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Asymmetric conjugate additions of carbon and oxygen nucleophiles to (*R*)-(−)-5-[(1*R*,2*S*,5*R*)-menthyloxy]-2(5*H*)-furanone

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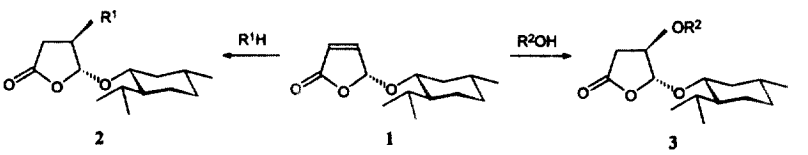
Abstract: Asymmetric conjugate additions of activated methyl compounds and primary alcohols to (*R*)-(−)-5-[(1*R*,2*S*,5*R*)-menthyloxy]-2(5*H*)-furanone with high diastereoselectivity are described. © 1997 Elsevier Science Ltd

Introduction

Since γ-butyrolactones are found as structural subunits in a wide variety of natural products with diverse biological activities,[1] and are frequently used as intermediates for the syntheses of biologically active compounds,[2] the synthesis of enantiopure γ-butyrolactones is an area of growing interest. One of the most effective approaches to obtain enantiopure γ-butyrolactones is asymmetric conjugate addition[3] of nucleophiles to chiral butenolides[2,4–9] that are prepared by using various readily available chiral starting materials.

In recent years, extensive research has been carried out outlining the asymmetric reactions of (*R*)-(−)-5-[(1*R*,2*S*,5*R*)-menthyloxy]-2(5*H*)-furanone[5] **1** (Scheme 1), which include Diels–Alder reactions,[5] 1,3-dipolar cycloadditions,[6] and conjugate additions of amine,[7] mercaptan[8] and organolithium.[9] High diastereoselectivity (de>99%) is obtained in these asymmetric reactions. The excellent asymmetric induction of **1** obviously results from the severe steric hindrance of the bulky menthyloxy, which enables the conjugate additions of nucleophiles to occur at the less hindered face of **1**. Reduction of some of these adducts leads to some multifunctional homochiral building blocks such as 2-amino-1,4-butanediols,[7] 2-mercapt-1,4-butanediols,[8] 3,4-epoxy-butanediols,[8] and 2-alkyl-1,4-butanediols.[9] In addition, because of its multifunctionality, **1** is a useful synthon for the synthesis of natural products and compounds with biological activity.[10]



R¹ = a. $C(NO_2H)CO_2Et$, b. $CH(CO_2Me)_2$, c. $CH(CO_2Et)_2$, d. $CCl(CO_2Et)_2$, e. CCl_3, f. $CH(CN)CO_2Et$, g. $CH(CN)CO_2R^3$
R² = a. Et, b. *n*-Pr, c. *n*-Bu, d. CH_2Ph, e. $CH_2CH{=}CH_2$
R³ = menthyl

Scheme 1.

Recently, we achieved the asymmetric conjugate addition of an activated methyl compound, ethyl nitroacetate, to **1**.[11] Studies on the derivatives of this adduct gave some interesting results.[11–13] In this paper, we report the asymmetric conjugate additions of other activated methyl compounds and primary alcohols to **1** with high diastereoselectivity, which give new and enantiopure γ-butyrolactones **2** and **3** (Scheme 1).

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Results and discussion

The initial attempts at the asymmetric conjugate addition of ethyl nitroacetate to **1**, which was expected to give **2a**, an intermediate for the synthesis of a natural product, were unsuccessful. This was because ethyl nitroacetate is much more acidic than other activated methyl compounds and so forms stable and insoluble salts[14] with the base catalysts, such as amines and alkali metal alkoxides in the presence of common protonic and aprotic solvents, which prevented the reaction from happening. Finally, this reaction was achieved by stirring the reactants at room temperature in the presence of the dipolar aprotic solvent DMF and a catalytic amount of NaOEt (2 N in EtOH), giving **2a** in 92% yield.[11] Although ethyl nitroacetate is a prochiral compound, it was found that complete tautomerization of the adduct (a diastereoisomeric mixture of the nitro form **2a**) to the chelated nitronic acid (the *aci*-nitro form **2a**) in its enantiopure form occurred when the reaction mixture was quenched with ice and water.[11]

Under the same reaction conditions as above, other activated methyl compounds also underwent this asymmetric conjugate addition successfully affording chiral γ-butyrolactones **2b–g** in 14–86% yields. It should be noted that the prochirality of the cyanoacetates resulted in a diastereoisomeric mixture of **2f** and **2g**, respectively, with a diastereoselectivity of 38% de for **2f** and 74% de for **2g** on the basis of the ^{1}H NMR spectra of the crude products.

In contrast to amines and mercaptans, alcohols are much weaker nucleophiles,[15] therefore it is not surprising that only a few examples concerning the conjugate additions of alcohols have been reported, which seemed to take place exclusively in the presence of excessive acids.[15,16] The limited success in the conjugate additions of alcohols urged us to study the asymmetric conjugate addition of alcohols to **1**, which has not been reported so far.

Acids are apparently not suitable catalysts for this purpose, because of the presence of acid sensitive functional groups such as lactone and acetal in **1**, and the potential epimerization of the C_5 stereogenic center. No reaction was observed to occur when **1** was treated with alcohols in the presence of weak bases such as Et_3N, K_2CO_3 and NaOH in various solvents. Eventually, this reaction was successfully completed at room temperature simply by mixing **1** and excessive primary alcohols in DMF with an iota of sodium alkoxide as the catalyst to furnish enantiomerically pure **3** in 82–97% yields.

However, it should be pointed out that the asymmetric conjugate additions of secondary and tertiary alcohols to **1** seemed sluggish under these conditions, which might be due to their larger steric hindrance. It was also very surprising that methanol failed to react with **1** even under various conditions. Interestingly, the photochemically generated radicals of secondary alcohols have been reported to undergo asymmetric conjugate additions to **1** producing a series of chiral tertiary alcohols.[17]

On the basis of the relevant studies,[7–9] we think that reduction of **3** with $LiAlH_4$ would generate the novel multifunctional homochiral building blocks various (*R*)- or (*S*)-2-alkyloxy-1,4-butanediols [when (+)- or (−)-menthol is used as the chiral auxiliary, respectively[5b]] which would not be easily obtained by alternative methods.

In all these chiral γ-butyrolactones **2** and **3**, a singlet ($J_{4,5}$=0) or a doublet with a small coupling constant ($J_{4,5} \leq 3.4$ Hz) was observed for the acetal hydrogen in the ^{1}H NMR spectra, which reveals the *trans* stereochemistry for the vicinal substituents.

In summary, asymmetric conjugate additions of carbon and oxygen nucleophiles to (*R*)-(−)-5-[(1*R*,2*S*,5*R*)-menthyloxy]-2(5*H*)-furanone were achieved with high diastereoselectivity giving new and enantiopure γ-butyrolactones **2a–e** and **3a–e**.

Experimental section

All reagents were of the best commercial grades available. (1*R*,2*S*,5*R*)-Menthyl cyanoacetate was a gift from Mr Z.-B. Zeng. Elemental analyses were performed on a Perkin–Elmer 240C micro analyzer. Infrared spectra were recorded on a Hitachi 260-50 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained at 200 MHz on a Varian-200 spectrometer in $CDCl_3$ with chemical shifts in ppm downfield

from TMS and coupling constants in Hz. Optical rotations were measured on a Perkin–Elmer 241MC polarimeter. Melting points (uncorrected) were taken on a Yanaco MP-500 apparatus. The syntheses and characterization of compounds **1** and **2a** are reported in a previous paper.[11b]

General procedure for preparation of compounds 2

To a well-stirred solution of an activated methyl compound (5.5 mmol) in DMF (4 mL) was added 2 N NaOEt (0.8 mL). To this mixture was then added compound **1** (1.2 g, 5 mmol) dissolved in DMF (4 mL). The progress of the reaction was monitored by TLC. After being stirred at room temperature for 6–24 h, the reaction mixture was dissolved in ether and washed with water, brine, and then dried (Na_2SO_4). Removal of solvent furnished the crude product which was purified by recrystallization from light petroleum ether or by column chromatography on silica gel using a mixture of light petroleum ether and ethyl acetate (7:1) as the eluent.

(4S,5R)-(−)-4-[1′,1′-(Bismethoxycarbonyl)methyl]-5-[(1R,2S,5R)-menthyloxy]-γ-butyrolactone ***2b***

Yield 86%; colorless crystals; mp 93.5–94.5°C; $[\alpha]_D^{25}$ −118 (*c* 0.76, $CHCl_3$); IR (KBr) 1780, 1750, 1740, 1720 cm^{-1}; ^1H NMR δ 0.6–1.5 (m, 14H), 1.65 (m, 2H), 2.10 (m, 2H), 2.45 (m, 1H), 2.95 (m, 2H), 3.50 (m, 2H), 3.78 (s, 6H), 5.59 (d, 1H, *J*=2.2); ^{13}C NMR δ 15.5, 20.8, 22.2, 23.0, 25.3, 31.2, 31.7, 34.2, 39.5, 41.2, 47.6, 51.9, 52.1, 52.9. 77.2, 101.9, 167.5, 167.6, 174.6; Anal. Calcd for $C_{19}H_{30}O_7$: C, 61.62; H, 8.11. Found: C, 61.73; H, 8.15.

(4S,5R)-(−)-4-[1′,1′-(Bisethoxycarbonyl)methyl]-5-[(1R,2S,5R)-menthyloxy]-γ-butyrolactone ***2c***

Yield 70%; colorless crystals; mp 86–87°C; $[\alpha]_D^{25}$ −105 (*c* 0.56, $CHCl_3$); IR (KBr) 1780, 1760, 1740, 1720 cm^{-1}; ^1H NMR δ 0.6–1.2 (m, 14H), 1.28 (t, 6H), 1.65 (m, 2H), 2.10 (m, 2H), 2.45 (m, 1H), 2.95 (m, 2H), 3.50 (m, 2H), 4.22 (q, 4H), 5.59 (d, 1H, *J*=2.0); ^{13}C NMR δ 13.6, 13.7, 15.3, 20.6, 21.9, 22.8, 25.1, 31.0, 31.4, 34.0, 39.3, 41.0, 47.4, 52.0, 61.6, 61.7, 76.9, 101.7, 166.8, 166.9, 174.2; Anal. Calcd for $C_{21}H_{34}O_7$: C, 63.32; H, 8.54. Found: C, 63.45; H, 8.52.

(4S,5R)-(−)-4-[1′-Chloro-1′,1′-(bisethoxycarbonyl)methyl]-5-[(1R,2S,5R)-menthyloxy]-γ-butyrolactone ***2d***

Yield 72%; colorless crystals; mp 81–82°C; $[\alpha]_D^{25}$ −94 (*c* 0.83, $CHCl_3$); IR (KBr) 1800, 1780, 1770, 1750 cm^{-1}; ^1H NMR δ 0.6–1.2 (m, 14H), 1.31 (t, 6H), 1.63 (m, 2H), 2.07 (m, 2H), 2.66 (dd, 1H, *J*=18.5, 4.6), 3.00 (dd, 1H, *J*=18.5, 9.6), 3.30 (ddd, 1H, *J*=9.6, 4.6, 2.4), 3.52 (dd, 1H, *J*=10.2, 4.0), 4.29 (q, 4H), 5.68 (d, 1H, *J*=2.4); ^{13}C NMR δ 13.7, 13.8, 15.6, 20.8, 22.2, 23.0, 25.4, 31.0, 31.2, 34.2, 39.2, 47.7, 48.1, 63.5, 63.6, 70.2, 77.2, 100.4, 164.9, 165.0, 174.1; Anal. Calcd for $C_{21}H_{33}O_7Cl$: C, 58.21; H, 7.62. Found: C, 58.45; H, 7.57.

(4S,5R)-(−)-4-Trichloromethyl-5-[(1R,2S,5R)-menthyloxy]-γ-butyrolactone ***2e***

Yield 14%; semisolid; $[\alpha]_D^{25}$ −142 (*c* 0.77, $CHCl_3$); IR (neat) 1800 cm^{-1}; ^1H NMR δ 0.6–1.5 (m, 14H), 1.60 (m, 2H), 2.05 (m, 2H), 2.82 (dd, 1H, *J*=18.8, 3.8), 3.01 (dd, 1H, *J*=18.8, 9.5), 3.49 (ddd, 1H, *J*=9.5, 3.8, 1.5), 3.59 (dd, 1H, *J*=10.4, 4.2), 5.81 (d, 1H, *J*=1.5); Anal. Calcd for $C_{15}H_{23}O_3Cl_3$: C, 50.35; H, 6.43. Found: C, 50.56; H, 6.48.

(4S,5R)-(−)-4-[(RS)-1′-Cyano-1′-ethoxycarbonylmethyl]-5-[(1R,2S,5R)-menthyloxy]-γ-butyrolactone ***2f***

Yield 86%; colorless crystals; mp 87–90°C; $[\alpha]_D^{25}$ −133 (*c* 0.66, $CHCl_3$); IR (KBr) 2250, 1800, 1750 cm^{-1}; ^1H NMR δ 0.6–1.2 (m, 14H), 1.35 (t, 3H), 1.60 (m, 2H), 2.05 (m, 2H), 2.50 (m, 1H), 2.90 (m, 2H), 3.54 (dd, 1H, *J*=10.2, 4.0), 3.65 (m, 1H), 4.30 (q, 2H), 5.67 (d, 1H, *J*=2.0); ^{13}C NMR δ 13.8, 15.5, 20.8, 22.1, 22.9, 25.3, 31.2, 31.4, 31.7, 34.1, 38.5, 39.4, 41.9, 47.5, 63.5, 77.7, 101.2, 114.0, 163.7, 172.9; Anal. Calcd for $C_{19}H_{29}NO_5$: C, 64.96; H, 8.26; N, 3.99. Found: C, 65.25; H, 8.29; N, 3.92.

(4S,5R)-(−)-4-[(RS)-1′-Cyano-1′-(1R,2S,5R)-menthyloxycarbonylmethyl]-5-[(1R,2S,5R)-menthyloxy]-γ-butyrolactone ***2g***

Yield 78%; colorless crystals; mp 163–164°C; $[\alpha]_D^{25}$ −178 (*c* 0.94, $CHCl_3$); IR (KBr) 2250, 1780, 1730 cm^{-1}; ^1H NMR δ 0.6–2.4 (m, 36H), 2.60 (m, 1H), 2.95 (m, 2H), 3.55 (dd, 1H, *J*=10.0, 4.0), 3.72 (d, 1H, *J*=5.6), 4.80 (dd, 1H, *J*=11.0, 4.2), 5.59 (d, 1H, *J*=3.4); ^{13}C NMR δ 15.5, 15.9, 20.7, 20.8, 21.8, 22.1, 22.9, 23.0, 25.3, 26.1, 31.2, 31.3, 31.4, 33.8, 34.1, 38.4, 39.7, 40.3, 41.9, 46.6, 47.5, 78.1, 78.4, 101.5, 114.0, 163.4, 172.5; Anal. Calcd for $C_{27}H_{43}NO_5$: C, 70.28; H, 9.33; N, 3.04. Found: C, 70.46; H, 9.41; N, 3.07.

General procedure for preparation of compounds 3

To a stirred solution of a primary alcohol (2 mL) in DMF (5 mL) was added a catalytic amount of metallic sodium (5.0 mg, 0.21 mmol). As soon as the sodium disappeared, compound **1** (1.0 g, 4.2 mmol) was added and the resulting red solution was stirred at room temperature for 3–24 h until the red color faded (the red color might be caused by the resulting enol anion of the furanone). Then the reaction mixture was dissolved in ether and washed with water, brine, and dried (Na_2SO_4). Removal of solvent afforded the crude product which was purified by recrystallization from light petroleum ether.

(4R,5R)-(−)-4-Ethoxy-5-[(1R,2S,5R)-menthyloxy]-γ-butyrolactone ***3a***

Yield 97%; colorless crystals; mp 93–94°C; $[\alpha]_{578}^{25}$ −146 (*c* 1.1, $CHCl_3$); IR (KBr) 1780 cm^{-1}; ^1H NMR δ 0.7–1.15 (m, 14H), 1.22 (t, 3H), 1.65 (m, 2H), 1.99 (m, 1H), 2.15 (m, 1H), 2.45 (dd, 1H, *J*=17.8, 1.4), 2.79 (dd, 1H, *J*=17.8, 6.0), 3.55 (q+dd, 3H), 3.90 (dd, 1H, *J*=6.0, 1.4), 5.55 (s, 1H); ^{13}C NMR δ 15.1, 15.5, 20.8, 22.2, 22.9, 25.4, 31.3, 34.1, 34.2, 39.5, 47.6, 64.8, 76.8, 78.7, 102.8, 174.9; Anal. Calcd for $C_{16}H_{28}O_4$: C, 67.61; H, 9.86. Found: C, 67.55; H, 9.89.

(4R,5R)-(−)-4-Propoxy-5-[(1R,2S,5R)-menthyloxy]-γ-butyrolactone ***3b***

Yield 90%; colorless crystals; mp 92–93°C; $[\alpha]_{578}^{25}$ −132 (*c* 0.86, $CHCl_3$); IR (KBr) 1780 cm^{-1}; ^1H NMR δ 0.6–1.8 (m, 21H), 2.00 (m, 1H), 2.15 (m, 1H), 2.45 (dd, 1H, *J*=18.0, 1.6), 2.77 (dd, 1H, *J*=18.0, 6.0), 3.43 (t, 2H, *J*=6.4), 3.54 (dd, 1H, *J*=10.6, 4.0), 3.91 (dd, 1H, *J*=6.0, 1.6), 5.55 (s, 1H); ^{13}C NMR δ 10.5, 15.5, 20.8, 22.2, 22.8, 23.0, 25.5, 31.3, 34.1, 34.2, 39.6, 47.6, 71.1, 76.7, 78.9, 102.8, 174.9; Anal. Calcd for $C_{17}H_{30}O_4$: C, 68.46; H, 10.07. Found: C, 68.35; H, 10.11.

(4R,5R)-(−)-4-Butoxy-5-[(1R,2S,5R)-menthyloxy]-γ-butyrolactone ***3c***

Yield 95%; colorless crystals; mp 73–74°C; $[\alpha]_{578}^{25}$ −128 (*c* 0.81, CH_2Cl_2); IR (KBr) 1780 cm^{-1}; ^1H NMR δ 0.7–1.8 (m, 23H), 2.00 (m, 1H), 2.15 (m, 1H), 2.45 (dd, 1H, *J*=17.8, 1.2), 2.79 (dd, 1H, *J*=17.8, 6.0), 3.47 (t, 2H, *J*=6.2), 3.54 (dd, 1H, *J*=10.0, 4.2), 3.91 (dd, 1H, *J*=6.0, 1.2), 5.56 (s, 1H); ^{13}C NMR δ 13.7, 15.4, 19.0, 20.7, 22.1, 22.8, 25.3, 31.1, 31.5, 34.0, 34.1, 39.4, 47.4, 69.1, 76.5, 78.7, 102.7, 174.9; Anal. Calcd for $C_{18}H_{32}O_4$: C, 69.23; H, 10.26. Found: C, 69.35; H, 10.28.

(4R,5R)-(−)-4-Benzyloxy-5-[(1R,2S,5R)-menthyloxy]-γ-butyrolactone ***3d***

Yield 82%; colorless crystals; mp 86–87°C; $[\alpha]_{578}^{25}$ −230 (*c* 1.0, hexane); IR (KBr) 1780 cm^{-1}; ^1H NMR δ 0.7–1.5 (m, 18H), 1.65 (m, 2H), 2.00 (m, 2H), 2.52 (dd, 1H, *J*=18.0, 1.4), 2.81 (dd, 1H, *J*=18.0, 5.8), 3.52 (dd, 1H, *J*=10.4, 4.2), 4.04 (dd, 1H, *J*=5.8, 1.4), 4.58 (s, 2H), 5.58 (s, 1H); ^{13}C NMR δ 15.5, 20.8, 22.2, 22.9, 25.4, 31.2, 34.2, 39.5, 47.5, 71.6, 76.7, 78.4, 102.7, 127.7, 128.1, 128.5, 136.8, 174.8; Anal. Calcd for $C_{21}H_{30}O_4$: C, 72.83; H, 8.67. Found: C, 72.88; H, 8.65.

(4R,5R)-(−)-4-Allyloxy-5-[(1R,2S,5R)-menthyloxy]-γ-butyrolactone ***3e***

Yield 85%; colorless crystals; mp 74–75°C; $[\alpha]_{578}^{25}$ −182 (*c* 1.0, $CHCl_3$); IR (KBr) 1780, 1640 cm^{-1}; ^1H NMR δ 0.7–1.5 (m, 14H), 1.7 (m, 2H), 2.00 (m, 1H), 2.10 (m, 1H), 2.47 (dd, 1H, *J*=17.8, 1.6), 2.79 (dd, 1H, *J*=17.8, 5.8), 3.54 (dd, 1H, *J*=10.4, 4.2), 4.03 (d+dd, 3H, *J*=5.4; 5.8, 1.6), 5.22 (dd, 1H, *J*=9.0, 1.4), 5.28 (dd, 1H, *J*=17.2, 1.4), 5.58 (s, 1H), 5.88 (m, 1H, *J*=17.2, 9.0, 5.4); ^{13}C NMR δ

15.5, 20.8, 22.2, 23.0, 25.4, 31.3, 34.1, 34.2, 39.5, 47.6, 70.2, 76.7, 78.3, 102.8, 117.7, 133.5, 174.7; Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.92; H, 9.46. Found: C. 69.10: H. 9.52.

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References

1. For reviews, see: (a) Davies-Coleman, M. T.; Rivett, D. E. A. *Prog. Chem. Nat. Prod.* **1989**, *55*, 1. (b) Jefford, C. W.; Jaggi, D.; Sledeski, A. W.; Boukouvalas, J. in *Studies in Natural Products Chemistry*, Rahman, A., Ed., Elsevier: Amsterdam, 1989, Vol. 3, pp. 157–171. (c) Yoshioka, H.; Mabry, T. J.; Timmermann, B. N. *Sesquiterpene Lactones*, University of Tokyo Press: Tokyo, 1973. (d) Grieco, P. A. *Synthesis* **1975**, 67. (e) Heywood, H.; Harborne, J. B.; Turner, B. L. *The Biology and Chemistry of the Compositae*, Academic Press: London, 1977, Vol. 1 and 2. (f) Fischer, N. H.; Oliver, C. J.; Fischer, H. D. in *Progress in the Chemistry of Organic Natural Products*, Herz, B.; Grisebach, H.; Kirby, G. W., Eds., Springer-Verlag: New York, 1979, Vol. 38, Chapter 2. (g) Hoffman, H. M. R.; Rabe, J. *Angew Chem., Int. Ed. Engl.* **1985**, *24*, 94. (h) Petragnani, N.; Ferraz, H. M. C.; Silva, G. V. J. *Synthesis* **1986**, 157.
2. Sanchez-Sancho, F.; Valverde, S.; Herradon, B. *Tetrahedron: Asymmetry* **1996**, *7*, 3209, and the references cited therein.
3. (a) Perlmutter, P. *Conjugate Addition Reactions in Organic Synthesis*, Pergamon Press: Oxford, 1992, Chapter 5. (b) Rossiter, B. E.; Swingle, N. M. *Chem. Rev.* **1992**, *92*, 771–806.
4. (a) Hizuka, M.; Hayashi, N.; Kamashita, T.; Suemune, H.; Sakai, K. *Chem. Pharm. Bull.* **1988**, *36*, 1550. (b) Hannesian, S.; Murray, P. J.; Sahoo, S. P. *Tetrahedron Lett.* **1985**, *26*, 5627. (c) Hannesian, S.; Murray, P. J. *J. Org. Chem.* **1987**, *52*, 1170. (d) Collis, M. P.; Hockless, D. C. R.; Perlmutter, P. *Tetrahedron Lett.* **1995**, *36*, 7133. (e) Collis, M. P.; Perlmutter, P. *Tetrahedron: Asymmetry* **1996**, *7*, 2117. (f) Casiraghi, G., Pinna, L.; Rassu, G.; Spanu, P.; Ulgheri, F. *Tetrahedron: Asymmetry* **1993**, *4*, 681. (g) Pelter, A.; Ward, R. S.; Sirit, A. *Tetrahedron: Asymmetry* **1994**, *5*, 1745.
5. (a) Feringa, B. L.; de Jong, J. C. *J. Org. Chem.* **1988**, *53*, 1125. (b) de Jong, J. C.; van Bolhuis, F.; Feringa, B. L. *Tetrahedron: Asymmetry* **1991**, *2*, 1247.
6. (a) de Lange, B.; Feringa, B. L. *Tetrahedron Lett.* **1988**, *29*, 5317. (b) Rispens, M. T.; Keller, E.; de Lange, B.; Zijlstra, R. W. J.; Feringa, B. L. *Tetrahedron: Asymmetry* **1994**, *5*, 607.
7. (a) Feringa, B. L.; de Lange, B. *Tetrahedron Lett.* **1988**, *29*, 1303. (b) de Lange, B.; van Bolhuis, F.; Feringa, B. L. *Tetrahedron* **1989**, *45*, 6799.
8. Feringa, B. L.; de Lange, B. *Tetrahedron* **1988**, *44*, 7213.
9. (a) Jansen, J. F. G. A.; Feringa, B. L. *Tetrahedron Lett.* **1989**, *30*, 5481. (b) Jansen, J. F. G. A.; Feringa, B. L. *Syn. Commun.* **1992**, *22*, 1367.
10. (a) Feringa, B. L.; de Lange, B.; Jansen, J. F. G. A.; de Jong, J. C.; Lubben, M.; Faber, W.; Schudde, E. P. *Pure Appl. Chem.* **1992**, *64*, 1865. (b) Feringa, B. L.; de Jong, J. C. *Bull. Soc. Chim. Belg.* **1992**, *101*, 627. (c) Krief, A.; Lecomte, P.; Demoute, J. P.; Dumont, W. *Synthesis* **1990**, 275. (d) Hoffmann, N.; Scharf, H. D. *Liebigs Ann. Chem.* **1991**, 1273.
11. (a) Kang, F. A.; Yin, C. L.; She, S. W. *Chin. Sci. Bull.* **1996**, *41*, 1847. (b) Kang, F. A.; Yin, C. L.; She, S. W. *J. Org. Chem.* **1996**, *61*, 5523.
12. (a) Kang, F. A.; Yin, C. L. *J. Chem. Soc., Chem. Commun.* **1997**, 579. (b) Kang, F. A.; Yin, C. L. *Tetrahedron* in press.
13. (a) Kang, F. A.; Yin, C. L. *J. Am. Chem. Soc.* **1997**, *119*, 8562. (b) Kang, F. A.; Yin, C. L. *Prog Nat. Sci.* in press.
14. (a) Joullie, M. M.; Nasfay, S.; Rypstat, L. *J. Am. Chem. Soc.* **1954**, *76*, 2990. (b) Davey, W.; Tivey, D. J. *J. Chem. Soc.* **1958**, 2276.

15. Weininger, S. J.; Stermitz, F. R. *Organic Chemistry,* Academic Press: New York, 1984, p. 718.
16. Darvesh, S.; Grant, A. S.; MaGee, D. I.; Valenta, Z. *Can. J. Chem.* **1989**, *67*, 2237.
17. Hoffmann, N. *Tetrahedron: Asymmetry* **1994**, *5*, 879.

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