
Oleg I. Afanasyev\textsuperscript{a}, Alexey A. Tsygankov\textsuperscript{a}, Dmitry L. Usanov\textsuperscript{b}, Dmitry S. Perekalin\textsuperscript{a}, Alexandra D. Samoylova\textsuperscript{c}, Denis Chusov\textsuperscript{*a,c}

\textsuperscript{a}A.N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences
Vavilova st. 28, Moscow, 119991, Russian Federation

\textsuperscript{b}c/a: Department of Chemistry and Chemical Biology, Harvard University
12 Oxford Street, Cambridge, MA 02138, USA

\textsuperscript{c}Moscow Chemical Lyceum, Tamozhenniy proezd 4, Moscow, Russian Federation E-mail: chusov@ineos.ac.ru or denis.chusov@gmail.com

Supporting Information

Table of contents

1. General information ...............................................................................................................................................2
2. Spectroscopic and analytical data .......................................................................................................................6
3. $^1$H, $^{13}$C NMR, mass and UV spectra of obtained compounds .................................................................16
1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and were used without further purification. THF was distilled over sodium/benzophenone. Commercial ruthenium chloride was additionally dried by refluxing in SOCl₂ with subsequent removal of thionyl chloride in high vacuum. Ethanol was dried over 3Å molecular sieves. Carbon monoxide of >98% purity was obtained from NII KM (Moscow, Russia). Reaction products were purified by column chromatography (Acros Organics, silica gel 0.06–0.200 mm). 

General procedure for reductive amination

Procedure: A glass vial in a 10 mL stainless steel autoclave was charged with 1.0 – 4.0 mol % of the catalyst, the corresponding solvent (the quality of solvents, is crucial for good yield of the reactions; THF and ethanol should be purified according to the general procedure in order to achieve good results), 100-200 mol % of the amine and 100-500 mol % of the cyclopropyl ketone (the use of a glass vial is crucial: interaction of the catalyst with the metal surface inside the autoclave can lead to decreased catalytic activity). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with the indicated pressure of CO. The reactor was placed into a preheated oil bath. After the indicated time, the reactor was cooled to room temperature and depressurized. The residue was purified by flash chromatography on silica gel using dichloromethane as eluent.

Complexes, tested as catalysts

Complexes, used in the catalyst screening are listed in figure S1. Compounds 3¹, 4³, 5³, 6⁴, 7⁵, 8 and 9⁶, 10⁷, 11⁸, 12⁹, 13¹⁰, 14¹¹, 18–20¹² were prepared according to the literature procedures.

⁵ Giordano, G.; Crabtree, R. H. Inorg. Synth. 1990, 28, 88 (we did not add Na₂CO₃).
Figure S1. Complexes used in the catalyst screening.

---


Rearrangement of cyclopropanemethylamines to pyrrolidines

![Rearrangement of cyclopropanemethylamines to pyrrolidines](image)

**General procedure**

A glass vial in a 10 mL stainless steel autoclave was charged with 1 – 10 mol % of the catalyst, THF (100 µL, the quality of the solvent is crucial for the yield of reactions – THF should be purified according to the general procedure in order to achieve good results) and aminomethylcyclopropane (2a) (28 mg, 100 mol %, 0.146 mmol). The use of a glass vial is crucial: interaction of the catalyst with the metal surface inside the autoclave can lead to decreased catalytic activity. The autoclave was sealed, flushed three times with 10 bar of the corresponding gas, and then charged with the indicated pressure. The reactor was placed into a preheated oil bath. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. The mixture was analyzed by $^1$H NMR. An example of a $^1$H NMR spectrum is enclosed.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Catalyst loading, mol %</th>
<th>T, °C</th>
<th>Gas (pressure)</th>
<th>Yield 1, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RuCl$_3$</td>
<td>2</td>
<td>130</td>
<td>N$_2$ (2 bar)</td>
<td>traces</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>2</td>
<td>130</td>
<td>N$_2$ (2 bar)</td>
<td>traces</td>
</tr>
<tr>
<td>3</td>
<td>17</td>
<td>2</td>
<td>130</td>
<td>N$_2$ (2 bar)</td>
<td>traces</td>
</tr>
<tr>
<td>4</td>
<td>AlCl$_3$</td>
<td>10</td>
<td>130</td>
<td>N$_2$ (2 bar)</td>
<td>traces</td>
</tr>
<tr>
<td>5</td>
<td>MgBr$_2$·Et$_2$O</td>
<td>10</td>
<td>130</td>
<td>N$_2$ (2 bar)</td>
<td>traces</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>-</td>
<td>130</td>
<td>N$_2$ (2 bar)</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>RuCl$_3$</td>
<td>4</td>
<td>160</td>
<td>CO (30 bar)</td>
<td>61</td>
</tr>
<tr>
<td>8</td>
<td>MgBr$_2$·Et$_2$O</td>
<td>10</td>
<td>160</td>
<td>CO (30 bar)</td>
<td>13</td>
</tr>
<tr>
<td>9</td>
<td>MgBr$_2$·Et$_2$O</td>
<td>10</td>
<td>160</td>
<td>N$_2$ (30 bar)</td>
<td>6</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>2</td>
<td>160</td>
<td>CO (30 bar)</td>
<td>33</td>
</tr>
<tr>
<td>11</td>
<td>20</td>
<td>2</td>
<td>160</td>
<td>N$_2$ (30 bar)</td>
<td>Complex mixture</td>
</tr>
<tr>
<td>12</td>
<td>AlCl$_3$</td>
<td>10</td>
<td>160</td>
<td>CO (30 bar)</td>
<td>Complex mixture</td>
</tr>
<tr>
<td>13</td>
<td>AlCl$_3$</td>
<td>10</td>
<td>160</td>
<td>N$_2$ (30 bar)</td>
<td>Complex mixture</td>
</tr>
<tr>
<td>14</td>
<td>17</td>
<td>1</td>
<td>160</td>
<td>CO (30 bar)</td>
<td>14</td>
</tr>
<tr>
<td>15</td>
<td>17</td>
<td>1</td>
<td>160</td>
<td>N$_2$ (30 bar)</td>
<td>27</td>
</tr>
</tbody>
</table>
1,4-bis(2-methylpyrrolidin-1-yl)benzene dihydrochloride (1k)

Ruthenium chloride (4.8 mg, 2 mol %, 18.5 µmol), p-phenylenediamine (100 mg, 100 mol %, 0.92 mmol) and cyclopropyl methyl ketone (275 µl, 300 mol %, 2.77 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL of water (HPLC grade) was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 160 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was dissolved in methanol, mixed with 3 ml of concentrated HCl, and evaporated to dryness. Crystallization from 1:1 (v/v) mixture of methanol and water gave 208 mg (71%) of off-white crystals of bispyrrolidine dihydrochloride. This compound is highly unstable on silica gel. Attempts to purify product as a free base via column chromatography resulted in decomposition of this compound. The free base and the protonated form generate very intensive dark to violet coloration in contact with silica gel or cellulose. Some applications of this feature can be imagined.

$^{1}H$ NMR (400 MHz, D$_2$O) $\delta$ 7.67 (s, 4H), 3.94 – 3.86 (m, 2H), 3.65 – 3.57 (m, 2H), 2.44 – 2.36 (m, 2H), 2.32 – 2.15 (m, 2H), 2.15 – 2.05 (m, 4H), 1.89 – 1.75 (m, 2H), 1.17 (d, $J = 6.5$ Hz, 6H).

$^{13}$C NMR (101 MHz, D$_2$O) $\delta$ 139.0, 124.1, 68.7, 58.5, 30.6, 21.4, 14.4.

Aqueous solution of bispyrrolidine dihydrochloride has interesting features. After dissolving (3 mg in 2 L of water) the solution rapidly began to change color from colorless to violet-blue (within 20 sec) and reached deep color in 10 minutes. Then gradual discoloration was observed, and the solution became colorless after 24 hours. Nevertheless, an NMR spectrum of a D$_2$O solution of this bispyrrolidine stored for 6 month at room temperature is the same as the spectrum of a freshly prepared solution. Therefore, the color can be assigned to some impurity with an extremely high extinction coefficient. A video is enclosed. When the maximum intensity of color was achieved, a UV/vis spectrum was measured. Four absorption maxima in the visible region at 612, 562, 523 and 478 nm with extinction coefficients of 16459, 15468, 8130 and 2829 respectively. The UV/vis spectrum is enclosed.

Solution of 1,4-bis(2-methylpyrrolidin-1-yl)benzene dihydrochloride (1.5 mg/L).

2. Spectroscopic and analytical data

1-(4-methoxyphenyl)-2-methylpyrrolidin-1-ium hexafluorophosphate

\[
\text{Rhodium catalyst (11)} \quad \text{(16.8 mg, 4 mol %, 32.4 μmol), p-anisidine (100 mg, 100 mol %, 0.81 mmol) and cyclopropyl methyl ketone (121 μL, 150 mol %, 1.22 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.3 mL of ethanol was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 110 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. 80 % yield of 1a by NMR (also 20% of N-(1-cyclopropylethyl)-4-methoxyaniline (2a) was detected).}
\]

0.5 ml (3.6 μmol) of trifluoroacetic anhydride was added dropwise to the solution of reaction mixture in DCM at 0°C. The reaction was allowed to warm to room temperature and concentrated in vacuum. The resulting brown oil was dissolved in methanol, and 0.5 mL of saturated aqueous solution of KPF6 was added. The solution was concentrated in vacuum, 5 mL of DCM was added, then the insoluble was filtered off, and the solution was concentrated to approximately 1 mL. The target compound was precipitated by gradual addition of Et2O as a brown oil, 176 mg (65%).

\(^1\)H NMR (400 MHz, CDCl3) δ 7.48 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 4.07 – 3.96 (m, 1H), 3.95 – 3.85 (m, 1H), 3.81 (s, 3H), 3.68 – 3.58 (m, 1H), 2.45 – 2.55 (m, 1H), 2.40 – 2.23 (m, 2H), 2.01 (m, 1H), 1.31 (d, J = 5.7 Hz, 3H).

\(^13\)C NMR (101 MHz, CDCl3) δ 161.0, 129.8, 123.0, 115.9, 69.8, 60.3, 55.8, 30.7, 21.3, 14.9.

2-methyl-1-(p-tolyl)pyrrolidine (1b) and N-(1-cyclopropylethyl)-4-methylaniline (2b)

\[
\text{Rhodium catalyst (11)} \quad \text{(19.4 mg, 4 mol %, 37.3 μmol), p-toluidine (100 mg, 100 mol %, 0.93 mmol) and cyclopropyl methyl ketone (138.7 μL, 150 mol %, 1.40 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.3 mL of ethanol was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 130 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. Yields were determined by NMR: 73 % of 1b and 25% of 2b. Spectra of the products were in agreement with the literature data.}
\]
2-methyl-1-(p-tolyl)pyrrolidine (1b)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.09 (d, $J = 8.3$ Hz, 2H), 6.57 (d, $J = 8.3$ Hz, 2H), 3.94 – 3.83 (m, 1H), 3.56 – 3.30 (m, 1H), 3.25 – 3.13 (m, 1H), 2.31 (s, 3H), 2.22 – 1.85 (m, 3H), 1.80-1.70 (m, 1H), 1.22 (d, $J = 6.2$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.4, 129.8, 124.3, 112.0, 53.8, 48.6, 33.3, 23.5, 20.3, 19.6.

N-(1-cyclopropylethyl)-4-methylaniline (2b)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.03 (d, $J = 8.2$ Hz, 2H), 6.58 (d, $J = 8.2$ Hz, 2H), 3.73 – 3.43 (br s, 1H), 2.99 (dt, $J = 6.3, 6.8$ Hz 1H), 2.29 (s, 3H), 1.27 (d, $J = 6.3$ Hz, 3H), 1.03-0.90 (m, 1H), 0.59-0.46 (m, 2H), 0.41-0.23 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.6, 129.8, 126.4, 113.8, 53.1, 20.5, 20.3, 18.0, 3.2, 2.7.

2-methyl-1-phenylpyrrolidine (1c) and N-(1-cyclopropylethyl)aniline (2c)

Rhodium catalyst (11) (22.3 mg, 4 mol %, 42.9 µmol), aniline (98 µL, 100 mol %, 1.07 mmol) and cyclopropyl methyl ketone (160 µL, 150 mol %, 1.61 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.3 mL of ethanol was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 110 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. Yields were determined by NMR: 56 % of 1c and 34% of 2c. Spectra of the products were in agreement with the literature data.$^{13}$

2-methyl-1-phenylpyrrolidine (1c)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.49 – 7.20 (m, 2H), 6.86 – 6.54 (m, 3H), 4.00 – 3.88 (m, 1H), 3.53 – 3.44 (m, 1H), 3.28 – 3.17 (m, 1H), 2.41 – 1.99 (m, 3H), 1.80 – 1.73 (m, 1H), 1.27 (d, $J = 6.2$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.3, 129.3, 115.2, 111.9, 53.7, 48.3, 33.2, 23.4, 19.5.

N-(1-cyclopropylethyl)aniline (2c)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22-7.11 (m, 2H), 6.74-6.65 (m, 1H), 6.61 (d, $J = 7.8$ Hz, 2H), 3.83-3.39 (br s, 1H), 3.01 (dt, $J = 6.2, 6.8$ Hz 1H), 1.25 (d, $J = 6.2$ Hz, 3H), 1.01-0.86 (m, 1H), 0.58-0.44 (m, 2H), 0.38-0.23 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.7, 129.4, 117.3, 113.6, 52.8, 20.3, 18.0, 3.2, 2.7

1-(2-methoxy-5-methylphenyl)-2-methylpyrrolidin-1-ium hexafluorophosphate and N-(1-cyclopropylethyl)-2-methoxy-5-methylaniline (2d)
Rhodium catalyst (11) (15.1 mg, 4 mol %, 29.2 µmol), p-cresidine (100 mg, 100 mol %, 0.73 mmol) and cyclopropyl methyl ketone (108 µL, 150 mol %, 1.09 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.3 mL of ethanol was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 130 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. 70 % yield by NMR (also 30% of N-(1-cyclopropylethyl)-2-methoxy-5-methylaniline was detected).

0.5 ml (3.6 µmol) of trifluoroacetic anhydride was added dropwise to the solution of the reaction mixture in DCM at 0°C. The reaction was allowed to warm to room temperature and concentrated in vacuum. The resulting brown oil was dissolved in methanol, and 0.5 mL of saturated aqueous solution of KPF₆ was added. The solution was concentrated in vacuum, 5 mL of DCM was added, then the insoluble residue was filtered off, and the solution was concentrated to approx. 1 mL. The target compound was precipitated by gradual addition of Et₂O and was obtained as a brown oil, 147 mg (58 %).

1-(2-methoxy-5-methylphenyl)-2-methylpyrrolidin-1-ium hexafluorophosphate

1H NMR (400 MHz, CDCl₃) δ 8.13 (s, 1H), 7.34 (s, 1H), 7.24 (d, J = 8.2 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 4.10 – 4.00 (m, 2H), 3.95 (s, 3H), 3.79 – 3.69 (m, 1H), 2.54 – 2.21 (m, 7H), 2.15 – 2.05 (m, 1H), 1.31 (d, J = 5.3 Hz, 3H).

N-(1-cyclopropylethyl)-2-methoxy-5-methylaniline (2d)

1H NMR (400 MHz, CDCl₃) δ 6.80 (d, J = 7.9 Hz, 1H), 6.68 (d, J = 7.9 Hz, 1H), 6.47 (d, J = 1.9 Hz, 1H), 3.85 (s, 3H), 3.15 – 2.90 (br s, 1H), 3.05 – 2.95 (m, 1H), 2.29 (s, 3H), 1.28 (d, J = 6.2 Hz, 3H), 0.97 – 0.87 (m, 1H), 0.60 – 0.45 (m, 2H), 0.40 – 0.25 (m, 2H).

2-methyl-1-(naphthalen-1-yl)pyrrolidine (1e) and N-(1-cyclopropylethyl)naphthalen-1-amine (2e)

Rhodium catalyst (11) (3.3 mg, 4 mol %, 6.4 µmol), naphtylamine (23 mg, 100 mol %, 0.16 mmol) and cyclopropyl methyl ketone (24 µL, 150 mol %, 0.24 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.1 mL of ethanol was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 110 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. Yields were determined by NMR: 58 % of 1e and 32 % of 2e. Spectra of the products were in agreement with the literature data.
**2-methyl-1-(naphthalen-1-yl)pyrrolidine (1e)**

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.34 (dd, $J = 6.2$, 3.5 Hz, 1H), 7.89 (dd, $J = 6.1$, 3.3 Hz, 1H), 7.66 – 7.36 (m, 4H), 7.12 (d, $J = 7.4$ Hz, 1H), 4.08 – 3.68 (m, 2H), 3.00 (d, $J = 5.5$ Hz, 1H), 2.44 – 2.20 (m, 1H), 2.18 – 2.02 (m, 1H), 1.98 – 1.88 (m, 1H), 1.85 – 1.69 (m, 1H), 1.16 (d, $J = 6.0$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.1, 134.9, 130.3, 128.2, 125.9, 125.7, 124.9, 124.7, 122.2, 114.3, 55.8, 55.5, 33.7, 23.6, 18.8.

**N-(1-cyclopropylethyl)naphthalen-1-amine (2e)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93-7.76 (m, 2H), 7.53-7.42 (m, 2H), 7.36 (t, $J = 7.7$ Hz, 1H), 7.24 (d, $J = 8.1$ Hz, 1H), 6.62 (d, $J = 7.5$ Hz, 1H), 3.20-3.08 (m, 1H), 1.38 (d, $J = 6.1$ Hz, 3H), 1.20-1.05 (m, 1H), 0.67-0.50 (m, 2H), 0.45-0.29 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.0, 134.6, 128.8, 126.7, 125.7, 124.6, 123.6, 120.1, 117.0, 105.0, 52.9, 20.1, 18.1, 3.3, 3.0.
4-methoxy-N-(3-(1-(4-methoxyphenyl)pyrrolidin-2-yl)propyl)aniline (If)

Ruthenium chloride (1.0 mg, 2 mol %, 4.8 µmol), p-anisidine (89 mg, 300 mol %, 0.72 mmol) and dicyclopentyl ketone (26.6 mg, 100 mol %, 0.24 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL of water (HPLC grade) was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 160 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. 77 % yield by NMR. The residue was purified by column chromatography (eluent: hexane:ethyl acetate 5:1 (v/v), Rf 0.4) to afford 55 mg (67 %) of the product as a yellowish oil.

**1H NMR (400 MHz, CDCl3) δ 6.85 (d, J = 9.0 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 6.59 (d, J = 8.8 Hz, 2H), 6.54 (d, J = 9.0 Hz, 2H), 3.77 (s, 3H), 3.76 (s, 3H), 3.63–3.57 (m, 1H), 3.48 – 3.39 (m, 1H), 3.17 – 3.08 (m, 3H), 2.07 – 1.90 (m, 3H), 1.86 – 1.78 (m, 2H), 1.68 – 1.62 (m, 2H), 1.43 – 1.35 (m, 1H).

**13C NMR (151 MHz, CDCl3) δ 152.2, 150.9, 142.6, 142.3, 115.2, 114.9, 114.4, 112.9, 59.0, 56.1, 55.9, 49.4, 45.2, 31.0, 30.6, 26.7, 23.7.

Mass spectrum (EI): Calc. m/z = 340; found m/z (%): 340 (4%) [M], 216 (1%), 176 (100%), 161 (10%), 136 (54%), 121 (19%), 77 (11%).

Ethyl 4-(2-methyl-5-phenylpyrrolidin-1-yl)benzoate (1g)

Ruthenium chloride (3.0 mg, 2 mol %, 14.5 µmol), ethyl 4-aminobenzoate (119 mg, 100 mol %, 0.72 mmol) and 2-phenylcyclopropyl methyl ketone (173.8 mg, 150 mol %, 1.08 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL of THF was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 110 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. 85 % yield of mixture of two diastereomers by NMR (ratio 1.9:1). The residue was purified by column chromatography (eluent: Toluene Rf 0.3) to afford 145 mg (68 %) of the product as a mixture of two diastereomers.
Major diastereomer:

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J = 8.9$ Hz, 2H), 7.43 – 7.08 (m, 5H), 6.51 (d, $J = 8.9$ Hz, 2H), 4.75 (t, $J = 7.1$ Hz, 1H), 4.31 (q, $J = 7.1$ Hz, 2H), 4.18 – 4.08 (m, 1H), 2.48 – 2.38 (m, 1H), 2.20 – 2.10 (m, 1H), 2.07 – 2.00 (m, 1H), 1.78 – 1.63 (m, 1H), 1.49 (d, $J = 6.3$ Hz, 3H), 1.35 (t, $J = 7.1$ Hz, 3H)

Minor diastereomer:

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 – 7.80 (m, 2H), 7.43 – 7.08 (m, 5H), 6.55 – 6.47 (m, 2H), 4.97 (d, $J = 8.4$ Hz, 1H), 4.43 – 4.35 (m, 1H), 4.31 (q, $J = 7.1$ Hz, 2H), 2.71 – 2.58 (m, 1H), 2.28 – 2.21 (m, 1H), 1.93 – 1.85 (m, 1H), 1.78 – 1.63 (m, 1H), 1.34 (t, $J = 7.1$ Hz, 3H), 1.31 (d, $J = 6.2$ Hz, 3H)

Combined $^{13}$C spectra

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.1, 150.5, 143.8, 143.4, 131.1, 131.1, 129.1, 128.8, 128.6, 126.9, 126.8, 125.9, 125.6, 117.5, 116.7, 112.7, 112.1, 65.8, 62.1, 60.1, 56.4, 54.4, 35.2, 33.0, 32.2, 29.6, 18.2, 14.5.

2-methyl-1-(1-(naphthalen-1-yl)ethyl)pyrrolidine (1h)

Ruthenium chloride (2.0 mg, 1 mol %, 9.6 µmol), α-naphtylethylamine (155 µL, 100 mol %, 0.96 mmol) and cyclopropyl methyl ketone (143.3 µL, 150 mol %, 1.45 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL of THF was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 140 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. NMR analysis revealed two diastereomers. NMR yield of major one is 45 % and of minor one – 9% NMR. The residue was purified by column chromatography (eluent: toluene: EtOAc 20:1 (v/v), Rf 0.3) to afford 83 mg (29 %) of the product as a yellowish oil.

Major diastereomer:

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.55 (d, $J = 8.1$ Hz, 1H), 7.90 (d, $J = 7.8$ Hz, 1H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.67 (d, $J = 6.7$ Hz, 1H), 7.59 – 7.45 (m, 3H), 4.71 – 4.63 (m, 1H), 3.15 – 3.00 (m, 1H), 2.73 – 2.56 (m, 2H), 2.18 – 1.95 (m, 1H), 1.81 – 1.63 (m, 2H), 1.54 (d, $J = 6.6$ Hz, 3H), 1.52 – 1.44 (m, 1H), 1.08 (d, $J = 6.2$ Hz, 3H).

Minor diastereomer:

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.59-8.51 (m, 1H), 7.92-7.87 (m, 1H), 7.82-7.77 (m, 1H), 7.72 (d, $J = 7.1$ Hz, 1H), 7.59 – 7.45 (m, 3H), 4.53-4.43 (m, 1H), 3.15-3.00 (m, 1H), 2.89-2.74 (m, 2H), 2.18-1.95 (m, 1H), 1.91-1.63 (m, 2H), 1.59 (d, $J = 6.6$ Hz, 3H), 1.52-1.44 (m, 1H), 1.05 (d, $J = 6.2$ Hz, 3H).
Combined $^{13}$C spectra

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 141.3, 134.1, 131.9, 131.5, 128.9, 128.7, 127.3, 127.1, 125.6, 125.5, 125.3, 125.2, 124.6, 124.4, 124.0, 56.6, 55.5, 55.3, 51.5, 48.9, 33.2, 23.1, 22.9, 22.1, 19.7, 18.7, 16.5.

1-benzhydryl-2-methylpyrrolidine (1i)$^{14}$

![1-benzhydryl-2-methylpyrrolidine (1i)](image)

Ruthenium chloride (2.0 mg, 1 mol %, 9.6 µmol), benzhydrilamine (166 µL, 100 mol %, 0.96 mmol) and cyclopropyl methyl ketone (143.3 µL, 150 mol %, 1.45 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL of THF was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 140 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. 64 % yield by NMR. The residue was purified by column chromatography (eluent: hexane: toluene 3:1 (v/v), Rf 0.2) to afford 140 mg (58 %) of the product as a yellowish oil, solidified after evaporation. Melting point 55 - 56°C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.55 – 7.10 (m, 10H), 4.72 (s, 1H), 3.05 – 2.95 (m, 1H), 2.85 – 2.67 (m, 1H), 2.48 – 2.38 (m, 1H), 2.07 – 1.94 (m, 1H), 1.91 – 1.60 (m, 2H), 1.52 – 1.39 (m, 1H), 0.92 (d, J = 6.3 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.5, 142.8, 128.6, 128.2, 128.2, 126.8, 126.7, 71.1, 56.0, 50.42, 32.6, 22.4, 18.2.

Mass spectrum (EI): Calc. m/z = 251; found m/z (%): 251 (5%), 236 (32%), 174 (21%), 167 (100%), 165 (70%), 152 (31%), 139 (5%), 115 (6%), 77 (14%), 51 (6%).

N,N-dimethyl-4-(2-methylpyrrolidin-1-yl)aniline (1I)

![N,N-dimethyl-4-(2-methylpyrrolidin-1-yl)aniline (1I)](image)

Ruthenium chloride (2.0 mg, 1 mol %, 9.6 µmol), $N^1,N^1$-dimethylbenzene-1,4-diamine (131 mg, 100 mol %, 0.97 mmol), cyclopropyl methyl ketone (143 µL, 150 mol %, 1.45 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL of THF was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 140 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. 85 % yield by NMR. The residue was purified by column chromatography (eluent: hexane-ethyl acetate –triethylamine 4:1:0.1 mixture (v/v), Rf 0.5) to afford 151 mg (76 %) of the product as a yellowish oil. This product is unstable and oxidizes in

$^{14}$ CAS : 1401951-36-7
Its NMR spectrum has poor resolution in DMSO and methanol, moderate in CDCl₃ and the signals can be resolved in unpolar C₆D₆.

¹H NMR (300 MHz, CDCl₃) δ 6.87 (d, J = 9.0 Hz, 2H), 6.62 (d, J = 9.0 Hz, 2H), 3.91 – 3.69 (m, 1H), 3.52 – 3.34 (m, 1H), 3.18 – 3.10 (m, 1H), 2.85 (s, 6H), 2.23 – 1.91 (m, 3H), 1.75 – 1.65 (m, 1H), 1.20 (d, J = 6.2 Hz, 3H).

¹H NMR (400 MHz, C₆D₆) δ 6.87 (d, J = 7.9 Hz, 2H), 6.63 (d, J = 7.9 Hz, 2H), 3.6 – 3.58 (m, 1H), 3.25 – 3.16 (m, 1H), 2.96 – 2.88 (m, 1H), 2.64 (s, 6H), 1.78 – 1.59 (m, 2H), 1.60 – 1.44 (m, 1H), 1.40 – 1.25 (m, 1H), 1.04 (d, J = 6.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 144.9, 141.2, 118.4, 113.6, 54.1, 48.9, 42.8, 34.2, 30.0, 24.0.

**N¹-(1-cyclopropylethyl)-N⁴,N⁴-dimethylbenzene-1,4-diamine (2l)**

![Diagram](image)

Ruthenium chloride (4.0 mg, 2 mol %, 15.3 µmol), N¹,N¹-dimethylbenzene-1,4-diamine (104 mg, 100 mol %, 0.765 mmol) and cyclopropyl methyl ketone (114 µL, 150 mol %, 1.15 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL of THF was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 140 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. 30 % yield by NMR. The residue was purified by column chromatography (eluent: hexane-ethyl acetate 5:1 mixture, Rf 0.3) to afford 12 mg (8 %) of the product as a yellowish oil. This product is unstable and oxidizes in air. Its NMR spectrum has poor resolution in CDCl₃ and the signals can be resolved in unpolar C₆D₆.

¹H NMR (400 MHz, C₆D₆) δ 6.74 (d, J = 7.7 Hz, 2H), 6.62 (d, J = 7.7 Hz, 2H), 2.61 (s, 6H), 1.11 (d, J = 6.3 Hz, 3H), 0.80 – 0.60 (m, 1H), 0.33 – 0.25 (m, 2H), 0.23 – 0.17 (m, 1H), 0.16 – 0.08 (m, 1H).

¹³C NMR (101 MHz, C₆D₆) δ 144.8, 140.3, 116.1, 116, 53.8, 42.1, 20.5, 18.1, 3.32, 2.69.

**5-(methyl(phenyl)amino)pentan-2-one (22)**

![Diagram](image)

Rhodium catalyst (11) (3.0 mg, 1 mol %, 5.8 µmol), N-methylaniline (63 µL, 100 mol %, 0.58 mmol) and cyclopropyl methyl ketone (251 µL, 500 mol %, 2.89 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.3 mL of ethanol was added and the autoclave was sealed, flushed three times with 5 bar of CO, and then charged with 3 bar CO. The reactor

---

¹⁵ CAS : 1156372-50-7

¹⁶ CAS : 57488-14-9
was placed into an oil bath preheated to 100 °C. After 48 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. 83% yield by NMR. The residue was purified by column chromatography (eluent: hexane:ethyl acetate 10:1 (v/v), Rf 0.2) to afford 58 mg (62 %) of the product as a yellowish oil.

1H NMR (400 MHz, CDCl₃) δ 7.29 – 7.22 (m, 2H), 6.87 – 6.60 (m, 3H), 3.35 (t, J = 7.3 Hz, 2H), 2.94 (s, 3H), 2.50 (t, J = 7.0 Hz, 2H), 2.15 (s, 3H), 1.94 – 1.85 (m, 2H).

13C NMR (101 MHz, CDCl₃) δ 208.5, 149.4, 129.3, 116.3, 112.3, 51.8, 40.7, 38.2, 30.1, 21.1. Mass spectrum (EI): Calc. m/z = 191; found m/z (%): 191 (5%); 121 (8%), 120 (100%), 104 (35%), 91 (17%), 77 (81%), 65 (11%), 51 (41%).

N₁,N₄-dimethyl-N¹,N₄-diphenylpentane-1,4-diamine (23)

Rhodium catalyst 11 (4 mg, 1 mol %, 8.7 µmol), N-methylaniline (188 µL, 200 mol %, 1.74 mmol), and cyclopropyl methyl ketone (86 µL, 100 mol %, 0.87 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL of EtOH was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 130 °C. After 48 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. 58 % yield by NMR.

1H NMR (400 MHz, CDCl₃) δ 7.28 – 7.20 (m, 4H), 6.83 – 6.57 (m, 6H), 4.01 – 3.92 (m, 1H), 3.22 (t, J = 7.2 Hz, 2H), 2.90 (s, 3H), 2.73 (s, 3H), 1.78 – 1.46 (m, 4H), 1.15 (d, J = 6.6 Hz, 3H).

13C NMR (101 MHz, CDCl₃) δ 150.6, 149.4, 129.3, 129.3, 116.4, 116.0, 113.1, 112.2, 53.2, 52.7, 38.3, 32.1, 29.8, 24.1, 17.4.

N-(4-methylbenzyl)-N-phenylaniline (24)

Ruthenium chloride (0.7 mg, 0.5 mol %, 2.7 µmol), diphenylamine (90.6 mg, 100 mol %, 0.54 mmol) and 4-methylbenzaldehyde (63 µL, 100 mol %, 0.54 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 70 µL of CH₃CN was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 60 bar CO. The reactor was placed into an oil bath preheated to 140 °C. After 8 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. 74 % yield by NMR. The residue was purified by column chromatography (eluent: hexane-toluene 40:1, Rf 0.25) to afford 99.6 mg (68 %) of the product as a yellowish oil.

1H NMR (400 MHz, CDCl₃) δ 7.40 – 7.27 (m, 6H), 7.25 – 7.15 (m, 6H), 7.07 (t, J = 7.1 Hz, 2H), 5.11 (s, 2H), 2.45 (s, 3H).
\( ^{13} \text{C NMR (101 MHz, CDCl}_3 \text{)} \delta 148.2, 136.4, 136.2, 129.4, 126.6, 121.4, 120.8, 56.2, 21.2. \)
3. $^1\text{H}, ^{13}\text{C}$ NMR, mass and UV spectra of obtained compounds
Cyclopropanemethylamines to pyrrolidines rearrangement – entry 7 (page S4) – reaction mixture (¹H NMR, CDCl₃, 400 MHz)
1-(4-methoxyphenyl)-2-methylpyrroldin-1-ium hexafluorophosphate (1H NMR, CDCl₃, 400 MHz)
1-(4-methoxyphenyl)-2-methylpyrrolidin-1-ium hexafluorophosphate ($^{13}$C NMR, CDCl$_3$, 101 MHz)
1-(2-methoxy-5-methylphenyl)-2-methylpyrrolidin-1-ium hexafluorophosphate (\(^1\)H NMR, CDCl\(_3\), 400 MHz)
4-methoxy-N-(3-(1-(4-methoxyphenyl)pyrrolidin-2-yl)propyl)aniline (1f) ($^1$H NMR, CDCl$_3$, 400 MHz)
4-methoxy-N-(3-(1-(4-methoxyphenyl)pyrrolidin-2-yl)propyl)aniline (1f) ($^{13}$C NMR, CDCl$_3$, 150 MHz)
4-methoxy-N-(3-(1-(4-methoxyphenyl)pyrrolidin-2-yl)propyl)aniline (1f) GC MS spectrum
2-methyl-1-(1-(naphthalen-1-yl)ethyl)pyrrolidine (1h) ($^1$H NMR, CDCl$_3$, 400 MHz)
2-methyl-1-(1-(naphthalen-1-yl)ethyl)pyrrolidine (1h) ($^{13}$C NMR, CDCl$_3$, 101 MHz) ($^1$H NMR, CDCl$_3$, 400 MHz)
1-benzhydryl-2-methylpyrrolidine (1i) ($^1$H NMR, CDCl$_3$, 400 MHz)
1-benzhydryl-2-methylpyrrolidine (1i) ($^{13}$C NMR, CDCl$_3$, 101 MHz)
1-benzhydryl-2-methylpyrroline (1i) GC MS spectrum

C:\Users\Yeika\p2017\af942.RAW Injection 1 + c Full ms [45.00-650.00] TIC

C:\Users\Yeika\p2017\af942.RAW Injection 1 + c Full ms [45.00-650.00] MS + spectrum 8.32

S28
N,N-dimethyl-4-(2-methylpyrrolidin-1-yl)aniline (11) (¹H NMR, CDCl₃, 400 MHz) – reaction mixture
N,N-dimethyl-4-(2-methylpyrrolidin-1-yl)aniline (11) (\textsuperscript{1}H NMR, CDCl\textsubscript{3}, 400 MHz)
N,N-dimethyl-4-(2-methylpyrrolidin-1-yl)aniline (11) ($^1$H NMR, C$_6$D$_6$, 400 MHz)
N,N-dimethyl-4-(2-methylpyrrolidin-1-yl)aniline (II) ($^1$H NMR, methanol-d$_4$, 400 MHz)
N,N-dimethyl-4-(2-methylpyrrolidin-1-yl)aniline (II) ($^{13}$C NMR, CDCl$_3$, 101 MHz)
$N^1$-(1-cyclopropylethyl)-$N^4,N^4$-dimethylbenzene-1,4-diamine (2l) ($^1$H NMR, C$_6$D$_6$, 400 MHz)
$N^1$-(1-cyclopropylethyl)-$N^4,N^4$-dimethylbenzene-1,4-diamine (2l) ($^{13}$C NMR, CDCl$_3$, 101 MHz)
5-(methyl(phenyl)amino)pentan-2-one (22) \(^1\text{H} \text{NMR, CDCl}_3, 400 \text{ MHz}\)
5-(methyl(phenyl)amino)pentan-2-one (22) ($^{13}$C NMR, CDCl$_3$, 101 MHz)
5-(methyl(phenyl)amino)pentan-2-one (22) GC MS spectrum
N\textsubscript{1},N\textsubscript{4}-dimethyl-N\textsubscript{1},N\textsubscript{4}-diphenylpentane-1,4-diamine (23) (\textsuperscript{1}H NMR, CDCl\textsubscript{3}, 400 MHz)
$N^1,N^4$-dimethyl-$N^1,N^4$-diphenylpentane-1,4-diamine (23) ($^{13}$C NMR, CDCl$_3$, 101 MHz)
N-(4-methylbenzyl)-N-phenylaniline (24) (¹H NMR, CDCl₃, 400 MHz)
$N$-(4-methylbenzyl)$-N$-phenylaniline (24) ($^{13}$C NMR, CDCl$_3$, 101 MHz)
UV/Vis. Spectrum of 1,4-bis(2-methylpyrrolidin-1-yl)benzene dihydrochloride (1k)