Efficient Synthesis of C_{10} Chiron by Lewis Acid Catalyzed Rearrangement of (+)-α-3,4-Epoxycarane

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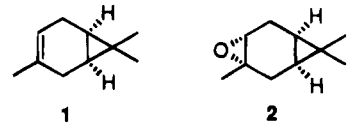
Asymmetric syntheses starting from optically active compounds are recognized as the chiral pool method. Over the last decades numerous reports have been published utilizing carbohydrates, amino acids, hydroxy acids, and terpenes as starting materials. However, optical purities of some monoterpene starting materials are not always high. For example, the optical purity of (1*S*)-(−)-α-pinene was determined to be less than 90% ee.[1] Naturally occurring (+)-3-carene (**1**) is an abundant chiral monoterpene, which is obtained from higher-boiling fractions of the oils of various *Pinus* species (Figure 1). Numerous attempts have been made at preparation of optically active useful compounds from **1**.[2] However, the optical purity of **1** has yet to be unequivocally determined.[3] In most of the previous studies starting from **1**, the cyclopropane moiety was incorporated into target molecules without cyclopropane ring opening.[2] Several studies on skeletal rearrangement of carene derivatives have been also made. (+)-α-3,4-Epoxycarane (**2**),[4] easily prepared from **1**, has been thought to be a candidate for the starting material of these rearrangements.[5] However, under the hitherto known conditions for the acid-catalyzed rearrangement of **2**, only carvenone (**3**) was obtained, with low optical purity.[5]

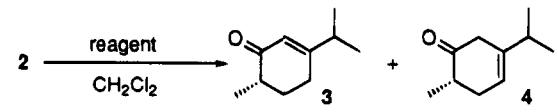
As part of our synthetic studies on tigliane and ingenane derivatives from **1**,[2a-c] we have been attempting to convert **2** into an optically active useful intermediate, using various Lewis acids as catalyst.[6] Among the Lewis acids we have examined, TMSOTf was found to promote the rearrangement of α-3,4-epoxycarane (**2**) at 0 °C (0.5 h), giving carvenone (**3**) (6%, 83% ee) and the β,γ-unsaturated ketone **4** (58%, 79% ee). Furthermore, it was found that the rearrangement proceeded nicely even at −78 °C (0.5 h) to afford **3** (4%, 99% ee) and **4** (75%, 96% ee). As shown in Table 1, run 5, the prolonged reaction time (12 h) improved the chemical yield of carvenone (**3**) only slightly, suggesting that efficient conversion of **4** to **3** would be unlikely under these reaction conditions. On the other hand, as shown in Table 1, run 6, the proton-catalyzed rearrangement of **2** resulted in the formation of **3** with 15% ee in 63% chemical yield, which is in accord with the reported result.[5] To the best of our knowledge, this is the first report concerning the isolation of the β,γ-unsaturated ketone **4** by a rearrangement of **2**. The optical purity of **3** was determined by HPLC using DAICEL CHIRALPAK AS (hexane−*i*-PrOH, 9:1). The optical purity of **4** was determined as follows. Reduction of **4** with either $LiAlH_4$ or K-Selectride gave the corresponding hydroxy derivatives **5** and **6** stereoselectively in high yield (Scheme 1). They were then converted to their corresponding 3,5-dinitrobenzoates **7** and **8**, respectively. The HPLC analysis of **7** and **8** using a DAICEL CHIRALCEL OD column (hexane−*i*-PrOH, 98:2) made possible the determination of the optical purity of **4** (96% ee), suggesting that **4** would be a potential chiron of high ee. The stereochemistry of **5** and **6** was determined from the ^{1}H-NMR spectra



1 2

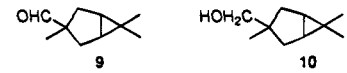
Figure 1.

Table 1. Acid-Catalyzed Rearrangement of 2 to 3 and 4



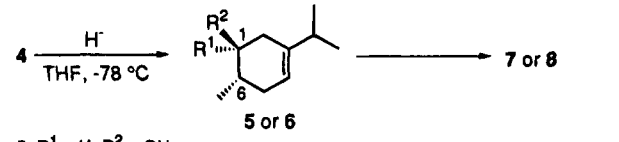
run	reagent (mol equiv)	T (°C)	time (h)	products: 3 yield, % (ee, %)	products: 4 yield, % (ee, %)
1	BF_3-OEt_2 (1.2)	0	1.5		[a]
2	Et_2AlCl (2.0)	0	1.0		[b]
3	TMSOTf (0.1)	0	0.5	6 (83)	58 (79)
4	TMSOTf (0.1)	−78	0.5	4 (99)	75 (96)
5	TMSOTf (0.1)	−78	12	10 (96)	69 (96)
6	TMSOTf (1.0), H_2O (0.05)	−78	0.5	63 (15)	trace

[a] A complex mixture was formed. [b] Compounds **9** (7%) and **10** (51%) were formed.



9 10

Scheme 1



5 or 6

5. R^1 = H, R^2 = OH
6. R^1 = OH, R^2 = H
7. R^1 = H, R^2 = *O*-3,5-dinitrobenzoyl
8. R^1 = *O*-3,5-dinitrobenzoyl, R^2 = H

reagent	5 : 6	yield, %
$LiAlH_4$	5 : 1	94
$K(s\text{-}C_4H_9)_3BH$	1 : 18	90

(1) Brown, H. C.; Jadhav, P. K.; Desai, H. C. *J. Org. Chem.* **1982**, *47*, 4583–4584.

(2) For recent examples, see the following references: (a) Sugita, K.; Shigeno, K.; Neville, C. F.; Sasai, H.; Shibasaki, M. *Synlett* **1994**, 325–329. (b) Shigeno, K.; Sasai, H.; Shibasaki, M. *Tetrahedron Lett.* **1992**, *33*, 4937–4940. (c) Shigeno, K.; Ohne, K.; Yamaguchi, T.; Sasai, H.; Shibasaki, M. *Heterocycles* **1992**, *33*, 161–171. (d) Paquette, L. A.; Ross, R. J.; Shi, Y.-J. *J. Org. Chem.* **1990**, *55*, 1589–1598. (e) Funk, R. L.; Olmstead, T. A.; Parvez, M. *J. Am. Chem. Soc.* **1988**, *110*, 3298–3300. (f) Maas, D. D.; Blagg, M.; Wiemer, D. F. *J. Org. Chem.* **1984**, *49*, 853–856. (g) Salaun, J. *Chem. Rev.* **1989**, *89*, 1247–1270. (h) Larock, R. C.; Song, H.; Kim, S.; Jacobson, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 834. (i) Ho, T.-L. *Enantioselective Synthesis. Natural Products from Chiral Terpenes*; John Wiley & Sons, Inc.: New York, 1992; pp 185–204.

(3) In a recent paper, Brown described that optical rotation of (+)-3-carene rose from +15° to +17.3° (neat) after recrystallization of the corresponding bis(caranyl)borane. See: Brown, H. C.; Racherla, U. S.; Liao, Y.; Khanna, V. V. *J. Org. Chem.* **1992**, *57*, 6608–6614.

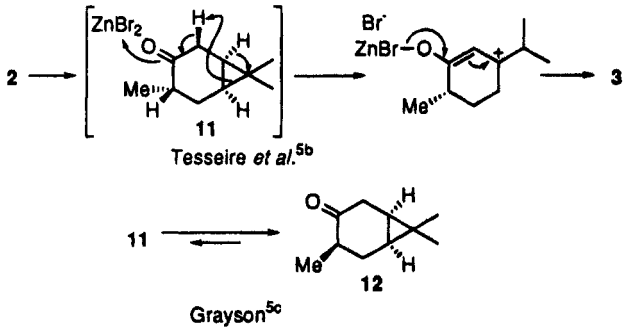
(4) (a) Arbuzov, B. A.; Mikhailov, B. M. *J. Prakt. Chem.* **1930**, *127*, 1–15. (b) Cocker, W.; Grayson, D. H., *J. Chem. Soc., Perkin Trans. 1* **1965**, 1217. (c) Brown, H. C.; Suzuki, A. *J. Am. Chem. Soc.* **1966**, *89*, 1933–1941.

(5) (a) Kropp, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 4926–4934. (b) Teisseire, P.; Galfre, A.; Plattier, M.; Rouillier, P.; Corbier, B. *Recherches* **1967**, *16*, 119–58. (c) Grayson, D. H. *Proc. R. Ir. Acad.* **1983**, *83B*, 85–92.

(6) Optical rotation of starting (+)-3-carene: $[\alpha]^{23}_D$ +15.4° (neat).

0022-3263/95/1960-0465$09.00/0

Scheme 2



(J_{HC_1,HC_6} = 9.5 Hz for **7** and 2.3 Hz for **8**), and their absolute configuration was confirmed by Mosher's method (see Experimental Section).[7] From these results it can be also concluded that the optical purity of (+)-3-carene is higher than 99% ee.

Regarding the mechanism of rearrangement of **2** to the enone **3**, Tesseire *et al.* proposed that the $ZnBr_2$-catalyzed rearrangement would take place through (−)-*trans*-caran-4-one (**11**) (Scheme 2).[5b] Grayson supported this mechanism by isolation of **11** using concd cold H_2SO_4 as a catalyst and also observed that **11** was easily epimerized into the thermodynamically more stable (−)-*cis*-caran-4-one (**12**).[5c,8] However, the precise reaction pathway from **2** to **3** remained unclear. The isolation of optically active **4**, in our studies, does not support the mechanism previously proposed (Scheme 2).[5] We succeeded in isolating (−)-*trans*-caran-4-one (**11**) from the reaction mixture of the TMSOTf-catalyzed rearrangement of **2** (5%, Table 1, run 4). Furthermore, it was found that treatment of **11** with TMSOTf (0.1 mol equiv) in CH_2Cl_2 at −78 °C for 1 h produced only carvenone (**3**) of 91% ee in 8% yield, together with recovery of **11** (65%). None of the β,γ-unsaturated ketone **4** was detected in the reaction mixture. This result also suggested that the β,γ-unsaturated ketone **4** would be formed through the different pathway from that proposed by Tesseire *et al.* Although the precise mechanism for the formation of **4** with 96% ee is not clear at present, it seems likely that the rearrangement proceeds through the tertiary carbocation (**13**) formed by the opening of the cyclopropane ring.[9] Finally, we investigated the transformation of **4** with 96% ee to **3** of high enantiomeric excess. The results are summarized in Table 2. The isomerization promoted by 1 mol equiv of TMSOTf at −78 °C (24 h) was found to give **3** of 82% ee in only 8% yield. After due consideration of the above-mentioned results, carvenone (**3**) of high ee appeared to be formed through (−)-*trans*-caran-4-one (**9**), albeit in rather low efficiency. Transformation of **4** to **3** was found to be best carried out on exposure to 2.5 mol equiv of DBU in CH_2Cl_2 at −78 to −70 °C for 40 h, affording **3** of 87% ee in 61% yield.

In conclusion, we have revealed the reaction course from (+)-3,4-epoxycarane (**2**) to **3** and **4** with the aid of TMSOTf. Optically active **3** and **4** will be useful synthetic intermediates for the preparation of terpenoids and other bioactive compounds. Furthermore, we have determined the high optical purity of (+)-3-carene.

(7) Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092–4096. Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Org. Chem.* **1991**, *56*, 1296–1298.

(8) Allinger's MM2 calculation indicates that **12** (E = 84.22 kJ/mol) is about ΔE = 8.52 kJ/mol more stable than **11** (E = 92.74 kJ/mol).

(9) The following mechanistic course is speculated at present. We are very grateful to the reviewer for bringing it our attention.

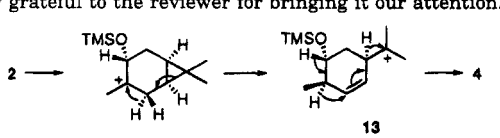


Table 2. Isomerization of 4 to 3

$$4 \xrightarrow[CH_2Cl_2]{\text{reagent}} 3$$

run	reagent (mol equiv)	T (°C)	time (h)	3 yield (%)	3 ee (%)
1	TMSOTf (1.0)	−40	48	56	19
2	TMSOTf (1.0)	−78	24	8	82
3	DBU (2.0)	−78 → −50	40	81	72
4	DBU (2.5)	−78 → −70	40	61	87

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were measured with Me_4Si as internal reference and $CDCl_3$ as solvent. All solvents used in reactions were dried prior to use.

Typical Experimental Procedure for the Rearrangement of (+)-α-3,4-Epoxycarane (2) with TMSOTf. To a stirred solution of the epoxide **2**, synthesized as described earlier[4a] (0.4 mL, 2.33 mmol), in CH_2Cl_2 (10 mL) was added TMSOTf (0.044 mL, 0.23 mmol) at −78 °C. After being stirred for 30 min at the same temperature, aqueous $NaHCO_3$ solution and ether were added to the reaction mixture. The organic layer was separated, washed with brine, and concentrated. The oily residue was purified by silica gel column chromatography (hexane–ether, 10:1) to give **4** (273 mg, 75%), **3** (15 mg, 4%), and **11** (19 mg, 5%).

The analytical and spectral data for **4** were as follows: $[\alpha]^{20}_D$ +112° (*c* 1.51, $CHCl_3$) (96% ee); IR (neat) ν 2963, 1717 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.02 (dd, J = 7.0, 0.9 Hz, 6H), 1.09 (d, J = 6.6 Hz, 3H), 2.00–2.16 (m, 1H), 2.24 (sept, J = 7.0 Hz, 1H), 2.48–2.67 (m, 2H), 2.76 (d, J = 20.1 Hz, 1H), 2.92 (bd, J = 20.1, 1H), 5.51–5.58 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ 14.1, 21.0, 21.1, 33.8, 34.1, 40.8, 42.3, 117.7, 117.8, 212.8; MS *m/z* 152 (M^+); HRMS calcd for $C_{10}H_{16}O$ 152.1202, found 152.1199.

The analytical and spectral data for known **3**[5a] were as follows: $[\alpha]^{20}_D$ −85.9° (*c* 0.87, $CHCl_3$) (99% ee); IR (neat) ν 2964, 1671 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.10 (d, J = 6.9 Hz, 6H), 1.14 (d, J = 6.9 Hz, 3H), 1.62–1.75 (m, 1H), 2.02–2.12 (m, 1H), 2.25–2.45 (m, 4H), 5.85 (s, 1H); MS *m/z* 152 (M^+).

The analytical and spectral data for known **11**[5a] were as follows: $[\alpha]^{25}_D$ −61.0° (*c* 0.79, $CHCl_3$); IR (neat) ν 2932, 1714 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.84 (dt, J = 6.2, 8.6 Hz, 1H), 0.93 (s, 3H), 1.03–1.11 (m, 1H), 1.07 (s, 3H), 1.23 (d, J = 7.2 Hz, 3H), 1.72 (dt, J = 5.4, 14.5 Hz, 1H), 1.98–2.13 (m, 2H), 2.18–2.28 (m, 1H), 2.58 (dd, J = 8.6, 18.2 Hz, 1H).

Reaction of 11 with TMSOTf. To a stirred solution of (−)-*trans*-caran-4-one (**11**) (30 mg, 0.20 mmol) in CH_2Cl_2 (1.5 mL) was added TMSOTf (4 μL, 0.02 mmol) at −78 °C. After being stirred 1 h at the same temperature, aqueous $NaHCO_3$ solution and ether were added to the reaction mixture. The organic layer was separated, washed with brine, and concentrated. The oily residue was purified by silica gel column chromatography (hexane–ether, 10:1) to give **3** of 91% ee (2.3 mg, 8%) and recovered of **11** (20 mg, 65%).

Isomerization of 4 to 3. To a stirred solution of the β,γ-unsaturated ketone **4** (20 mg, 0.13 mmol) in CH_2Cl_2 (1 mL) was added DBU (0.049 mL, 0.33 mmol) at −78 °C. After being stirred for 40 h at −78 to −70 °C, the reaction mixture was quenched by the addition of 1 N HCl, and ether was then added. The organic layer was separated, washed with brine, and concentrated. The oily residue was purified by silica gel column chromatography (hexane–ether, 10:1 to give **3** of 87% ee (12.1 mg, 61%).

Reduction of 4 with $LiAlH_4$. To a stirred solution of the β,γ-unsaturated ketone **4** (70 mg, 0.46 mmol) in THF (1.0 mL) was added $LiAlH_4$ (17.5 mg, 0.46 mmol) at −78 °C. After being stirred for 30 min at the same temperature, the reaction mixture was quenched by the addition of Na_2SO_4–$10H_2O$ (1.0 g), and water was then added. The mixture was extracted with AcOEt (10 mL × 3). The organic extracts were washed with brine, dried

(Na_2SO_4), and evaporated. Purification of the resulting residue, by flash chromatography (SiO_2, AcOEt–hexane, 1:2), gave the hydroxy derivatives **5** (56 mg, 79%) and **6** (11 mg, 15%).

The analytical and spectral data for **5** were as follows: IR (neat) υ 3352, 2959 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.99 (d, J = 6.9 Hz, 6H), 1.02 (d, J = 6.6 Hz, 3H), 1.57–2.35 (m, 6H) 3.51 (m, 1H), 5.30–5.32 (m, 1H); HRMS calcd for $C_{10}H_{18}O-H_2O$ 136.1252, found 136.1253.

Reduction of 4 with K-Selectride. To a stirred solution of the β,γ-unsaturated ketone **4** (70 mg, 0.46 mmol) in THF (1.0 mL) was added 1.0 M K-Selectride THF solution (0.45 mL, 0.45 mmol) at −78 °C. After being stirred for 30 min at the same temperature, the reaction mixture was quenched by the addition of H_2O_2 (2.0 mL), and then water was added. The mixture was extracted with AcOEt (10 mL × 3). The organic extracts were washed with brine, dried (Na_2SO_4), and evaporated. Purification of the resulting residue, by flash chromatography (SiO_2, AcOEt–hexane, 1:2), gave the hydroxy derivatives **5** (3.4 mg, 5%) and **6** (61 mg, 85%). The analytical and spectral data for **6** were as follows: IR (neat) υ 3363, 2923 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.97 (d, J = 6.3 Hz, 6H), 0.99 (d, J = 6.9 Hz, 3H), 1.79–2.30 (m, 6H), 3.87–3.89 (m, 1H), 5.38–5.39 (m, 1H); HRMS calcd for $C_{10}H_{18}O$ 154.1358, found 154.1363.

Synthesis of the 3,5-Dinitrobenzoate 7. To a stirred solution of the hydroxy derivative **5** (80 mg, 0.519 mmol) in CH_2Cl_2 (5.0 mL) was added Et_3N (219 μL, 1.56 mmol), DMAP (32 mg, 0.260 mmol) and 3,5-dinitrobenzoyl chloride (179 mg, 0.779 mmol) at 0 °C. After being stirred for 1.5 h, the reaction mixture was treated with aqueous $NaHCO_3$ (10 mL) solution and extracted with AcOEt (10 mL × 3). The organic extracts were washed with brine, dried (Na_2SO_4) and concentrated. Purification of the resulting residue, by flash chromatography (SiO_2, AcOEt-hexane, 1:50), gave the 3,5-dinitrobenzoate derivative **7** (137 mg, 76%) as yellow crystals.

The analytical and spectral data for **7** were as follows: mp 81–82 °C; IR (KBr) υ 3106, 2961, 1718, 1546, 1342, 1287 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.02 (d, J = 6.9 Hz, 6H), 1.03 (d, J = 6.6 Hz, 3H), 1.85–2.27 (m, 4H), 2.35 (dt, J = 17.5, 5.2 Hz, 1H), 2.49 (bdd, J = 17.5, 5.2 Hz, 1H), 5.11 (ddd, J = 5.2, 9.5, 8.5 Hz, 1H), 5.41 (m, 1H), 9.17 (d, J = 2.0 Hz, 2H), 9.23 (t, J = 2.0 Hz, 1H); MS m/z 195 ($M^+ - C_7H_3N_2O_5$). Anal. Calcd for $C_{17}H_{20}N_2O_8$: C, 58.62; H, 5.78; N, 8.04. Found: C, 58.72; H, 5.74; N, 8.01.

Synthesis of the 3,5-Dinitrobenzoate 8. To a stirred solution of the hydroxy derivative **6** (50 mg, 0.324 mmol) in CH_2Cl_2 (5.0 mL) was added Et_3N (135 μL, 0.972 mmol), DMAP (20 mg, 0.162 mmol), and 3,5-dinitrobenzoyl chloride (112 mg, 0.486 mmol) at 0 °C. After being stirred for 1.5 h, the reaction mixture was treated with aqueous $NaHCO_3$ (10 mL) solution and extracted with AcOEt (10 mL × 3). The organic extracts were washed with brine, dried (Na_2SO_4), and evaporated. Purification of the resulting residue, by flash chromatography (SiO_2, AcOEt–hexane, 1:50), gave the 3,5-dinitrobenzoate derivative **8** (93 mg, 83%) as yellow crystals.

The analytical and spectral data for **8** were as follows: mp 88–89 °C; IR (KBr) υ 3108, 2963, 1721, 1545, 1345, 1287 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.99 (dd, J = 6.6, 2.0 Hz, 6H), 1.04 (d, J = 6.3 Hz, 3H), 2.03–2.46 (m, 6H), 5.41 (dt, J = 2.0, 4.6 Hz, 1H), 5.48 (m, 1H), 9.12 (d, J = 2.3 Hz, 2H), 9.22 (t, J = 2.3 Hz, 1H); MS m/z 195 ($M^+ - C_7H_3N_2O_5$). Anal. Calcd for $C_{17}H_{20}N_2O_8$: C, 58.62; H, 5.78; N, 8.04. Found: C, 58.46; H, 5.64; N, 8.06.

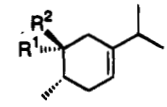
Determination of the Absolute Configuration of the Hydroxy Derivatives 5 and 6. Synthesis of (*R*)- and (*S*)-MTPA Esters of 5 and 6. To a stirred solution of hydroxy derivative **5** (10 mg, 0.065 mmol) in THF (0.5 mL) was added DCC (27 mg, 0.13 mmol), DMAP (2.6 mg, 0.021 mmol) and (*R*)-MTPA (15 mg, 0.065 mmol) at room temperature. After being stirred for 1 h, the reaction mixture was filtered over Celite and the organic layer was evaporated. The residue was purified by flash chromatography (SiO_2, AcOEt–hexane, 1:80) to give the (*R*)-MTPA ester **14** (22.7 mg, 94%). The other corresponding MTPA esters were also synthesized based on above procedure.

The spectral data for the (*R*)-MTPA ester **14** were as follows: ^1H-NMR ($CDCl_3$) δ 0.83 (d, J = 6.6 Hz, 3H), 0.99 (d, J = 6.6 Hz, 6H), 1.74–1.96 (m, 3H), 2.08–2.27 (m, 2H), 2.44 (dd, J = 5.5, 17.0 Hz, 1H), 3.58 (d, J = 1.2 Hz, 3H), 4.98 (m, 1H), 5.34 (m, 1H), 7.38–7.42 (m, 3H), 7.51–7.57 (m, 2H).

The spectral data for the (*S*)-MTPA ester **15** were as follows: ^1H-NMR ($CDCl_3$) δ 0.95 (d, J = 6.6 Hz, 6H), 0.97 (d, J = 6.3 Hz, 3H), 1.70–2.04 (m, 3H), 2.10–2.29 (m, 2H), 2.42 (dd, J = 5.5, 17.0 Hz, 1H), 3.55 (d, J = 1.3 Hz, 3H), 4.95 (m, 1H), 5.32 (m, 1H), 7.38–7.42 (m, 3H), 7.52–7.57 (m, 2H).

The spectral data for the (*R*)-MTPA ester **16** were as follows: ^1H-NMR ($CDCl_3$) δ 0.92 (dd, J = 6.6, 1.6 Hz, 6H), 0.95 (d, J = 6.6 Hz, 3H), 1.80–2.01 (m, 2H), 2.06–2.17 (m, 2H), 2.22–2.35 (m, 2H), 3.51 (d, J = 1.2 Hz, 3H), 5.27 (m, 1H), 5.36 (m, 1H), 7.38–7.42 (m, 3H), 7.51–7.55 (m, 2H).

The spectral data for the (*S*)-MTPA ester **17** were as follows: ^1H-NMR ($CDCl_3$) δ 0.86 (d, J = 6.6 Hz, 3H), 0.99 (dd, J = 6.9, 1.7 Hz, 6H), 1.81–2.00 (m, 2H), 2.08–2.27 (m, 2H), 2.33 (m, 2H), 3.55 (d, J = 1.3 Hz, 3H), 5.27 (m, 1H), 5.44 (m, 1H), 7.32–7.42 (m, 3H), 7.52–7.56 (m, 2H).



δ	methyl	isopropyl
14	0.83	0.99
15	0.97	0.95
Δδ	+0.14 (Δδ > 0)	- 0.04 (Δδ < 0)

14. R^1 = H, R^2 = O-(*R*)-MTPA
15. R^1 = H, R^2 = O-(*S*)-MTPA
16. R^1 = O-(*R*)-MTPA, R^2 = H
17. R^1 = O-(*S*)-MTPA, R^2 = H

δ	methyl	isopropyl
16	0.95	0.92
17	0.86	0.99
Δδ	- 0.09 (Δδ < 0)	+ 0.07 (Δδ > 0)

These NMR spectra confirmed the absolute configuration.[7]

Supplementary Material Available: Proton and ^{13}C NMR spectra of the compounds **4–8** and **14–17** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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