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7B %\$' % \$' &+ 5ž&\$% "\$\* "&\*

<i UbZYb[ ' >] Ub[ "7i ! 7UhU mmYX H\FYY!

7cadcbYbh 7UgWUXY 5bbi `Uh] cb FYUW] cb. 5b

9bhf m hc : i bVh] cbU ] nYX Dmf ] X] bYg" >"

Cf[ " 7\Ya" "&\$% ž , \$ , +\*! , ++% "

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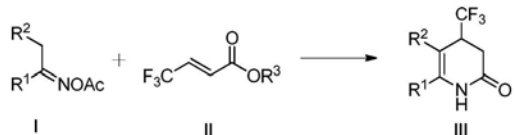
f&\$\$\* "\$%&

f&\$\$\* "\$%&

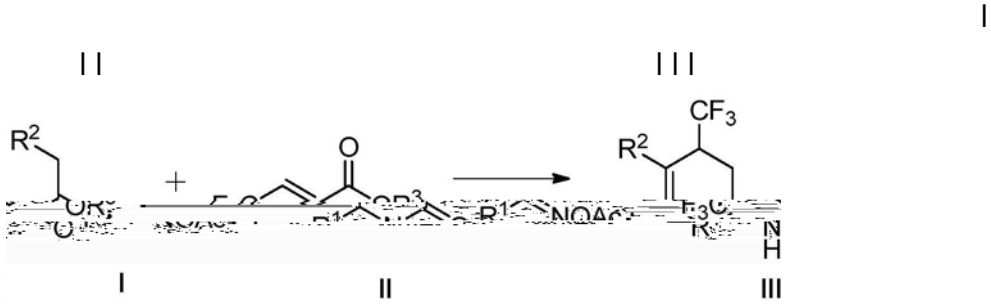
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CN 108299285 B



1. III



6,7,8 2 2 4 ( 0 ) 4 4 3 3

R<sup>3</sup>

2. 1 III  
CuCl CuBr CuI CuOAc

3. 1 III  
DMF DMSO

4. 1 III  
60 120

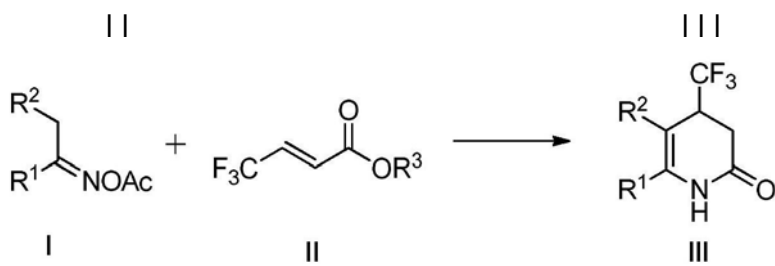
5. 1 III

1M HCl

III

C H C X( )

III



R<sup>1</sup>

R<sup>2</sup> H

R<sup>3</sup>

O

R<sup>1</sup> C<sub>11</sub>f

S ñyPci @

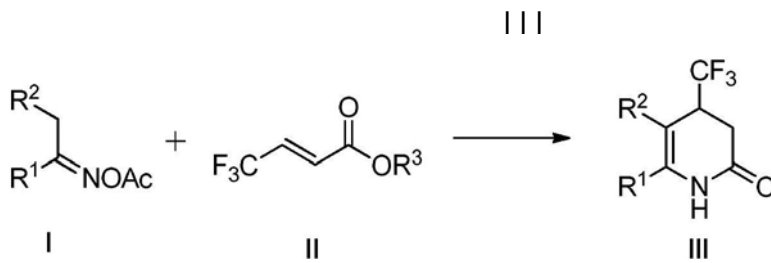
I I II 1:1 2  
 I II 1:1.1 1:2  
 20mol 10mol I 10 50mol 10  
 25mol I  
 II I  
 III I  
 (0.20mmol) II (0.2 0.4mmol) Cu<sup>I</sup> (0.02 0.04mmol , 10 20mol ) Zn  
 (0.02 0.05mmol , 10 25mol ) DMSO(2  
 3.5mL) 60 120 12 36  
 H<sub>2</sub>O(2.0mL) 1MHCl (aq, 3mL)  
 (4 10mL) (EA: PE 5: 1)  
 III  
 III  
 III Cu(I)  
 CF<sub>3</sub> [3+3]  
 4  
 4



1 2 3 4

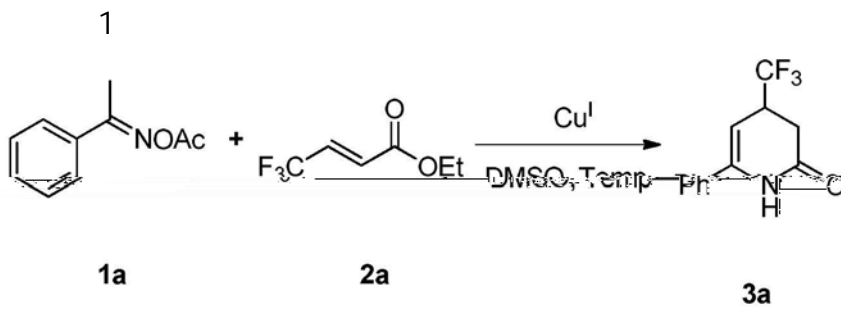
O S N

(Z) (E) ) R S (Z) (E)



I (0.02 0.04mmol , 10 20ml ) II (0.2 0.4mmol ) CuCl (0.2 0.4mmol ) Zn(0.02 0.05mmol , 10 25ml ) DMSO(2 3.5ml) 60 120 12 36 H<sub>2</sub>O(2.0ml)

1M HCl (aq, 3ml) (4 10ml) (EA: PE 5: 1)



1a(0.20mmol) 2a(0.24mmol) CuCl (0.02mmol 10ml ) Zn(0.05mmol 25ml ) DMSO(3.5ml) 80 24

H<sub>2</sub>O(2.0ml) 1M HCl (aq, 3ml) (4 10ml) (EA: PE 5: 1)

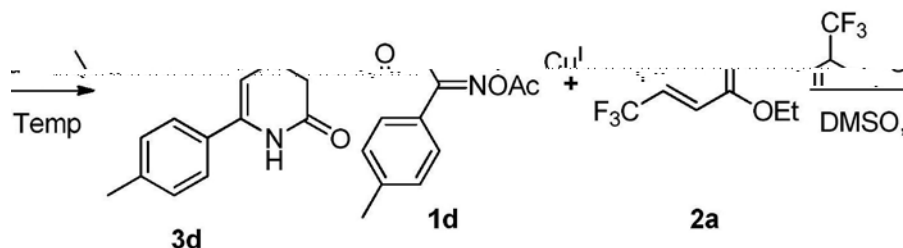
(35mg, 72 )

3a

mp 144 146 . <sup>1</sup>H NMR(400MHz, CDCl<sub>3</sub>) 7.82(s, 1H) , 7.48 7.41(m 5H) ,

5. 27(d, J 3.0 Hz, 1H), 3.45 3.34(m, 1H), 2.84 2.72(m, 2H).  $^{13}\text{C}$  NMR(100MHz,  $\text{CDCl}_3$ ) 168.7, 140.5, 134.0, 129.7, 129.0, 126.4(q, J 277.8 Hz), 125.4, 94.9(q, J 2.9 Hz), 37.9 (q, J 29.4 Hz), 29.8(q, J 2.5 Hz).  $^{19}\text{F}$  NMR(565MHz,  $\text{CDCl}_3$ ) 74.86(d, J 8.0 Hz). HRMS:  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{12}\text{H}_{11}\text{F}_3\text{NO}^+$ : 242.0787, found 242.0787.

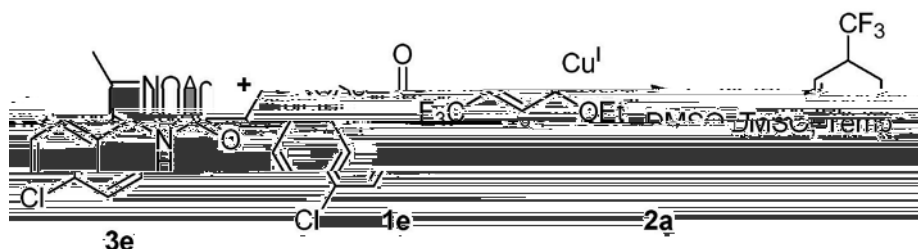
2



1d (0.20 mmol)      2a (0.4 mmol)    CuCl (0.03 mmol)    Zn  
(0.02 mmol)      DMSO (3 mL)  
100      14  
H<sub>2</sub>O (2.0 mL)      1M HCl (aq, 3 mL)      (4 10 mL)  
(EA: PE 5:1)      3d (38 mg, 75 %)

mp 100-102.  $^1\text{H}$  NMR(400MHz,  $\text{CDCl}_3$ ) 7.92(s, 1H), 7.35(d, J 8.0 Hz, 2H), 7.22(d, J 8.0 Hz, 2H), 5.23(d, J 3.8 Hz, 1H), 3.41 3.34(m, 1H), 2.83 2.71(m, 2H), 2.38(s, 3H).  $^{13}\text{C}$  NMR(100MHz,  $\text{CDCl}_3$ ) 168.9, 140.5, 139.8, 131.2, 129.6, 126.5(q, J 277.7 Hz), 125.2, 94.1(q, J 2.9 Hz), 37.8(q, J 29.4 Hz), 29.8(q, J 2.5 Hz).  $^{19}\text{F}$  NMR (565MHz,  $\text{CDCl}_3$ ) 73.24(d, J 8.6 Hz). HRMS:  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{13}\text{H}_{13}\text{F}_3\text{NO}^+$ : 256.0944, found 256.0946.

3

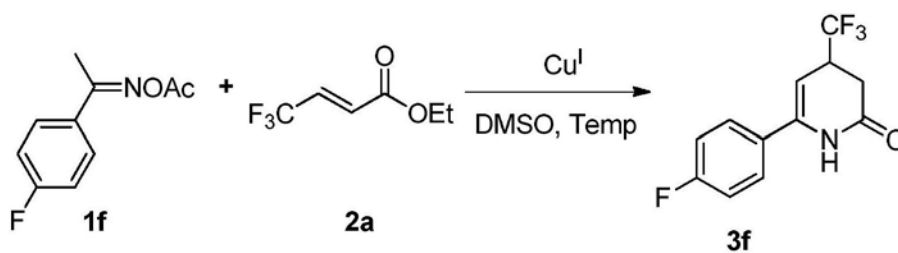


1e (0.20 mmol)      2a (0.4 mmol)    CuCl (0.03 mmol)    Zn  
(0.02 mmol)      DMSO (3 mL)  
100      14  
H<sub>2</sub>O (2.0 mL)      1M HCl (aq, 3 mL)      (4 10 mL)  
(EA: PE 5:1)      3e (39 mg, 71 %)

mp 196-198.  $^1\text{H}$  NMR(400MHz,  $\text{CDCl}_3$ ) 8.08(s, 1H), 7.43 7.38(m, 4H), 5.26(d, J 4.0 Hz, 1H), 3.44 3.33(m, 1H), 2.84 2.72(m, 2H).  $^{13}\text{C}$  NMR(100MHz,  $\text{CDCl}_3$ ) 168.9, 139.7, 135.8, 132.5, 129.3, 126.3(q, J 277.8 Hz), 126.8, 95.4(q, J 2.8 Hz), 37.9 (q, J 29.5 Hz), 29.7(q, J 2.5 Hz).  $^{19}\text{F}$  NMR(565MHz,  $\text{CDCl}_3$ ) 73.15(d, J 8.5 Hz). HRMS:  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{F}_3\text{NO}^+$ : 276.0398, found 276.0399.

4





1f (0.20mmol)      2a(0.4mmol)    CuCl (0.03mmol)    Zn  
 (0.02mmol)      DMSO(3mL)

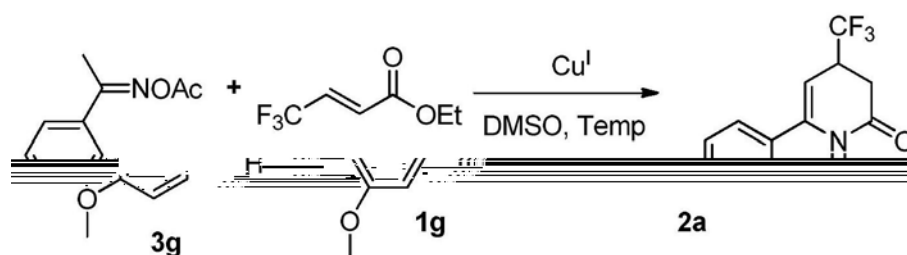
100      14  
 H<sub>2</sub>O(2.0mL)

1MHCl (aq, 3mL)      (4 10mL)  
 (EA: PE 5: 1)

3f (36mg, 70 %)

mp 122-124 °C. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) 8.09(s, 1H), 7.48-7.44(m, 2H), 7.13-7.09(m, 2H), 5.21(d, J = 3.6Hz, 1H), 3.44-3.32(m, 1H), 2.83-2.71(m, 2H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) 168.9, 163.5(d, J = 250.1Hz), 139.8, 130.3(d, J = 3.4Hz), 127.5(d, J = 8.4Hz), 126.4(q, J = 277.8Hz), 116.1(d, J = 21.9Hz), 94.9(q, J = 1.6Hz), 37.8(q, J = 29.4Hz), 29.7(q, J = 2.5Hz). <sup>19</sup>F NMR (565MHz, CDCl<sub>3</sub>) 73.22(s), 110.60(m). HRMS: [M+H]<sup>+</sup> calculated for C<sub>12</sub>H<sub>10</sub>F<sub>4</sub>NO<sup>+</sup>: 260.0693, found 260.0697.

5



1g(0.20mmol)      2a(0.4mmol)    CuCl (0.03mmol)    Zn  
 (0.02mmol)      DMSO(3mL)

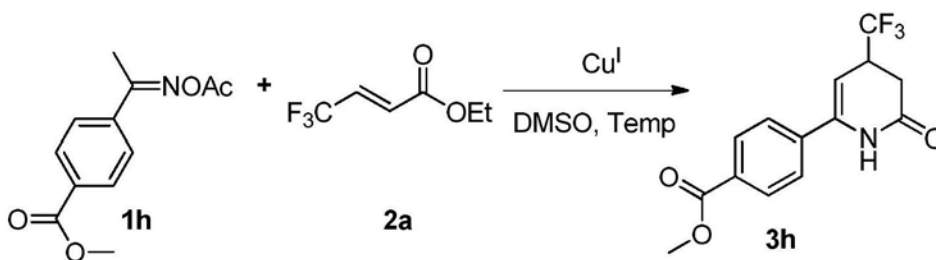
100      14  
 H<sub>2</sub>O(2.0mL)

1MHCl (aq, 3mL)      (4 10mL)  
 (EA: PE 5: 1)

3g(41mg, 76 %)

mp 96-98 °C. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) 7.76(s, 1H), 7.40-7.38(m, 2H), 6.94-6.92(m, 2H), 5.17(d, J = 4.1Hz, 1H), 3.82(s, 3H), 3.43-3.31(m, 1H), 2.83-2.71(m, 2H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) 168.8, 160.7, 140.1, 126.7, 126.5, 126.4(q, J = 277.7Hz), 114.3, 93.4(q, J = 2.9Hz), 55.4, 37.8(q, J = 29.4Hz), 29.9(q, J = 2.5Hz). <sup>19</sup>F NMR (565MHz, CDCl<sub>3</sub>) 73.28(d, J = 6.8Hz). HRMS: [M+H]<sup>+</sup> calculated for C<sub>13</sub>H<sub>13</sub>F<sub>3</sub>NO<sup>+</sup>: 272.0893, found 272.0894.

6



1h (0.20mmol)      2a (0.4mmol)    CuCl (0.02mmol)    Zn  
(0.05mmol)      DMSO(3mL)

100      24

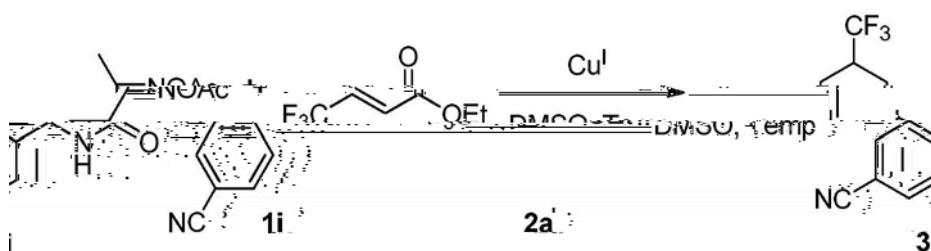
H<sub>2</sub>O(2.0mL)      1MHCl (aq, 3mL)      (4 10mL)

(EA: PE 5: 1)

3h(45mg, 75 %)

mp 122-124 °C. <sup>1</sup>H NMR(400MHz, CD<sub>3</sub>OD) 8.05(d, J = 8.4Hz, 1H), 7.63(d, J = 8.4Hz, 1H), 5.43(d, J = 4.9Hz, 1H), 3.92(s, 3H), 2.87(dd, J = 16.8, 7.8Hz, 1H), 2.70(dd, J = 16.8, 6.8Hz, 1H). <sup>13</sup>C NMR(100MHz, CD<sub>3</sub>OD) 171.2, 167.9, 142.2, 140.1, 132.0, 130.9, 128.2(q, J = 277.3Hz), 127.2, 97.9(q, J = 2.6Hz), 52.8, 38.6(q, J = 29.2Hz), 30.5(q, J = 2.4Hz). <sup>19</sup>F NMR(565MHz, CDCl<sub>3</sub>) 73.45(d, J = 8.8Hz). HRMS: [M-H]<sup>+</sup> calculated for C<sub>14</sub>H<sub>13</sub>F<sub>3</sub>NO<sub>3</sub><sup>+</sup>: 300.0842, found 300.0845.

7



1i (0.20mmol)      2a (0.4mmol)    CuCl (0.02mmol)    Zn  
(0.05mmol)      DMSO(3mL)

100      24

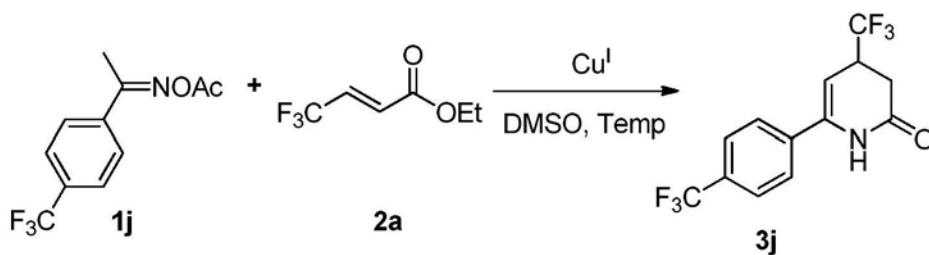
H<sub>2</sub>O(2.0mL)      1MHCl (aq, 3mL)      (4 10mL)

(EA: PE 5: 1)

3i (30mg, 56 %)

mp 148-150 °C. <sup>1</sup>H NMR(400MHz, CD<sub>3</sub>OD) 7.78(d, J = 8.5Hz, 1H), 7.69(d, J = 8.5Hz, 1H), 5.46(d, J = 4.9Hz, 1H), 3.64-3.53(m, 1H), 2.87(dd, J = 16.9, 7.8Hz), 2.71(dd, J = 16.9, 6.9Hz, 1H). <sup>13</sup>C NMR(100MHz, CD<sub>3</sub>OD) 169.7, 140.3, 138.7, 132.3, 126.8(q, J = 277.5Hz), 117.9, 112.5, 97.4(q, J = 2.7Hz), 37.2(q, J = 29.3Hz), 29.1(q, J = 2.5Hz). <sup>19</sup>F NMR(565MHz, CDCl<sub>3</sub>) 73.58(d, J = 8.8Hz). HRMS: [M-H]<sup>+</sup> calculated for C<sub>13</sub>H<sub>13</sub>F<sub>3</sub>N<sub>2</sub>O<sup>+</sup>: 267.0740, found 267.0736.

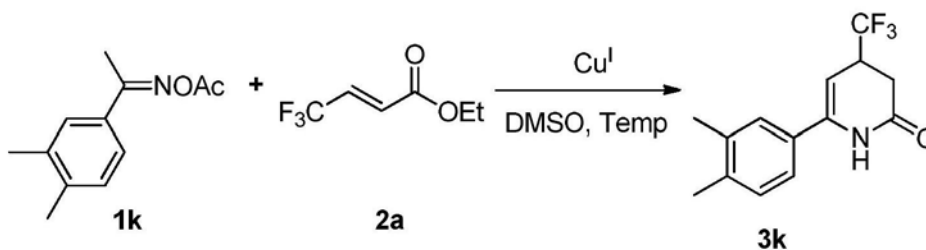
8



1j (0.20mmol)      2a(0.4mmol)    CuCl (0.02mmol)    Zn  
 (0.04mmol)      DMSO(3mL)  
 120      24  
 H<sub>2</sub>O(2.0mL)      1MHCl (aq, 3mL)      (4 10mL)

(EA: PE 5: 1)      3j (36mg, 56%)  
 mp 188-190 °C. <sup>1</sup>H NMR(400MHz, CD<sub>3</sub>OD) 7.74-7.69(m, 4H), 5.43(d, J = 4.9Hz, 1H), 3.64-3.52(m, 1H), 2.88(dd, J = 16.9, 7.8Hz, 1H), 2.71(dd, J = 16.9, 6.9Hz, 1H). <sup>13</sup>C NMR(100MHz, CDCl<sub>3</sub>) 169.8, 140.5, 138.1, 130.8(d, J = 32.5Hz), 126.4, 126.8(q, J = 277.3Hz), 125.3(q, J = 3.8Hz), 124.0(q, J = 266.0Hz), 96.6(q, J = 2.6Hz), 37.2(q, J = 29.2Hz), 29.1(q, J = 2.3Hz). <sup>19</sup>F NMR(565MHz, CDCl<sub>3</sub>) 63.23(s, 1H), 73.61(d, J = 8.9Hz). HRMS: [M+H]<sup>+</sup> calculated for C<sub>13</sub>H<sub>10</sub>F<sub>6</sub>NO<sup>+</sup>: 310.0661, found 310.0658.

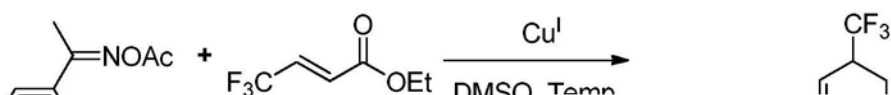
9



1k(0.20mmol)      2a(0.4mmol)    CuCl (0.02mmol)    Zn  
 (0.04mmol)      DMSO(3mL)  
 120      24  
 H<sub>2</sub>O(2.0mL)      1MHCl (aq, 3mL)      (4 10mL)

(EA: PE 5: 1)      3k(69mg, 74%)  
 mp 132-134 °C. <sup>1</sup>H NMR(400MHz, CDCl<sub>3</sub>) 7.68(s, 1H), 7.23-7.16(m, 3H), 5.23(d, J = 3.2Hz, 1H), 3.43-3.32(m, 1H), 2.83-2.71(m, 2H), 2.29-3.28(m, 6H). <sup>13</sup>C NMR(100MHz, CDCl<sub>3</sub>) 168.7, 140.4, 138.6, 137.4, 131.6, 130.2, 126.5(q, J = 277.6Hz), 126.4, 122.6, 93.9(q, J = 2.9Hz), 37.8(q, J = 29.3Hz), 29.9(q, J = 2.4Hz), 19.8, 19.6. <sup>19</sup>F NMR(565MHz, CDCl<sub>3</sub>) 73.26(d, J = 8.3Hz). HRMS: [M+H]<sup>+</sup> calculated for C<sub>14</sub>H<sub>15</sub>F<sub>3</sub>NO<sup>+</sup>: 270.1100, found 270.1102.

10



11 (0.20mmol)      2a(0.4mmol)     $\text{CuCl}$  (0.02mmol)     $\text{Zn}$   
(0.04mmol)      DMSO(3mL)

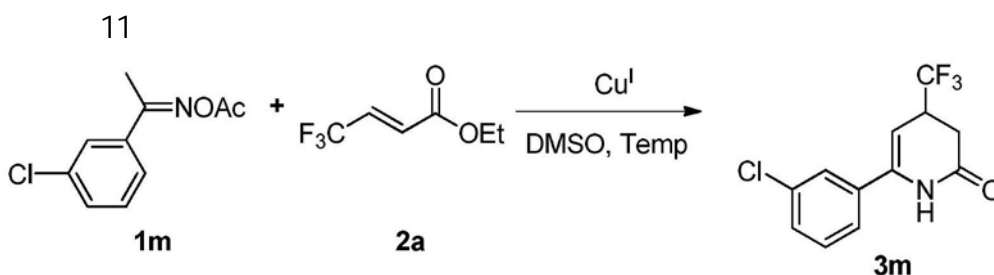
100      20

$\text{H}_2\text{O}$ (2.0mL)      1MHCl (aq, 3mL)      (4 10mL)

(EA: PE 5: 1)

3l (45mg, 75 %)

$^1\text{H NMR}$ (400MHz,  $\text{CDCl}_3$ ) 8.05(s, 1H), 7.05 7.03(m 1H), 6.96 6.95(m 1H), 6.90 6.87(m 1H), 5.19(d, J = 3.9Hz, 1H), 3.93(s, 1H), 3.90(s, 3H), 3.43 3.31(m 1H), 2.82 2.70(m 2H).  $^{13}\text{C NMR}$ (100MHz,  $\text{CDCl}_3$ ) 169.8, 150.3, 149.3, 140.4, 126.8, 126.5 (q, J = 277.7Hz), 118.1, 111.2, 108.5, 93.6(q, J = 2.6Hz), 56.0, 59.9, 37.8(q, J = 29.2Hz), 29.9(q, J = 2.2Hz).  $^{19}\text{F NMR}$ (565MHz,  $\text{CDCl}_3$ ) 73.22(d, J = 8.8Hz). HRMS:  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{14}\text{H}_{15}\text{F}_3\text{NO}_3^+$ : 302.0999, found 302.0999.



1m(0.20mmol)      2a(0.3mmol)     $\text{CuCl}$  (0.03mmol)     $\text{Zn}$   
(0.03mmol)      DMSO(3mL)

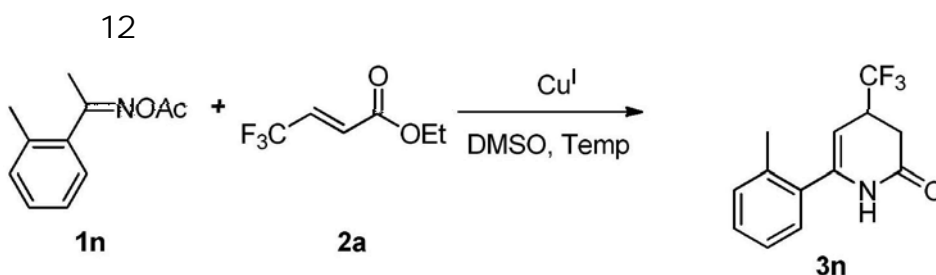
100      22

$\text{H}_2\text{O}$ (2.0mL)      1MHCl (aq, 3mL)      (4 10mL)

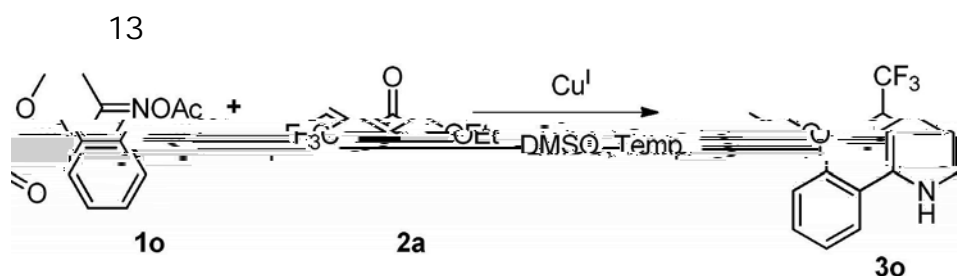
(EA: PE 5: 1)

3m(39mg, 71 %)

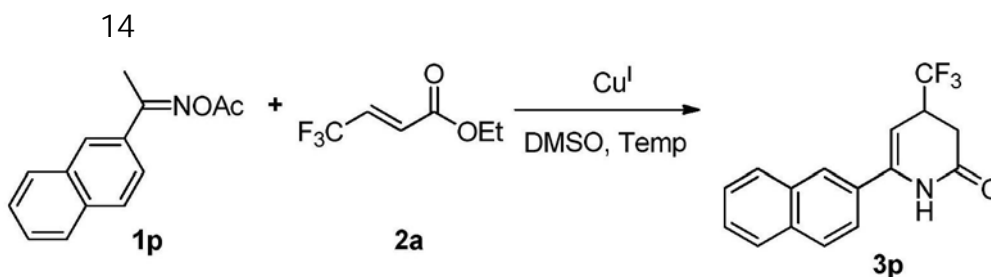
mp 128 130.  $^1\text{H NMR}$ (400MHz,  $\text{CDCl}_3$ ) 8.07(s, 1H), 7.47 7.46(m 1H), 7.41 7.35(m 3H), 5.29(d, J = 2.8Hz, 1H), 3.46 3.34(m 1H), 2.84 2.72(m 2H).  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ ) 168.8, 139.5, 135.8, 135.1, 130.3, 129.8, 126.3(q, J = 277.7Hz), 125.8, 123.5, 96.0(q, J = 2.9Hz), 37.8(q, J = 29.5Hz), 29.7(q, J = 2.5Hz).  $^{19}\text{F NMR}$ (565MHz,  $\text{CDCl}_3$ ) 73.13(d, J = 8.7Hz). HRMS:  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{12}\text{H}_{10}\text{ClF}_3\text{NO}^+$ : 276.0398, found 276.0394.



1n (0.20mmol) 2a (0.4mmol) CuCl (0.03mmol) Zn  
 (0.03mmol) DMSO (3mL)  
 110 22  
 H<sub>2</sub>O (2.0mL) 1MHCl (aq, 3mL) (4 10mL)  
 (EA: PE 5: 1) 3n (39mg, 76 )  
 mp 124 126 °C. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) 7.32 7.19 (m 1H), 7.16 (s, 1H),  
 4.94 (d, J 3.8Hz, 1H), 3.42 3.30 (m 1H), 2.84 2.72 (m 2H), 2.35 (s, 3H). <sup>13</sup>C NMR (100MHz,  
 CDCl<sub>3</sub>) 167.9, 140.7, 135.9, 134.4, 130.7, 129.5, 128.7, 126.5 (q, J 277.9Hz), 126.2,  
 96.6 (q, J 2.7Hz), 37.8 (q, J 29.3Hz), 29.6 (q, J 2.5Hz), 19.5. <sup>19</sup>F NMR (565MHz, CDCl<sub>3</sub>)  
 73.22 (d, J 6.4Hz). HRMS: [M+H]<sup>+</sup> calculated for C<sub>13</sub>H<sub>13</sub>F<sub>3</sub>NO<sup>+</sup>: 256.0944, found  
 256.0948.

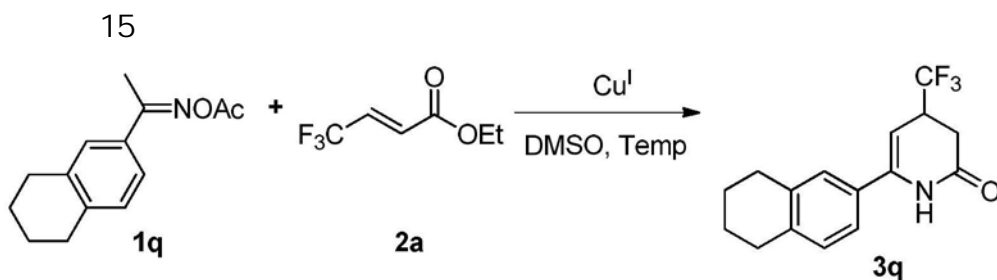


1o (0.20mmol) 2a (0.4mmol) CuCl (0.03mmol) Zn  
 (0.04mmol) DMSO (3mL)  
 100 22  
 H<sub>2</sub>O (2.0mL) 1MHCl (aq, 3mL) (4 10mL)  
 (EA: PE 5: 1) 3o (40mg, 74 )  
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) 7.71 (s, 1H), 7.35 7.31 (m 1H), 7.05 7.03 (m  
 1H), 6.98 6.94 (m 2H), 5.27 (d, J 2.9Hz, 1H), 3.84 (s, 3H), 3.44 3.33 (m 1H), 2.84 2.72  
 (m 2H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) 168.6, 160.0, 140.4, 135.5, 130.1, 126.4 (q, J  
 279.4Hz), 117.7, 115.4, 110.9, 95.0 (q, J 2.9Hz), 55.4, 37.9 (q, J 29.4Hz), 29.8 (q, J  
 2.5Hz). <sup>19</sup>F NMR (565MHz, CDCl<sub>3</sub>) 73.22 (d, J 4.5Hz). HRMS: [M+H]<sup>+</sup> calculated for  
 C<sub>13</sub>H<sub>13</sub>F<sub>3</sub>NO<sub>2</sub><sup>+</sup>: 272.0893, found 272.0896.



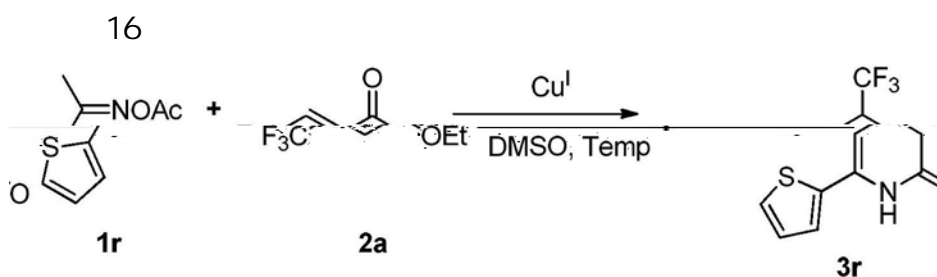
1p (0.20mmol) 2a (0.4mmol) CuCl (0.03mmol) Zn  
 (0.04mmol) DMSO (3mL)  
 100 22  
 H<sub>2</sub>O (2.0mL) 1MHCl (aq, 3mL) (4 10mL)  
 (EA: PE 5: 1) 3p (46mg, 79 )

mp 192-194.  $^1\text{H NMR}$  (400 MHz,  $\text{CD}_3\text{OD}$ ) 8.01 (s, 1H), 7.93-7.86 (m, 4H), 7.62-7.60 (m, 1H), 7.54-7.50 (m, 2H), 5.45 (d, J = 4.9 Hz, 1H), 3.62-3.51 (m, 1H), 2.90 (dd, J = 16.8, 7.8 Hz, 1H), 2.73 (dd, J = 16.8, 6.7 Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CD}_3\text{OD}$ ) 171.4, 142.8, 135.1, 134.5, 132.9, 129.6, 129.5, 128.3 (q, J = 277.6), 128.7, 127.9, 127.7, 126.1, 124.6, 96.6 (q, J = 2.7 Hz), 38.6 (q, J = 29.0 Hz), 30.7 (q, J = 2.5 Hz).  $^{19}\text{F NMR}$  (565 MHz,  $\text{CDCl}_3$ ) 73.56 (d, J = 8.8 Hz). HRMS:  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{14}\text{H}_{13}\text{F}_3\text{NO}^+$ : 268.0944, found 268.0945.



1q (0.20 mmol)      2a (0.3 mmol)    CuCl (0.02 mmol)    Zn  
(0.04 mmol)      DMSO (3 mL)  
100                  23  
 $\text{H}_2\text{O}$  (2.0 mL)      1M HCl (aq, 3 mL)      (4-10 mL)  
(EA: PE = 5:1)                                  3q (42 mg, 71%)

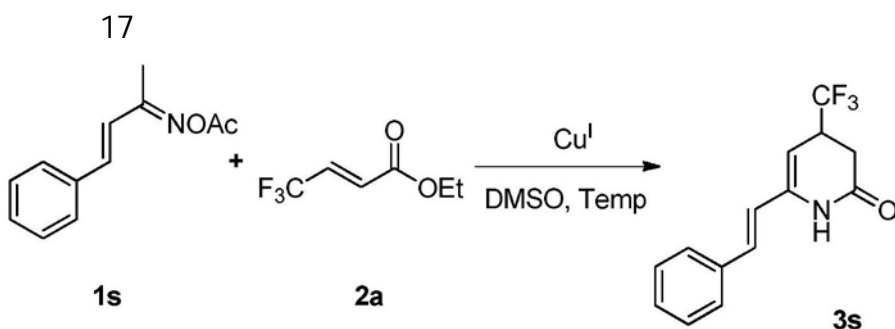
mp 188-190.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) 7.56 (s, 1H), 7.17-7.15 (m, 2H), 7.11-7.09 (m, 1H), 5.22 (d, J = 3.3 Hz, 1H), 3.43-3.31 (m, 1H), 2.83-2.71 (m, 6H), 1.83-1.79 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) 168.6, 140.5, 139.2, 138.0, 131.2, 129.8, 126.5 (q, J = 277.6), 125.9, 122.3, 93.9 (q, J = 2.8 Hz), 37.9 (q, J = 29.3 Hz), 29.9 (q, J = 2.6 Hz), 29.4, 29.2, 22.9 (d, J = 2.3 Hz).  $^{19}\text{F NMR}$  (565 MHz,  $\text{CDCl}_3$ ) 73.26 (d, J = 8.5 Hz). HRMS:  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{16}\text{H}_{17}\text{F}_3\text{NO}^+$ : 296.1257, found 296.1256.



1r (0.20 mmol)      2a (0.3 mmol)    CuCl (0.02 mmol)    Zn  
(0.04 mmol)      DMSO (3 mL)  
100                  24  
 $\text{H}_2\text{O}$  (2.0 mL)      1M HCl (aq, 3 mL)      (4-10 mL)  
(EA: PE = 5:1)                                  3r (28 mg, 57%)

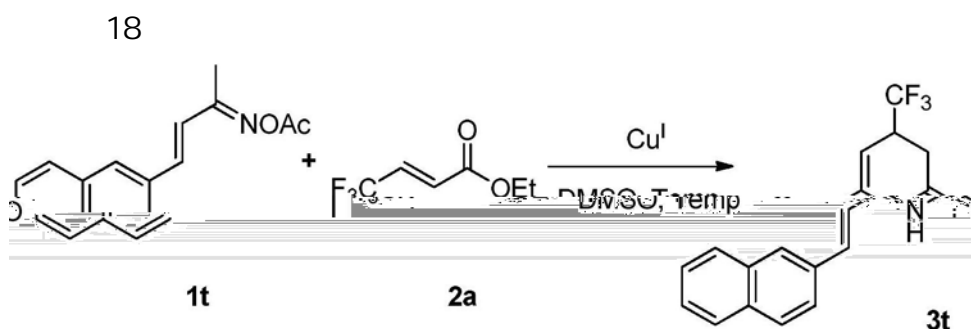
mp 130-132.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) 8.14 (s, 1H), 7.32-7.30 (m, 1H), 7.27-7.26 (m, 1H), 7.08-7.05 (m, 1H), 5.34 (d, J = 3.9 Hz, 1H), 3.42-3.35 (m, 1H), 2.86-2.73 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) 168.6, 136.7, 134.8, 127.8, 126.3 (q, J = 277.6 Hz), 126.3, 124.4, 94.1 (q, J = 2.9 Hz), 37.8 (q, J = 29.6 Hz), 29.9 (q, J = 2.4 Hz).  $^{19}\text{F NMR}$

(565MHz, CDCl<sub>3</sub>) 73.11(d, J 8.1Hz). HRMS: [M-H]<sup>+</sup>calculated for C<sub>10</sub>H<sub>9</sub>F<sub>3</sub>NOS<sup>+</sup>: 248.0351, found 248.0350.



1s (0.20mmol) 2a (0.2mmol) CuCl (0.02mmol) Zn  
(0.04mmol) DMSO (3mL)  
100 24  
H<sub>2</sub>O (2.0mL) 1MHCl (aq, 3mL) (4 10mL)  
(EA: PE 5:1) 3s (43mg, 81%)

mp 168-170. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) 8.32(s, 1H), 7.46-7.44(m, 2H), 7.39-7.35(m, 2H), 7.32-7.29(m, 1H), 6.83(d, J 16.6Hz, 1H), 6.57(d, J 16.6Hz, 1H), 5.16(d, J 4.1Hz, 1H), 3.45-3.32(m, 1H), 2.84-2.72(m, 2H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) 168.7, 138.1, 135.6, 129.0, 128.8, 128.7, 126.8, 126.2(q, J 277.9), 121.4, 99.2(q, J 2.9Hz), 37.9(q, J 29.5Hz), 30.0(q, J 2.4Hz). <sup>19</sup>F NMR (565MHz, CDCl<sub>3</sub>) 73.09(d, J 7.8Hz). HRMS: [M-H]<sup>+</sup>calculated for C<sub>18</sub>H<sub>15</sub>F<sub>3</sub>NO<sup>+</sup>: 268.0944, found 268.0945.

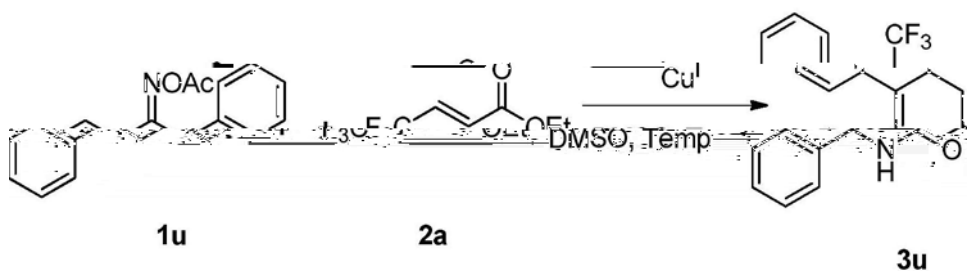


1t (0.20mmol) 2a (0.25mmol) CuCl (0.02mmol) Zn  
(0.05mmol) DMSO (3.5mL)  
80 24  
H<sub>2</sub>O (2.0mL) 1MHCl (aq, 3mL) (4 10mL)  
(EA: PE 5:1) 3t (49mg, 77%)

mp 186-188. <sup>1</sup>H NMR (400MHz, (CD<sub>3</sub>)<sub>2</sub>CO) 8.77(s, 1H), 7.95-7.88(m, 4H), 7.80-7.78(m, 1H), 7.52-7.50(m, 2H), 7.35(d, J 16.7Hz, 1H), 6.99(d, J 16.6Hz, 1H), 5.32(d, J 4.4Hz, 1H), 3.68-3.58(m, 1H), 2.84(dd, J 15.6, 9.0Hz, 1H), 2.65(dd, J 16.7, 6.7Hz, 1H). <sup>13</sup>C NMR (100MHz, (CD<sub>3</sub>)<sub>2</sub>CO) 168.4, 140.4, 135.0, 134.7, 134.4, 129.9(d, J 2.0Hz), 129.5, 129.1, 128.7, 128.2, 128.1(q, J 277.2Hz), 127.5, 127.3, 124.4, 123.5(q, J 5.3Hz), 99.5(q, J 3.9Hz), 38.4(q, J 28.6Hz), 30.7(q, J 2.0Hz). <sup>19</sup>F NMR (565MHz, CDCl<sub>3</sub>) 73.72(s). HRMS: [M-H]<sup>+</sup>calculated for C<sub>18</sub>H<sub>15</sub>F<sub>3</sub>NO<sup>+</sup>: 318.1100, found

318.1101.

19



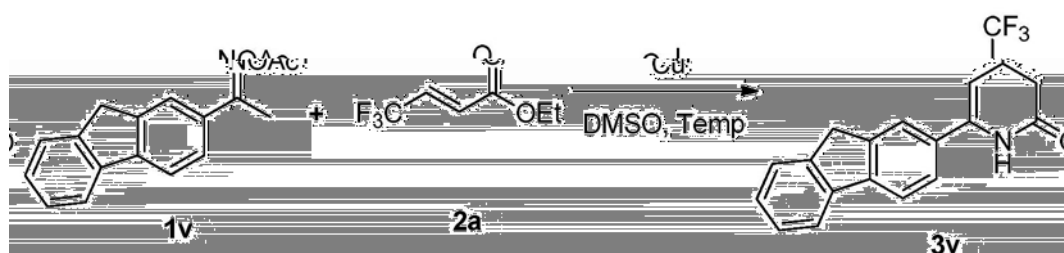
1u(0.20mmol)      2a(0.25mmol)      CuCl(0.02mmol)      Zn  
(0.05mmol)      DMSO(3.5mL)

80      36  
H<sub>2</sub>O(2.0mL)      1MHCl(aq, 3mL)      (4 10mL)

(EA: PE 5: 1)      3u(20mg, 31%)

mp 142-144 °C. <sup>1</sup>H NMR(400MHz, CDCl<sub>3</sub>) 7.26-7.25(m, 2H), 7.23(s, 1H), 7.16-7.13(m, 6H), 7.06-7.05(m, 2H), 3.55-3.46(m, 1H), 3.07-2.94(m, 2H). <sup>13</sup>C NMR(100MHz, CDCl<sub>3</sub>) 167.8, 138.2, 138.0, 135.0, 129.8, 129.0, 128.7, 128.6, 128.2, 126.8(q, J = 265.1), 110.9, 108.6, 43.2(q, J = 27.8Hz), 30.8(q, J = 2.4Hz, 1H). <sup>19</sup>F NMR(565MHz, CDCl<sub>3</sub>) 70.37(d, J = 8.6Hz). HRMS: [M-H]<sup>+</sup> calculated for C<sub>18</sub>H<sub>15</sub>F<sub>3</sub>NO<sup>+</sup>: 318.1100, found 318.1098.

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1v(0.20mmol)      2a(0.25mmol)      CuCl(0.02mmol)      Zn  
(0.05mmol)      DMSO(3.5mL)

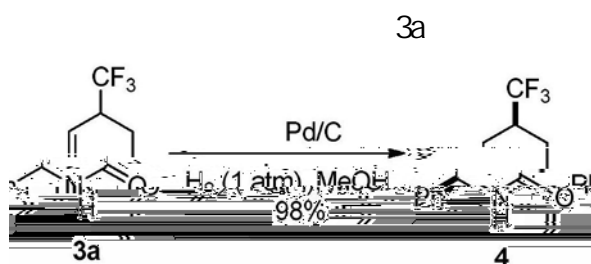
80      30  
H<sub>2</sub>O(2.0mL)      1MHCl(aq, 3mL)      (4 10mL)

(EA: PE 5: 1)      3v(47mg, 75%)

mp 180-182 °C. <sup>1</sup>H NMR(400MHz, DMSO) 9.88(s, 1H), 7.94-7.91(m, 2H), 7.77(s, 1H), 7.62-7.56(m, 2H), 7.42-7.32(m, 2H), 5.32(d, J = 4.8Hz, 1H), 3.94(s, 2H), 3.73-3.65(m, 1H), 2.82(dd, J = 16.6, 7.8Hz, 1H), 2.56(dd, J = 16.7, 6.4Hz, 1H). <sup>13</sup>C NMR(100MHz, CDCl<sub>3</sub>) 168.3, 143.4, 143.2, 142.1, 141.6, 140.4, 132.5, 127.2, 127.1(q, J = 277.6), 126.9, 125.2, 124.7, 122.7, 120.4, 120.0, 93.6(q, J = 2.1Hz), 36.4, 36.3(q, J = 27.9Hz), 29.7(q, J = 1.8Hz). <sup>19</sup>F NMR(565MHz, CDCl<sub>3</sub>) 73.24(d, J = 8.9Hz). HRMS: [M-H]<sup>+</sup> calculated for C<sub>19</sub>H<sub>15</sub>F<sub>3</sub>NO<sup>+</sup>: 330.1100, found 330.1101.

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3a (0.2 mmol) (30 mL) 10 Pd/C  
(100 mg) 12 h. 4  
(45 mg, 98%). mp 124–126 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 7.42–7.36 (m, 4H), 7.35–7.30 (m, 1H), 4.60 (dd, J = 11.6, 4.1 Hz, 1H), 3.03–2.96 (m, 1H), 2.64–2.58 (m, 1H), 2.51–2.43 (m, 1H), 2.27–2.23 (m, 1H), 1.67 (dd, J = 24.8, 12.7 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 172.2, 142.9, 130.0, 129.3, 128.1 (q, J = 275.8 Hz), 127.5, 57.5, 38.6 (q, J = 28.6 Hz), 32.4 (d, J = 2.6 Hz), 30.9 (d, J = 2.4 Hz). HRMS: [M+H]<sup>+</sup> calculated for C<sub>12</sub>H<sub>13</sub>F<sub>3</sub>NO: 244.0944, found 244.0945.