Facile, Asymmetric Addition of Acetylene to Aldehydes: *In Situ* Generation of Reactive Zinc Acetylide

by **Hiroshi Sasaki**, **Dean Boyall**, and **Erick M. Carreira***

Laboratorium für Organische Chemie, Universitätstrasse 16, ETH-Zentrum, CH-8092 Zürich

This study documents a process in which acetylene is employed directly in nucleophilic additions to aldehydes to give adducts in high levels of enantiomeric induction, up to 98% ee. To the best of our knowledge, this represents the first time in which acetylene itself has been utilized in such ligand-controlled enantioselective additions.

Introduction. – Optically active propargylic alcohols constitute a versatile and useful class of building blocks for asymmetric synthesis[1]). The presence of a C≡C bond in these compounds offers a diversity of options for further synthetic elaboration [2]. In this regard, propargylic alcohols can be transformed into the corresponding *cis*- or *trans*-allylic alcohols by a variety of semireductive methods [3]. The rich organometallic chemistry to which the C≡C bond can be subjected further expands the scope and versatility of propargylic alcohols [4]. Thus, not only can internal acetylenes readily participate in metallation reactions [5], but, also, more recently, they have been demonstrated to participate in metathesis reactions, giving rise to cycloalkynes [6]. There have been three general approaches to the preparation of optically active propargylic alcohols, namely, biocatalytic resolutions of propargylic esters [7], ynone reduction with stoichiometric as well as catalytic reductants [8][9], and alkyne additions to aldehydes [10–15][2]). Of these, the latter approach is inherently the most efficient, as the new stereogenic center and the C,C bond form concomitantly. We have been studying methods for the direct addition of terminal alkynes to C=N and C=O bonds and have recently disclosed that, in the presence of $Zn(OTf)_2$, amine base, and amino alcohol ligands, additions to aldehydes and nitrones may be carried out in an enantioselective manner [12]. The additions work well for a broad range of aldehydes and functionalized terminal alkynes. In continuing investigations of this system, we set out to investigate whether acetylene itself, C_2H_2, would participate in these addition reactions, and whether these additions in turn could be carried out in an enantioselective manner. Herein, we describe the realization of such a process in which C_2H_2 is employed directly in nucleophilic additions to aldehydes to give adducts in high levels of enantiomeric induction (up to 98% ee; *Scheme 1*): To the best of our knowledge, this represents the first time in which C_2H_2 itself has been utilized in such ligand-controlled enantioselective additions.

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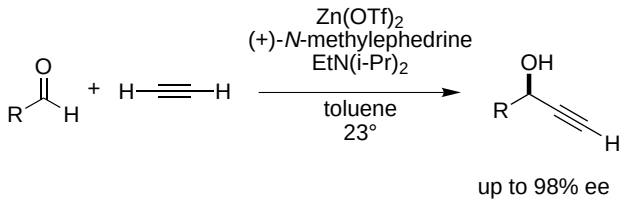
[1]) For selected examples of the use of optically active propargylic alcohols, see [1].

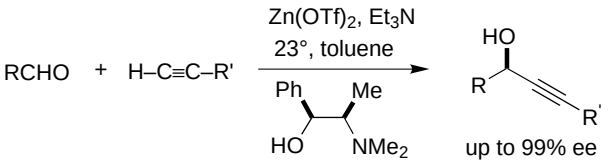
[2]) An alternative strategy for the preparation of optically active propargylic alcohols involves addition to alkynals (see [15]).

Scheme 1



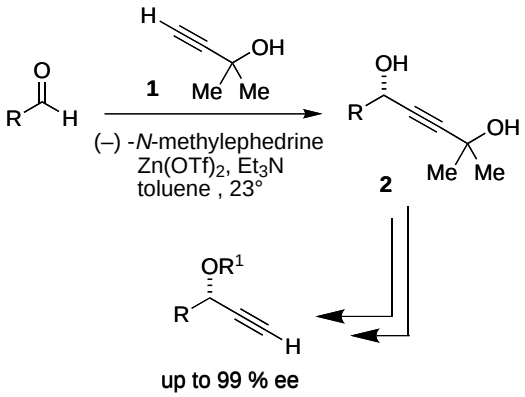
Results and Discussion. – The enantioselective addition of borylalkynes to aldehydes has been reported in a study by *Corey* in which a chiral oxazaborolidine was employed as catalyst and chiral additive [10b]. More recently, researchers at *Merck* have reported remarkably selective additions of lithiated phenylacetylene to aromatic aldehydes as well as of lithiated cyclopropylacetylene to trifluoromethyl ketones in the presence of chiral amino alcohols, such as (1*R*,2*S*)-2-(1,2-diphenylpyrrolidin-1-yl)-ethanol and (1*S*,2*R*)-2-(1,3-dihydroisoindol-2-yl)-1,2-diphenylethanol, to give optically active secondary and tertiary alcohols, respectively [11]. We have documented a new procedure in which a Zn-acetylide is generated *in situ* under mild conditions directly from a terminal alkyne. This organozinc species undergoes highly enantioselective additions to a range of aldehydes in the presence of (+)- or (−)-*N*-methylephedrine (*Scheme 2*).

Scheme 2



In recent work, we have also disclosed that 2-methylbut-3-yn-2-ol (**1**), a readily available and inexpensive commodity bulk chemical, also participates in the addition reactions; by a facile, thermal fragmentation reaction of **2**, these addition reactions provide access to optically active terminal alkynes as useful building blocks for asymmetric synthesis (*Scheme 3*) [12d]. However, although C_2H_2 is as a commodity chemical with a worldwide production exceeding 300,000 tons/year and one of the least expensive carbon sources, its use in enantioselective aldehyde additions has not been the subject of extensive investigations. Its use in asymmetric additions has been reported only rarely, with the addition reactions displaying poor selectivity [16][17]. The use of C_2H_2 in aldehyde addition reactions would provide adducts possessing much versatility as building blocks for synthesis of complex molecules. In addition to transformations involving the C≡C bond, terminal alkyne adducts can participate in subsequent C−C bond-forming reactions; as such, the production of optically active propargylic alcohols derived from C_2H_2 provide general access to a large family of propargylic alcohols.

Scheme 3



At the outset of our investigations described herein, we had little information regarding the structural requirements of a zinc-alkynilide, generated under the conditions we have described, to participate successfully in enantioselective addition reactions. In this respect, given the known propensity for C_2H_2 to undergo double metallation and form multinuclear aggregates, there was concern over whether this simplest of alkynes would participate in the *in situ* activation/deprotonation and subsequent nucleophilic additions.

In preliminary experiments, a solution of toluene was saturated with C_2H_2 gas at 0° by bubbling for 10–15 min. This solution was subsequently treated with $Zn(OTf)_2$, $EtN(i\text{-}Pr)_2$, and (+)- or (−)-*N*-methylephedrine followed by an aldehyde. Under these conditions, adducts were isolated as a 1:1 mixture of the desired alk-1-yn-3-ols and 1,4-diols, the products of double addition of an equivalent of C_2H_2 to 2 equiv. of aldehyde. We then proceeded to investigate whether increasing the concentration of dissolved C_2H_2 would lead to minimization of the 1,4-diol products of double addition with concomitant improvement in the yield of the monoaddition adducts. In this regard, a mixture of aldehyde, $Zn(OTf)_2$, $EtN(i\text{-}Pr)_2$, and (+)- or (−)-*N*-methylephedrine in toluene was cooled to −40° and bubbled with C_2H_2 for 20 min, and the reaction vessel was sealed and allowed to warm to 23°. Under these conditions, the formation of monoadducts from the addition of C_2H_2 and aldehydes was optimized, giving propargylic alcohols in up to 98% ee (*Scheme 4* and *Table*). Because some of the substrates we investigated afforded low-molecular-weight, volatile alcohol adducts **4**, the isolated yields were only modest. However, we found that this problem could be circumvented if, when following the addition reaction, the unpurified products were treated with 3,5-dinitrobenzoyl chloride (DMAP, Et_3N) to afford the corresponding propargylic esters **5** (*Scheme 4*). These protected adducts were more easily handled and, in some cases, crystalline.

In contrast to the addition reactions we have reported for substituted terminal alkynes, the additions involving C_2H_2 are uniformly slower. For aliphatic aldehydes, the reactions reach completion in 7 days, while, for aromatic and conjugated aromatic aldehydes, the reactions were observed to reach only 35% conversion in 14 days. We speculate that the dramatic rate differences between terminal, substituted alkynes and

Scheme 4

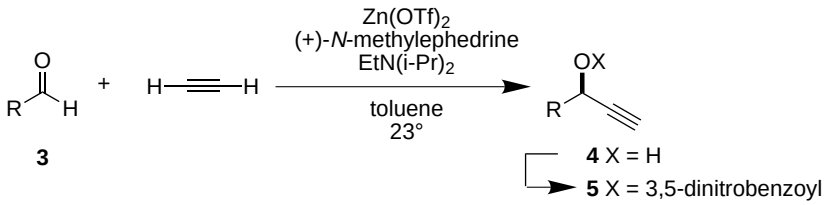
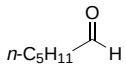
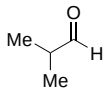
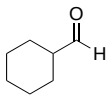
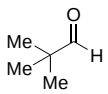
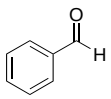
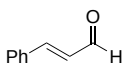
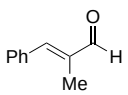


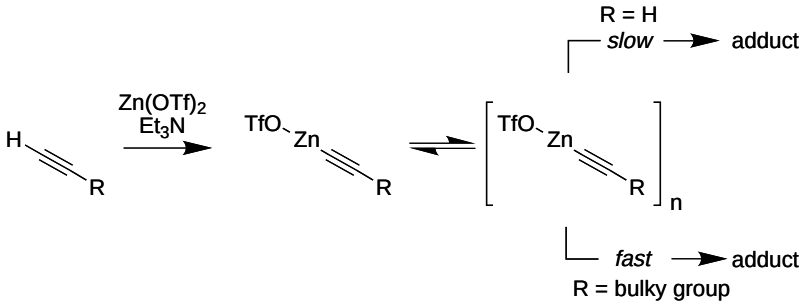
Table. *Enantioselective Additions of Acetylene with Aldehydes* (see *Scheme 4*)[a])

Entry	**3**	Reaction time [d]	Recovery of **3** [%]	Yield [%] of **4** or **5**		ee [%][f])
1		7	0[b])	30[d])	**4a**	97
2		7	0[b])	76[e])	**5a**	98
3		7	0[b])	70[c])	**4b**	98
4		7	0[b])	92[e])	**5b**	98
5		14	32[c])	35[c])	**4c**	97
6		14	41[c])	34[c])	**4d**	92
7		14	61[c])	28[c])	**4e**	91

[a]) The C_2H_2 addition reaction was conducted with 1.1 equiv. $Zn(OTf)_2$, 1.2 equiv. (+)-*N*-methylephedrine, 1.2 equiv. $EtN(i\text{-}Pr)_2$, and excess C_2H_2 (saturated at $-40°$) in toluene (0.05M) at 23°. [b]) Determined by TLC. [c]) Isolated yield after CC. [d]) Determined by GC with dodecane as internal standard. [e]) Isolated yield as the corresponding 3,5-dinitrobenzoates. [f]) Determined by ^{1}H-NMR analysis of the corresponding (*S*)- or (*R*)-*Mosher* esters. Absolute configuration of the products was established by correlation with known compounds or by analogy.

C_2H_2 may result from the formation of unreactive aggregates of the sterically unhindered metallated species derived from C_2H_2. Interestingly, we have noted that, in previous studies, the more hindered alkynes react at an appreciably faster rate (*Scheme 5*). Thus, in contrast to the results with C_2H_2, the use of (*tert*-butyl)ethyne lead to significant rate enhancement that may result from significant perturbation of the putative equilibrium between unreactive aggregates and reactive species [18][3]). It is interesting to note that, above $-25°$, monolithium acetylide is known to disproportionate into the more stable dilithiated carbide and C_2H_2 [19]. Irrespective of the rate, it is interesting to note that, in all cases, the enantioselectivities were observed to be high (91–98% ee). Thus, neither the structure of the alkyne nor of the aldehyde appears to have a dramatic impact on the optical purity of the adduct isolated from the reaction.

Scheme 5



Conclusion. – We have documented highly enantioselective additions of C_2H_2 to aldehydes to give propargylic alcohols in up to 98% ee. These results underscore the versatility of the novel process we have described for the *in situ* generation of zinc-acetylides from terminal alkynes in the presence of $Zn(OTf)_2$, and amine bases. Additionally, the high selectivities observed with C_2H_2 further highlight the unique aspects of the enantioselective additions in which both hindered and unhindered terminal alkynes afford products in high levels of asymmetric induction. To the best of our knowledge, this represents the first report in which C_2H_2 is used directly in enantioselective addition reaction with aldehydes.

The generous support of ETH-Zentrum and *F. Hoffmann-La Roche AG* is gratefully acknowledged. We thank *UBE Industries Ltd.*, Tokyo, Japan for sponsoring *H. S.*

Experimental Part

General. All aldehydes were distilled prior to use. Zinc(II) triflate, (+)-*N*-methylephedrine, and (+)-(*R*)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (MTPA) were purchased from *Fluka*. $EtN(i\text{-}Pr)_2$ and Et_3N were distilled from KOH prior to use. Toluene and CH_2Cl_2 were purified by passage through activated alumina column prior to use. Acetylene was purified by passing through conc. H_2SO_4 and then KOH. Air- and moisture-sensitive liquids were transferred *via* syringe. Organic solns. were concentrated by rotary evaporation below 50°.

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[3]) Studies of the solution and crystal structures of lithiated acetylenes reveal that the aggregation state of acetylenes varies as a function of the substitution (for examples, see [18]).

Chromatographic purification of products was carried out by forced-flow column chromatography (CC) on *Fluka* silica gel *60* (230–400 mesh). Thin-layer chromatography (TLC) was performed on *Merck* 0.25-mm silica gel *60F* plates (230–400 mesh). Visualization of the developed chromatogram was performed either with UV light or by staining with phosphomolybdic acid or anisaldehyde. GC: *Varian 3400*; *Supelco SPB-5* capillary column. Optical rotations: *JASCO DIP-1000* digital polarimeter operating at 589 nm. M.p.: *Büchi 510* melting-point apparatus; uncorrected. IR Spectra: *Perkin-Elmer Spectrum-RX1 FT-IR* spectrometer; KBr pellets or thin films on NaCl; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Varian Mercury-300* (300 MHz for ^1H and 75 MHz for ^{13}C), chemical shifts (δ) in ppm (referenced internally to solvent signals), and coupling constant J in Hz. Elemental analysis was performed by the analytical laboratory at ETH-Zentrum.

General Procedure for the Nucleophilic Addition of C_2H_2 to Aldehydes. – A 100-ml glass pressure-reaction tube was charged with $Zn(OTf)_2$ (1.00 g, 2.75 mmol), dried by evacuation and heating with a heat-gun, and then purged with N_2. (+)-*N*-Methylephedrine (538 mg, 3.00 mmol), toluene (50 ml), and $EtN(i\text{-}Pr)_2$ (0.81 g, 6.3 mmol) were added, and the mixture was stirred at r.t. (23°) for 2 h under N_2. To the resulting suspension was added the aldehyde (2.50 mmol). The mixture was cooled at −40° and saturated with C_2H_2 by bubbling for 20 min before the reactor was closed tightly. The resulted suspension was stirred at r.t. for 7–14 d. The reactor was cooled at −40° and opened carefully. To the reaction mixture was added sat. aq. NH_4Cl soln. (20 ml) dropwise, and the mixture was allowed to warm to r.t. with stirring for 2 h. The two layers were separated, and the org. layer was washed with brine (10 ml) and dried (Na_2SO_4) to afford the crude propargylic alcohol soln. in toluene.

*(*R*)-Oct-1-yn-3-ol* (**4a**). The reaction was carried out for 7 d. The yield of **4a** was 30% determined by GC analysis of the unpurified toluene solution. Removal of toluene by rotary evaporation and purification by CC (silica gel; hexane/AcOEt 95:5–50:50) afforded crude **4a**, which was purified by bulb-to-bulb distillation. Colorless oil. B.p. 95°/40 mmHg. $[\alpha]_D^{27} = +5$ ($c = 0.545$, $CHCl_3$) [20]. IR (thin film): 3311, 2932, 2862, 2116, 1468, 1027. ^1H-NMR ($CDCl_3$, 300 MHz): 4.37 (*td*, $J = 6.5, 2.2, 1$ H); 2.46 (*d*, $J = 2.2$, 1 H); 1.82 (br. *s*, 1 H); 1.8–1.6 (*m*, 2 H); 1.6–1.4 (*m*, 2 H); 1.4–1.2 (*m*, 4 H); 0.90 (*t*, $J = 7.0$, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 85.2; 73.0; 62.5; 37.7; 31.5; 24.7; 22.6; 14.0. Anal. calc. for $C_8H_{14}O$: C 76.14, H 11.18; found: C 75.92, H 11.48.

A small amount of the alcohol was converted to the corresponding *Mosher* ester ((*S*)-MTPA chloride, 4-(dimethylamino)pyridine (DMAP), CH_2Cl_2, 40°). The optical purity was 97% ee determined by ^1H-NMR analysis of the acetylenic proton of the corresponding ester derived from (*S*)-MTPA chloride (2.54 ppm (major), 2.49 ppm (minor)).

*(*R*)-1-(1-Methylethyl)prop-2-ynyl 3,5-Dinitrobenzoate* (**5a**). The reaction was carried out for 7 d. The resulting propargylic alcohol soln. in toluene was divided 4:1 by volume. To the larger portion was added Et_3N (0.63 g, 6.2 mmol), DMAP (99 mg, 0.81 mmol), and 3,5-dinitrobenzoyl chloride (1.46 g, 6.33 mmol), and the mixture was stirred at r.t. for 24 h. The resulting suspension was filtered, and the filtrate was washed with sat. aq. NH_4Cl (20 ml) and brine (10 ml), and then dried (Na_2SO_4). Removal of toluene by rotary evaporation and purification by CC (silica gel; toluene) afforded **5a** (445 mg, 1.52 mmol; 76%). To the smaller portion was added *N,N′*-dicyclohexylcarbodiimide (DCC; 336 mg, 1.63 mmol), DMAP (35 mg, 0.29 mmol), and (*R*)-MTPA (365 mg, 1.56 mmol), then the mixture was stirred at r.t. for 32 h. The resulting suspension was filtered, and the filtrate was concentrated and purified by passing through short silica-gel plug (hexane/AcOEt 80:20) to give the (*R*)-MTPA ester for ^1H-NMR analysis.

Data of **5a**: colorless solid [21]. M.p. 112°. $[\alpha]_D^{27} = +11$ ($c = 0.560$, $CHCl_3$). IR (KBr): 3416, 3303, 3106, 2981, 2128, 1727, 1633, 1545, 1470, 1347, 1286, 1172, 1074, 977, 720, 694, 657. ^1H-NMR ($CDCl_3$, 300 MHz): 9.25 (*t*, $J =$ 2.2, 1 H); 9.17 (*d*, $J = 2.2$, 2 H); 5.52 (*dd*, $J = 5.6, 2.2$, 1 H); 2.56 (*d*, $J = 2.2$, 1 H); 2.24 (*sept. d*, $J = 6.8, 5.6$, 1 H); 1.17 (*d*, $J = 6.8$, 3 H); 1.12 (*d*, $J = 6.8$, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 161.6; 148.7; 133.6; 129.6; 122.6; 78.5; 75.6; 71.5; 32.4; 18.2; 17.6. Anal. calc. for $C_{13}H_{12}N_2O_6$: C 53.43, H 4.14, N 9.59; found: C 53.80, H 4.40, N 9.52.

The optical purity was 98% ee determined by ^1H-NMR analysis of the acetylenic proton of the corresponding (*R*)-MTPA ester (2.54 ppm (major), 2.48 ppm (minor)).

*(*R*)-1-Cyclohexylprop-2-yn-1-ol* (**4b**). The reaction was carried out for 7 days. Removal of toluene by rotary evaporation and purification by CC (silica gel; hexane/AcOEt 95:5–60:40) afforded **4b** (241 mg, 1.74 mmol, 70%). Colorless solid [22]. M.p. 56°. $[\alpha]_D^{25} = +10$ ($c = 0.500$, Et_2O). IR (KBr): 3380, 3284, 2930, 2849, 2110, 1450, 1338, 1294, 1265, 1029, 985, 892, 652. ^1H-NMR ($CDCl_3$, 300 MHz): 4.18 (*td*, $J = 5.8, 2.1$, 1 H); 2.48 (*d*, $J = 2.1$, 1 H); 2.0–1.5 (*m*, 7 H); 1.4–0.9 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 84.0; 73.6; 67.0; 43.9; 28.4; 27.9; 26.3; 25.9; 25.8. Anal. calc. for $C_9H_{14}O$: C 78.21, H 10.21; found: C 78.29; H 10.22.

A small amount of the alcohol was converted to the corresponding *Mosher* ester ((*S*)-MTPA chloride, DMAP, CH_2Cl_2, 40°). The optical purity was 98% ee determined by ^1H-NMR analysis of the acetylenic proton of the corresponding ester derived from (*S*)-MTPA chloride (2.54 ppm (major), 2.48 ppm (minor)).

*(*R*)-1-(*tert*-Butyl)prop-2-ynyl 3,5-Dinitrobenzoate* (**5b**). The reaction was carried out for 7 d. The resulting propargylic alcohol soln. in toluene was divided 4:1 by volume. To the larger portion was added Et_3N (0.65 g, 6.4 mmol), DMAP (91 mg, 0.74 mmol), and 3,5-dinitrobenzoyl chloride (1.46 g, 6.33 mmol), and the mixture was stirred at r.t. for 24 h. The resulting suspension was filtered, and the filtrate was washed with sat. aq. NH_4Cl (20 ml) and brine (10 ml), and then dried (Na_2SO_4). Removal of toluene by rotary evaporation and purification by CC (silica gel; toluene) afforded **5b** (564 mg, 1.84 mmol, 92%). To the smaller portion was added DCC (336 mg, 1.63 mmol), DMAP (35 mg, 0.29 mmol), and (*R*)-MTPA (365 mg, 1.56 mmol), then the mixture was stirred at r.t. for 32 h. The resulting suspension was filtered, and the filtrate was concentrated and purified by passage through short silica-gel plug (hexane/AcOEt 80:20) to give the (*R*)-MTPA ester for ^{1}H-NMR analysis.

Data of **5b**: Colorless solid. M.p. 128°. $[\alpha]_D^{27} = +13$ ($c = 0.520$, $CHCl_3$). IR (KBr): 3418, 3304, 2975, 2128, 1722, 1632, 1543, 1347, 1283, 1167, 1073, 962, 918, 721, 695, 653. ^{1}H-NMR ($CDCl_3$, 300 MHz): 9.25 (*t*, $J = 2.2$, 1 H); 9.17 (*d*, $J = 2.2$, 2 H); 5.41 (*d*, $J = 2.2$, 1 H); 2.54 (*d*, $J = 2.2$, 1 H); 1.15 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 161.7; 148.8; 133.6; 129.5; 122.6; 78.6; 75.5; 74.4; 35.4; 25.6. Anal. calc. for $C_{14}H_{14}N_2O_6$: C 54.90, H 4.61, N 9.15; found: C 54.87, H 4.81, N 9.09.

The optical purity was 98% ee determined by ^{1}H-NMR analysis of the acetylenic proton of the corresponding (*R*)-MTPA ester (2.54 ppm (major), 2.48 ppm (minor)).

*(*S*)-1-Phenylprop-2-yn-1-ol* (**4c**). The reaction was carried out for 14 d. Removal of toluene by rotary evaporation and purification by ((silica gel; hexane/AcOEt 85:15 – 50:50) afforded PhCHO (86.0 mg, 0.810 mmol, 32%) and **4c** (116 mg, 0.878 mmol, 35%). A small amount of the alcohol was converted to the corresponding *Mosher* ester ((*S*)-MTPA chloride, DMAP, CH_2Cl_2, 40°).

Data of **4c**: Colorless oil [23]. B.p. 120°/18 mmHg. $[\alpha]_D^{27} = +29$ ($c = 0.600$, $CHCl_3$). IR (thin film): 3292, 2118, 1493, 1455, 1022, 698, 649. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.6 – 7.5 (*m*, 2 H); 7.5 – 7.3 (*m*, 3 H); 5.47 (*d*, $J =$ 2.2, 1 H); 2.68 (*d*, $J = 2.2$, 1 H); 2.35 (*d*, $J = 5.0$, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 140.0; 128.7; 128.6; 126.6; 83.5; 74.9; 64.5. Anal. calc. for C_9H_8O: C 81.79, H 6.10; found: C 81.68, H 6.14.

The optical purity was 97% ee determined by ^{1}H-NMR analysis of the acetylenic proton of the corresponding ester derived from (*S*)-MTPA chloride (2.75 ppm (major), 2.70 ppm (minor)).

*(1*E*,3*R*)-1-Phenylpent-1-en-4-yn-3-ol* (**4d**). The reaction was carried out for 14 d. Removal of toluene by rotary evaporation and purification by CC (silica gel; hexane/AcOEt 85:15 – 50:50) afforded cinnamaldehyde (135 mg, 1.02 mmol, 41%) and **4d** (135 mg, 0.853 mmol; 34%). A small amount of the alcohol was converted to the corresponding *Mosher* ester ((*S*)-MTPA chloride, DMAP, CH_2Cl_2, 40°).

Data of **4d**: Colorless solid [24]. M.p. 67°. $[\alpha]_D^{27} = +2$ ($c = 0.510$, $CHCl_3$) [25]. IR (thin film): 3293, 2118, 1493, 1449, 1093, 1013, 966, 750, 693. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.5 – 7.2 (*m*, 5 H); 6.81 (*dd*, $J = 15.9$, 1.2, 1 H); 6.31 (*dd*, $J = 15.9$, 5.9, 1 H); 5.07 (*m*, $J = 5.9$, 1 H); 2.65 (*d*, $J = 2.2$, 1 H); 2.15 (*d*, $J = 6.5$, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 135.9; 132.4; 128.7; 128.3; 127.5; 126.9; 82.8; 74.7; 62.8. Anal. calc. for $C_{11}H_{10}O$: C 83.52, H 6.37; found: C 83.65, H 6.43.

The optical purity was 92% ee determined by ^{1}H-NMR analysis of the acetylenic proton of the corresponding ester derived from (*S*)-MTPA chloride (2.72 ppm (major), 2.68 ppm (minor)).

*(1*E*,3*S*)-2-Methyl-1-phenylpent-1-en-4-yn-3-ol* (**4e**). The reaction was carried out for 14 d. Removal of toluene by rotary evaporation and purification by CC (silica gel; hexane/AcOEt 85:15 – 50:50) afforded (*E*)-2-methylcinnamaldehyde (223 mg, 1.52 mmol, 61%) and **4e** (122 mg, 0.708 mmol, 28%). Colorless oil. B.p. 110°/0.5 mmHg. $[\alpha]_D^{27} = -4$ ($c = 0.955$, $CHCl_3$). IR (thin film): 3292, 2118, 1490, 1447, 1010, 752, 700. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.4 – 7.2 (*m*, 5 H); 6.72 (*s*, 1 H); 4.94 (*m*, 1 H); 2.61 (*d*, $J = 2.5$, 1 H); 2.11 (br. *s*, 1 H); 2.02 (*d*, $J = 1.6$, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 137.0; 136.3; 129.0; 128.2; 127.5; 126.9; 82.9; 74.5; 68.1; 14.0. Anal. calc. for $C_{12}H_{12}O$: C 83.69, H 7.02; found: C 83.41, H 7.27.

A small amount of the alcohol was converted to the corresponding *Mosher* ester ((*S*)-MTPA chloride, DMAP, CH_2Cl_2, 40°). The optical purity was 91% ee determined by ^{1}H-NMR analysis of the acetylenic proton of the corresponding (*R*)-MTPA ester derived from (*S*)-MTPA chloride (2.69 ppm (major), 2.65 ppm (minor)).

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