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Synthetic Approach to (−)-Cuparenone by Rhodium-Catalyzed Cyclization

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(−)-α-Cuparenone, (**17**) was synthesized from the olefinic aldehyde (**9**) by utilizing a rhodium-catalyzed cyclization as a key step. The optically active aldehyde (**7**) was prepared by employing an asymmetric [2,3]sigmatropic rearrangement of a quaternary L-prolinol derivative. The aldehyde (**7**) was also converted into its antipodal form (**24**) in several steps.

Keywords——(−)-α-cuparenone; cyclopentanone synthesis; asymmetric [2,3]sigmatropic rearrangement; tris(triphenylphosphine)rhodium chloride; rhodium-catalyzed cyclization

Synthesis of the cyclopentanone ring system continues to attract interest because of the presence of this ring system in numerous naturally occurring terpenoids. Recently, Sakai and his co-workers have described[1] a conversion of olefinic aldehydes into the corresponding cyclopentanone derivatives by employing tris(triphenylphosphine)rhodium chloride[2] as a catalyst, and this synthetic tool was successfully applied to a facile synthesis of prostanoid derivatives.[3] Moreover, the use of a rhodium catalyst bearing chiral ligands in this type of cyclization brought about an asymmetric induction to afford an optically active cyclopentanone derivative.[4] We have also investigated an application of the above synthetic strategy to a synthesis of naturally occurring terpenoids and here wish to report a synthesis of (−)-[5] and (+)-α-cuparenone.[6]

The requisite olefinic aldehyde (**7**) in an optically active form was prepared as follows. Condensation of the acid (**1**)[7] with methyl (*S*)-prolinate[8] in dichloromethane in the presence of 2,2-dipyridyl disulfide and triphenylphosphine (PPh_3)[9] afforded the amide (**2**) in 94.5% yield; this product was also prepared by the mixed anhydride method[10] in 73% yield. Reduction of the amide (**2**) with lithium aluminium hydride afforded the amino-alcohol (**3**), which was converted to its benzyl ether (**4**) by treatment with benzyl bromide in toluene–dimethyl sulfoxide (DMSO) in the presence of sodium hydride in 76.9% overall yield. An asymmetric [2,3]sigmatropic rearrangement of the quaternary salt (**5**), prepared from the ether (**4**) and cyanomethyl benzenesulfonate, was carried out according to Hiroi and Nakazawa[10b] to give optically active **7**, after acid-catalyzed hydrolysis of the intermediate **6**. The optical yield of **7** was determined based on the nuclear magnetic resonance (NMR) spectrum of the mandelate (**26**) derived from the alcohol (**25**) and (*R*)-(−)-*O*-methylmandelic acid.[11] The reaction conditions and yields are summarized in the table.

The aldehyde (**7**) was treated with (methoxymethyl)triphenylphosphonium chloride in tetrahydrofuran (THF) in the presence of *n*-butyllithium to yield the enol ether (**8**),[12] acid-catalyzed hydrolysis of which gave rise to the homologous aldehyde (**9**). First, the rhodium-catalyzed cyclopentanone synthesis was attempted with the α,α-dimethyl aldehyde (**10**), which was obtained from **9** by treatment with methyl iodide in the presence of potassium hydride[12] in THF, together with **11** and **8**. However, none of the desired product was obtained under various reaction conditions.[13] On the other hand, the treatment of the aldehyde (**9**) with

TABLE. Asymmetric Induction in the [2,3]Sigmatropic Rearrangement Reaction of the Allylic Quaternary Amine (**5**)[d]

Time (h)	Solvent (DMSO : THF, v/v)	Temp. (°C)	Yield[a] (%) of **7**	$[\alpha]_D^{20}$[b]	ee
20	1 : 2[c]	−10—0	29	+4.23	5.6
20	1 : 30	−35	44.3	+6.95	9.2
10	1 : 10	−78	23	+10.4	13.8
72	1 : 30	−78	49.7	+10.7	14.2

a) Isolated yield from the allylic amine (**4**). *b*) The specific optical rotations were obtained in dry dichloromethane, at the concentration of 1 g/100 ml. *c*) This solvent system (reported by Hiroi and Nakazawa[10b]) solidified at −78 °C, so we could not carry out the rearrangement under such reaction conditions. *d*) Cyanomethyl benzenesulfonate was more effective than chloroacetonitrile as an alkylating reagent to form the quaternary salt. ee, enantiomeric excess.

tris(triphenylphosphine)rhodium chloride in methylene chloride resulted in cyclization to furnish the cyclopentanone (**13**) in 42% yield. In order to accomplish the synthesis of cuparenone, **13** was converted to the (*n*-butylthio)methylidene derivative (**15**) *via* **14**.[14] Methylation of **15** with methyl iodide in the presence of potassium *tert*-butoxide in *tert*-butanol gave the α,β-dimethylated ketone (**16**),[15] which, on removal of the protecting group, afforded (−)-α-cuparenone (**17**), $[\alpha]_D^{20}$ −15.56° [lit.,[5] $[\alpha]_D$ −169.9° ($CHCl_3$)]. Thus, we had achieved the chiral synthesis of (−)-α-cuparenone, although the enantiomeric excess was low. Since the aldehyde (**7**) could be transformed into (−)-α-cuparenone, the absolute configuration of the major product was assigned as **7**. The prolinol derivative (**4**) was alternatively prepared[16] from the allylic alcohol (**18**) and *O*-benzylprolinol,[17] because the above low enantioselectivity might arise from the partial epimerization of the ester group of **2** during the subsequent reduction with lithium aluminium hydride. The optical rotation of **4** prepared by the latter synthetic route, however, was the same as that of **4** obtained before.

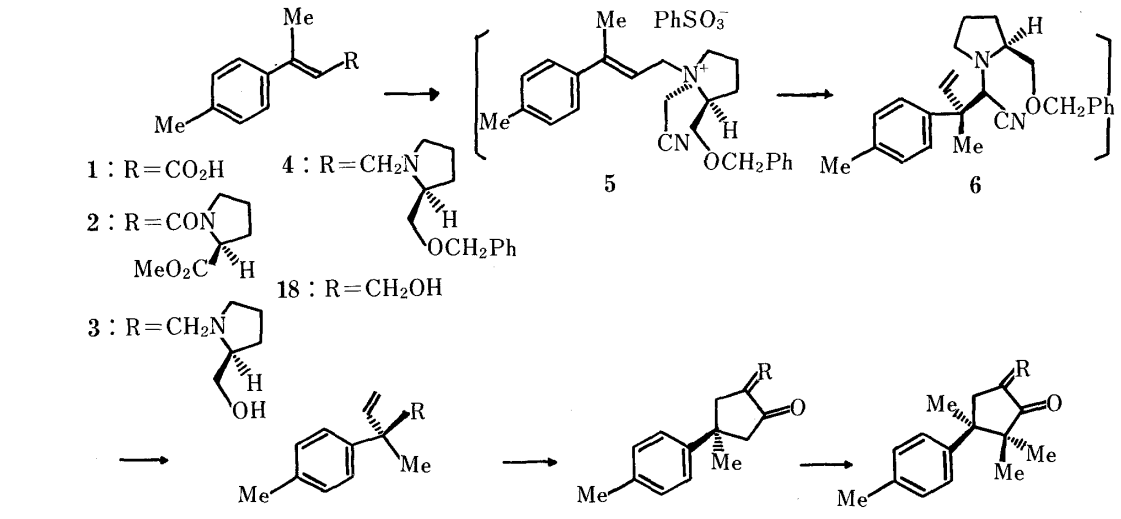

Chart 1

Furthermore, the aldehyde (**7**) was converted to its enantiomer to accomplish the synthesis of (+)-α-cuparenone. The ethylene ketal (**19**) of **7** was treated with diborane followed by alkaline hydrogen peroxide to afford the alcohol[18] (**20**) together with **21** in 95% yield, in the ratio of *ca.* 3 : 1. The acid hydrolysis of **20** gave the lactol (**22**). Wittig reaction of **22** with triphenylphosphonium methylide yielded the olefinic alcohol (**23**), which was then oxidized with pyridinium chlorochromate to give the aldehyde (**24**) with 14% enantiomeric excess. Since the antipode of **24** had already been converted into (−)-α-cuparenone, this synthesis also constitutes a formal synthesis of (+)-α-cuparenone.

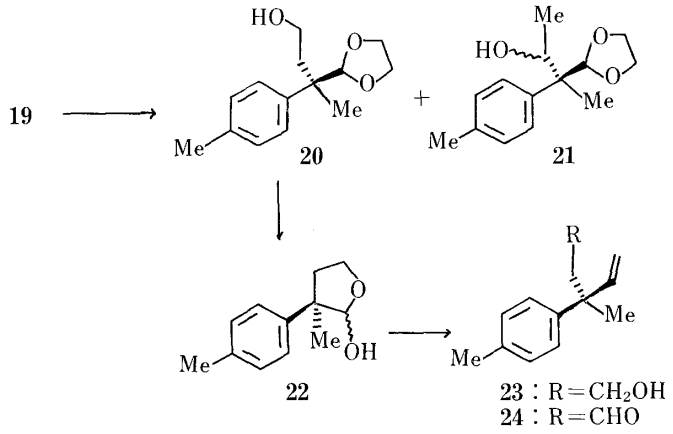

Chart 2

Experimental

Infrared (IR) spectra were obtained with a Hitachi 260-10 spectrophotometer, NMR spectra with JEOL PMX-60, JEOL JNM FX-100 and JNM-GX-400 instruments (tetramethylsilane as internal standard), and mass spectra (MS) with a JEOL JMS D-300 spectrometer. Melting points were determined with a Yanagimoto micro melting point apparatus. Optical rotations were measured with a JASCO DIP 181 instrument.

Methyl *N*-[(*E*)-3-*p*-Tolyl-2-butenoyl]-(*S*)-prolinate (2)——(a) Et_3N (0.8 ml, 5.68 mmol) was added dropwise to a stirred solution of **1** (1 g, 5.68 mmol) in anhydrous $CHCl_3$ (70 ml) under nitrogen at −15 °C. Stirring was continued for 15 min, then methyl chloroformate (0.45 ml, 5.68 mmol) was added dropwise, and the resulting mixture was stirred for 30 min. Then a solution of methyl (*S*)-prolinate (735 mg, 5.68 mmol) in anhydrous $CHCl_3$ (70 ml) was added dropwise at −10 °C, and the resulting mixture was further stirred for 2 h at −10 °C. The organic layer was washed with saturated $NaHCO_3$ solution and brine, then dried over Na_2SO_4. Evaporation of the solvent gave a crude oil (1.33 g), which was precipitated from ether–hexane (1 : 1, v/v, 12 ml/g) to afford **2** (1.2 g, 73%) as a white powder, mp 70—71 °C (from ether–hexane). *Anal.* Calcd for $C_{17}H_{21}NO_3$: C, 71.05; H, 7.37; N, 4.87. Found: C, 70.99; H, 7.42; N, 4.88. IR ($CHCl_3$): 1740, 1640, 1610 cm^{-1}. NMR ($CDCl_3$) δ: 1.68—2.18 (4H, m, pyrrolidine $-C\underline{H}_2C\underline{H}_2-$), 2.31 (6H, s), 3.45—3.85 (2H, m, $N-C\underline{H}_2-$), 3.71 (3H, s), 4.28—4.68 (1H, m, $-N-C-\underline{H}$), 6.28 (1H, br s), 7.08 (2H, d, J=8 Hz), 7.35 (2H, d, J=8 Hz). MS *m/e*: 287 (M^+). $[\alpha]_D^{20}$ −58.7° (*c*=0.6, MeOH). $[\alpha]_D^{20}$ −61.1° (*c*=1.0, MeOH) was obtained after recrystallization twice from ether–hexane.

(b) A solution of **1** (500 mg, 2.84 mmol) and PPh_3 (745 mg, 2.84 mmol) in anhydrous CH_2Cl_2 (30 ml) was added dropwise to a stirred solution of methyl (*S*)-prolinate (367 mg, 2.84 mmol) and 2,2-dipyridyl disulfide (625 mg, 2.84 mmol) in anhydrous CH_2Cl_2 (40 ml) under nitrogen at 0 °C, and the resulting mixture was stirred for 1 h at 0 °C. The organic layer was washed with 10% HCl, saturated $NaHCO_3$ solution and brine, then dried over Na_2SO_4. Evaporation of the solvent gave a crude oil, which was chromatographed on silica gel (50 g) with benzene–ethyl acetate (10 : 1, v/v) as the eluant to give **2** (770 mg, 94.5%), $[\alpha]_D^{20}$ −59.1° (*c*=0.7, MeOH). The compound obtained was identical with an authentic sample.

***O*-Benzyl-*N*-[(*E*)-3-*p*-tolyl-2-butenyl]-(*S*)-prolinol (4)**——(a) A solution of **2** (1.315 g, 4.58 mmol) in anhydrous ether (30 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (350 mg, 9.16 mmol) in anhydrous ether (30 ml) under nitrogen at 0 °C, and the resulting mixture was stirred for 1 h at room temperature, then refluxed for 16 h. The reaction mixture was diluted with ether (100 ml), and excess reagent was decomposed by the addition of 20% NaOH solution. After the insoluble materials had been filtered off on a celite pad, the filtrate was washed with brine, and dried over Na_2SO_4. Evaporation of the solvent gave a crude oil (1.2 g), which was chromatographed on silica gel (50 g) with ethyl acetate–methanol (1 : 10, v/v) as the eluant to afford *N*-[(*E*)-3-*p*-tolyl-2-butenyl]-(*S*)-prolinol (**3**)

(1.04 g, 92.7%) as a brownish oil. IR ($CHCl_3$): 3400, 1640 cm^{-1}. NMR ($CDCl_3$) δ: 1.56—1.93 (4H, m, pyrrolidine $-CH_2CH_2-$), 2.03 (3H, s), 2.29 (3H, s), 2.46—3.81 (7H, m), 5.81 (1H, t, $J=7$ Hz, $C=CH$), 7.03 (2H, d, $J=8$ Hz), 7.23 (2H, d, $J=8$ Hz). A stirred solution of **3** (528 mg, 2.16 mmol) and 60% NaH in oil (95.2 mg, 238 mmol) in anhydrous toluene–anhydrous DMSO (20:1, v/v, 52.5 ml) was refluxed for 30 min under nitrogen, and then cooled to room temperature. Next, benzyl bromide (0.26 ml, 2.16 mmol) was added dropwise and the resulting mixture was refluxed for 6 h. After cooling to room temperature, the reaction mixture was diluted with benzene (100 ml). The organic layer was washed with 10% KOH solution and brine, and dried over Na_2SO_4. Evaporation of the solvent gave a crude oil, which was chromatographed on silica gel (15 g) with benzene containing 30—60% ethyl acetate as the eluant, to give **4** (598 mg, 83%) as a colorless oil. *Anal.* Calcd for $C_{23}H_{25}NO$: C, 74.27; H, 8.13: N, 3.77. Found: C, 73.87; H, 8.26; N, 3.67. IR ($CHCl_3$): 1640 cm^{-1}. NMR ($CDCl_3$) δ: 1.51—1.88 (4H, m, pyrrolidine $-CH_2CH_2-$), 2.01 (3H, s), 2.31 (3H, s), 2.58—3.93 (7H, m, N–CH, N–CH_2–, N–CH_2–(C=C), and C–CH_2–O), 4.50 (2H, s, $ArCH_2O-$), 5.87 (1H, t, $J=6$ Hz), 7.01 (2H, d, $J=8$ Hz), 7.25 (2H, d, $J=8$ Hz), 7.25 (5H, s). MS *m/e*: 335 (M^+). $[\alpha]_D^{20}$ $-28.2°$ ($c=1.9$, MeOH). The prolinol (**4**) was crystallized as its hydrochloride, and recrystallization from ether–ethanol (20:1, v/v) afforded the pure prolinol (**4**) hydrochloride, mp 116—117 °C, $[\alpha]_D^{20}$ $+9.7°$ ($c=0.4$, MeOH).

(b) A solution of bromine (0.27 ml, 5.23 mmol) in anhydrous CH_3CN (3 ml) was added dropwise to a stirred suspension of PPh_3 (1.37 g, 5.23 mmol) in anhydrous CH_3CN (5 ml) under nitrogen at 0 °C. Then a solution of **18** (848 mg, 5.23 mmol) in anhydrous CH_3CN (6 ml), a solution of *O*-benzyl (*S*)-prolinol (1 g, 5.23 mmol) in anhydrous CH_3CN (4 ml), and a solution of Et_3N (1.5 ml, 10.5 mmol) in anhydrous CH_3CN (2 ml) at 0 °C were added. The mixture was stirred for 1 h at 0 °C, and then refluxed for 48 h. The insoluble materials were filtered off and the filtrate was diluted with ether (100 ml). The organic layer was washed with water, 10% KOH solution and brine, then dried over Na_2SO_4. Evaporation of the solvent gave a brownish oil, which was chromatographed on silica gel (30 g) with chloroform as the eluant to afford **4** (390 mg, 21%) as a colorless oil, $[\alpha]_D^{20}$ $-28.9°$ ($c=1.8$, MeOH), which was identical with an authentic sample.

(2*R*)-2-Methyl-2-*p*-tolyl-3-butenal (7)——Cyanomethyl benzenesulfonate (80%) (1.8 g, 7.2 mmol) was added to a solution of the allylic amine (**4**) (2.19 g, 6.5 mmol) in anhydrous DMSO (5 ml) under nitrogen, and the resulting mixture was stirred for 18 h at 45 °C. A solution of the salt (**5**) in anhydrous DMSO (5 ml) was diluted with anhydrous THF (150 ml) and cooled to −78 °C. After addition of potassium *tert*-butoxide (1.65 g, 14.6 mmol), the resulting mixture was further stirred for 20 h at −78 °C. The reaction mixture was diluted with ethyl acetate (200 ml), and the organic layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave the rearranged amine (**6**) as an oil, which was chromatographed on silica gel (80 g). Elution with benzene afforded **6** (1.4 g) as a crude oil, which was used for the next step without further purification. Further elution with methanol gave the starting allylic amine (**4**) (0.9 g). The above rearranged amine (**6**) (1.4 g) in THF (30 ml) was treated with a warm solution of oxalic acid (30%, v/v, 30 ml) and the resulting mixture was heated under reflux for 2 h. After cooling to room temperature, the reaction mixture was diluted with ether (100 ml), and the organic layer was washed with brine, and dried over Na_2SO_4. Evaporation of the solvent gave a crude oil (811 mg), which was chromatographed on silica gel (30 g) with hexane containing 10—40% benzene as the eluant to afford **7** (565 mg, 49.7%) as a colorless oil. *Anal.* Calcd for $C_{12}H_{14}O \cdot 0.1H_2O$: C, 81.88; H, 8.13. Found: C, 82.01; H, 8.39. High resolution MS *m/e*: Calcd for $C_{12}H_{14}O$: M^+ 174.1044. Found: M^+ 174.1039. IR ($CHCl_3$): 1720, 1630 cm^{-1}. NMR ($CDCl_3$) δ: 1.45 (3H, s), 2.28 (3H, s), 5.07 (1H, d. $J=17$ Hz, $^{H}\!>\!C=C\!<^{H}_{H}$), 5.28 (1H, d, $J=10$ Hz, $^{H}\!>\!C=C\!<^{H}_{H}$), 6.17 (1H, dd, $J=10$, 17 Hz, $^{H}\!>\!C=C\!<^{H}_{H}$), 7.09 (4H, s), 9.47 (1H, s). MS *m/e*: 174 (M^+). $[\alpha]_D^{20}$ $+10.7°$ ($c=1.1$, CH_2Cl_2).

(3*R*)-3-Methyl-3-*p*-tolyl-4-pentenal (9)——A solution of *n*-BuLi in hexane (129 mg/ml) (26.3 mg, 52.9 mmol) was added dropwise to a stirred suspension of (methoxymethyl)triphenylphosphonium chloride (16.9 g, 52.9 mmol) in anhydrous THF (200 ml) under nitrogen at 0 °C. Next, a solution of **7** (2.3 g, 13.2 mmol) in anhydrous THF (30 ml) was added dropwise at 0 °C and the resulting mixture was stirred for 2 h at the same temperature. The reaction mixture was diluted with ether (300 ml), and the organic layer washed with brine, and dried over Na_2SO_4. Evaporation of the solvent gave a crude oil, which was chromatographed on silica gel (300 g). Elution with hexane containing 10% benzene afforded one of the geometric isomers of (3*R*)-(*E*,*Z*)-1-methoxy-3-methyl-3-*p*-tolylpenta-1,4-diene (**8**). IR ($CHCl_3$): 1660, 1630 cm^{-1}. NMR ($CDCl_3$) δ: 1.53 (3H, s), 2.25 (3H, s), 3.32 (3H, s), 4.45 (1H, d, $J=6$ Hz, $^{H}\!>\!C=C(OMe)H$), 4.96 (1H, d, $J=17$ Hz, $^{H}\!>\!C=C\!<^{H}_{H}$), 4.97 (1H, d, $J=10$ Hz, $^{H}\!>\!C=C\!<^{H}_{H}$), 5.80 (1H, d, $J=6$ Hz, $>C=C(OMe)H$), 6.20 (1H, dd, $J=10$, 17 Hz, $^{H}\!>\!C=C\!<^{H}_{H}$), 7.00 (2H, d, $J=8$ Hz), 7.37 (2H, d, $J=8$ Hz). Further elution afforded the other isomer. IR ($CHCl_3$): 1670, 1650 cm^{-1}. NMR ($CDCl_3$) δ: 1.47 (3H, s), 2.31 (3H, s), 3.50 (3H, s), 4.80—5.13 (3H, m, $^{H}\!>\!C=C\!<^{H}_{H}$, $^{H}\!>\!C=C\!<^{H}_{H}$, and $>C=C(OMe)H$), 6.79—6.24 (2H, m, $^{H}\!>\!C=C\!<^{H}_{H}$ $^{H}\!>\!C=C(OMe)H$), 7.00 (2H, d, $J=8$ Hz), 7.20 (2H, d, $J=8$ Hz). A solution of the above mixture in THF (100 ml) and 10% HCl (100 ml) was stirred for 30 min at room temperature. The reaction mixture was diluted with ether (100 ml), and the organic layer was washed with water and brine, then dried over Na_2SO_4. Evaporation of the solvent gave a

crude oil, which was chromatographed on silica gel (100 g). Elution with hexane–benzene (1 : 1, v/v) afforded **9** (1.8 g, 72.6%) as a colorless oil. *Anal.* Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.46; H, 8.70. IR ($CHCl_3$): 1710, 1630 cm^{-1}. NMR ($CDCl_3$) δ: 1.50 (3H, s), 2.32 (3H, s), 2.73 (2H, d, J=3 Hz, 2-H_2), 5.09 (1H, dd, J=1, 17 Hz, $H>C=C<\underline{H}$), 5.17 (1H, dd, J=1, 10 Hz, $H>C=C<\underline{H}$), 6.13 (1H, dd, J=10, 17 Hz, $\underline{H}>C=C<H$), 7.10 (2H, d, J=10 Hz), 7.27 (2H, d, J=10 Hz), 9.58 (1H, t, J=3 Hz). MS *m/e*: 188 (M^+). $[\alpha]_D^{20}$ −1.21° (*c*=1.1, CH_2Cl_2) from **7** with $[\alpha]_D^{20}$ +10.7°; $[\alpha]_D^{20}$ −0.67° (*c*=2.0, CH_2Cl_2) from **7** with $[\alpha]_D^{20}$ +6.95°.

(3*R*)-Trimethyl-3-*p*-tolyl-2,2,3-4-pentenal (10)——(a) A solution of **9** (100 mg, 0.53 mmol) in anhydrous THF (1 ml) was added dropwise to stirred suspension of potassium hydride (0.11 ml, 0.97 mmol) in anhydrous THF (1 ml) under nitrogen at room temperature, and the resulting mixture was stirred for 15 min. Then a solution of methyl iodide (0.063 ml, 1.01 mmol) in anhydrous THF (1 ml) was added dropwise at room temperature, and the resulting mixture was further stirred for 1 h. The reaction mixture was diluted with ether and the organic layer was washed with saturated ammonium chloride solution, saturated $NaHCO_3$ solution and brine, then dried over Na_2SO_4. Evaporation of the solvent gave a yellowish oil, which was chromatographed on silica gel (10 g). Elution with hexane containing 10—20% benzene afforded **8** as a geometric mixture and (3*R*)-(*E*,*Z*)-1-methoxy-2,3-dimethyl-3-*p*-tolyl-1,4-pentadiene (**11**) (as a geometric mixture) (total 70 mg) as an inseparable mixture (1 : 1, from the ratio of peaks in the NMR spectrum). IR ($CHCl_3$): 1660, 1650 cm^{-1}. NMR ($CDCl_3$) δ: 1.47 (9H, s, 3-Me×2 and 2-Me), 2.28 (6H, s, ArMe×2), 3.48 and 3.54 (each 3H, each s, each OMe), 4.57—5.20 (5H, m, $H>C=C<\underline{H}$×2 and $\underline{H}>C=C(H)OMe$), 5.68—6.33 (4H, m, $\underline{H}>C=C<H$×2 and $C=C(OMe)\underline{H}$×2), 6.98 (4H, d, J=8 Hz, Ar$\underline{H}$×2), 7.27 (4H, d, J=8 Hz, Ar$\underline{H}$×2). MS *m/e*: 202 (M^+) for **8** and 216 (M^+) for **11**. Further elution gave **10** (20 mg, 17.4%) as a colorless oil. High-resolution MS *m/e*: Calcd for $C_{15}H_{20}O$: M^+ 216.1513. Found: M^+ 216.1498. IR ($CHCl_3$): 1715, 1630 cm^{-1}. NMR ($CDCl_3$) δ: 0.98 (6H, s), 1.47 (3H, s), 2.26 (3H, s), 4.98 (1H, d, J=17 Hz, $H>C=C<\underline{H}$), 5.14 (1H, d, J=11 Hz, $H>C=C<\underline{H}$), 6.46 (1H, dd, J=11, 17 Hz, $\underline{H}>C=C<H$), 6.93 (2H, d, J=9 Hz), 7.07 (2H, d, J=9 Hz), 9.39 (1H, s). MS *m/e*: 216 (M^+). $[\alpha]_D^{20}$ −4.8° (*c*=0.72, $CHCl_3$), which was derived from **9** with $[\alpha]_D^{20}$ −0.67°.

(b) A mixture of **8** and **11** (70 mg), 10% HCl (1 ml), and THF (1 ml) was stirred for 1 h at 50 °C. The reaction mixture was diluted with ether, and the organic layer was washed with brine, and dried over Na_2SO_4. Evaporation of the solvent gave a crude oil, which was chromatographed on silica gel (10 g) with hexane containing 20% benzene as the eluant to afford **9** and (3*R*)-2,3-dimethyl-3-*p*-tolyl-4-pentenal (**12**) (total 30 mg) as an inseparable oily mixture (1 : 1, from the ratio of peaks in the NMR spectrum). IR ($CHCl_3$): 1715, 1635 cm^{-1}. NMR ($CDCl_3$) δ: 0.93 and 0.98 (each 1.5H, d, J=6 Hz), 1.43 and 1.50 (each 3H, s), 2.30 (6H, s, ArMe×2), 2.67—3.07 (1H, m, 2H), 2.72 (2H, d, J=2 Hz, 2-H_2), 4.83—5.33 (4H, m, $H>C=C<\underline{H}$×2), 5.80—6.43 (2H, m, $\underline{H}>C=C<H$×2), 7.11 (8H, s), 9.45 (1H, d, J=2 Hz), 9.55 (1H, t, J=2 Hz). MS *m/e*: 188 (M^+) for **9** and 202 (M^+) for **12**.

(c) A solution of **9** and **12** (1 : 1) (238 mg, 0.61 mmol×2) in anhydrous THF (2 ml) was added dropwise to a stirred suspension of potassium hydride (0.23 ml, 2 mmol) in anhydrous THF (1 ml) under nitrogen at room temperature. After stirring for 15 min, a solution of methyl iodide (0.14 ml, 2.2 mmol) in anhydrous THF (2 ml) was added dropwise, and the resulting suspension was stirred for 15 min at room temperature. The reaction mixture was diluted with ether, and the organic layer was washed with saturated ammonium chloride solution, saturated $NaHCO_3$ and brine, then dried over Na_2SO_4. Evaporation of the solvent gave a crude oil, which was chromatographed on silica gel (10 g) with hexane containing 10—20% benzene as the eluant. The first eluate afforded an inseparable mixture of **8** and **11** (122 mg, 1 : 4.8 from the ratio of peaks in the NMR spectrum). The second eluate afforded **10** (84 mg, 32%), which was identical with an authentic sample.

(3*S*)-3-Methyl-3-*p*-tolylcyclopentan-1-one (13)——Tris(triphenylphosphine)chlororhodium (550 mg, 0.6 mmol) was added to a stirred solution of **9** (300 mg, 1.6 mmol) in anhydrous CH_2Cl_2 (10 ml), and the resulting mixture was stirred at room temperature for 16 h under nitrogen. The reaction mixture was concentrated under reduced pressure to leave the residue, which was treated with hexane. After the insoluble material had been filtered off, the filtrate was washed with water and brine, and dried over Na_2SO_4. Evaporation of the solvent gave a crude oil, which was chromatographed on silica gel (70 g) with benzene containing 10—20% hexane as the eluant to give **13** (126 mg, 42%) as a colorless oil. *Anal.* Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.57; H, 8.61. IR ($CHCl_3$): 1730 cm^{-1}. NMR ($CDCl_3$) δ: 1.33 (3H, s), 2.24 (2H, s, 2-H_2), 2.28 (3H, s), 2.48 (2H, d, J=4 Hz, 5-H_2), 7.08 (4H, s). MS *m/e*: 188 (M^+). $[\alpha]_D^{20}$ −3.5° (*c*=0.1, CH_2Cl_2) from **9** with $[\alpha]_D^{20}$ −1.21°; $[\alpha]_D^{20}$ −1.05° (*c*=0.1, CH_2Cl_2) from **9** with $[\alpha]_D^{20}$ −0.67°.

(−)-α-Cuparenone (17)——A solution of **13** (450 mg, 2.4 mmol) and ethyl formate (45 ml) in anhydrous benzene (10 ml) was added to a stirred suspension of sodium methoxide (900 mg, 16.7 mmol) in anhydrous benzene (30 ml) under nitrogen at 0 °C and the resulting mixture was stirred for 12 h at room temperature. Water was added to the reaction mixture and the aqueous layer was separated, washed with ether and then acidified with conc. HCl. The

resulting oily suspension was extracted with ether. The ethereal layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was chromatographed on silica gel (50 g) with benzene as the eluant to give (3*S*)-5-hydroxymethylidene-3-methyl-3-*p*-tolylcyclopentan-1-one (**14**) (490 mg, 94.8%) as a colorless oil. IR ($CHCl_3$): 1680, 1600 cm^{-1}. NMR ($CDCl_3$) δ: 1.36 (3H, s), 2.30 (3H, s), 2.51—3.08 (4H, m, 2-H_2 and 4-H_2), 7.01—7.28 (1H, br s, C=C<u>H</u>), 7.07 (4H, s), 9.01—9.48 (1H, br s, O<u>H</u>). A solution of **14** (490 mg, 2.27 mmol) in benzene (20 ml) containing *n*-butylmercaptan (225 mg, 2.5 mmol) and a catalytic amount of *p*-toluenesulfonic acid was refluxed for 1 h with a Dean–Stark apparatus. The reaction mixture was washed with saturated $NaHCO_3$ solution and brine, and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (20 g) with benzene as the eluant to afford (3*S*)-5-*n*-butylthiomethylidene-3-methyl-3-*p*-tolylcyclopentan-1-one (**15**) (587 mg, 89.8%) as a colorless oil. IR ($CHCl_3$): 1690, 1580 cm^{-1}. NMR ($CDCl_3$) δ; 1.28 (3H, s), 2.28 (3H, s), 2.58 (2H, d, J=2 Hz, 4-H_2), 2.74 (2H, s, J=2 Hz, 2-H_2), 7.01 (4H, s), 7.35 (1H, t, J=2 Hz, C=C<u>H</u>). MS *m/e*: 288 (M^+). A solution of **15** (487 mg, 1.7 mmol) in anhydrous *tert*-butanol (10 ml) was added to a stirred solution of potassium *tert*-butoxide (1.2 g, 9.8 mmol) in anhydrous *tert*-butanol (50 ml), and the resulting mixture was stirred for 5 min under nitrogen at room temperature. After addition of methyl iodide (1.5 ml, 24 mmol), the whole was refluxed for 2.5 h. Removal of the solvent gave a residue, which was extracted with ether. The ethereal layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was chromatographed on silica gel (20 g) with hexane containing 30% benzene to give (3*S*)-5-*n*-butylthiomethylidene-2,2,3-trimethyl-3-*p*-tolylcyclopentan-1-one (**16**) (330 mg, 61.4%) as a colorless oil. IR ($CHCl_3$): 1690, 1580 cm^{-1}. NMR ($CDCl_3$) δ: 0.62, 1.19 and 1.23 (each 3H, s), 2.29 (3H, s), 2.54 (2H, d, J=2 Hz, 4-H_2), 6.99 (2H, d, J=8 Hz), 7.15 (2H, d, J=8 Hz), 7.42 (1H, t, J=2 Hz, C=C<u>H</u>). MS *m/e*: 316 (M^+). A mixture of **16** (411 mg, 1.3 mmol), 25% KOH solution (6 ml) and diethylene glycol (6 ml) was refluxed for 15.5 h under nitrogen. After being cooled, the reaction mixture was extracted with ether (100 ml × 2). The ether solution was washed with brine (100 ml × 3) and dried over Na_2SO_4. Evaporation of the solvent gave an oily yellow residue (280 mg), which was chromatographed on silica gel (15 g) with benzene containing 50% hexane as the eluant to afford (−)-α-cuparenone [(3*S*)-2,2,3-trimethyl-3-*p*-tolylcyclopentan-1-one)] (**17**) (226 mg, 80.5%) as a colorless oil. IR ($CHCl_3$): 1720 cm^{-1}. NMR ($CDCl_3$) δ: 0.61, 1.16, and 1.27 (each 3H, s), 1.66—2.14 (2H, m, 4-H_2), 2.30 (3H, s), 2.41—2.68 (2H, m, 5-H_2), 7.03 (2H, d, J=8 Hz), 7.23 (2H, d, J=8 Hz). MS *m/e*: 216 (M^+), 145 ($M^+ - 71$), whose spectral data were identical with those reported;[19] $[\alpha]_D^{20}$ −15.56° (*c*=1.3, $CHCl_3$) (lit.,[5] $[\alpha]_D^{20}$ −169.9° ($CHCl_3$)) from **13** with $[\alpha]_D^{20}$ −1.05°. The optical purity of this compound was 9.16%.

(3*R*)-4,4-Ethylenedioxy-3-methyl-3-*p*-tolylbut-1-ene (19)——A solution of **7** (700 mg, 4.0 mmol, $[\alpha]_D^{20}$ +10.7°), ethylene glycol (2.5 g, 40 mmol), and a catalytic amount of *p*-toluenesulfonic acid in benzene (70 ml) was refluxed for 14 h with a Dean–Stark water separator. The reaction mixture was cooled to room temperature, and treated with saturated $NaHCO_3$ and ether. The organic layer was separated, washed with brine, and dried over Na_2SO_4. Evaporation of the solvent gave a crude oil, which was chromatographed on silica gel (30 g) with benzene containing 30% hexane as the eluant to afford **19** (842 mg, 96.6%) as a colorless oil. *Anal.* Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.11; H, 8.47. IR ($CHCl_3$): 1635 cm^{-1}. NMR ($CDCl_3$) δ: 1.43 (3H, s), 2.28 (3H, s), 3.77 (4H, s), 5.05 (1H, s, 4-H), 5.08 (1H, dd, J=1, 17 Hz, $^{H}\!>\!C\!=\!C\!<^{\underline{H}}_{H}$), 5.15 (1H, dd, J=1, 12 Hz, $^{H}\!>\!C\!=\!C\!<^{H}_{\underline{H}}$), 6.17 (1H, ddd, J=1, 12, 17 Hz, $^{\underline{H}}\!>\!C\!=\!C\!<^{H}$), 7.02 (2H, d, J=8 Hz), 7.45 (2H, d, J=8 Hz). MS *m/e*: 218 (M^+). $[\alpha]_D^{20}$ −2.0° (*c*=1.0, $CHCl_3$).

(3*S*)-4,4-Ethylenedioxy-3-methyl-3-*p*-tolylbutan-1-ol (20)——A solution of borane–THF complex (1 M) (13.5 ml, 13.5 mmol) was added dropwise to a stirred solution of **19** (900 mg, 4.13 mmol, $[\alpha]_D^{20}$ −2.0°) in anhydrous THF (10 ml) under nitrogen at room temperature. After being stirred for 1 h, the reaction mixture was treated with 6 N NaOH solution (10 ml), and 30% H_2O_2 solution (10 ml), and the whole was stirred for 2 h at room temperature. The reaction mixture was diluted with ether, and the organic layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was chromatographed on silica gel (10 g) with benzene containing 5—10% ethyl acetate as the eluant. The first elution afforded (2*RS*, 3*S*)-4,4-ethylenedioxy-3-methyl-3-*p*-tolylbutan-2-ol (**21**) (22.4 mg, 23%) as a diastereomixture, which was separated carefully by rechromatography on silica gel (50 g) with benzene containing 5% ethyl acetate as the eluant to give one of the diastereoisomers (**21**) (135 mg) as a colorless oil. IR ($CHCl_3$): 3500 cm^{-1}. NMR ($CDCl_3$) δ: 1.04 (3H, d, J=7 Hz, 2-M<u>e</u>), 1.27 (3H, s, 3-M<u>e</u>), 2.30 (4H, s, ArM<u>e</u> and O<u>H</u>), 3.80 (4H, s), 3.95—4.39 (1H, m, 2-H), 5.25 (1H, s, 4-H), 7.05 (2H, d, J=8 Hz), 7.37 (2H, d, J=8 Hz). MS *m/e*: 203 ($M^+ - 33$), and the other isomer (**21**) (89 mg) as a colorless oil. IR ($CHCl_3$): 3500 cm^{-1}. NMR ($CDCl_3$) δ: 0.83 (3H, d, J=7 Hz, 2-M<u>e</u>), 1.34 (3H, s, 3-M<u>e</u>), 2.30 (3H, s), 3.29 (1H, br s, O<u>H</u>), 3.80 (4H, s), 4.41 (1H, q, J=7 Hz, 2-<u>H</u>), 5.10 (1H, s, 4-H), 7.05 (2H, d, J=8 Hz), 7.37 (2H, d, J=8 Hz). MS *m/e*: 203 ($M^+ - 33$). The second eluate afforded (3*S*)-4,4-ethylenedioxy-3-methyl-3-*p*-tolylbutan-1-ol (**20**) (704 mg, 72.3%) as a colorless oil. High-resolution MS *m/e*: Calcd for $C_{14}H_{20}O_3$: M^+ 236.1411. Found: M^+ 236.1389. IR ($CHCl_3$): 3450 cm^{-1}. NMR ($CDCl_3$) δ: 1.34 (3H, s), 1.81 (1H, s, O<u>H</u>), 1.88—2.34 (2H, m, 2-H_2), 2.28 (3H, s), 3.34—3.68 (2H, m, 1-H_2), 3.77 (4H, s), 5.86 (1H, s, 4-H), 7.01 (2H, d, J=8 Hz), 7.24 (2H, d, J=8 Hz). MS *m/e*: 236 (M^+). $[\alpha]_D^{20}$ +0° (*c*=1.2, $CHCl_3$).

(3*S*)-2-Hydroxy-3-methyl-3-*p*-tolyltetrahydrofuran (22)——A catalytic amount of *p*-toluenesulfonic acid was added to a stirred solution of **20** (700 mg, 2.97 mmol, $[\alpha]_D^{20}$ +0°) in acetone (40 ml) containing water (7 ml) at room temperature, and the resulting mixture was stirred for 15 h at 45—50 °C. After removal of the solvent, the residue was

extracted with ether, and the organic layer was washed with saturated $NaHCO_3$ and brine, then dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was chromatographed on silica gel (100 g) with benzene containing 5% ethyl acetate as the eluant to afford **22** (520 mg, 91.3%) as a colorless oil. IR ($CHCl_3$): 3400 cm^{-1}. NMR ($CDCl_3$) δ: 1.28 and 1.38 (each 3H, s), 1.72—2.75 (4H, m, 4-H_2 × 2), 2.33 (6H, s), 2.88 and 3.57 (each 1H, d, J=3, 4 Hz, OH × 2), 3.72—4.35 (4H, m, 5-H_2), 5.36 and 5.38 (each 1H, d, J=3, 4 Hz, 2-H × 2), 7.07 (4H, d, J=7 Hz), 7.27 (4H, d, J=7 Hz). MS *m/e*: 192 (M^+).

(3*S*)-3-Methyl-3-*p*-tolyl-4-pentenol (23)——A solution of *n*-BuLi in hexane (129 mg/ml) (13.2 ml, 26.6 mmol) was added dropwise to a stirred suspension of methyltriphenylphosphonium bromide (9.67 g, 27 mmol) in anhydrous THF (40 ml) under nitrogen at 0 °C. The mixture was stirred for 30 min, then a solution of **22** (520 mg, 2.7 mmol) in anhydrous THF (10 ml) was added dropwise, and the resulting mixture was further stirred for 2 h at room temperature. The reaction mixture was treated with ether (500 ml) and water (20 ml), and the organic layer was washed with saturated ammonium chloride solution, saturated $NaHCO_3$ solution and brine, then dried over Na_2SO_4. Evaporation of the solvent gave a crude oil, which was chromatographed on silica gel (15 g) with benzene containing 5% ethyl acetate as the eluant to afford **23** (410 mg, 80%) as a colorless oil. *Anal.* Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 81.68; H, 9.72. IR ($CHCl_3$): 3400, 1630 cm^{-1}. NMR ($CDCl_3$) δ: 1.37 (3H, s), 1.91 (1H, s, O<u>H</u>), 2.04 (2H, t, J=7 Hz, 2-H_2), 2.31 (3H, s), 3.54 (2H, t, J=7 Hz, 1-H_2), 5.04 (1H, dd, J=1, 17 Hz, $^{H}\!>\!C\!=\!C\!<^{H}_{\underline{H}}$), 5.10 (1H, dd, J=1, 10 Hz, $^{H}\!>\!C\!=\!C\!<^{H}_{\underline{H}}$), 6.06 (1H, dd, J=10, 17 Hz, $^{\underline{H}}\!>\!C\!=\!C\!<^{H}_{H}$), 7.09 (2H, d, J=9 Hz), 7.24 (2H, d, J=9 Hz). MS *m/e*: 190 (M^+). $[\alpha]_D^{20}$ +2.77° (c=1.7, $CHCl_3$) from **20** with $[\alpha]_D^{20}$ ±0°.

(3*S*)-3-Methyl-3-*p*-tolyl-4-pentenal (24)——Pyridinium chlorochromate (187 mg, 0.87 mmol) was added in one portion to a stirred solution of **23** (110 mg, 0.58 mmol, $[\alpha]_D^{20}$ +2.77°) in anhydrous CH_2Cl_2 (5 ml) under nitrogen at room temperature, and the resulting mixture was stirred for 2 h at the same temperature. Removal of the solvent gave a black solid, which was extracted with ether (30 ml × 3) until it became granular. The combined organic layer was washed with brine (50 ml × 2) and dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was chromatographed on silica gel (2 g) with benzene as the eluant to afford **24** (100 mg, 92%) as a colorless oil; $[\alpha]_D^{20}$ +1.35° (c=1.3, CH_2Cl_2), whose spectral data (IR, NMR, and MS) were identical with those of its antipode.

(*E*)-*p*-Tolyl-2-buten-1-ol (18)——$LiAlH_4$ (200 mg, 5.26 mmol) was added in small portions to a stirred solution of the cinnamic acid (**1**) (1 g, 5.68 mmol) in anhydrous ether (15 ml) and anhydrous THF (4 ml) under nitrogen at 0 °C, and the resulting mixture was stirred for 20 min at 0 °C. Ether (100 ml) was added to the reaction mixture, followed by dropwise addition of 10% NaOH solution with vigorous stirring. The resulting suspension was filtered. The filtrate was washed with water, 10% HCl solution (100 ml), and brine (100 ml × 2), and dried over Na_2SO_4. Evaporation of the solvent gave a crude oil, which was chromatographed on silica gel (30 g) with benzene as the eluant to afford **18** (610 mg, 66.3%) as a colorless oil. High-resolution MS *m/e*: Calcd for $C_{11}H_{14}O$: M^+ 162.1043. Found: M^+ 162.1043. IR ($CHCl_3$): 3400, 1640 cm^{-1}. NMR ($CDCl_3$) δ: 1.95 (3H, s, C=C(Ar)Me), 2.26 (3H, s), 3.05 (1H, s, O<u>H</u>), 4.22 (2H, d, J=6 Hz, 1-H_2), 5.85 (1H, t, J=6 Hz, ArC=C<u>H</u>), 6.95 (2H, d, J=8 Hz), 7.18 (2H, d, J=8 Hz). MS *m/e*: 162 (M^+).

(2*R*)-2-Methyl-2-*p*-tolyl-3-buten-1-ol (25)——$NaBH_4$ (245 mg, 0.65 mmol) was added to a stirred solution of **7** (210 mg, 1.2 mmol) in ethanol (10 ml) at 0 °C, and the resulting mixture was stirred for 1 h at 0 °C. The reaction mixture was diluted with ether (100 ml) and several drops of acetic acid, then the organic layer was washed with brine, and dried over Na_2SO_4. Evaporation of the solvent gave a crude oil, which was chromatographed on silica gel (10 g) with benzene as the eluant to afford **25** (207 mg, 97.5%) as a colorless oil. High-resolution MS *m/e*: Calcd for $C_{12}H_{16}O$: M^+ 176.1201. Found: M^+ 176.1203. IR ($CHCl_3$): 3400. 1635 cm^{-1}. NMR ($CDCl_3$) δ: 1.37 (3H, s), 1.60 (1H, s, O<u>H</u>), 2.29 (3H, s), 3.67 (2H, s, 1-H_2), 5.03 (1H, d, J=18 Hz, $^{\underline{H}}\!>\!C\!=\!C\!<^{H}_{\underline{H}}$), 5.15 (1H, d, J=11 Hz, $^{H}\!>\!C\!=\!C\!<^{H}_{\underline{H}}$), 6.00 (1H, dd, J=11, 18 Hz, $^{\underline{H}}\!>\!C\!=\!C\!<^{H}_{H}$), 7.00 (2H, d, J=8 Hz), 7.17 (2H, d, J=8 Hz). MS *m/e*: 176 (M^+). $[\alpha]_D^{20}$ −1.14° (c=1.6, $CHCl_3$) from **7** with $[\alpha]_D^{20}$ +4.23°; $[\alpha]_D^{20}$ −2.4° (c=1.2, $CHCl_3$) from **7** with $[\alpha]_D^{20}$ +10.7°.

(2*R*)-2-Methyl-2-*p*-tolyl-3-butenyl (*R*)-α-methoxyphenylacetate (26)——A mixture of (*R*)-(−)-α-methoxyphenylacetic acid (225 mg, 1.36 mmol), $[\alpha]_D^{20}$ −141.7° (c=0.6, EtOH, 94.4% enantiomerically pure), thionyl chloride (2.8 ml), and anhydrous benzene (20 ml) was refluxed vigorously for 1 h and then concentrated under reduced pressure. A solution of the alcohol (**25**) (110 mg, 0.625 mmol) in benzene (2 ml) and pyridine (1 ml) was added to a solution of the acid chloride prepared in benzene (5 ml) at room temperature, and the resulting mixture was allowed to stand at the same temperature for 30 min. After dilution with benzene (10 ml), the mixture was washed with water, 10% hydrochloric acid, and brine, then dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was chromatographed on silica gel (10 g) with benzene as the eluant to afford **26** (197 mg, 97.3%) as a colorless oil. *Anal.* Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.58; H, 7.55. IR ($CHCl_3$): 1730, 1630 cm^{-1}. NMR ($CDCl_3$) δ: 1.18 (3H, s), 2.18 (3H, s), 3.21 (3H, s), 4.15 (2H, br s, 1-H_2), 4.51 (1H, s, α-H), 4.76 (1H, d, J=17 Hz, $^{H}\!>\!C\!=\!C\!<^{H}_{\underline{H}}$),

4.90 (1H, d, J=10 Hz, $\overset{H}{>}C=C\overset{H}{<}$), 5.76 (1H, dd, J=10, 17 Hz, $\overset{H}{>}C=C\overset{H}{<}$), 6.89 (4H, s), 7.10 (5H, s); 400 MHz NMR ($CDCl_3$) δ of (2*R*)-**26**: 1.29037 (3H, s, 2-Me), 4.67723 (1H, s, α-H); 400 MHz NMR ($CDCl_3$) δ of (2*S*)-**26**: 1.29953 (3H, s, 2-Me), 4.68578 (1H, s, α-H). MS *m/e*: 324 (M^+).

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