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Epoxy Derivatives of {(5-[(1-Phenylethyl)aminocarbonyl]-cyclopent-2-en-1-yl}methyl Acetates

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Abstract—Diastereoisomeric [(1*R*,5*S*)-5-{[(1*R*)-1-phenylethyl]aminocarbonyl}cyclopent-2-en-1-yl]methyl acetate and [(1*S*,5*R*)-5-{[(1*R*)-1-phenylethyl]aminocarbonyl}cyclopent-2-en-1-yl]methyl acetate reacted with *m*-chloroperoxybenzoic acid to give the corresponding stereoisomeric α- and β-epoxy derivatives, which were identified on the basis of their spectral parameters.

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In the preceding communication we described the synthesis of individual bicyclic hydroxy lactams **Ia** and **Ib** [1] from readily accessible dichlorobicyclobutanone derivative **II** and (+)-α-methylbenzylamine (Scheme 1). Chiral functionalized cyclopentene building blocks are increasingly used in target-oriented syntheses [2–4]. In the present work we examined epoxidation of compounds **Ia** and **Ib** with *m*-chloroperoxybenzoic acid. It is known that the synthetic potential of epoxy compounds, especially cyclic ones, is very broad (isomerization, nucleophilic cleavage, electrophile-promoted rearrangements, etc. [5–7]), so that versatile functionalization of the cyclopentene fragment in **Ia** and **Ib** becomes possible.

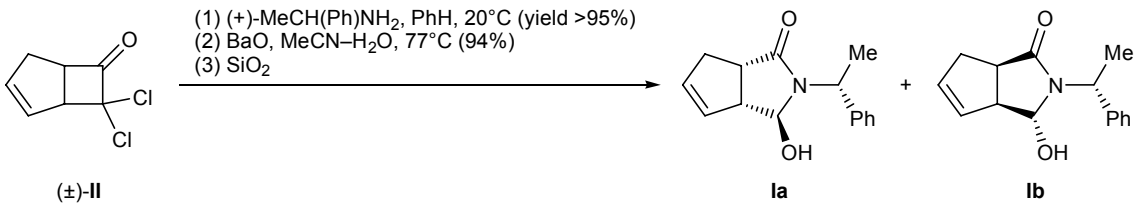
However, epoxidation of **Ia** and **Ib** was not selective. Therefore, compounds **Ia** and **Ib** were reduced with sodium tetrahydridoborate, and alcohols **IIIa** and **IIIb** thus obtained were converted into acetates **IVa** and **IVb** that are more convenient to handle with (Scheme 2).

Acetates **IVa** and **IVb** smoothly and rapidly reacted with *m*-chloroperoxybenzoic acid to produce two couples of stereoisomeric epoxides **V**/**VI** and **VII**/**VIII** (Scheme 3); in each couple, the more polar stereoisomer slightly prevailed (~8 : 7). Compounds **V** and **VI**, as well as **VII** and **VIII**, were characterized by anomalously strongly different R_f values, and they were readily separated by column chromatography on silica gel.

Although allylic BocNH and trichloroacetamide groups, as well as homoallylic hydroxy group, are known to act as *cis* directors in the epoxidation of cyclopentene systems with *m*-chloroperoxybenzoic acid [8–10], the corresponding effect in dihomoallylic amides **IVa** and **IVb** is insignificant. Presumably, the stereoselectivity in the epoxidation of **IVa** and **IVb** is determined not only by the effect of heteroatom but also by steric factors, which act in the opposite directions.

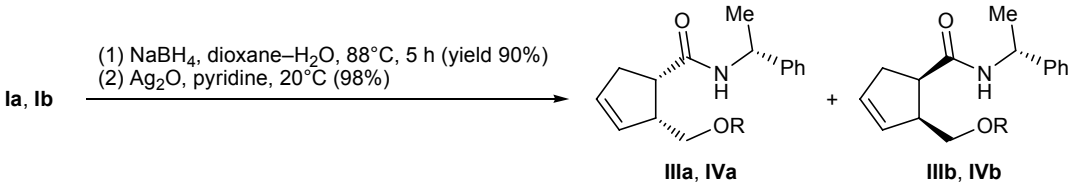
The structures of stereoisomeric epoxy derivatives **V**/**VI** and **VII**/**VIII** were assigned on the basis of their ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR spectrum of *cis*-epoxide **V**, the 2-H signal (δ 3.03 ppm) is located in a weaker field (see figure) than the corresponding

Scheme 1.



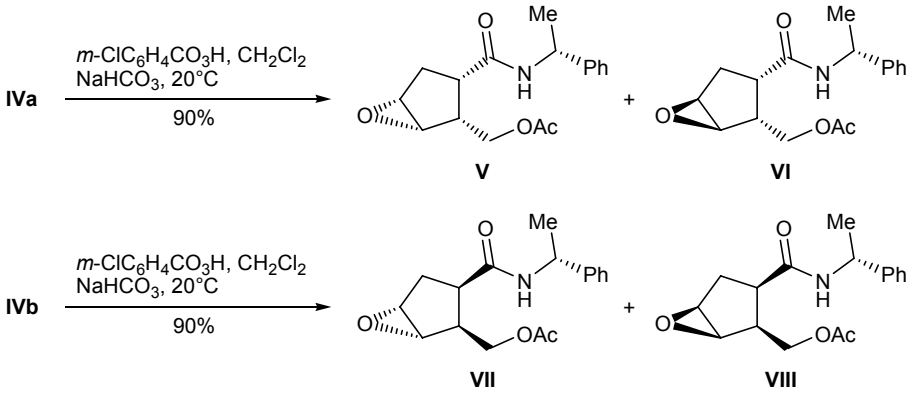
(±)-**II** **Ia** **Ib**

Scheme 2.

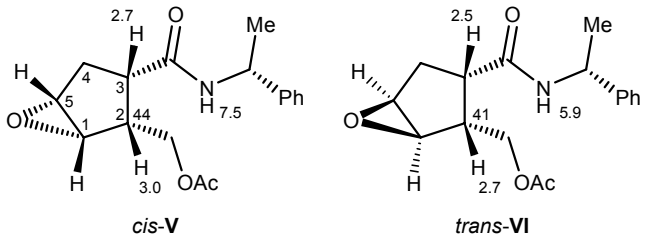


III, R = H; **IV**, R = Ac.

Scheme 3.



signal of isomeric *trans*-epoxide **VI** (δ 2.70 ppm). This is the result of through-space electron-withdrawing effect of the oxirane oxygen atom on the vicinal 2-H proton in *trans* isomer **VI**. Shielding effect of the oxirane oxygen atom on the vicinal *cis*-proton is also reflected in the chemical shift of C^2: δ_C 44 and 31 ppm for *cis*-**V** and *trans*-**VI**, respectively. The same applies to diastereoisomer couple **VII**/**VIII**. Furthermore, the amide NH proton in *cis*-epoxides **V** and **VIII** resonates in a weaker field (δ ~7.5 ppm) as compared to *trans* isomers **VI** and **VII** (δ ~5.9 ppm). The downfield position of the amide proton signal in the spectra of *cis*-epoxides **V** and **VIII** isomers is likely to be related to its participation in intramolecular hydrogen bond with the oxygen atom; no analogous hydrogen bonding is possible in *trans*-epoxides **VI** and **VII**. Finally, anomalously large difference in the R_f values of the *cis* and *trans* isomers may be rationalized in terms of higher polarity of the former and their better sorption on silica gel surface due to arrangement of functional groups at one side of the five-membered ring.



Chemical shifts of some protons in the ^{1}H NMR spectra of isomeric compounds *cis*-**V** and *trans*-**VI**.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples prepared as thin films or dispersions in mineral oil. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer at 300 and 75.47 MHz, respectively, using $CDCl_3$ as solvent and tetramethylsilane as internal reference. The mass spectra were obtained on a Shimadzu LCMS-2010 EV instrument (samples were introduced as solutions in ethanol). Thin-layer chromatography was performed on Sorbfil plates. The optical rotations were measured on a Perkin–Elmer 241 MS polarimeter. The purity of the products was checked by GLC on a Chrom 5 chromatograph.

Compounds Ia and Ib. A solution of 1.09 g (9 mmol) of (+)-α-methylbenzylamine in 10 ml of benzene was added to a solution of 1.5 g (8.5 mmol) of dichloro ketone **II** in 40 ml of benzene, and the mixture was stirred for 4 h at room temperature, the progress of the reaction being monitored by TLC. The mixture was evaporated, and the precipitate was washed with hexane. We thus isolated 2.4 g (95%) of a mixture of diastereoisomers **Ia** and **Ib** as yellow

crystals. The product was dissolved in 50 ml of acetonitrile, a solution of 3.7 g (24 mmol) of barium oxide in 15 ml of water was added, and the mixture was stirred for 20 h on heating under reflux (TLC). The organic solvent was distilled off, and the aqueous phase was extracted with ethyl acetate (3×45 ml). The extracts were combined, dried over $MgSO_4$, and evaporated under reduced pressure, and the residue was subjected to chromatography on silica gel using petroleum ether–ethyl acetate (7:3) as eluent.

(3*S*,3a*R*,6a*S*)-3-Hydroxy-2-[(1*R*)-phenylethyl]-3,3a,6,6a-tetrahydrocyclopenta[*c*]pyrrol-1(2*H*)-one (Ia). Yield 0.9 g (46%), colorless crystals, mp 120–121°C, $[\alpha]_D^{20}$ = +37.8° (*c* = 0.8, MeOH). IR spectrum, ν, cm^{-1}: 3244 (OH), 2922, 2852, 1651 (C=O), 1616, 1456, 1336, 1303, 1273, 1222, 1058, 805, 698. ^{1}H NMR spectrum, δ, ppm: 1.56 d (3H, CH_3, *J* = 5.7 Hz), 2.15–2.35 br.s (1H, OH), 2.54–2.84 m (2H, 6-H), 3.13–3.24 m (1H, 3a-H), 3.23 t (1H, 6a-H, *J* = 7.08 Hz), 5.06–5.17 br.s (1H, 3-H), 5.35 q (1H, C**H**Ph, *J* = 7.05 Hz), 5.59–5.67 m (1H, 5-H), 5.75–5.85 m (1H, 4-H), 7.20–7.54 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 17.05 (CH_3), 35.64 (C^6), 42.85 (C^{6a}), 49.94 (**C**HPh), 53.32 (C^{3a}), 84.38 (C^3), 126.96, 127.23, 128.07 (Ph), 128.73 (C^5), 132.65 (C^4), 141.21 (Ph), 177.35 (C=O). Mass spectrum (APCI), *m*/*z* (I_{rel}, %): 244 $[M + H]^+$ (100), 226 (43), 198 (33.3), 177 (16.7), 161 (15), 121 (11.7), 93 (16.7), 65 (8.3). Found, %: C 73.97; H 6.63; N 5.35. $C_{15}H_{17}NO_2$. Calculated, %: C 74.07; H 6.70; N 5.76.

(3*R*,3a*S*,6a*R*)-3-Hydroxy-2-[(1*R*)-phenylethyl]-3,3a,6,6a-tetrahydrocyclopenta[*c*]pyrrol-1(2*H*)-one (Ib). Yield 0.92 g (47%), yellow crystals, mp 105–107°C, $[\alpha]_D^{20}$ = +142.4° (*c* = 0.65, MeOH). IR spectrum, ν, cm^{-1}: 3232, 2922, 2852, 1647, 1456, 1327, 1290, 1215, 1058, 802, 702. ^{1}H NMR spectrum, δ, ppm: 1.68 d (3H, CH_3, *J* = 6.8 Hz), 2.54–2.84 m (2H, 6-H), 3.21–3.33 m (1H, 3a-H), 3.39 t (1H, 6a-H, *J* = 9.08 Hz), 3.73–4.03 br.s (1H, OH), 4.63–4.73 br.s (1H, 3-H), 5.34 q (1H, C**H**Ph, *J* = 7.05 Hz) 5.33–5.49 m (1H, 5-H), 5.72–5.84 m (1H, 4-H), 7.13–7.35 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 18.66 (CH_3), 35.70 (C^6), 42.83 (C^{6a}), 49.96 (**C**HPh), 54.17 (C^{3a}), 84.83 (C^3), 127.316, 127.43, 128.40 (Ph), 128.61 (C^5), 132.30 (C^4), 139.79 (Ph), 177.27 (C=O). Mass spectrum (APCI), *m*/*z* (I_{rel}, %): 244 $[M + H]^+$ (100), 226 (39), 198 (35.3), 177 (13.7), 161 (18.1), 121 (12.8), 93 (13.2), 65 (9.3). Found, %: C 73.28; H 6.36; N 5.25. $C_{15}H_{17}NO_2$. Calculated, %: C 74.07; H 6.70; N 5.76.

(1*S*,2*R*)-2-Hydroxymethyl-*N*-[(1*R*)-1-phenylethyl]cyclopent-3-ene-1-carboxamide (IIIa). Compound **Ia**, 85 mg (0.35 mmol), was dissolved in 6 ml of aqueous dioxane (1:1), 130 mg (3.4 mmol) of sodium tetrahydridoborate was added, and the mixture was heated for 5 h under reflux (TLC), evaporated to a small volume, and extracted with methylene chloride (3×10 ml). The extracts were combined, dried over $MgSO_4$, filtered, and evaporated, and the residue was subjected to chromatography on silica gel using petroleum ether–ethyl acetate (1:1) as eluent. Yield 77 mg (90%), colorless crystals, mp 132–134°C, $[\alpha]_D^{20}$ = –1.8° (*c* = 1.05, MeOH). IR spectrum, ν, cm^{-1}: 3313 (OH, NH), 2945 (CH_3), 2852 (CH_3), 1643 (C=O), 1531, 1454 (CH_3), 1375 (CH_3), 1276, 1037, 764, 704, 547. ^{1}H NMR spectrum, δ, ppm: 1.55 d (3H, CH_3, *J* = 9.0 Hz), 2.44–2.86 m (2H, 5-H), 2.98–3.10 t (2H, 2-H, 1-H, *J* = 6.0 Hz), 3.53–3.74 m (3H, CH_2OH), 5.19 quint (1H, C**H**Ph, *J* = 7.5, 6.0 Hz), 5.58–5.65 m (1H, 4-H), 5.85–5.92 m (1H, 3-H), 6.01–6.12 m (1H, NH), 7.27–7.43 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 21.28 (CH_3), 36.64 (C^5), 47.48 (C^1), 49.07 (**C**HPh), 51.29 (C^2), 62.61 (CH_2O), 126.08, 127.43, 128.53 (Ph), 130.40 (C^4), 131.14 (C^3), 142.77 (Ph), 174.40 (C=O). Mass spectrum (APCI), *m*/*z* (I_{rel}, %): 246 $[M + H]^+$ (100), 228 (96.5). Found, %: C 72.85; H 7.56; N 5.49. $C_{15}H_{19}NO_2$. Calculated, %: C 73.47; H 7.76; N 5.71.

(1*R*,2*S*)-2-(Hydroxymethyl)-*N*-[(1*R*)-1-phenylethyl]cyclopent-3-ene-1-carboxamide (IIIb) was synthesized in a similar way from 130 mg (0.54 mmol) of compound **Ib**. Yield 116 mg (89%), colorless crystals, mp 115–117°C, $[\alpha]_D^{20}$ = +168.5° (*c* = 0.425, MeOH). IR spectrum, ν, cm^{-1}: 3261 (OH, NH), 2951 (CH_3), 2922, 2852 (CH_3), 1639 (C=O), 1556, 1454 (CH_3), 1375 (CH_3), 1232, 1056, 759, 748, 698. ^{1}H NMR spectrum, δ, ppm: 1.53 d (3H, CH_3, *J* = 9.0 Hz), 2.45–2.50 m (1H, 5-H), 2.70–2.80 m (1H, 5-H), 2.95–3.03 m (1H, 2-H), 3.05 t (1H, 1-H, *J* = 9.0 Hz), 3.41–3.61 m (3H, CH_2OH), 5.18 quint (1H, C**H**Ph, *J* = 7.5, 6.0 Hz), 5.55–5.61 m (1H, 4-H), 5.86–5.92 m (1H, 3-H), 6.04–6.12 m (1H, NH), 7.62–7.78 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 21.64 (CH_3), 36.79 (C^5), 47.49 (C^1), 49.08 (**C**HPh), 51.35 (C^2), 62.62 (CH_2O), 126.16, 127.45, 128.70 (Ph), 130.49 (C^4), 131.21 (C^3), 143.05 (Ph), 174.59 (C=O). Mass spectrum (APCI), *m*/*z* (I_{rel}, %): 246 $[M + H]^+$ (100), 228 (96.5). Found, %: C 73.15; H 7.67; N 5.49. $C_{15}H_{19}NO_2$. Calculated, %: C 73.47; H 7.76; N 5.71.

[(1*R*,5*S*)-5-{[(1*R*)-1-Phenylethyl]aminocarbonyl}-cyclopent-2-en-1-yl]methyl acetate (IVa). Compound **IIIa**, 400 mg (1.6 mmol), was dissolved in 15 ml of pyridine, 0.65 ml (6.4 mmol) of acetic anhydride was

added, and the mixture was stirred for 5 h (TLC). The mixture was evaporated under reduced pressure, and the residue was subjected to chromatography on silica gel using petroleum ether–ethyl acetate (1:1) as eluent. Yield 450 mg (98%), colorless crystals, mp 97–99°C, $[\alpha]_D^{20}$ = –56.2° (*c* = 1.0, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3325 (NH), 2962, 2860, 1739 (C=O), 1641 (C=O), 1525, 1454, 1377, 1236, 1033, 702. ^1H NMR spectrum, δ, ppm: 1.50 d (3H, C**H**$_3$CH, *J* = 5.7 Hz), 1.99 s (3H, CH_3CO), 2.38–2.48 m (1H, 4-H, *J* = 5.7 Hz), 2.71–2.82 m (1H, 4-H), 3.04 q (1H, 5-H, *J* = 9.1 Hz), 3.10–3.23 m (1H, 1-H), 4.05 d.d (1H, CH_2O, *J* = 5.7, 11.6 Hz), 4.20 d.d (1H, CH_2O, *J* = 5.8, 11.8 Hz), 5.13 quint (1H, C**H**Ph, *J* = 7.05), 5.58–5.64 m (1H, 3-H), 5.80–5.87 m (1H, 2-H), 5.99–6.13 br.s (1H, NH), 7.20–7.36 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 20.7 (**C**H_3CO), 21.6 (**C**H_3CH), 35.1 (C^4), 46.1 (C^1), 47.3 (C^5), 48.7 (**C**HPh), 64.9 (CH_2O), 126.2, 127.2, 128.6 (Ph), 129.8 (C^3), 131.7 (C^2), 143.1 (Ph), 170.7 (**C**OCH_3), 171.4 (CON). Mass spectrum (APCI), *m*/*z* (I_{rel}, %): 288 $[M + H]^+$ (100), 228 (91.5), 125 (2.1), 93 (2.0). Found, %: C 70.94; H 7.55; N 4.69. $C_{17}H_{21}NO_3$. Calculated, %: C 71.08; H 7.32; N 4.88.

[(1*S*,5*R*)-5-{[(1*R*)-1-phenylethyl]aminocarbonyl}-cyclopent-2-en-1-yl]methyl acetate (IVb) was synthesized in a similar way from 350 mg (1.4 mmol) of hydroxy amide **IIIb**. Yield 393 mg (98%), colorless crystals, mp 103–105°C, $[\alpha]_D^{20}$ = +135.6° (*c* = 1.075, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3292 (NH), 2953, 2852, 1728 (C=O), 1639 (C=O), 1548, 1456, 1377, 1255, 1240, 1041, 759, 719, 698. ^1H NMR spectrum, δ, ppm: 1.50 d (3H, C**H**$_3$CH, *J* = 4.76 Hz), 1.85 s (3H, CH_3CO), 2.46–2.56 d.d (1H, 4-H, *J* = 15.4, 5.48 Hz), 2.72–2.82 m (1H, 4-H), 3.05 q (1H, 5-H, *J* = 7.1 Hz), 3.13–3.21 m (1H, 1-H), 4.00 d.d (1H, CH_2O, *J* = 6.4, 11.6 Hz), 4.11 d.d (1H, CH_2O, *J* = 6.4, 11.8 Hz), 5.14 quint (1H, C**H**Ph, *J* = 7.15 Hz), 5.58–5.63 m (1H, 3-H), 5.83–5.86 m (1H, 2-H), 5.91–5.96 br.s (1H, NH), 7.23–7.37 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 20.7 (**C**H_3CO), 21.8 (**C**H_3CH), 35.4 (C^4), 46.2 (C^1), 47.2 (C^5), 48.8 (**C**HPh), 64.2 (CH_2O), 126.2, 127.3, 128.6 (Ph), 129.9 (C^3), 131.6 (C^2), 143.1 (Ph), 170.7 (**C**OCH_3), 171.5 (CON). Mass spectrum (APCI), *m*/*z* (I_{rel}, %): 288 $[M + H]^+$ (100), 228 (73.5), 125 (4.3), 93 (3.6). Found, %: C 71.02; H 7.15; N 4.71. $C_{17}H_{21}NO_3$. Calculated, %: C 71.08; H 7.32; N 4.88.

Compounds V and VI. A solution of 572 mg (3.3 mmol) of *m*-chloroperoxybenzoic acid and 272 mg (3.3 mmol) of sodium hydrogen carbonate in 10 ml of methylene chloride was added to a solution of 317 mg (1.3 mmol) of acetate **IVa** in 10 ml of methylene chloride. The mixture was stirred for 8 h at room temperature (TLC), washed with 15 ml of a saturated solution of $Na_2S_2O_3$ and 15 ml of a 5% aqueous solution of $NaHCO_3$, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was subjected to chromatography on silica gel using petroleum ether–ethyl acetate (1:1) as eluent.

{(1*S*,2*R*,3*S*,5*R*)-3-{[(1*R*)-Phenylethyl]aminocarbonyl}-6-oxabicyclo[3.1.0]hex-2-yl}methyl acetate (V). Yield 163 mg (48%), colorless crystals, mp 95–97°C, $[\alpha]_D^{20}$ = +49.9° (*c* = 0.875, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3288 (NH), 2953, 2924, 2852, 1735 (C=O), 1645 (C=O), 1521, 1458, 1377, 1240, 1037, 854, 704. ^1H NMR spectrum, δ, ppm: 1.45 d (3H, C**H**$_3$CH, *J* = 6.6 Hz), 1.98 s (3H, CH_3CO), 2.22 d.d.d (1H, 4-H, *J* = 1.25, 10.2, 14.0 Hz), 2.34 d.d (1H, 4-H, *J* = 1.2, 14.2 Hz), 2.71 t.d (1H, 3-H, *J* = 6.3, 10.2 Hz), 3.03 t.d (1H, 2-H, *J* = 1.5, 10.5 Hz), 3.47–3.59 m (1H, 5-H), 3.60–3.67 m (1H, 1-H), 4.01 d.d (1H, CH_2O, *J* = 9.1, 11.2 Hz), 4.14 d.d (1H, CH_2O, *J* = 6.4, 10.4 Hz), 4.99 quintet (1H, C**H**Ph, *J* = 6.95 Hz), 7.20–7.36 m (5H, Ph), 7.50 d (1H, NH, *J* = 6.95 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.6 (**C**H_3CO), 21.9 (**C**H_3CH), 32.3 (C^4), 42.6 (C^3), 44.2 (C^2), 48.8 (**C**HPh), 57.7 (C^5), 59.5 (C^1), 61.9 (CH_2O), 126.1, 127.1, 128.6 (Ph), 143.2 (Ph), 170.3 (**C**OCH_3), 171.9 (CON). Mass spectrum (APCI), *m*/*z* (I_{rel}, %): 304 $[M + H]^+$ (100), 244 (46.8). Found, %: C 67.24; H 6.55; N 4.27. $C_{17}H_{21}NO_4$. Calculated, %: C 67.33; H 6.93; N 4.62.

{(1*R*,2*R*,3*S*,5*S*)-3-{[(1*R*)-Phenylethyl]aminocarbonyl}-6-oxabicyclo[3.1.0]hex-2-yl}methyl acetate (VI). Yield 140 mg (42%), colorless crystals, mp 167–169°C, $[\alpha]_D^{20}$ = –14.1° (*c* = 0.871, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3298 (NH), 2953, 2924, 2852, 1743 (C=O), 1643 (C=O), 1554, 1458, 1377, 1228, 1041, 840, 700. ^1H NMR spectrum, δ, ppm: 1.50 d (3H, C**H**$_3$CH, *J* = 6.95 Hz), 2.04 s (3H, CH_3CO), 2.18 d.d.d (1H, 4-H, *J* = 1.2, 10.2, 16.1 Hz), 2.28 d.d (1H, 4-H, *J* = 1.8, 16.2 Hz), 2.57 t.d (1H, 3-H, *J* = 6.6, 9.1 Hz), 2.73 t.d (1H, 2-H, *J* = 2.1, 9.9 Hz), 3.44–3.55 m (2H, 5-H, 1-H), 3.97 d.d (1H, CH_2O, *J* = 8.3, 11.6 Hz), 4.23 d.d (1H, CH_2O, *J* = 6.3, 11.5 Hz), 5.11 quint (1H, C**H**Ph, *J* = 6.95 Hz), 5.87–6.00 br.s (1H, NH), 7.23–7.36 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 22.8 (**C**H_3CO), 23.6 (**C**H_3CH), 30.9 (C^4), 42.2 (C^3), 41.3 (C^2), 50.0 (**C**HPh), 56.9 (C^5), 58.3 (C^1), 62.5 (CH_2O), 124.5, 125.8, 127.0 (Ph), 143.5 (Ph), 169.6 (**C**OCH_3), 170.3 (CON). Mass spectrum (APCI), *m*/*z* (I_{rel}, %): 304 $[M + H]^+$ (100), 244 (83.2). Found, %: C 66.99; H 6.67; N 4.35. $C_{17}H_{21}NO_4$. Calculated, %: C 67.33; H 6.93; N 4.62.

Compounds **VII** and **VIII** were synthesized in a similar way from 420 mg (1.46 mmol) of **IVb**.

{(1*S*,2*S*,3*R*,5*R*)-3-{[(1*R*)-Phenylethyl]aminocarbonyl}-6-oxabicyclo[3.1.0]hex-2-yl]methyl acetate (VII). Yield 190 mg (43%), colorless crystals, mp 143–145°C, $[\alpha]_D^{20}$ = +114.2° (*c* = 0.9, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3296 (NH), 2952, 2922, 2851, 1746 (C=O), 1641 (C=O), 1554, 1458, 1377, 1226, 1039, 826, 700. ^{1}H NMR spectrum, δ, ppm: 1.48 d (3H, C**H**$_3$CH, *J* = 6.95 Hz), 1.96 s (3H, CH_3CO), 2.16 d (2H, 4-H, *J* = 8.76 Hz), 2.57 q (1H, 3-H, *J* = 8.6 Hz), 2.70 t.d (1H, 2-H, *J* = 4.9, 8.1 Hz), 3.44–3.47 m (1H, 5-H), 3.52–3.57 m (1H, 1-H), 3.86 d.d (1H, CH_2O, *J* = 8.5, 11.5 Hz), 4.06 d.d (1H, CH_2O, *J* = 4.8, 11.8 Hz), 5.10 quint (1H, C**H**Ph, *J* = 7.25 Hz), 5.87–5.99 br.s (1H, NH), 7.24–7.38 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 20.7 (**C**H_3CO), 21.8 (**C**H_3CH), 29.3 (C^4), 40.8 (C^3), 41.2 (C^2), 49.0 (**C**HPh), 56.0 (C^5), 58.0 (C^1), 61.8 (CH_2O), 126.1, 127.4, 128.7 (Ph), 143.0 (Ph), 169.8 (**C**OCH_3), 170.5 (CON). Mass spectrum (APCI), *m*/*z* (I_{rel}, %): 304 $[M + H]^+$ (100), 244 (89.3). Found, %: C 67.03; H 6.65; N 4.34. $C_{17}H_{21}NO_4$. Calculated, %: C 67.33; H 6.93; N 4.62.

{(1*R*,2*S*,3*R*,5*S*)-3-{[(1*R*)-Phenylethyl]aminocarbonyl}-6-oxabicyclo[3.1.0]hex-2-yl}methyl acetate (VIII). Yield 211 mg (47%), colorless crystals, mp 100–102°C, $[\alpha]_D^{20}$ = +51.2° (*c* = 0.9, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3234 (NH), 2953, 2924, 2852, 1733 (C=O), 1646 (C=O), 1526, 1377, 1236, 1033, 849, 710. ^{1}H NMR spectrum, δ, ppm: 1.50 d (3H, C**H**$_3$CH, *J* = 6.89 Hz), 2.08 s (3H, CH_3CO), 2.18 d.d (1H, 4-H, *J* = 10.2, 16.3 Hz), 2.28 d.d (1H, 4-H, *J* = 1.8, 16.2 Hz), 2.79 t.d (1H, 3-H, *J* = 6.7, 9.7 Hz), 3.04 t.d (1H, 2-H, *J* = 2.1, 9.8 Hz), 3.66 s (2H, 5-H, 1-H), 4.27 d.d (1H, CH_2O, *J* = 9.2, 11.0 Hz), 4.40 d.d (1H, CH_2O, *J* = 6.2, 11.4 Hz), 5.00 quint (1H, C**H**Ph, *J* = 7.29 Hz), 7.22–7.36 m (5H, Ph), 7.55 d (1H, NH, *J* = 7.55 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.7 (**C**H_3CO), 22.3 (**C**H_3CH), 32.2 (C^4), 42.5 (C^3), 44.3 (C^2), 48.8 (**C**HPh), 57.7 (C^5), 59.5 (C^1), 61.5 (CH_2O), 125.9, 127.0, 128.6 (Ph), 143.6 (Ph), 170.6 (**C**OCH_3), 171.6 (CON). Mass spectrum (APCI), *m*/*z* (I_{rel}, %): 304 $[M + H]^+$ (100), 244 (66.7). Found, %: C 67.12; H 6.72; N 4.55. $C_{17}H_{21}NO_4$. Calculated, %: C 67.33; H 6.93; N 4.62.

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