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2017.06.16

CN 107089950 A

2017.08.25

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CA 2294023 A1, 1998.12.30,

W0 2005085204 A1, 2005.09.15,

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Zhang, X.

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612-616.

Jun-Long Zhan, Meng-Wei Wu, Fei Chen,  
and Bing Han.Cu-Catal yzed [ 3 + 3]  
Annul ati on for the Synthesi s of  
Pyr i mi di nes vi a. J. Org. Chem .2016,(  
81 ), 11994-12000.

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140

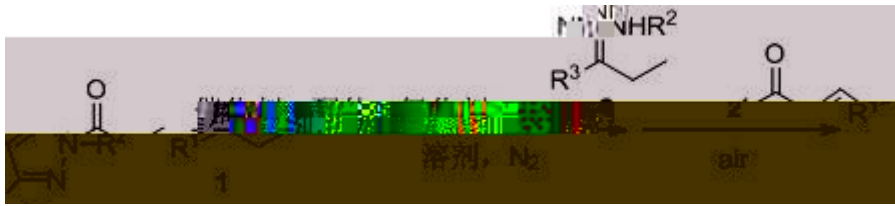
100-

100-140

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1. 4  
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 100 140 2 100  
 140 4 3



R<sup>1</sup> 2 3 C<sub>5-6</sub>

R<sup>2</sup> C<sub>1-4</sub>

R<sup>3</sup>

2

2,2' 2,2,6,6  
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 , 1 2  
 1 1.2 1: 0.1 0.2 0.1: 1 2

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1

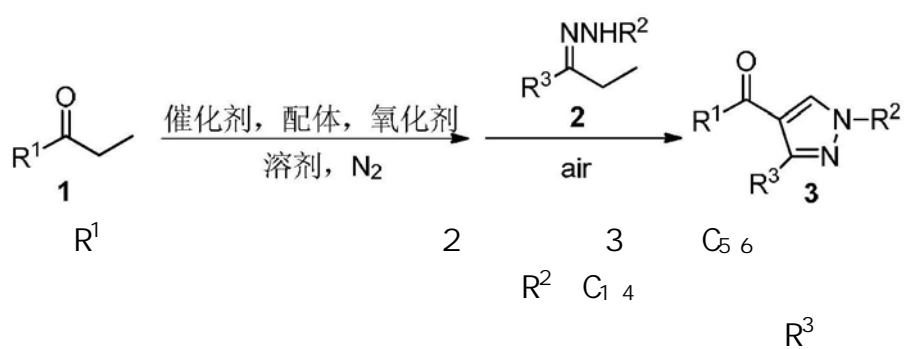
100 140

2

100 140

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2

2, 2'

2, 2, 6, 6

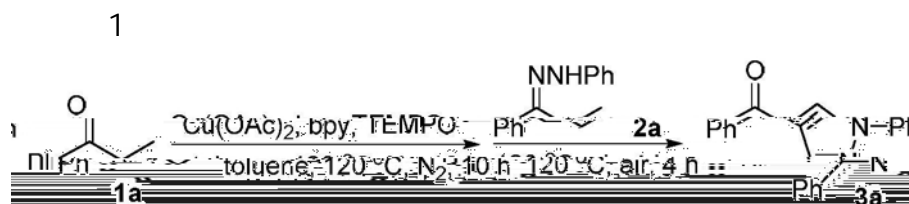
(TEMPO)

1

2

1 1.2 1: 0.1 0.2 0.1: 1 2

(1)



15mL 1a (0.5mmol, 67mg) (Cu(OAc)<sub>2</sub>, 0.05mmol, 9mg) 2,  
 2' (bpy, 0.05mmol, 8mg) 2, 2, 6, 6 (TEMPO, 0.5mmol, 78mg)  
 (toluene, 3mL) 120 10h  
 2a (0.5mmol, 112mg) 120  
 4h 10mL (10mL 3)  
 ( / 20/1)

1, 3 4 3a (68mg, 42 ) <sup>1</sup>H NMR  
 (400MHz, CDCl<sub>3</sub>) : 7.32 7.42(m, 6H), 7.47 7.54(m, 3H), 7.72 7.74(m, 2H), 7.79(d, J  
 8.0Hz, 2H), 7.84(d, J 7.6Hz, 2H), 8.28(s, 1H). <sup>13</sup>C NMR (150MHz, CDCl<sub>3</sub>) : 119.6, 121.2,  
 127.6, 128.2, 128.4, 128.6, 128.9, 129.5, 129.7, 132.1, 132.3, 132.6, 138.9, 139.3,  
 154.0, 190.1. HRMS: cal cd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: 347.1155[MNa]<sup>+</sup>, found: 347.1157

2  
 15mL 1a (0.5mmol, 67mg) Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy  
 (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)  
 120 10h 2a (0.5mmol, 112mg)  
 120 4h 10mL (10mL 3)  
 ( / 20/1) 1, 3 4 3a (97mg, 60 )

3  
 15mL 1a (0.6mmol, 80mg) Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy  
 (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)  
 120 10h 2a (0.5mmol, 112mg)  
 120 4h 10mL (10mL 3)  
 ( / 20/1) 1, 3 4 3a (105mg, 65 )

4  
 15mL 1a(0.6mmol, 80mg) Cu(OAc)<sub>2</sub>(0.1mmol, 18mg) bpy  
 (0.05mmol, 8mg) TEMPO(1.0mmol, 156mg) (3mL)  
 120 10h 2a(0.5mmol, 112mg)  
 120 4h 10mL (10mL 3)  
 ( /  
 20/1) 1,3 4 3a(49mg, 30 )

5  
 15mL 1a(0.6mmol, 80mg) Cu(OAc)<sub>2</sub>(0.1mmol, 18mg) bpy  
 (0.05mmol, 8mg) TEMPO(0.5mmol, 78mg) (3mL)  
 120 10h 2a(0.5mmol, 112mg)  
 120 4h 10mL (10mL 3)  
 ( /  
 20/1) 1,3 4 3a(117mg, 72 )

6  
 15mL 1a(0.6mmol, 80mg) Cu(OAc)<sub>2</sub>(0.1mmol, 18mg) bpy  
 (0.05mmol, 8mg) TEMPO(0.5mmol, 78mg) (3mL)  
 100 10h 2a(0.5mmol, 112mg)  
 100 4h 10mL (10mL 3)  
 ( /  
 20/1) 1,3 4 3a(94mg, 58 )

7  
 15mL 1a(0.6mmol, 80mg) Cu(OAc)<sub>2</sub>(0.1mmol, 18mg) bpy  
 (0.05mmol, 8mg) TEMPO(0.5mmol, 78mg) (3mL)  
 140 10h 2a(0.5mmol, 112mg)  
 140 4h 10mL (10mL 3)  
 ( /  
 20/1) 1,3 4 3a(102mg, 63 )

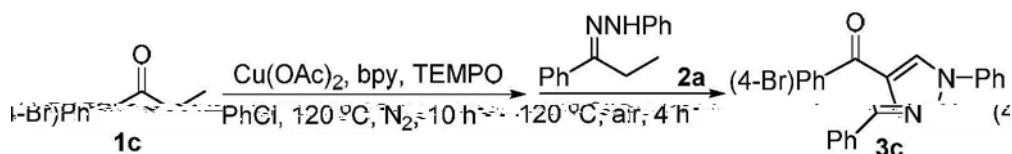
8



15mL 1b(0.6mmol, 91mg) Cu(OAc)<sub>2</sub>(0.1mmol, 18mg) bpy  
 (0.05mmol, 8mg) TEMPO(0.5mmol, 78mg) (3mL)  
 120 10h 2a(0.5mmol, 112mg)  
 120 4h 10mL (10mL 3)  
 ( /  
 20/1) 1,3 4 (4 ) 3b(130mg, 76 )

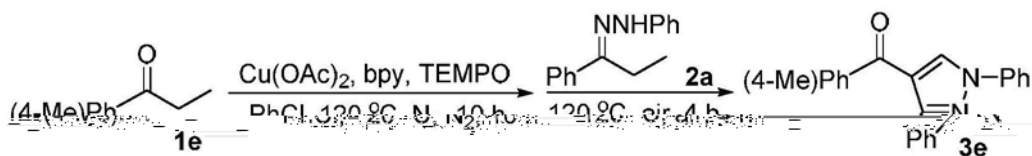
$^1\text{H NMR}$  (600MHz,  $\text{CDCl}_3$ ) : 7.03(t, J = 8.4Hz, 2H), 7.30-7.32(m, 3H), 7.34(t, J = 7.2Hz, 1H), 7.47(t, J = 7.8Hz, 2H), 7.66-7.68(m, 2H), 7.77-7.80(m, 2H), 7.82-7.84(m, 2H), 8.27(s, 1H).  $^{13}\text{C NMR}$  (150MHz,  $\text{CDCl}_3$ ) : 115.5(d,  $^2J_{\text{CF}}$  = 21.9Hz), 119.6, 121.1, 127.6, 128.2, 128.7, 128.9, 129.7, 132.0, 132.1(d,  $^3J_{\text{CF}}$  = 9.9Hz), 132.2, 135.0(d,  $^4J_{\text{CF}}$  = 3.3Hz), 139.2, 153.8, 165.5(d,  $^1J_{\text{CF}}$  = 252.6Hz), 188.6. HRMS: calcd for  $\text{C}_{22}\text{H}_{15}\text{FN}_2\text{O}$ : 365.1061 [M+Na] $^+$ , found: 365.1031

9



15mL  
 (0.05mmol, 8mg) TEMPO(0.5mmol, 78mg) 120 120  
 1c(0.6mmol, 127mg) PhI, 120 °C,  $\text{N}_2$ , 10 h  
 10h 4h 10mL  
 Cu(OAc) $_2$ (0.1mmol, 18mg) bpy (3mL)  
 2a(0.5mmol, 112mg) (10mL 3)  
 ( /  
 20/1) 1,3 4 (4 ) 3c(150mg, 75 )

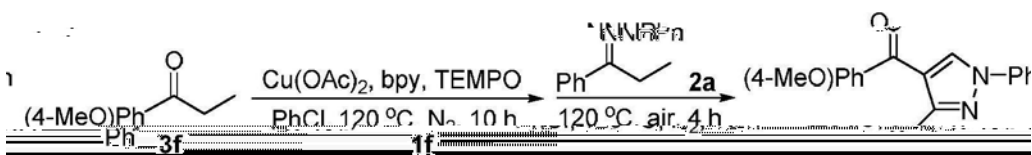
$^1\text{H NMR}$  (400MHz,  $\text{CDCl}_3$ ) : 7.33-7.34(m, 3H), 7.37(t, J = 7.6Hz, 1H), 7.48-7.53(m, 4H), 7.67-7.70(m, 4H), 7.78(dd,  $J_1$  = 8.8Hz,  $J_2$  = 1.2Hz, 2H), 8.28(s, 1H).



15mL  
(0.05mmol, 8mg) TEMPO(0.5mmol, 78mg)  
120  
120  
1e(0.6mmol, 89mg) Cu(OAc)<sub>2</sub>(0.1mmol, 18mg) bpy  
(3mL)  
10h  
4h 10mL  
2a(0.5mmol, 112mg)  
(10mL 3)  
( /  
20/1) 1,3 4 (4 ) 3e(110mg, 65 )

<sup>1</sup>H NMR(400MHz, CDCl<sub>3</sub>) : 2.38(s, 3H), 7.19(d, J = 8.0Hz, 2H), 7.32-7.35(m, 4H), 7.47(t, J = 8.0Hz, 2H), 7.74-7.78(m, 6H), 8.24(s, 1H). <sup>13</sup>C NMR(100MHz, CDCl<sub>3</sub>) : 21.7, 119.5, 121.4, 127.4, 128.2, 128.6, 128.9, 129.1, 129.6, 129.7, 132.0, 132.2, 136.3, 139.3, 143.5, 153.8, 189.8. HRMS: calcd for C<sub>23</sub>H<sub>19</sub>N<sub>2</sub>O 339.1492[MH]<sup>+</sup>, found: 339.1474

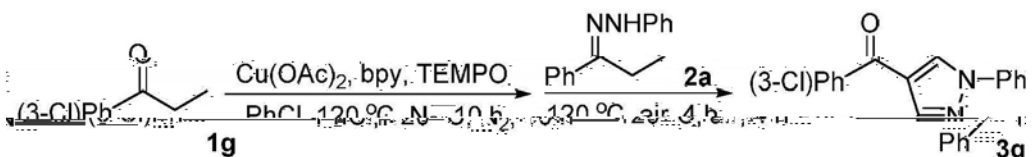
12



15mL  
(0.05mmol, 8mg) TEMPO(0.5mmol, 78mg)  
120  
120  
1f(0.6mmol, 98mg) Cu(OAc)<sub>2</sub>(0.1mmol, 18mg) bpy  
(3mL)  
10h  
4h 10mL  
2a(0.5mmol, 112mg)  
(10mL 3)  
( /  
10/1) 1,3 4 (4 ) 3f(106mg, 60 )

<sup>1</sup>H NMR(400MHz, CDCl<sub>3</sub>) : 3.85(s, 3H), 6.87(dd, J<sub>1</sub> = 1.2Hz, J<sub>2</sub> = 7.2Hz, 2H), 7.32-7.34(m, 3H), 7.37(d, J = 7.2Hz, 1H), 7.50(t, J = 8.0Hz, 2H), 7.71-7.73(m, 2H), 7.79(d, J = 7.6Hz, 2H), 7.85(dd, J<sub>1</sub> = 6.8Hz, J<sub>2</sub> = 2.0Hz, 2H), 8.26(s, 1H). <sup>13</sup>C NMR(150MHz, CDCl<sub>3</sub>) : 55.5, 113.6, 119.5, 121.5, 127.4, 128.2, 128.5, 128.8, 129.6, 131.4, 131.6, 132.0, 132.2, 139.4, 153.6, 163.4, 188.9. HRMS: calcd for C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>Na: 377.1260[M+Na]<sup>+</sup>, found: 377.1228

13



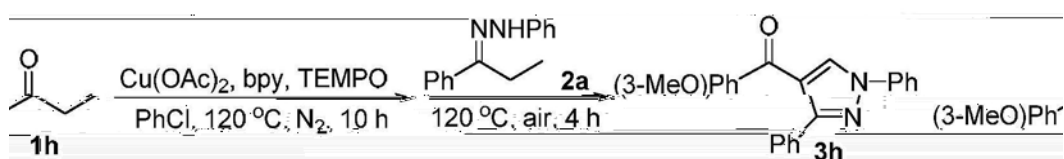
15mL  
(0.05mmol, 8mg) TEMPO(0.5mmol, 78mg)  
120  
120  
1g(0.6mmol, 101mg) Cu(OAc)<sub>2</sub>(0.1mmol, 18mg) bpy  
(3mL)  
10h  
4h 10mL  
2a(0.5mmol, 112mg)

120 4h 10mL (10mL 3)

20/1) 1,3 4 (3 ) 3g(143mg, 80 )

$^1\text{H NMR}$  (600MHz,  $\text{CDCl}_3$ ) : 7.31(t, J 7.8Hz, 1H), 7.33 7.35(m 3H), 7.38(t, J 7.8Hz, 1H), 7.47(dd,  $J_1$  7.8Hz,  $J_2$  1.2Hz, 1H), 7.50(t, J 7.8Hz, 2H), 7.66 7.69(m 3H), 7.78 7.80(m 3H), 8.31(s, 1H).  $^{13}\text{C NMR}$  (150MHz,  $\text{CDCl}_3$ ) : 119.7, 120.9, 127.6, 127.7, 128.2, 128.8, 129.0, 129.4, 129.6, 129.7, 131.9, 132.3, 132.5, 134.6, 139.2, 140.4, 154.1, 188.6. HRMS: calcd for  $\text{C}_{22}\text{H}_{15}\text{Cl N}_2\text{O Na}$ : 381.0765[MNa] $^+$ , found: 381.0769

14



15mL 1h (0.6mmol, 98mg)  $\text{Cu}(\text{OAc})_2$  (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)

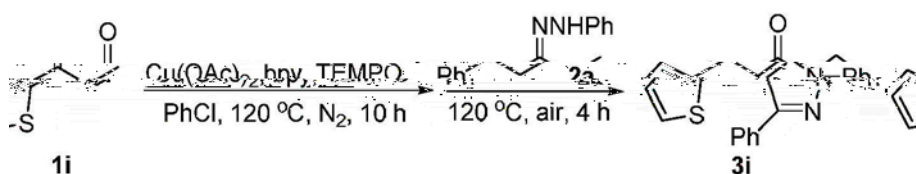
120 10h 2a (0.5mmol, 112mg)

120 4h 10mL (10mL 3)

10/1) 1,3 4 (3 ) 3h(110mg, 62 )

$^1\text{H NMR}$  (400MHz,  $\text{CDCl}_3$ ) : 3.66(s, 3H), 6.94 6.97(m 1H), 7.16 7.27(m 6H), 7.31(d, J 7.6Hz, 1H), 7.37(t, J 8.0Hz, 2H), 7.62 7.68(m 4H), 8.18(s, 1H).  $^{13}\text{C NMR}$  (150MHz,  $\text{CDCl}_3$ ) : 55.4, 113.7, 119.3, 119.6, 121.2, 122.3, 127.6, 128.2, 128.7, 128.9, 129.4, 129.7, 132.2, 132.4, 139.3, 140.2, 154.0, 159.7, 189.7. HRMS: calcd for  $\text{C}_{23}\text{H}_{19}\text{N}_2\text{O}_2$ : 355.1441[MH] $^+$ , found: 355.1434

15



15mL 1i (0.6mmol, 84mg)  $\text{Cu}(\text{OAc})_2$  (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)

120 10h 2a (0.5mmol, 112mg)

120 4h 10mL (10mL 3)

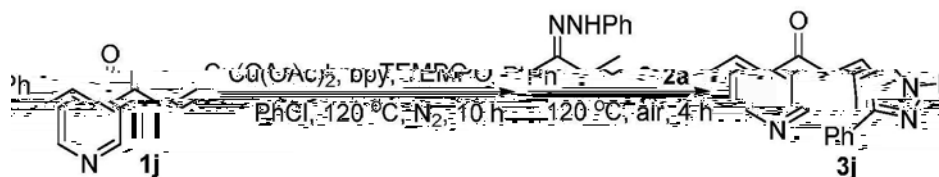
20/1) 3i (135mg, 82 )  $^1\text{H NMR}$

(400MHz,  $\text{CDCl}_3$ ) : 7.06 7.09(m 1H), 7.35 7.40(m 4H), 7.52(t, J 8.0Hz, 2H), 7.62(dd,  $J_1$  1.2Hz,  $J_2$  4.0Hz, 1H), 7.66(dd,  $J_1$  0.8Hz,  $J_2$  4.8Hz, 1H), 7.78 7.82(m 4H), 8.40(s, 1H).  $^{13}\text{C NMR}$  (150MHz,  $\text{CDCl}_3$ ) : 119.6, 121.1, 127.6, 128.0, 128.3, 128.7, 128.8, 129.7,



131.2, 132.0, 133.9, 134.0, 139.3, 145.0, 153.4, 181.4. HRMS: calcd for  $C_{20}H_{14}N_2OSNa$ : 353.0719[MNa]<sup>+</sup>, found: 53.0707

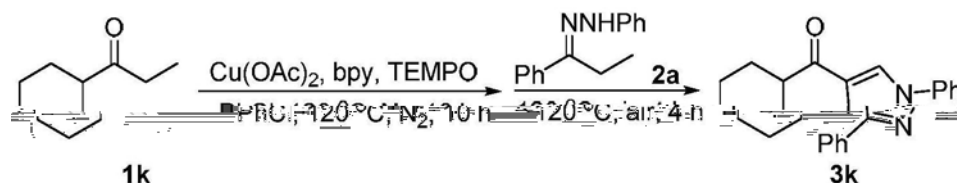
16



15mL  
 1j (0.6mmol, 81mg) Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy  
 (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)  
 120 10h 2a (0.5mmol, 112mg)  
 120 4h 10mL (10mL 3)

10/1) 3j (102mg, 63%) <sup>1</sup>H NMR  
 (400MHz, CDCl<sub>3</sub>): 7.31-7.38(m, 5H), 7.48(t, J = 8.0Hz, 2H), 7.67-7.69(m, 2H), 7.78(d, J = 8.0Hz, 2H), 8.05(d, J = 7.6Hz, 1H), 8.35(s, 1H), 8.71(s, 1H), 9.02(s, 1H). <sup>13</sup>C NMR  
 (100MHz, CDCl<sub>3</sub>): 119.6, 120.9, 123.4, 127.8, 128.3, 128.9, 129.1, 129.7, 131.8, 132.5, 134.4, 136.6, 139.1, 150.3, 152.8, 154.1, 188.1. HRMS: calcd for C<sub>21</sub>H<sub>16</sub>N<sub>3</sub>O 326.1288[MH]<sup>+</sup>, found: 326.1276

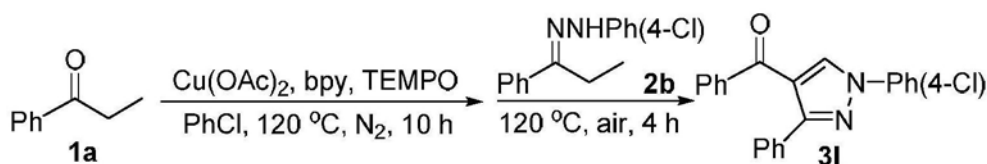
17



15mL  
 1k (0.6mmol, 84mg) Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy  
 (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)  
 120 10h 2a (0.5mmol, 112mg)  
 120 4h 10mL (10mL 3)

10/1) 3k (79mg, 48%) <sup>1</sup>H NMR  
 (600MHz, CDCl<sub>3</sub>): 1.13-1.24(m, 3H), 1.45-1.51(m, 2H), 1.64-1.66(m, 1H), 1.76-1.79(m, 2H), 1.83-1.85(m, 2H), 2.78-2.82(m, 1H), 7.36(t, J = 7.8Hz, 1H), 7.42-7.46(m, 3H), 7.49(t, J = 7.8Hz, 2H), 7.73(dd, J<sub>1</sub> = 7.8Hz, J<sub>2</sub> = 1.2Hz, 2H), 7.78(d, J = 7.2Hz, 2H), 8.42(s, 1H). <sup>13</sup>C NMR (150MHz, CDCl<sub>3</sub>): 25.7, 25.8, 29.4, 48.9, 119.7, 121.7, 127.6, 128.1, 128.8, 129.3, 129.6, 130.9, 132.7, 139.3, 153.9, 199.0. HRMS: calcd for C<sub>22</sub>H<sub>23</sub>N<sub>2</sub>O 331.1805[MH]<sup>+</sup>, found: 331.1789

18



15mL  
(0.05mmol, 8mg) TEMPO(0.5mmol, 78mg) 120 120 20/1)

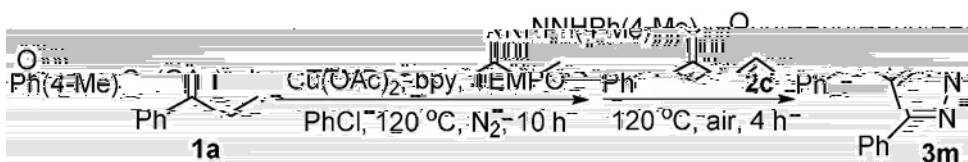
1a(0.6mmol, 80mg) Cu(OAc)<sub>2</sub>(0.1mmol, 18mg) bpy (3mL) 10h 4h 10mL

2b(0.5mmol, 129mg) (10mL 3)

3l (143mg, 80)

<sup>1</sup>H NMR(600MHz, CDCl<sub>3</sub>) : 7.32 7.34(m 3H), 7.39(t, J 7.2Hz, 2H), 7.45(d, J 7.8Hz, 2H), 7.52(t, J 6.6Hz, 1H), 7.70 7.74(m 4H), 7.82(d, J 7.2Hz, 2H), 8.25(s, 1H). <sup>13</sup>C NMR(150MHz, CDCl<sub>3</sub>) : 120.7, 121.6, 128.2, 128.4, 128.7, 128.9, 129.5, 129.8, 131.9, 132.1, 132.7, 133.1, 137.8, 138.7, 154.2, 189.9. HRMS: cal cd for C<sub>22</sub>H<sub>15</sub>Cl N<sub>2</sub>O: 381.0765[MNa]<sup>+</sup>, found: 381.0747

19



15mL  
(0.05mmol, 8mg) TEMPO(0.5mmol, 78mg) 120 120 20/1)

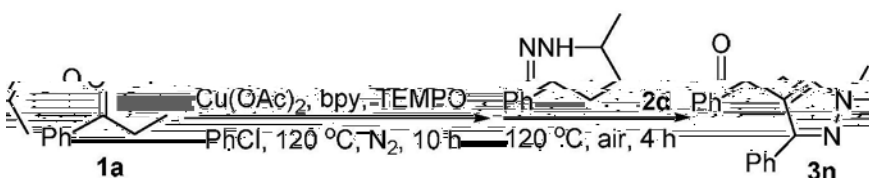
1a(0.6mmol, 80mg) Cu(OAc)<sub>2</sub>(0.1mmol, 18mg) bpy (3mL) 10h 4h 10mL

2c(0.5mmol, 119mg) (10mL 3)

3m(118mg, 70)

<sup>1</sup>H NMR(600MHz, CDCl<sub>3</sub>) : 2.41(s, 3H), 7.29(d, J 7.8Hz, 2H), 7.32 7.34(m 3H), 7.40(t, J 7.2Hz, 2H), 7.52(t, J 7.2Hz, 1H), 7.66(d, J 7.8Hz, 2H), 7.73(d, J 6.0Hz, 2H), 7.83(d, J 7.2Hz, 2H), 8.24(s, 1H). <sup>13</sup>C NMR(150MHz, CDCl<sub>3</sub>) : 21.0, 119.5, 121.0, 128.1, 128.3, 128.5, 128.9, 129.5, 130.1, 132.2, 132.3, 132.6, 137.0, 137.5, 139.0, 153.8, 190.1. HRMS: cal cd for C<sub>23</sub>H<sub>19</sub>N<sub>2</sub>O: 339.1492[MH]<sup>+</sup>, found: 339.1475

20



15mL  
(0.05mmol, 8mg) TEMPO(0.5mmol, 78mg) 120 120

1a(0.6mmol, 80mg) Cu(OAc)<sub>2</sub>(0.1mmol, 18mg) bpy (3mL) 10h 4h 10mL

2d(0.5mmol, 95mg)

120

4h 10mL

(10mL 3)

( /

20/1)

1

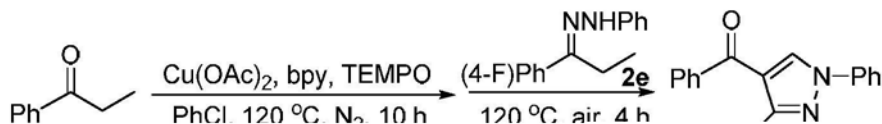
3

4

3n(104mg, 72 )

$^1\text{H NMR}$  (600MHz,  $\text{CDCl}_3$ ) : 1.51(d, J 6.6Hz, 6H), 4.48 4.50(m, 1H), 7.19 7.21(m, 3H), 7.28(t, J 7.2Hz, 2H), 7.40(t, J 6.6Hz, 1H), 7.55(d, J 6.6Hz, 2H), 7.68(d, J 7.2Hz, 2H), 7.74(s, 1H).  $^{13}\text{C NMR}$  (150MHz,  $\text{CDCl}_3$ ) : 21.8, 53.4, 118.0, 127.0, 127.1, 127.2, 127.9, 128.3, 131.2, 131.5, 131.7, 138.2, 151.6, 189.2. HRMS: cal cd for  $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}$  291.1492[MH] $^+$ , found: 291.1468

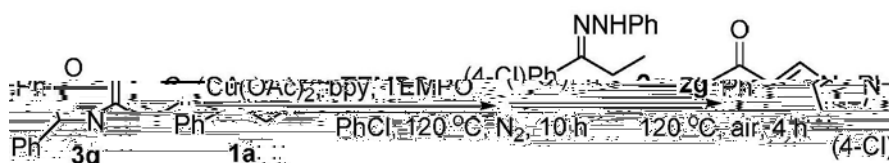
21



15mL 1a (0.6mmol, 80mg)  $\text{Cu}(\text{OAc})_2$  (0.1mmol, 18mg) bpy  
(0.05mmol, 8mg) TEMPO 0.6 - 0.7, 8mg a p1 J M

152.9, 189.7. HRMS: cal cd for  $C_{22}H_{16}BrN_2O$  403.0441 [M-H]<sup>+</sup>, found: 403.0464

23



15 mL 1a (0.6 mmol, 80 mg)  $Cu(OAc)_2$  (0.1 mmol, 18 mg) bpy (0.05 mmol, 8 mg) TEMPO (0.5 mmol, 78 mg) (3 mL)

120 10 h 2g (0.5 mmol, 129 mg) 120 4 h 10 mL (10 mL 3)

( / 20/1) 1 3 (4 ) 4 3q (140 mg, 78 )

<sup>1</sup>H NMR (600 MHz,  $CDCl_3$ ): 7.31 (d, J 8.4 Hz, 2H), 7.35 (t, J 7.2 Hz, 1H), 7.42 (t, J 7.2 Hz, 2H), 7.47 (t, J 7.8 Hz, 2H), 7.54 (d, J 7.2 Hz, 1H), 7.72 (m, 4H), 7.83 (d, J 7.2 Hz, 2H), 8.24 (s, 1H). <sup>13</sup>C NMR (150 MHz,  $CDCl_3$ ): 119.6, 121.1, 127.7, 128.4, 128.5, 129.5, 129.7, 130.3, 130.7, 132.6, 132.8, 134.7, 138.9, 139.1, 152.9, 189.8. HRMS: cal cd for  $C_{22}H_{16}ClN_2O$  359.0946 [M-H]<sup>+</sup>, found: 359.0924

24



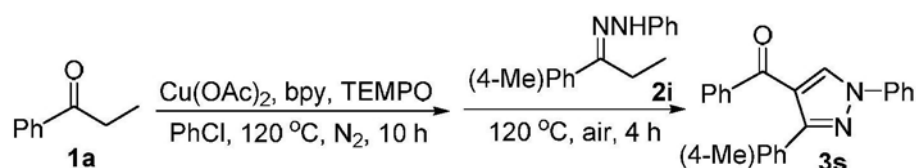
15 mL 1a (0.6 mmol, 80 mg)  $Cu(OAc)_2$  (0.1 mmol, 18 mg) bpy (0.05 mmol, 8 mg) TEMPO (0.5 mmol, 78 mg) (3 mL)

120 10 h 2h (0.5 mmol, 146 mg) 120 4 h 10 mL (10 mL 3)

( / 20/1) 1 3 (4 ) 4 3r (174 mg, 89 )

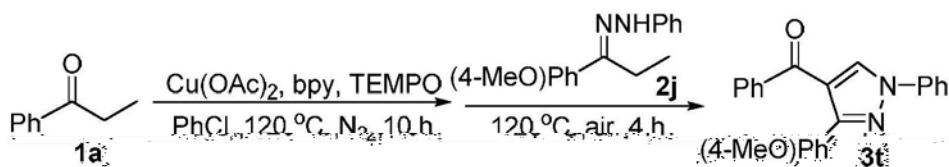
<sup>1</sup>H NMR (600 MHz,  $CDCl_3$ ): 7.38 (t, J 7.2 Hz, 1H), 7.44 (t, J 7.2 Hz, 2H), 7.50 (t, J 7.2 Hz, 2H), 7.57 (t, J 7.2 Hz, 1H), 7.61 (d, J 7.8 Hz, 2H), 7.77 (d, J 8.4 Hz, 2H), 7.85 (d, J 7.8 Hz, 2H), 7.91 (d, J 7.8 Hz, 2H), 8.28 (s, 1H). <sup>13</sup>C NMR (100 MHz,  $CDCl_3$ ): 119.6, 121.3, 124.2 (q, <sup>1</sup>J<sub>C-F</sub> 270.6 Hz), 125.1 (q, <sup>3</sup>J<sub>C-F</sub> 4.4 Hz), 127.9, 128.6, 129.2, 129.4, 129.7, 130.4 (q, <sup>2</sup>J<sub>C-F</sub> 32 Hz), 132.7, 132.9, 135.7 (q, <sup>4</sup>J<sub>C-F</sub> 1.5 Hz), 138.8, 139.1, 152.6, 189.6. HRMS: cal cd for  $C_{23}H_{16}F_3N_2O$  393.1209 [M-H]<sup>+</sup>, found: 393.1218

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15mL 1a (0.6mmol, 80mg) Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy  
 (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)  
 120 10h 2i (0.5mmol, 119mg)  
 120 4h 10mL (10mL 3)  
 ( /  
 20/1) 1 3 (4 ) 4 3s (140mg,  
 83 )  
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) : 2.34(s, 3H), 7.14(d, J 7.8Hz,  
 2H), 7.33(t, J 7.2Hz, 1H), 7.39(t, J 7.8Hz, 2H), 7.46(t, J 7.8Hz, 2H), 7.51(t, J  
 7.8Hz, 1H), 7.64(d, J 7.8Hz, 2H), 7.76(d, J 7.8Hz, 2H), 7.84(d, J 7.2Hz, 2H), 8.23(s,  
 1H). <sup>13</sup>C NMR (150MHz, CDCl<sub>3</sub>) : 21.4, 119.6, 121.1, 127.4, 128.4, 128.8, 128.9, 129.2,  
 129.5, 129.6, 132.3, 132.6, 138.5, 139.1, 139.3, 154.1, 190.0. HRMS: calcd for C<sub>23</sub>H<sub>19</sub>N<sub>2</sub>O  
 339.1492[MH]<sup>+</sup>, found: 339.1506

26



15mL 1a (0.6mmol, 80mg) Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy  
 (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)  
 120 10h 2j (0.5mmol, 127mg)  
 120 4h 10mL (10mL 3)  
 ( /  
 10/1) 1 3 (4 ) 4 3t (124mg,  
 70 )  
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) : 3.81(s, 3H), 6.88(d, J 9.2Hz,  
 2H), 7.34(t, J 7.6Hz, 1H), 7.41(t, J 7.6Hz, 2H), 7.48(t, J 8.0Hz, 2H), 7.53(t, J  
 7.6Hz, 1H), 7.72(d, J 8.8Hz, 2H), 7.76(d, J 7.6Hz, 2H), 7.84(d, J 7.2Hz, 2H), 8.24(s,  
 1H). <sup>13</sup>C NMR (150MHz, CDCl<sub>3</sub>) : 55.3, 113.6, 119.5, 120.9, 124.6, 127.4, 128.4, 129.5,  
 129.6, 130.3, 132.4, 132.6, 139.1, 139.3, 153.8, 160.0, 190.1. HRMS: calcd for C<sub>23</sub>H<sub>19</sub>N<sub>2</sub>O  
 355.1441[MH]<sup>+</sup>, found: 355.1442

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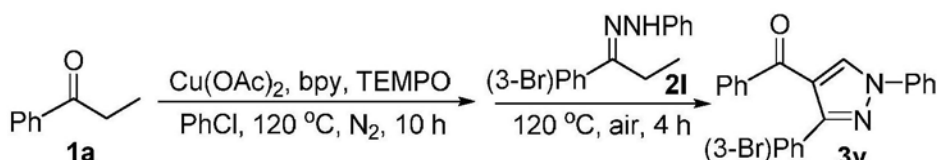


15mL 1a (0.6mmol, 80mg) Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy  
 (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)  
 120 10h 2k (0.5mmol, 121mg)  
 120 4h 10mL (10mL 3)  
 ( /

20/1) 1 3 (3 ) 4 3u(121mg, 71 )

$^1\text{H NMR}$  (600MHz,  $\text{CDCl}_3$ ) : 6.90 6.94(m 1H) , 7.17 7.20(m 1H) , 7.25(t, J 7.2Hz, 1H) , 7.32(t, J 7.8Hz, 2H) , 7.38(t, J 7.8Hz, 2H) , 7.43 7.45(m 3H) , 7.66(d, J 8.4Hz, 2H) , 7.74(d, J 7.2Hz, 2H) , 8.16(s, 1H) .  $^{13}\text{C NMR}$  (150MHz,  $\text{CDCl}_3$ ) : 115.5 (d,  $^2\text{J}_{\text{CF}}$  20.7Hz) , 115.8(d,  $^2\text{J}_{\text{CF}}$  23.0Hz) , 119.6, 121.2, 124.8(d,  $^4\text{J}_{\text{CF}}$  3.3Hz) , 127.7, 128.5, 129.5, 129.6(d,  $^3\text{J}_{\text{CF}}$  8.7Hz) , 129.7, 132.5, 132.8, 134.3(d,  $^3\text{J}_{\text{CF}}$  8.7Hz) , 138.9, 139.1, 152.7(d,  $^4\text{J}_{\text{CF}}$  2.2Hz) , 162.6(d,  $^1\text{J}_{\text{CF}}$  242.7Hz) , 189.8. HRMS: cal cd for  $\text{C}_{22}\text{H}_{16}\text{FN}_2\text{O}$  343.1241 [MH] $^+$ , found: 343.1242

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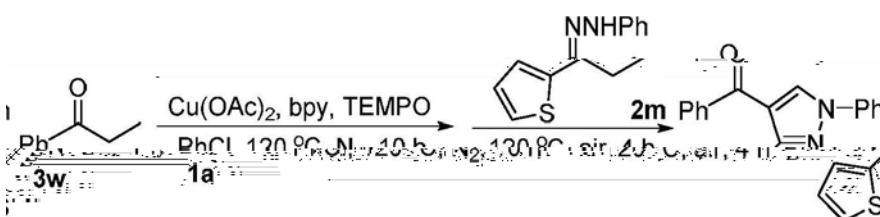


15mL 1a (0.6mmol, 80mg)  $\text{Cu}(\text{OAc})_2$  (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL) 120 10h 120 4h 10mL 2l (0.5mmol, 151mg) (10mL 3) ( /

20/1) 1 3 (3 ) 4 3v(159mg, 79 )

$^1\text{H NMR}$  (600MHz,  $\text{CDCl}_3$ ) : 7.20(t, J 7.8Hz, 1H) , 7.37(t, J 7.8Hz, 1H) , 7.40 7.46(m 3H) , 7.50(t, J 7.2Hz, 2H) , 7.55(t, J 7.8Hz, 1H) , 7.67(d, J 7.8Hz, 1H) , 7.77(d, J 7.8Hz, 2H) , 7.83(d, J 7.8Hz, 2H) , 7.96(s, 1H) , 8.27(s, 1H) .  $^{13}\text{C NMR}$  (150MHz,  $\text{CDCl}_3$ ) : 119.6, 121.3, 122.2, 127.7, 127.8, 128.5, 129.4, 129.6, 129.7, 131.6, 131.7, 132.6, 132.8, 134.1, 138.9, 139.1, 152.5, 189.8. HRMS: cal cdf or  $\text{C}_{22}\text{H}_{16}\text{BrN}_2\text{O}$  403.0441 [MH] $^+$ , found: 403.0440

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15mL 1a (0.6mmol, 80mg)  $\text{Cu}(\text{OAc})_2$  (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL) 120 10h 120 4h 10mL 2m (0.5mmol, 115mg) (10mL 3) ( /

20/1) 1 3 ( 2 ) 4 3v(133mg, 81 )

g 5 A, nQ(3 m $^{\text{f}}$  5

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7.93–7.94(m, 1H), 8.17(s, 1H).  $^{13}\text{C}$  NMR(150MHz,  $\text{CDCl}_3$ ) : 119.6, 120.4, 126.8, 127.5, 127.7, 128.6, 128.9, 129.4, 129.7, 132.6, 132.9, 134.2, 139.0, 139.5, 148.3, 189.5. HRMS: calcd for  $\text{C}_{20}\text{H}_{14}\text{N}_2\text{OSNa}$ : 353.0719  $[\text{M}+\text{Na}]^+$ , found: 353.0706