## Acylation/Cyclization of 1,6-Dienes with Ethers under Catalyst- and Base-Free Conditions

Xun-Jie Huang,<sup>*a*</sup> Fu-Hua Qin,<sup>*a*</sup> Yi Liu,<sup>*a*</sup> Shi-Ping Wu,<sup>*a*</sup> Qiang Li,<sup>*b*</sup> and Wen-Ting Wei<sup>\**a*</sup>

 <sup>a</sup> State Key Laboratory Base of Novel Functional Materials and Preparation Science, State Key Laboratory for Managing Biotic and Chemical Threats to the Quality and Safety of Agro-products, School of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, P. R. China.
 <sup>b</sup> Institution of Functional Organic Molecules and Materials, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, P. R. China. E-mail: weiwenting@nbu.edu.cn

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#### (A) Typical experimental procedure for the acylation/cyclization

To a Schlenk tube were added 1,6-dienes 1 (0.2 mmol), ethers 2 (2.0 mL) and TBHP (anhydrous, 5 M in decane, 2.0 equiv). Then the tube was stirred at 120 °C sealed in air for the indicated time until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the solution was concentrated under reduced pressure, and the mixture was purified by flash column chromatography over silica gel (hexane/ethyl acetate = 4:1) to a  $\Box$  ord the desired product 3.

#### (B) Study of thermal degradation profiles of the crude mixture

To a Schlenk tube were added 1,6-diene **1a** (0.2 mmol), ethers **2a** (2.0 mL) and TBHP (anhydrous, 5 M in decane, 2.0 equiv). Then the tube was stirred at 120 °C sealed in air for 24 h. After the reaction was finished, the crude mixture was detected through thermal gravimetric analyzer (Figure **1**). It was found that 1-ethoxy-1-hydroperoxyethane and TBHP has completely decomposed in the reaction system, which was further confirmed by the use of KI/HOAc solution.



Figure 1. Thermal degradation profiles of the crude mixture

#### (C) Analytical data

3,4-Dimethyl-3-(2-oxopropyl)-1-phenylpyrrolidin-2-one (3aa),  $p_{hr} = \int_{0}^{1} \int_{0}^{1} \int_{0}^{1} yellow oil (0.0387 g, 79\% yield, d.r. > 20:1); {}^{1}H NMR (500 MHz, CDCl_3) & 7.63 (d, J = 8.5 Hz, 2H), 7.37 (t, J = 8.0 Hz, 2H), 7.15 (t, J = 7.5 Hz, 1H), 3.96-3.92 (m, 1H), 3.47-3.44 (m, 1H), 2.86 (d, J = 18.0 Hz, 1H), 2.73 (d, J = 18.5 Hz, 1H), 2.51-2.47 (m, 1H), 2.16 (s, 3H), 1.30 (s, 3H), 1.02 (d, J = 7.0 Hz, 3H); {}^{13}C NMR (125 MHz, CDCl_3) & 207.1, 177.4, 139.7, 128.8, 124.5, 120.1, 53.4, 47.1, 46.7, 36.0, 30.8, 23.5, 15.4; HRMS$ *m/z*(ESI) calcd for C<sub>15</sub>H<sub>20</sub>NO<sub>2</sub> ([M+H]<sup>+</sup>) 246.1489, found 246.1491.

**3,4-Dimethyl-3-(2-oxobutyl)-1-phenylpyrrolidin-2-one** (3ab), yellow solid (0.0368 g, 71% yield, d.r. > 20:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.62 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.16-7.11 (m, 1H), 3.96-3.93 (m, 1H), 3.47-3.45 (m, 1H), 2.85 (d, *J* = 18.0 Hz, 1H), 2.70 (d, *J* = 18.0 Hz, 1H), 2.52-2.44 (m, 2H), 2.08-1.99 (m, 1H), 1.33 (s, 3H), 1.28 (d, *J* = 4.0 Hz, 3H), 1.02 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 209.9, 177.4, 139.7, 128.8, 124.5, 120.1, 53.4, 47.1, 45.4, 36.7, 31.4, 23.6, 15.4, 7.8; HRMS *m/z* (ESI) calcd for C<sub>16</sub>H<sub>22</sub>NO<sub>2</sub> ([M+H]<sup>+</sup>) 260.1645, found 260.1649.

 $\begin{array}{l} \textbf{h} = 1 \\ \textbf{h}$ 

1.01 (d, J = 7.0 Hz, 3H), 0.90 (t, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 209.4, 177.4, 139.8, 128.8, 124.5, 120.1, 53.4, 47.1, 45.9, 45.5, 36.0, 23.5, 17.3, 15.5, 13.7; HRMS m/z (ESI) calcd for C<sub>17</sub>H<sub>24</sub>NO<sub>2</sub> ([M+H]<sup>+</sup>) 274.1802, found 274.1800.

3,4-Dimethyl-1-phenyl-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin-2-one (4ae), yellow solid (0.0443 g, 81% yield, d.r. > 20:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.64-7.62 (m, 2H), 7.36-7.33 (m, 2H), 7.11 (t, J = 7.5 Hz, 1H), 4.11-4.06 (m, 1H), 3.89-3.80 (m, 2H), 3.70-3.65 (m, 1H), 3.36 (t, J = 9.0 Hz, 1H), 2.62-2.58 (m, 1H), 2.06-2.00 (m, 1H), 1.93-1.88 (m, 2H), 1.84-1.80 (m, 1H), 1.77-1.73 (m, 1H), 1.53-1.49 (m, 1H), 1.11 (d, J = 7.0 Hz, 3H), 1.08 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) *δ*: 178.8, 139.9, 128.7, 124.1, 119.7, 75.4, 67.5, 52.5, 47.0, 42.4, 33.9, 32.7, 25.4, 17.2, 13.2; HRMS m/z (ESI) calcd for C<sub>17</sub>H<sub>24</sub>NO<sub>2</sub>([M+H]<sup>+</sup>) 274.1802, found 274.1804.

## 3,4-Dimethyl-1-phenyl-3-((tetrahydro-2*H*-pyran-2-

yl)methyl)pyrrolidin-2-one (4af), yellow oil (0.0414 g, 72% yield, d.r. > 20:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.63 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 7.5Hz, 2H), 7.14 (t, J = 7.5 Hz, 1H), 3.97-3.93 (m, 1H), 3.86-3.82 (m, 1H), 3.75-3.71 (m, 1H), 3.50-3.44 (m, 1H), 3.38-3.34 (m, 1H), 2.51-2.45 (m, 2H), 1.72-1.63 (m, 3H), 1.60-1.51 (m, 4H), 1.29 (s, 3H), 1.01 (d, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 177.4, 139.7, 128.8, 124.5, 120.0, 67.2, 62.4, 53.3, 47.1, 45.8, 35.9, 30.7, 25.5, 20.7, 19.7, 15.6; HRMS m/z (ESI) calcd for C<sub>18</sub>H<sub>26</sub>NO<sub>2</sub>([M+H]<sup>+</sup>) 288.1958, found 288.1954.

# $\begin{array}{c} \textbf{3-((1,4-Dioxan-2-yl)methyl)-3,4-dimethyl-1-phenylpyrrolidin-2-} \\ \textbf{one (4ag), yellow oil (0.0393 g, 68\% yield, d.r. > 20:1); ^1H NMR (500 \\ \end{array}$

MHz, CDCl<sub>3</sub>)  $\delta$ : 7.63 (d, J = 9.5 Hz, 2H), 7.36 (t, J = 8.0 Hz, 2H), 7.13 (t, J = 7.5 Hz, 1H), 3.84-3.78 (m, 2H), 3.74-3.62 (m, 5H), 3.39-3.32 (m, 2H), 2.51-2.46 (m, 1H), 1.81-1.76 (m, 1H), 1.55-1.51 (m, 1H), 1.10 (d, J = 7.0 Hz, 3H), 1.07 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 178.6, 139.7, 128.8, 124.2, 119.7, 72.2, 71.5, 66.6, 66.3, 52.4, 46.3, 38.2, 34.3, 17.1, 13.1; HRMS *m/z* (ESI) calcd for C<sub>17</sub>H<sub>24</sub>NO<sub>3</sub>([M+H]<sup>+</sup>) 290.1751, found 290.1755.



### 1-(4-Methoxyphenyl)-3,4-dimethyl-3-(2-

**oxopropyl)pyrrolidin-2-one (3ba)**, yellow oil (0.0440 g, 80% yield, d.r. > 20:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.52-7.50 (m,

2H), 6.91-6.90 (m, 2H), 3.91-3.88 (m, 1H), 3.80 (s, 3H), 3.42-3.39 (m, 1H), 2.84 (d, J = 18.5 Hz, 1H), 2.73 (d, J = 18.5 Hz, 1H), 2.49-2.45 (m, 1H), 2.16 (s, 3H), 1.29 (s, 3H), 1.02 (d, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) & 207.1, 177.0, 156.7, 132.9, 122.0, 114.1, 55.5, 53.8, 46.8 (2), 36.2, 30.8, 23.5, 15.2; HRMS *m/z* (ESI) calcd for C<sub>16</sub>H<sub>22</sub>NO<sub>3</sub> ([M+H]<sup>+</sup>) 276.1594, found 276.1596.

3,4-Dimethyl-3-(2-oxopropyl)-1-(*p*-tolyl)pyrrolidin-2-one (3ca),
 yellow solid (0.0409 g, 79% yield, d.r. > 20:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.50 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H),
 3.93-3.90 (m, 1H), 3.43-3.40 (m, 1H), 2.85 (d, J = 18.0 Hz, 1H), 2.72 (d, J = 18.0 Hz, 1H),

1H), 2.49-2.46 (m, 1H), 2.33 (s, 3H), 2.15 (s, 3H), 1.29 (s, 3H), 1.01 (d, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 207.2, 177.1, 137.2, 134.2, 129.4, 120.2, 53.5, 47.0, 46.7, 36.0, 30.9, 23.3, 20.9, 15.4; HRMS *m*/*z* (ESI) calcd for C<sub>16</sub>H<sub>22</sub>NO<sub>2</sub>([M+H]<sup>+</sup>) 260.1645, found 260.1647.



#### 1-(4-(tert-Butyl)phenyl)-3,4-dimethyl-3-(2-

**oxopropyl)pyrrolidin-2-one (3da)**, yellow oil (0.0470 g, 78% yield, d.r. > 20:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.56-7.54 (m, 2H), 7.40-7.38 (m, 2H), 3.96-3.92 (m, 1H), 3.45-3.42 (m, 1H), 2.87 (d, *J* = 18.0 Hz, 1H), 2.72 (d, *J* = 18.0 Hz, 1H), 2.51-2.47 (m, 1H), 2.16 (s, 3H), 1.31 (s, 9H), 1.29 (s, 3H), 1.01 (d, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 207.2, 177.2, 147.4, 137.1, 125.7, 119.7, 53.3, 47.0, 46.6, 35.9, 34.4, 31.3, 30.9, 23.2, 15.5; HRMS *m/z* (ESI) calcd for C<sub>19</sub>H<sub>28</sub>NO<sub>2</sub> ([M+H]<sup>+</sup>) 302.2115, found 302.2117.

## 1-(4-Fluorophenyl)-3,4-dimethyl-3-(2-oxopropyl)pyrrolidin-

**2-one (3ea)**, yellow oil (0.0374 g, 71% yield, d.r. > 20:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.59-7.57 (m, 2H), 7.06 (t, J = 8.5 Hz, 2H), 3.92-3.88 (m, 1H), 3.45-3.42 (m, 1H), 2.84 (d, J = 18.5 Hz, 1H), 2.74 (d, J = 18.5 Hz, 1H), 2.49-2.45 (m, 1H), 2.16 (s, 3H), 1.29 (s, 3H), 1.02 (d, J = 7.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 207.1, 177.4, 159.0 (d,  $J_{C-F} = 242.5$  Hz), 135.7, 121.9 (d,  $J_{C-F} = 8.0$  Hz), 115.5 (d,  $J_{C-F} = 22.3$  Hz), 53.7, 47.0, 46.7, 35.9, 30.7, 23.9, 15.2; <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$ : -117.8; HRMS *m/z* (ESI) calcd for C<sub>15</sub>H<sub>19</sub>FNO<sub>2</sub>([M+H]<sup>+</sup>) 264.1394, found 264.1392.

**1-(4-Chlorophenyl)-3,4-dimethyl-3-(2-oxopropyl)pyrrolidin-2-one (3fa)**, yellow solid (0.0402 g, 72% yield, d.r. > 20:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.59-7.58 (m, 2H), 7.33-7.31 (m, 2H),

3.91-3.87 (m, 1H), 3.45-3.42 (m, 1H), 2.83 (d, *J* = 18.0 Hz, 1H), 2.73 (d, *J* = 18.5 Hz, 1H), 2.49-2.45 (m, 1H), 2.15 (s, 3H), 1.29 (s, 3H), 1.02 (d, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 207.0, 177.5, 138.3, 129.6, 128.8, 121.2, 53.3, 47.0, 46.9, 35.9,

30.7, 23.9, 15.2; HRMS *m*/*z* (ESI) calcd for C<sub>15</sub>H<sub>19</sub>ClNO<sub>2</sub> ([M+H]<sup>+</sup>) 280.1099, found 280.1101.



**Figure 2.** H-H Noesy: there is strong NOE between  $CH_{3a}$  and  $H_b$ 

1-(4-Bromophenyl)-3,4-dimethyl-3-(2-oxopropyl)pyrrolidin-<br/>2-one (3ga), yellow solid (0.0452 g, 70% yield, d.r. > 20:1); <sup>1</sup>H<br/>NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.54 (d, J = 9.0 Hz, 2H), 7.47 (d, J =<br/>9.0 Hz, 2H), 3.91-3.87 (m, 1H), 3.45-3.42 (m, 1H), 2.84 (d, J = 18.5 Hz, 1H), 2.74 (d,<br/>J = 18.5 Hz, 1H), 2.49-2.45 (m, 1H), 2.15 (s, 3H), 1.28 (s, 3H), 1.01 (d, J = 7.0 Hz,<br/>3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 206.9, 177.5, 138.8, 131.8, 121.5, 117.3, 53.2,<br/>47.0, 46.9, 35.9, 30.7, 23.9, 15.1; HRMS m/z (ESI) calcd for C<sub>15</sub>H<sub>19</sub>BrNO<sub>2</sub> ([M+H]<sup>+</sup>)<br/>324.0594, found 324.0596.

#### 4-(3,4-Dimethyl-2-oxo-3-(2-oxopropyl)pyrrolidin-1-



**yl)benzonitrile (3ha)**, yellow oil (0.0330 g, 61% yield, d.r. > 20:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.80 (d, *J* = 9.0 Hz, 2H),

7.65 (d, J = 9.0 Hz, 2H), 3.94-3.91 (m, 1H), 3.52-3.49 (m, 1H), 2.85 (d, J = 18.5 Hz,

1H), 2.77 (d, J = 18.5 Hz, 1H), 2.51-2.47 (m, 1H), 2.15 (s, 3H), 1.30 (s, 3H), 1.03 (d, J = 7.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 206.7, 178.3, 143.5, 132.9, 119.5, 118.9, 107.2, 53.0, 47.3, 46.9, 35.7, 30.5, 24.4, 15.0; HRMS *m*/*z* (ESI) calcd for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub> ([M+H]<sup>+</sup>) 271.1441, found 271.1439.

**3,4-Dimethyl-3-(2-oxopropyl)-1-(***m***-tolyl)pyrrolidin-2-one (3ia)**, yellow oil (0.0404 g, 78% yield, d.r. > 20:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.42 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 3.88-3.84 (m, 1H), 3.39-3.36 (m, 1H), 2.78 (d, *J* = 18.0 Hz, 1H), 2.65 (d, *J* = 18.0 Hz, 1H), 2.43-2.39 (m, 1H), 2.29 (s, 3H), 2.09 (s, 3H), 1.22 (s, 3H), 0.94 (d, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 207.2, 177.3, 139.6, 138.7, 128.7, 125.4, 120.9, 117.2, 53.5, 47.1, 46.7, 35.9, 30.9, 23.4, 21.6, 15.4; HRMS *m/z* (ESI) calcd for C<sub>16</sub>H<sub>22</sub>NO<sub>2</sub> ([M+H]<sup>+</sup>) 260.1645, found 260.1643.

**3,4-Dimethyl-3-(2-oxopropyl)-1-tosylpyrrolidin-2-one (3ja)**, yellow oil (0.0355 g, 55% yield, d.r. > 20:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.85 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 3.92-3.88 (m, 1H), 3.43-3.40 (m, 1H), 2.60 (d, J = 18.5 Hz, 1H), 2.49 (d, J = 18.5 Hz, 1H), 2.36 (s, 3H), 2.34-2.29 (m, 1H), 1.94 (s, 3H), 1.04 (s, 3H), 0.80 (d, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 206.0, 177.2, 145.1, 134.7, 129.6, 128.2, 51.7, 46.9, 46.6, 35.9, 30.3, 23.3, 21.7, 14.7; HRMS *m/z* (ESI) calcd for C<sub>16</sub>H<sub>22</sub>NO<sub>4</sub>S ([M+H]<sup>+</sup>) 324.1264, found 324.1266.



 $CDCl_3$ )  $\delta$ : 7.61 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.15 (t, J = 7.5 Hz, 1H), 3.59 (d, J = 9.5 Hz, 1H), 3.41 (d, J = 9.5 Hz, 1H), 2.97 (d, J = 17.0 Hz, 1H), 2.61 (d, J = 17.0 Hz, 1H), 2.21 (s, 3H), 1.26 (s, 3H), 1.24 (s, 3H), 1.09 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 207.5, 177.5, 139.6, 128.9, 124.5, 119.8, 59.3, 50.6, 46.5, 38.4, 31.9, 24.9, 22.7, 18.0; HRMS m/z (ESI) calcd for C<sub>16</sub>H<sub>22</sub>NO<sub>2</sub> ([M+H]<sup>+</sup>) 260.1645, found 260.1649.



(d, J = 9.5 Hz, 1H), 3.38 (d, J = 9.5 Hz, 1H), 2.96 (d, J = 16.5 Hz, 1H), 2.62-2.57 (m, J = 16.5 Hz, 100 Hz), 2.62-2.57 (m, J = 16.5 Hz, 100 Hz), 2.62-2.57 (m, J = 16.5 Hz), 2.62-2.57 (m, J = 16.5 Hz), 2.62-2.57 (m, J = 16.5 Hz), 2.52-2.57 (m, J = 16.5 Hz), 2.52-2.57 (m, J =3H), 2.21 (s, 3H), 1.59-1.56 (m, 2H), 1.37-1.32 (m, 2H), 1.25 (s, 3H), 1.23 (s, 3H), 1.08 (s, 3H), 0.90 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 207.6, 177.3, 139.3, 137.2, 128.8, 119.8, 59.4, 50.5, 46.5, 38.5, 35.0, 33.7, 31.9, 24.9, 22.7, 22.3, 18.0, 14.0; HRMS m/z (ESI) calcd for  $C_{20}H_{30}NO_2([M+H]^+)$  316.2271, found 316.2273.



#### 1-(4-Fluorophenyl)-3,4,4-trimethyl-3-(2-

oxopropyl)pyrrolidin-2-one (3ma), yellow oil (0.0432 g, 78% yield); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.58-7.55 (m, 2H), 7.06 (t, J = 8.5 Hz, 2H), 3.56 (d, J = 9.5 Hz, 1H), 3.37 (d, J = 9.5 Hz, 1H), 2.96 (d, J = 17.0 Hz, 1H), 2.62 (d, J = 17.0 Hz, 1H), 2.21 (s, 3H), 1.25 (s, 3H), 1.24 (s,1.09 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 207.4, 177.4, 159.0 (d,  $J_{CF}$  = 242.8 Hz), 135.6, 121.5 (d,  $J_{C-F}$  = 7.8 Hz), 115.5 (d,  $J_{C-F}$  = 22.3 Hz), 59.6, 50.4, 46.5, 38.4, 31.8,

24.8, 22.8, 18.1; <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ: -117.7; HRMS m/z (ESI) calcd for C<sub>16</sub>H<sub>21</sub>FNO<sub>2</sub> ([M+H]<sup>+</sup>) 278.1551, found 278.1555.



#### 3,4,4-Trimethyl-3-(2-oxopropyl)-1-(4-

(trifluoromethyl)phenyl)pyrrolidin-2-one (3na), yellow oil (0.0471 g, 72% yield); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) &: 7.77 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 9.0 Hz, 2H), 3.60 (d, J = 9.5 Hz, 1H), 3.44 (d, J =9.0 Hz, 1H), 2.96 (d, J = 17.0 Hz, 1H), 2.63 (d, J = 17.0 Hz, 1H), 2.21 (s, 3H), 1.27 (s, 3H), 1.25 (s, 3H), 1.10 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 207.1, 178.1, 130.9, 128.8, 126.0 (q,  $J_{C-F} = 2.8$  Hz), 124.0 (q,  $J_{C-F} = 67.4$  Hz), 119.1, 59.1, 50.6, 46.5, 38.3, 31.7, 24.9, 22.8, 18.2; <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ: -62.1; HRMS m/z (ESI) calcd for C<sub>17</sub>H<sub>21</sub>F<sub>3</sub>NO<sub>2</sub> ([M+H]<sup>+</sup>) 328.1519, found 328.1517.

# Bn 3-Benzyl-4-methyl-3-(2-oxopropyl)-1-phenylpyrrolidin-2-one

(30a), colorless oil (0.0494 g, 77% yield, d.r. > 20:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.47 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.24-7.22 (m, 3H), 7.20-7.18 (m, 2H), 7.14 (t, J = 7.0 Hz, 1H), 3.27-3.25 (m, 2H), 3.05 (d, J = 13.5 Hz, 1H), 2.96 (d, J = 13.5 Hz, 1H), 2.91-2.82 (m, 2H), 2.65-2.61 (m, 1H), 2.16 (s, 3H), 0.93 (d, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 207.2, 176.1, 139.3, 137.0, 130.4, 128.8, 128.3, 126.9, 124.7, 120.6, 53.7, 51.5, 47.0, 43.4, 32.1, 30.8, 15.7; HRMS m/z (ESI) calcd for  $C_{21}H_{24}NO_2([M+H]^+)$  322.1802, found 322.1804.

## 4-Methyl-3-(2-oxopropyl)-1,3-diphenylpyrrolidin-2-one **(3pa)**, yellow oil (0.0448 g, 73% yield, d.r. > 20:1); <sup>1</sup>H NMR (500 MHz,

CDCl<sub>3</sub>)  $\delta$ : 7.60 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 7.5 Hz, 2H), 7.37-7.30 (m, 5H), 7.24

(t, J = 7.5 Hz, 1H), 7.14 (t, J = 8.0 Hz, 1H), 3.87-3.84 (m, 1H), 3.47-3.45 (m, 1H), 3.37 (d, J = 18.0 Hz, 1H), 3.29-3.27 (m, 1H), 3.04 (d, J = 18.0 Hz, 1H), 2.00 (s, 3H), 1.21 (d, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 206.7, 174.8, 140.7, 139.6, 128.8, 128.6, 127.2, 126.6, 124.6, 120.1, 55.2, 53.3, 47.5, 34.8, 31.2, 16.1; HRMS *m/z* (ESI) calcd for C<sub>20</sub>H<sub>22</sub>NO<sub>2</sub> ([M+H]<sup>+</sup>) 308.1645, found 308.1647.

(D) Spectra

3,4-Dimethyl-3-(2-oxopropyl)-1-phenylpyrrolidin-2-one (3aa)



3,4-Dimethyl-3-(2-oxobutyl)-1-phenylpyrrolidin-2-one (3ab)



3,4-Dimethyl-3-(2-oxopentyl)-1-phenylpyrrolidin-2-one (3ac)



3,4-Dimethyl-1-phenyl-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin-2-one (4ae)



3,4-Dimethyl-1-phenyl-3-((tetrahydro-2*H*-pyran-2-yl)methyl)pyrrolidin-2-one (4af)



3-((1,4-Dioxan-2-yl)methyl)-3,4-dimethyl-1-phenylpyrrolidin-2-one (4ag)



1-(4-Methoxyphenyl)-3,4-dimethyl-3-(2-oxopropyl)pyrrolidin-2-one (3ba)



3,4-Dimethyl-3-(2-oxopropyl)-1-(*p*-tolyl)pyrrolidin-2-one (3ca)



1-(4-(*tert*-Butyl)phenyl)-3,4-dimethyl-3-(2-oxopropyl)pyrrolidin-2-one (3da)



1-(4-Fluorophenyl)-3,4-dimethyl-3-(2-oxopropyl)pyrrolidin-2-one (3ea)



1-(4-Chlorophenyl)-3,4-dimethyl-3-(2-oxopropyl)pyrrolidin-2-one (3fa)



1-(4-Bromophenyl)-3,4-dimethyl-3-(2-oxopropyl)pyrrolidin-2-one (3ga)



4-(3,4-Dimethyl-2-oxo-3-(2-oxopropyl)pyrrolidin-1-yl)benzonitrile (3ha)



3,4-Dimethyl-3-(2-oxopropyl)-1-(*m*-tolyl)pyrrolidin-2-one (3ia)



3,4-Dimethyl-3-(2-oxopropyl)-1-tosylpyrrolidin-2-one (3ja)



3,4,4-Trimethyl-3-(2-oxopropyl)-1-phenylpyrrolidin-2-one (3ka)



1-(4-Butylphenyl)-3,4,4-trimethyl-3-(2-oxopropyl)pyrrolidin-2-one (3la)



1-(4-Fluorophenyl)-3,4,4-trimethyl-3-(2-oxopropyl)pyrrolidin-2-one (3ma)



3,4,4-Trimethyl-3-(2-oxopropyl)-1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one (3na)



3-Benzyl-4-methyl-3-(2-oxopropyl)-1-phenylpyrrolidin-2-one (3oa)



4-Methyl-3-(2-oxopropyl)-1,3-diphenylpyrrolidin-2-one (3pa)

