# **Supporting Information**

# Synthesis of oxazoles by silver catalysed oxidative decarboxylation-cyclization of α-oxocarboxylates and isocyanides

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## **General Considerations**

All manipulations were carried out using standard Schlenk techniques. Unless otherwise stated, analytical grade solvents and commercially available reagents were used to conduct the reactions. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum ether (bp. 60-90 °C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum ether to the ethyl acetate. All new compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS. The known compounds were characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. The chemical shifts (δ) were given in part per million relative to internal tetramethyl silane (TMS, 0 ppm for <sup>1</sup>H), CDCl<sub>3</sub> (77.3 ppm for <sup>13</sup>C). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument and accurate masses were reported for the molecular ion + Hydrogen (M+H).

## **Experimental Procedures**

#### **1.** Preparation of substituted α-oxocarboxylic acids:

All kinds of substituted  $\alpha$ -oxocarboxylic acids were prepared from oxidation of corresponding methyl ketones with SeO<sub>2</sub> according to the reported procedure.<sup>1</sup>

#### **2.** Preparation of substituted α-oxocarboxylates:

All the substituted  $\alpha$ -oxocarboxylic acids were reacted with KOH (1:1) in *i*PrOH for 3h, and the desired  $\alpha$ -oxocarboxylates was obtained by removing the *i*PrOH.<sup>2</sup>

#### 3. General procedure for oxazoles synthesis:

A mixture of  $\alpha$ -oxocarboxylates **1a** (0.25 mmol, 47.1 mg), ethyl 2-isocyanoacetate **2a** (0.50 mmol, 56.6 mg), Ag<sub>2</sub>CO<sub>3</sub> (0.025 mmol, 6.9 mg), 1,10-phen (0.125 mmol, 22.5 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.75 mmol, 202.7mg) in DMF (1.0 mL) was stirred under an N<sub>2</sub> atmosphere at 80 °C for 12 h. After completion of the reaction, as indicated by TLC and GC-MS, the solid was filtered off and washed with ethyl acetate. After removal of the solvent of the filtrate, the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1) to afford **3a** in 88% yield.

## **Mechanism Study**

#### 1. operando IR

Procedure for the stepwise reaction between **1a**, Ag<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and **2a**:

An oven-dried three necked reaction vessel was fitted with a magnetic stirring bar. The IR probe was inserted through an adapter into the middle neck; the other two necks were capped by septa for injections and a nitrogen line. The reaction vessel was kept at 60 °C and was allowed to be vacuumed and purged with nitrogen for three times. Then 4.0 mL DMSO and oxophenylacetate **1a** (0.50 mmol, 94.1 mg), Ag<sub>2</sub>CO<sub>3</sub> (0.05 mmol, 13.8 mg), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (1.5 mmol, 405.5 mg) were added in via syringes. The data collection was started. After 10 min, ethyl 2-isocyanoacetate **2a** (1.0 mmol, 113 .1 mg) was also added. *Operando* IR spectra were recorded over the course of the reaction

(Figure S1 and Figure S2).

Figure S1



**Figure S1.** The 3D-Kinetic profile of the reaction of **1a** (1.0 mmol), Ag<sub>2</sub>CO<sub>3</sub> (0.1 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (3.0 mmol) and **2a** (2.0 mmol) in DMSO (4.0 mL) at 60 °C; the reaction was monitored by *operando* IR.



**Figure S2**. (A) The absorbance of component **A** in 3D-Kinetic profile; (B) Spectra of the component **A** (green curve) and standard sample (benzoyl-acylium salt, red curve).

ConcIRT spectra of the authentic samples of oxophenylacetate **1a**, ethyl 2isocyanoacetate **2a** and product **3a**:



Figure S3. Standard IR spectra of oxophenylacetate 1a, ethyl 2-isocyanoacetate 2a and product

3a.

### 2. EPR experiments

Procedure: X band, 9.4 GHz, at 160 K

- 1. Blank experiment: to a 25 mL schlenk tube equipped with a stir bar,  $Ag_2CO_3$  (0.025 mmol, 6.9 mg) was added under N<sub>2</sub> atmosphere, then 1.0 mL DMF was injected to the tube. The reaction was conducted at 80 °C for 2 h. Then sample 0.5 mL from it and preserved in liquid nitrogen for EPR exam.
- Experiment: to a 25 mL schlenk tube equipped with a stir bar, a mixture of Ag<sub>2</sub>CO<sub>3</sub> (0.025 mmol, 6.9 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.75 mmol, 202.7 mg) was added under N<sub>2</sub> atmosphere, then 1.0 mL DMF was injected to the tube. The reaction was conducted at 80 °C for 2 h. Then sample 0.5 mL from it and preserved in liquid nitrogen for EPR exam.

### 3. Radical inhibiting experiments

Procedure: to a 25 mL schlenk tube equipped with a stir bar, a mixture of potassium oxophenylacetate **1a** (0.25 mmol, 47.1 mg),  $Ag_2CO_3$  (0.025 mmol, 6.9 mg), 1,10-phen (0.0125 mmol, 22.5 mg),  $K_2S_2O_8$  (0.5 mmol, 135.2 mg) and radical trapping reagent (TEMPO or BHT 0.5 mmol, 78.1 mg or 110.2 mg) were under N<sub>2</sub> atmosphere, then 2.0 mL DMF was injected to the tube. After 5 min, ethyl 2-isocyanoacetate **2a** (0.50 mmol, 56.6 mg) was added to the tube under N<sub>2</sub>. Then the reaction was conducted at 80 °C for 20 h. After completion of the reaction, it was analysis by GC using biphenyl as the internal standard.

## **Characterization of Products**



47.8 mg (0.25 mmol scale). <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 8.06-8.03 (m, 2H), 7.90 (s, 1H), 7.46-7.44 (m, 3H), 4.40 (q, J = 7.2 Hz, 2H), 1.39 ppm (t, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (100 M, in CDCl<sub>3</sub>): 162.1, 155.7, 149.3, 130.7, 128.7, 128.6, 126.9, 61.6, 14.4 ppm.<sup>3</sup>



43.9 mg (0.25 mmol scale). <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 7.97-7.95 (m, 2H), 7.89 (s, 1H), 7.28-7.26 (m,

2H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.40 ppm (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 M, in CDCl<sub>3</sub>): 162.2, 156.0, 148.9, 141.0, 129.3, 128.6, 126.2, 124.0, 61.5, 21.7, 14.4 ppm. HRMS (ESI) calculated [M]<sup>+</sup>: 231.0895; found [M+H]<sup>+</sup>: 232.0961.



38.1 mg (0.25 mmol scale). <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 7.79 (s, 1H), 7.38-7.36 (m, 1H), 7.33-7.29 (m, 1H), 7.23-7.18 (m, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.19 (s, 3H), 1.19 ppm (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 M, in CDCl<sub>3</sub>): 161.6, 150.1, 138.1, 131.0, 130.7, 130.5, 128.5, 126.7, 125.6, 61.3, 20.2, 14.2 ppm. HRMS (ESI) calculated [M]<sup>+</sup>: 231.0895; found [M+H]<sup>+</sup>: 232.0959.



49.5 mg (0.25 mmol scale). <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 8.05-8.03 (m, 2H), 7.84 (s, 1H), 6.97-6.95 (m, 2H), 4.39 (q, J = 7.2 Hz, 2H), 3.83 (s, 3H), 1.38 ppm (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 M, in CDCl<sub>3</sub>): 162.4, 161.4, 156.0, 148.6, 130.3, 125.5, 119.4, 114.0, 61.5, 55.6, 14.5 ppm.<sup>3</sup>



42.0 mg (0.25 mmol scale). <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 7.91 (s, 1H), 7.47-7.41 (m, 2H), 7.04-6.95 (m, 2H), 4.28 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 1.25 ppm (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 M, in CDCl<sub>3</sub>): 161.9, 157.6, 153.0, 150.0, 132.2, 131.6, 128.8, 120.4, 116.3, 111.3, 61.1, 55.7, 14.3 ppm. HRMS (ESI) calculated [M]<sup>+</sup>: 247.0845; found [M+H]<sup>+</sup>: 248.0902.



44.9 mg (0.25 mmol scale). <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 8.22-8.20 (m, 2H), 7.96 (s, 1H), 7.72-7.70 (m,

2H), 4.42 (q, J = 7.2 Hz, 2H), 1.40 ppm (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 M, in CDCl<sub>3</sub>): 161.9, 154.1, 149.8, 132.2 (q,  $J_{CF} = 32.6$  Hz), 130.6, 130.2, 129.0, 128.2, 125.7 (q,  $J_{CF} = 3.7$  Hz), 124.0 (q,  $J_{CF} = 270.7$ Hz), 62.0, 14.4 ppm. <sup>19</sup>F NMR (400 M, in CDCl<sub>3</sub>): -63.1 ppm. HRMS (ESI) calculated [M]<sup>+</sup>: 285.0613; found [M+H]<sup>+</sup>: 286.0674.



42.8 mg (0.25 mmol scale). <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 8.06-8.03 (m, 2H), 7.92 (s, 1H), 7.45-7.42 (m, 2H), 4.41 (q, *J* = 6.8 Hz, 2H), 1.40 ppm (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 M, in CDCl<sub>3</sub>): 162.1, 154.7, 149.3, 136.9, 130.0, 129.0, 127.1, 125.4, 61.9, 14.5 ppm. HRMS (ESI) calculated [M]<sup>+</sup>: 251.0349; found [M+H]<sup>+</sup>: 252.0412.



40.9 mg (0.25 mmol scale). <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 8.01 (s, 1H), 7.51-7.48 (m, 2H), 7.45-7.40 (m, 1H), 7.37-7.34 (m, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.23 ppm (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 M, in CDCl<sub>3</sub>): 161.1, 150.4, 134.3, 132.2, 131.7, 129.9, 126.5 (2C), 61.3, 14.0 ppm. HRMS (ESI) calculated [M]<sup>+</sup>: 251.0349; found [M+H]<sup>+</sup>: 252.0416.



52.6 mg (0.25 mmol scale). <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 7.99-7.95 (m, 2H), 7.92 (s, 1H), 7.61-7.58 (m, 2H), 4.41 (q, *J* = 7.2 Hz, 2H), 1.40 ppm (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 M, in CDCl<sub>3</sub>): 161.8, 154.4, 149.1, 131.7, 129.8, 126.9, 125.5, 125.0, 61.6, 14.2 ppm. HRMS (ESI) calculated [M]<sup>+</sup>: 294.9844; found [M+H]<sup>+</sup>: 295.9904.



51.8 mg (0.25 mmol scale). <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 8.22-8.21 (m, 1H), 8.02-8.00 (m, 1H), 7.92 (s, 1H), 7.56-7.54 (m, 1H), 7.34-7.29 (m, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.38 ppm (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 M, in CDCl<sub>3</sub>): 161.8, 153.8, 149.5, 133.5, 131.4, 130.1, 128.7, 127.5, 127.2, 122.6, 61.8, 14.4 ppm. HRMS (ESI) calculated [M]<sup>+</sup>: 294.9844; found [M+H]<sup>+</sup>: 295.9903.



51.5 mg (0.25 mmol scale). <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 7.92 (s, 1H), 7.85-7.80 (m, 4H), 4.41 (q, *J* = 6.8 Hz, 2H), 1.41 ppm (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 M, in CDCl<sub>3</sub>): 162.1, 154.9, 149.4, 138.0, 130.1, 127.3, 126.4, 97.5, 61.9, 14.5 ppm. HRMS (ESI) calculated [M]<sup>+</sup>: 342.9705; found [M+H]<sup>+</sup>: 343.9767.



42.7 mg (0.25 mmol scale). <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 8.06-8.04 (m, 2H), 7.89 (s, 1H), 7.45-7.26 (m, 2H), 3.91 ppm (s, 3H); <sup>13</sup>C NMR (100 M, in CDCl<sub>3</sub>): 162.5, 155.8, 149.2, 130.7, 128.6, 128.5, 126.7, 126.4, 52.5 ppm. HRMS (ESI) calculated [M]<sup>+</sup>: 203.0582; found [M+H]<sup>+</sup>: 204.0647.



19.1 mg (0.25 mmol scale). <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 7.77 (s, 1H), 7.35-7.27 (m, 5H), 4.44 (q, *J* = 7.2 Hz, 2H), 4.42 (s, 2H), 1.43 ppm (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 M, in CDCl<sub>3</sub>): 158.0, 149.6, 136.2, 129.0, 128.7, 127.5, 127.3, 61.4, 32.2, 14.5 ppm. HRMS (ESI) calculated [M]<sup>+</sup>: 231.0895; found [M+H]<sup>+</sup>: 232.0952.



10.1 mg (0.25 mmol scale). <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 7.73 (s, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 2.62 (s, 3H), 1.37 ppm (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 M, in CDCl<sub>3</sub>): 162.4, 156.7, 149.0, 127.5, 61.2, 14.5, 12.1 ppm. HRMS (ESI) calculated [M]<sup>+</sup>: 155.0582; found [M+H]<sup>+</sup>: 156.0655.



30.1 mg (0.25 mmol scale). <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 8.07-8.06 (m, 1H), 7.81 (s, 1H), 7.52-7.51 (m, 1H), 7.15-7.12 (m, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.42 ppm(t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 M, in CDCl<sub>3</sub>): 162.0, 148.4, 130.7, 130.1, 128.3, 128.0, 124.7, 61.6, 14.5 ppm. HRMS (ESI) calculated [M]<sup>+</sup>: 223.0303; found [M+H]<sup>+</sup>: 224.0369.



42.8 mg (0.25 mmol scale). <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 8.65 (s, 1H), 8.09-8.06 (m, 1H), 7.93-7.87 (m, 4H), 7.53-7.50 (m, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.41 ppm (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 M, in CDCl<sub>3</sub>): 162.2, 155.7, 149.2, 134.1, 132.9, 129.2, 129.1, 128.2, 127.8, 127.7, 127.0, 126.8, 125.0, 124.1, 61.6, 14.5 ppm. HRMS (ESI) calculated [M]<sup>+</sup>: 267.0895; found [M+H]<sup>+</sup>: 268.0955.

## References

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## NMR and HRMS Spectra of Products



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)







































































