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Asymmetric Synthesis of Valilactone

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Abstract—Total synthesis of (–)-valilactone, an efficient pancreatic lipase inhibitor, was accomplished with the use of Keck allylation in the key step of construction of the target carbon skeleton.

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In the past decades, much attention has been given to natural β-lactones (oxetan-2-ones) due to their antibacterial and immunomodulating activity, phytotoxicity, and the ability to inhibit animal and human enzymes [1–3]. Tetrahydrolipstatin (orlistat, **I**), tetrahydroesterastin (**II**), panclicin D (**III**), and valilactone (**IV**) are striking representatives of esters derived from amino acids and δ-hydroxy-β-lactones, which differ by the acid residue and side-chain structure; all asymmetric centers in their molecules have *S* configuration [4]. Compounds **I**–**IV** and their analogs are pancreatic lipase inhibitors and therefore may be used as weight-reducing agents in obesity [4, 5].

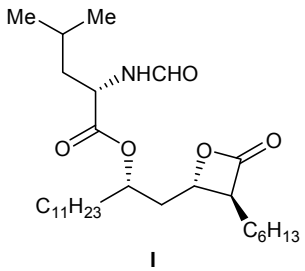
Valilactone (**IV**) was isolated from the microbial strain MG147-CF2 which is similar to *Streptomyces albolongus* [6]. Compound **IV** reacts with serine residues in pancreatic lipase, so that fatty acids are retained as triglycerides and are not assimilated, which leads to weight loss. The inhibitory activity of valilactone toward pancreatic lipase is lower by 3 orders of magnitude than that of tetrahydrolipstatin (**I**); however, among lactones **I**–**IV** only tetrahydrolipstatin (**I**, Xenical®) is commercially available [4, 5].

Four schemes for the total synthesis of valilactones have been reported. These schemes utilized π-allyl tricarbonyl iron complexes [7, 8], acyl iron complex with a chiral auxiliary [4], Mukayama reaction accompanied by lactonization [9], and preparation of *anti*-1,3-diol with subsequent lactone ring closure via activation of the hydroxy group [5].

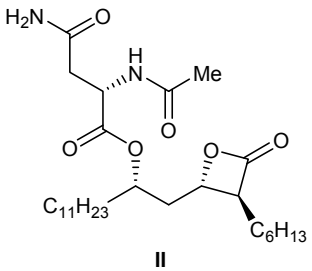
In the present work, the starting material was an allylic synthetic building block, methyl 3-[(tributylstannyl)methyl]but-3-enoate (**V**), which was prepared in 5 steps [10, 11] from ethyl 3,3-diethoxypropionic acid (**VI**) (Scheme 1). Compound **V** was used previously in the synthesis of massoia lactone [12], dihydrokavain [13], and insect pheromones with methyl-branched carbon skeleton [14].

The key step in the proposed scheme is asymmetric allylation of hexanal (**VII**) with stannane **V** according to Keck [15, 16] (Scheme 1). Unlike the known procedure, no trifluoroacetic acid was added, and the amount of the catalyst was reduced to 5 mol %. These conditions ensured formation of hydroxy ester **VIII** in 82% yield with more than 99% enantioselectivity, as followed from the intensity ratio of the MeO proton signals (δ 3.47 and 3.49 ppm) in the ^{1}H NMR spectrum of the acylation product of **VIII** with (*S*)- and (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chlorides (Mosher's acid chloride) [17].

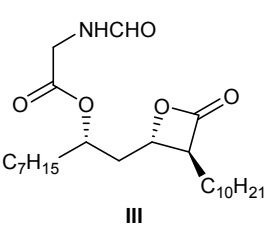
Protection of the hydroxy group in **VIII** by silylation with *tert*-butyl(chloro)dimethylsilane and subse-



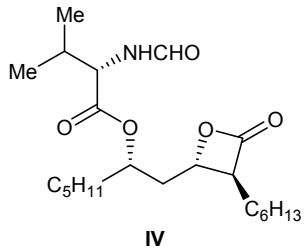
I



II

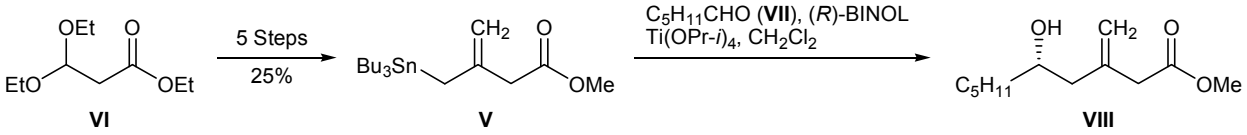


III



IV

Scheme 1.



quent ozonolysis of ester **IX** gave protected keto ester (**X**) (Scheme 2). It should be noted that silylated δ-hydroxy-β-oxo esters are useful intermediate products for the synthesis of many biologically active compounds, such as goniothalamin [18], antifungal drug (6*S*)-5,6-dihydro-6-[(2*R*)-2-hydroxy-6-phenylhexyl]-2*H*-pyran-2-one [19], parasorbic acid and colletodiol [20], lactone analogs of compactin and mevinolin [21, 22], and many others [23, 24].

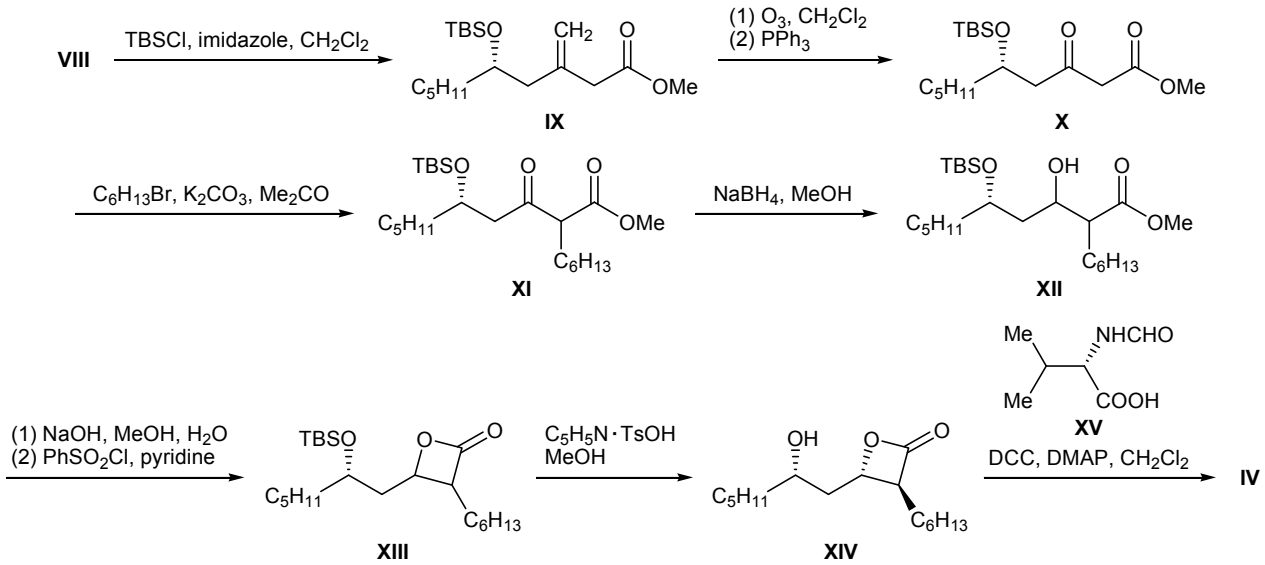
The alkylation of **X** with hexyl bromide, followed by nonselective reduction of ketone **XI**, afforded ester **XII**. Diastereoisomeric silylated oxetan-2-one derivatives **XIII** were obtained in moderate yield according to the standard procedure for the preparation of four-membered lactones via Adam's lactonization [25, 26]. Removal of the *tert*-butyl(dimethyl)silyl protection from **XIII** by the action of tetrabutylammonium fluoride in tetrahydrofuran gave a complex mixture of products, whereas treatment of **XIII** in methanol with pyridinium *p*-toluenesulfonate (PPTS) smoothly produced a mixture of diastereoisomeric hydroxy lactones which were separated by chromatography. By analogy with tetrahydrolipstatin [27], non-targeted *trans*-lactone was eluted first, next followed compound **XIV**, and then a mixture of *cis*-lactones was isolated; the yield of targeted isomer **XIV** was 34% .

The structure of **XIV** was confirmed by comparing its spectral parameters with those reported in [4], as well as by the spin–spin coupling constant for *trans*-oriented protons in the oxetane ring (J = 4 Hz). The synthesis of valilactone was completed by esterification with *N*-formyl-L-valine (**XV**) [28] via activation with *N*,*N*′-dicyclohexylcarbodiimide (DCC) in the presence of 4-dimethylaminopyridine (DMAP).

The overall yield of valilactone (**IV**) starting from ester **VI** was 3.1% (14 steps) or 12.4% calculated on allylic building block **V** (9 steps). The proposed synthetic approach to valilactone is not inferior to the other syntheses described in [4, 5, 7–9]. In particular, the first total synthesis of **IV** ensured as poor yield as 0.6% in 13 steps. The procedure described in the present work is advantageous due to experimental simplicity and the use of inexpensive and accessible reagents; furthermore, it requires neither expensive and toxic catalysts nor enzymatic transformations.

In summary, a new approach has been developed to the synthesis of natural oxetan-2-one derivative, valilactone (**IV**), which is potentially efficient pancreatic lipase inhibitor and anti-obesity drug. The proposed scheme may be successfully applied to the preparation of tetrahydrolipstatin (**I**, orlistat), tetrahydroesterastin (**II**), and panclicin D (**III**).

Scheme 2.



EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded from solutions in chloroform-*d* on a Bruker AC-400 spectrometer operating at 400 and 100 MHz, respectively. The IR spectra were recorded from solutions in carbon tetrachloride using a Bruker Vertex 70 instrument. The optical rotations were measured on an SM-3 polarimeter (scale division value 0.05°) at room temperature. Individual products were isolated by chromatography on silica gel (70–230 mesh). All solvents were purified and dried by standard methods and were distilled prior to use.

Methyl (5*S*)-5-hydroxy-3-methylidenedecanoate (VIII). A 0.1 M solution of titanium(IV) isopropoxide, 2.9 mL (294 μmol), was added to a mixture of 168 mg (588 μmol) of (*R*)-BINOL and 1.5 g of activated 4-Å molecular sieves (preliminarily calcined at 125–130°C under an oil-pump vacuum) in 50 mL of anhydrous methylene chloride, and the mixture was heated for 1 h under reflux with vigorous stirring. The resulting catalyst-containing mixture was cooled to –78°C, 1.76 g (12 mmol) of hexanal (**VII**) in 10 mL of anhydrous methylene chloride was added, the mixture was stirred for 15 min, 6.15 g (15.6 mmol) of stannane **V** [10] in 20 mL of anhydrous methylene chloride was added, and the mixture was left to stand for 5 days in a refrigerator at –25°C without stirring. The mixture was then treated under vigorous stirring with a saturated aqueous solution of $NaHCO_3$ (100 mL), the organic phase was separated, the aqueous phase was extracted with methylene chloride (3×30 mL), and the extracts were combined with the organic phase, washed with brine (50 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the product was isolated by chromatography using petroleum ether–ethyl acetate (40:1 to 5:1) as eluent. Yield 2.10 g (82%), $[\alpha]_D$ = –3.9° (*c* = 1.6, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3446, 1739, 1245, 1199, 1161. ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, CH_3, *J* = 6.9 Hz), 1.24–1.49 m [8H, $CH_3(C\mathbf{H}_2)_4$], 2.14 d.d (1H, 4-H, *J* = 14.1, 9.7 Hz), 2.33 d.d (1H, 4-H, *J* = 14.1, 2.1 Hz), 3.07 d and 3.14 d (1H each, 2-H, *J* = 15.6 Hz), 3.66–3.72 m (1H, 5-H), 3.69 s (3H, CH_3O), 5.04 s and 5.07 s (1H each, CH_2=). ^{13}C NMR spectrum, δ_C, ppm: 14.0 (CH_3), 22.6 (CH_2), 25.4 (CH_2), 31.8 (CH_2), 37.1 (CH_2), 41.5 (CH_2), 44.7 (CH_2), 52.0 (OCH_3), 69.1 (CH), 117.5 (=CH_2), 139.3 (C^3), 172.3 (C=O). Found, %: C 67.30; H 10.32. $C_{12}H_{22}O_3$. Calculated, %: C 67.26; H 10.35.

Methyl 3-{(2*S*)-2-[*tert*-butyl(dimethyl)silyloxy]-heptyl}but-3-enoate (IX). Ester **VIII**, 0.43 g (2 mmol), was dissolved in 10 mL of anhydrous methylene chloride, 0.3 g (3.5 mmol) of imidazole and 0.45 g (3 mmol) of *tert*-butyl(dimethyl)silyl chloride were added, and the mixture was stirred for 12 h and treated with water (30 mL). The organic phase was separated, the aqueous phase was extracted with methylene chloride (3×5 mL), the extracts were combined with the organic phase and dried over $MgSO_4$, the solvent was distilled off under reduced pressure, and the product was isolated by chromatography using petroleum ether–ethyl acetate (80:1) as eluent. Yield 0.58 g (88%), $[\alpha]_D$ = +40.1° (*c* = 1.8, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1743, 1258, 1158, 1094. ^{1}H NMR spectrum, δ, ppm: 0.02 s and 0.04 s (3H each, CH_3Si), 0.86–0.92 m [12H, *t*-BuSi, $C\mathbf{H}_3(CH_2)_4$], 1.22–1.45 m [8H, $CH_3(C\mathbf{H}_2)_4$], 2.24–2.27 m (2H, 3-CH_2), 3.07 d and 3.12 d (1H each, 2-H, *J* = 15.1 Hz), 3.68 br.s (3H, CH_3O), 3.74–3.82 m (1H, CHOSi), 4.95 br.s (2H, CH_2=). ^{13}C NMR spectrum, δ_C, ppm: –4.5 (2C, CH_3), 14.0 (CH_3), 18.1 (C), 22.6 (CH_2), 24.9 (CH_2), 25.9 (3C, CH_3), 32.0 (CH_2), 36.8 (CH_2), 42.1 (CH_2), 43.6 (CH_2), 51.7 (OCH_3), 71.0 (CH), 116.5 (C^4), 139.7 (C^3), 171.9 (C=O). Found, %: C 65.82; H 11.02. $C_{18}H_{36}O_3Si$. Calculated, %: C 65.80; H 11.04.

Methyl (5*S*)-5-[*tert*-butyl(dimethyl)silyloxy]-3-oxodecanoate (X). A solution of 2.30 g (7.0 mmol) of compound **IX** in 50 mL of methylene chloride was cooled to –78°C, an ozone/oxygen mixture was passed through the solution over a period of 1.5 h until persistent blue color, and oxygen was then passed to remove excess ozone. Triphenylphosphine, 1.84 g (15.6 mmol), was added in portions under vigorous stirring, and the mixture was allowed to slowly warm up to room temperature (over a period of 3 h) and treated with water (30 mL). The organic phase was separated, the aqueous phase was extracted with methylene chloride (2×10 mL), the extracts were combined with the organic phase and dried over $MgSO_4$, the solvent was distilled off under reduced pressure, and the product was isolated by chromatography on silica gel using petroleum ether–ethyl acetate (90:1) as eluent. Yield 2.17 g (94%), $[\alpha]_D$ = –4.0° (*c* = 1.0, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1753, 1720, 1255, 1072. ^{1}H NMR spectrum, δ, ppm: 0.02 s and 0.06 s (3H each, CH_3Si), 0.86 br.s (9H, *t*-BuSi), 0.88 t [3H, $C\mathbf{H}_3(CH_2)_4$, *J* = 6.6 Hz], 1.22–1.34 m [6H, $CH_3(C\mathbf{H}_2)_3$], 1.41–1.49 m (2H, 6-H), 2.59 d.d (1H, 4-H, *J* = 15.2, 4.9 Hz), 2.69 d.d (1H, 4-H, *J* = 15.2, 6.9 Hz), 3.47 d and 3.51 d (1H each, 2-H, *J* = 15.7 Hz), 3.73 br.s (3H, CH_3O), 4.13–4.20 m (1H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: –4.6 (2C, CH_3), 14.1 (CH_3), 18.5 (C), 22.6 (CH_2), 26.1

(3C, CH_3), 27.3 (CH_2), 30.9 (CH_2), 37.5 (CH_2), 49.1 (CH_2), 51.4 (CH_2), 52.3 (CH_3), 66.8 (C^5), 167.4 (C=O), 171.9 (C=O). Found, %: C 61.79; H 10.34. $C_{17}H_{34}O_4Si$. Calculated, %: C 61.77; H 10.37.

Methyl (2*RS*,5*S*)-5-[*tert*-butyl(dimethyl)silyloxy]-2-hexyl-3-oxodecanoate (XI). A mixture of 0.66 g (2 mmol) of keto ester **X**, 0.57 g (4 mmol) of calcined K_2CO_3, and 0.66 g (4 mmol) of hexyl bromide in 10 mL of anhydrous acetone was heated for 1 h under reflux with vigorous stirring. The mixture was treated with water (20 mL) and extracted with methylene chloride (3×10 mL), the combined extracts were dried over $MgSO_4$, the solvent was distilled off under reduced pressure, and the product was isolated by chromatography on silica gel using petroleum ether–ethyl acetate (100:1) as eluent. Yield 0.75 g (90%). IR spectrum, ν, cm^{-1}: 1717, 1463, 1378, 1256, 1142, 1056. ^1H NMR spectrum, δ, ppm: 0.01 s and 0.02 s (3H each, CH_3Si), 0.87 t [3H, C**H**$_3(CH_2)_5$, J = 6.4 Hz], 0.87 br.s (9H, *t*-BuSi), 0.88 t [3H, C**H**$_3(CH_2)_4$, J = 6.9 Hz], 1.26–1.43 m [14H, $CH_3(CH_2)_3$, $CH_3(CH_2)_4$], 1.76–1.89 m (4H, 6-H, 2-CH_2), 2.57 d.d (1H, 4-H, J = 17.5, 5.1 Hz), 2.70 d.d (1H, 4-H, J = 17.5, 6.1 Hz), 3.39–3.47 m (1H, 2-H), 3.66 br.s (3H, CH_3O), 4.12–4.13 m (1H, 5-H). Found, %: C 66.64; H 11.15. $C_{23}H_{46}O_4Si$. Calculated, %: C 66.61; H 11.18.

Methyl (2*RS*,3*RS*,5*S*)-5-[*tert*-butyl(dimethyl)-silyloxy]-2-hexyl-3-hydroxydecanoate (XII). A solution of 0.83 g (2 mmol) of keto ester **XI** in 20 mL of methanol was cooled to 0°C, 0.09 g (2.3 mmol) of $NaBH_4$ was added, and the mixture was kept for 0.5 h, treated with a saturated solution of ammonium chloride (20 mL), and extracted with methylene chloride (3×10 mL). The combined extracts were washed with a saturated aqueous solution of $NaHCO_3$ (50 mL) and dried over $MgSO_4$, the solvent was distilled off under reduced pressure, and the product was isolated by chromatography on silica gel using petroleum ether–ethyl acetate (25:1) as eluent. Yield 0.73 g (87%). IR spectrum, ν, cm^{-1}: 3436, 1738, 1256. ^1H NMR spectrum, δ, ppm: 0.07 s and 0.08 s (3H each, CH_3Si), 0.85–0.89 m [15H, C**H**$_3(CH_2)_5$, *t*-BuSi, C**H**$_3(CH_2)_4$], 1.20–1.31 m [14H, $CH_3(CH_2)_3$, $CH_3(CH_2)_4$], 1.43–1.68 m (4H, 6-H, 2-CH_2), 2.39–2.47 m (1H, 2-H), 3.46 br.s (1H, OH), 3.71 br.s (3H, CH_3O), 3.81–3.92 m (1H, 3-H), 3.96–4.06 m (1H, 5-H). Found, %: C 66.32; H 11.59. $C_{23}H_{48}O_4Si$. Calculated, %: C 66.29; H 11.61.

(3*RS*,4*RS*)-4-{(2*S*)-2-[*tert*-Butyl(dimethyl)silyloxy]heptyl}-3-hexyloxetan-2-one (XIII). Hydroxy ester **XII**, 0.42 g (1 mmol), was dissolved in 2.5 mL of methanol, 2.5 mL of 1 M aqueous sodium hydroxide was added, and the mixture was heated for 2 h under reflux. The mixture was cooled, neutralized with 2.5 mL of 1 M aqueous HCl, diluted with 5 mL of water, and extracted with diethyl ether (3×5 mL). The extracts were combined and dried over $MgSO_4$, the solvent was distilled off, the residue was dissolved in 10 mL of pyridine, the solution was cooled to 0°C, 0.46 g (2.6 mmol) of benzenesulfonyl chloride was added in one portion, and the mixture was stirred for 24 h at room temperature. The mixture was treated with water (30 mL) and extracted with diethyl ether (3×10 mL), the combined extracts were dried over $MgSO_4$, the solvent was distilled off under reduced pressure, and the product (a 1.4:1 mixture of diastereoisomers) was isolated by chromatography on silica gel using petroleum ether–ethyl acetate (100:1) as eluent. Yield 0.31 g (80%). IR spectrum, ν, cm^{-1}: 1823, 1100, 1073. ^1H NMR spectrum, δ, ppm: 0.04 s (1.2H, CH_3Si), 0.05 s (3H, CH_3Si), 0.06 s (3H, CH_3Si), 0.80–0.93 m [36H, C**H**$_3(CH_2)_5$, *t*-BuSi, C**H**$_3(CH_2)_4$], 1.21–1.91 m [43.2H, $CH_3(CH_2)_4$, $CH_3(CH_2)_5$], 2.02–2.36 m (4.8H, 4-CH_2), 3.14–3.27 m (2.4H, 3-H), 3.59–3.66 m (0.4H, CHOSi), 3.79–3.86 m (2H, CHOSi), 4.42–4.46 m (1.4H, 4-H), 4.71–4.78 m (1H, 4-H). Found, %: C 68.72; H 11.51. $C_{22}H_{44}O_3Si$. Calculated, %: C 68.69; H 11.53.

(3*S*,4*S*)-3-Hexyl-4-[(2*S*)-2-hydroxyheptyl]oxetan-2-one (XIV). Pyridinium *p*-toluenesulfonate, 0.05 g (0.2 mol), was added to a solution of 0.77 g (2 mmol) of lactone **XIII** in 6 mL of methanol, and the mixture was heated for 2 h at 50°C. A few drops of triethylamine were added, the mixture was evaporated under reduced pressure, and the target diastereoisomer was isolated by chromatography using petroleum ether–ethyl acetate (40:1) as eluent. Yield 0.18 g (34%), $[\alpha]_D$ = –16.3° (c = 0.5, $CHCl_3$). The spectral parameters of the product were consistent with those reported in [4].

(2*S*,2′*S*,3′*S*)-1-(3-Hexyl-4-oxooxetan-2-yl)heptan-2-yl (*S*)-*N*-formyl-3-methylbutanoate [IV, (–)-valilactone]. A solution of 0.1 g (0.4 mmol) of lactone **XIV** in 0.5 mL of anhydrous methylene chloride was added in one portion at room temperature to a mixture of 0.08 g (0.6 mmol) of *N*-formyl-L-valine (**XV**) [28], 0.12 g (0.6 mmol) of *N*,*N*′-dicyclohexylcarbodiimide, and 9 mg (0.07 mmol) of 4-dimethylaminopyridine in 1 mL of anhydrous methylene chloride. After 24 h, the mixture was treated with water (10 mL), the organic phase was separated, the aqueous phase was extracted with diethyl ether (3×5 mL), the extracts were com-

bined with the organic phase and dried over $MgSO_4$, the solvent was distilled off under reduced pressure, and the product was isolated by chromatography on silica gel using petroleum ether–ethyl acetate (2:1) as eluent. Yield 0.11 g (86%), $[\alpha]_D = -33.5°$ ($c = 0.9$, $CHCl_3$). The spectral parameters of the product were consistent with those given in [4].

REFERENCES

1. Pommier, A. and Pons, J.-M., *Synthesis*, 1995, p. 729.
2. Yang, H.W., Zhao, C., and Romo, D., *Tetrahedron*, 1997, vol. 53, p. 16471.
3. Yang, H.W. and Romo, D., *Tetrahedron*, 1999, vol. 55, p. 6403.
4. Case-Green, S.C., Davies, S.G., Roberts, P.M., Russell, A.J., and Thomson, J.E., *Tetrahedron: Asymmetry*, 2008, vol. 19, p. 2620.
5. Wu, Y. and Sun, Y.-P., *J. Org. Chem*., 2006, vol. 71, p. 5748.
6. Kitahara, M., Asano, M., Naganawara, H., Maeda, K., Hamada, M., Aoyagi, T., Umezawa, H., Iitaka, Y., and Nakamura, H., *J. Antibiot*., 1987, vol. 40, p. 1647.
7. Bates, R.W., Fernandez-Moro, R., and Ley, S.V., *Tetrahedron Lett*., 1991, vol. 32, p. 2651.
8. Bates, R.W., Fernandez-Moro, R., and Ley, S.V., *Tetrahedron*, 1991, vol. 47, p. 9929.
9. Ma, G., Zancanella, M., Oyola, Y., Richardson, R.D., Smith, J.W., and Romo, D., *Org. Lett*., 2006, vol. 8, p. 4497.
10. Mineeva, I.V. and Kulinkovich, O.G., *Russ. J. Org. Chem*., 2008, vol. 44, p. 1261.
11. Mineyeva, I.V. and Kulinkovich, O.G., *Tetrahedron Lett*., 2010, vol. 51, p. 1836.
12. Mineeva, I.V., *Russ. J. Org. Chem*., 2012, vol. 48, p. 977.
13. Mineeva, I.V., *Russ. J. Org. Chem*., 2013, vol. 49, p. 712.
14. Mineeva, I.V., *Russ. J. Org. Chem*., 2013, vol. 49, p. 253.
15. Keck, G.E. and Yu, T., *Org. Lett*., 1999, vol. 1, p. 289.
16. Sanchez, C.C. and Keck, G.E., *Org. Lett*., 2005, vol. 7, p. 3053.
17. Dale, J.A., Dull, D.L., and Mosher, H.S., *J. Org. Chem*., 1969, vol. 34, p. 2543.
18. Sato, M., Sunami, S., Sugita, Y., and Kaneko, C., *Chem. Pharm. Bull*., 1994, vol. 42, p. 839.
19. Sabitha, G., Srinivas, C., Sudhakar, K., Rajkumar, M., Maruthi, C., and Yadav, J.S., *Synthesis*, 2007, p. 3886.
20. Sakaki, J., Sugita, Y., Sato, M., and Kaneko, C., *Tetrahedron*, 1991, vol. 47, p. 6197.
21. Johnson, W.S., Kelson, A.B., and Elliott, J.D., *Tetrahedron Lett*., 1988, vol. 29, p. 3757.
22. Sabitha, G., Sundhakar, K., Srinivas, Ch., and Yadav, J.S., *Synthesis*, 2007, p. 705.
23. Soriente, A., De Rosa, M., Villano, R., and Scettri, A., *Tetrahedron: Asymmetry*, 2000, vol. 11, p. 2255.
24. Soriente, A., De Rosa, M., Stanzione, M., Villano, R., and Scettri, A., *Tetrahedron: Asymmetry*, 2001, vol. 12, p. 959.
25. Adam, W., Baeza, J., and Ju-Chao, L., *J. Am. Chem. Soc*., 1972, vol. 94, p. 2000.
26. Ghosh, A.K., Shurrush, K., and Kulkarni, S., *J. Org. Chem*., 2009, vol. 74, p. 4508.
27. Barbier, P. and Schneider, F., *Helv. Chim. Acta*, 1987, vol. 70, p. 196.
28. Muramatsu, I., Murakami, M., Yoneda, T., and Hagiani, A., *Bull. Chem. Soc. Jpn*., 1965, vol. 38, p. 244.