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Highly Diastereoselective Metal-Free Catalytic Synthesis of Drug-Like Spiroimidazolidinone

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Abstract—A four-step procedure has been developed for the synthesis of (*S*)-3-isopropyl-1-[(*R*)-1-phenylethyl)-1,4-diazaspiro[4.5]decan-2-one with high diastereoselectivity (up to 95% *de*) from (*S*)-α-aminoisovaleric acid (L-valine). Quantum chemical computations of the synthesized compound have been performed using Gaussian 09 software package.

Keywords: spiroimidazolidinone, L-valine, catalysis, diastereoselectivity, DFT quantum chemical computations, B3LYP/6-31G(*d*).

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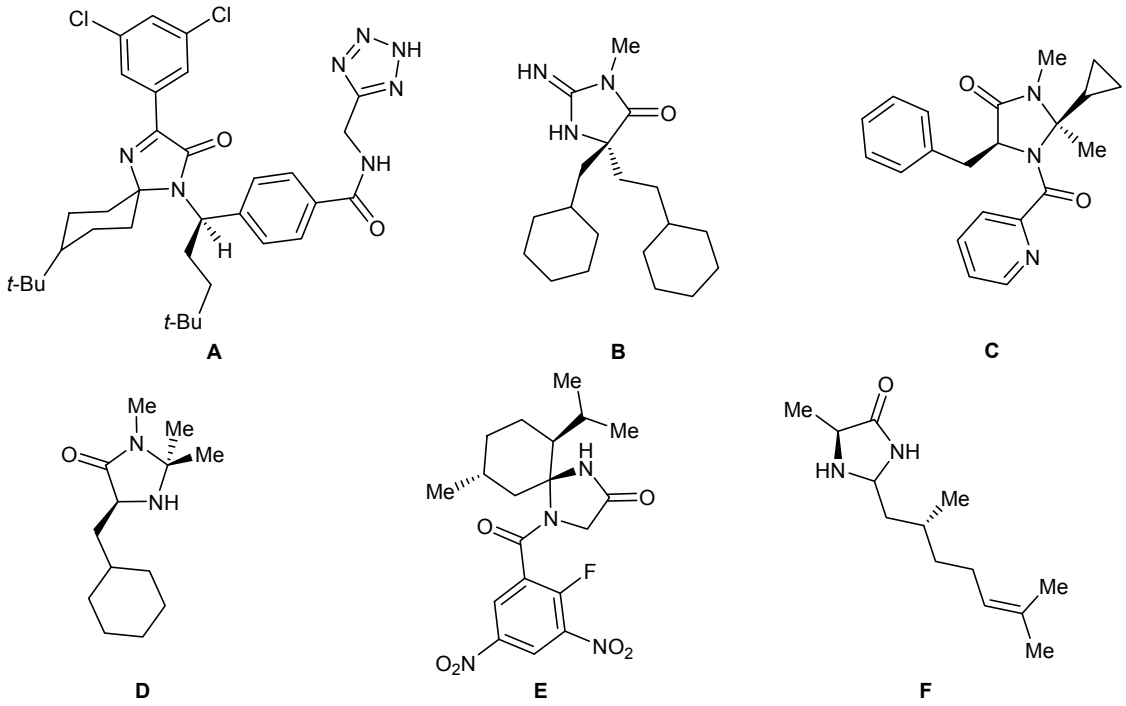
The design and synthesis of cyclic amides are a major perspective for the exploration and understanding of their applications [1]. Cyclic amides whose active centers contain amino acids with primary amino substructure are used as natural catalysts for the synthesis of carbohydrates [2, 3]. Chiral α-amino acids are fundamentally important structures in diverse applications [4]. A wide range of synthetic methods have been developed over the last decades to provide access to not only naturally occurring α-amino acids and their enantiomers [5, 6] but also to unnatural amino acid derivatives [7]. Amino acids and their derivatives such as amides (peptides) are widely used as organocatalysts [8–15]. A cyclic amide moiety, particularly imidazolidinone, is present in many biologically active natural products and pharmaceutically important compounds [16]. Examples are spiroimidazolones **A** [antagonist of human glucagon receptor (hGCGR)] [17] and **B** [BACE1 (β-secretase) inhibitor for the treatment of Alzheimer's disease] [18]. Diastereoisomeric imidazolidinones have been studied as a core unit of many pharmacological agents [19–22]. Chiral imidazolidinones **C** [23] and **D** [24] are successfully used in aminocatalysis, and imidazolidinone **E** is an analog of Sanger and Marfey reagents for analysis of D- and L-amino acids [25]. The imidazolidinone scaffold offers many opportunities for tuning and modification of steric requirements with regard to stereochemistry of a catalytic system like **F** [26] which has been tested as fragrance delivery system.

The construction of a quaternary stereogenic center in imidazolidinones seems to be a challenging problem, which is evidenced by increased interest from synthetic organic chemists over the last 10 years [27, 28]. Asymmetric synthetic strategies ranging from classical diastereoselective auxiliary-controlled methods to modern approaches involving enantioselective catalysis have been reported. These methods include allylic substitution [29], conjugate addition [30–32], and nucleophilic allylation [33, 34].

Therefore, search for efficient methodologies for the synthesis of imidazolidinone derivatives with specific biological activities has been undertaken [35]. The developed methods for the synthesis of imidazolidinones from chiral α-amino acids involve the use of amidophosphane precatalysts [36, 37]. Different reagents were utilized for the synthesis of disubstituted chiral *N*-aryl and *N*-alkylamines (including α- and β-amino acids) which can be further converted to differently functionalized imidazolidinones. The direct coupling reaction is one of the most common reactions for C–C and C–N bond formation [38–40].

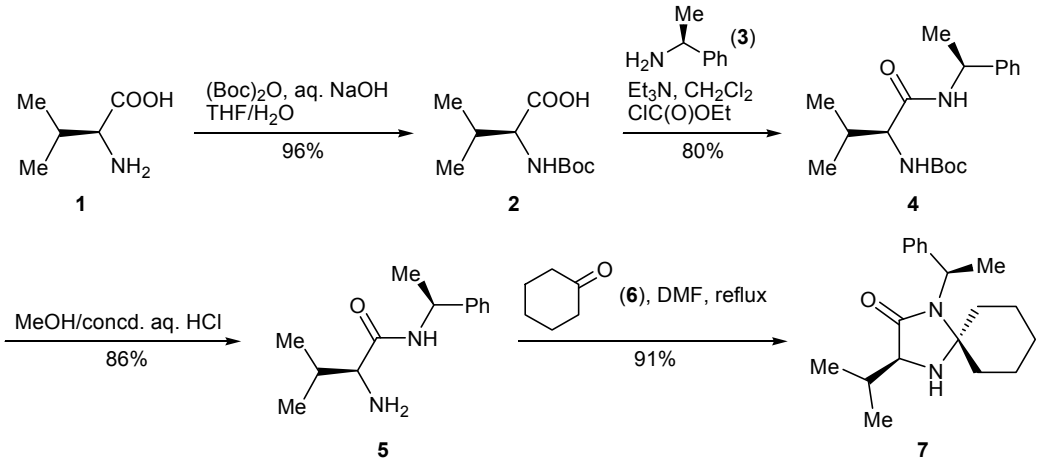


Much effort has been devoted to the development of highly asymmetric coupling reactions both in metal [41] and metal-free catalytic conditions [42, 43]. The coupling of different Boc-protected amino acids with primary amines under controlled conditions provides required intermediates [44] in high yields, and the Boc protecting group can be directly removed to afford chiral amines [45–48].

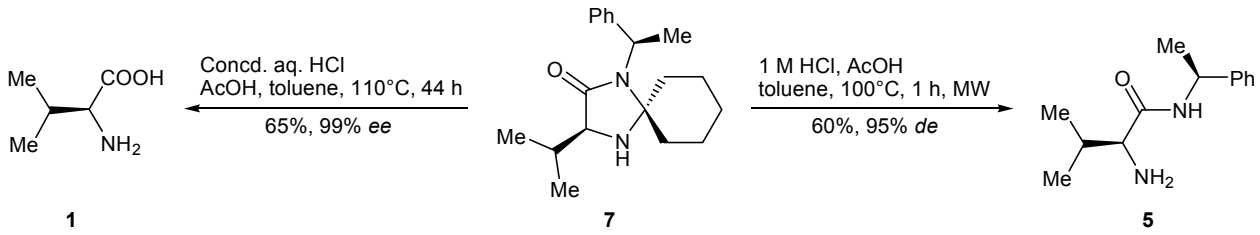
In this work, we focused on the synthesis of imidazolidinone heterocycle as a chiral auxiliary starting from an amino acid (Scheme 1). For this purpose, L-valine (**1**) was protected with Boc anhydride to obtain chiral protected amino acid **2**. Amino acid **2** was coupled with chiral amine **3** to afford compound **4** which was deprotected by treatment with concentrated aqueous HCl in methanol, and intermediate **5** thus formed was cyclized with cyclohexanone (**6**) to desired spiroimidazolidinone **7**. The diastereoisomeric purity of **7** was estimated at 95% *de* by chiral HPLC.

Chiral amino acid **1** (L-valine) was obtained from imidazolidinone **7** under harsh acidic conditions (110°C, 44 h) without loss of enantiomeric excess (99% *ee*) (Scheme 2). (*S*)-2-Amino-3-methyl-*N*-[(*S*)-1-phenylethyl]butanamide (**5**) can be generated in moderate yield from imidazolidinone **7** through cleavage of the N–C bond in the presence of 1 M aqueous HCl under microwave irradiation for only 1 h at 100°C (96% *de*).

Scheme 1.



Scheme 2.



The electronic structure of spiroimidazolidinone **7** was analyzed by quantum chemical calculations with the help of Gaussian 09 software package. Geometry optimization was carried out at the DFT level in the B3LYP/6-31G(*d*) approximation. The energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and molecular electrostatic potential (MEP) of **7** were analyzed. The HOMO and LUMO surfaces are shown in Fig. 1. The HOMO (E_{HOMO} = –5.93 eV) is localized mostly on the imidazolidinone heterocycle, while the LUMO (E_{LUMO} = –0.41 eV) is localized on the benzene ring. The energy gap is 5.44 eV, which makes the molecule more stable toward ionization.

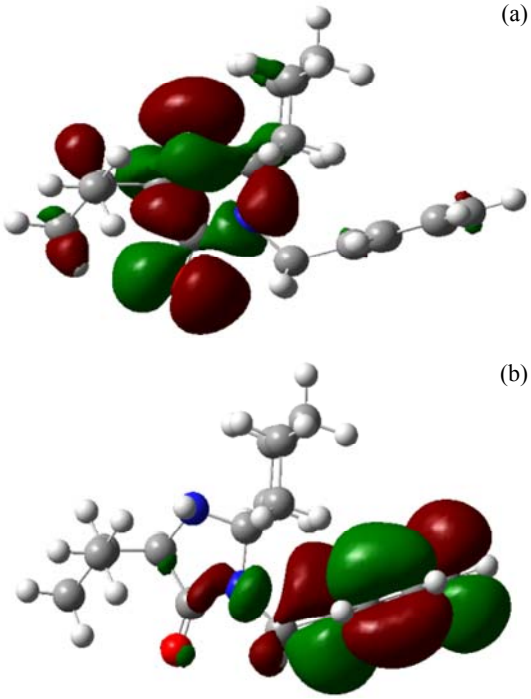


Fig. 1. (a) HOMO and (b) LUMO structures of imidazolidinone **7**.

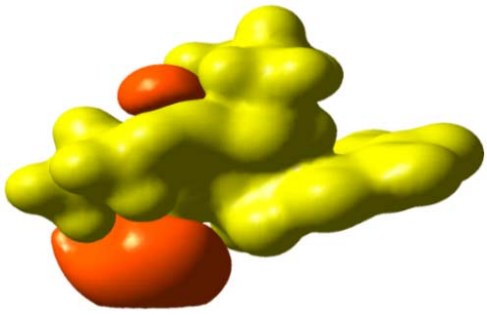


Fig. 2. MEP map of imidazolidinone **7** molecule; negative region is shown in red, and positive, in yellow.

The molecular electrostatic potential (MEP) map [49–51] of **7** was constructed for the most stable conformer at the same level of theory [DFT B3LYP/6-31G(*d*)]. Figure 2 shows two negative regions, one of which is near the carbonyl oxygen atom and the other is near the NH nitrogen atom. These two regions are nucleophilic, and they tend to form hydrogen bonds by accepting hydrogen atoms from nearest donor counterparts. Out of these, electrostatic potential shows positive regions. Thus, there are many regions that can be involved in interactions with various targets.

In summary, a novel drug-like imidazolidinone has been synthesized from a chiral amino acid (L-valine) and (*S*)-(–)-α-methylbenzylamine in a good yield (91%) with high diastereoselectivity (up to 95% *de*). Quantum chemical calculations, including molecular orbital and electrostatic potential map analysis, have been performed to elucidate features of its probable binding to specific sites (biological targets) of proteins, nucleic acids, receptors, and enzymes.

EXPERIMENTAL

All solvents and starting materials were purchased from Sigma–Aldrich. All reactions were carried out in a nitrogen atmosphere. The ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker AV-400 spectrometer at 400 and 100.5 Hz, respectively, using chloroform-*d* as solvent and reference (δ 7.26 ppm, δ_C 77.16 ppm). The melting points were measured in capillary tubes with a Gallenkamp melting point apparatus and are uncorrected. The high-resolution mass spectra (electrospray ionization) were re-

corded using a Waters Micromass LCT instrument. The IR spectra were recorded in the range 4000–700 cm^{-1} on a Perkin Elmer Paragon 100 FTIR spectrophotometer. Microwave-assisted reactions were accomplished using a Smith Creator™ EXP reactor and Smith process vials™ (Sheffield, UK). The products were purified by flash column chromatography on silica gel 60 (230–400 mesh). HPLC analyses were carried out using an Alltima C18 column (4.6 mm× 250 mm, 3 μm); 5–95% MeCN/0.1% aqueous TFA (10 min), then hold 6 min; UV detection at λ 256 nm; room temperature. The optical rotations were measured at λ 589 nm. Analytical TLC was performed using plates precoated with silica gel 60 UV 254 nm; spots were visualized by treatment with aqueous potassium permanganate and under UV light.

(*S*)-2-[(*tert*-Butoxycarbonyl)amino]-3-methylbutanoic acid (2) [52–54]**.** An aqueous solution of 2.5 g (63.8 mmol) of sodium hydroxide was added to a solution of 2.5 g (21.2 mmol) of (*S*)-α-aminoisovaleric acid (**1**) in 50 mL of THF, and 5.1 g (23.4 mmol) of Boc anhydride was then added. The mixture was stirred for 14 h at room temperature, acidified with 1 N aqueous HCl, and extracted with ethyl acetate (3×25 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. Yield 4.4 g (96%), oily mate-rial, $[\alpha]_D^{20}$ = –9.6° (*c* = 1, DMF). IR spectrum, ν, cm^{-1}: 3446–3289 br (O–H), 2936 (C–H), 2861 (C–H), 1715 s (C=O). ^{1}H NMR spectrum, δ, ppm: 0.96 d (3H, CH_3, *J* = 6.8 Hz), 1.00 d (3H, CH_3, *J* = 6.8 Hz), 1.45 s (9H, *t*-Bu), 2.18–2.21 m (1H, CH), 4.24–4.27 m (1H, CH), 8.10 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 19.0, 28.3 (3C), 31.2, 58.4, 80.0, 155.8, 176.6. Mass spectrum: *m*/*z* 218.3436 $[M + H]^+$. $C_{10}H_{19}NO_4$. Calculated: *M* + H 218.3440.

***tert*-Butyl ((*S*)-3-methyl-1-oxo-1-{[(*S*)-1-phenylethyl]amino}butan-2-yl)carbamate 4** [55, 56]**.** Triethylamine, 2.8 mL (20.1 mmol), was added under nitrogen to a cold solution of 4.0 g (18.4 mmol) of acid **2** in 75 mL of methylene chloride. Ethyl chloroformate, 1.9 mL (20.1 mmol), was then slowly added, the mixture was stirred for 1 h at room temperature, 2.4 mL (18.4 mmol) of of (*S*)-(–)-α-methylbenzylamine was added, and the mixture was additionally stirred for 2 h at room temperature. The organic layer was washed with aqueous $NaHCO_3$ and brine, extracted with ethyl acetate, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude compound was purified by column chromatography (ethyl acetate–petroleum ether, 4:6; R_f 0.2). Yield 3.2 g (80%), white solid, mp 133–136°C, $[\alpha]_D^{20}$ = +27.4° (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3352 s (N–H), 3062 (C–H_{arom}), 2932 (C–H), 2861 (C–H), 1685 s (C=O), 1604 (C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.91 d (3H, CH_3, *J* = 6.6 Hz), 0.96 d (3H, CH_3, *J* = 6.6 Hz), 1.40 s (9H, *t*-Bu), 1.48 d (3H, CH_3, *J* = 6.8 Hz), 2.10–2.15 m (1H, CH), 4.42 d (1H, CH, *J* = 4.3 Hz), 5.04–5.11 m (1H, CH), 7.22–7.33 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 19.4, 21.9, 28.3 (3C), 30.5, 50.8, 63.3, 79.2, 125.7, 127.3, 128.6, 142.9, 155.9, 170.6. Mass spectrum: *m*/*z* 321.2178 $[M + H]^+$. $C_{18}H_{29}N_2O_3$. Calculated: *M* + H 321.2180.

(*S*)-2-Amino-3-methyl-*N*-[(*S*)-1-phenylethyl]-butanamide (5). A solution of 2.5 g (12.5 mmol) of carbamate **4** in 15 mL of methanol was cooled to 0°C, 1.3 mL (11.7 mmol) of 10 N aqueous HCl was added dropwise, and the mixture was stirred for 4 h at room temperature. The mixture was then evaporated under reduced pressure, and the residue was neutralized with aqueous $NaHCO_3$ and extracted with ethyl acetate. The ethyl acetate layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, and the crude product was purified by column chromatography (ethyl acetate–petroleum ether, 4:6; R_f 0.4). Yield 2.1 g (86%), gummy material, $[\alpha]_D^{20}$ = –115.4° (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3353 s (N–H), 3085 (C–H_{arom}), 3062 (C–H_{arom}), 2978 (C–H), 2881 (C–H), 1686 (C=O), 1614 (C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.87 d (3H, CH_3, *J* = 7.0 Hz), 1.01 d (3H, CH_3, *J* = 7.0 Hz), 1.31 br.s (2H, NH_2), 1.51 d (3H, CH_3 *J* = 6.8 Hz), 2.35 d.d (1H, CH, *J* = 6.9, 3.7 Hz), 3.24 d (1H, CH, *J* = 3.7 Hz), 5.16 d.t (1H, CH, *J* = 15.2, 6.9 Hz), 7.27–7.29 m (1H, H_{arom}), 7.33–7.36 m (2H, H_{arom}), 7.37 m (2H, H_{arom}), 7.36 d (1H, NH, *J* = 5.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 15.9, 19.7, 22.1, 30.8, 48.1, 60.0, 126.2 (C_{arom}), 127.2 (CH_{arom}), 128.6 (CH_{arom}), 143.4, 173.3. Mass spectrum: *m*/*z* 221.1654 $[M + H]^+$. $C_{13}H_{21}N_2O$. Calculated: *M* + H 221.1667.

(3*S*)-1-[(*R*)-1-Phenylethyl]-3-(propan-2-yl)-1,4-diazaspiro[4.5]decan-2-one (7). A mixture of 2.2 g (10.0 mmol) of **5** and 1.0 mL of cyclohexanone (**6**) in 15.0 mL of DMF was refluxed for 5 h. The mixture was concentrated on a rotary evaporator, and the residue was treated thrice with 10 mL of isopropyl alcohol, followed by evaporation, to remove DMF completely. The product was purified by flash chromatography on silica gel (ethyl acetate–petroleum ether, 4:6; R_f 0.3). Yield 2.0 g (91%), viscous oil. IR spectrum, ν, cm^{-1}: 3351 s (N–H), 3062 (C–H_{arom}), 3028 (C–H_{arom}), 2932 (C–H), 2861 (C–H), 1685 (C=O), 1638

(C=C_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 0.95 d (3H, CH_3, J = 6.8 Hz), 1.05 d (3H, CH_3, J = 6.9 Hz), 1.78–1.55 m (10H, CH_2) 1.85 d (3H, CH_3, J = 3.6 Hz), 2.20–2.16 m (1H, CH) 3.45 d (1H, CH, J = 3.7 Hz), 4.42 d.d (1H, CH, J = 14.2, 7.1 Hz), 7.23 t (1H, H_{arom}, J = 7.3 Hz), 7.31 t (2H, H_{arom}, J = 7.4 Hz), 7.45 d (2H, H_{arom}, J = 8.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.9, 19.2, 19.7, 23.1 (2C), 24.9, 37.7, 52.4 (2C, CH_2), 62.5 (CH), 78.6, 126.8, 128.2, 142.7 (CH), 178.4. Mass spectrum: m/z 301.2274 $[M + H]^+$. $C_{19}H_{28}N_2O$. Calculated: M + H 301.2276.

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CONFLICT OF INTERESTS

The authors declare no conflict of interests.

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