

## Enantioselective synthesis of a substituted cyclopentanone with all-carbon quaternary stereocenter

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Dedicated to Prof. Oleg Rakin on the occasion of his 65<sup>th</sup> birthday

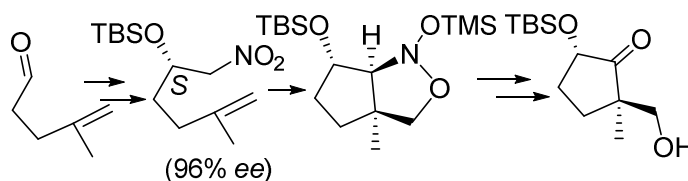
Received 05-17-2017

Accepted 07-01-2017

Published on line 07-23-2017

### Abstract

The enantioselective synthesis of a substituted cyclopentanone with an all-carbon quaternary stereocenter was performed using an asymmetric nitroaldol condensation involving metal-complex catalysis and stereocontrolled silyl nitronate intramolecular [3+2] cycloaddition reaction in the key steps of the synthesis.

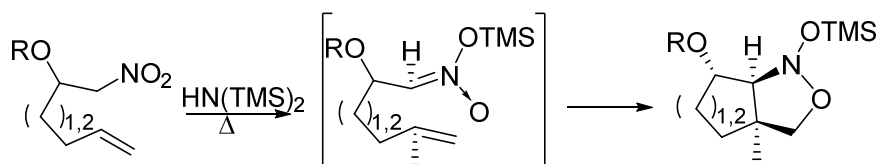


**Keywords:** Enantioselective synthesis; substituted cyclopentanone; silyl nitronate; intramolecular cycloaddition

## Introduction

Enantioselective construction of all-carbon quaternary stereocenters, i.e. centers in which the carbon atom bears four different carbon substituents, remains one of the most challenging subjects in modern synthetic chemistry because creation of such centers is complicated by steric repulsion between the carbon substituents.<sup>1</sup> However there is a strong demand for the development of effective methods for the asymmetric synthesis of organic compounds containing such structural units which were revealed in a variety of natural compounds and bioactive molecules. In particular, many terpenoids,<sup>1-5</sup> alkaloids<sup>1,6,7</sup> and prostaglandin analogs<sup>8</sup> contain substituted cyclopentane fragments containing such chiral centers.

Currently, there are few direct C-C bond formation reactions that have been successfully applied for the construction of all-carbon quaternary stereocenters.<sup>1,9,10</sup> Among them the enantioselective catalysis for allylic alkylation,<sup>1,9-13</sup> conjugation addition,<sup>14,15</sup> Diels–Alder reactions<sup>16</sup> and some other reactions have been used.<sup>17,18</sup> There are significantly fewer examples of efficient control of the stereogenic process and stereochemistry of the newly formed quaternary center directed by chiral center or centers present initially in the starting materials.<sup>19-21</sup> Nevertheless, using the substrate-controlled stereo-induction of an easily accessible stereogenic center is a very attractive strategy to create another one that is more difficult to establish by conventional methods. We surmised that the advantages of this approach could additionally be shown using an annulation reaction by intramolecular dipolar [3+2] cycloaddition of silyl nitronates generated from chiral unsaturated nitro compounds. Previously we have demonstrated<sup>22,23</sup> a strong stereocontrol of the formation of substituted cyclopentane and cyclohexane rings in such cycloadditions directed by a substituent on the corresponding nitronate derived from the starting nitroolefin (*cf.* refs 24,25) (Scheme 1).

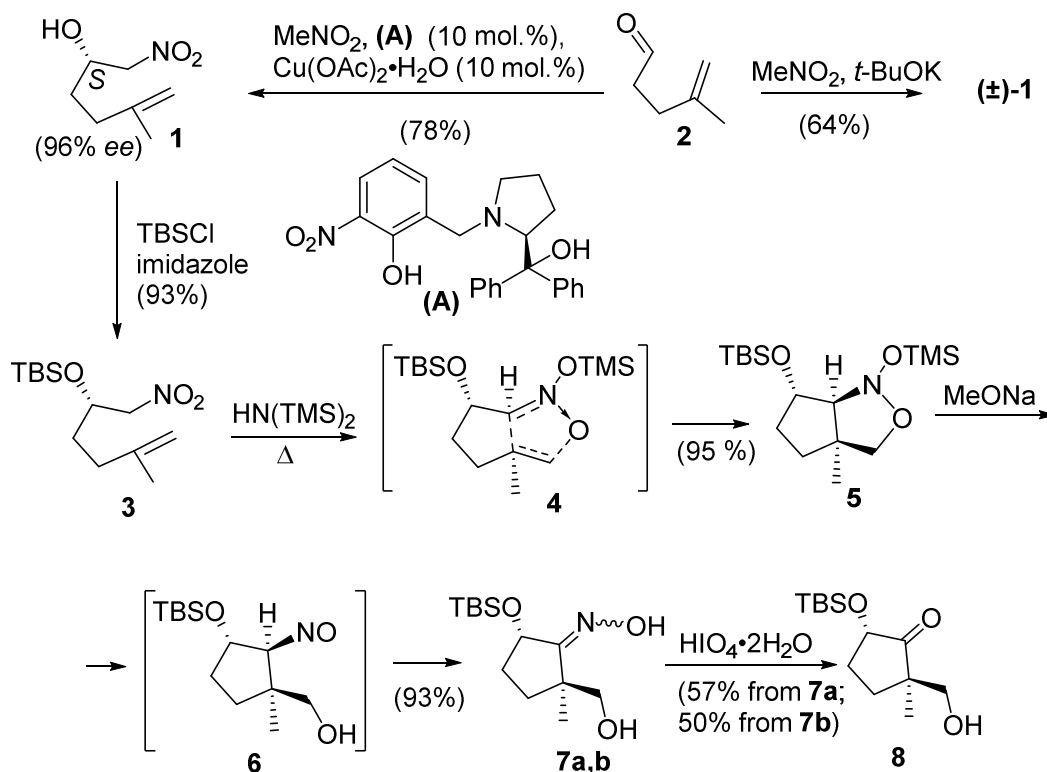


### Scheme 1

Herein we describe an application of the intramolecular silyl nitronate cycloaddition reaction in the synthesis of a highly enantioenriched (~96 % *ee*) substituted cyclopentanone with an all-carbon quaternary stereocenter in the molecule.

## Results and Discussion

The key unsaturated nitroalcohol **1** (96 % *ee*, HPLC data) in the synthesis of the target compound was obtained by enantioselective Henry reaction of 4-methylpentenal **2** with nitromethane promoted by a catalytic system proposed earlier<sup>26</sup> for a similar process (Scheme 2). The absolute configuration of the newly obtained compound **1** was assigned by analogy with that of its homologue synthesized under the same reaction conditions.<sup>26</sup> For further measurement of the enantiomeric excess by chiral HPLC, racemic nitroalcohol ( $\pm$ )-**1** was obtained by a convenient procedure.

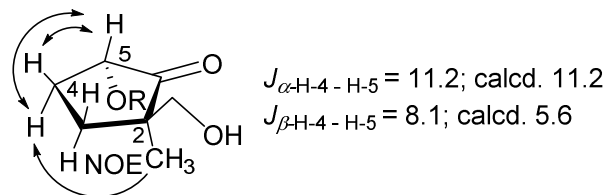


## Scheme 2

The nitroalcohol **1** thus obtained was converted into silyl ether **3**. Heating the latter with 1,1,1,3,3,3-hexamethyldisilazane at 115 °C yields (*via* formation of nitronate **4**) a rather labile cyclopentaisoxazolidine **5**. The intramolecular cycloaddition proceeds highly stereoselectively with formation of the sole stereoisomer with *trans*-disposition of the OTBS substituent relative to the annulated isoxazolidine ring (*cf.* refs. 22-25). Further transformation of cyclopentaisoxazolidine **5** consisted in isoxazolidine fragment opening upon the action of sodium methoxide as described earlier for related compounds (*cf.* ref. 23). In this case it gives a mixture of isomeric oximes **7a,b** (*anti*-/*syn*- ≈ 12 : 1, <sup>1</sup>H NMR data) through initial formation of plausible nitroso intermediate **6**. The configuration of the C=N double bond in isomers **7a** and **7b** was established from <sup>13</sup>C NMR spectroscopic data, because it is known<sup>27,28</sup> that the oxime hydroxyl group exerts a substantial shielding effect on the adjacent  $\alpha$ -carbon atom.

Deoximation of oximes **7a** and **7b** was carried out in the absence of a solvent by triturating with HIO<sub>4</sub>·2H<sub>2</sub>O in a mortar for a short time (*cf.* ref. 29) to give desired cycloalkanone **8** in moderate yields in both cases. Enantiomeric excess of ketone **8** is apparently not less than 96 % *ee* since chiral center which was initially in the starting nitroalcohol **1** and the newly induced quaternary stereocenter was not affected during the subsequent stages of the synthesis.

The relative configuration of cyclopentanone **8** substituents was additionally confirmed by 1D NOE experiment. Methyl group at C(2) shows considerable NOE with H-4  $\alpha$ -hydrogen (Fig. 1). Its *trans*-orientation to H-5 was established by comparison of coupling constants between hydrogens H-4 and H-5 and these constants values calculated by DFT method using B3LYP functional and aug-cc-pvtz basis set.



**Figure 1.** Structure of cyclopentanone (**8**).

## Conclusions

In summary, we have developed a highly diastereoselective and enantioselective synthesis of a substituted cyclopentanone containing an all-carbon quaternary stereocenter. To the best of our knowledge, this is the first example of the construction of a cyclopentane core with such a structural feature using an intramolecular [3+2] cycloaddition reaction of silyl nitronate generated from an available enantioenriched nitro compound. We believe this methodology has potential to be utilized for the synthesis a number of natural cyclopentanoids.

## Experimental Section

**General.** All reactions involving moisture-sensitive chemicals were carried out under positive pressure of argon with magnetic stirring. Commercially available chemicals were used without further purification. Solvents, including petroleum ether with bp 40-70 °C, were purified and dried using standard procedures. Starting 4-methylpent-4-enal was prepared according to known procedure.<sup>30</sup> Melting points were measured with a Kofler hot-stage apparatus. HRMS spectra (ESI) were obtained with a Bruker micrOTOF II mass spectrometer. IR spectra were recorded with Bruker ALPHA-T spectrometer. Optical rotation values were measured on a Jasco P-2000 polarimeter. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub> at 303 K on a Bruker AM-300 spectrometer. Chemical shifts were reported relative to CHCl<sub>3</sub> ( $\delta_{\text{H}} = 7.27$  and  $\delta_{\text{C}} = 77.0$ ) or C<sub>6</sub>H<sub>6</sub> ( $\delta_{\text{H}} = 7.17$  and  $\delta_{\text{C}} = 128.6$ ). TLC was performed on silica-coated glass plates (Merck, silica gel 60 F254). Visualization was accomplished by treating the plates with KMnO<sub>4</sub> (0.5% in H<sub>2</sub>O). Flash chromatography was performed on silica gel 60 (Merck, 230–400 mesh) with the indicated eluents. For analytical HPLC a chiral phase Kromasil<sup>®</sup> 3 CelluCoat (column 4.6×150 mm) was used. Sonication was performed with an ultrasonic bath UZV-1/100-TN at 44 kHz (75 W).

**(2S)-5-Methyl-1-nitrohex-5-en-2-ol (1).** A suspension of ligand (**A**) (0.61 g, 1.51 mmol) and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.33 g, 1.65 mmol) in anhydrous *i*-PrOH (50 mL) was ultrasonicated for 10 min at 20 °C, then aldehyde **2** (2.94 g, 29.96 mmol) and MeNO<sub>2</sub> (16 ml) were added to the formed solution. The reaction mixture was kept for 40 h at 20 °C until complete consumption of the starting aldehyde (TLC monitoring), and concentrated under reduced pressure. Purification of the residue by column chromatography over silica gel (elution with petroleum ether/*t*-BuOMe, 3:1) afforded nitro alcohol **1** in the yield of 3.72 g (78%), oil, *R*<sub>f</sub> 0.23 (petroleum ether/*t*-BuOMe, 3:1), bp 65-68 °C (0.08 Torr),  $[\alpha]_{\text{D}}^{20} +5.8$  (*c* 1.00, CH<sub>2</sub>Cl<sub>2</sub>). IR (neat): 3425, 2969-2858, 1650, 1556, 1447, 1423, 1383, 1206, 1100, 891 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  4.77 (s, 1 H, H-6), 4.71 (s, 1 H, H'-6), 4.26-4.51 (m, 3 H, 2×H-1, H-2), 2.88 (br. s, 1 H, OH), 2.17 (m, 2H, H-4), 1.74 (s, 3H, CH<sub>3</sub>), 1.66 (m, 2H, H-3). <sup>13</sup>C NMR (75

MHz, CDCl<sub>3</sub>):  $\delta$  141.40 (C-5), 110.99 (C-6), 80.59 (C-1), 68.34 (C-2), 33.27 (C-4), 31.44 (C-3), 22.25 (CH<sub>3</sub>). HRMS (ESI) calcd. for C<sub>7</sub>H<sub>13</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 160.0968, found 160.0972. HPLC: hexane/*i*-PrOH, 98/2, flow rate 1.5 mL/min, 30 °C,  $\lambda$  = 210 nm,  $t_r$  = 9.3 (minor);  $t_r$  = 9.7 min (major); calcd. 96% *ee*.

**(±)-5-Methyl-1-nitrohex-5-en-2-ol ((±)-1)**. To a solution of aldehyde **2** (1.27 g, 12.94 mmol) and MeNO<sub>2</sub> (1.63 g, 26.77 mmol) in a mixture of *t*-BuOH and THF (1 : 1, 7 ml), stirred under argon at 20 °C, *t*-BuOK (0.14 g, 1.25 mmol) was added in a small portions. The reaction mixture was stirred at 20 °C for 1.5 h and then diluted with water and extracted with *t*-MeO*Bu*. The extract was washed with water and brine, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. Purification of the residue by column chromatography over silica gel (gradient elution with petroleum ether → petroleum ether/*t*-BuOMe, 7:3) afforded 1.31 g (64 %) nitroalcohol **(±)-1** as a colorless liquid, bp 69-72 °C (0.09 Torr), physical characteristics of which (boiling point, NMR spectra and retention times of enantiomers) were almost the same as above described for the optically active product.

**(5S)-5-*t*-Butyl(dimethyl)silyloxy-2-methyl-6-nitrohex-1-ene (3)**. Imidazole (2.86 g, 42.0 mmol) was added to a stirred solution of nitro alcohol **1** (3.18 g, 19.98 mmol) and TBSCl (3.16 g, 20.97 mmol) in DMF (15 mL) under argon at 20 °C. The reaction mixture was stirred at 20 °C for 15 h and then diluted with water and extracted with *t*-MeO*Bu*. The extract was washed with water and brine, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. Purification of the residue by column chromatography over silica gel (gradient elution with petroleum ether → petroleum ether/*t*-BuOMe, 9:1) afforded silyl ether **3** in the yield of 5.08 g (93%), oil,  $R_f$  0.52 (petroleum ether/*t*-BuOMe, 9:1), bp 78-80 °C (0.08 Torr),  $[\alpha]_D^{28}$  +26.9 (c 1.00, CH<sub>2</sub>Cl<sub>2</sub>). IR (neat): 2955-2859, 1650, 1558, 1473, 1386, 1258, 1115, 981, 838, 811, 779 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  4.77 (s, 1 H, H-1), 4.71 (s, 1 H, H'-1), 4.41 (m, 3 H, H-5, H-6), 2.07 (m, 2H, H-3), 1.74 (s, 3H, CH<sub>3</sub>), 1.71 (m, 2H, H-4), 0.87 (s, 9 H, CH<sub>3</sub>CSi), 0.09, 0.04 (s, 6 H, CH<sub>3</sub>Si). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 144.40 (C-2), 110.67 (C-1), 80.95 (C-6), 69.74 (C-5), 33.09 (C-3), 32.60 (C-4), 25.61 (CH<sub>3</sub>CSi) 22.25 (CH<sub>3</sub>), 17.90 (CH<sub>3</sub>CSi), -4.68, -5.19 (CH<sub>3</sub>Si). HRMS (ESI) calcd. for C<sub>13</sub>H<sub>27</sub>NO<sub>3</sub>Si [M + H]<sup>+</sup>: 274.1833; found 274.1839.

**(3a*S*,6*S*,6a*S*)-6-*t*-Butyl(dimethyl)silyloxy-3a-methyl-1-(trimethylsilyloxy)perhydrocyclopenta[*c*]isoxazole (5)**. A stirred under argon mixture of compound **3** (3.82 g, 13.97 mmol), Et<sub>3</sub>N (1.67 g, 16.50 mmol), HMPA (0.5 g, 2.79 mmol) and HMDS (18 mL), was heated at 115 °C for 10 h and then concentrated under reduced pressure. The residue was distilled off. Compound **5** was obtained in a yield of 4.58 g (95%) as a colorless oil with bp 85-89 °C (0.08 Torr). IR (neat): 2957-2858, 1462, 1251, 1072, 921, 881, 841, 776 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  4.10 (d, 1 H, H-3,  $J$  = 8.0), 4.03 (m, 1 H, H-6), 3.95 (d, 1 H, H'-3,  $J$  = 8.0), 3.69 (d, 1 H, H-6a,  $J$  = 7.9), 1.49–2.03 (m, 4 H, H-4, H-5), 1.16 (s, 3 H, CH<sub>3</sub>), 0.87 (s, 9 H, CH<sub>3</sub>CSi), 0.12, 0.08 and 0.04 (s, 15 H, CH<sub>3</sub>Si). HRMS (ESI) calcd. for C<sub>16</sub>H<sub>35</sub>NO<sub>3</sub>Si<sub>2</sub> [M + H]<sup>+</sup>: 346.2228; found 346.2229.

**(1*E*,2*S*,5*S*)-5-*t*-Butyl(dimethyl)silyloxy-2-(hydroxymethyl)-1-(hydroxyimino)-2-methylcyclopentane (7a) and (1*Z*,2*S*,5*S*)-5-*t*-butyl(dimethyl)silyloxy-2-(hydroxymethyl)-1-(hydroxyimino)-2-methylcyclopentane (7b)**. To a stirred under argon suspension of MeONa (1.24 g, 23.04 mmol) in PhH (25 mL), a solution of isoxazolidine **5** (4.48 g, 13.0 mmol) in PhH (10 mL) was added dropwise at 20 °C. The reaction mixture was stirred at 20 °C for 2 h and neutralized with 10% aqueous HCl. The aqueous layer was separated and extracted with EtOAc. Combined organic layers were washed with water and brine dried with NaSO<sub>4</sub>, and the solvent was removed under reduced pressure. Column chromatography of the residue over silica gel (elution with EtOAc) afforded oximes **7a** and **7b**. Oxime **7a** (yield 3.05 g, 86%), colorless crystals, mp 76-77 °C (from petroleum ether),  $[\alpha]_D^{28}$  +110.6 (c 1.00, CH<sub>3</sub>OH). IR (KBr): 3331, 2954-2859, 1472-1346, 1254, 1132, 1078, 1032, 943, 836, 776 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  9.65 (br.s, 1 H, NOH), 5.05 (t, 1 H, H-5,  $J$  = 3.8), 3.70 (br.s 1 H, OH), 3.62 (d, 1 H, HCO,  $J$  = 10.1), 3.55 (d, 1 H, H'CO,  $J$  = 10.1), 1.51-1.81 (m, 4 H, H-3, H-4), 1.43 (s, 3H, CH<sub>3</sub>), 0.99 (s, 9 H, CH<sub>3</sub>CSi), 0.28, 0.33 (s, 6 H, CH<sub>3</sub>Si). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 170.17 (C=NOH), 69.87 (CH<sub>2</sub>O), 69.51 (C-5), 46.39 (C-2), 33.68,

33.72 (C-3, C-4), 26.67 ( $\text{CH}_3\text{-CSi}$ ), 24.75 ( $\text{CH}_3\text{-2}$ ), 19.00 ( $\text{CH}_3\text{CSi}$ ),  $-4.04$ ,  $-4.31$  ( $\text{CH}_3\text{Si}$ ). HRMS (ESI) calcd. for  $\text{C}_{13}\text{H}_{27}\text{NO}_3\text{Si}$  [ $\text{M} + \text{H}$ ] $^+$ : 274.1833 and [ $\text{M} + \text{Na}$ ] $^+$ : 296.1652; found 274.1837 and 296.1655. Oxime **7b** (yield 0.25 g, 7%), colorless crystals, m.p. 57-58 °C (from petroleum ether),  $[\alpha]_{\text{D}}^{28} +32.7$  (c 1.00,  $\text{CH}_3\text{OH}$ ). IR (KBr): 3264, 2858-2956, 1362-1472, 1253, 1138, 1091, 1045, 992, 937, 839, 781, 670  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 9.65$  (br.s, 1 H, NOH), 4.54 (t, 1 H, H-5,  $J = 6.6$ ), 4.09 (d, 1 H, HCO,  $J = 10.7$ ), 3.58 (d, 1 H, H'CO,  $J = 10.7$ ), 3.18 (br.s 1 H, OH), 1.64–1.95 (m, 4 H, H-3, H-4), 1.41 (s, 3H,  $\text{CH}_3$ ), 0.99 (s, 9 H,  $\text{CH}_3\text{CSi}$ ), 0.33, 0.29 (s, 6 H,  $\text{CH}_3\text{Si}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 167.82$  (C=NOH), 76.06 (C-5), 68.66 ( $\text{CH}_2\text{O}$ ), 48.73 (C-2), 34.11, 33.43 (C-3, C-4), 26.74 ( $\text{CH}_3\text{CSi}$ ), 20.61 ( $\text{CH}_3\text{-2}$ ), 19.03 ( $\text{CH}_3\text{CSi}$ ),  $-3.99$ ,  $-3.73$  ( $\text{CH}_3\text{Si}$ ). HRMS (ESI) calcd. for  $\text{C}_{13}\text{H}_{27}\text{NO}_3\text{Si}$  [ $\text{M} + \text{H}$ ] $^+$ : 274.1833 and [ $\text{M} + \text{Na}$ ] $^+$ : 296.1652; found 274.1821 and 296.1647.

**(2R,5S)-5-*t*-Butyl(dimethyl)silyloxy-2-hydroxymethyl-2-methylcyclopentan-1-one (8)**. A: Oxime **7a** (0.60 g, 2.19 mmol) and  $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$  (0.25 g, 1.09 mmol) was thoroughly mixed and ground in an agate mortar for 2 min. The resulting homogeneous oily material was extracted with *t*-BuOMe. The extract was washed with solution of  $\text{Na}_2\text{S}_2\text{O}_3$ , water and brine dried with  $\text{Na}_2\text{SO}_4$ , and the solvent was removed under reduced pressure. Purification of the residue by column chromatography over silica gel (gradient elution with  $\text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2/t\text{-BuOMe}$ , 9:1) afforded cyclopentanone **8** in the yield of 0.32 g (57%), colorless crystals, mp 46-47 °C (from petroleum ether),  $[\alpha]_{\text{D}}^{28} +75.1$  (c 1.00,  $\text{CH}_2\text{Cl}_2$ ). IR (KBr): 3468, 2967-2858, 1751, 1463, 1362, 1254, 1173, 1147, 1054, 995, 839, 780.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 4.05$  (d.d, 1 H, H-5,  $J = 10.9$ ,  $J = 8.2$ ), 3.65 (d, 1 H, HCO,  $J = 10.6$ ), 3.39 (d, 1 H, H'CO,  $J = 10.6$ ), and 1.94–2.28 1.62–1.88 (both m, 4 H, H-3, and H-4), 1.03 (s, 3 H,  $\text{CH}_3$ ), 0.92 (s, 9 H,  $\text{CH}_3\text{CSi}$ ), 0.14 (s, 3 H,  $\text{CH}_3\text{Si}$ ), 0.09 (s, 3 H,  $\text{CH}_3\text{Si}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 220.30$  (C=O), 77.10 (C-2), 67.60 ( $\text{CH}_2\text{O}$ ), 48.13 (C-5), 28.68, 26.97, (C-3, C-4), 25.81 ( $\text{CH}_3\text{CSi}$ ), 20.26 ( $\text{CH}_3\text{-5}$ ), 18.43 ( $\text{CH}_3\text{CSi}$ ),  $-4.51$ ,  $-4.99$ , ( $\text{CH}_3\text{Si}$ ). HRMS (ESI) calcd. for  $\text{C}_{13}\text{H}_{26}\text{O}_3\text{Si}$  [ $\text{M} + \text{H}$ ] $^+$ : 259.1724 and [ $\text{M} + \text{Na}$ ] $^+$ : 281.1543; found 259.1721 and 281.1535. B: The sample of cyclopentanone **8** with almost the same characteristics (m.p., optical rotation and NMR spectra) was prepared by similar procedure from oxime **7b** in the yield 50%.

## Acknowledgements

This work was supported by the Russian Foundation for Basic Research (Project No. 13-03-00197).

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