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Asymmetric synthesis of 6-formyl-1-alkoxycarbonylbicyclo[3.1.0]hex-2-ene-2-carboxylic acids by a novel buffer-mediated rearrangement

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Abstract—Asymmetric synthesis of 6-formyl-1-alkoxycarbonylbicyclo[3.1.0]hex-2-ene-2-carboxylic acids has been achieved and the absolute configurations of the products of a novel buffer-mediated rearrangement have been established.

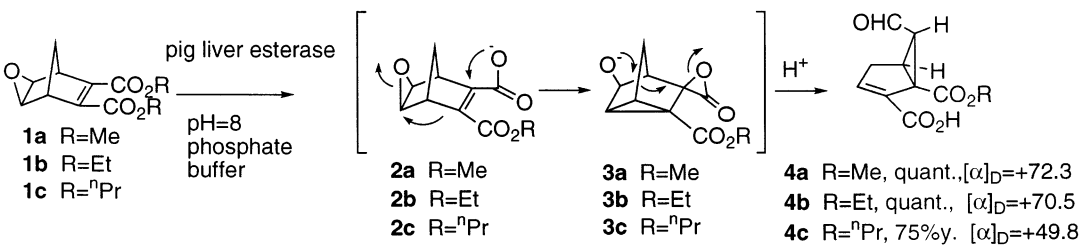
1. Introduction

Enzymatic reactions have been proficient tools for the development of elegant asymmetric syntheses of many important classes of natural products and pharmaceuticals.[1] In particular, enzymatic monohydrolysis of *meso* diesters is a versatile enantioselective reaction, as it enables unique regiospecific conversions at later steps.

Many enzymatic reactions applied in organic synthesis induce only simple chemoselective conversion of a limited number of functional groups. However, we discovered the first chemoenzymatic rearrangement which undergoes complete skeletal conversion to produce the enantiomerically enriched monoesters, 6-formyl-1-(alkoxycarbonyl)bicyclo-[3.1.0]hex-2-ene-2-carboxylic acids, **4a**–**4c**, during the asymmetric enzymatic monohydrolysis of the dialkyl 5,6-epoxybicyclo[2.2.1]hept-2-ene-2,3-dicarboxylates, **1a**–**1c**, applying pig liver esterase (PLE).[2–5] The structures of the rearranged products have been confirmed based on their ^{1}H, ^{13}C NMR and IR spectroscopic data, as well as by X-ray crystallographic analysis of an acetal derivative of rearranged product **4a** (Scheme 1).[5]

The preparation of the core structure in these rearranged products, bicyclo[3.1.0]hex-2-ene-*endo*-carboaldehyde, **8**, by peracid oxidation of norbornadiene was reported by Meinwald et al. earlier (Scheme 2).[6,7]

This rearranged compound, **8**, has been known to be a useful synthetic building block which produces an important class of bioactive molecules such as nucleoside analogues[8] or reactive species for further skeletal conversions for production of prostaglandin derivatives.[9] Therefore, similar synthetic versatility is expected for the rearranged products **4a**–**4c**. Moreover, the advantage of our chemoenzymatic rearrangement is that it can introduce optical activity by enzymatic asymmetric monohydrolysis. However, the absolute



Scheme 1.

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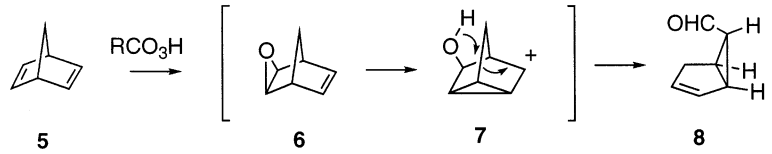


Scheme 2.

configurations of the predominant enantiomers of the rearranged products after the enzymatic hydrolysis remained unknown. Establishing the absolute configurations is expected to be essential for further synthetic development in the application of these rearranged products.

Herein, we report the asymmetric synthesis of optically pure 6-formyl-1-(alkoxycarbonyl)bicyclo-[3.1.0]hex-2-ene-2-carboxylic acids, **4a′**–**4c′**, starting from a naturally available D-mannitol derivative. Based on these absolute configurations, we have determined the absolute configurations of 6-formyl-1-(alkoxycarbonyl)bicyclo-[3.1.0]hex-2-ene-2-carboxylic acids, **4a**–**4c**, which were obtained by the novel chemoenzymatic rearrangement initiated by PLE monohydrolysis of the *meso* epoxy diesters dialkyl 5,6-epoxybicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate. This is an indispensable start for synthetic development of this asymmetric rearrangement.

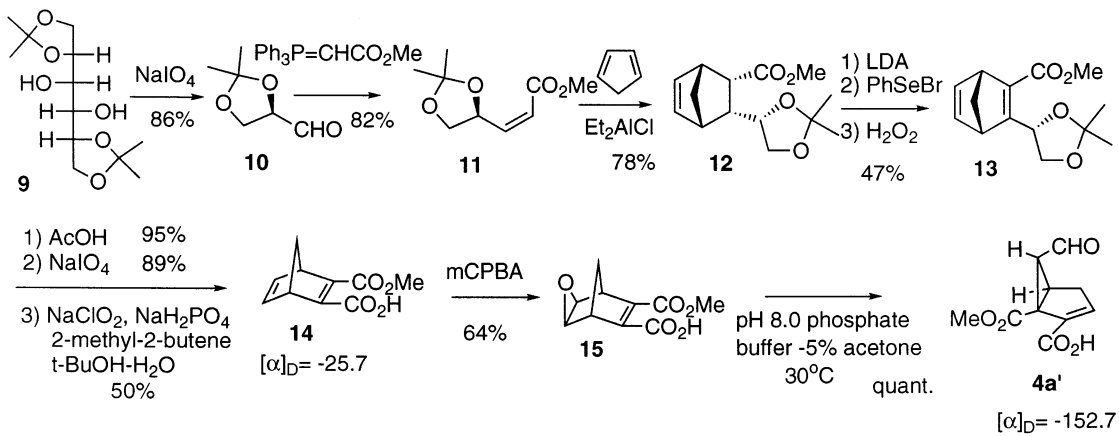
2. Results and discussion

From earlier studies, we know that this rearrangement is mediated by a buffer medium after enzymatic asymmetric desymmetrization.[10] Therefore, our synthesis was focused on asymmetric synthesis of half-esters **2a**–**2c** starting from a natural chiral auxiliary. Since the signs of specific rotations were all positive for **4a**–**4c**, the determination of the absolute configuration of the predominant enantiomers was accomplished by referring to the signs of the optical rotation of the authentic rearrangement products under the same conditions.

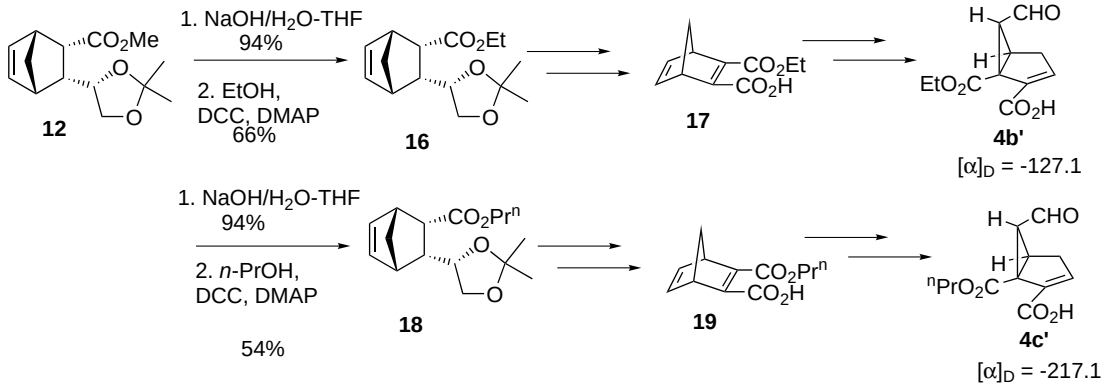
Our synthesis started with a D-mannitol derivative as a chiral precursor. As reported by Mann et al.,[11] commercially available 1,2:5,6-di-*O*-isopropylidene-D-mannitol, **9**, was submitted to oxidative cleavage with sodium periodate to produce aldehyde **10**, in 86% yield, which was reacted with a Wittig reagent to give olefin **11** in 82% yield.[11] Subsequently, following Ortuño's method, **11** was reacted with excess cyclopentadiene in the presence of a Lewis acid (Et_2AlCl), which afforded the corresponding Diels–Alder adduct, **12**, in 78% yield with high stereoselectivity.[12,13] The Diels–Alder adduct, **12**, was treated with LDA, and the resultant lithium enolate was reacted with PhSeBr to afford the mixture of epimers, which was subsequently treated with hydrogen peroxide and glacial acetic acid to give the corresponding α,β-unsaturated ester, **13**, in 47% yield over three steps. Deprotection of the isopropylidene group of **13** with 90% acetic acid at room temperature for 2 days afforded the corresponding diol in 95% yield. This diol was submitted to oxidative cleavage with aqueous sodium periodate to afford the corresponding aldehyde in 89% yield, which was then oxidized to afford carboxylic acid **14** in 50% yield.

The more electron-rich C_5–C_6 olefinic bond in **14** was epoxidized with *m*-CPBA in diluted CH_2Cl_2 solution at room temperature for 2 days, and afforded enantiomerically pure 5,6-*exo*-epoxy-3-(methoxycarbonyl)bicyclo-[2.2.1]hept-2-ene-2-carboxylic acid, **15**, in 64% yield (Scheme 3).

This enantiomerically pure monoester was dissolved in pH 8 phosphate buffer containing 5% acetone, and the mixture was incubated at 37°C for 4 h. Usual work-up afforded the rearranged product, **4a′**, in a quantitative yield [with the specific rotation $[\alpha]_D = -152.7$ ($c = 0.74$ MeOH)] in 100% e.e. Based on these data, the absolute configuration of the predominant enantiomer of the rearranged product **4a** formed by the PLE chemoenzy-



Scheme 3.



Scheme 4.

matic rearrangement was determined to be opposite from the rearranged product produced by our asymmetric synthesis, as depicted in Scheme 1.

In addition, the corresponding ethyl ester and *n*-propyl ester were prepared by changing the ester group in **12**, as in Scheme 4. We found that usual saponification tends to afford an undesirable mixture, but the ester group can be cleanly hydrolyzed to the corresponding carboxylic acid in 94% yield by applying the THF–aqueous NaOH system developed by Niwayama.[14] Then the acid was reacted with ethyl alcohol and *n*-propyl alcohol in the presence of an equivalent of DCC and a catalytic amount of *N*,*N*-DMAP to produce the corresponding ethyl and *n*-propyl ester. The corresponding ethyl and *n*-propyl esters, **4b**′ and **4c**′, were both prepared successfully following the same procedure.

In conclusion, we have established the absolute configuration of the rearranged products, **4a**–**4c**, obtained by enzymatic asymmetric desymmetrization of symmetric **1a**–**1c**. These rearranged products, which can be obtained easily by one-pot enzymatic monohydrolysis of **1a**–**1c**, are expected to be useful chiral building blocks. We are currently investigating improvement of the enantiomeric purities of the products from the chemoenzymatic rearrangement and the results will be reported in due course.

3. Experimental

3.1. General procedures

Melting points are uncorrected. ^{1}H NMR at 300 MHz and ^{13}C NMR at 75 MHz spectra were measured as solutions in $CDCl_3$ using TMS as an internal standard. The IR spectra were recorded on an FTIR instrument. Optical rotations were measured with a Perkin–Elmer 241 polarimeter.

3.2. Synthesis of 13

Compound **12** was prepared according to the reported procedures.[11–13]

A solution of BuLi in hexane (1.6 M, 11.0 mL, 17.0 mmol) was added dropwise to a solution of diisopropylamine (2.38 mL, 17.0 mmol) in anhydrous THF (45 mL), cooled to −78°C under a nitrogen atmosphere, and the mixture was stirred for 30 min, after which a solution of ester **12** (1.6 g, 6.7 mmol) in anhydrous THF (15 mL) was added. After stirring at −78°C for 90 min, a solution of phenylselenyl bromide (4 g, 20.1 mmol) in anhydrous THF (15 mL) was added. The resultant solution was stirred at −78°C for 5 h, the reaction mixture was neutralized with saturated aqueous ammonium chloride, and the organic layers were separated. The organic phase was dried with magnesium sulfate, filtered and the filtrate evaporated in vacuo. The residue was purified by column chromatography (10:1 hexane–ethyl acetate) to afford a mixture of the epimeric selenides. Subsequently, to an ice-cooled solution of the mixture of the epimers in THF (35 mL), 30% hydrogen peroxide (6.0 mL) and glacial acetic acid (0.25 mL) were added, and the resultant solution was stirred for 90 min. The reaction mixture was neutralized with saturated aqueous sodium bicarbonate and extracted with dichloromethane. The organic solvents were removed and the residue was purified by column chromatography (10:1 hexane–ethyl acetate) to afford the conjugated ester **13** (752 mg, 47.4% yield). Colorless oil. $[\alpha]_D^{22} = -80.2$ ($c = 2.2$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 6.7$–6.9 (2H, m), 5.48 (1H, t, $J = 6.9$ Hz), 4.27 (1H, dd, $J = 6.9$, 8.1 Hz), 3.86 (2H, br.s), 3.70 (3H, s), 3.70 (1H, dd, $J = 6.9$, 8.1 Hz) 1.98 (2H, br.s), 1.50 (3H, s), 1.38 (3H, s). ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 169.0$, 165.3, 143.2, 142.2, 141.6, 109.9, 72.2, 71.6, 68.5, 52.5, 51.4, 51.2, 26.3, 25.3. IR (neat, cm^{-1}) 2984, 2942, 2875, 1711, 1635, 1563, 1440, 1244, 1063, 863. HRMS calcd for $C_{14}H_{19}O_4$ $(M+H)^+$: 251.1283. Found 251.1297.

3.3. Synthesis of 14

A solution containing **13** (733 mg, 2.93 mmol) in 90% acetic acid (40 mL) was stirred at rt for 2 days and the reaction mixture was evaporated to dryness. The residue was dissolved in absolute ethanol (10 mL) and the solvent was removed. This process was repeated twice. The crude diol was purified by column chromatography (1:1 hexane–ethyl acetate) to afford a pure

diol (585 mg, 95%). A solution of this diol (572 mg, 2.72 mmol) in THF (15 mL) was added dropwise to a suspension of sodium periodate (1.0 g, 4.7 mmol) in THF (7 mL) and water (3 mL). After additional stirring at rt for 2 h, the precipitated solid was removed by filtration and washed with ether. The solvent was removed and the residue was extracted with dichloromethane. After evaporation, the crude reaction mixture was purified by column chromatography (10:1 hexane–ethyl acetate) to afford aldehyde (432 mg, 89%).

A solution containing sodium chloride (1.4 g, 15.5 mmol) and sodium dihydrogenphosphate (1.46 g, 12.1 mmol) in water (6 mL) was added dropwise to a stirred solution containing the aldehyde obtained above (350 mg, 1.97 mmol) and 2-methyl-2-butene (8.5 mL, 80.2 mmol) in *tert*-butanol (30 mL). The mixture was stirred at rt for 18 h and the volatile components were evaporated. The residue was poured into water and washed with hexane. The aqueous phase was acidified with 10% aqueous HCl and extracted with dichloromethane. The organic extracts were combined and, in turn, extracted with saturated aqueous sodium carbonate. Subsequently, the combined aqueous phases were acidified with HCl and then extracted with dichloromethane. After evaporation of the solvent, the crude residue was purified by column chromatography (1:1 hexane–ethyl acetate) to afford half-ester **14** (190 mg, 50%). White solid (mp 108–109°C). $[\alpha]_D^{22}=-25.7$ ($c=1.9$, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz) $\delta=6.8$–6.9 (2H, m), 4.2 (1H, br.s), 4.1 (1H, br.s), 3.93 (3H, s), 2.21 (1H, dt, $J=7.2$, 1.2 Hz), 2.12 (1H, dt, $J=7.2$, 1.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta=167.84$, 164.00, 162.85, 149.62, 142.64, 141.78, 72.52, 54.78, 53.43, 53.13. IR (neat, cm^{-1}); 3018, 3000–2500, 2946, 2880, 2731, 2660, 1726, 1640, 1563, 1449, 1339, 1301, 882. Anal. calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.71; H, 5.34%.

3.4. Synthesis of 4a′

m-CPBA (80%, 816 mg, 3.78 mmol) was added to a stirred solution of half-ester **14** (170 mg, 0.88 mmol) in dichloromethane (40 mL) at rt and the mixture stirred for 2 days. The mixture was saturated with sodium chloride and extracted with ethyl acetate. After evaporation of the solvent, the crude reaction mixture was purified by column chromatography (2:1 hexane–ethyl acetate, 100:1 ethyl acetate–acetic acid) to afford epoxide **15** (117 mg, 64%).

Epoxide **15** (20 mg, 0.095 mmol) was dissolved in 19 mL of phosphate buffer (pH 8.0) containing 1.0 mL of acetone, and the mixture was incubated at 37°C for 4 h. The reaction mixture was acidified with 2N hydrochloric acid, extracted with ethyl acetate, and then dried over magnesium sulfate. Evaporation under reduced pressure afforded **4a′** in a quantitative yield from **15**. Colorless oil. $[\alpha]_D^{22}=-152.7$ ($c=0.74$, MeOH). ^1H NMR (300 MHz, $CDCl_3$): $\delta=9.39$ (1H, d, $J=3.6$), 6.8 (1H, m), 3.77 (3H, s), 2.9 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=196.77$, 169.59, 167.86, 147.12, 131.86, 52.73, 44.48, 34.78, 34.69, 33.41. IR (neat, cm^{-1}); 3857, 3400–2500, 1711, 1619, 1445, 1264. HRMS calcd for $C_{10}H_{14}O_5N$ $(M+NH_4)^+$: 228.0862. Found 228.0852.

3.5. Synthesis of 16

Ester **12** (2.43 g, 9.64 mmol) was dissolved in THF (19 mL). Water (190 mL) and aqueous NaOH (0.25N, 78 mL) was added. The reaction mixture was stirred at rt for 1 day and the reaction mixture was acidified with 2N aqueous hydrochloric acid, saturated with sodium chloride, extracted with ethyl acetate, and dried with sodium sulfate. After evaporation of the solvent, the crude reaction mixture was purified by column chromatography (2:1 hexane–ethyl acetate) to afford the corresponding acid (2.15 g, 94%). The acid formed above (2.15 g, 9.03 mmol) was added to a solution of DMAP (135 mg, 1.25 mmol) in dichloromethane (40 mL) at rt, and absolute ethanol (1.35 mL, 24 mmol) and DCC (2.1 g, 10 mmol) were added. The reaction mixture was stirred at rt for 3 h. The solid was filtered off and the filtrate was successively washed with water, 5% AcOH, and brine. After evaporation of the solvent, the crude reaction mixture was purified by column chromatography (10:1 hexane–ethyl acetate) to afford ethyl ester **16** (1.58 g, 66%). Colorless oil. ^1H NMR ($CDCl_3$, 300 MHz) $\delta=6.2$–6.3 (2H, m), 3.9–4.2 (2H, m), 3.91 (1H, dd, $J=8.1$, 5.1 Hz), 3.8 (1H, m), 3.63 (1H, dd, $J=8.1$ Hz, $J=5.1$ Hz), 3.05 (2H, br, s), 2.98 (1H, dd, $J=10.0$ Hz, $J=3.0$ Hz), 2.47 (1H, dt, $J=3.0$ Hz, $J=10.0$ Hz), 1.2–1.5 (2H, m), 1.42 (3H, s), 1.26 (3H, s), 1.21 (3H, t, $J=7.2$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta=173.35$, 135.65, 135.29, 108.16, 77.15, 69.31, 60.23, 49.23, 48.55, 47.00, 46.18, 46.15, 27.22, 25.08, 14.14. IR (neat, cm^{-1}) 2984, 2942, 2875, 1735, 1459, 1373, 1153, 1071. HRMS calcd for $C_{15}H_{23}O_4$ $(M+H)^+$: 267.1596. Found 267.1593.

Starting from ethyl ester **16**, the half-ester **17** and, subsequently, the rearranged product **4b′** were prepared in the same way as **14** and **4a′**.

3.6. Half-ester 17

White solid (mp 67–68°C; yield: 29% from **16**). $[\alpha]_D^{22}=-15.4$ ($c=2.7$, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz) $\delta=6.8$–6.9 (2H, m) 4.36 (2H, dq, $J=6.9$, 12.0 Hz), 4.2 (1H, br. s), 4.1 (1H, br. s), 2.23 (1H, d, $J=7.2$ Hz), 2.15 (1H, d, $J=7.2$ Hz), 1.39 (3H, t, $J=6.9$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta=167.74$, 162.67, 162.09, 151.38, 142.70, 141.72, 72.64, 63.31, 54.71, 53.36, 13.90. IR (neat, cm^{-1}); 3050–2660, 1730, 1644, 1563, 1435, 1297. Anal. calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.22; H, 6.02%.

3.7. Rearranged product 4b′

Colorless oil (yield: 55% from **17**). $[\alpha]_D^{22}=-127.1$ ($c=3.1$, MeOH). ^1H NMR (300 MHz, $CDCl_3$): $\delta=9.36$ (1H, d, $J=3.9$), 6.8 (1H, m), 4.25 (1H, dq, $J=10.8$, 7.2), 4.13 (1H, dq, $J=10.8$, 7.2), 2.9 (3H, m), 2.6 (1H, m) 1.23 (3H, t, $J=7.2$). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=197.0$, 169.0, 168.4, 146.8, 132.0, 61.8, 44.7, 34.7,

34.6, 33.4, 14.0. IR (neat, cm^{-1}) 3587, 3500–2500, 2976, 2931, 1711, 1620, 1434, 1264. HRMS calcd for $C_{11}H_{16}O_5N$ $(M+NH_4)^+$: 242.1039. Found 242.1044.

3.8. Synthesis of 18

The acid (2.456 g, 10.3 mmol) obtained in the synthesis of **16** above was added to a solution of DMAP (155 mg, 1.44 mmol) in dichloromethane (35 mL) at rt, to which 1-propanol (0.93 mL, 21.4 mmol) and DCC (2.4 g, 11.4 mmol) were added. The reaction mixture was stirred at rt for 3 h and the solid was removed by filtration. The filtrate was successively washed with water, 5% AcOH and brine. After evaporation of the solvent, the crude reaction mixture was purified by column chromatography (10:1 hexane–ethyl acetate) to afford **18** (1.557 g, 54%). Colorless oil. ^1H NMR ($CDCl_3$, 300 MHz) $\delta=$ 6.3–6.2 (2H, m), 4.1–3.7 (4H, m), 3.62 (1H, dd, $J=8.1$ Hz, $J=5.1$ Hz), 3.09 (2H, br, s), 2.99 (1H, dd, $J=10.0$ Hz, $J=3.0$ Hz), 2.47 (1H, dt, $J=3.0$ Hz, $J=10$ Hz), 1.7–1.5 (2H, m), 1.2–1.5 (2H, m), 1.42 (3H, s), 1.26 (3H, s), 0.92 (3H, t, $J=7.2$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta=173.46$, 135.64, 135.34, 108.16, 77.15, 69.31, 65.97, 49.20, 48.59, 47.06, 46.16, 46.12, 27.22, 25.08, 21.90, 10.47. IR (neat, cm^{-1}) 2975, 2937, 2860, 1735, 1454, 1378, 1158, 1068. Anal. calcd for $C_{16}H_{24}O_4$: C, 68.55; H, 8.63. Found: C, 68.72; H, 8.56%.

Starting from *n*-propyl ester **18**, the half-ester **19** and, subsequently, the rearranged product **4c′** were prepared in the same way as **14** and **4a′**.

3.9. Half-ester 19

Colorless oil (yield: 9% from **17**). $[\alpha]_D^{22}=-10.2$ ($c=1.87$, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz) $\delta=6.8$–6.9 (2H, m), 4.2–4.3 (3H, m), 4.1 (1H, br. s), 2.21 (1H, d, $J=8.7$ Hz), 2.10 (1H, d, $J=8.7$ Hz), 1.76 (2H, sextet, $J=7.5$ Hz) 0.99 (3H, t, $J=7.5$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta=167.77$, 162.65, 162.11, 151.41, 142.80, 141.66, 72.60, 68.68, 54.69, 53.34, 21.65, 10.28. IR (neat, cm^{-1}) 3100–2600, 1728, 1637, 1603, 1439, 1292. Anal. calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 65.14; H, 6.60%.

3.10. Rearranged product 4c′

Colorless oil (yield: 75% from **17**). $[\alpha]_D^{22}=-217.1$ ($c=$ 0.35, MeOH). ^1H NMR (300 MHz, $CDCl_3$): $\delta=9.39$ (1H, d, $J=3.9$), 6.9 (1H, m), 4.19 (1H, dt, $J=10.8$, 7.2), 4.05 (1H, dt, $J=10.8$, 7.2), 2.9 (3H, m), 2.6 (1H, m), 1.66 (2H, sextet, $J=7.2$), 0.93 (3H, t, $J=7.2$). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=197.0$, 169.2, 168.4, 146.8, 132.0, 67.4, 44.7, 34.8, 34.7, 33.4, 21.8, 10.3. IR (neat, cm^{-1}) 3587, 3500–2500, 2971, 2925, 1711, 1626, 1428, 1270. HRMS calcd for $C_{12}H_{15}O_5N$ $(M+H)^+$: 239.0919. Found 239.0906.

Acknowledgements

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