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Supporting Information

## Copper-catalyzed oxidative cyclization of vinyl azides with benzylic

## C<sub>sp3</sub>-H bonds for the synthesis of substituted phenanthridines

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#### **Table of Contents**

General Information	<b>S2</b>
Starting Materials	<b>S2</b>
Characterization of New Starting Materials	<b>S</b> 3
Optimization of Reaction Conditions	<b>S4</b>
Investigation of the Reaction Mechanism	<b>S6</b>
Reference	<b>S7</b>
<sup>1</sup> H NMR and <sup>13</sup> C NMR Spectra of the Products <b>3</b>	<b>S8</b>
<sup>1</sup> H NMR and <sup>13</sup> C NMR Spectra of the Products <b>4</b>	S22
<sup>1</sup> H NMR and <sup>13</sup> C NMR Spectra of the Products <b>6</b>	<b>S31</b>

### **General Information**

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Advance III-400 in solvents as indicated. Chemical shift are reported in ppm from TMS with the solvent resonance as internal standard (CDCl<sub>3</sub>: <sup>1</sup>H NMR:  $\delta = 7.26$ ; <sup>13</sup>C NMR:  $\delta = 77.0$ ). IR spectra were recorded on a Bruker Tensor 27 spectrometer and only major peaks are reported in cm<sup>-1</sup>. HRMS were obtained on a Q-TOF micro spectrometer or Orbitrap mass spectrometer. All reactions were conducted in oven-dried Schlenk-tube under an atmosphere of nitrogen. Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Column chromatography was carried out on silica gel.

### **Starting Materials**

All of vinyl azides **2** were synthesized according to the literature, and the NMR spectroscopy were in full accordance with the data in the literature.<sup>1</sup>

### **Characterization of New Starting Materials**



**2d:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.55-7.52 (m, 2H), 7.47-7.43 (m, 2H), 7.40-7.32 (m, 4H), 4.95 (d, *J* = 1.2 Hz, 1H), 4.80 (d, *J* = 0.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 145.4, 139.4, 139.2, 133.7, 131.4, 130.4, 130.2, 130.1, 129.5, 127.8, 121.7, 103.9 ppm; IR (KBr):  $v_{max}$  2925, 2123, 2095, 1625 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>14</sub>H<sub>11</sub>BrN<sub>3</sub> [M+H]<sup>+</sup> 300.0131, found 300.0136.



**2h:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.43-7.33$  (m, 8H), 4.95 (d, J = 3.2 Hz, 1H), 4.80 (d, J = 2.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 144.7$ , 142.2, 139.3, 135.1, 132.3, 131.2, 130.4, 128.6, 128.3, 127.9, 127.4, 104.0 ppm; IR (KBr):  $v_{max}$  3061, 2925, 2124, 2094, 1620 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>14</sub>H<sub>11</sub>ClN<sub>3</sub> [M+H]<sup>+</sup> 256.0636, found 256.0637.

### **Optimization of Reaction Conditions**

#### **General Procedure**

A 10 mL oven-dried Schlenk-tube equipped with a magnetic sir bar was charged with catalyst (See Table S1). Then, the tube was evacuated and backfilled with nitrogen (three times). After that, vinyl azide **2a** (0.25 mmol, 1.0 equiv), toluene and oxidants (See Table S1) in 1 mL solvent were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred for 24 h at 65 °C. The mixture was then diluted with EtOAc and transferred to a separatory funnel. The organic phase was washed successively with H<sub>2</sub>O and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure. The resulting residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/50 to 1/20) to afford the product **3a** as a yellow oil.

**Table S1** Optimization of the reaction conditions<sup>a</sup>

$ \begin{array}{c}     \hline & \\      \hline & \\      \hline & \\     \hline & \\     \hline & \\     \hline & \\     \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\       \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\       \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\      \hline & \\       \hline & \\       \hline & \\       \hline \\ \hline \hline & \\       \hline \\ \hline \hline \hline \hline \\ \hline \hline \hline \hline \hline \\ \hline \\ \hline \hline$				
	1a	2a	3a	
Entry	Catalyst (mol%)	Oxidant (equiv.)	Solvent	$\operatorname{Yield}^{b}(\%)$
1	$Cu(OAc)_2(5)$	TBPB (2)	CH <sub>3</sub> CN	6 <sup>c</sup>
2	$Cu(OAc)_2(5)$	TBPB (2)	EtOAc	9 <sup>c</sup>
3	$Cu(OAc)_2(5)$	TBPB (2)	DMF	0°
4	$Cu(OAc)_2(5)$	TBPB (2)	DMSO	<5°
5	$Cu(OAc)_2(5)$	TBPB (2)	PhCl	80
6	$Cu(OAc)_2(5)$	TBPB (2)	PhCF <sub>3</sub>	10 <sup>c</sup>
7	$Cu(OAc)_2(5)$	TBPB (2)	-	25 <sup>c</sup>
8	$Cu(OAc)_2(5)$	TBPB (2)	-	$45^d$
9	$Cu(OAc)_2(5)$	TBPB (2)	-	58
10	$Cu(OAc)_2(5)$	TBPB (2)	-	43 <sup>e</sup>
11	$Cu(OAc)_2(5)$	TBHP (2)	-	12
12	$Cu(OAc)_2(5)$	DTBP (2)	-	0
13	Cu(acac) <sub>2</sub> (5)	TBPB (2)	-	62 (61) <sup>f</sup>
14	$CuSO_4(5)$	TBPB (2)	-	50
15	$CuCl_2(5)$	TBPB (2)	-	53
16	CuO (5)	TBPB (2)	-	51
17	CuCl (5)	TBPB (2)	-	57
18	Cu <sub>2</sub> O (5)	TBPB (2)	-	50
19	$Fe(acac)_2(5)$	TBPB (2)	-	45
20	$FeCl_3(5)$	TBPB (2)	-	53
21	$Fe(OAc)_2(5)$	TBPB (2)	-	44
22	$Cu(acac)_2(10)$	TBPB (2)	-	59
23	$Cu(acac)_2(2)$	TBPB (2)	-	54
24	$Cu(acac)_2(10)$	-	-	0
25	-	TBPB (2)	-	35

<sup>a</sup> Reaction conditions: 5 mol% of catalyst, 2a (0.25 mmol, 1.0 equiv.), oxidant (2.0 equiv.), toluene (1a, 1.0 mmol, 4.0 equiv.), solvent

(1.0 mL), 65 °C, 24 h, under N<sub>2</sub>. <sup>b</sup> Yield of isolated product. <sup>c</sup> at 100 °C. <sup>d</sup> at 80 °C. <sup>e</sup> at 50 °C. <sup>f</sup> Yield on a 1 mmol scale is given in parentheses.

## **Investigation of the Reaction Mechanism**



When the TEMPO was added to the reaction of 1a with 2a under the standard conditions, only small amount of the desired product 3a was isolated. The result indicates that the radical intermediate might be involved in the catalytic cycle of the reaction.



When the BHT was added to the reaction of **1a** with **2a** under the standard conditions, only trace amount of the desired product **3a** was detected. The result indicates that the radical intermediate might be involved in the catalytic cycle of the reaction.

# References

1 Y.-F. Wang, G. H. Lonca, M. L. Runigo and S. Chiba, Org. Lett., 2014, 16, 4272.

## <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of the Products 3









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# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of the Products 4

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#### S23

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# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of the Starting Materials 2d and 2h

![](_page_36_Figure_1.jpeg)

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