JOC*Note*

Radical-Mediated Opening of 2,3-Epoxy Alcohols Using Cp_2TiCl: Stereoselective Construction of Quaternary Chiral Centers†

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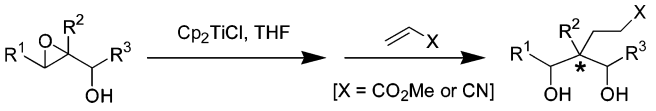
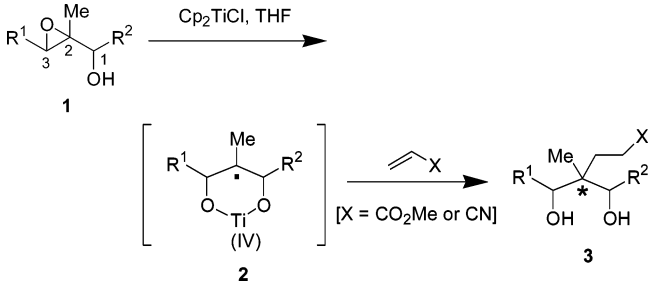


Radical-mediated opening of chiral 2,3-epoxy alcohols regioselectively at the 2-position using Cp_2TiCl and trapping the intermediate radical with methyl acrylate and acrylonitrile led to the stereoselective formation of tetrasubstituted chiral centers.

There have been many reports in recent years on the radical-mediated opening of epoxides using Ti(III) reagents and its application in the synthesis of many natural products.[1,2] The reaction that was reported in 1988[3] was extended later to various 2,3-epoxy alcohols that led to the development of a facile method for the synthesis of chiral allylic alcohols.[4] Interestingly, when the same reaction was carried out by us for an extended period of time, a different class of products, namely, chiral 1,3-diols, were obtained from both di- and trisubstituted 2,3-epoxy alcohols.[5] This was successfully employed by us to construct the 1,3-diol moieties of many polyketide natural products.[6] The fact that even in this radical-induced epoxide ring-opening reaction of the trisubstituted 2,3-epoxy alcohols excellent diastereoselectivity was observed in the hydrogen abstraction step, resulting in the chiral induction in the 2-position, prompted us to investigate the stereoselection in the quenching of the intermediate radicals with other trapping agents. In this note, we report that during the opening of trisubstituted epoxy alcohols **1** the radical intermediates **2** could be successfully trapped using methyl acrylate or acrylonitrile to prepare 1,3-diols **3** with chiral quaternary carbon centers in the 2-position stereoselectively, especially with 1,3-syn diols and in good yields (Scheme 1). With 1,3-anti diols, the major product had a syn relationship between the 2-methyl and the adjacent hydroxyl group, which carried the smaller substituent. This is in accordance with what we have seen earlier during the hydrogen abstraction process where syn,syn product was formed almost exclusively from 1,3-syn diols and syn,anti (or anti,syn) was formed from 1,3-anti diols, depending on the sizes of the substituents R^1 and R^2.[5]

SCHEME 1



The details of the process are outlined in Scheme 2. A syn epoxy alcohol **4**[5] on ring opening with $Cp_2Ti(III)Cl$, generated in situ from Cp_2TiCl_2 following the reported procedure,[5] gave a radical intermediate that was trapped with methyl acrylate to furnish a mixture of lactones **5** and **6** in a 2:1 ratio (determined from the ^1H NMR spectrum of the mixture) in 75% yield. Reduction of the mixture with lithium aluminum hydride (LAH) furnished a triol intermediate as a single isomer, which was converted to the acetonide **7** in 80% yield. The ^{13}C NMR spectrum of **7** showed the gem dimethyls of the acetonide unit

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(1) For a recent review, see: Barrero, A. F.; Quílez del Moral, J.; Sánchez, E. M.; Arteaga, J. F. *Eur. J. Org. Chem.* **2006**, 1627−1641.

(2) For some recent works, see: (a) Barrero, A. F.; Quílez del Moral, J. F.; Sánchez, E. M.; Arteaga, J. F. *Org. Lett.* **2006**, *8*, 669−672. (b) Banerjee, B.; Roy, S. C. *Eur. J. Org. Chem.* **2006**, 489−497. (c) Justicia, J.; Oller-López, J. L.; Campaña, A. G.; Oltra, J. E.; Cuerva, J. M.; Buñuel, E.; Cárdenas, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 14911−14921. (d) Justicia, J.; Oltra, J. E.; Cuerva, J. M. *J. Org. Chem.* **2005**, *70*, 8265−8272. (e) Jana, S.; Guin, C.; Roy, S. C. *J. Org. Chem.* **2005**, *70*, 8252−8254. (f) Nishiguchi, G. A.; Little, R. D. *J. Org. Chem.* **2005**, *70*, 5249−5256. (g) Justicia, J.; Oltra, J. E.; Barrero, A. F.; Guadaño, A.; González-Coloma, A.; Cuerva, J. M. *Eur. J. Org. Chem.* **2005**, 712−718. (h) Gansäuer, A.; Rinker, B.; Ndene-Schiffer, N.; Pierobon, M.; Grimme, S.; Gerenkamp, M.; Mück-Lichtenfeld, C. *Eur. J. Org. Chem.* **2004**, 2337−2351. (i) Fernández-Mateos, A.; Burón, L. M.; Martín de la Nava, E. M.; Clemente, R. R.; González, R. R.; González, F. S. *Synlett* **2004**, 2553−2557. (j) Bermejo, F.; Sandoval, C. *J. Org. Chem.* **2004**, *69*, 5275−5280. (k) Barrero, A. F.; Rosales, A.; Cuerva, J. M.; Oltra, J. E. *Org. Lett.* **2003**, *5*, 1935−1938. (l) Gansäuer, A.; Pierobon, M.; Bluhm, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3206−3208. (m) Gansäuer, A.; Rinker, B. *Tetrahedron* **2002**, *58*, 7017−7026. (n) Parrish, J. D.; Little, R. D. *Org. Lett.* **2002**, *4*, 1439−1442. (o) Roy, S. C.; Rana, K. K.; Guin, C. *J. Org. Chem.* **2002**, *67*, 3242−3248. (p) Barrero, A. F.; Oltra, J. E.; Cuerva, J. M.; Rosales, A. *J. Org. Chem.* **2002**, *67*, 2566−2571. (q) Barrero, A. F.; Cuerva, J. M.; Alvarez-Manzaneda, E. J.; Oltra, J. E.; Chahboun, R. *Tetrahedron Lett.* **2002**, *43*, 2793−2796. (r) Joubert, B. M.; Buckner, F. S.; Matsuda, S. P. T. *Org. Lett.* **2001**, *3*, 1957−1960. (s) Yang, D.; Xu, M. *Org. Lett.* **2001**, *3*, 1785−1788. (t) Barrero, A. F.; Cuerva, J. M.; Herrador, M. M.; Valdivia, M. V. *J. Org. Chem.* **2001**, *66*, 4074−4078. (u) Hardouin, C.; Chevallier, F.; Rousseau, B.; Doris, E. *J. Org. Chem.* **2001**, *66*, 1046−1048. (v) Gansäuer, A.; Bluhm, H.; Pierobon, M. *J. Am. Chem. Soc.* **1998**, *120*, 12849−12859. (w) Gansäuer, A.; Pierobon, M.; Bluhm, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 101−103.

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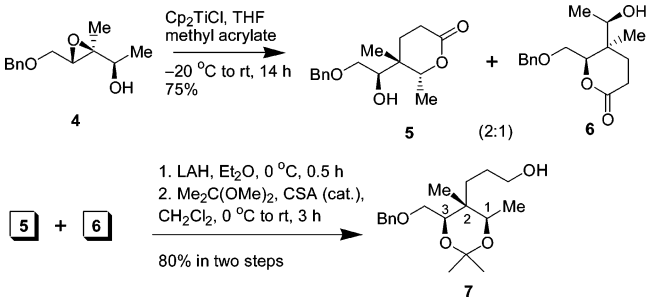
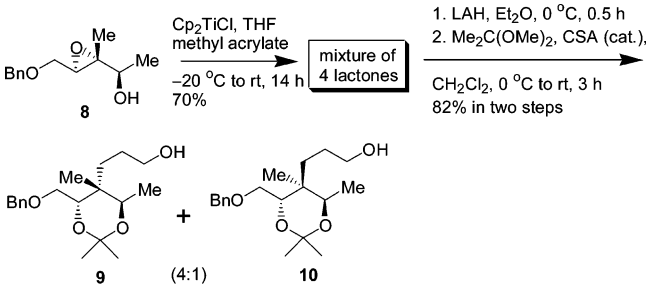
SCHEME 2



SCHEME 3

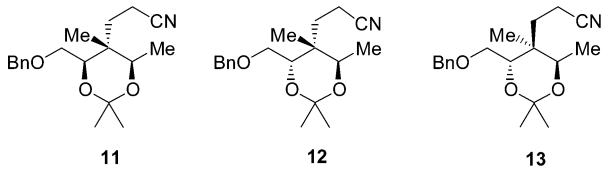


at 30.0 and 19.6 ppm and the ketal carbon at 98.4 ppm, proving the syn relationship between C_1-OH and C_3-OH.[7]

The stereochemistry of the tetrasubstituted C-2 position was determined by ^1H NOE difference spectroscopic studies. While irradiation of the C1−C*H*$_3$ signal of compound **7** at δ 1.04 enhanced the peak of the C2−C*H*$_3$ singlet at δ 0.85, irradiation of the C2−C*H*$_3$ peak showed NOEs of C1−C*H*$_3$ and C4−*H* (3.62 ppm) and C4−*H*′ (3.36 ppm) resonances. Thus, the radical intermediate formed during the ring opening of **4** was quenched exclusively from the same side as that observed earlier with hydrogen abstraction.[5,6d]

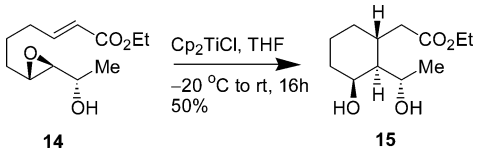
In contrast, the anti epoxy alcohol **8**[5] on ring opening with $Cp_2Ti(III)Cl$ and quenching the radical intermediate with methyl acrylate, following the same method as that described for **4**, furnished a mixture of four lactones (Scheme 3) that was reduced directly without separation using LAH to give a mixture of two triols in a 4:1 ratio, determined from the ^1H NMR spectrum of the mixture. The mixture, which could not be separated at the triol stage, remained inseparable even after it was transformed into its acetonides, **9** and **10**. Determination of the stereochemistry of the tetrasubstituted C-2 position from the ^1H NMR spectrum of the mixture of acetonides, **9** and **10**, or from ^1H NOE difference spectroscopic studies was difficult because of their twist-boat conformation. However, on the basis of our earlier studies on proton abstraction products,[5,6d] the major product in this case was assigned to the structure **9** with C1−OH and C2−CH_3 having a syn relationship and the minor product probably having them in the anti orientation as in **10**.

As expected, quenching of the radical intermediate obtained from **4** with acrylonitrile gave only one isomer that was transformed into the acetonide **11** in 40% overall yield from **4**, presumably with the same stereochemistry as that in **7**. The anti epoxy alcohol **8**, on the other hand, led to a mixture of two products **12** and **13** in a ∼2:1 ratio and in 45% overall yield, with the major one probably having the same stereochemistry as that in **9**.

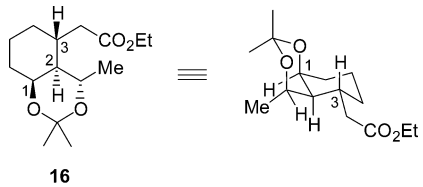


With disubstituted 2,3-epoxy alcohols, both syn and anti, no diastereoselectivity was observed during the radical quenching step, with either methyl acrylate or acrylonitrile. However, an intramolecular version of this reaction with disubstituted anti epoxy alcohol **14**[8] was successfully carried out with good selectivity as shown in Scheme 4. Compound **14** on ring opening with $Cp_2Ti(III)Cl$ gave a radical intermediate that underwent a facile ring-closing reaction to furnish the six-membered cyclic compound **15** as the major product in 50% isolated yield, along with some other unidentified minor compounds.

SCHEME 4



The stereochemistry of **15** was determined from the ^3J values of C1−*H*, which did not show any large coupling with any of its vicinal protons suggesting that its equatorial orientation was in a chair-type conformation. Furthermore, diol **15** was converted into an acetonide **16** to assign the stereochemistries of the C2 and C3 centers. While C1−*H* in **16** appeared as a quartet with ∼3 Hz coupling confirming its equatorial position, the O−C*H*−Me showed a dq with ∼6 Hz couplings with both methyl protons and C2−*H*. That the C2 center has *S* stereochemistry can be concluded from the fact that diol **15** could be easily converted into the acetonide **16**, which otherwise would have been difficult to make. Finally, an equatorial orientation of the C3 substituent is possibly more stable than an axial one. The latter orientation would be expected to give rise to a lactone during the formation of **15**. That there was no lactone formed in the reaction provides additional support in favor of the proposed *R* stereochemistry for the C3 carbon.



The method developed here can be extended to the synthesis of quaternary chiral centers present in many natural products[9] as well as to the stereoselective synthesis of many substituted cyclohexane ring-containing compounds.

Experimental Section

General Procedure for the Epoxide Opening. To a suspension of Cp_2TiCl_2 (841 mg, 3.38 mmol) in dry THF (13 mL) at room temperature were added sequentially freshly fused $ZnCl_2$ (457 mg,

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(8) Synthesis of the epoxy alcohol **14** is described in the Supporting Information.

(9) Trost, B. M.; Jiang, C. *Synthesis* **2006**, 369−396.

3.38 mmol) and Zn powder (442 mg, 6.76 mmol) with stirring under a nitrogen atmosphere. After stirring for 0.5 h, the reaction mixture developed a dark green color and was cooled to −20 °C. Then, epoxy alcohol (1.13 mmol), dissolved in dry THF (4 mL), was added to the reaction mixture followed by the addition of the dry and freshly distilled radical quencher (20 equiv of the epoxy alcohol) at the same temperature. The reaction was continued at −20 °C for 2 h, allowed to warm slowly to room temperature, and stirred for 14 h. It was then quenched with 1 N HCl (10 mL) and extracted with diethyl ether. The combined organic extracts were washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography to furnish the pure products, which were characterized by standard spectroscopic methods.

Synthesis of 5 and 6. According to the general procedure of epoxide opening described above, compound **4**, using methyl acrylate as a radical quencher, gave an inseparable mixture of lactones **5** and **6** (in 2:1 ratio) in 75% yield. R_f = 0.4 (silica gel, 50% EtOAc in hexane). IR (KBr): ν_{max} 3447 (b), 2922, 1722, 1635, 1379, 1215 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, major product **5**): δ 7.38−7.23 (m, 5H), 4.55 (ABq, 2H), 4.37 (q, J = 6.7 Hz), 3.71 (dd, J = 9.1, 2.3 Hz, 1H), 3.57 (dd, J = 9.1, 2.3 Hz, 1H), 3.36 (t, J = 9.1 Hz, 1H), 2.51−2.42 (m, 2H), 1.97−1.82 and 1.52−1.41 (two m, 2H), 1.39 (d, J = 6.7 Hz, 3H), 1.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, mixture of **5** and **6**): δ 171.4, 171.1, 137.5, 137.4, 128.5, 127.9, 127.7, 85.06, 82.3, 74.0, 73.5, 73.0, 70.7, 70.4, 69.2, 29.6, 28.2, 26.5, 26.3, 25.7, 18.5, 17.6, 16.7, 16.4. MS (ESI): *m*/*z* (%) 279 (10) $[M + H]^+$, 296 (100) $[M + NH_4]^+$, 301 (60) $[M + Na]^+$. HRMS (ESI): calcd for $C_{16}H_{23}O_4$ $[M + H]^+$, 279.1596; found, 279.1600.

Synthesis of Acetonide 7. The mixture of lactones **5** and **6** (200 mg, 0.72 mmol) was taken in dry Et_2O (4 mL). It was cooled to 0 °C. Then, lithium aluminum hydride (54.6 mg, 1.44 mmol) was added and stirred for 0.5 h at 0 °C. The reaction was quenched carefully with saturated Na_2SO_4 solution (2 mL) at 0 °C and extracted with EtOAc. The combined organic layer was washed with H_2O and brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, 90% EtOAc in hexane as eluant) to afford the triol as a colorless oil, which was used directly in the next step.

The triol was dissolved in dry CH_2Cl_2 (3 mL) and cooled to 0 °C. Then, 2,2-dimethoxypropane (0.35 mL, 2.9 mmol) was added to it followed by (±)-camphor-10-sulfonic acid (16.7 mg, 0.07 mmol). The reaction was allowed to come to room temperature and was stirred for 3 h. Then, it was cooled to 0 °C, quenched with saturated $NaHCO_3$ solution, and extracted with EtOAc. The combined organic extracts were washed with H_2O and brine, dried (Na_2SO_4), and concentrated in vacuo. Chromatographic purification (SiO_2, 20% EtOAc in hexane as eluant) afforded pure **7** (162 mg, 80% from **5** and **6**) as a colorless oil. R_f = 0.4 (silica gel, 30% EtOAc in hexane). IR (KBr): ν_{max} 3445, 2987, 2925, 2857, 1632, 1457 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38−7.24 (m, 5H), 4.54 (ABq, 2H), 4.04 (dd, J = 6.0, 3.8 Hz, 1H), 3.93 (q, J = 6.3 Hz, 1H), 3.62 (dd, J = 10.6, 3.8 Hz, 1H), 3.53−3.43 (m, 2H), 3.36 (dd, J = 10.6, 6.0 Hz, 1H), 1.66−1.22 (m, 2H), 1.45 (s, 3H), 1.37 (s, 3H), 1.04 (d, J = 6.3 Hz, 3H), 0.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.4, 128.3, 127.8, 127.6, 98.4, 74.5, 73.2, 70.2, 70.0, 63.2, 37.2, 30.8, 30.0, 26.1, 19.6, 14.5, 13.5. MS (ESI): *m*/*z* (%) 323 (20) $[M + H]^+$, 340 (100) $[M + NH_4]^+$, 345 (10) $[M + Na]^+$. HRMS (ESI): calcd for $C_{19}H_{30}O_4Na$ $[M + Na]^+$, 345.2041; found, 345.2047.

Synthesis of Acetonides 9 and 10. The mixture of four lactones obtained from **8** using methyl acrylate as the radical quencher following the general procedure of epoxide opening described above was converted to an inseparable mixture of acetonides **9** and **10**, using the same protocol as that used for the synthesis of **7**, in a 4:1 ratio and in 82% yield. R_f = 0.4 (silica gel, 30% EtOAc in hexane). IR (KBr): ν_{max} 3453 (b), 2929, 1636, 1456, 1378, 1227, 1108 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, major isomer **9**): δ 7.34−7.18 (m, 5H), 4.53 (ABq, 2H), 3.81 (dd, J = 7.5, 3.4 Hz, 1H), 3.66−3.34 (m, 5H), 1.8−1.4 (m, 4H), 1.37 (s, 3H), 1.32 (s, 3H), 1.06 (d, J = 6.7 Hz, 3H), 0.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, major isomer **9**): δ 138.5, 128.2, 127.5, 127.4, 100.8, 73.5, 73.2, 72.0, 70.1, 63.7, 40.7, 30.0, 27.6, 24.3, 24.0, 17.3, 14.4. MS (LCMS): *m*/*z* (%) 345 (70) $[M + Na]^+$. HRMS (ESI): calcd for $C_{19}H_{30}O_4Na$ $[M + Na]^+$, 345.2041; found, 345.2035.

Synthesis of Acetonide 11. Ring opening of **4** using acrylonitrile as the radical quencher gave an intermediate diol as a single isomer, which was transformed into acetonide **11** following the same procedure as that used in the synthesis of **7** in 40% overall yield from **4**. R_f = 0.6 (silica gel, 20% EtOAc in hexane). IR (KBr): ν_{max} 2925, 2861, 2247, 1105 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.4−7.24 (m, 5H), 4.49 (ABq, 2H), 3.98−3.84 (m, 1H), 3.91 (q, J = 6.2 Hz, 1H), 3.55 (dd, J = 10.2, 6.1 Hz, 1H), 3.33 (dd, J = 10.2, 4.2 Hz, 1H), 2.48−2.16 (m, 2H), 1.90−1.56 (m, 2H), 1.43 (s, 3H), 1.34 (s, 3H), 1.05 (d, J = 6.2 Hz, 3H), 0.84 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.8, 128.5, 127.9, 127.7, 119.6, 98.6, 73.6, 70.2, 69.9, 37.7, 30.3, 29.8, 29.6, 19.5, 14.7, 12.7, 11.8. MS (ESI): *m*/*z* (%) 318 (10) $[M + H]^+$, 335 (100) $[M + NH_4]^+$. HRMS (ESI): calcd for $C_{19}H_{28}NO_3$ $[M + H]^+$, 318.2069; found, 318.2063.

Synthesis of Acetonides 12 and 13. Acetonides **12** and **13** were prepared as an inseparable mixture of diastereomers in a 2:1 ratio and in 45% overall yield from **8** using acrylonitrile as the radical quencher in the same way as that used for the synthesis of **11**. R_f = 0.6 (silica gel, 20% EtOAc in hexane). IR (KBr): ν_{max} 2984, 2933, 2246, 1381, 1225, 1105 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, mixture of **12** and **13**): δ 7.40−7.24 (m, 5H), 4.64−4.40 (m, 2H), 3.78−3.40 (m, 4H), 2.52−2.32 (m, 2H), 1.82−1.60 (m, 2H), 1.33 and 1.30 (two s, total 9H), 1.07 (two d, J = 6.1 Hz, total 3H), 0.87 and 0.79 (two s, total 3H). ^{13}C NMR (75 MHz, $CDCl_3$, mixture of **12** and **13**): δ 137.9, 137.7, 128.4, 127.8, 127.76, 127.73, 127.6, 127.6, 120.1, 101.2, 101.1, 74.9, 73.5, 71.7, 71.4, 69.6, 68.9, 68.8, 41.4, 41.1, 30.1, 29.8, 29.6, 24.1, 24.0, 23.94, 23.90, 17.5, 17.3, 15.6, 14.3, 12.8, 12.6. MS (LCMS): *m*/*z* (%) 318 (60) $[M + H]^+$. HRMS (ESI): calcd for $C_{19}H_{28}NO_3$ $[M + H]^+$, 318.2069; found, 318.2060.

Synthesis of 15. Activated Zn powder (863 mg, 13.2 mmol), freshly fused $ZnCl_2$ (894 mg, 6.6 mmol). and Cp_2TiCl_2 (1.6 g, 6.6 mmol) were taken in dry THF (65 mL) and stirred for 0.5 h at room temperature. The color of the reaction mixture turned into deep green. Then, it was cooled to −20 °C and compound **14** (500 mg, 2.2 mmol) in dry THF (10 mL) was added. The reaction mixture was allowed to come to room temperature slowly. Then, it was stirred for 15 h. The reaction was quenched with 1 N HCl and extracted with Et_2O. The combined organic layer was washed with H_2O and brine, dried (Na_2SO_4), and concentrated in vacuo. Purification by column chromatography (SiO_2, 26% EtOAc in hexane eluant) provided the 1,3-diol **15** as a pure colorless oil (252 mg, 50% yield). R_f = 0.65 (silica gel, 50% EtOAc in hexane). $[\alpha]^{27}_D$ = −7.54 (*c* 0.5 in $CHCl_3$). IR (KBr): ν_{max} 3387, 2229, 2857, 1731 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.40−4.34 (m, 1H), 4.15 (q, J = 7.1 Hz, 2H), 4.02−3.88 (m, 1H), 3.86−3.72 (bs, 2H), 2.54−2.22 (m, 3H), 1.92−1.66 (m, 3H), 1.54−1.38 (m, 1H), 1.32−1.05 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.27 (d, J = 6.7 Hz, 3H), 0.99−0.87 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.0, 67.4, 66.3, 60.9, 50.9, 39.5, 33.6, 32.8, 29.1, 20.2, 19.9, 14.1. MS (ESI): *m*/*z* (%) 231 (100) $[M + H]^+$, 253 (10) $[M + Na]^+$. HRMS (ESI): calcd for $C_{12}H_{23}O_4$ $[M + H]^+$, 231.1596; found, 231.1603.

Synthesis of 16. Diol **15** (200 mg, 0.87 mmol) was dissolved in dry CH_2Cl_2 (4 mL) and cooled to 0 °C. 2,2-Dimethoxypropane (0.43 mL, 3.48 mmol) was added to it, followed by the addition of (±)-camphor-10-sulfonic acid (21 mg, 0.09 mmol). The reaction was allowed to come to room temperature slowly and was stirred for 1 h. Then, it was cooled to 0 °C, quenched with saturated $NaHCO_3$ solution, and extracted with EtOAc. The combined organic extracts were washed with H_2O and brine, dried (Na_2SO_4), and concentrated

in vacuo. Chromatographic purification (SiO_2, 10% EtOAc in hexane) afforded pure **16** (188 mg, 80%). $R_f = 0.6$ (silica gel, 15% EtOAc in hexane). IR (KBr): ν_{max} 2983, 2934, 1736, 1375, 1230 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 4.13 (q, $J = 7.1$ Hz, 2H), 4.04−3.96 (m, 1H), 3.74−3.59 (dq, $J = 6.0$ Hz, 1H), 2.35 (dd, $J = 3.0$, 13.4 Hz, 1H), 2.2−1.8 (m, 2H), 1.76−1.42 (m, 3H), 1.37 (s, 3H), 1.32 (s, 3H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.24 (d, $J = 6.0$ Hz, 3H), 1.20−1.10 (m, 2H), 1.04−0.82 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.7, 100.1, 69.1, 63.8, 60.2, 48.5, 39.2, 34.9, 30.9, 29.9, 26.6, 24.1, 23.4, 20.0, 14.2. MS (ESI): *m*/*z* (%) 271 (10) $[M + H]^+$. HRMS (ESI): calcd for $C_{15}H_{26}O_4Na$ $[M + Na]^+$, 293.1728; found, 293.1733.

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Supporting Information Available: General experimental procedures, complete experimental details for the synthesis of **14**, and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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