Reversal of facial selectivity in the kinetic resolution of olefin *via* asymmetric dihydroxylation (AD) reaction: Synthesis of optically active (−)-mintlactone and (+)-isomintlactone by AD reaction from intrinsically disfavoured diastereoface of alkene[†]

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Reversal of diastereofacial selectivity in the kinetic resolution of 4-methyl-1-(carbethoxymethylene)cyclohexane **6** has been observed during asymmetric dihydroxylation reaction using different chiral auxiliaries. The AD reaction of **6** proceeds from a favoured diastereoface when DHQD$_2$-TP or DHQD-CLB are used, whereas unfavoured diastereofacial selection is observed when DHQD$_2$-PHAL is used as chiral auxiliary. Similarly, AD reaction of ethyl α-(4-methylcyclohex-1-ene)propionate **5** proceeds *via* unfavoured diastereoface; resulting in axial dihydroxylation, to afford (−)-mintlactone **1** and (+)-isomintlactone **2**.

In continuation of our efforts to explore the synthetic potential of asymmetric dihydroxylation reactions[1,2] we envisaged the total synthesis of the optically active (−)-mintlactone **1**, (+)-isomintlactone **2** *via* the kinetic resolution of the disymmetric olefin **5**.

(-)-Mintlactone-1   **(+)-Isomintlactone-2**
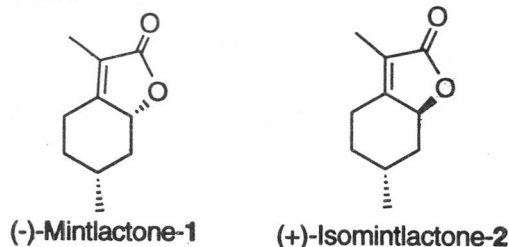
Retrosynthetic analysis of the natural products **1** and **2** indicates that olefin **5** (Scheme I) would act as a logical precursor to the synthesis of mintlactone **1** and isomintlactone **2** *via* asymmetric dihydroxylation. The olefins **5** can be obtained by the kinetic resolution (KR) of the unsaturated ester **6** followed by stereoselective methylation.

The kinetic resolution of racemic alkenes has been reported using asymmetric dihydroxylation reaction[3]. The k_{rel}[4] depends upon the nature of the substrate and chiral ligands and follows double diastereoselection rule[5]. The stereochemistry of the diol formed in the reaction follows mechanistic mnemonic[6]. Quite recently, a few exceptions to the stereoselection rule based on mechanistic mnemonic have appeared, and mismatched double diastereoselection has been found to be the favoured pathway[7]. Examination of previous substrates subjected to kinetic resolution shows the presence of a racemic or chiral carbon present at an allylic or homoallylic position which eventually acts as directing group for the incoming oxidant[7].

Recently, the facial selectivity of the AD reaction has been also found to alter even in the absence of preexisting chiral centre in the substrate which perhaps influences the reaction trajectory of the incoming oxidant and depends upon the nature of heterocyclic linker joining the two alkaloid moieties together[8].

Results and Discussion

In the present article we wish to report the kinetic resolution of the substrate **6** in which the chiral centre is far away from the reaction site *via* AD reaction. The olefin **6** was prepared by a known method from 4-methylcyclohexanone[9]. The knetic resolution of olefin **6** was carried out using 1, 4-(9-*O*-bis-dihydroquinidinyl)terephthalate (DHQD$_2$-TP), dihydroquinidine 4-chlorobenzoate (DHQD-CLB) and 1, 4-bis(9-*O*-dihydroquinidyl)phthalazine (DHQD$_2$PHAL) and their respective pseudoenantiomers as chiral ligands (Scheme II). All the reactions were carried out at *ca*
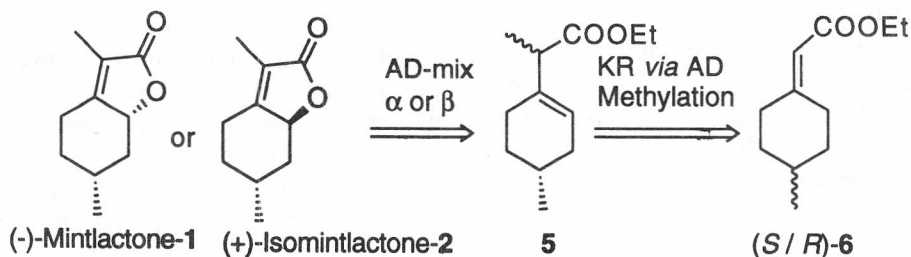
Scheme I—Retrosynthetic approach for the synthesis of (−)-mintlactone **1** and (+)-Isomintlactone **2**
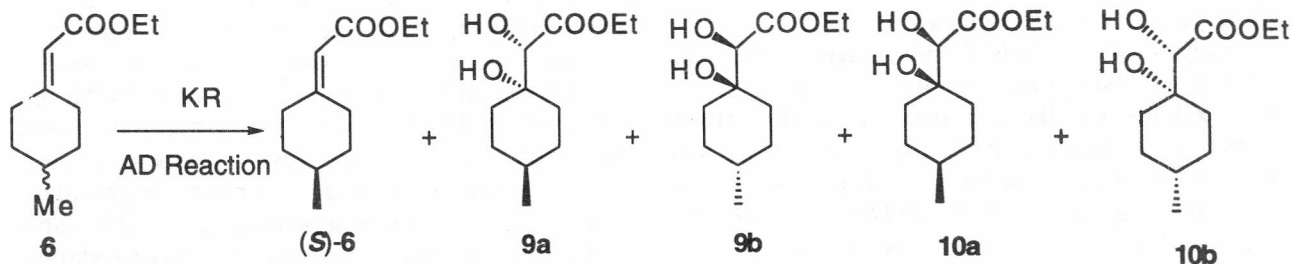
Scheme II—Kinetic resolution 1-(carbethoxymethylene)-4-methylcyclohexane **6**

20°C in *t*-BuOH-H$_2$O (1:1) as solvent using K$_3$Fe(CN)$_6$-K$_2$CO$_3$ as co-oxidant. The reactions were carried out to 50-75% conversion. The extent of conversion was followed by capillary gas chromatography (GC). The unreacted olefin **6** and the diols (**9a/b/10a/b**) were isolated by flash chromatography. The enantiomeric excess of the recovered olefin was determined by GC using β-cyclodextrin chiral stationary phase. The configuration of the olefin was determined by comparison of optical rotation with the compound of known configuration[10]. The results are summarized in Table I. In Table I, k_{rel} indicates the ratio of rate constants for the fast *versus* slow reacting enantiomers and reveals the extent of conversion required to get the desired enantiomeric purity of the unreacted substrate. From the knowledge of double diastereoselection[5] and the mechanistic mnemonic[6], one would expect a faster AD reaction of (R)-olefin **6** in the presence of DHQ$_2$-TP, leaving behind the unreacted (S)-olefin **6** which has been found to be the case. Analysis suggests that the diol formed in the kinetic resolution of **6** with DHQ$_2$-TP predominantly arises from equatorial dihydroxylation leading to the formation of **9a/b** (Scheme II).

Dihydroxylation carried out in the absence of chiral auxiliary also resulted in the preferential formation of the diol **9a/b** arising from equatorial dihydroxylation. Similar results were observed when DHQ-CLB was used. As expected, use of pseudoenantiomeric chiral auxiliaries DHQD$_2$-TP

Sl. No.	L*	% Conver.[a]	k_{rel}[b]	% ee[c]	Conf.[d]	$[\alpha]_D^{25}$ (CHCl$_3$)
1	DHQ$_2$-TP	50	1.50	14	S	+6.3°(c 0.81)
2	DHQ$_2$-TP	70	1.42	21	S	+12.0°(c 0.8)
3	DHQD$_2$-TP	50	1.59	16	R	−7.8°(c 1.18)
4.	DHQD$_2$-CLB	50	1.59	16	R	−7.8°(c 1.8)
5	DHQ-CLB	70	1.40	20	S	+11.3°(c 1.66)
6.	DHQ$_2$-PHAL	58	3.67	53	R	−31.2°(c 0.28)
7.	DHQ$_2$-PHAL	75	4.26	85	R	−50.5°(c 1.12)
8.	DHQD$_2$-PHAL	60	4.10	60	S	+35.6°(c 0.52)

Table I—Kinetic resolution of olefin **6** using different chiral ligands (L*)

(a) Conversions (%) were followed by capillary GLC.
(b) Relative rate was calculated using the equation $k_{rel} = \ln (1-c) (1-ee)/\ln (1-c) (1+ee)$ where c is the percent conversion/ 100 and ee is percent enantiomeric excess/100.
(c) The % ee was determined by capillary gas chromatography using β-cyclodextrin as stationary phase.
(d) Configuration was assigned by comparison of optical rotation with the known compound.

and DHQD-CLB furnished the opposite enantiomer. Unfortunately, the enantiomeric excess of recovered olefin 6 was unsatisfactory even after 70% conversion. Thus, we carried out the kinetic resolution of (±)-6 with DHQ₂-PHAL and DHQD₂-PHAL. Interestingly, use of DHQ₂-PHAL in KR led to the recovery of 23% olefin 6 in 85% ee, however, that of opposite optical antipode (R)-6 (vide supra) (Table I, entry 7 vs entries 2 and 5) after 75% conversion. Similarly, use of DHQD₂-PHAL resulted in the recovery of alkene (S)-6 (Table I, entry 8 vs entries 3 and 4).

Analysis of the diols formed suggests that the product is arising preferentially from the axial dihydroxylation of alkene, furnishing the diol 10a/b as the major product. It is important to note that k_{rel} for the kinetic resolution of 6 using either of the chiral ligands DHQD₂-PHAL and DHQ₂-PHAL is ca 4.0 at ca 60% conversion (Table I, entries 6 and 8). The kinetic resolution observed in this case is due to the dihydroxylation of fast reacting olefin from an intrinsically disfavoured diastereoface which means that contrary to the favoured matched double asymmetric reaction which is expected to be fast reaction, the mismatch double asymmetric reaction is dominant. Although such a mismatch diastereoselection is not unprecedented[3,5] no explanation has been suggested so far in any such case of the reversal of facial selectivity in the AD reaction.

The (R)-6 (85% ee) isolated from the kinetic resolution of (±)-6 (Table I, entry 7) was used for

the synthesis of − -mintlactone 1 and (+)-isomintlactone 2, which are the active constituents of peppermint oil and spearmint oil which are used as commercial flavouring agents[11]. Several racemic[9,12] and chiral[13] syntheses of (+)-mintlactone and (−)-isomintlactone have been reported. Our synthetic route for the preparation of the optically active (+)-mintlactone and (−)-isomintlactone, using the optically active (R)-6-olefin is shown in Scheme III.

The optically active olefin (R)-6 (85% ee) was alkylated using LDA/MeI in THF to furnish a mixture of diastereoisomeric alkenes 5a/5b. Asymmetric dihydroxylation of alkenes 5a/5b using DHQD₂-PY furnished the γ-hydroxylactone 12 which was dehydrated using catalytic amount of p-toluenesulfonic acid to furnish (−)-mintlactone 1 and (+)-isomintlactone 2 in 3:1 ratio (89% yield). Similarly, asymmetric dihydroxylation of alkene 5a/5b with DHQ₂-PHAL followed by dehydration of γ-hydroxylactone 11 furnished a mixture of 1 and 2 in 1:1 ratio (86% yield). The enantiomeric excess of 1 and 2 was determined by comparison of optical rotation with the reported value[13a]. Formation of 1 and 2 in the AD reaction of 5a/5b using either DHQD₂-PHAL or DHQ₂-PHAL clearly suggests that the alkenes 5a and 5b are present in nearly 1:1 ratio and axial dihydroxylation has proceeded from the intrinsically disfavoured diastereoface. Although alkene (R)-6 has 85% ee, the deprotonation of (R)-6 using LDA may proceed from either of the faces
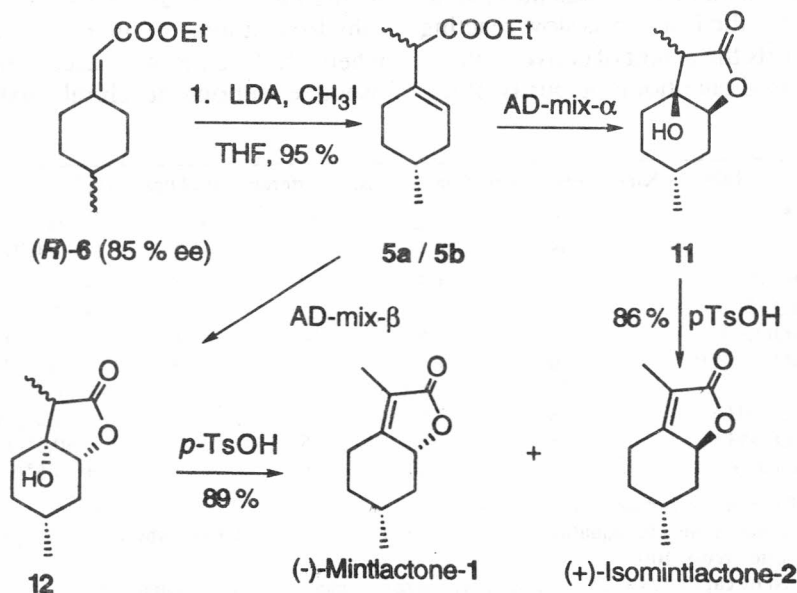
Scheme III—Synthesis of (−)-mintlactone 1 and (+)-isomintlactone 2
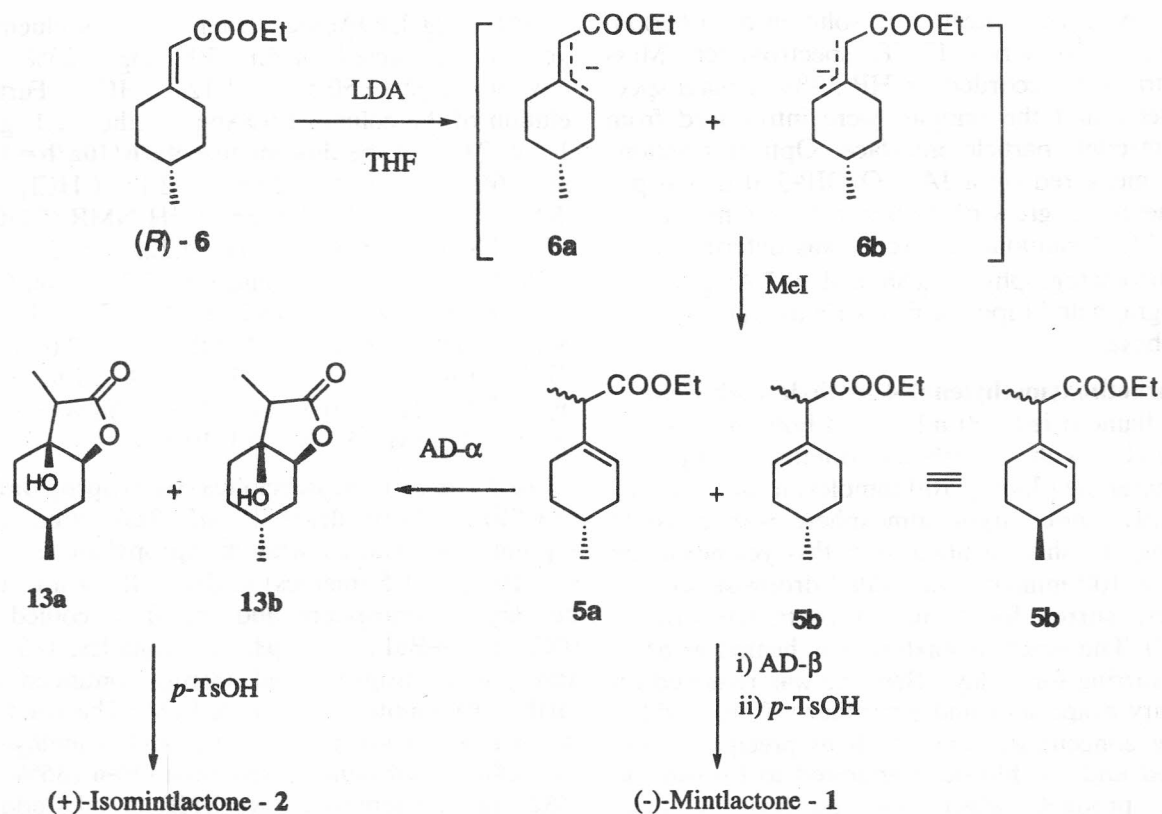
Scheme IV—Mechanism of racemization of 1-(carbethoxymethylene)-4-methyl cyclohexane **6** during methylation and its effect on the formation of (–)-**1** and (+)-**2**

giving rise to intermediates **6a** and **6b** which upon methylation gave a mixture of alkenes **5a** and **5b** as shown in Scheme IV.

The creation of new chiral centre α to COOEt does not play a key role in the synthetic strategy, since the chirality of this centre is lost in the subsequent dehydration step. Thus, the migration of double bond during deprotonation of (R)-**6** into six-membered ring plays a crucial role on the stereoselective formation of **5a** *vs* **5b**. Since deprotonation can take place from either side of the six-membered ring to give **6a** or **6b**, it would lead to eventual racemization of the chiral centre in 4-methylcyclohexyl ring to furnish **5a/5b**. In fact, one would expect a complete racemization of the carbon bearing the methyl group, and the formation of both (–)-mintlactone **1** and (+)-isomintlactone **2** using either DHQD$_2$-PHAL or DHQ$_2$-PHAL. Formation of **1** and **2** suggests that asymmetric dihydroxylation of both **5a** and **5b** proceeded *via* axial dihydroxylation from an unfavoured diastereoface leading predominantly to the formation of (–)-mintlactone **1** when DHQD$_2$-PHAL is used and (+)-isomintlactone **2** when DHQ$_2$-PHAL is employed.

In conclusion, we have observed an unusual reversal of facial selectivity in the kinetic resolution of racemic alkene in which chiral centre is far away from the reaction site. Attempt has been made to utilize the recovered alkene from kinetic resolution for the synthesis of the optically active (–)-mintlactone **1** and (+)-isomintlactone **2** *via* an interesting and unusual disfavoured axial asymmetric dihydroxylation reaction of **5a/5b**. The reason for the formation of a mixture of **1** and **2** has been attributed to the unselective deprotonation of (R)-**6** giving rise to a mixture of **5a/5b**.

Experimental Section

General. All b.ps are uncorrected. Flash chromatography was carried out on silical gel SRL (230-400 mesh). TLC analyses were carried out on precoated Merck Kieselgel 60 F-254 plates. All solvents were dried and distilled before use. ^{1}H NMR spectra were recorded on a Varian Gemini (200 MHz) FT-NMR instrument in CDCl$_3$ with TMS as internal standard. ^{13}C NMR spectra were recorded on the same instrument (50 MHz) in CDCl$_3$ solution. IR (ν_{max} in cm^{-1})

were recorded as neat or in solution on a Perkin-Elmer 1600 series FT-IR spectrometer. Mass spectra were recorded on HP 5989 A mass spectrometer and the samples were introduced from LC through particle interface. Optical rotations were measured on a JASCO DIP-370 digital polarimeter. Progress of the reaction was monitored by GLC. Enantiomeric excess was determined by gas chromatography using Shimadzu 17 AF gas chromatograph and Lipodex-β-dextrin as chiral stationary phase.

1-(carbethoxymethylene)-4-methylcyclohexane 6.

A flame dried 100 mL round bottom flask was charged with (carbethoxymethylene)triphenyl phosphorane (3.48 g, 100 mmoles) in dry benzene (20 mL) under argon atmosphere with constant stirring. Freshly distilled 4-methylcyclohexanone (1.12 g, 100 mmoles) was added dropwise and the mixture stirred for 5 min at room temperature (30°C). The reaction mixture was heated at 65°C with stirring for 4 days. Benzene was removed on a rotary evaporator and pet. ether (50 mL) added to the concentrate. The resultant precipitate was filtered and the filtrate evaporated to furnish the crude product, which was purified by flash chromatography using a mixture of ethyl acetate and pet. ether (1:19) as eluent to furnish a colourless liquid (1.4 g, 77%), b.p. 125°C (2 mm, Kugel ruher); IR (Neat): 1716, 1649 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ5.61 (s, 1H), 4.15 (q, $J=$ 8.75 Hz, 2H), 3.72 (m, 1H), 2.35-1.75 (m, 6H), 1.6 (m, 1H), 1.28 (t, $J=$8.75 Hz, 3H), 1.1 (m, 1H), 0.93 (d, $J=$7.5 Hz, 3H); ^{13}C NMR (CDCl$_3$) : δ 166.3, 162.6, 112.9, 59.0, 37.0, 36.3, 35.5, 32.0, 28.6, 21.3, 14.0; MS (relative intensity): m/z 183 (M+1, 64%), 182 (M$^+$, 100%).

General procedure for the kinetic resolution of alkene. To a double jacketed reactor connected to a cooling system maintained at 20°C was added a mixture of K$_3$Fe(CN)$_6$ (3.52 g, 10.71 mmoles) and K$_2$CO$_3$ (1.48 g, 10.71 mmoles) in t-BuOH-H$_2$O (1:1, 70 mL) and the mixture stirred until all the solids dissolved to form an orange coloured solution. To the reaction mixture cinchona alkaloid derivative (DHQ)$_2$-PHAL (40 mg) dissolved in 0.5 mL t-BuOH and OsO$_4$ (40 μL, 0.5 M) were added. The racemic olefin 6 (1.3 g, 7.14 mmoles) was added in one portion and vigorous stirring continued for 24 hr at 20°C. The reaction mixture was quenched with sodium metabisulfite (5 g), extracted with EtOAc (4×25 mL), washed with brine (25 mL), dried over Na$_2$SO$_4$, filtered and evaporated. The unreacted olefin and the diol were separated by flash chromatography over sili-

ca gel using EtOAc-pet. ether (1:19) as eluent to get the unreacted olefin (302 mg, 23% recovery), $[\alpha]_D^{26}$ − 50.5° (c 1.12, CHCl$_3$). Further elution of the column EtOAc-pet. ether (1:1) gave 1.1 g (71%) of the diol mixture(9a/b/10a/b = 1:3), m.p. 66-68°C; $[\alpha]_D^{24}$ − 26.6° (c 2.15, CHCl$_3$); IR (KBr): 3534, 3443, 1719 cm^{-1}; ^{1}H NMR (CDCl$_3$) : δ 4.28 (q, $J=$8.3 Hz, 2H), 4.22, 3.9 (2s, 1H), 2.35 (bs, 2H, D$_2$O exchangeable), 2.2-1.1 (m, 9H), 1.4(t, $J=$8.2 Hz, 3H), 0.92 and 0.9 (2s, 3H); ^{13}C NMR (CDCl$_3$): δ 173.4, 173.0, 73.5, 77.0, 72.7, 72.3, 61.4, 61.2, 33.3, 33.1, 32.4, 31.9, 30.4, 30.3, 29.5, 22.1, 20.5, 14.0; MS (relative intensity): m/z 181 (M-35, 9%), 113 (100%).

Ethyl a-(4-methylcyclohex-1-enyl)propionate (5a/5b). A flame dried 25 mL flask fitted with septum was charged with diisopropylamine (152 mg, 197 μL, 1.5 mmoles) in dry THF (4 mL) under argon atmosphere and the flask cooled to 0°C, and n-BuLi (685 μL, 1.6 mmoles, 0.6 M) added to it dropwise and stirring continued for further 30 minutes to generate LDA. The reaction mixture was cooled to − 20°C and 4-methyl-1-(carbethoxymethylene)cyclohexane (R)-6 (85% ee) (182 mg, 1 mmoles) in dry THF (1 mL) added dropwise with continuous stirring. The reaction mixture was stirred for 1 hr at ca 0°C and then cooled to − 78°C. Methyl iodide (75 μL, 1.2 mmoles) was then added slowly and stirring continued for 5 hr during which the reaction mixture was allowed to warm upto room temperature. The reaction was quenched by adding cold water and the mixture extracted with ether (3 × 10 ml), washed with brine (10 ml), dried over Na$_2$SO$_4$, filtered and evaporated. The yellow oil obtained was purified by flash chromatography on silica gel using a mixture of ethyl acetate and petroleum ether (1:4) as eluent to furnish a mixture of 5a and 5b as a pale yellow liquid (188 mg, 95%), b.p. 175° (2 mm, K R); $[\alpha]_D^{28}$ + 48.2 (c 0.39, CHCl$_3$); IR (KBr): 1735 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 5.51 (bs, 1H), 4.2 (q, $J=$7.9 Hz, 2H), 3.05 (q, $J=$7.5 Hz, 1H), 2.15-1.9 (m, 4H), 1.8-1.5 (m, 3H), 1.25 (t, $J=$7.8 Hz, 3H), 1.21 (d, $J=$7.5 Hz, 3H), 0.95 (d, $J=$5.2 Hz, 3H); ^{13}C NMR (CDCl$_3$): δ 174.0, 135.7, 122.5, 122.3, 59.7, 46.4, 46.1, 33.4, 30.6, 27.8, 25.9, 25.7, 21.1, 15.4, 15.1, 14.0, 13.7; MS (relative intensity): m/z 196 (M$^+$, 10%), 81 (100%).

(6R, 7aR)−3, 6-Dimethyl-5, 6, 7, 7a-tetrahydro-2(4H)-benzofuranone (Mintlactone 1). To a double jacketed reactor connected with cooling system maintained at 20°C was added a mixture of K$_3$Fe(CN)$_6$ (987 mg, 3 mmoles) and K$_2$CO$_3$

(414 mg, 3 mmoles) in *t*-BuOH-H_2O (1:1, 10 mL), and the whole mixture stirred well until all the solids dissolved to form an orange coloured solution. Cinchona alkaloid derivative (DHQD)$_2$-PY (20 mg) and OsO_4 (20 μL, 0.5 *M*) were added with stirring. The olefin **5a/5b** (170 mg, 0.86 mmol) was then added and stirring continued for 20 hr. The reaction was quenched with sodium metabisulfite (1.5 g), extracted with ethyl acetate (3 × 15 mL), washed with brine (15 mL), dried over Na_2SO_4 and evaporated. The crude lactol obtained was dissolved in dry toluene (3 mL) and the solution refluxed for 3 hr with azeotropic removal of water in the presence of catalytic *p*-TsOH (25 mg) (TLC monitored). The reaction mixture was cooled to room temperature and toluene removed under vacuum. The syrup obtained was chromatographed over silica gel using EtOAc-pet. ether (1:4) as eluent to afford a mixture of mintlactone-**1** and isomintlactone-**2** in 3:1 ratio as a pale yellow oil (127 mg, 89%); $[\alpha]_D^{27}$ − 17.4° (*c* 0.85, EtOH) [lit.[13a] for optically pure **1** $[\alpha]$ − 51.8 (*c* 10, EtOH) and for optically pure **2** $[\alpha]_D^{25}$ + 73.5° (*c* 1.5, EtOH)]; IR (Neat) ν : 1755, 1688 cm^{-1}; ^{1}H NMR (CDCl$_3$) : δ4.9-4.6 (m, 1H), 2.9-2.6 (m, 1H), 2.5-2.1 (m, 2H), 1.95 (m, 1H), 1.8 (s, 3H), 1.75-1.1 (m, 3H), 1.1 (d, *J*= 7.5 Hz, 3H); ^{13}C NMR (CDCl$_3$) : δ 175.0, 162.5, 120.0, 79.9, 42.0, 39.5, 34.5, 32.6, 29.8, 25.9, 21.7, 21.2, 17.2, 8.2; MS (relative intensity) : m/z 167 (M + 1, 100%).

(6R, 7S)-3, 6-Dimethyl-5, 6, 7, 7a-tetrahydro-2(4H)-benzofuranone (Isomintlactone 2). The olefin **5a/5b** (90 mg, 0.46 mmole) was dihydroxylated in the presence of (DHQ)$_2$-PHAL and dehydrated and purified as described in the case of mintlactone to furnish a colourless solid (65 mg, 86%), m.p. 60-69°C which consisted of a mixture of isomintlactone and mintlactone in 1:1 ratio; $[\alpha]_D^{27}$ + 8.04° (*c* 0.67, EtOH) [lit.[13a] for optically pure **2** $[\alpha]_D$ + 73.5 (*c* 1.5, EtOH)]; IR (KBr): 1754, 1687 cm^{-1}; ^{1}H NMR (CDCl$_3$) : δ 4.9-4.55 (m, 1H), 2.85-2.6 (m, 1H), 2.5-2.05 (m, 2H), 2.0-1.1 (m, 7H), 1.82 (s, 3H), 1.0 (d, *J*= 7 Hz, 3H); ^{13}C NMR (CDCl$_3$) : δ 175.0, 162.5, 119.0, 79.71, 77.27, 41.7, 39.2, 34.4, 34.2, 31.3, 29.3, 28.6, 26.9, 25.1, 24.1, 21.4, 20.9, 20.7, 16.9, 7.8; MS (relative intensity): m/z 167 (M + 1, 47%), 166 (M$^+$, 53%), 165 (M$^+$-1,62%), 154 (23%), 149(75%), 137(48%), 121(33%), 109(72%), 95(82%), 81(100%).

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4 $k_{rel} = \ln (1\text{-}c) (1\text{-}ee)/\ln (1\text{-}c) (1 + ee)$ where c is the percentage conversion/100 and ee is the percentage enantiomeric excess/100.

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