

# Reactions of *N*-Vinylpyrrolidone with Arenes under Superelectrophilic Activation Conditions

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**Abstract**—Reactions of *N*-vinylpyrrolidone (1-ethenylpyrrolidine-2-one) with arenes under the action of the Brønsted superacid CF<sub>3</sub>SO<sub>3</sub>H (triflic acid, TfOH) or strong Lewis acids AlX<sub>3</sub> (X = Cl, Br) at room temperature for 1.5 h afford *N*-(1-arylethyl)pyrrolidones as products of hydroarylation of the *N*-vinyl group in 11–85% yields. The key intermediate of this transformation is O,C-diprotonated form of *N*-vinylpyrrolidone, which is a highly reactive electrophile, according to DFT calculations. In the absence of arenes in TfOH, *N*-vinylpyrrolidone underwent devinylation to form NH-pyrrolidone.

**Keywords:** vinylpyrrolidone, pyrrolidone derivatives, triflic acid, hydroarylation, carbocations

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## INTRODUCTION

The pyrrolidine heterocyclic core is a part of many naturally occurring biologically active compounds such as nicotine, atropine, proline, hydroxyproline, and many others. Amount of pyrrolidine derivatives is especially high in carrots, tobacco leaves, and plants of the Solanaceae family. The pyrrolidone (pyrrolidine-2-one) structure is actively used in pharmacy for creation of nootropic drugs, the most famous of which is piracetam [1, 2].

However, up to 95% of all pyrrolidone produced in industry is used for the synthesis of just one compound, *N*-vinylpyrrolidone (1-ethenylpyrrolidine-2-one) **1** [3, 4] (Scheme 1). This substance is an important precursor and intermediate in the production of technological auxiliaries and additives. It is mainly used for the synthesis of polyvinylpyrrolidone and copolymers with vinyl acetate and methacrylate [3–9].

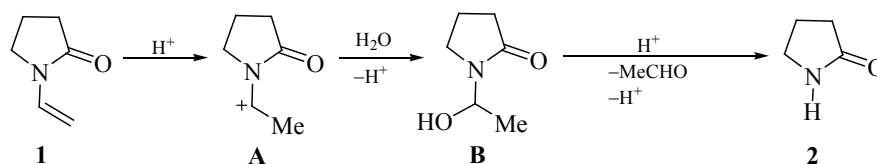
Pharmaceutical industry consumes a significant amount of the monomer **1** for the production of polyvinylpyrrolidone-iodine complex (Povidone-iodine), topical antiseptic and disinfectant with a wide spectrum of action [10]. *N*-Vinylpyrrolidone is used as a reactive

solvent for UV-curable polymers, in the production of inks, paints and adhesives, as well as an additive in the cosmetics industry due to its low toxicity and good solubility in water [4]. Thus, development of new methods for synthesis of pyrrolidone derivatives is an actual goal in organic chemistry, medicine, and materials science.

It was previously found that *N*-vinylpyrroles [11] and *N*-vinylpyrrolidone **1** [12, 13] were devinylated to furnish the corresponding NH derivatives under acid hydrolysis conditions. In [13], it was suggested that slow protonation of the carbon-carbon double bond of compound **1** occurred in Brønsted acids to give rise to carbocation **A**, which rapidly formed alcohol **B**. The latter was decomposed under the action of acid to give NH-pyrrolidone **2** and acetic aldehyde (Scheme 1).

However, up to the moment, reactions of *N*-vinylpyrrolidone **1** in low nucleophilic Brønsted superacids, trifluoromethanesulfonic (CF<sub>3</sub>SO<sub>3</sub>H, TfOH) and fluorosulfonic (FSO<sub>3</sub>H) acids, have not been investigated. Based on our previous work on the electrophilic hydroarylation of carbon-carbon double bond conjugated with heterocyclic system or included in it [14–19], we undertook this study on transformations

Scheme 1.



of *N*-vinylpyrrolidone **1** under the superelectrophilic activation conditions.

The main objectives of this work were to generate reactive cationic intermediates from *N*-vinylpyrrolidone **1** under the action of Brønsted superacids TfOH, FSO<sub>3</sub>H, strong Lewis acids AlX<sub>3</sub> (X = Cl, Br), as well as acidic zeolites in order to involve cations in reactions with aromatic nucleophiles; and to study cations experimentally by NMR and theoretically by quantum chemical calculations using the density functional theory (DFT) method.

## RESULTS AND DISCUSSION

In the beginning, reaction of *N*-vinylpyrrolidone **1** with benzene under the action of various Brønsted and Lewis acids, and acidic zeolite was investigated (Table 1). Brønsted acids H<sub>2</sub>SO<sub>4</sub>, TfOH, or Lewis acids AlCl<sub>3</sub>, AlBr<sub>3</sub> at room temperature for 1.5–2 h led to *N*-(1-phenylethyl) pyrrolidone **3a**, as a product of hydrophenylation of C=C bond of the starting compound **1**. The highest yield of 85% of compound **3a** was achieved using AlCl<sub>3</sub> (Table 1, entry 3). In the reaction with acidic zeolite CBV-720, a devinylation of compound **1** was observed to form

pyrrolidone **2** in a small yield of 22% with significant amount of oligomeric material (entry 5).

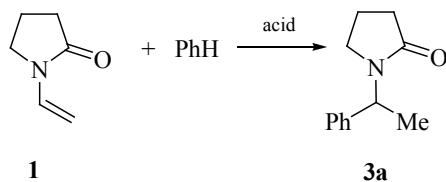
The reaction needs a use of an excess of benzene (or other arenes, see below in Table 2), since upon using of equivalent amounts of compound **1** and arenes a large amount of devinylation product, NH-pyrrolidone **2**, is formed.

Then reactions of *N*-vinylpyrrolidone **1** with other aromatic compounds (*o*-, *m*-, *p*-xylenes, anisole, veratrole, 1,2-dichlorobenzene) were carried out. It turned out that, unlike benzene, other arenes under the action of Lewis acids AlX<sub>3</sub> (X = Cl, Br) and sulfuric acid H<sub>2</sub>SO<sub>4</sub>, gave mixtures of oligomeric substances.

The corresponding compounds **3a–3j**, products of hydroarylation of C=C bond of compound **1**, were obtained in TfOH at room temperature for 1.5 h in total yields of regioisomers of 11–55% (Table 2, entries 1, 4, 7, 10, 12, 14). Decreasing reaction temperature down to –40°C in TfOH did not lead to an increase in yields of target compounds **3**, while a complete conversion of the starting substance **1** was achieved in 4 h (entries 2, 5, 8).

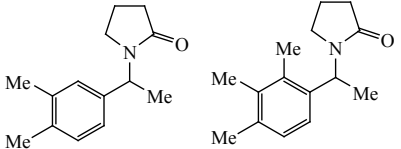
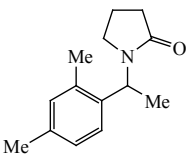
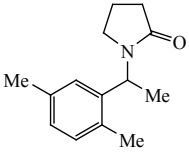
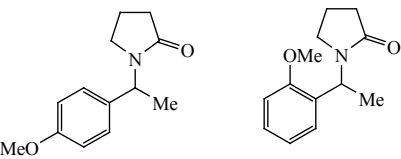
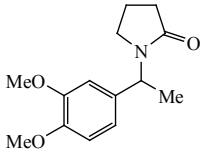
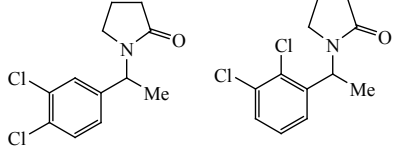
Carrying out this reaction in stronger acid FSO<sub>3</sub>H at –80°C (fluorosulfonation of aromatic moieties

**Table 1.** Reactions of *N*-vinylpyrrolidone **1** with benzene under the action of various Brønsted and Lewis acids, and acidic zeolite

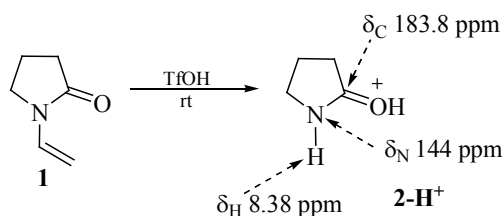


Entry	Benzene (equiv.)	Reaction conditions			Yield of <b>3a</b> , %
		acid (equiv.)	temperature, °C	time, h	
1	2	H <sub>2</sub> SO <sub>4</sub> (70)	20	2	53
2	3	TfOH (25)	20	1.5	60
3	45	AlCl <sub>3</sub> (6)	20	1.5	85
4	45	AlBr <sub>3</sub> (8)	20	1.5	78
5	60	Zeolite CBV-720 (5)	130	1	Pyrrolidone <b>2</b> (22%)

**Table 2.** Reactions of *N*-vinylpyrrolidone **1** with arenes in TfOH and FSO<sub>3</sub>H leading to 1-(1-arylethyl)pyrrolidine-2-ones **3a–3j**

Entry	Arene (equiv.)	Reaction conditions			Reaction products, yield (%)
		acid (equiv.)	<i>T</i> , °C	time, h	
1	<i>o</i> -Xylene (2)	TfOH (25)	20	1.5	 <b>3b</b> (30%) + <b>3c</b> (16%)
2	<i>o</i> -Xylene (2)	TfOH (25)	−40	4	<b>3b</b> (31%) + <b>3c</b> (15%)
3	<i>o</i> -Xylene (2.5)	FSO <sub>3</sub> H (38)	−80	1	<b>3b</b> (31%) + <b>3c</b> (15%)
4	<i>m</i> -Xylene (2)	TfOH (25)	20	1.5	 <b>3d</b> (50%)
5	<i>m</i> -Xylene (2)	TfOH (25)	−40	4	<b>3d</b> (20%)
6	<i>m</i> -Xylene (2.5)	FSO <sub>3</sub> H (38)	−80	1	<b>3d</b> (4%)
7	<i>p</i> -Xylene (2)	TfOH (25)	20	1.5	 <b>3e</b> (47%)
8	<i>p</i> -Xylene (2)	TfOH (25)	−40	4	<b>3e</b> (55%)
9	<i>p</i> -Xylene (2.5)	FSO <sub>3</sub> H (38)	−80	1	<b>3e</b> (14%)
10	Anisole (2)	TfOH (25)	20	1.5	 <b>3f</b> (37%) + <b>3g</b> (10%)
11	Anisole (2.5)	FSO <sub>3</sub> H (38)	−80	1	<b>3f</b> (5%) + <b>3g</b> (5%)
12	Veratrole (2)	TfOH (25)	20	1.5	 <b>3h</b> (29%)
13	Veratrole (2.5)	FSO <sub>3</sub> H (38)	−80	1	Oligomeric compounds
14	1,2-Dichlorobenzene (2)	TfOH (25)	20	1.5	 <b>3i</b> (7%) + <b>3j</b> (4%)

Scheme 2.



takes place at higher temperatures) required a shorter reaction time in 1 h. However, in most cases, yields of substances **3** were decreased due to the formation of a large number of oligomers (entries 3, 6, 9, 11, 13). Thus, the most effective acidic reagent for the hydroarylation of *N*-vinylpyrrolidone **1** was found to be the Brønsted superacid TfOH. It should be also noted that mixtures of electrophilic aromatic substitution regioisomers **3b**, **3c**, **3f**, **3g**, and **3i**, **3j** were obtained in reactions with *o*-xylene, anisole, and 1,2-dichlorobenzene, respectively (entries 1, 10, 14).

It should be noted that in all these reactions, a complete conversion of the starting compound **1** was achieved (Table 2). Under the access of arenes, the formation of NH-pyrrolidone **2** was not observed. These reactions were accompanied by the formation of oligomeric materials, that led to a decrease in the yields of target compounds **3**.

Investigation of protonation of *N*-vinylpyrrolidone **1** in TfOH at room temperature by means of NMR showed that cation **2-H<sup>+</sup>** was rapidly formed upon dissolving of substance **1** in TfOH in NMR tube. This cation is *O*-protonated form of NH-pyrrolidone **2**, which is obtained by devinylation of compound **1** (Scheme 2), similar to data of work [13] on this reaction in aqueous

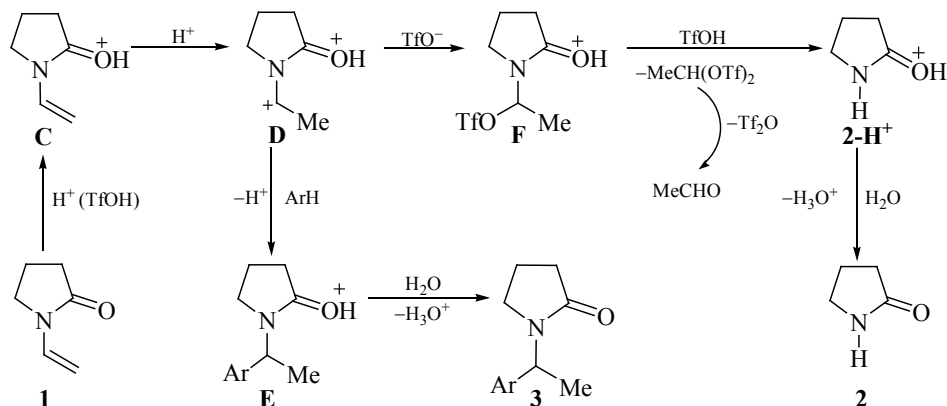
solutions of other Brønsted acids. In NMR experiments, we were not able to catch other intermediate cationic species.

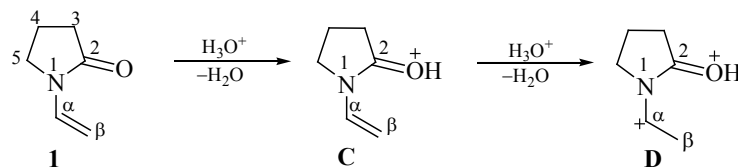
Based on the experimental data obtained (Tables 1 and 2, Scheme 2), the following mechanism of transformations of *N*-vinylpyrrolidone **1** in TfOH may be proposed (Scheme 3). Stepwise protonation of carbonyl oxygen and then carbon of the vinyl group gives rise to cations **C** (*O*-protonated form) and **D** (*O,C*-diprotonated form), respectively. In the presence of arenes, species **D** reacts via electrophilic substitution to form *O*-protonated form **E**, hydrolysis of the latter leads to hydroarylation product **3**. In the absence of aromatic nucleophiles, dication **D** reacts with triflate ion leading to species **F**, which eliminates acetaldehyde and is turned into *O*-protonated form of pyrrolidone **2-H<sup>+</sup>**, hydrolysis of the reaction solution finally results pyrrolidone **2** (Scheme 3).

Additionally, quantum chemical calculations using density functional theory (DFT) were carried out to evaluate electrophilic properties and reactivity of cations **C** and **D** generated upon protonation of *N*-vinylpyrrolidone **1**. Gibbs energies  $\Delta G_{298}$  of protonation reactions, electronic and orbital characteristics (charge distribution, HOMO–LUMO energies, contributions of atomic orbitals into LUMO, global electrophilicity index  $\omega$  [20]) were calculated (Table 3).

Calculation of Gibbs energies  $\Delta G_{298}$  of protonation reactions of compound **1** has revealed that the formation of species **C** is thermodynamically very favorable, since the value of  $\Delta G_{298}$  for the reaction **1**→**C** is  $-90.8$  kJ/mol. Further protonation of cation **C** with the formation of dication **D** is not so thermodynamically favorable,  $\Delta G_{298}$  value of the reaction **C**→**D** is  $14.7$  kJ/mol. However,

Scheme 3.



**Table 3.** Selected calculated (DFT) electronic characteristics of cations **C** and **D** generated upon protonation of vinylpyrrolidone **1**, and values of Gibbs energies of protonation reactions

Characteristic	C	D	Characteristic	C	D
$E_{\text{HOMO}}$ , eV	-7.66	-10.58	$q(\text{C}^\beta)$ , $e^b$	-0.36	-0.68
$E_{\text{LUMO}}$ , eV	-2.08	-5.12	$k(\text{N}^1)_{\text{LUMO}}$ , % <sup>c</sup>	1.7	2.5
$\omega$ , eV <sup>a</sup>	2.1	5.6	$k(\text{C}^2)_{\text{LUMO}}$ , % <sup>c</sup>	21.3	27.5
$q(\text{N}^1)$ , $e^b$	-0.40	-0.40	$k(\text{C}^\alpha)_{\text{LUMO}}$ , % <sup>c</sup>	2.4	28.6
$q(\text{C}^2)$ , $e^b$	0.75	0.88	$k(\text{C}^\beta)_{\text{LUMO}}$ , % <sup>c</sup>	3.8	1.5
$q(\text{C}^\alpha)$ , $e^b$	-0.02	0.43	$\Delta G_{298}$ , kJ/mol	<b>1</b> → <b>C</b> : -90.8	<b>C</b> → <b>D</b> : 14.7

<sup>a</sup> Global electrophilicity index  $\omega = (E_{\text{HOMO}} + E_{\text{LUMO}})^2 / 8(E_{\text{LUMO}} - E_{\text{HOMO}})$ .

<sup>b</sup> Natural charges.

<sup>c</sup> Contribution of atomic orbital into LUMO.

this value of the Gibbs energy is not so high, and the generation of species **D** may take place in superacid TfOH.

Dication **D** has a high electrophilicity index  $\omega$  of 5.6 eV (Table 3), i.e. it is a superelectrophile [21], and therefore it reacts easily and quickly with aromatic nucleophiles even at low temperatures of -80 and -40°C (Table 2). The high electrophilic properties of the cationic center  $\text{C}^\alpha$  in species **D** are determined by both charge [ $q(\text{C}^\alpha) = 0.43 e$ ] and orbital [ $k(\text{C}^\alpha)_{\text{LUMO}}$  28.6%] parameters.

It should be specially mentioned that, taking into account a great practical value of pyrrolidone derivatives as  $\gamma$ -lactam antibiotics [22], considerable attention is paid to the synthesis of medicinally relevant *N*-benzylpyrrolidones that are structurally similar to compounds **3**. The known synthetic approaches for preparation of these compounds are mainly based on multicomponent reactions [23–28] or Ni-catalyzed hydroarylation of *N*-vinylpyrrolidone [29].

## CONCLUSIONS

As a result of this work, a novel method for the synthesis of medicinally relevant *N*-(1-arylethyl)pyrrolidones was developed by hydroarylation of side chain N-carbon-carbon double bond of *N*-vinylpyrrolidone in its reaction with arenes under the action of superacid TfOH,  $\text{FSO}_3\text{H}$  or aluminum halogenides  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ .

## EXPERIMENTAL

NMR spectra of solutions of compounds in  $\text{CDCl}_3$  and  $(\text{CD}_3)_2\text{CO}$  were recorded on a Bruker AVANCE 500 spectrometers (at 500 and 125 MHz for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, respectively) or Bruker AVANCE III 400 (at 400 and 100 MHz for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, respectively) at 25°C. Chemical shifts of  $^{15}\text{N}$  nuclei were obtained from the  $^1\text{H}$ - $^{15}\text{N}$  HSQC and  $^1\text{H}$ - $^{15}\text{N}$  HMBC spectra recorded on a Bruker AVANCE III 400 spectrometer at 40 MHz for  $^{15}\text{N}$ . NMR spectra in TfOH were recorded on a Bruker AVANCE III 400 spectrometer (400 and 100 MHz for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, respectively) using  $\text{CH}_2\text{Cl}_2$  as an internal standard. Chromato-mass spectra (GC-MS) were recorded on a Bruker instrument. High-resolution mass spectra (HRMS) were recorded on a Bruker Maxis ESI-TOF instrument. The reaction progress was monitored by TLC on Silufol UV-254 plates with a UV indicator. Column chromatography was performed on Chemapol 40/100 silica gel (0.04–0.10 mm) or on Macherey-Nagel 60 silica gel (0.04–0.063 mm) using mixtures of petroleum ether–diethyl ether as an eluent. Preparative thin-layer chromatography was performed on a glass plate using Chemapol 5/40 silica gel (0.005–0.4 mm) with a UV indicator using mixtures of petroleum ether–diethyl ether as an eluent.

**DFT calculations.** All computations were carried out at the DFT/HF hybrid level of theory using hybrid

exchange functional B3LYP by using GAUSSIAN 2009 program packages [30]. The geometries optimization was performed using the 6-311+G(2d,2p) basis set (standard 6-311G basis set added with polarization (d,p) and diffuse functions). Optimizations were performed on all degrees of freedom and solvent phase optimized structures were verified as true minima with no imaginary frequencies. The Hessian matrix was calculated analytically for the optimized structures in order to prove the location of correct minima and to estimate the thermodynamic parameters. Solvent-phase calculations used the Polarizable Continuum Model (PCM, solvent—water).

**General procedure for the synthesis of *N*-(1-arylethyl)pyrrolidine-2-ones 3a–3j by reaction of *N*-vinylpyrrolidone 1 with arenes in TfOH.** *N*-Vinylpyrrolidone 1 (53 mg, 0.48 mmol) was added to a solution of arene (0.96 mmol, 2.0 equiv.; for benzene 112 mg, 1.44 mmol, 3.0 equiv.) in TfOH (1.0 mL, 25 equiv.). The resulting solution was stirred at room temperature for 1.5 h, then the reaction mixture was poured into water (50 mL). The reaction products were extracted with EtOAc (3 × 30 mL), the combined extracts are washed with water (2 × 30 mL), saturated aqueous solution of NaHCO<sub>3</sub> (30 mL), water (50 mL) and dried with Na<sub>2</sub>SO<sub>4</sub>. The combined extracts were concentrated in vacuum; the residue was subjected to chromatographic separation on silica gel by column or preparative thin-layer chromatography. Reaction of compound 1 with benzene was carried out in a similar way in sulfuric acid H<sub>2</sub>SO<sub>4</sub> at room temperature for 2 h as indicated in Table 1 (entry 1).

**General procedure for the synthesis of *N*-(1-arylethyl)pyrrolidine-2-ones 3b–3g by reaction of *N*-vinylpyrrolidone 1 with arenes in FSO<sub>3</sub>H.** Arene (1.56 mmol, 2.5 equiv.) was dissolved in FSO<sub>3</sub>H (1 mL, 38 equiv.) pre-cooled to –80°C; then solution of *N*-vinylpyrrolidone 1 (50 mg, 0.45 mmol) in dichloromethane (0.5 mL) was added. The resulting mixture was stirred at –80°C (dry ice-acetone bath) for 1 h. Then the reaction mixture was poured into HCl<sub>aq</sub> (15 mL) pre-cooled to –80°C. The reaction products were extracted with EtOAc (3 × 30 mL), the combined extracts were washed with water (2 × 30 mL), saturated aqueous solution of NaHCO<sub>3</sub> (30 mL), water (50 mL) and dried with Na<sub>2</sub>SO<sub>4</sub>. The combined extracts were concentrated in vacuum, the residue was subjected to chromatographic separation on silica gel by column or preparative thin-layer chromatography.

**General procedure for the synthesis of *N*-(1-phenylethyl)pyrrolidine-2-one 3a by reaction of *N*-vinylpyrrolidone 1 with benzene under the action of AlCl<sub>3</sub> or AlBr<sub>3</sub>.** *N*-Vinylpyrrolidone 1 (53 mg, 0.48 mmol) was added to a mixture of AlCl<sub>3</sub> (385 mg, 2.88 mmol) or AlBr<sub>3</sub> (1 g, 3.84 mmol) in benzene (2 mL) and stirred at room temperature for 1.5 h, then the reaction mixture was poured into water (50 mL). The reaction products were extracted with EtOAc (3 × 30 mL), the combined extracts were washed with water (2 × 30 mL), saturated aqueous solution of NaHCO<sub>3</sub> (30 mL), water (50 mL) and dried with Na<sub>2</sub>SO<sub>4</sub>. The combined extracts were concentrated in vacuum, the residue was subjected to chromatographic separation on silica gel by column or preparative thin-layer chromatography.

**Synthesis of pyrrolidone 2 from *N*-vinylpyrrolidone 1 under the action of zeolite CBV-720 in benzene.** A mixture of *N*-vinylpyrrolidone 1 (60 mg, 0.54 mmol), CBV-720 zeolite (449 mg) and benzene (3 mL) was heated at 130°C in a high-pressure glass tube for 1 h while stirring. After cooling to room temperature the resulting mixture was filtered through a Schott filter. The zeolite was boiled with methanol (10 mL) for 30 min, then filtered. The boiling and filtration of the zeolite was repeated twice more. The combined extracts were concentrated in vacuum, the residue was subjected to chromatographic separation on silica gel by column or preparative thin-layer chromatography.

**Pyrrolidin-2-one (2).** Yield 10 mg (22%), oil [31, 32]. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 500 MHz), δ, ppm: 2.08–2.13 m (2H, CH<sub>2</sub>), 2.26–2.29 m (2H, CH<sub>2</sub>), 3.38 t (2H, CH<sub>2</sub>, *J* 7.1 Hz), 6.50 s (1H, NH). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 125 MHz), δ<sub>C</sub>, ppm: 20.9, 30.1, 42.3, 179.3. Mass spectrum (HRMS-ESI), *m/z*: 86.0601 [*M* + H]<sup>+</sup> (calcd for C<sub>4</sub>H<sub>8</sub>NO: 86.0600).

***N*-(1-Phenylethyl)pyrrolidin-2-one (3a).** Yield 54 mg (60%) in TfOH, 77 mg (85%) using AlCl<sub>3</sub>, 71 mg (78%) using AlBr<sub>3</sub>, oil [23]. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz), δ, ppm: 1.51 d (3H, CH<sub>3</sub>, *J* 7.1 Hz), 1.87–1.98 m (2H, NCH<sub>2</sub>CH<sub>2</sub>), 2.38–2.44 m (2H, COCH<sub>2</sub>), 2.95–3.00 m (1H, NCHH), 3.29–3.33 m (1H, NCHH), 5.48 q (1H, PhCH, *J* 7.1 Hz), 7.25–7.34 m (5H<sub>Ar</sub>). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz), δ<sub>C</sub>, ppm: 15.9, 17.6, 31.4, 42.2, 48.9, 126.7, 127.4, 128.2, 139.9, 174.3. Mass spectrum (HRMS-ESI), *m/z*: 190.1232 [*M* + H]<sup>+</sup> (calcd for C<sub>12</sub>H<sub>15</sub>NO: 190.1226).

***N*-[1-(3,4-Dimethylphenyl)ethyl]pyrrolidin-2-one (3b) and *N*-[1-(2,3-dimethylphenyl)ethyl]pyrrolidin-**

**2-one 3c** were obtained as a mixture of isomers for the ratio of 1 : 0.54. Yield 47 mg (46%), oil.

***N*-[1-(3,4-Dimethylphenyl)ethyl]pyrrolidin-2-one (3b)**. Yield 30%. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz), δ, ppm: 1.47–1.48 m (3H, CH<sub>3</sub>), 1.81–1.99 m (2H, CH<sub>2</sub>), 2.23 s (3H, CH<sub>3</sub>), 2.24 s (3H, CH<sub>3</sub>), 2.35–2.43 m (2H, CH<sub>2</sub>), 2.96–3.00 m (1H, CH<sub>2</sub>), 3.28–3.32 m (1H, CH<sub>2</sub>), 5.42 q (1H, PhCH, *J* 7.1 Hz), 7.01–7.10 m (3H, H-Ar). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz), δ<sub>C</sub>, ppm: 16.4, 17.9, 19.4, 19.9, 31.6, 42.4, 48.8, 124.4, 128.6, 129.4, 129.7, 135.8, 137.8, 174.4. Mass spectrum (GC-MS), *m/z* (*I*<sub>rel.</sub>, %): 217 (83) [*M*]<sup>+</sup>, 202 (100), 174 (58), 159 (27), 132 (81), 105 (25), 117 (35), 91 (33).

***N*-[1-(2,3-Dimethylphenyl)ethyl]pyrrolidin-2-one (3c)**. Yield 16%. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz), δ, ppm: 1.47–1.50 m (3H, CH<sub>3</sub>), 1.81–1.99 m (2H, CH<sub>2</sub>), 2.15 s (3H, CH<sub>3</sub>), 2.28 s (3H, CH<sub>3</sub>), 2.35–2.43 m (2H, CH<sub>2</sub>), 2.68–2.72 m (1H, CH<sub>2</sub>), 3.17–3.22 m (1H, CH<sub>2</sub>), 5.58 q (1H, PhCH, *J* 6.9 Hz), 7.01–7.20 m (3H, H-Ar). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz), δ<sub>C</sub>, ppm: 14.7, 16.6, 18.0, 20.9, 31.5, 42.7, 46.8, 124.1, 125.3, 136.1, 136.7, 137.3, 137.6, 173.8. Mass spectrum (GC-MS), *m/z* (*I*<sub>rel.</sub>, %): 217 (19) [*M*]<sup>+</sup>, 202 (35), 117 (31), 132 (100), 98 (10), 91 (17), 69 (8), 41 (13). Mass spectrum (HRMS-ESI), *m/z*: 218.1545 [*M* + H]<sup>+</sup> (calcd for C<sub>14</sub>H<sub>19</sub>NO: 218.1539).

***N*-[1-(2,4-Dimethylphenyl)ethyl]pyrrolidin-2-one (3d)**. Yield 49 mg (50%), oil. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 500 MHz), δ, ppm: 1.47 d (3H, CH<sub>3</sub>, *J* 7.0 Hz), 1.79–1.93 m (2H, CH<sub>2</sub>), 2.22 s (3H, CH<sub>3</sub>), 2.29 s (3H, CH<sub>3</sub>), 2.37 t (2H, CH<sub>2</sub>, *J* 8.4 Hz), 2.70–2.75 m (1H, CH<sub>2</sub>), 3.18–3.23 m (1H, CH<sub>2</sub>), 5.50 q (1H, PhCH, *J* 7.1 Hz), 6.98–7.00 m (2H, H-Ar), 7.20 d (1H, H-Ar, *J* 7.7 Hz). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 125 MHz), δ<sub>C</sub>, ppm: 16.0, 17.9, 19.1, 20.9, 31.3, 42.6, 46.3, 126.1, 126.3, 131.5, 134.6, 173.7. Mass spectrum (GC-MS), *m/z* (*I*<sub>rel.</sub>, %): 217 (33) [*M*]<sup>+</sup>, 205 (67), 189 (33), 175 (44), 91 (25), 57 (100), 55 (52), 41 (48). Mass spectrum (HRMS-ESI), *m/z*: 218.1541 [*M* + H]<sup>+</sup> (calcd for C<sub>14</sub>H<sub>19</sub>NO: 218.1539).

***N*-[1-(2,5-Dimethylphenyl)ethyl]pyrrolidin-2-one (3e)**. Yield 76 mg (47%), oil. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 500 MHz), δ, ppm: 1.62 d (3H, CH<sub>3</sub>, *J* 7.0 Hz), 1.92–2.10 m (2H, CH<sub>2</sub>), 2.34 s (3H, CH<sub>3</sub>), 2.46 s (3H, CH<sub>3</sub>), 2.35 t (2H, CH<sub>2</sub>, *J* 8.2 Hz), 2.53 t (2H, *J* 8.3 Hz), 2.85–2.90 m (1H, CH<sub>2</sub>), 3.33–3.38 m (1H, CH<sub>2</sub>), 5.65 q (1H, PhCH, *J* 7.0 Hz), 7.13 d (1H, H-Ar, *J* 7.8 Hz), 7.17 d (1H, H-Ar, *J* 7.8 Hz). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 125 MHz), δ<sub>C</sub>, ppm: 16.2, 17.9, 18.7, 21.2, 31.3, 42.7, 46.5, 126.9, 128.2, 130.6, 134.2, 135.1, 137.4, 173.8.

Mass spectrum (GC-MS), *m/z* (*I*<sub>rel.</sub>, %): 217 (19) [*M*]<sup>+</sup>, 202 (27), 177 (46), 132 (100), 98 (10), 91 (13), 69 (6), 41 (8). Mass spectrum (HRMS-ESI), *m/z*: 218.1545 [*M* + H]<sup>+</sup> (calcd for C<sub>14</sub>H<sub>19</sub>NO: 218.1539).

***N*-[1-(4-Methoxyphenyl)ethyl]pyrrolidin-2-one (3f) and *N*-[1-(2-methoxyphenyl)ethyl]pyrrolidin-2-one (3g)** were obtained as a mixture of isomers for the ratio of 1 : 0.3. Yield 49 mg (47%), oil.

***N*-[1-(4-Methoxyphenyl)ethyl]pyrrolidin-2-one (3f)**. Yield 37%, oil. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz), δ, ppm: 1.49 d (3H, CH<sub>3</sub>, *J* 7.2 Hz), 1.85–2.03 m (2H, CH<sub>2</sub>), 2.36–2.43 m (2H, CH<sub>2</sub>), 2.93–2.99 m (1H, CH<sub>2</sub>), 3.25–3.32 m (1H, CH<sub>2</sub>), 3.80 s (3H, OCH<sub>3</sub>), 5.45 q (1H, PhCH, *J* 7.2 Hz), 6.94 d (2H, H-Ar, *J* 8.9 Hz), 7.84 d (2H, H-Ar, *J* 7.8 Hz). Mass spectrum (GC-MS), *m/z* (*I*<sub>rel.</sub>, %): 219 (52) [*M*]<sup>+</sup>, 204 (100), 135 (75), 161 (23), 176 (29), 91 (29), 77 (21), 41 (21).

***N*-[1-(2-Methoxyphenyl)ethyl]pyrrolidin-2-one (3g)**. Yield 10%, oil. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz), δ, ppm: 1.48–1.50 m (3H, CH<sub>3</sub>), 1.85–1.96 m (2H, CH<sub>2</sub>), 2.36–2.43 m (2H, CH<sub>2</sub>), 2.93–2.99 m (1H, CH<sub>2</sub>), 3.25–3.32 m (1H, CH<sub>2</sub>), 3.25–3.32 m (1H, CH<sub>2</sub>), 3.81 s (3H, OCH<sub>3</sub>), 5.62 q (1H, PhCH, *J* 7.2 Hz), 6.80 t (1H, H-Ar, *J* 7.6 Hz), 6.85–6.88 m (1H, H-Ar), 7.21 d (1H, H-Ar, *J* 8.6 Hz). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz), δ<sub>C</sub>, ppm: 16.2, 16.3, 17.7, 17.9, 22.5, 29.5, 31.3, 44.90, 48.3, 110.4, 113.5, 113.6, 120.0, 120.3, 127.2, 128.1, 128.6, 130.5, 132.0, 132.2, 135.0, 206.7. Mass spectrum (GC-MS), *m/z* (*I*<sub>rel.</sub>, %): 219 (85) [*M*]<sup>+</sup>, 204 (96), 176 (48), 135 (100), 119 (67), 105 (56), 91 (77), 77 (58). Mass spectrum (HRMS-ESI), *m/z*: 242.1156 [*M* + Na]<sup>+</sup> (calcd for C<sub>13</sub>H<sub>17</sub>NO<sub>2</sub>: 242.1151).

***N*-[1-(3,4-Dimethoxyphenyl)ethyl]pyrrolidin-2-one (3h)**. Yield 34 mg (29%), oil. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz), δ, ppm: 1.49 d (3H, CH<sub>3</sub>, *J* 7.1 Hz), 1.85–2.04 m (2H, CH<sub>2</sub>), 2.38–2.44 m (2H, CH<sub>2</sub>), 2.94–3.00 m (1H, CH<sub>2</sub>), 3.28–3.34 m (1H, CH<sub>2</sub>), 3.86 s (3H, OCH<sub>3</sub>), 3.87 s (3H, OCH<sub>3</sub>), 5.45 q (1H, PhCH, *J* 7.1 Hz), 6.79–6.87 m (3H, H-Ar). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz), δ<sub>C</sub>, ppm: 16.4, 18.1, 31.7, 42.4, 48.9, 56.0, 56.1, 111.0, 111.1, 119.0, 133.1, 148.6, 149.2, 174.5. Mass spectrum (HRMS-ESI), *m/z*: 272.1260 [*M* + Na]<sup>+</sup> (calcd for C<sub>14</sub>H<sub>19</sub>NO<sub>3</sub>: 272.1257).

***N*-[1-(3,4-Dichlorophenyl)ethyl]pyrrolidin-2-one (3i) and *N*-[1-(2,3-dichlorophenyl)ethyl]pyrrolidin-2-one (3j)** were obtained as a mixture of isomers for the ratio of 1 : 0.5. Yield 14 mg (11%), oil.

**N-[1-(3,4-Dichlorophenyl)ethyl]pyrrolidin-2-one**

**(3i).** Yield 7%, oil. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz), δ, ppm: 1.49 d (3H, CH<sub>3</sub>, *J* 7.2 Hz), 1.89–2.05 m (2H, CH<sub>2</sub>), 2.37–2.44 m (2H, CH<sub>2</sub>), 2.96–3.01 m (1H, CH<sub>2</sub>), 3.30–3.35 m (1H, CH<sub>2</sub>), 5.44 q (1H, PhCH, *J* 7.2 Hz), 7.13 d. d (1H, H-Ar, *J* 1.8, 8.3 Hz), 7.37 d (1H, H-Ar, *J* 1.8 Hz), 7.40 d (H, H-Ar, *J* 8.3 Hz). Mass spectrum (GC-MS), *m/z* (*I*<sub>rel</sub>, %): 257 (94) [*M*]<sup>+</sup>, 242 (100), 172 (60), 137 (52), 112 (40), 98 (100), 69 (81), 41 (67).

**N-[1-(2,3-Dichlorophenyl)ethyl]pyrrolidin-2-one**

**(3j).** Yield 4%. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz), δ, ppm: 1.53 d (3H, CH<sub>3</sub>, *J* 6.9 Hz), 1.89–2.05 m (2H, CH<sub>2</sub>), 2.37–2.44 m (2H, CH<sub>2</sub>), 2.81–2.86 m (1H, CH<sub>2</sub>), 3.22–3.27 m (1H, CH<sub>2</sub>), 5.59 q (1H, PhCH, *J* 6.9 Hz), 7.22 t (1H, H-Ar, *J* 7.8 Hz), 7.31 d (1H, H-Ar, *J* 7.8 Hz), 7.42 d. d (H, H-Ar, *J* 1.6, 7.8 Hz). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz), δ<sub>C</sub>, ppm: 16.0, 16.3, 17.7, 17.9, 30.9, 31.0, 42.0, 43.3, 47.9, 48.1, 125.8, 126.4, 126.9, 128.7, 129.5, 130.3, 131.3, 132.5, 132.5, 133.6, 139.8, 140.6, 174.0, 174.4. Mass spectrum (GC-MS), *m/z* (*I*<sub>rel</sub>, %): 257 (3) [*M*]<sup>+</sup>, 242 (5), 224 (35), 222 (100), 205 (8), 186 (5), 173 (6). Mass spectrum (HRMS-ESI), *m/z*: 258.0446 [*M* + H]<sup>+</sup> (calcd for C<sub>12</sub>H<sub>13</sub>Cl<sub>2</sub>NO: 258.0447).

**NMR spectra of cation 2-H<sup>+</sup>.** <sup>1</sup>H NMR spectrum (400 MHz, CF<sub>3</sub>SO<sub>3</sub>H), δ, ppm: 2.51 m (2H, CH<sub>2</sub>), 3.10 t (2H, CH<sub>2</sub>CO, *J* 8.3 Hz), 3.96 t (2H, CH<sub>2</sub>N, *J* 7.5 Hz), 8.38 s (1H, NH). <sup>13</sup>C NMR spectrum (100 MHz, CF<sub>3</sub>SO<sub>3</sub>H), δ<sub>C</sub>, ppm: 19.5, 30.5, 48.1, 183.8. <sup>15</sup>N NMR spectrum (40 MHz, CF<sub>3</sub>SO<sub>3</sub>H): δ<sub>N</sub> 144.0 ppm.

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## CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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