

1-Chloroalkyl *p*-Tolyl Sulfoxides as Acetylide Anion Equivalent: A Novel Synthesis Including Asymmetric Synthesis of Propargylic Alcohols from Carbonyl Compounds

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Addition of the carbanion of 1-chloroalkyl *p*-tolyl sulfoxide to carbonyl compounds gave the adducts, which were heated in refluxing toluene or xylene to give vinyl chlorides in high overall yield. Dehydrochlorination of the vinyl chlorides with excess *n*-BuLi afforded propargylic alcohols in high yields. Asymmetric synthesis of both enantiomers of the propargylic alcohols was realized using optically active 1-chloroalkyl *p*-tolyl sulfoxide and aldehyde.

Acetylenes are very important compounds in synthetic organic chemistry.¹⁾ In the acetylenes, propargylic alcohols, including optically active ones, are now recognized to be quite useful building blocks in natural product synthesis.²⁾ Many methods for synthesizing propargylic alcohols have been reported; however, in view of the usefulness of propargylic alcohols in organic synthesis, new methods are eagerly sought.

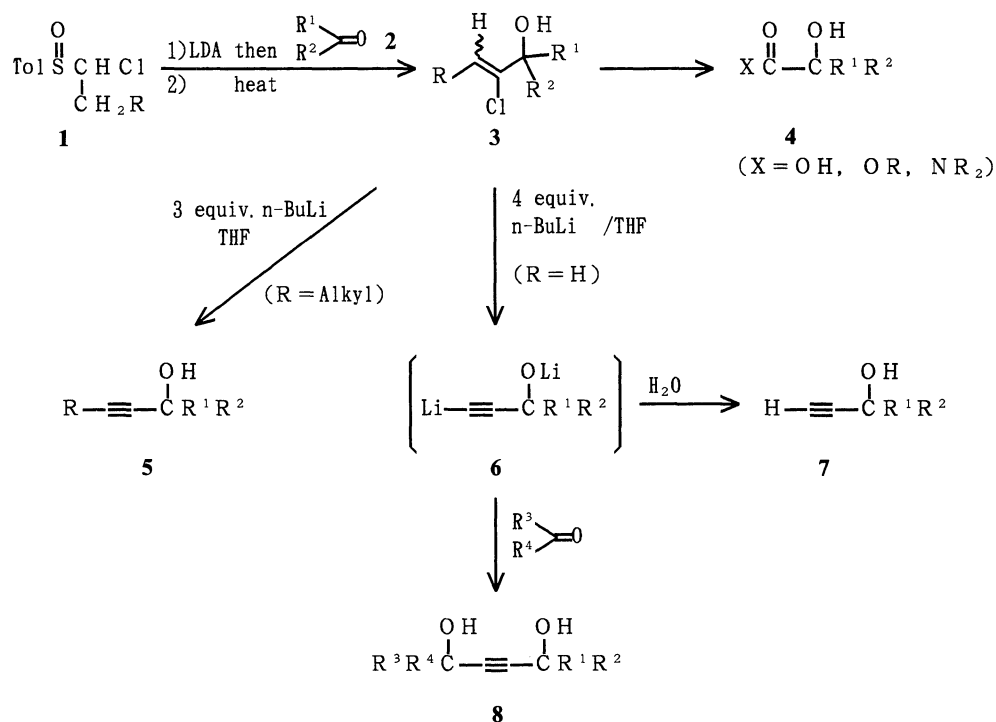
We recently reported some new synthetic methods using 1-chloroalkyl *p*-tolyl sulfoxides **1**.³⁾ For example, ozonolysis of vinyl chlorides **3**, which were synthesized from **1** and carbonyl compounds **2** through chloro alcohols, gave α -hydroxy carboxylic acids and their derivatives **4** in high yields.⁴⁾ In this method **1** acted as a hydroxycarbonyl-, alkoxycarbonyl-, and formamide anion equivalent (Scheme 1). In continuation of our

study concerning the use of 1-chloroalkyl aryl sulfoxides in organic synthesis, we report here a novel synthesis of propargylic alcohols (**5**, **7**, and **8**) from **1** and carbonyl compounds through vinyl chloride **3**. In this method **1** acts as an acetylide anion and acetylide dianion equivalent.

Results and Discussion

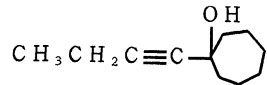
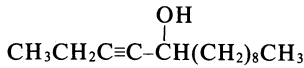
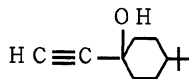
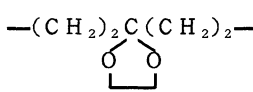
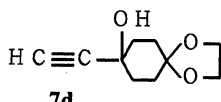
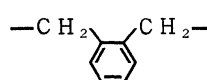
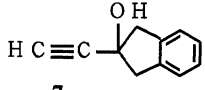
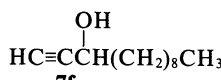
A Synthesis of Propargylic Alcohols from Carbonyl Compounds and 1-Chloroalkyl *p*-Tolyl Sulfoxides.

The synthesis of 1-(1-butylnyl)-1-cycloheptanol **5a** from cycloheptanone and 1-chlorobutyl *p*-tolyl sulfoxide (**1**; R=Et) as acetylide anion equivalent is reported as a representative example. 1-Chlorobutyl *p*-tolyl sulfoxide, easily prepared from butyl *p*-tolyl sulfide,⁵⁾ was treated with lithium diisopropylamide (LDA) in THF at



Scheme 1.

Table 1. Synthesis of Propargylic Alcohols **5** and **7** from **1** and Carbonyl Compound **2** through Vinyl Chlorides **3**

	1 R	2		3 (Yield/%) ^{a)}	<i>n</i> -BuLi (equiv)	Conditions ^{b)}	5 or 7 (Yield/%)
		R ¹	R ²				
a	Et	-(CH ₂) ₆ -		3a (77)	(3)	A	 5a (92)
b	Et	CH ₃ (CH ₂) ₈	H	3b-L (34) ^{c)}	(3)	A	 5b (99)
				3b-P (46) ^{c)}	(3)	B	5b (51)
c	H	-(CH ₂) ₂ CH(CH ₂) ₂ - +		3c (80)	(4)	A	 7c (85)
d	H			3d (92)	(4)	C	 7d (95)
e	H			3e (90)	(4)	D	 7e (92)
f	H	CH ₃ (CH ₂) ₈	H	3f (91)	(4)	E	 7f (93)

a) Two-step overall yield from **1** and carbonyl compound **2** through chloro alcohol. Isolated yield. b) Conditions: A, -35 to 0 °C (2 h) then 0 °C (0.5 h); B, -35 °C to room temperature (4 h) then at room temperature (0.75 h); C, -45 to -35 °C (0.7 h); D, -50 to -40 °C (0.7 h); E, -40 to -10 °C (2 h). c) L: less polar isomer, P: more polar isomer.

-60 °C followed by addition of cycloheptanone to give the adduct, which was then heated in refluxing toluene for 5 min to afford cleanly the vinyl chloride **3a** (R=Et, R¹=R²=(CH₂)₆-) in 77% overall yield.

As vinylic hydrogen is relatively more acidic than that of saturated carbon, it might be expected that on treatment of vinyl chloride **3** with a strong base elimination of hydrogen chloride takes place to afford propargylic alcohol **5**.⁶⁾ The vinyl chloride **3a** was treated with a variety of bases (such as LDA, *t*-BuOK, *n*-BuLi etc.) under various conditions, and three-equivalents of *n*-BuLi in THF at low temperature (below 0 °C) was found to be the best conditions to give **5a** (Table 1) in 92% yield. Interestingly, treatment of **3a** with *n*-BuLi in hexane gave a quite sluggish and incomplete reaction even at room temperature.

Representative examples of the synthesis of propargylic alcohols **5** and **7** from carbonyl compounds are summarized in Table 1. As shown in the Table 1, various kinds of propargylic alcohols are synthesized in good overall yield. In the step of the elimination of hydrogen chloride, some difference in the reaction was found between the stereoisomers (Entry b). Generally speaking, the elimination giving monosubstituted acetylenes (**7c**-**7f**) is more reactive than that giving disub-

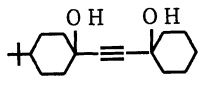
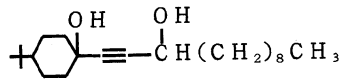
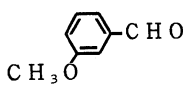
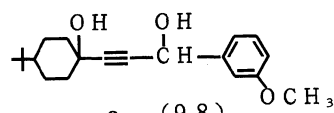
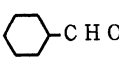
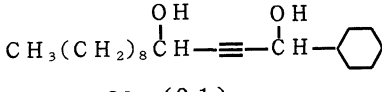
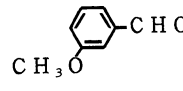
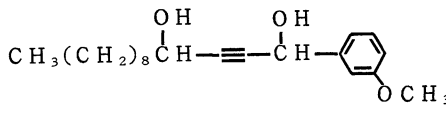
stituted acetylenes (**5a**, **5b**).

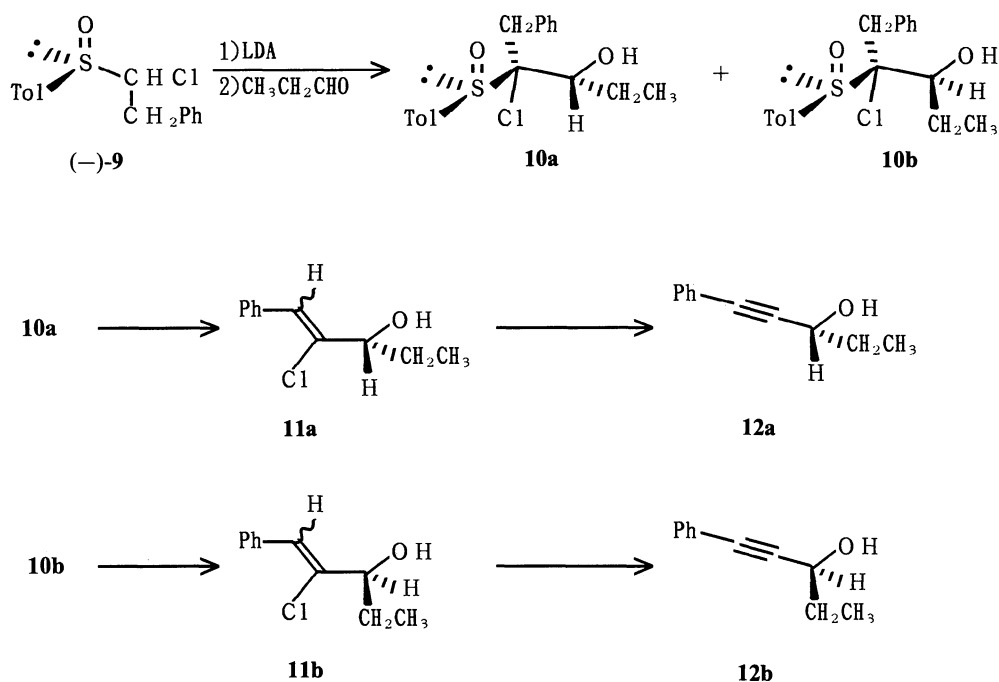
The elimination of hydrogen chloride from vinyl chloride (**3**: R=H) derived from 1-chloroethyl *p*-tolyl sulfoxide (**1**: R=H) gave propargylic alcohol dianion **6**. This dianion **6** was trapped with carbonyl compounds at -15 °C to afford acetylenic diol **8** in good yields. As shown in Table 2, this reaction gave almost quantitative yields with aldehydes; however, the yields was 72% with cyclohexanone because of its high enolizability. It is worth noting that 1-chloroethyl *p*-tolyl sulfoxide (**1**: R=H) acts as dianion of acetylene.

Asymmetric Synthesis of Both Enantiomers of Propargylic Alcohols. Asymmetric synthesis is one of the most important subjects in modern organic synthesis. We recently reported some new methods for synthesis of optically active 1-chloroalkyl *p*-tolyl sulfoxide.^{3a,3b,4)} Here we describe an asymmetric synthesis of both enantiomers of propargylic alcohols (**12a** and **12b**) using the above-mentioned method from (-)-**9** (Scheme 2).⁷⁾

Treatment of (-)-1-chloro-2-phenylethyl *p*-tolyl sulfoxide **9** (over 98% ee) with LDA in THF at -60 °C followed by addition of propanal afforded two adducts, which were easily separated by silica-gel column chromatography to give the less polar adduct **10a** (41%) and the more polar adduct **10b** (53%). The absolute stereo-

Table 2. Synthesis of Acetylenic Diol **8** from Vinyl Chloride **3**

Entry	Vinyl chloride 3	Carbonyl compound	8 (Yield/%)
1	3c		 8a (72)
2		$\text{CH}_3(\text{CH}_2)_8\text{CHO}$	 8b (88)
3			 8c (98)
4	3f		 8d (91)
5			 8e (96)



Scheme 2.

chemistry of **10a** and **10b** were presumed as depicted in Scheme 2 based on the experiences gained from the study with α,β -epoxy sulfoxides.^{3a)} Thermal elimination of the sulfinyl group in **10a** and **10b** in refluxing toluene

under N_2 for 20 min afforded cleanly the desired vinyl chlorides **11a** (single isomer) and **11b** (*E/Z*-mixture), both in 99% yield. Elimination of hydrogen chloride from **11b** was carried out with three equivalents of *n*-

BuLi at -35 to 0°C for 2 h to afford (*S*)-(-)-1-phenyl-1-pentyn-3-ol **12b** in 92% yield. The specific rotation of (-)-**12b** ($[\alpha]_D^{24} -20.0^\circ$ (c 2.6, Et₂O) was consistent with that of the reported value ($[\alpha]_D^{25} -13.7^\circ$ (c 2.0, Et₂O); 70% ee).^{7g)} Similar treatment of **11a** with *n*-BuLi gave (*R*)-(+)-**12a** ($[\alpha]_D^{26} +19.3^\circ$ (c 2.3, Et₂O) in 96% yield.

Unfortunately, as the addition of the carbanion of 1-chloroethyl *p*-tolyl sulfoxide with aldehyde gave an inseparable diastereomeric mixture of the adducts, this method could not be used for the asymmetric synthesis of the propargylic alcohols of type 7. However, because of its overall simplicity and high overall yields, we believe that the presented method will prove valuable in the synthesis of propargylic alcohols in racemic and optically active form.

Experimental

All melting points are uncorrected. ¹H NMR spectra were measured in a CDCl₃ solution with a JEOL FX-100 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel BW-127 ZH (Fuji-Devison) containing 2% fluorescence reagent 254 and quartz column were used for column chromatography, and products having UV absorption were detected by UV irradiation. In experiments requiring dry solvents, THF was distilled from diphenylketyl; toluene, xylene, and diisopropylamine were dried over CaH₂ and distilled.

1-(1-Chloro-1-butenyl)-1-cycloheptanol (3a). A solution of 1-chlorobutyl *p*-tolyl sulfoxide **1** ($R = \text{CH}_2\text{CH}_3$; 1.15 g; 5 mmol) in 2 ml of THF was added dropwise to a solution of LDA (6 mmol) in 6 ml of THF under N₂ at -60°C with stirring. The reaction mixture was stirred at -60°C for 10 min, then cycloheptanone (6 mmol) was added to the mixture. The reaction mixture was stirred for 10 min, then the reaction was quenched with sat. aqueous NH₄Cl. The whole was extracted with ether–benzene and the organic layer was washed once with sat. aqueous NH₄Cl. The solution was dried over MgSO₄ and then the solvent was evaporated under vacuum to give the residue, which was purified by silica-gel column chromatography to afford 1.51 g (88%) of chloro alcohol.

A solution of the chloro alcohol (1.46 g; 4.26 mmol) in 15 ml of toluene was refluxed under N₂ for 5 min. The toluene was evaporated under vacuum to leave a residue, which was purified by flash chromatography (hexane:AcOEt=10:1) to give 0.75 g (87%) of **3a** (single isomer; *E/Z* not determined) as a colorless oil. IR (neat) 3380 (OH), 1645 (C=C) cm⁻¹; ¹H NMR $\delta = 1.01$ (3H, t, $J = 7$ Hz), 1.2–2.2 (13H, m), 2.17 (2H, quintet, $J = 7$ Hz), 5.79 (1H, t, $J = 7$ Hz); MS m/z (%) 202 (M⁺, 26), 173 ([M–C₂H₅]⁺, 84), 145 (100). Found: m/z 202.1131. Calcd for C₁₁H₁₉ClO: M, 202.1124.

4-Chloro-3-tetradecen-5-ol (3b). Addition of the carbanion of 1-chlorobutyl *p*-tolyl sulfoxide to decanal gave less polar adduct and more polar adduct; these were easily separated by silica-gel column chromatography. The less polar adduct: 42% yield; mp 66 – 67°C (AcOEt–Hexane); IR (KBr) 3470 cm⁻¹; ¹H NMR $\delta = 3.80$ (1H, t, $J = 5$ Hz); Found: C, 65.14; H, 9.42; Cl, 9.19; S, 8.08%. Calcd for C₂₁H₃₅ClO₂S: C, 65.12; H, 9.12; Cl, 9.16; S, 8.28%. The more polar adduct: 51% yield; colorless oil; IR (neat) 3400 cm⁻¹; ¹H NMR $\delta = 3.76$ (1H, dd, $J = 8, 2$ Hz). Thermal elimination of the sulfanyl group of the

less polar adduct in refluxing xylene for 15 min gave **3b-L** as a colorless oil in 80% yield (*E/Z*-mixture; ratio about 10:1). IR (neat) 3350 (OH), 1655 (C=C) cm⁻¹; ¹H NMR $\delta = 0.87$ (3H, t, $J = 7$ Hz), 1.01 (3H, t, $J = 7$ Hz), 1.1–1.9 (16H, m), 2.21 (2H, quintet, $J = 7$ Hz), 4.11 (0.9H, t, $J = 7$ Hz), 4.54 (0.1H, t, $J = 7$ Hz), 5.71 (1H, t, $J = 7$ Hz); MS m/z (%) 246 (M⁺, 2), 211 ([M–Cl]⁺, 8), 119 (100). Found: m/z 246.1751. Calcd for C₁₄H₂₇ClO: M, 246.1749. In a similar way, the more polar adduct gave **3b-P** as a colorless oil in 96% yield (*E/Z*-mixture; ratio about 2:1). IR (neat) 3350 (OH), 1655 (C=C) cm⁻¹; ¹H NMR $\delta = 4.11$ (2/3H, t, $J = 7$ Hz), 4.54 (1/3H, t, $J = 7$ Hz), 5.70 (1/3H, t, $J = 7$ Hz), 5.72 (2/3H, t, $J = 7$ Hz); MS and high resolution mass spectral data are quite similar to those of **3b-L**.

1-(1-Chlorovinyl)-4-*t*-butyl-1-cyclohexanol (3c). Addition of the carbanion of 1-chloroethyl *p*-tolyl sulfoxide to 4-*t*-butylcyclohexanone gave the adduct in 83% yield as colorless crystals; mp 215 – 216°C (AcOEt–hexane). IR (KBr) 3360 (OH) cm⁻¹; ¹H NMR $\delta = 0.89$ (9H, s), 1.44, 2.43 (each 3H, s). Found: C, 63.56; H, 8.47; Cl, 10.13; S, 8.87%. Calcd for C₁₉H₂₉ClO₂S: C, 63.93; H, 8.19; Cl, 9.93; S, 8.98%. Thermal elimination of the sulfanyl group of this adduct in refluxing xylene for 20 min gave **3c** as a colorless crystals, mp 51 – 52°C (AcOEt–hexane). IR (KBr) 3375 (OH), 1630 (C=C) cm⁻¹; ¹H NMR $\delta = 0.89$ (9H, s), 1.0–1.9 (10H, m), 5.24, 5.46 (each 1H, d, $J = 2$ Hz); MS m/z (%) 216 (M⁺, 1), 181 (5), 142 (12), 107 (20), 57 (100). Found: m/z 216.1288. Calcd for C₁₂H₂₁ClO: M, 216.1279.

Vinyl Chloride (3d, 3e, 3f). These vinyl chlorides were reported in the Ref. 8.

1-(1-Butynyl)-1-cycloheptanol (5a). To a solution of vinyl chloride **3a** (61 mg; 0.3 mmol) in 3 ml of dry THF under N₂ was added *n*-BuLi (0.9 mmol) dropwise with stirring at -35°C . The reaction mixture was stirred and allowed to warm to 0°C in 2 h, and finally stirred at 0°C for 30 min. The reaction was quenched with sat. aqueous NH₄Cl. The whole was extracted with ether–benzene and the organic layer was dried over MgSO₄. The product was purified by silica-gel column chromatography to afford 46 mg (92%) of **5a** as a colorless oil. IR (neat) 3370 (OH), 2230 (C≡C) cm⁻¹; ¹H NMR $\delta = 1.13$ (3H, t, $J = 7$ Hz), 1.3–2.1 (13H, m), 2.21 (2H, q, $J = 7$ Hz); MS m/z (%) 166 (M⁺, 3), 151 ([M–CH₃]⁺, 4), 137 ([M–C₂H₅]⁺, 42), 109 (100). Found: m/z 166.1357. Calcd for C₁₁H₁₈O: M, 166.1357.

Propargylic Alcohol (5b, 7c–7f). These propargylic alcohols were synthesized from corresponding vinyl chlorides with three or four equivalents of *n*-BuLi in a similar way as described above for the synthesis of **5a**. The conditions and the yields are summarized in Table 1.

3-Tetradecyn-5-ol (5b). Colorless oil; IR (neat) 3340 (OH), 2225 (C≡C) cm⁻¹; ¹H NMR $\delta = 0.88$ (3H, t, $J = 7$ Hz), 1.13 (3H, t, $J = 7$ Hz), 1.2–1.8 (13H, m), 2.22 (2H, dq, $J = 7, 2$ Hz), 4.31 (1H, m); MS m/z (%) 210 (M⁺, trace), 181 ([M–C₂H₅]⁺, 7), 83 (100). Found: m/z 210.1972. Calcd for C₁₄H₂₆O: M, 210.1981.

1-Ethynyl-4-*t*-butyl-1-cyclohexanol (7c). Low melting solid; IR (KBr) 3530, 3420, 3320, 3260 (OH), 2100 (C≡C) cm⁻¹; ¹H NMR $\delta = 0.86$ (9H, s), 1.0–2.2 (10H, m), 2.41 (1H, s); MS m/z (%) 180 (M⁺, trace), 165 (1.5), 106 (44), 57 (100). Found: m/z 180.1515. Calcd for C₁₂H₂₀O: M, 180.1513.

4-Ethynyl-4-hydroxyl-1-cyclohexanone Ethylene Acetal (7d). Colorless oil; IR (neat) 3450, 3320, (OH), 2125 (C≡C) cm⁻¹; ¹H NMR $\delta = 1.6$ –2.1 (8H, m), 2.48 (1H, s), 3.94 (4H, s); MS m/z (%) 182 (M⁺, 0.4), 154 (2), 125 (2), 99 (100). Found:

m/z 182.0942. Calcd for $C_{10}H_{14}O_3$: M, 182.0942.

2-Ethynyl-2-indanol (7e). Colorless crystals; mp 91–92.5 °C (AcOEt–hexane); IR (KBr) 3450, 3290 (OH), 2125 (C≡C) cm^{-1} ; 1H NMR δ =2.52 (1H, s), 3.26, 3.40 (each 2H, d, J =17 Hz), 7.17 (4H, s); MS m/z (%) 158 (M^+ , 51), 129 (18), 105 (100). Found: C, 83.35; H, 6.27%. Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37%.

1-Dodecyn-3-ol (7f). Colorless oil; IR (neat) 3330 (OH), 2130 (C≡C) cm^{-1} ; 1H NMR δ =0.87 (3H, t, J =7 Hz), 1.0–2.0 (17H, m), 2.45 (1H, d, J =2 Hz), 4.35 (1H, dq, J =7, 2 Hz); MS m/z (%) 182 (M^+ , trace), 181 (0.3), 121 (14), 43 (100). Found: m/z 182.1660. Calcd for $C_{12}H_{22}O$: 182.1669.

1-[2-(1-Hydroxycyclohexyl)ethyl]-4-*t*-butyl-1-cyclohexanol (8a). To a solution of the vinyl chloride **3c** (54 mg; 0.25 mmol) in 3 ml of dry THF at –25 °C under N_2 was added *n*-BuLi (1 mmol) with stirring. The reaction mixture was stirred and allowed to warm to –15 °C in 1 h. To this reaction mixture was added cyclohexanone (0.3 mmol) and the mixture was stirred at –15 °C for 10 min. The reaction was quenched with sat. aqueous NH_4Cl and the whole was extracted with ether–benzene. The product was purified by silica-gel column chromatography to give 50 mg (72%) of **8a** as colorless crystals; mp 164.5–165 °C (AcOEt–hexane). IR (KBr) 3390 (OH) cm^{-1} , the signal due to C≡C stretching vibrations could not be observed; 1H NMR δ =0.85 (9H, s), 1.0–2.3 (20H, m); MS m/z (%) 278 (M^+ , 14), 260 (14), 232 (19), 203 (45), 162 (63), 57 (100). Found: C, 77.66; H, 10.97%. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86%.

1-(3-Hydroxy-1-dodecynyl)-4-*t*-butyl-1-cyclohexanol (8b). Colorless crystals; mp 73–74 °C (hexane); IR (KBr) 3370 (OH) cm^{-1} ; 1H NMR δ =0.85 (9H, s), 0.88 (3H, t, J =7 Hz), 1.0–2.2 (27H, m), 4.35 (1H, t, J =7 Hz); MS m/z (%) 336 (M^+ , 0.8), 318 [$M-H_2O$] $^+$, 3), 303 (5), 57 (100). Found: C, 78.70; H, 12.24%. Calcd for $C_{22}H_{40}O_2$: C, 78.51; H, 11.98%.

1-[3-Hydroxy-3-(3-methoxyphenyl)-1-propynyl]-4-*t*-butyl-1-cyclohexanol (8c). Colorless crystals; mp 104–105 °C (AcOEt–hexane) IR (KBr) 3360 (OH) cm^{-1} ; 1H NMR δ =0.85 (9H, s), 0.9–2.2 (10H, m), 3.79 (3H, s), 5.41 (1H, d (+ D_2O singlet), J =6 Hz), 6.7–7.4 (4H, m); MS m/z (%) 316 (M^+ , 100), 298 [$M-H_2O$] $^+$, 5), 283 (4), 241 (15), 200 (48). Found: C, 75.97; H, 8.87%. Calcd for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92%.

1-Cyclohexyl-2-tridecyne-1,4-diol (8d). Colorless oil; IR (neat) 3310 (OH) cm^{-1} ; 1H NMR δ =0.88 (3H, t, J =7 Hz), 1.0–2.0 (27H, m), 4.16 (1H, d, J =4 Hz), 4.38 (1H, t, J =5 Hz); MS m/z (%) 294 (M^+ , 0.3), 276 [$M-H_2O$] $^+$, 1.5), 233 (1.5), 194 (60), 83 (100). Found: m/z 294.2553. Calcd for $C_{19}H_{34}O_2$: M, 294.2556.

1-(3-Methoxyphenyl)-2-tridecyne-1,4-diol (8e). Colorless oil; IR (neat) 3340 (OH) cm^{-1} ; 1H NMR δ =0.87 (3H, t, J =7 Hz), 1.1–1.9 (16H, m), 3.79 (3H, s), 4.40 (1H, dt, J =6, 1 Hz), 5.44 (1H, s), 6.7–7.4 (4H, m); MS m/z (%) 318 (M^+ , 15), 138 (100). Found: m/z 318.2199. Calcd for $C_{20}H_{30}O_3$: M, 318.2193.

(2*R*, 3*R*, *R*_s)-2-Chloro-1-phenyl-2-(*p*-tolylsulfinyl)-3-pentanol (10a) and (2*R*, 3*S*, *R*_s)-Isomer (10b). The carbanion of (–)-1-chloro-2-phenylethyl *p*-tolyl sulfoxide (**9**; 98% ee) was reacted with propanal in a similar way as described above to give two adducts **10a** (41%) and **10b** (53%). These products were easily separated by silica-gel column chromatography.

10a: Colorless oil; IR (neat) 3400 (OH), 1080, 1040, 1015 (SO) cm^{-1} ; 1H NMR δ =0.93 (3H, t, J =7 Hz), 1.4–1.8 (4H, m), 2.44 (3H, s), 3.36 (1H, d, J =15 Hz), 3.82 (1H, dd, J =8, 4 Hz),

4.13 (1H, d, J =15 Hz), 7.2–7.7 (5H, m); [α]_D²⁷ –128.1° (*c* 0.2, acetone).

10b: Colorless crystals; mp 156–157 °C (AcOEt–hexane); IR (KBr) 3430 (OH), 1080, 1050, 1030 (SO) cm^{-1} ; 1H NMR δ =0.90 (3H, t, J =7 Hz), 1.3–1.8 (2H, m), 1.8–2.3 (2H, m), 2.41 (3H, s), 3.34 (1H, d, J =15 Hz), 3.38 (1H, dd, J =8, 2 Hz), 3.41 (1H, d, J =15 Hz), 7.1–7.7 (5H, m). Found: C, 64.03; H, 6.03; Cl, 10.59; S, 9.25%. Calcd for $C_{18}H_{21}ClO_2S$: C, 64.18; H, 6.28; Cl, 10.52; S, 9.52%. [α]_D²⁵ –68.0° (*c* 1.0, acetone).

(3*R*)-2-Chloro-1-phenyl-1-penten-3-ol (11a) and (3*S*)-Isomer (11b). Thermal elimination of **10a** in refluxing toluene for 20 min gave **11a** in 99% yield as a colorless oil (single isomer; *E/Z* not determined). IR (neat) 3380 (OH), 1645 (C=C) cm^{-1} ; 1H NMR δ =0.96 (3H, t, J =7 Hz), 1.79 (2H, m), 4.21 (1H, t, J =7 Hz), 6.70 (1H, s), 7.2–7.7 (5H, m); MS m/z (%) 196 (M^+ , 29), 167 (100), 31 (85). Found: m/z 196.0652. Calcd for $C_{11}H_{13}ClO$: M, 196.0654. [α]_D²³ +10.4° (*c* 0.7, acetone). Similar treatment of **10b** in refluxing toluene for 10 min gave **11b** in 99% yield as a colorless oil (a mixture of geometrical isomers; ratio about 2:1; *E/Z* not determined). IR (neat) 3380 (OH), 1650 (C=C) cm^{-1} ; 1H NMR δ =0.89 (1H, t, J =7 Hz), 0.96 (2H, t, J =7 Hz), 1.79 (2H, m), 4.21 (2/3H, t, J =7 Hz), 4.59 (1/3H, t, J =7 Hz), 6.71 (2/3H, s), 6.85 (1/3H, s), 7.1–7.7 (5H, m); MS m/z (%) 196 (M^+ , 31), 167 (100), 131 (80). Found: m/z 196.0646. Calcd for $C_{11}H_{13}ClO$: M, 196.0654. [α]_D²⁵ +15.3° (*c* 0.9, acetone).

(3*R*)-1-Phenyl-1-pentyn-3-ol (12a) and (3*S*)-Isomer (12b). To a solution of **11a** (60 mg; 0.3 mmol) in 3 ml of dry THF at –50 °C under N_2 was added *n*-BuLi (0.9 mmol) dropwise with stirring. The reaction mixture was then stirred at –35 °C and allowed to warm to 0 °C in 2 h, and finally at 0 °C for 30 min. The reaction was quenched with sat. aqueous NH_4Cl , and the usual workup gave **12a** (46 mg; 96%) as a colorless oil. IR (neat) 2350 (OH), 2240 (C≡C) cm^{-1} ; 1H NMR δ =1.07 (3H, t, J =7 Hz), 1.82 (2H, m), 4.53 (1H, t, J =6 Hz), 7.1–7.5 (4H, m); MS m/z (%) 160 (M^+ , 15), 131 (100), 103 (26). Found: m/z 180.0893. Calcd for $C_{11}H_{12}O$: M, 180.0888. [α]_D²⁶ +19.3° (*c* 2.3, Et₂O).

Vinyl chloride **11b** gave (–)-(3*S*)-isomer **12b** in 92% yield. [α]_D²⁴ –20.0° (*c* 2.6, Et₂O). The IR and NMR spectra were superimposable on those of **12a**.

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