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CN 107089950 B

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2019. 12. 24

(21) 201710458815. 8

(56)

(22) 2017. 06. 16

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(65)

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Wang, Z.

(73)

Chen, G.

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Zhang, X.

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Fan, X. .Synthesi s of 3-acySynthesi s

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612-616.

( ) 41139

Jun-Long Zhan, Meng-Wei Wu, Fei Chen,  
and Bing Han. Cu-Catal yzed [ 3 + 3]

(51)Int. Cl .

Annul ati on for the Synthesi s of

C07D 231/12 (2006. 01)

Pyri mi di nes vi a. J. Org. Chem .2016,(

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C07D 401/06 (2006. 01)

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C07D 409/04 (2006. 01)

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4

4

100

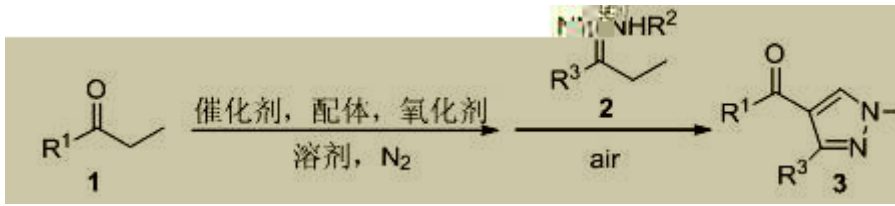
140

100 140

4

4

1. 4  
, 1  
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  
2. 1 4  
, 1 2  
1 1. 2 1: 0.1 0.2 0.1: 1 2

4

[0001]

4

[0002]

4

4

[0003]

4

4

[0004]

4

2

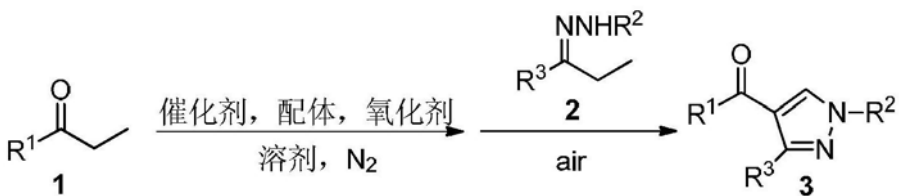
100 140

100 140

4

3

[0005]



[0006]

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

(TEMPO)

[0007]

1

2

1 1.2 1: 0.1 0.2 0.1: 1 2

[0008]

(1)

4

(2)

(3)

(4)

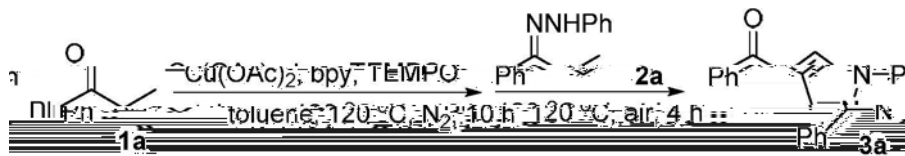
4

[0009]

[0010]

1

[0011]



[0012]

2'

(toluene, 3mL)

4h

10mL

1a (0.5mmol, 67mg)

2a (0.5mmol, 112mg)

(10mL 3)

( / 20/1)

(Cu(OAc)<sub>2</sub>, 0.05mmol, 9mg)

(bpy, 0.05mmol, 8mg)

120

120

120

10h

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: calcd 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

[0013]

2

[0014]

120

120

120

15mL

10h

4h

20/1)

[0015]

3

[0016]

120

120

120

15mL

10h

4h

20/1)

1a (0.5mmol, 67mg)

2a (0.5mmol, 112mg)

1, 3 4

1a (0.6mmol, 80mg)

2a (0.5mmol, 112mg)

1, 3 4

Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)

2a (0.5mmol, 112mg) (10mL 3) ( /

3a (97mg, 60%)

Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)

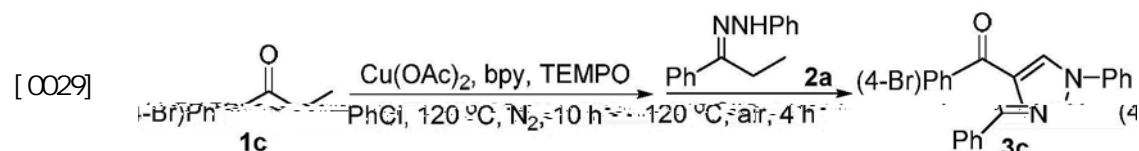
2a (0.5mmol, 112mg) (10mL 3) ( /

3a (105mg, 65%)

[0017]	4							
[0018]	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 )				
[0019]	5							
[0020]	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 )				
[0021]	6							
[0022]	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 )				
[0023]	7							
[0024]	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 )				
[0025]	8							
[0026]	o							
[0027]	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 [MNa] $^+$ , found: 365.1031

[0028] 9



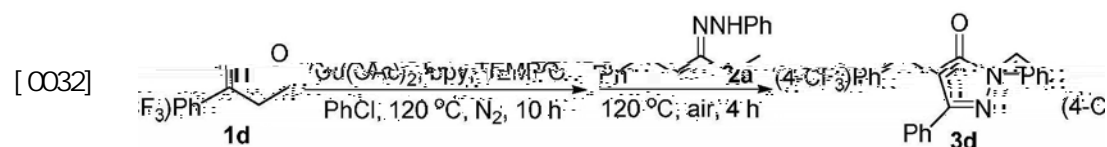
[0030] 15mL 1c (0.6mmol, 127mg)  $\text{Cu}(\text{OAc})_2$  (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)

120 10h 2a (0.5mmol, 112mg)  
120 4h 10mL (10mL 3)

( /  
20/1) 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).  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ ) : 119.6, 121.0, 127.6, 127.7, 128.2, 128.8, 128.9, 129.7, 131.0, 131.6, 131.9, 132.2, 137.6, 139.2, 153.9, 188.9. HRMS: calcd for  $\text{C}_{22}\text{H}_{16}\text{BrN}_2\text{O}$ : 403.0441 [MH] $^+$ , found: 403.0452

[0031] 10



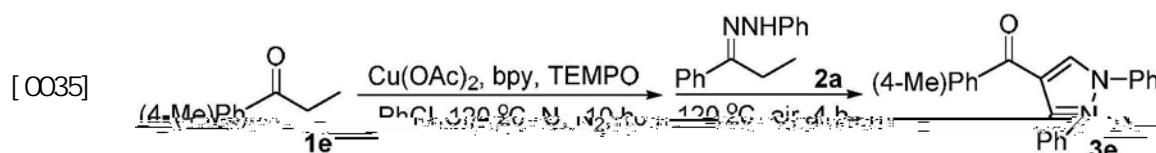
[0033] 15mL 1d (0.6mmol, 121mg)  $\text{Cu}(\text{OAc})_2$  (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)

120 10h 2a (0.5mmol, 112mg)  
120 4h 10mL (10mL 3)

( /  
20/1) 1, 3 4 (4 ) 3d (167mg, 85 )

$^1\text{H NMR}$  (400MHz,  $\text{CDCl}_3$ ) : 7.31-7.38(m, 4H), 7.46-7.50(m, 2H), 7.62(d, J = 8.0Hz, 2H), 7.66-7.69(m, 2H), 7.76-7.78(m, 2H), 7.87(d, J = 8.0Hz, 2H), 8.29(s, 1H).  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ ) : 119.6, 120.9, 123.6(q,  $^1J_{\text{CF}}$  = 271.3Hz), 125.4(q,  $^3J_{\text{CF}}$  = 3.7Hz), 127.8, 128.2, 128.8, 129.0, 129.6, 129.7, 131.8, 132.6, 133.8(q,  $^2J_{\text{CF}}$  = 32.8Hz), 139.1, 141.9, 154.2, 188.8. HRMS: calcd for  $\text{C}_{23}\text{H}_{16}\text{F}_3\text{N}_2\text{O}$ : 393.1209 [MH] $^+$ , found: 393.1210

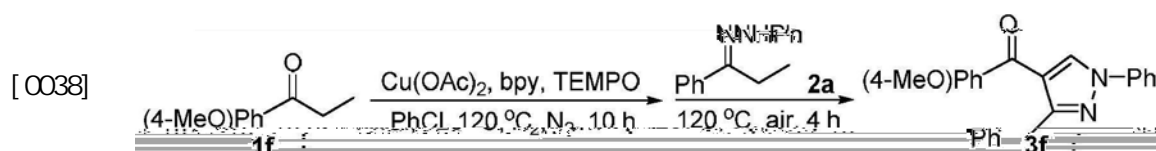
[0034] 11



[0036] 15mL 1e (0.6mmol, 89mg) 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 ) 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 [M]<sup>+</sup>, found: 339.1474

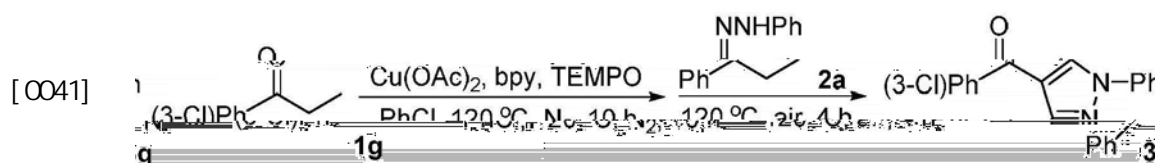
[0037] 12



[0039] 15mL 1f (0.6mmol, 98mg) 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) 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

[0040] 13

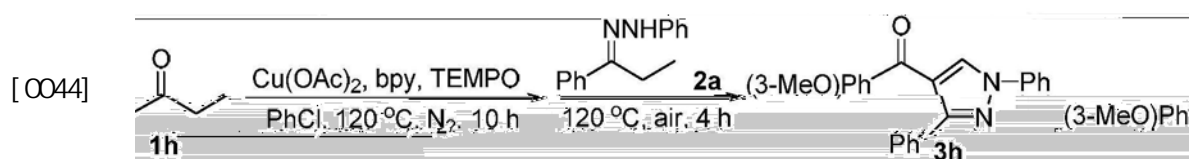


[0042] 15mL 1g (0.6mmol, 101mg) Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)  
120 10h 2a (0.5mmol, 112mg)

120 4h 10mL (10mL 3)  
 ( /  
 20/1) 1,3 4 (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

[0043] 14



[0045] 15mL 1h (0.6mmol, 98mg)  $\text{Cu}(\text{OAc})_2$  (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)

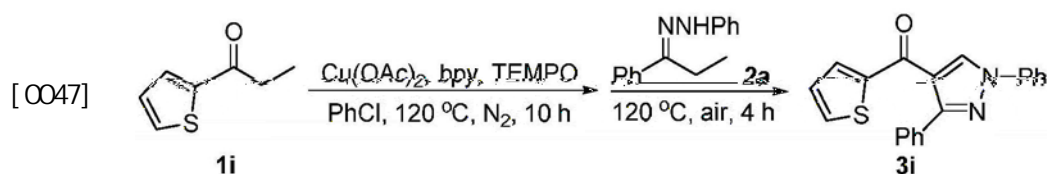
120 10h 2a (0.5mmol, 112mg)

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

[0046] 15



[0048] 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)

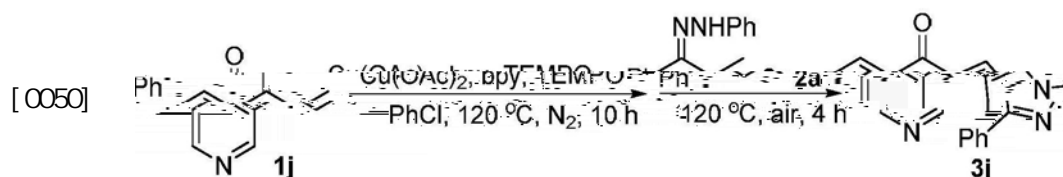
( /  
 20/1) 3i (135mg, 82 )  $^1\text{H NMR}$

(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: cal cdf or  $C_{20}H_{14}N_2OSNa$ : 353.0719[MNa]<sup>+</sup>, found: 53.0707

[0049] 16

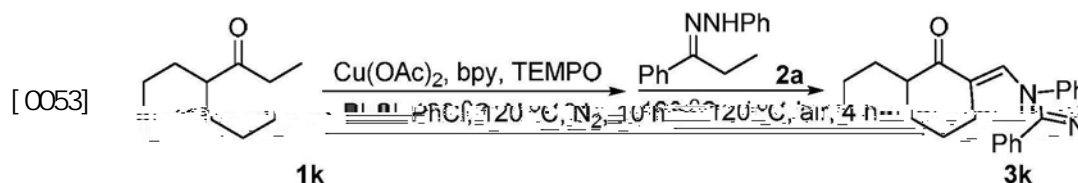


[0051] 15mL 1j (0.6mmol, 81mg) Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)

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: cal cd for C<sub>21</sub>H<sub>16</sub>N<sub>3</sub>O 326.1288[MH]<sup>+</sup>, found: 326.1276

[0052] 17

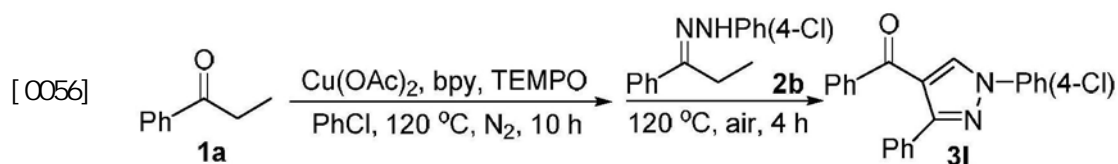


[0054] 15mL 1k (0.6mmol, 84mg) Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)

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: cal cd for C<sub>22</sub>H<sub>23</sub>N<sub>2</sub>O 331.1805[MH]<sup>+</sup>, found: 331.1789

[0055] 18



[0057] 15mL 1a (0.6mmol, 80mg) Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)  
120 10h 2b (0.5mmol, 129mg)  
120 4h 10mL (10mL 3)  
( /  
20/1) 1 (4 ) 3 4 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 Na: 381.0765[MNa]<sup>+</sup>, found: 381.0747

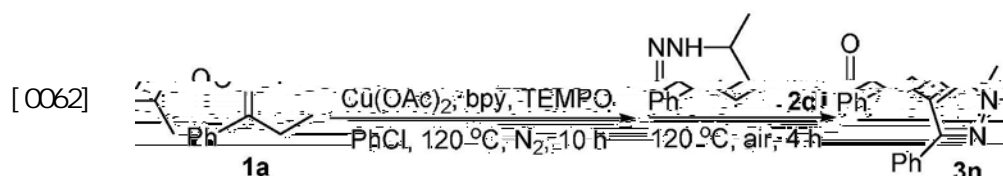
[0058] 19



[0060] 15mL 1a (0.6mmol, 80mg) Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)  
120 10h 2c (0.5mmol, 119mg)  
120 4h 10mL (10mL 3)  
( /  
20/1) 1 (4 ) 3 4 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

[0061] 20

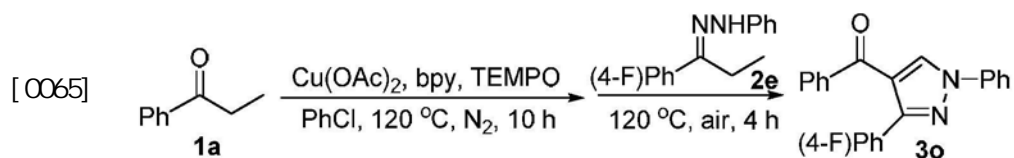


[0063] 15mL 1a (0.6mmol, 80mg) Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)  
120 10h 2d (0.5mmol, 95mg)

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

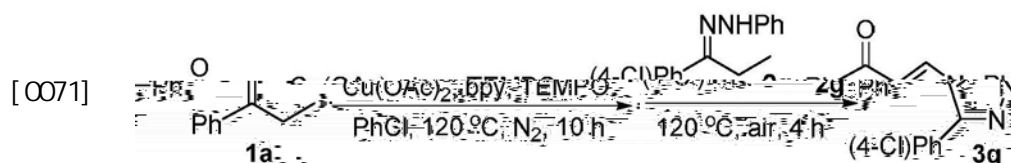
[0064] 21



[0066] 15mL 1a(0.6mmol, 80mg)  $\text{Cu}(\text{OAc})_2$ (0.1mmol, 18mg) bpy  
 (0.05mmol, 8mg) TEMPO, 11 - m07, 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

[0070] 23



[0072] 15mL 1a (0.6mmol, 80mg) Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)

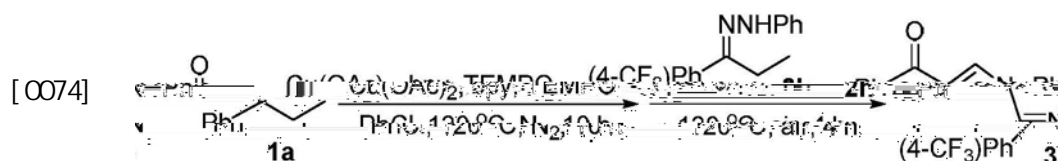
120 10h 2g (0.5mmol, 129mg)

120 4h 10mL (10mL 3)

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

<sup>1</sup>H NMR (600MHz, CDCl<sub>3</sub>) : 7.31(d, J 8.4Hz, 2H), 7.35(t, J 7.2Hz, 1H), 7.42(t, J 7.2Hz, 2H), 7.47(t, J 7.8Hz, 2H), 7.54(d, J 7.2Hz, 1H), 7.72 7.75(m, 4H), 7.83(d, J 7.2Hz, 2H), 8.24(s, 1H). <sup>13</sup>C NMR (150MHz, CDCl<sub>3</sub>) : 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

[0073] 24



[0075] 15mL 1a (0.6mmol, 80mg) Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)

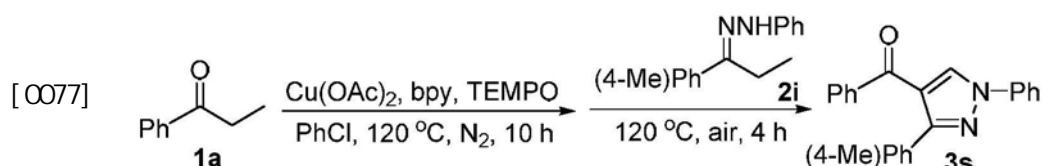
120 10h 2h (0.5mmol, 146mg)

120 4h 10mL (10mL 3)

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

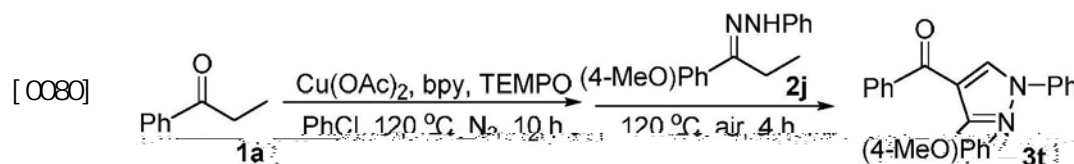
<sup>1</sup>H NMR (600MHz, CDCl<sub>3</sub>) : 7.38(t, J 7.2Hz, 1H), 7.44(t, J 7.2Hz, 2H), 7.50(t, J 7.2Hz, 2H), 7.57(t, J 7.2Hz, 1H), 7.61(d, J 7.8Hz, 2H), 7.77 (d, J 8.4Hz, 2H), 7.85(d, J 7.8Hz, 2H), 7.91(d, J 7.8Hz, 2H), 8.28(s, 1H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) : 119.6, 121.3, 124.2(q, <sup>1</sup>J<sub>CF</sub> 270.6Hz), 125.1(q, <sup>3</sup>J<sub>CF</sub> 4.4Hz), 127.9, 128.6, 129.2, 129.4, 129.7, 130.4(q, <sup>2</sup>J<sub>CF</sub> 32Hz), 132.7, 132.9, 135.7(q, <sup>4</sup>J<sub>CF</sub> 1.5Hz), 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

[0076] 25



[0078] 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

[0079] 26



[0081] 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<sub>2</sub> 355.1441[MH]<sup>+</sup>, found: 355.1442

[0082] 27

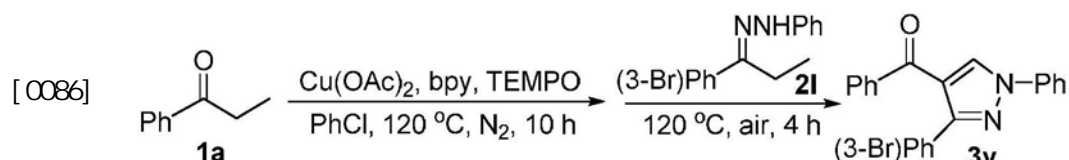


[0084] 15mL 1a (0.6mmol, 80mg) Cu(OAc)<sub>2</sub> (0.1mmol, 18mg) bpy (0.05mmol, 8mg) TEMPO (0.5mmol, 78mg) (3mL)  
 120 10h 2k (0.5mmol, 121mg)  
 120 4h 10mL (10mL 3)  
 ( /

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

[0085] 28

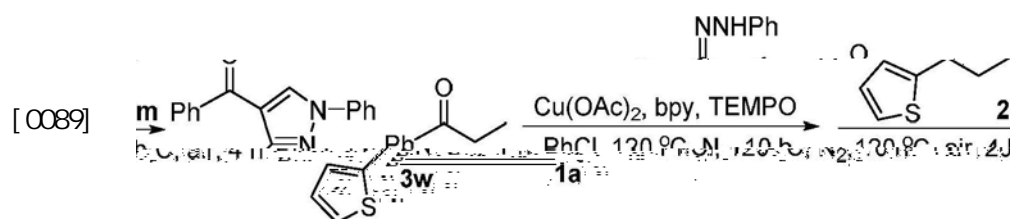


[0087] 15mL 1a (0.6mmol , 80mg)  $\text{Cu}(\text{OAc})_2$  (0.1mmol , 18mg) bpy (0.05mmol , 8mg) TEMPO (0.5mmol , 78mg) (3mL)  
120 10h 2l (0.5mmol , 151mg)  
120 4h 10mL (10mL 3)

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

[0088] 29



[0090] 15mL 1a (0.6mmol , 80mg)  $\text{Cu}(\text{OAc})_2$  (0.1mmol , 18mg) bpy (0.05mmol , 8mg) TEMPO (0.5mmol , 78mg) (3mL)  
120 10h 2m (0.5mmol , 115mg)  
120 4h 10mL (10mL 3)

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

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7.93-7.94(m, 1H), 8.17(s, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ): 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 [0091]