738 (m) cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 5.63 (m, 2H), 5.35 (d, J = 9.1 Hz, 2H), 4.86 (dd, J = 4.0, 1.8 Hz, 2H), 4.35 (s, 1H), 3.72-3.35 (m, 8H), 1.94 (s, 3H), 1.10 (q, J = 7.1 Hz, 12H); ¹³C NMR (50 MHz, CDCl₃): δ 194.6, 131.3, 129.3, 104.4, 65.5, 63.2, 57.1, 54.2, 21.6, 15.9, 15.8; MS (EI): m/z 260 (18), 259 (65), 216 (12), 215 (22), 214 (35), 213 (40), 202 (73), 201 (40), 185 (40), 171 (85), 160 (23), 155 (38), 143 (30), 142 (40), 141 (45), 131 (87), 125 (80), 115 (78), 114 (90), 104 (90), 99 (80), 98 (65), 87 (60), 83 (70), 73 (85); HRMS calcd for C₁₃H₂₃O₅ [M⁺ - EtO⁻] 259.1545, found 259.1543.

Reduction of 7. Formation of (Z)-5,5-diethoxy-4-hydroxypent-2-enyl acetate (10). Acetate **7** (0.23 g, 1.0 mmol) was added to a stirred mixture of Lindlar's catalyst (0.08 g) and potassium carbonate (0.08 g) in ethyl acetate (10 mL), which was kept stirring under a hydrogen atmosphere for 30 min. The product mixture was filtered through a Celite plug, and the solvent was removed *in vacuo* on a rotary evaporator, which left **10** (0.23 g, 99%) as a clear oil.

10. IR (film): ν_{\max} 3469 (m), 3028 (w), 2977 (s), 2931 (m), 2897 (m), 1740 (s), 1481 (w), 1445 (m), 1373 (s), 1240 (s), 1119 (s), 1066 (s), 1030 (s), 887 (w) cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 5.92-5.60 (m, 2H), 4.78-4.11 (m, 4H), 3.81-3.53 (m, 4H), 2.60 (s, 1H), 2.07 (s, 3H), 1.24 (m, 6H); ¹³C NMR (50 MHz, CDCl₃): δ 170.7, 131.1, 127.8, 104.4, 71.2, 68.6, 63.8, 60.8, 20.7, 15.1; MS (EI): m/z 130 (5), 129 (25), 104 (8), 103 (100), 101 (8), 87 (48), 75 (70), 71 (12), 60 (8), 59 (25), 55 (6); HRMS m/z calcd for C₇H₁₃O₂ [M⁺ - C₅H₁₁O₂⁻] 129.0916, found 129.0914.

Reduction of 9. Formation of (Z)-5,5-diethoxypent-2-ene-1,4-diol (11). Diol **9** (0.50 g, 2.7 mmol) was added to a stirred mixture of Lindlar's catalyst (0.10 g) and potassium carbonate

(0.10 g) in ethyl acetate (10 mL) and kept stirring under a hydrogen atmosphere for 50 min. The product mixture was filtered through a Celite plug, and the solvent was removed *in vacuo* on a rotary evaporator, which left **11** (0.50 g, 99%) as a yellowish oil.

11. IR (film): ν_{\max} 3395 (s), 3021 (w), 2977 (s), 2930 (s), 2885 (s), 1652 (w), 1445 (m), 1392 (m), 1374 (m), 1345 (m), 1275 (m), 1121 (s), 1066 (s), 1027 (s), 945 (m), 885 (w), 843 (w), 762 (w), 720 (w) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 5.91-5.81 (m, 1H), 5.61-5.51 (m, 1H), 4.45-4.13 (m, 4H), 3.83-3.46 (m, 6H), 1.22 (q, $J = 7.0$ Hz, 6H); ^{13}C NMR (50 MHz, CDCl_3): δ 132.6, 129.4, 104.2, 68.2, 64.3, 63.3, 58.2, 15.0, 14.9; MS (EI): m/z 145 (8), 143 (8), 129 (8), 128 (15), 127 (85), 126 (10), 115 (15), 105 (30), 104 (92), 97 (60), 89 (10), 86 (60), 85 (90), 81 (90), 76 (82), 71 (52), 69 (48), 61 (16), 60 (100), 59 (60); HRMS m/z calcd for $\text{C}_7\text{H}_{13}\text{O}_3$ [$\text{M}^+ - \text{EtO}^-$] 145.0865, found 145.0868.

Reduction of 6. Formation of (Z)-5,5-diethoxy-4-oxopent-2-enyl acetate (12). Acetate **6** (0.20 g, 2.0 mmol) was added to a stirred mixture of Lindlar's catalyst (0.08 g) and quinoline (0.08 g) in ethyl acetate (10 mL) and kept stirring under hydrogen for 30 min. The reaction mixture was filtered through a Celite plug, and the solvent was then removed *in vacuo* on a rotary evaporator. Filtration through a silica plug, to remove the quinoline, and removal of the solvent gave acetate **12** (0.20 g, >99%) as a pure oil.

12. IR (film): ν_{\max} 2980 (m), 2932 (m), 2884 (m), 2253 (w), 1742 (s), 1711 (s), 1619 (s), 1444 (w), 1415 (m), 1372 (s), 1320 (m), 1233 (s), 1174 (m), 1102 (s), 1062 (s), 1042 (s), 914 (s), 842 (w), 792 (w), 734 (s) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 6.60 (dt, $J = 12.1, 2.4$ Hz, 1H), 6.32 (dt, $J = 11.7, 4.8$ Hz, 1H), 5.17 (dd, $J = 4.8, 2.4$ Hz, 2H), 4.65 (s, 1H), 3.75-3.50 (m, 4H), 2.10 (s, 3H), 1.25 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (50 MHz, CDCl_3): δ 195.0, 170.5, 146.5, 122.0, 102.2, 63.7, 63.1, 20.7, 15.0; MS (EI): m/z 142 (8), 125 (20), 115 (5), 105 (5), 104 (38), 103 (100), 97 (62), 96 (12), 85 (20), 76 (12), 75 (92), 69 (20), 68 (18), 58 (10), 57 (28); HRMS m/z calcd for $\text{C}_9\text{H}_{13}\text{O}_4$ [$\text{M}^+ - \text{EtO}^-$] 185.0811, found 185.0814.

Hydrogenation of mixtures of derivatives of 2a

Reduction of a 1:1 mixture of 2a and 4. 4,4,5,5-Tetraethoxypent-2-yn-1-ol (**2a**) (0.130 g, 0.50 mmol) and 4,4,5,5-tetraethoxypent-2-ynyl acetate (**4**) (0.151 g, 0.50 mmol) were dissolved in ethyl acetate (2 mL), to which were added Lindlar catalysts (0.005 g) and K_2CO_3 (0.0003 g). Hydrogen was bubbled through the reaction mixture and the reaction was monitored by TLC. After 5 hours all the acetate (**4**) was consumed and the reaction was stopped. The Lindlar catalysts and K_2CO_3 were then filtered from the reaction mixture and ethyl acetate was evaporated. NMR-analysis of the crude mixture showed that it contained a 1:4:5 mixture of (Z)-**3a**, **2a**, and (Z)-**5**. The product mixture was subjected to flash chromatography (80:20; hexane-ethyl acetate) which afforded (Z)-4,4,5,5-tetraethoxypent-2-en-1-ol ((Z)-**3a**) (0.023g, 18%) as a clear liquid and (Z)-4,4,5,5-tetraethoxypent-2-enyl acetate ((Z)-**5**) (0.135 g, 90%) as a clear liquid.

Reduction of a 1:1 mixture of 7 and 9. Acetate **7** (0.115 g, 0.50 mmol) and diol **9** (0.094 g, 0.50 mmol) were dissolved in ethyl acetate (2 mL) mixed with Lindlar catalysts (0.005 g) and K_2CO_3 (0.0003 g). H_2 gas was bubbled through the reaction mixture while the reaction was followed by TLC. After 30 min all the acetate was consumed, and the reaction was then stopped. The catalysts and K_2CO_3 were filtered from the reaction mixture and ethyl acetate was evaporated. NMR analysis of the crude mixture showed that it contained the corresponding allylic alcohols, (*Z*)-5,5-diethoxy-4-hydroxypent-2-enyl acetate (**10**) and (*Z*)-5,5-diethoxypent-2-ene-1,4-diol (**11**), in at ratio 2:1. The product mixture was subjected to flash chromatography (90:10; hexane-ethyl acetate) giving 0.107 g (92%) of pure **10** as a clear liquid and 0.044 g (46%) of pure **11** as a yellowish oil.

Reduction of a 1:1 mixture of 4 and 6. Ketal **4** (0.151 g, 0.5 mmol) and ketone **6** (0.114 g, 0.5 mmol) were dissolved in ethyl acetate (2 mL) together with Lindlar catalysts (0.005 g) and K_2CO_3 (0.0003 g). H_2 -gass was bubbled through the reaction mixture for 30 min. The reaction was monitored by TLC and stopped when all of the more reactive alkyne, conjugated ynone **6**, had been consumed. The Lindlar catalysts and K_2CO_3 were then filtered from the reaction mixture and ethyl acetate was evaporated on a rotary evaporator. NMR analysis of the crude mixture showed that it contained the hydrogenated products (*Z*)-**5** and **12** in a 1:8 ratio. The product mixture was subjected to flash chromatography (90:10; hexane-ethyl acetate) and pure **12** (0.103 g, 91%) as a clear liquid and (*Z*)-**5** (0.020 g, 12%) as a clear liquid were obtained.

Reduction of propargylic alcohols (2**) to (*E*)-allylic alcohols ((*E*)-**3**). General procedure**

The propargylic alcohol was added dropwise to a mixture of lithium aluminium hydride (LAH) (1.5 equiv.) in dry THF (40 mL) at $-15\text{ }^\circ\text{C}$. The reaction mixture was left stirring at this temperature for 24 h before being quenched by slow addition of an excess of ethanol (10 mL). Most of the solvent were evaporated on a rotary evaporator and the residue was taken up into water (25 mL). The hydrolysate was extracted with dichloromethane (3 x 25 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated *in vacuo* on a rotary evaporator. The crude product was purified by flash chromatography (80:20, hexane-ethyl acetate).

(*E*)-4,4,5,5-Tetraethoxypent-2-en-1-ol ((*E*)-3a**).** Alcohol **2a** (0.60 g, 2.3 mmol) and LAH (0.13 g, 3.4 mmol) gave (*E*)-**3a** (0.59 g, 98%) as a clear liquid.

(*E*)-3a**.** IR (film): ν_{max} 3442 (m), 2973 (s), 2885 (s), 1454 (m), 1385 (m), 1337 (m), 1273 (w), 1078 (s), 922 (m), 880 (m), 812 (w) cm^{-1} ; ^1H NMR (200 MHz, $CDCl_3$): δ 6.16 (dt, $J = 5.2, 15.8$ Hz, 1H), 5.72 (dt, $J = 1.5, 15.8$ Hz, 1H), 4.44 (s, 1H), 4.18 (dd, $J = 1.5, 5.2$ Hz, 2H), 3.82-3.39 (m, 8H), 2.83 (bs, 1H), 1.22 (t, $J = 7.1$ Hz, 6H), 1.17 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 133.9, 126.4, 103.3, 100.1, 64.4, 62.4, 56.2, 14.9, 14.8; MS (EI): m/z 217 (3), 187 (1), 171 (1), 159 (44), 142 (10), 127 (7), 103 (100), 97 (23), 85 (57), 75 (63), 69 (22), 58 (16), 47 (71); HRMS m/z calcd $C_{11}H_{21}O_4$ [$M^+ - EtO$] 217.1440, found 217.1434

(*E*)-5,5,6,6-Tetraethoxyhex-3-en-2-ol ((*E*)-3b**).** Alcohol **2b** (0.50 g, 1.8 mmol) and LAH (0.10 g, 2.6 mmol) gave (*E*)-**3b** (0.47 g, 93%) as a clear liquid.

(E)-3b. IR (reflective): ν_{\max} 3426 (w), 2974 (w), 2930 (w), 2883 (w), 1729 (w), 1633 (w), 1445 (w), 1374 (w), 1260 (w), 1151 (m), 1110 (s), 1062 (s), 975 (m), 926 (w), 706 (w) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 6.06 (dd, $J = 15.8$ Hz, 6.1 Hz, 1H), 5.66 (dd, $J = 15.8$ Hz, 1.2 Hz, 1H), 4.42 (s, 1H), 4.40-4.29 (m, 1H), 3.91-3.36 (m, 8H), 1.32-1.07 (m, 15H); ^{13}C NMR (50 MHz, CDCl_3): δ 139.2, 122.8, 103.9, 100.8, 65.1, 62.4, 56.1, 14.9, 14.8, 14.4; MS (EI): m/z 231 (12), 215 (8), 187 (40), 186 (55), 185 (75), 174 (75), 169 (10), 160 (45), 157 (80), 154 (15), 139 (92), 125 (30), 115 (70), 111 (90), 104 (95), 97 (80), 95 (50), 87 (60), 81 (80), 76 (78); HRMS m/z calcd for $\text{C}_{12}\text{H}_{23}\text{O}_4$ [$\text{M}^+ - \text{EtO}^-$] 231.1596 found 231.1601.

(E)-1,1,2,2-Tetraethoxyundec-3-en-5-ol ((E)-3e). Alcohol **2e** (0.60 g, 1.7 mmol) and LAH (0.10 g, 2.6 mmol) gave **(E)-3e** (0.49 g, 81%) as a clear liquid.

(E)-3e. IR (film): ν_{\max} 3501 (m), 2974 (s), 2929 (s), 2870 (s), 2858 (s), 2242 (w), 1635 (w), 1480 (m), 1440 (m), 1430 (m), 1389 (m), 1376 (m), 1327 (m), 1294 (w), 1250 (w), 1220 (w), 1119 (s), 1075 (s), 1019 (s), 950 (m), 921 (m), 878 (w), 804 (w), 765 (w) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 6.04 (dd, $J = 15.8$, 6.0 Hz, 1H), 5.70 (dd, $J = 15.8$, 6.0 Hz, 1H), 4.58-4.50 (m, 1H), 4.44 (s, 1H), 3.89-3.40 (m, 8H), 2.82 (bs, 1H), 1.50-1.20 (m, 22H), 0.90 (t, $J = 6.1$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3): δ 139.6, 125.7, 102.4, 101.8, 65.2, 65.0, 64.1, 55.8, 55.6, 35.7, 30.8, 28.4, 25.0, 22.1, 15.0, 14.9, 13.8; MS (EI): m/z 256 (30), 243 (70), 231 (10), 226 (55), 215 (20), 197 (40), 181 (25), 170 (50), 169 (100), 153 (35), 142 (40), 129 (35), 113 (50), 109 (78), 104 (60), 95 (40), 86 (20), 85 (20), 83 (55), 81 (60); HRMS m/z calcd for $\text{C}_{17}\text{H}_{33}\text{O}_4$ [$\text{M}^+ - \text{EtO}^-$] 301.2379, found 301.2386.

(E)-4,4,5,5-Tetraethoxy-1-phenylpent-2-en-1-ol ((E)-3f). Alcohol **2f** (0.51 g, 1.5 mmol) and LAH (0.10 g, 2.6 mmol) gave **(E)-3f** (0.37 g, 72%) as a clear liquid.

(E)-3f. IR (film): ν_{\max} 3446 (m), 3035 (w), 2973 (s), 2885 (s), 1674 (w), 1596 (w), 1568 (w), 1521 (m), 1453 (m), 1382 (m), 1337 (m), 1273 (w), 1078 (s), 922 (m), 881 (m), 812 (w), 788 (w) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.41-7.36 (m, 2H), 7.35-7.28 (m, 2H), 7.27-7.21 (m, 1H), 6.19 (dd, $J = 15.7$, 6.3 Hz, 1H), 5.84 (d, $J = 15.7$, 1H), 5.26 (d, $J = 6.3$ Hz, 1H), 4.43 (s, 1H), 3.77-3.39 (m, 8H), 2.93 (bs, 1H), 1.27-1.09 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3): δ 142.7, 136.5, 128.1, 127.2, 127.1, 126.3, 103.4, 100.3, 74.2, 64.5, 64.4, 56.5, 56.4, 15.2, 15.1; MS (EI): m/z 247 (12), 236 (30), 218 (10), 189 (20), 173 (8), 162 (15), 132 (15), 115 (30), 103 (190), 90 (10), 75 (50); HRMS m/z calcd for $\text{C}_{11}\text{H}_{21}\text{O}_4$ [$\text{M}^+ - \text{EtO}^-$] 293.1750, found 293.1741.

(E)-5,5,6,6-Tetraethoxy-2-methylhex-3-en-2-ol ((E)-3g). Alcohol **2g** (0.25 g, 0.87 mmol) and LAH (0.05 g, 1.3 mmol) gave **(E)-3g** (0.14 g, 54%) as a clear liquid.

(E)-3g. IR (film): ν_{\max} 3434 (s), 2974 (s), 2929 (s), 2887 (s), 2241 (w), 1678 (w), 1448 (m), 1272 (s), 1278 (m), 1214 (m), 1125 (s), 1072 (s), 913 (m), 788 (w) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 6.16 (d, $J = 16.0$ Hz, 1H), 5.67 (d, $J = 16.0$ Hz, 1H), 4.43 (s, 1H), 3.80-3.41 (m, 8H), 1.34 (s, 6H), 1.30-1.15 (m, 12H); ^{13}C NMR (50 MHz, CDCl_3): δ 141.1, 123.2, 104.7, 101.2, 65.0, 62.2, 56.2, 31.8, 14.9, 14.8; MS (EI): m/z 201 (7), 199 (10), 198 (8), 187 (38), 183 (2), 169 (8), 158 (2), 141 (50), 127 (10), 113 (90), 103 (50), 97 (52), 95 (42), 87 (8), 81 (13), 75 (92), 67 (30), 55 (20), 47 (100), 43 (80); HRMS m/z calcd for $\text{C}_{13}\text{H}_{25}\text{O}_4$ [$\text{M}^+ - \text{EtO}^-$] 245.1751, found 245.1760.

(E)-6,6,7,7-Tetraethoxy-3-ethylhept-4-en-3-ol ((E)-3h). Alcohol **2h** (0.25 g, 0.87 mmol) and LAH (0.05 g, 1.3 mmol) gave **(E)-3h** (0.14 g, 54%) as a clear liquid.

(E)-3h. IR (film): ν_{\max} 3422 (m), 2975 (s), 2933 (s), 2880 (s), 1650 (w), 1478 (w), 1439 (w), 1370 (w), 1293 (w), 1270 (w), 1115 (s), 1078 (s), 1049 (s), 982 (m), 920 (w), 887 (w), 790 (w) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 5.93 (d, $J = 15.9$ Hz, 1H), 5.60 (d, $J = 15.9$ Hz, 1H), 4.45 (s, 1H), 3.80-3.50 (m, 8H), 2.85 (bs, 1H), 1.53 (dq, $J = 7.1, 1.9$ Hz, 4H), 1.24 (t, $J = 6.0$ Hz, 12H), 0.91 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (50 MHz, CDCl_3): δ 140.2, 123.8, 104.3, 102.3, 72.9, 62.7, 56.4, 33.0, 15.1, 14.9, 8.3; MS (EI): m/z 244 (10), 232 (10), 227 (40), 215 (70), 199 (10), 197 (15), 186 (30), 181 (15), 169 (50), 157 (50), 153 (60), 142 (55), 135 (15), 125 (85), 113 (70), 95 (100), 83 (80), 75 (90); HRMS calcd for $\text{C}_{15}\text{H}_{29}\text{O}_4$ [$\text{M}^+ - \text{EtO}^-$] 273.2066, found 273.2058.

Reduction of propargylic alcohols (2) to homoallylic alcohols (13). General procedure

The propargylic alcohol was added dropwise to a mixture of LAH (3.0 equiv.) in dry, refluxing (35 °C) diethyl ether. The reaction mixture was left stirring at reflux until the reaction was complete (20 min). Most of the solvent was evaporated on a rotary evaporator and the residue was mixed with water (30 mL), and then extracted with dichloromethane (3 x 30 mL). The combined organic phases were dried (MgSO_4), filtered, and concentrated *in vacuo* on a rotary evaporator. The crude product was purified by flash chromatography (80:20, hexane-ethyl acetate). TLC analyses indicated that the products were pure, but the ^1H - and ^{13}C -NMR spectra showed that the compounds contained one or several minor contaminants.

(E)-4,5,5-Triethoxypent-3-en-1-ol (13a). 4,4,5,5-Tetraethoxypent-2-yn-1-ol (**2a**) (1.50 g, 6.5 mmol) and LAH (0.76 g, 20.0 mmol) in ether (50 mL) gave **13a** (0.99 g, 70%) as a clear liquid.

13a. IR (film): ν_{\max} 3432 (m), 2976 (s), 2928 (s), 2879 (s), 1663 (m), 1478 (w), 1445 (m), 1386 (m), 1333 (m), 1163 (s), 1114 (s), 1061 (s), 992 (w), 887 (w), 812 (w) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 5.00 (s, 1H), 4.59 (t, $J = 8.1$ Hz, 1H), 3.79-3.46 (m, 8H), 2.97 (bs, 1H), 2.44 (dt, $J = 6.3, 8.1$ Hz, 2H), 1.32 (t, $J = 7.0$ Hz, 3H), 1.24 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (50 MHz, CDCl_3): δ 153.5, 99.3, 97.2, 62.5, 62.3, 62.2, 28.2, 14.8, 14.2; MS (EI) m/z ; 217 (1), 187 (2), 172 (25), 159 (13), 142 (26), 127 (84), 115 (17), 103 (100), 85 (57), 75 (82), 69 (66), 57 (30), 47 (91); HRMS calcd for $\text{C}_9\text{H}_{17}\text{O}_3$ [$\text{M}^+ - \text{EtO}^-$] 173.1178, found 173.1175.

(E)-5,6,6-Triethoxyhex-4-en-2-ol (13b). 5,5,6,6-Tetraethoxyhex-3-yn-2-ol (**2b**) (0.40 g, 1.46 mmol) and LAH (0.17 g, 4.48 mmol) in ether (30 mL) gave **13b** (0.25 g, 74%) as a clear liquid.

13b. IR (film): ν_{\max} 3428 (s), 2972 (s), 2928 (s), 2895 (s), 1959 (w), 1662 (m), 1447 (m), 1384 (m), 1332 (m), 1230 (m), 1071 (s), 945 (m), 890 (m), 851 (m), 822 (m), 691 (m) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 4.99 (s, 1H), 4.62 (t, $J = 8.3$ Hz, 1H), 3.81-3.46 (m, 6H), 2.93 (bs, 1H), 2.38-2.30 (m, 2H), 1.31 (t, $J = 7.0$ Hz, 2H), 1.24 (t, $J = 7.0$ Hz, 3H), 1.23 (t, $J = 7.0$ Hz, 3H), 1.19 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3): δ 153.6, 99.4, 97.0, 67.4, 62.4, 62.3, 62.2, 34.4, 22.5, 14.7, 14.1; MS (EI): m/z 231 (1), 187 (41), 129 (33), 113 (82), 103 (87), 97 (83), 87 (65), 75 (88), 69 (100), 55 (83); HRMS calcd for $\text{C}_{10}\text{H}_{19}\text{O}_3$ [$\text{M}^+ - \text{EtO}^-$] 187.1334, found 187.1329.

(E)-1,1,2-Triethoxyundec-2-en-5-ol (13e). 1,1,2,2-Tetraethoxyundec-3-yn-5-ol (**2e**) (1.01 g, 2.9 mmol) and LAH (0.33 g, 8.7 mmol) in ether (50 mL) gave **13e** (0.82 g, 93%) as a clear liquid.

13e. IR (film): ν_{\max} 3442 (m), 2975 (s), 2928 (s), 2860 (s), 2249 (w), 1962 (w), 1664 (m), 1457 (m), 1444 (m), 1390 (m), 1332 (m), 1295 (m), 1229 (m), 1116 (s), 1070 (s), 952 (w), 919 (w), 878 (w), 814 (w), 736 (m), 700 (w) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 4.98 (s, 1H), 4.61 (t, $J = 8.3$ Hz, 1H), 3.84-3.46 (m, 6H), 2.38-2.30 (m, 2H), 1.45-1.17 (m, 20H), 0.88 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3): δ 154.1, 99.7, 97.1, 71.5, 62.8, 62.6, 62.5, 37.0, 31.8, 29.3, 25.7, 22.5, 22.4, 15.0, 14.9, 14.4, 14.0; MS (EI): m/z 299 (38), 271 (10), 254 (18), 241 (79), 214 (40), 209 (53), 197 (14), 181 (22), 167 (29), 151 (25), 142 (38), 128 (52), 109 (82), 85 (100), 69(78), 57 (77); HRMS calcd for $\text{C}_{15}\text{H}_{28}\text{O}_3$ [$\text{M}^+ - \text{EtOH}$] 256.2038, found 256.2046.

(E)-4,5,5-Triethoxy-1-phenylpent-3-en-1-ol (13f). 4,4,5,5-Tetraethoxy-1-phenylpent-2-yn-1-ol (**2f**) (0.27 g, 0.80 mmol) and LAH (0.09 g, 2.4 mmol) in ether (30 mL) gave **13f** (0.17 g, 72%) as a clear liquid.

13f. IR (film): ν_{\max} 3448 (m), 3061 (m), 3028 (m), 2976 (s), 2892 (s), 1662 (s), 1604 (w), 1484 (m), 1448 (m), 1386 (s), 1334 (m), 1298 (m), 1071 (s), 937 (m), 877 (m), 807 (m), 755 (m), 701 (m), 660 (w) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 7.38-7.19 (m, 5H), 4.93 (s, 1H), 4.69-4.49 (m, 2H), 3.76-3.42 (m, 6H), 2.68-2.59 (m, 2H), 1.28 (t, $J = 7.0$ Hz, 3H), 1.24 (t, $J = 7.0$ Hz, 3H), 1.22 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3): δ 151.3, 141.5, 128.0, 127.2, 125.6, 96.9, 95.4, 74.3, 62.6, 62.1, 57.8, 31.3, 18.0, 15.2, 14.2; MS (EI): m/z 249 (3), 221 (1), 203 (3), 191 (100), 175 (5), 163 (10), 145 (13), 129 (15), 117 (68), 103 (38), 91 (15), 75 (34); HRMS calcd for $\text{C}_{15}\text{H}_{21}\text{O}_3$ [$\text{M}^+ - \text{EtO}^-$] 249.1441, found 249.1488.

(E)-5,6,6-Triethoxy-2-methylhex-4-en-2-ol (13g). 5,5,6,6-Tetraethoxy-2-methylhex-3-yn-2-ol (**2g**) (0.50 g, 1.7 mmol) and LAH (0.20 g, 5.3 mmol) in ether (30 mL) gave **13g** (0.23 g, 54%) as a clear liquid.

13g. IR (film): ν_{\max} 3472 (m), 2976 (s), 2932 (m), 1732 (m), 1629 (w), 1459 (m), 1369 (m), 1283 (m), 1216 (m), 1105 (m), 1064 (s), 910 (w), 878 (w), 800 (w) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 4.93 (s, 1H), 4.61 (t, $J = 8.6$ Hz, 1H), 3.72-3.36 (m, 6H), 2.97 (bs, 1H), 2.26 (d, $J = 8.6$ Hz, 2H), 1.24 (s, 6H), 1.19-1.11 (m, 9H); ^{13}C NMR (50 MHz, CDCl_3): δ 150.1, 94.1, 92.8, 70.9, 64.2, 62.4, 62.1, 35.1, 29.2, 15.0, 14.8, 14.7; MS (EI) m/z 201 (20), 171 (5), 155 (10), 143 (13), 137 (18), 127 (22), 116 (70), 99 (89), 87 (67), 73 (96), 55 (100); HRMS calcd for $\text{C}_{13}\text{H}_{26}\text{O}_4$ [M^+] 246.1831, found 246.1825.

Supplementary information available

The ^1H -NMR and ^{13}C -NMR spectra of all new compounds are compiled as supplementary material and are available from the authors on request.

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