10.1071/CH18246\_AC

©CSIRO 2018

Australian Journal of Chemistry 2018, 71(8), 566-572

## **Supplementary Material**

## An Efficient Synthesis of Pyrrolidinone Derivatives in the Presence of 1,1'-Butylenebis(3-sulfo-3*H*-imidazol-1-ium) Chloride

Nader Ghaffari Khaligh,<sup>A,\*</sup> Kim Foong Chong,<sup>A</sup> Taraneh Mihankhah,<sup>B</sup> Salam Titinchi,<sup>C</sup> Mohd Rafie Johan,<sup>A</sup> and Juan Joon Ching<sup>A</sup>

<sup>A</sup> Nanotechnology and Catalysis Research Center, 3rd Floor, Block A, Institute of Postgraduate Studies, University of Malaya, 50603 Kuala Lumpur, Malaysia

<sup>B</sup> Environmental Research Laboratory, Department of Water and Environmental Engineering, School of Civil Engineering, Iran University of Science and Technology, 16765-163, Tehran, Iran

<sup>C</sup> Department of Chemistry, University of the Western Cape, Cape Town, South Africa

\* Corresponding author Tel.: +98-21-6643-1738; Fax: +98-21-6693-4046; Email: ngkhaligh@gmail.com and also ngkhaligh@um.edu.my

#### Experiment

#### General

Unless specified, all chemicals were analytical grade and purchased from Merck, Aldrich and Fluka Chemical Companies and used without further purification. Products were characterized by their physical constant and FT-IR, NMR and elemental analysis. The purity determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates. The purity determination of the products was accomplished by GC-MS on an Agilent 6890GC/5973MSD analysis instrument under 70 eV conditions. The FT-IR spectra were recorded on a Perkin Elmer 781 Spectrophotometer using KBr pellets for solid and neat for liquid samples in the range of 4000-400 cm<sup>-1</sup>. In all the cases the <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with Bruker Avance 400 MHz instrument. All chemical shifts are quoted in parts per million (ppm) relative to TMS using deuterated solvent. Microanalyses were performed on a Perkin-Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

#### The typical procedure for the synthesis of pyrrolidinones (2a-s)

A mixture of the aryl aldehyde (2.0 mmol), aniline derivatives (2.0 mmol), diethyl acetylenedicarboxylate (2.0 mmol, 340 mg) and [BBSI]Cl catalyst (1.0 mmol%, 9.1 mg) was stirred in 2 mL ethanol (96%) for 30 min. After the completion

of the reaction (monitored by TLC), the crude products were extracted by EtOAc ( $3 \times 10$  mL). Then the extracted organic phases were collected and dried on anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under vacuum rotary vaporization and the product purified by flash chromatography or recrystallized from hot ethanol to get the pure products. All the known products have spectral and physical data consistent with those reported in the literature as well as the samples prepared from previously reported methods.

#### **Recycling catalyst**

After extraction of the product, the volatiles were removed in vacuum and the remaining ionic liquid was collected, dried and reused for the next run.

## <sup>1</sup>H NMR and <sup>13</sup>C NMR spectral data of new and known compounds (The NMR spectra were recorded in 400 MHz Bruker instrument and CDCl3 or DMSO-d6 were used as NMR solvent).

Ethyl-1-phenyl-2-(4-chlorophenyl)-4-hydroxy-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (2a) [29]



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.20 (t, *J* =7.0 Hz, 3H), 4.20 (q, *J* = 7.0 Hz, 2H), 5.72 (s, 1H), 7.11-7.17 (m, 3H), 7.22-7.30 (m, 4H), 7.43 (d, *J* = 8.0 Hz, 2H), 9.04 (br s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 13.6, 60.5, 61.1, 112.5, 122.0, 125.8, 128.6, 128.7, 128.9, 133.4, 134.1, 135.8, 156.3, 162.4, 164.6 ppm.

Ethyl-1,2-diphenyl-4-hydroxy-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (2b) [29]



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.19 (t, *J* = 7.0 Hz, 3H), 4.20 (q, *J* = 7.0 Hz, 2H), 5.74 (s, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.19-7.32 (m, 7H), 7.49 (d, *J* = 8.0 Hz, 2H), 9.10 (br s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 13.9, 61.2, 61.5, 113.3, 122.3, 125.8, 127.5, 128.5, 128.6, 129.1, 135.1, 136.2, 156.4, 162.9, 164.9 ppm.

Ethyl-1-phenyl-2-p-tolyl-4-hydroxy-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (2c) [31]



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.20 (t, *J* = 7.1 Hz, 3H), 2.26 (s, 3H), 4.19 (q, J = 7.2 Hz, 2H), 5.70 (s, 1H), 7.03-7.11 (m, 5H), 7.24-7.28 (m, 2H), 7.47 (d, *J* = 7.6 Hz, 2H), 9.02 (br s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 13.9, 21.1, 61.2, 61.3, 113.2, 122.2, 125.7, 127.4, 128.9, 128.3, 132.1, 136.4, 138.3, 156.4, 162.7, 165.1 ppm.

Ethyl-1-phenyl-2-(4-trifluoromethylphenyl)-4-hydroxy-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (2d) [30]



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.19 (t, *J* = 7.2 Hz, 3H), 4.20 (q, *J* = 7.2 Hz, 2H), 5.81 (s, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0, 2H), 9.10 (br s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 14.2, 60.2, 60.4, 112.0, 122.7, 124.3 (<sup>*I*</sup>*J*<sub>C-F</sub> = 244.7 Hz), 125.5, 125.7, 125.9, 128.6 (<sup>2</sup>*J*<sub>C-F</sub> = 27 Hz), 129.0, 129.2 (<sup>3</sup>*J*<sub>C-F</sub> = 8 Hz), 136.4, 142.0, 152.5, 162.3, 164.2 ppm.

Ethyl-1-phenyl-2-(4-methoxyphenyl)-4-hydroxy-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (2e) [29]



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.20 (t, *J* = 7.2 Hz, 3H), 3.72 (s, 3H), 4.19 (q, *J* = 7.2 Hz, 2H), 5.70 (s, 1H), 6.76 (d, *J* = 8.8 Hz, 2H), 7.08-7.14 (m, 3H), 7.24-7.29 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 9.06 (br s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 14.7, 56.1, 56.2, 61.4, 112.2, 113.8, 124.0, 125.7, 126.4, 130.2, 131.3, 137.3, 152.4, 162.5, 164.1 ppm. *Ethyl-1-phenyl-2-(4-hydroxyphenyl)-4-hydroxy-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate* (**2***f*) [*31*]



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.20 (t, *J* = 7.00 Hz, 3H), 3.51 (br s, 1H), 4.25 (q, *J* = 7.00 Hz, 2H), 5.59 (s, 1H), 7.10-7.37 (m, 9H), 9.05 (br s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 13.9, 60.5, 62.5, 110.5, 122.2, 123.1, 127.6, 129.1, 129.3, 136.8, 138.8, 145.7, 163.1, 165.2 ppm.

Ethyl-1-phenyl-2-(4-nitrophenyl)-4-hydroxy-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (2g) [31]



<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 1.06 (t, *J* =7.0 Hz, 3H), 3.86 (br s, 1H), 4.01 (q, *J* = 7.0 Hz, 2H), 6.27 (s, 1H), 7.08 (t, *J* = 7.0 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.56-7.59 (m, 4H), 8.05 (d, *J* =8.4 Hz, 2H) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 14.3, 60.1, 60.2, 111.6, 122.9, 123.8, 126.1, 129.6, 130.2, 136.6, 145.3, 147.6, 154.1, 162.4, 164.5 ppm.

Ethyl-1-phenyl-2-(4-bromophenyl)-4-hydroxy-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (2h) (New spectra Data)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.17 (t, *J* =7.2 Hz, 3H), 4.25 (q, *J* = 7.2 Hz, 2H), 5.62 (s, 1H), 7.08-7.16 (m, 3H), 7.30-7.48 (m, 6H), 9.14 (br s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 14.0, 60.5, 61.5, 113.5, 122.2, 123.3, 125.6, 129.1, 129.3, 131.8, 133.8, 137.3, 154.7, 161.8, 164.2 ppm.

Ethyl-1-phenyl-2-(2-nitrophenyl)-4-hydroxy-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (2i) [30]



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.20 (t, *J* =7.1 Hz, 3H), 4.20 (q, *J* = 7.0 Hz, 2H), 5.64 (s, 1H), 7.09-7.69 (m, 9H), 9.10 (br s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 14.3, 55.0, 60.5, 112.3, 122.6, 125.3, 126.2, 127.9, 129.6, 131.7, 134.3, 136.8, 150.4, 153.9, 160.2, 162.4, 164.7 ppm.

Ethyl-1-phenyl-2-(2-chlorophenyl)-4-hydroxy-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (2j) [31]



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.18 (t, *J* =7.2 Hz, 3H), 4.18 (q, *J* = 7.2 Hz, 2H), 6.44 (s, 1H), 7.01-7.56 (m, 9H), 9.22 (br s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 13.8, 56.6, 61.4, 112.6, 119.4, 121.8, 126.0, 127.0, 127.5, 129.1, 129.7, 132.9, 136.1, 157.4, 162.8, 165.2 ppm.

Ethyl-1-phenyl-2-(2-methoxyphenyl)-4-hydroxy-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (2k) [30]



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.40 (t, *J* =7.2 Hz, 3H), 3.90 (s, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 6.31 (s, 1H), 6.83 (t, J = 7.6 Hz, 2H), 6.98-7.10 (m, 2H), 7.17-7.21 (m, 1H), 7.25 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 7.6 Hz, 2H), 9.11 (br s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 14.3, 56.4, 60.1, 112.3, 121.0, 122.0, 124.5, 125.7, 129.1, 129.7, 136.9, 153.8, 158.3, 162.4, 164.6 ppm.

Ethyl-1-benzyl-4-hydroxy-5-oxo-2-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (21) [29]



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 0.98 (t, *J* =7.2 Hz, 3H), 3.55 (d, *J* =14.8 Hz, 1H), 3.90 (q, *J* = 7.2 Hz, 2H), 4.83 (s, 1H), 5.15 (d, *J* =14.8 Hz, 1H), 7.04-7.47 (m, 10H), 9.04 (br s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 14.0, 44.1, 59.7, 60.0, 109.1, 127.6, 128.0, 128.2, 128.5, 128.6, 128.7, 128.9, 134.6, 136.7, 136.8, 161.5, 165.3 ppm.

Methyl-1,2-diphenyl-4-hydroxy-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (2m) [21]



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 3.74 (s, 3H), 5.73 (s, 1H), 7.10 (t, J= 7.8 Hz, 1H), 7.23-7.28 (m, 7H), 7.46 (d, J = 7.8 Hz, 2H), 9.01 (br s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 52.0, 61.7, 112.7, 122.2, 125.8, 127.4, 128.5, 128.6, 129.0, 135.0, 136.1, 156.1, 162.7, 165.1 ppm.

 $Methyl-1-phenyl-2-p-tolyl-4-hydroxy-5-oxo-2, 5-dihydro-1H-pyrrole-3-carboxylate (\mathbf{2n}) (New \ compound)$ 



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 2.28 (s, 3H), 3.74 (s, 3H), 5.73 (s, 1H), 7.08-7.22 (m, 5H), 7.25-7.30 (m, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 9.04 (br s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 21.2, 52.3, 61.7, 113.5, 122.1, 125.6, 127.3, 128.9, 129.4, 131.7, 136.2, 138.6, 157.5, 163.5, 165.2 ppm.

Ethyl-1-phenyl-2-(benzo[d][1,3]dioxol-5-yl)-4-hydroxy-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate (20) [29]



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.23 (t, *J* =7.0 Hz, 3H), 4.22 (q, *J* = 7.0 Hz, 2H), 5.60 (s, 1H), 5.91 (s, 2H), 6.65-6.79 (m, 2H), 7.13-7.17 (m, 2H), 7.35-7.39 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 9.04 (br s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 14.2, 61.2, 61.5, 101.4, 107.2, 108.4, 113.2, 122.0, 122.8, 126.1, 128.8, 129.2, 136.5, 148.0, 148.2, 156.5, 162.9, 165.2 ppm.

 $\label{eq:expansion} Ethyl-1-(4-nitrophenyl)-4-hydroxy-5-oxo-2-(4-trifluoromethylphenyl)-2, 5-dihydro-1H-pyrrole-3-carboxylate~(2q)~[30]$ 



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.22 (t, J = 7.2 Hz, 3H), 4.23 (q, J = 7.2 Hz, 2H), 5.88 (s, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 9.2 Hz, 2H), 8.14 (d, J = 9.2 Hz, 2H), 9.15 (br s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 14.0, 60.5, 61.9, 113.5, 120.6, 123.5 (<sup>1</sup>J<sub>C-F</sub> = 265 Hz), 126.0 (<sup>3</sup>J<sub>C-F</sub> = 4 Hz), 127.8, 130.9, 131.3 (<sup>2</sup>J<sub>C-F</sub> = 32 Hz), 138.7, 141.6, 144.4, 155.8, 163.0, 164.5 ppm;

Ethyl-1-p-tolyl-4-hydroxy-5-oxo-2-(4-trifluoromethylphenyl)-2,5-dihydro-1H-pyrrole-3-carboxylate (2r) [30]



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.19 (t, *J* = 7.2 Hz, 3H), 2.26 (s, 3H), 4.20 (q, *J* = 7.2 Hz, 2H), 5.77 (s, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 9.11 (br s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 13.8, 20.7, 61.0, 61.2, 112.3, 122.1, 123.8 ( ${}^{I}J_{C-F}$  = 270.8 Hz), 125.5, 125.6 ( ${}^{3}J_{C-F}$  = 4 Hz), 127.9, 129.5, 130.0, 130.4 ( ${}^{2}J_{C-F}$  = 32 Hz), 133.2, 136.0, 139.5, 156.6, 162.5, 164.6 ppm;

 $\label{eq:expectation} Ethyl-1-(4-methoxyphenyl)-4-hydroxy-5-oxo-2-(4-trifluoromethylphenyl)-2, 5-dihydro-1H-pyrrole-3-carboxylate~(2s)~[30]$ 



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 1.14$  (t, J = 7.2 Hz, 3H), 3.69 (s, 3H), 4.15 (q, J = 7.2 Hz, 2H), 5.72 (s, 1H), 6.77 (d, J = 9.2 Hz, 2H), 7.28 (t, J = 9.2 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 14.4$ , 55.6, 60.2, 61.0, 111.8, 114.4, 123.6, 124.0 ( ${}^{1}J_{C-F} = 269$  Hz), 125.6 ( ${}^{3}J_{C-F} = 7$  Hz), 128.4, 128.5, 128.7, 129.0, 129.2 ( ${}^{2}J_{C-F} = 27$  Hz), 142.2, 153.8, 157.4, 162.4, 164.2 ppm.

# <sup>1</sup>HNMR and <sup>13</sup>C NMR copies of 2h and (2n) (The NMR spectra were recorded in 400 MHz Bruker instrument and CDCl<sub>3</sub> were used as NMR solvent).

*Ethyl-1-phenyl-2-(4-bromophenyl)-4-hydroxy-5-oxo-2,5-dihydro-1H-pyrrole-3-carboxylate* (2h)







 $Methyl-1-phenyl-2-p-tolyl-4-hydroxy-5-oxo-2, 5-dihydro-1H-pyrrole-3-carboxylate~({\it 2n})$ 



