# **Electronic Supplementary Information**

### Merging Gold Catalysis, Organocatalytic Oxidation, and Lewis Acid Catalysis for Chemodivergent Synthesis of Functionalized Oxazoles from N-Propargylamides

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#### **1. General Information**

Unless specified, all metal complexes, reagents, and starting materials were purchased from commercial sources and used as received.  $Ph_3PAuCl^1$  and  $Ph_3PAuNTf_2^2$  were prepared according to the published methods. Metal salts were stored in a nitrogen atmosphere dry box. Acetonitrile, methanol, toluene, THF, Et<sub>2</sub>O, and CH<sub>2</sub>Cl<sub>2</sub> were dried by filtration through alumina according to the procedure of Grubbs.<sup>3</sup> All reactions were carried out under an atmosphere of nitrogen in glassware, which had been oven-dried. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at ambient temperature using 500 MHz spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the  $\delta$  scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integrations. High-resolution mass spectra (HRMS) were recorded with a Waters Micromass GCT Premier using an electron impact (EI) technique or an Agilent 1290 using an electrospray ionization (ESI) technique by peak matching.

<sup>(1)</sup> Zalesskiy, S. S.; Sedykh, A. E.; Kashin, A. S.; Ananikov. V. P. J. Am. Chem. Soc. 2013, 135, 3550.

<sup>(2)</sup> Mezailles, N.; Ricard, L.; Gagosz, F. Org. Lett. 2005, 19, 4133.

<sup>(3)</sup> Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Organometallics 1996, 15, 1518.

#### 2. Synthesis of Substrates

#### 2.1 Synthesis of *N*-Propargylamides<sup>4</sup>

$$R-COOH + CI \xrightarrow{O}_{O} CI \xrightarrow{DMF (1 \text{ mol}\%)}_{O} R \xrightarrow{O}_{R} CI \xrightarrow{H_2N}_{NEt_3} R \xrightarrow{O}_{H}$$

To a solution of carboxylic acid (5 mmol) in DCM (20 mL) was added dropwise oxalyl chloride (6.5 mmol) and DMF (1 mol %) sequentially at room temperature in a round bottom flask. The resulting mixture was stirred at room temperature for 3 h and monitored by TLC analysis. After reaction was completed, the solvent was removed in vacuo. Concentration led to the acid chloride, which was used directly for the next step.

Propargylic amine was dissolved in dry DCM (20 ml) and 1 equiv of Et<sub>3</sub>N and 2 mol% DMAP were added. After cooling to 0 °C, the acid chloride was added dropwise and the mixture was stirred for 15 min at 0 °C and for further 5 h at room temperature. After the reaction was completed, water was added and the mixture was extracted three times with DCM. The combined organic phases were dried over MgSO<sub>4</sub>. After filtration and the solvent was removed in vaccuo. The product was purified either by column chromatography or by recrystallization.

#### 2.2 Synthesis of Methyleneoxazoline 52



To a solution of *N*-propargylamide **1** (2 mmol) in dry DCM was added PPhAuNTf<sub>2</sub> (2 mol %). The resulting mixture was stirred at room temperature for 12 h. The product was purified by silica gel chromatography (PE/ EA = 20:1 as eluent) affording product **524** in 85% yield (270 mg) as a solid.

<sup>(4)</sup> Hashmi, A. S. K.; Jimes, M. C. B.; Schuster, A. M.; Rominger. F. J. Org. Chem. 2012, 77, 6394.

#### 2.3 Preparation of Oxazole 53



To a solution of *N*-propargylamide **1** (2 mmol) in dry DCE was added FeCl<sub>3</sub> (50 mol %). The resulting mixture was stirred at 80 °C for 2h. The reaction mixture was diluted with water. The aqueous layer was extracted with  $CH_2Cl_2$  (3x10 mL), and the combined organic layers were washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Silica gel chromatography (PE/ EA) gave the desired oxazole **53**<sup>5</sup> (220 mg) as a white solid in 71% yield.

#### 2.4 Preparation of Aldoxime 54



In a dry Schlenk, *N*-propargylamide **1** (5 mmol) and NIS (1.2 equiv) were dissolved in 20 mL DCE. The resulting mixture was stirred at room temperature for 2 h and then stirred at 80 °C under an  $O_2$  atmosphere until the consumption of starting materials monitored by TLC. After the reaction was completed, the solvent was evaporated and the residue was purified by column chromatography (petroleum ether/EtOAc: 30/1), giving aldehyde **4**<sup>6</sup> (484 mg) as a white solid in 61% yield.

To a solution of aldehyde **4** (2 mmol) in EtOH (20 mL) was added hydroxylamine hydrochloride (6 mmol), Na<sub>2</sub>CO<sub>3</sub> (3 mmol) and water (9 mL). The resulting mixture was stirred at 95 °C for 3 h. The reaction mixture was diluted with water. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x10 mL), and the combined organic layers were washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Silica gel chromatography (PE/ EA) gave the desired Oxime **54** (338 mg) in 90% yield as a white solid. <sup>1</sup>H NMR (**500 MHz, DMSO**)  $\delta$  11.77 (s, 1H), 8.23 (s, 1H), 8.14-7.97 (m, 2H), 7.65-7.47 (m, 4H). <sup>13</sup>C NMR (**126 MHz, DMSO**)  $\delta$  163.1, 162.0, 146.3, 143.9, 139.0, 135.4, 134.6, 132.97, 132.92, 130.8, 130.60, 130.57, 127.7, 127.6, 126.9, 126.8. HRMS (ESI+) *m/z* calcd for C<sub>10</sub>H<sub>9</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M + H]<sup>+</sup>): 189.0659, found: 189.0651.

<sup>(5)</sup> Senadi, G. C.; Hu, W-P.; Hsiao, J-S.; Vandavasi, J. K.; Chen, C-Y.; Wang. J.-J. Org. Lett. **2007**, *9*, 1887.

<sup>(6)</sup> Hu, Y.; Yi, R.; Wang, C.; Xin, X.; Wu, F.; Wan. B. J. Org. Chem. 2014, 79, 3052.

#### 3. General Procedure for Au/NHPI/LA Catalysis

#### 3.1 5-Oxazolecarbonitrile Synthesis Catalyzed by Au/NHPI/Ni Ternary System



**Conditions A:** A sealable Schlenk tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg), Ni(acac)<sub>2</sub> (0.015 mmol, 3.9 mg), propargylic amide **1** (0.2 mmol, 31.8 mg), NHPI (0.06 mmol, 9.8 mg), MgO (0.6 mmol, 36.3 mg), CH<sub>3</sub>CN (1 mL) and 'BuONO (0.6 mmol, 66  $\mu$ L), were added under nitrogen. The Schlenk tube was sealed and immersed into an oil bath preheated at 50 °C for 3 h. After the reaction was completed, the solvent was evaporated and the organic product purified by column chromatography (petroleum ether/EtOAc: 30/1), giving the expected product **2** (24 mg, 70%) as a white solid.

#### 3.2 5-Oxazolecarboxamide Synthesis Catalyzed by Au/NHPI/Cu Ternary System



**Conditions B:** A sealable Young-type tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg), Cu(OAc)<sub>2</sub> (0.03 mmol, 6.0 mg), propargylic amide **1** (0.2 mmol, 31.8 mg), NHPI (0.06 mmol, 9.8 mg), THF (1 mL) and 'BuONO (0.6 mmol, 66  $\mu$ L) were added under nitrogen. Then Young-type tube was sealed and immersed into an oil bath preheated at 80 °C overnight. After the reaction was completed, the reaction mixture was diluted with water. The aqueous layer was extracted with EA (3x10 mL), and the combined organic layers were washed with sat. NaHCO<sub>3</sub>, water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc: 1/2), giving the expected product **3** (26 mg, 68%) as a white solid.

#### 4. Optimization of the Reaction Conditions

#### Table S1. Optimization of the Reaction Conditions<sup>a</sup>



<sup>a</sup>Reaction conditions: *N*-propargylbenzamide **1** (0.2 mmol), gold catalyst (5 mol %), NHPI (30 mol %), Lewis acid (5–15 mol %), and 'BuONO (3 equiv) in anhydrous solvent (1 mL) at 50 °C or 80 °C under N<sub>2</sub> atomosphere unless otherwise specified. <sup>*h*</sup>GC yield. <sup>c</sup>Acid additives tested: Pd(OAc)<sub>2</sub>, PdCl<sub>2</sub>, CuO, CuCl<sub>2</sub>, CuSO<sub>4</sub>, ZnCl<sub>2</sub>, Zn(OTf)<sub>2</sub>, Sc(OTf)<sub>3</sub>, NiCl<sub>2</sub>, FeCl<sub>2</sub>, FeCl<sub>3</sub>, Mn(OAc)<sub>2</sub>·2H<sub>2</sub>O, Mn(acac)<sub>3</sub>, AlCl<sub>3</sub>, BF<sub>3</sub>·Et<sub>2</sub>O, HOAc, and CF<sub>3</sub>CO<sub>2</sub>H. <sup>*d*</sup>MgO (3 equiv) was added. <sup>*e*</sup>Isolated yield. <sup>*f*</sup>A Å MS (150 mg) was added. <sup>*g*</sup>Silver salts (5 mol %) were used *in situ* to activate the neutral gold complexes. <sup>*h*</sup>Without NHPI or 'BuONO. NHPI = *N*-hydroxyphthalimide. Tf = trifluoromethanesulfonyl. acac = acetylacetonate. IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene. JohnPhos = 2-(di-*tert*-butylphosphino)biphenyl. MTBE = methyl *tert*-butyl ether

#### 5. Mechanistic Experiments

#### **5.1 Control Experiments**

#### **Reaction of Vinyl–Gold Complex 55**



A sealable Schlenk tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then Ni(acac)<sub>2</sub> (0.00375 mmol, 1 mg), vinyl-Au complex **55**<sup>7</sup> (0.05 mmol, 26.2 mg), NHPI (0.015 mmol, 2.5 mg), MgO (0.15 mmol, 9 mg), CH<sub>3</sub>CN (0.3 mL) and 'BuONO (0.15 mmol, 17  $\mu$ L), were added under nitrogen. The Schlenk tube was sealed and immersed into an oil bath preheated at 50 °C for 3 h. The reaction was analyzed directly by GC and TLC.

#### **Reaction of Internal Alkyne Substrate 58**



A sealable Schlenk tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg), Ni(acac)<sub>2</sub> (0.015 mmol, 3.9 mg), internal alkyne **58**<sup>8</sup> (0.2 mmol, 47 mg), NHPI (0.06 mmol, 9.8 mg), MgO (0.6 mmol, 36.3 mg), CH<sub>3</sub>CN (1 mL) and 'BuONO (0.6 mmol, 66  $\mu$ L), were added under nitrogen. The Schlenk tube was sealed and immersed into an oil bath preheated at 50 °C for 3 h. After the reaction was completed, the solvent was evaporated and the organic product purified by column chromatography (petroleum ether/EtOAc: 4/1), giving the ketone **59** (12.5 mg, 25%) as a yellow solid. Trace amounts of ketone **59** can be obtained under the same condition without PPh<sub>3</sub>AuNTf<sub>2</sub>.

<sup>(7)</sup> Hashmi, A. S. K.; Schuster, A. M.; Rominger, F. Angew. Chem., Int. Ed. 2009, 48, 8247.

<sup>(8)</sup> Sinai, Á.; Vangel, D.; Gáti, T.; Bombicz, P.; Novák. Z. Org. Lett. 2015, 17, 4136.

Phenyl(2-phenyloxazol-5-yl)methanone (CAS: 1509895-03-7) (59)<sup>9</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.25-8.18 (m, 2H), 8.05-7.98 (m, 2H), 7.89 (d, J = 7.7 Hz, 1H), 7.71-7.61 (m, 1H), 7.59-7.48 (m, 5H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  181.4, 164.8, 149.0, 137.6, 136.9, 133.2, 131.9, 128.99, 128.97, 128.8, 127.5, 126.2.

#### **5.2 Isotope Labeling Experiments**



A sealable Schlenk tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg), propargylic amide **1**- $d^{10}$  (0.2 mmol, 32 mg), NHPI (0.06 mmol, 9.8 mg), MgO (0.6 mmol, 36.3 mg), CH<sub>3</sub>CN (1 mL) and 'BuONO (0.6 mmol, 66 µL), were added under nitrogen. The Schlenk tube was sealed and immersed into an oil bath preheated at 50 °C for 3 h. Then filtered over a small column of silica gel and the solvent was removed from vacuum. The residue was analyzed directly by crude NMR giving the **4**-*d* (75% D).



<sup>(9)</sup> Bathula, S. R.; Reddy, M. P.; Viswanadham, K. K. D. R.; Sathyanarayana, P.; Reddy, M. S. *Eur. J. Org. Chem.* **2013**, 4552.

<sup>(10)</sup> Hashmi, A. S. K.; Weyrauch, J. P.; Frey, W.; Bats, J. W. Org. Lett. 2004, 6, 4391.



A sealable Schlenk tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg), propargylic amide **1-***d* (0.1 mmol, 18 mg), propargylic amide **56** (0.1 mmol, 14 mg), NHPI (0.06 mmol, 9.8 mg), MgO (0.6 mmol, 36.3 mg), CH<sub>3</sub>CN (1 mL) and 'BuONO (0.6 mmol, 66  $\mu$ L), were added under nitrogen. The Schlenk tube was sealed and immersed into an oil bath preheated at 50 °C for 3 h. Then filtered over a small column of silica gel and the solvent was removed from vacuum. The residue was analyzed directly by crude NMR giving the **4-***d* (75% D) and **57** (0% D). The ratio of **4-***d* and **57** was 4:1.





A sealable Schlenk tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg), propargylic amide **1-d(N)** (0.2 mmol, 32 mg), NHPI (0.06 mmol, 9.8 mg), CH<sub>3</sub>CN (1 mL) and 'BuONO (0.6 mmol, 66  $\mu$ L), were added under nitrogen. The Schlenk tube was sealed and immersed into an oil bath preheated at 50 °C for 3 h. Then filtered over a small column of silica gel and the solvent was removed from vacuum. The residue was analyzed directly by crude NMR giving the **4** (0% D).





A sealable Schlenk tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg), propargylic amide **1** (0.2 mmol, 31.8 mg), NHPI (0.06 mmol, 9.8 mg), D<sub>2</sub>O (1 mmol, 18 mg), CH<sub>3</sub>CN (1 mL) and 'BuONO (0.6 mmol, 66  $\mu$ L), were added under nitrogen. The Schlenk tube was sealed and immersed into an oil bath preheated at 50 °C for 3 h. Then filtered over a small column of silica gel and the solvent was removed from vacuum. The residue was analyzed directly by crude NMR giving the **4** (0% D)



#### 5.3<sup>31</sup>P NMR study

a) A sealable Schlenk tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg) was added followed with CDCl<sub>3</sub> (1 mL) under nitrogen. The Schlenk tube was sealed and immersed into an oil bath preheated at 50 °C for 20 mins. The residue was analyzed directly by crude <sup>31</sup>P NMR to give a 30.48 ppm peak.

b) A sealable Schlenk tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg) and 'BuONO (0.6 mmol, 66  $\mu$ L) were added followed with CDCl<sub>3</sub> (1 mL) under nitrogen. The Schlenk tube was sealed and immersed into an oil bath preheated at 50 °C for 20 mins. The residue was analyzed directly by crude <sup>31</sup>P NMR to give two peaks: 30.48 ppm and -50.0 ppm.



a)

S12

According to the <sup>31</sup>P NMR data, we speculate the another possible pathway maybe involved in the catalytic cycle:



#### 5.4 Analysis of EPR spectra

EPR measurements: EPR spectra were recorded at room temperature on a JEOL JES-FA200 spectrometer (9074 MHz): Mod. Amplitude = 5 G; Time Constan = 100 msec; Sweep time = 60 sec; Power = 1 mw. DMPO (5, 5-dimethyl-1-pyrroline *N*-oxide) was employed as the radical trap. The assignment of the radicals in Figure S1-S7 was referred to the simulations in Figure S8 correspondingly.

To further understand the details of the radical reaction, a series of mechanistic studies by electron paramagnetic resonance (EPR) spectroscopy was performed under various conditions (Figures S1-S7). Firstly, a very strong EPR signal of NO species was observed in the reaction mixture of Conditions A without of addition of NHPI and DMPO (Figure S3b), however, the control experiments under absolute Conditions A and Conditions A in the absence of TBN just gave very weak or no EPR signal at all (Figure S1b and S2b). These results suggested that the TBN is the source of NO radicals and NHPI is the scavenger of NO radical. The *N*-centered TBN radical was configured by the characteristic isotropic g-value (2.0056) and hyperfine coupling constant a<sub>iso</sub> (28.5 G). When the free-radical spin-trapping agent DMPO was added to the above three reaction mixtures, a superposition of EPR signals of the trapping radicals was observed under absolute Conditions A and the condition in the absence of NHPI (Figure S1a and S3a). Data analysis suggests that both N-centered radical and O-centered radical were generated and quickly trapped by DMPO to form the relatively stable radical A  $(a_{N1} = 13.6 \text{ G}, a_{H\beta} = 19.5 \text{ G}, a_{N2} = 2.35 \text{ G})$  and B  $(a_{N1} = 13.6 \text{ G}, a_{H\beta} = 10.5 \text{ G})$ . Further EPR experiments were performed under absolute Conditions B as well as in the absence of TBN or NHPI. Once again, with the addition of free radical spin trapping agent DMPO, both N-centered radical and O-centered radical were generated and trapped by DMPO to form relatively stable radicals A and B as well (Figure S4), which is consistent to Conditions A. And the condition in the absence of TBN only gave the clear N-centered radical signal ( $a_{N1} =$ 13.6 G,  $a_{H\beta} = 19.5$  G,  $a_{N2} = 2.35$  G) (Figure S5), suggesting that O-centered radical comes

from TBN, and the formation of *N*-centered radical is independent to TBN; in another word, the result suggests that NHPI promotes the formation of *N*-centered radical. However, without the addition of NHPI in the reaction mixture, only *O*-centered radical is detected ( $a_{N1} = 13.6$  G,  $a_{H\beta} = 10.5$  G) (Figure S6), that means that either *N*-centered radical is not formed or it is consumed by TBN. In order to understand the role of Au catalyst in this transformation, one experiment without PPh<sub>3</sub>AuNTf<sub>2</sub> is carried out as well (Figure S7), this time both *N*-centered radical and *O*-centered radical are detected, indicating that Au will not affect the radical formation.

# EPR spectrum of reaction system under standard conditions for Conditions A (a)



S15

**Figure S1**. EPR spectra (X band, 9.07 GHz, RT) of conditions: A sealable Schlenk tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg), Ni(acac)<sub>2</sub> (0.015 mmol, 3.9 mg), proparpylic amide **1** (0.2 mmol, 31.8 mg), NHPI (0.06mmol, 9.8 mg), MgO (0.6 mmol, 36.3 mg), CH<sub>3</sub>CN (1 mL) and 'BuONO (0.6 mmol, 66  $\mu$ L) were added under nitrogen. The Schlenk tube was sealed and immersed into an oil bath preheated at 50 °C for 0.5 h. (a) 0.05mL of this reaction solution was taken out into a small tube, followed by the addition of 0.05 mL DMPO (1\*10<sup>-2</sup> M). Then, this mixture was used for EPR measurement. (b) The reaction mixture was directly used for EPR measurement without addition of DMPO.

Note: (a) Figure S1 shows that both N-centered radical and O-centered radical were detected under the above conditions. (b) Without DMPO, very weak NO radical detected.





**(a)** 



S16

**Figure S2**. EPR spectra (X band, 9.7 GHz, RT) of conditions: A sealable Schlenk tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg), Ni(acac)<sub>2</sub> (0.015 mmol, 3.9 mg), proparpylic amide **1** (0.2 mmol, 31.8 mg), NHPI (0.06 mmol, 9.8 mg), MgO (0.6 mmol, 36.3 mg), CH<sub>3</sub>CN (1 mL) were added under nitrogen. The Schlenk tube was sealed and immersed into an oil bath preheated at 50 °C for 0.5 h. (a) 0.05 mL of this reaction solution was taken out into a small tube, followed by the addition of 0.05 mL DMPO (1\*10<sup>-2</sup> M). Then, this mixture was used for EPR measurement. (b) The reaction mixture was directly used for EPR measurement without addition of DMPO.

Note: (a) Figure S2 shows that no radical signal was observed above the noise level, indicating NO radical comes from TBN. (b) Without DMPO, no radical was detected, indicating NO comes from TBN.



**(a)** 



**(b)** 



**Figure S3**. EPR spectra (X band, 9.7 GHz, RT) of conditions: A sealable Schlenk tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg), Ni(acac)<sub>2</sub> (0.015 mmol, 3.9 mg), proparpylic amide **1** (0.2 mmol, 31.8 mg), MgO (0.6 mmol, 36.3 mg), CH<sub>3</sub>CN (1 mL) and 'BuONO (0.6 mmol, 66  $\mu$ L) were added under nitrogen. The Schlenk tube was sealed and immersed into an oil bath preheated at 50 °C for 0.5 h. (a) 0.05 mL of this reaction solution was taken out into a small tube, followed by the addition of 0.05 mL DMPO (1\*10<sup>-2</sup> M). Then, this mixture was used for EPR measurement. (b) The reaction mixture was directly used for EPR measurement without addition of DMPO.

Note: (a) Figure S3 shows that both N-centered radical and O-centered radical signals were observed under the above reaction conditions. It means that NHPI is the radical trapper for both radicals. (b) Without DMPO, strong NO EPR signal observed, suggesting the accumulation of NO radical in the absence of NHPI, and also suggesting that NHPI is the scavenger of NO radical.



EPR spectrum of reaction system under standard conditions for Conditions B

**Figure S4**. EPR spectra (X band, 9.7 GHz, RT) of conditions: A sealable Schlenk tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg), Cu(OAc)<sub>2</sub> (0.03 mmol, 6.0 mg), **1** (0.2 mmol, 31.8 mg), NHPI (0.06 mmol, 9.8 mg), THF (1 mL) and <sup>t</sup>BuONO (0.6 mmol, 66  $\mu$ L) were added under nitrogen. The Schlenk tube was sealed and immersed into an oil bath preheated at 80 °C for 2 hr. 0.05 mL of this

reaction solution was taken out into a small tube, followed by the addition of 0.05 mL DMPO ( $1*10^{-2}$  M). Then, this mixture was used for EPR measurement.

Note: Figure S4 shows that both N-centered radical and O-centered radical existed in the reaction mixture. It means that propargylamide (1a) was the substrate which could provide the N-centered radical, at the same time, combined with Figure S5, it suggests that O-centered radical comes from tBuONO.

EPR spectrum of reaction system for Conditions B without 'BuONO

**Figure S5**. EPR spectra (X band, 9.7 GHz, RT) of conditions: A sealable Schlenk tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg), Cu(OAc)<sub>2</sub> (0.03 mmol, 6.0 mg), **1** (0.2 mmol, 31.8 mg), NHPI (0.06mmol, 9.8 mg), THF (1 mL) were added under nitrogen. The Schlenk tube was sealed and immersed into an oil bath preheated at 80 °C for 2 hr. 0.05 mL of this reaction solution was taken out into a small tube, followed by the addition of 0.05 mL DMPO (1\*10<sup>-2</sup> M). Then, this mixture was used for EPR measurement.

Note: Figure S5 shows that N-centered radical signal was clearly observed in the absence of tBuONO. It means that the formation of N-centered radical was not affected by tBuONO or it was not related to tBuONO, in another word, NHPI might be responsible to the formation of N-centered radical.

EPR spectrum of reaction system for Conditions B without NHPI



**Figure S6**. EPR spectra (X band, 9.7 GHz, RT) of conditions: A sealable Schlenk tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg), Cu(OAc)<sub>2</sub> (0.03 mmol, 6.0 mg), **1** (0.2 mmol, 31.8 mg), THF (1 mL) and <sup>t</sup>BuONO (0.6 mmol, 66  $\mu$ L) were added under nitrogen. The Schlenk tube was sealed and immersed into an oil bath preheated at 80 °C for 2 hr. 0.05 mL of this reaction solution was taken out into a small tube, followed by the addition of 0.05 mL DMPO (1\*10<sup>-2</sup> M). Then, this mixture was used for EPR measurement.

Note: Figure S6 shows that only ROO radical signal was observed, it means that the formations of N-centered radical and O-centered radical are both related to NHPI, or suggests that either N-centered and O-centered radicals were not formed in the absence of NHPI or they were quenched by TBN due to the absence of NHPI.



EPR spectrum of reaction system for Conditions B without PPh<sub>3</sub>AuNTf<sub>2</sub>

**Figure S7**. EPR spectra (X band, 9.7 GHz, RT) of conditions: A sealable Schlenk tube was dried under vacuum using a heatgun, and evacuated and back-filled with nitrogen for two or three times. Then Cu(OAc)<sub>2</sub> (0.03 mmol, 6.0 mg), **1** (0.2 mmol, 31.8 mg), THF (1 mL) and 'BuONO (0.6 mmol, 66  $\mu$ L) were added under nitrogen. The Schlenk tube was sealed and immersed into an oil bath preheated at 80 °C for 2 hr. 0.02 mL of this reaction solution was taken out into a small tube, followed by the addition of 0.05 mL DMPO (2\*10<sup>-2</sup> M). Then, this mixture was used for EPR measurement.

Note: Figure S7 shows that both N-centered radical signal and ROO radical signal were observed. It means that the formation of radicals were independent of Au catalyst, that is Au catalyst is not responsible to the formation of radicals, which is consistent to the mechanism we proposed.

## Stimulations



Figure S8. Stimulations and Experimental results

#### 5.5 Attempt toTrap N-Centered Radical



A sealable Schlenk tube was dried under vacuum using a heatgun. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg), **61**<sup>11</sup> (0.2 mmol, 49 mg), NHPI (0.06 mmol, 9.8 mg), MgO (0.6 mmol, 36.3 mg), CH<sub>3</sub>CN (1 mL) and 'BuONO (0.6 mmol, 66  $\mu$ L), were added under air. The Schlenk tube was sealed and immersed into an oil bath preheated at 50 °C for 3 h. After the reaction was completed, the solvent was evaporated and the organic product purified by column chromatography (petroleum ether/EtOAc: 4/1), giving the product **62** (11 mg, 19%) as a white solid. <sup>1</sup>**H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.47-7.33 (m, 4H), 6.47 (s, 1H), 5.79 (dd, *J* = 7.7, 6.4 Hz, 1H), 3.54-3.29 (m, 2H), 2.06-2.00 (m, 1H), 1.96-1.85 (m, 1H), 1.75 (tdd, *J* = 10.5, 7.5, 3.8 Hz, 1H), 1.71-1.57 (m, 1H). <sup>13</sup>**C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  157.4 (d, *J* = 36.9 Hz), 137.3, 129.2, 129.0, 126.4, 115.7 (d, *J* = 288.0 Hz), 84.8, 39.3, 31.5, 25.2.



A sealable Schlenk tube was dried under vacuum using a heatgun. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg), **63**<sup>11</sup>(0.2 mmol, 39 mg), NHPI (0.06 mmol, 9.8 mg), MgO (0.6 mmol, 36.3 mg), CH<sub>3</sub>CN (1 mL) and 'BuONO (0.6 mmol, 66  $\mu$ L), were added under air. The Schlenk tube was sealed and immersed into an oil bath preheated at 50 °C for 3 h. The reaction was analyzed directly by GC-MS with starting material remained and no product **64** can be detected.



A sealable Schlenk tube was dried under vacuum using a heatgun. Then PPh<sub>3</sub>AuNTf<sub>2</sub> (0.01 mmol, 7.4 mg), ethylbenzene **65** (0.2 mmol, 21 mg), NHPI (0.06 mmol, 9.8 mg), MgO (0.6 mmol, 36.3 mg), CH<sub>3</sub>CN (1 mL) and 'BuONO (0.6 mmol, 66  $\mu$ L), were added under air. The Schlenk tube was sealed and immersed into an oil bath preheated at 50 °C for 3 h. The reaction was analyzed directly by GC-MS, product **66** and **67** can be detected.

<sup>(11)</sup> Chu, J. C. K.; T. Rovis. Nature 2007, 539, 272.

#### 6. Transformation of 5-Oxazolecarbonitrile 2



Synthesis of **2-phenyloxazole-5-carboxamide 3**.<sup>12</sup> A 25 mL round bottom Schlenk flask equipped with a magnetic stirring bar was charged with **2** (34 mg, 0.2 mmol), 'BuOK (67 mg, 0.6 mmol) and 'BuOH (3 mL). The reaction mixture was stirred at rt under nitrogen atmosphere for 12 h. Upon completion as indicated by TLC analysis, the reaction mixture was cooled to room temperature and cold water (10 mL) was added. The mixture was then extracted with EA. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated, and purified with silica gel column chromatography, eluting with PE: EA (1/2), to provide pure **3** as a pale yellow solid (34 mg, 90%).



Synthesis of **2-phenyloxazole-5-carboxylic acid 49**.<sup>13</sup> A 25 mL round bottom Schlenk flask equipped with a magnetic stirring bar was charged with **2** (34 mg, 0.2 mmol), KOH (34 mg, 0.6 mmol) and EtOH (3 mL). The reaction mixture was stirred at reflux temperature under nitrogen atmosphere for 12 h. Upon completion as indicated by TLC analysis, the reaction mixture was cooled to room temperature and cold water (10 mL) was added. The mixture was then extracted with EA. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated, and purified with silica gel column chromatography, eluting with CHCl<sub>3</sub>/EtOH (10/1), to provide pure **49**<sup>14</sup> as a pale yellow solid (28 mg, 74%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.18-8.02 (m, 2H), 7.78 (s, 1H), 7.67-7.55 (m, 3H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  162.1, 154.8, 143.9, 132.0, 130.1, 129.9, 127.0, 126.9.

<sup>(12)</sup> Midya, G. C.; Kapat, A.; Maiti, S.; Dash, J. J. Org. Chem. 2015, 80, 4148.

<sup>(13)</sup> Morita, H.; Shiotani. S. J. Heterocycl. Chem. 1987, 24, 373.

<sup>(14)</sup> Zhang, F.; Greaney, M. F. Org. Lett. 2010, 12, 4745.



Synthesis of **5-(4,5-dihydro-1***H***-imidazol-2-yl)-2-phenyloxazole**.<sup>15</sup> A 25 mL round bottom Schlenk flask equipped with a magnetic stirring bar was charged with **2** (34 mg, 0.2 mmol), *p*-toluenesulfonic acid monohydrate (57 mg, 0.3 mmol) and ethylenediamine (3.5 mL). The reaction mixture was stirred at reflux temperature under nitrogen atmosphere for 5 h. Upon completion as indicated by TLC analysis, the reaction mixture was cooled to room temperature and cold water (10 mL) was added. The mixture was then extracted with CHCl<sub>3</sub> (3 x 10 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated, and purified with silica gel column chromatography, eluting with CHCl<sub>3</sub>/EtOH (7/1), to provide pure **50** as a pale yellow solid (26 mg, 61%). <sup>1</sup>H NMR (**500 MHz, CDCl<sub>3</sub>**)  $\delta$  8.11-8.02 (m, 2H), 7.69 (s, 1H), 7.52-7.39 (m, 3H), 3.81 (s, 4H). <sup>13</sup>C NMR (**126 MHz, CDCl<sub>3</sub>**)  $\delta$  162.6, 154.7, 142.6, 131.2, 129.9, 128.9, 126.8, 126.5, 49.8, 29.7. HRMS (ESI+) *m/z* calcd for C<sub>12</sub>H<sub>12</sub>N<sub>3</sub>O<sup>+</sup> ([M + H]<sup>+</sup>): 214.0975, found: 214.0970.



Synthesis of **2-phenyl-5-(1***H***-tetrazol-5-yl)oxazole**.<sup>16</sup> A 25 mL round bottom Schlenk flask equipped with a magnetic stirring bar was charged with **2** (34 mg, 0.2 mmol), NaN<sub>3</sub> (26 mg, 0.4 mmol), NH<sub>4</sub>Cl (21.4 mg, 0.4 mmol) and DMF (2 mL). The reaction mixture was stirred at 120 °C under nitrogen atmosphere for 14 h. Upon completion as indicated by TLC analysis, the reaction mixture was cooled to room temperature, cold water (20 mL) was added and acidified with 2 M HCl until PH<1. The mixture was then extracted with EA (3 x 10 mL). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated, to provide pure **51** as a white solid (39 mg, 92%). <sup>1</sup>H NMR (**500 MHz, DMSO**)  $\delta$  8.15-8.10 (m, 2H), 8.10 (s, 1H), 7.67-7.61 (m, 3H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  162.9, 148.3, 139.2, 132.2, 130.4, 130.0, 127.1, 126.5. HRMS (ESI+) *m/z* calcd for C<sub>10</sub>H<sub>8</sub>N<sub>5</sub>O<sup>+</sup> ([M + H]<sup>+</sup>): 214.0723, found: 214.0724.

<sup>(15)</sup> Nasr-Esfahani, M.; Montazerozohori, M.; Mehrizi, S. J. Heterocycl. Chem. 2011, 48, 249.

<sup>(16)</sup> Zhou, W.; Zhang, L.; Jiao, N. Angew. Chem., Int. Ed. 2009, 48, 7094.

#### 7. Characterization of Products



**2-Phenyloxazole-5-carbonitrile (CAS: 1391828-42-4) (2)** was obtained as a white solid (24 mg, 70%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.11-8.06 (m, 2H), 7.81 (s, 1H), 7.60-7.48 (m, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.8, 139.0, 132.3, 129.1, 127.3, 125.5, 124.1, 109.5. HRMS (ESI+) *m*/*z* calcd for C<sub>10</sub>H<sub>7</sub>N<sub>2</sub>O<sup>+</sup> ([M + H]<sup>+</sup>): 171.0553, found: 171.0557.



2-(p-Tolyl)oxazole-5-carbonitrile (5) was obtained as a white solid

(22 mg, 61%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 (d, J = 8.2 Hz, 2H), 7.79 (s, 1H), 7.31 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  165.1, 143.0, 139.1, 129.8, 127.3, 123.8, 122.8, 109.6, 21.7. HRMS (EI) m/z calcd for C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O<sup>+</sup> ([M]<sup>+</sup>): 184.0631, found: 184.0630.



**2-(4-Isopropylphenyl)oxazole-5-carbonitrile (6)** was obtained as a white solid (24 mg, 56%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (d, J = 8.4 Hz, 2H), 7.82 (s, 1H), 7.46-7.35 (m, 2H), 3.05-2.96 (m, 1H), 1.31 (d, J = 6.9 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.9, 153.6, 138.8, 127.2, 127.0, 123.6, 122.9, 109.4, 34.0, 23.4. HRMS (EI) m/zcalcd for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O<sup>+</sup> ([M]<sup>+</sup>): 212.0944, found: 212.0945.



**2-(4-(***Tert***-butyl)phenyl)oxazole-5-carbonitrile** (7) was obtained as a white solid (33 mg, 74%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (d, J = 8.5 Hz, 2H), 7.79 (s, 1H), 7.53 (d, J = 8.6 Hz, 2H), 1.36 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  165.1, 156.1, 139.1, 127.2, 126.1, 123.9, 122.8, 109.6, 35.1, 31.1. HRMS (EI) *m/z* calcd for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sup>+</sup> ([M]<sup>+</sup>): 226.1101, found: 226.1106.



2-(4-Fluorophenyl)oxazole-5-carbonitrile (CAS:1391828-24-2)

(8) was obtained as a white solid (20 mg, 52%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.24-7.99 (m, 2H), 7.80 (s, 1H), 7.21 (t, J = 8.6 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  165.1 (d, J = 254.5 Hz), 164.0, 139.0, 129.7 (d, J = 9.1 Hz), 124.3, 121.9 (d, J = 3.0 Hz), 116.5 (d, J = 22.5 Hz), 109.4.



**2-(4-Chlorophenyl)oxazole-5-carbonitrile (CAS:1391750-56-3)** (9) was obtained as a white solid (20 mg, 50%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.05-7.99 (m, 2H), 7.81 (s, 1H), 7.55-7.46 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 163.9, 139.1, 138.7, 129.5, 128.6, 124.4, 123.9, 109.3.



**2-(4-Bromophenyl)oxazole-5-carbonitrile (10)** was obtained as a white solid (31 mg, 63%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.03-7.89 (m, 2H), 7.81 (s, 1H), 7.72-7.62 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.0, 139.0, 132.5, 128.7, 127.2, 124.4, 109.3. HRMS (EI) *m/z* calcd for C<sub>10</sub>H<sub>5</sub>BrN<sub>2</sub>O<sup>+</sup> ([M]<sup>+</sup>): 247.9580, found: 227.9592.



**2-(4-Formylphenyl)oxazole-5-carbonitrile (11)** was obtained as a white solid (19 mg, 48%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  10.11 (s, 1H), 8.27 (d, J = 8.4 Hz, 2H), 8.04 (d, J = 8.5 Hz, 2H), 7.88 (s, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  191.1, 163.5, 139.2, 138.5, 130.2, 127.9, 125.1, 109.1, 100.0. HRMS (EI) m/z calcd for C<sub>11</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 198.0424, found: 198.0426.



2-(4-Cyanophenyl)oxazole-5-carbonitrile (CAS:1391828-41-3)

(12) was obtained as a white solid (25 mg, 64%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.21 (d, J = 8.6 Hz, 2H), 7.88 (s, 1H), 7.83 (d, J = 8.6 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  162.7, 139.2, 132.9, 129.1, 127.8, 125.2, 117.7, 115.6, 108.9.



2-(3-Chlorophenyl)oxazole-5-carbonitrile (CAS:1391750-61-0)

(13) was obtained as a white solid (27 mg, 67%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.09 (t, J = 1.8 Hz, 1H), 7.98 (dd, J = 7.8, 1.2 Hz, 1H), 7.83 (s, 1H), 7.54 (ddd, J = 8.0, 2.0, 1.1 Hz, 1H), 7.46 (t, J = 7.9 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  163.5, 139.0, 135.4, 132.3, 130.5, 127.4, 127.1, 125.4, 124.6, 109.2.



**2-(o-Tolyl)oxazole-5-carbonitrile (CAS:1391740-00-3) (14)** was obtained as a white solid (26 mg, 70%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (dd, J = 8.1, 1.2 Hz, 1H), 7.85 (s, 1H), 7.44 (td, J = 7.6, 1.3 Hz, 1H), 7.34 (dt, J = 7.1, 3.3 Hz, 2H), 2.70 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  165.2, 138.67, 138.66, 132.0, 131.8, 129.6, 126.3, 124.4, 123.7, 109.7, 22.1.



2-(2,6-Difluorophenyl)oxazole-5-carbonitrile (15) was obtained as a

white solid (24 mg, 59%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (s, 1H), 7.54 (tt, J = 8.5, 6.1 Hz, 1H), 7.10 (t, J = 8.6 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.9 (dd, J = 260.4, 5.0 Hz), 157.3-156.4 (m), 138.5 (s), 133.9 (t, J = 10.6 Hz), 125.0 (s), 112.6 (dd, J = 21.4, 3.9 Hz), 109.0 (s), 104.7 (d, J = 14.9 Hz). HRMS (EI) m/z calcd for C<sub>10</sub>H<sub>4</sub>F<sub>2</sub>N<sub>2</sub>O<sup>+</sup> ([M]<sup>+</sup>): 206.0286, found: 206.0292.



**2-(3,4-Dichlorophenyl)oxazole-5-carbonitrile (16)** was obtained as a white solid (22 mg, 46%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.19 (d, J = 2.0 Hz, 1H), 7.92 (dd, J = 8.4, 2.0 Hz, 1H), 7.83 (s, 1H), 7.60 (d, J = 8.4 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  162.7, 139.0, 137.0, 133.9, 131.3, 129.1, 126.3, 125.3, 124.8, 109.0. HRMS (EI) m/z calcd for C<sub>10</sub>H<sub>4</sub>Cl<sub>2</sub>N<sub>2</sub>O<sup>+</sup> ([M]<sup>+</sup>): 237.9695, found: 237.9709.



**2-(3,4-Dimethylphenyl)oxazole-5-carbonitrile (17)** was obtained as a white solid (27 mg, 68%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.86 (d, J = 1.2 Hz, 1H), 7.80 (dd, J = 7.8, 1.7 Hz, 1H), 7.26 (d, J = 7.9 Hz, 1H), 2.34 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  165.3, 141.8, 139.0, 137.7, 130.4, 128.3, 124.9, 123.7, 123.1, 109.7, 20.0, 19.7. HRMS (EI) m/z calcd for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O<sup>+</sup> ([M]<sup>+</sup>): 198.0788, found: 198.0788.



**2-(Benzo**[*d*][1,3]dioxol-5-yl)oxazole-5-carbonitrile (18) was obtained as a white solid (30 mg, 70%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.76 (s, 1H), 7.65 (dd, J = 8.2, 1.7 Hz, 1H), 7.50 (d, J = 1.7 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 6.07 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.6, 151.2, 148.3, 139.1, 123.6, 122.9, 119.5, 109.6, 108.9, 107.3, 102.0. HRMS (EI) *m/z* calcd for C<sub>11</sub>H<sub>6</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> ([M]<sup>+</sup>): 214.0373, found: 214.0380.



**2-(Naphthalen-2-yl)oxazole-5-carbonitrile (19)** was obtained as a white solid (22 mg, 50%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.61 (s, 1H), 8.11 (dd, J = 8.6, 1.7 Hz, 1H), 7.96 (dd, J = 8.1, 3.7 Hz, 2H), 7.89 (d, J = 7.8 Hz, 1H), 7.85 (s, 1H), 7.65-7.55 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  165.1, 139.2, 134.9, 132.7, 129.1, 129.0, 128.4, 128.3, 127.9, 127.2, 124.2, 123.2, 122.7, 109.5. HRMS (EI) *m/z* calcd for C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>O<sup>+</sup> ([M]<sup>+</sup>): 220.0631, found: 220.0631.



#### 2-(Furan-3-yl)oxazole-5-carbonitrile (CAS:1391828-48-0) (20) was

obtained as white solid (16 mg, 50%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (dd, J = 1.3, 0.7 Hz, 1H), 7.76 (s, 1H), 7.54 (t, J = 1.7 Hz, 1H), 6.90 (dd, J = 1.9, 0.7 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.2, 144.7, 144.6, 138.8, 123.5, 114.2, 109.3, 108.5.



2-(Thiophen-3-yl)oxazole-5-carbonitrile (CAS:1391828-49-1) (21)

was obtained as a white solid (18 mg, 52%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.13 (dd, J = 3.0, 1.1 Hz, 1H), 7.78 (s, 1H), 7.65 (dd, J = 5.1, 1.1 Hz, 1H), 7.46 (dd, J = 5.1, 3.0 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  161.5, 138.9, 129.0, 127.6, 127.5, 126.1, 123.5, 109.5.



2-(Adamantan-1-yl)oxazole-5-carbonitrile (22) was obtained as a

white solid (34 mg, 74%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 (s, 1H), 2.11 (s, 3H), 2.04 (d, J = 2.6 Hz, 6H), 1.78 (q, J = 12.4 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  174.8, 137.6, 123.6, 109.6, 40.0, 36.5, 36.2, 27.7. HRMS (EI) m/z calcd for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sup>+</sup> ([M]<sup>+</sup>): 228.1257, found: 228.1267.



**2-Phenyloxazole-5-carboxamide (CAS:39819-42-6)**<sup>17</sup> (3) was obtained as a white solid (26 mg, 68%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.19 (s, 1H), 8.17-8.13 (m, 2H), 7.90 (s, 1H), 7.75 (s, 1H), 7.64-7.58 (m, 3H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  162.5, 159.0, 146.4, 132.4, 132.3, 130.1, 127.5, 127.2.

<sup>(17)</sup> Mohamed, H; Ons, M.; Yosra, E-T.; Rayda, S.; Neji, G.; Moncef, N. *JSciFoodAgric* **2009**, 89, 897.



2-(p-Tolyl)oxazole-5-carboxamide (24) was obtained as a

white solid (26 mg, 65%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.18 (s, 1H), 8.03 (d, J = 8.2 Hz, 2H), 7.87 (s, 1H), 7.75 (s, 1H), 7.41 (d, J = 8.0 Hz, 2H), 2.39 (d, J = 21.5 Hz, 3H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  162.8, 159.2, 146.2, 142.6, 132.4, 130.8, 127.6, 124.6, 22.1. HRMS (EI) m/z calcd for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 202.0737, found: 202.0739.



**2-(4-Isopropylphenyl)oxazole-5-carboxamide (25)** was obtained as a white solid (27 mg, 59%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.19 (s, 1H), 8.07 (d, J = 8.3 Hz, 2H), 7.87 (s, 1H), 7.75 (s, 1H), 7.48 (d, J = 8.3 Hz, 2H), 3.09-2.92 (m, 1H), 1.26 (d, J = 6.9 Hz, 6H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  162.8, 159.2, 153.2, 146.2, 132.4, 128.2, 127.8, 124.9, 34.5, 24.6. HRMS (EI) *m*/*z* calcd for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 230.1050, found: 230.1057.



**2-(4-(***Tert***-butyl)phenyl)oxazole-5-carboxamide (26)** was obtained as a white solid (37 mg, 75%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.17 (s, 1H), 8.10-8.04 (m, 2H), 7.88 (s, 1H), 7.73 (s, 1H), 7.65-7.59 (m, 2H), 1.35 (s, 9H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  162.7, 159.1, 155.3, 146.2, 132.3, 127.4, 126.9, 124.5, 35.7, 31.8. HRMS (EI) *m*/*z* calcd for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 244.1206, found: 244.1213.





obtained as a white solid (23 mg, 52%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.16 (s, 1H), 8.08 (d, J = 8.9 Hz, 2H), 7.84 (s, 1H), 7.72 (s, 1H), 7.15 (d, J = 8.9 Hz, 2H), 3.88 (d, J = 1.7 Hz, 3H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  162.79, 162.77, 159.2, 145.9, 132.4, 129.5, 119.8, 115.7, 56.5. HRMS (EI) m/z calcd for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3<sup>+</sup></sub> ([M]<sup>+</sup>): 218.0686, found: 218.0687.



**2-(4-Ethoxyphenyl)oxazole-5-carboxamide** (28) was obtained as a white solid (19 mg, 41%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.12 (s, 1H), 8.07 (d, J = 8.9 Hz, 2H), 7.83 (s, 1H), 7.68 (s, 1H), 7.13 (d, J = 8.9 Hz, 2H), 4.15 (q, J = 7.0 Hz, 2H), 1.39 (t, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  162.7, 162.0, 159.1, 145.8, 132.4, 129.4, 119.6, 116.0, 64.4, 15.5. HRMS (EI) m/z calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> ([M]<sup>+</sup>): 232.0842, found: 232.0853.



2-(4-Fluorophenyl)oxazole-5-carboxamide (29) was obtained

as a white solid (25 mg, 60%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.23 (s, 1H), 8.19 (dd, J = 8.7, 5.5 Hz, 2H), 7.88 (s, 1H), 7.77 (s, 1H), 7.44 (t, J = 8.8 Hz, 2H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  164.60 (d, J = 249.8 Hz), 161.5, 158.8, 146.1, 132.1, 129.9 (d, J = 9.1 Hz), 123.5 (d, J = 2.9 Hz), 117.1 (d, J = 22.3 Hz). HRMS (EI) m/z calcd for C<sub>10</sub>H<sub>7</sub>FN<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 206.0486, found: 206.0496.



**2-(4-Chlorophenyl)oxazole-5-carboxamide (30)** was obtained as a white solid (28 mg, 64%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.23 (s, 1H), 8.17-8.12 (m, 2H), 7.91 (d, J = 8.5 Hz, 1H), 7.76 (s, 1H), 7.70-7.65 (m, 2H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  161.8, 159.2, 146.7, 137.4, 132.6, 130.5, 129.5, 126.1. HRMS (EI) *m/z* calcd for C<sub>10</sub>H<sub>7</sub>ClN<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 222.0191, found: 222.0202.



**2-(4-Bromophenyl)oxazole-5-carboxamide (31)** was obtained as a white solid (28 mg, 53%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.22 (s, 1H), 8.12-8.05 (m, 2H), 7.91 (s, 1H), 7.84-7.80 (m, 2H), 7.77 (s, 1H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  161.7, 158.9, 146.6, 133.2, 132.4, 129.4, 126.4, 126.1. HRMS (EI) *m/z* calcd for C<sub>10</sub>H<sub>7</sub>BrN<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 265.9685, found: 265.9697.



**2-(4-(Trifluoromethyl)phenyl)oxazole-5-carboxamide (32)** was obtained as a white solid (26 mg, 51%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.35 (d, J = 8.1 Hz, 2H), 8.28 (s, 1H), 8.03-7.95 (m, 3H), 7.82 (s, 1H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  161.1, 158.8, 147.0, 132.5, 132.0 (d, J = 32.0 Hz), 130.8, 128.3, 127.5-126.9 (m), 124.8 (d, J = 272.5 Hz). HRMS (EI) m/z calcd for C<sub>11</sub>H<sub>7</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 256.0454, found: 256.0468.



2-(4-Formylphenyl)oxazole-5-carboxamide (33) was

obtained as a white solid (23 mg, 54%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  10.13 (s, 1H), 8.36 (dd, J = 8.3, 1.5 Hz, 2H), 8.27 (s, 1H), 8.13 (dd, J = 8.3, 1.5 Hz, 2H), 7.98 (d, J = 0.6 Hz, 1H), 7.82 (s, 1H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  193.6, 161.4, 158.8, 147.1, 138.6, 132.7, 131.9, 131.1, 128.1. HRMS (EI) m/z calcd for C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3<sup>+</sup></sub> ([M]<sup>+</sup>): 216.0529, found: 216.0537.



**2-(4-Cyanophenyl)oxazole-5-carboxamide** (34) was obtained as a white solid (31 mg, 72%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.31 (s, 1H), 8.29 (d, J = 8.6 Hz, 6H), 8.08-8.04 (m, 6H), 7.96 (s, 2H), 7.84 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  161.1, 159.1, 147.2, 134.3, 132.9, 131.1, 128.3, 119.4, 114.6. HRMS (EI) *m/z* calcd for C<sub>11</sub>H<sub>7</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 213.0533, found: 213.0545.



2-(3-Chlorophenyl)oxazole-5-carboxamide (35) was obtained

as a white solid (28 mg, 64%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.29 (s, 1H), 8.20 (t, J = 1.8 Hz, 1H), 8.09 (dt, J = 7.6, 1.4 Hz, 1H), 7.91 (s, 1H), 7.81 (s, 1H), 7.68 (ddd, J = 8.1, 2.0, 1.2 Hz, 1H), 7.64 (t, J = 7.8 Hz, 1H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  161.3, 159.2, 146.8, 135.1, 132.7, 132.4(X2), 129.2, 127.2, 126.3. HRMS (EI) m/z calcd for C<sub>10</sub>H<sub>7</sub>ClN<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 222.0191, found: 222.0206.



2-(o-Tolyl)oxazole-5-carboxamide (36) was obtained as a white

solid (19 mg, 48%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.20-8.07 (m, 1H), 7.93 (s, 1H), 7.74 (s, 1H), 7.55-7.45 (m, 1H), 7.45-7.37 (m, 1H), 2.69 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  162.8, 159.1, 145.9, 138.5, 132.7, 132.1, 131.8, 129.9, 127.2, 126.1, 22.6. HRMS (EI) *m*/*z* calcd for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 202.0737, found: 202.0746.



2-(2,6-Difluorophenyl)oxazole-5-carboxamide (37) was obtained

as a white solid (23 mg, 51%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.15 (s, 1H), 8.05 (s, 1H), 7.82 (s, 1H), 7.79-7.69 (m, 1H), 7.39 (t, J = 8.6 Hz, 1H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  161.0 (dd, J = 255.7, 5.4 Hz), 158.7, 154.1 (t, J = 2.5 Hz), 147.3, 135.2 (t, J = 10.6 Hz), 131.9, 113.8 (dd, J = 20.7, 3.9 Hz), 106.1 (t, J = 16.6 Hz). HRMS (EI) m/z calcd for C<sub>10</sub>H<sub>6</sub>F<sub>2</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 224.0392, found: 224.0396.



2-(3,4-Dichlorophenyl)oxazole-5-carboxamide (38) was

obtained as a white solid (26 mg, 50%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.37 (d, J = 2.0 Hz, 1H), 8.27 (s, 1H), 8.09 (dd, J = 8.4, 2.0 Hz, 1H), 7.92 (s, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.81 (s, 1H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  160.3, 158.8, 146.9, 135.1, 133.1, 132.6, 132.5, 129.1, 127.6, 127.5. HRMS (EI) *m*/*z* calcd for C<sub>10</sub>H<sub>6</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 255.9801, found: 255.9818.



2-(3,4-Dimethylphenyl)oxazole-5-carboxamide (39) was

obtained as a white solid (21 mg, 45%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.18 (s, 1H), 7.90 (s, 1H), 7.85 (s, 1H), 7.87-7.83 (m, 1H), 7.73 (s, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 2.32 (s, 1H), 2.30 (s, 1H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  162.7, 159.0, 145.7, 141.1, 138.0, 132.1, 130.9, 128.1, 124.9, 124.5, 20.2, 20.0. HRMS (EI) *m*/*z* calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 216.0893, found: 216.0904.



2-(Benzo[d][1,3]dioxol-5-yl)oxazole-5-carboxamide (40) was

obtained as a white solid (32 mg, 70%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.17 (s, 1H), 7.83 (s, 1H), 7.77-7.68 (m, 2H), 7.64 (d, J = 1.6 Hz, 1H), 7.13 (dd, J = 8.2, 5.2 Hz, 1H), 6.18 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  162.4, 159.1, 151.0, 149.0, 146.0, 132.4, 122.8, 121.2, 110.0, 107.4, 103.0. HRMS (EI) *m*/*z* calcd for C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup> ([M]<sup>+</sup>): 232.0479, found: 232.0490.



**2-(Naphthalen-2-yl)oxazole-5-carboxamide (41)** was obtained as a white solid (23 mg, 48%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.77 (d, J = 0.9 Hz, 1H), 8.25 (s, 1H), 8.22 (dd, J = 8.6, 1.7 Hz, 1H), 8.13 (dd, J = 9.2, 2.5 Hz, 2H), 8.05 (dd, J = 6.2, 3.2 Hz, 1H), 7.96 (s, 1H), 7.79 (s, 1H), 7.72-7.64 (m, 2H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  162.6, 159.0, 146.5, 134.9, 133.5, 132.4, 129.9, 129.7, 128.9, 128.8, 128.2, 127.7, 124.5, 124.1. HRMS (EI) *m/z* calcd for C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 238.0737, found: 238.0748.





solid (21 mg, 60%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.51 (dd, J = 1.5, 0.8 Hz, 1H), 8.08 (s, 1H), 7.95-7.91 (m, 1H), 7.85 (s, 1H), 7.73 (s, 1H), 7.02 (dd, J = 1.9, 0.7 Hz, 1H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  159.0, 158.2, 146.3, 145.6, 145.3, 131.9, 115.5, 109.5. HRMS (EI) m/z calcd for C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> ([M]<sup>+</sup>): 178.0373, found: 178.0380.



2-(Thiophen-3-yl)oxazole-5-carboxamide (43) was obtained as a

white solid (25 mg, 65%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.36 (dd, J = 2.9, 1.2 Hz, 1H), 8.17-8.10 (m, 1H), 7.85 (s, 1H), 7.80 (dd, J = 5.0, 3.0 Hz, 1H), 7.74 (s, 1H), 7.69 (dd, J = 5.1, 1.2 Hz, 1H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  159.7, 159.1, 145.6, 132.1, 129.6, 129.2, 129.1, 126.9. HRMS (EI) *m*/*z* calcd for C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup> ([M]<sup>+</sup>): 194.0144, found: 194.0146.



(E)-2-Styryloxazole-5-carboxamide (44) was obtained as a white

solid (26 mg, 60%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.10 (s, 1H), 7.86 (s, 1H), 7.78-7.74 (m, 2H), 7.72 (s, 1H), 7.51-7.40 (m, 3H), 7.22 (d, *J* = 16.4 Hz, 1H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  162.8, 159.0, 145.7, 139.0, 135.8, 132.4, 130.7, 129.9, 128.6, 114.4. HRMS (EI) *m*/*z* calcd for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2<sup>+</sup></sub> ([M]<sup>+</sup>): 214.0737, found: 214.0741.



2-(Tert-butyl)oxazole-5-carboxamide (45) was obtained as a white

solid (20 mg, 60%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  7.95 (s, 1H), 7.64 (s, 1H), 7.61 (s, 1H), 1.37 (s, 9H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  172.9, 159.3, 146.0, 130.6, 34.6, 29.1. HRMS (EI) *m*/*z* calcd for C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 168.0893, found: 168.0900.



2-(Adamantan-1-yl)oxazole-5-carboxamide (46) was obtained

as a white solid (38 mg, 78%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 (s, 1H), 6.27 (s, 2H), 2.09 (s, 3H), 2.04 (d, J = 2.5 Hz, 3H), 1.82-1.72 (m, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  172.5, 159.3, 143.9, 131.6, 40.2, 36.3, 36.0, 27.8. HRMS (EI) m/z calcd for C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 246.1363, found: 246.1372.





solid (16 mg, 36%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  7.98 (s, 1H), 7.65 (s, 1H), 7.61 (s, 1H), 7.33-7.28 (m, 2H), 7.26 (t, J = 4.1 Hz, 2H), 7.24-7.19 (m, 1H), 3.13 (ddd, J = 7.3, 5.5, 1.9 Hz, 2H), 3.10-3.06 (m, 2H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  166.2, 159.2, 146.2, 141.2, 131.0, 129.4, 129.3, 127.3, 32.9, 30.3. HRMS (EI) m/z calcd for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 216.0893, found: 216.0894.


2-(1-(6-Methoxynaphthalen-2-yl)ethyl)oxazole-5-c

**arboxamide (48)** was obtained as a white solid (28 mg, 47%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  7.98 (s, 1H), 7.83 (dd, J = 8.7, 4.2 Hz, 2H), 7.75 (d, J = 4.1 Hz, 2H), 7.62 (s, 1H), 7.43 (dd, J = 8.5, 1.8 Hz, 1H), 7.33 (d, J = 2.5 Hz, 1H), 7.19 (dd, J = 9.0, 2.6 Hz, 1H), 4.55 (d, J = 7.2 Hz, 1H), 3.89 (s, 3H), 1.73 (d, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  168.2, 158.6, 157.7, 145.9, 137.1, 133.8, 130.4, 129.7, 128.9, 127.7, 126.5, 125.9, 119.3, 106.2, 55.6, 39.2, 20.3. HRMS (EI) m/z calcd for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> ([M]<sup>+</sup>): 296.1155, found: 296.1172.

## 8. Crystal Structure of 5-Oxazolecarbonitrile 14





Bond precision: C-C= 0.0022 A Wavelength=0.71073

Cell: a=7.8533(8) b=17.4662(14) c=13.5621(15) alpha=90 beta=97.846(8) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	1842.9(3)	1842.9(3)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C11 H8 N2 O	?
Sum formula	C11 H8 N2 O	C11 H8 N2 O
Mr 184.19	184.19	
Dx,g cm-3	1.328	1.435
Z 8 8		

Mu (mm-1)	0.088	0.088		
F0	768.0	768.0		
F000'	768.31			
h,k,lmax	9,21,16	9,21,16		
Nref 3765	3760			
Tmin,Tmax				
Tmin'				
Correction method= Not given				
Data completenes	ss= 0.999			
Theta(max)= $26.3$	370			
R(reflections)=0	.0464( 2533)			
wR2(reflections)=	= 0.1386( 3760)			
S = 1.033 Npar	= 255			

## 9. NMR Spectra
























































































gg











54







