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2017.12.05

CN 107892674 A

2018.04.10

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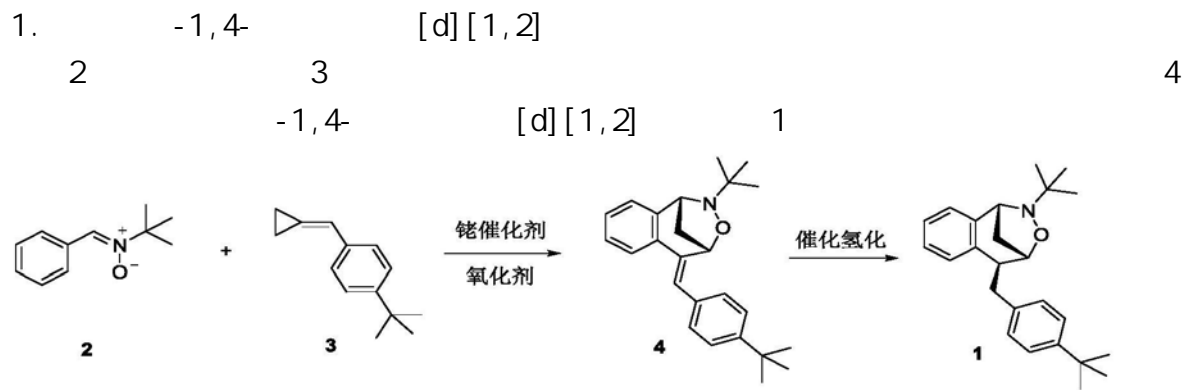
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CN 101693712 A, 2010.04.14  
Fang Xi e et al ..Nitron e Directing  
Groups i n Rhodi um(I



2. 1 -1,4- [d][1,2]
3. 1 -1,4- [d][1,2]
- 30 50 2 3 0.02-1 1 2.5
4. 1 -1,4- [d][1,2]
5. 1 -1,4- [d][1,2]
- 4 [d][1,2] 1
- 1,4-



0-100

30-50

0.1-2.0

4

1,4-

[d][1,2]

1

1)

[d][1,2]

1

1,4-

2)

1

Cp\* Rh(OAc)<sub>2</sub> (7.0mg, 0.010mmol, 0.050equiv), AgOAc (80mg, 0.500mmol, 2.50equiv) 25mL 1mL CF<sub>3</sub>CH<sub>2</sub>OH 10  
2(0.200mmol, 1.00equiv) 3(0.500mmol, 2.50equiv)

40

24h

15mL

4

84

<sup>1</sup>H NMR <sup>13</sup>C NMR

95

<sup>1</sup>H NMR(400MHz, CDCl<sub>3</sub>) 7.80(d, J 7.8Hz, 1H), 7.44(s, 4H), 7.29(s, 1H), 7.25(t, J 7.6Hz, 1H), 7.18(t, J 7.3Hz, 1H), 7.09(d, J 7.3Hz, 1H), 5.46(d, J 5.5Hz, 1H), 4.31(d, J 4.9Hz, 1H), 2.33(s, 1H), 2.02(t, J 10.2Hz, 1H), 1.35(s, 9H), 1.18(s, 9H). <sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) 150.1, 142.4, 136.9, 134.0, 132.8, 129.4, 127.6, 127.5, 125.9, 125.3, 124.7, 123.7, 73.3, 59.7, 58.8, 37.9, 34.6, 31.4, 26.8. HRMS(ESI, m/z): C<sub>25</sub>H<sub>32</sub>NO[M-H]<sup>+</sup>: 362.2478, : 362.2480.

4(40mg)

2mL

5mg 5 Pd/C

(TLC )

(PE: EA 10: 1)

1

52

<sup>1</sup>H NMR

(400MHz, CDCl<sub>3</sub>) 7.35(m 5H), 7.23(dt, J 7.5, 1.2Hz, 1H), 7.12(t, J 7.4Hz, 1H), 7.04(d, J 7.3Hz, 1H), 4.39(dd, J 5.9, 2.9Hz, 1H), 4.22(d, J 5.0Hz, 1H), 3.24-2.97(m 3H), 2.39-2.28(m 1H), 1.85(d, J 11.0Hz, 1H), 1.34(s, 9H), 1.18(s, 9H). <sup>13</sup>C NMR(101MHz, CDCl<sub>3</sub>) 148.7, 142.6, 138.2, 137.5, 129.4, 129.0, 127.6, 126.0, 125.3, 125.2, 73.4, 58.9, 58.8, 48.7, 38.0, 37.2, 34.4, 31.5, 26.8. HRMS(ESI, m/z): calcd for C<sub>25</sub>H<sub>34</sub>NO[M-H]<sup>+</sup>: 364.2635, found 364.2628.

2

Cp\*Rh(OAc)<sub>2</sub> (7.0mg, 0.010mmol, 0.050equiv), AgNO<sub>2</sub> (85mg, 0.500mmol, 2.50equiv) 25mL 1mL CF<sub>3</sub>CH<sub>2</sub>OH 10  
 2(0.200mmol, 1.00equiv) 3(0.500mmol, 2.50equiv)  
 50 24h, 15mL  
 4 85 <sup>1</sup>H NMR <sup>13</sup>C NMR 95

<sup>1</sup>H NMR(400MHz, CDCl<sub>3</sub>) 7.80(d, J 7.8Hz, 1H), 7.44(s, 4H), 7.29(s, 1H), 7.25(t, J 7.6Hz, 1H), 7.18(t, J 7.3Hz, 1H), 7.09(d, J 7.3Hz, 1H), 5.46(d, J 5.5Hz, 1H), 4.31(d, J 4.9Hz, 1H), 2.33(s, 1H), 2.02(t, J 10.2Hz, 1H), 1.35(s, 9H), 1.18(s, 9H). <sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) 150.1, 142.4, 136.9, 134.0, 132.8, 129.4, 127.6, 127.5, 125.9, 125.3, 124.7, 123.7, 73.3, 59.7, 58.8, 37.9, 34.6, 31.4, 26.8. HRMS(ESI, m/z): C<sub>25</sub>H<sub>2</sub>NO[M-H]<sup>+</sup>: 362.2478, : 362.2480.

4(40mg) 2mL 4mg 10 Pd/C  
 (TLC )

(PE: EA 10:1) 1 59 <sup>1</sup>H NMR(400MHz, CDCl<sub>3</sub>) 7.35(m 5H), 7.23(dt, J 7.5, 1.2Hz, 1H), 7.12(t, J 7.4Hz, 1H), 7.04(d, J 7.3Hz, 1H), 4.39(dd, J 5.9, 2.9Hz, 1H), 4.22(d, J 5.0Hz, 1H), 3.24-2.97(m 3H), 2.39-2.28(m 1H), 1.85(d, J 11.0Hz, 1H), 1.34(s, 9H), 1.18(s, 9H). <sup>13</sup>C NMR(101MHz, CDCl<sub>3</sub>) 148.7, 142.6, 138.2, 137.5, 129.4, 129.0, 127.6, 126.0, 125.3, 125.2, 73.4, 58.9, 58.8, 48.7, 38.0, 37.2, 34.4, 31.5, 26.8. HRMS(ESI, m/z): calcd for C<sub>25</sub>H<sub>3</sub>NO[M-H]<sup>+</sup>: 364.2635, found 364.2628.

3

Cp\*Rh(OAc)<sub>2</sub> (7.0mg, 0.010mmol, 0.050equiv), Ag<sub>2</sub>CO<sub>3</sub> (55mg, 0.200mmol, 1.00equiv) 25mL 1mL CF<sub>3</sub>CH<sub>2</sub>OH 10  
 2(0.200mmol, 1.00equiv) 3(0.500mmol, 2.50equiv)  
 30 24h, 15mL  
 4 81 <sup>1</sup>H NMR <sup>13</sup>C NMR 95

<sup>1</sup>H NMR(400MHz, CDCl<sub>3</sub>) 7.80(d, J 7.8Hz, 1H), 7.44(s, 4H), 7.29(s, 1H), 7.25(t, J 7.6Hz, 1H), 7.18(t, J 7.3Hz, 1H), 7.09(d, J 7.3Hz, 1H), 5.46(d, J 5.5Hz, 1H), 4.31(d, J 4.9Hz, 1H), 2.33(s, 1H), 2.02(t, J 10.2Hz, 1H), 1.35(s, 9H), 1.18(s, 9H). <sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) 150.1, 142.4, 136.9, 134.0, 132.8, 129.4, 127.6, 127.5, 125.9, 125.3, 124.7, 123.7, 73.3, 59.7, 58.8, 37.9, 34.6, 31.4, 26.8. HRMS(ESI, m/z): C<sub>25</sub>H<sub>2</sub>NO[M-H]<sup>+</sup>: 362.2478, : 362.2480.

4(40mg) 2mL 5mg 5 Pd/C  
 (TLC )

(PE: EA 10:1) 1 57 <sup>1</sup>H NMR(400MHz, CDCl<sub>3</sub>) 7.35(m 5H), 7.23(dt, J 7.5, 1.2Hz, 1H), 7.12(t, J 7.4Hz, 1H), 7.04(d, J 7.3Hz, 1H), 4.39(dd, J 5.9, 2.9Hz, 1H), 4.22(d, J 5.0Hz, 1H), 3.24-2.97(m 3H), 2.39-2.28(m 1H), 1.85(d, J 11.0Hz, 1H), 1.34(s, 9H), 1.18(s, 9H). <sup>13</sup>C NMR(101MHz, CDCl<sub>3</sub>) 148.7, 142.6, 138.2,

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137.5, 129.4, 129.0, 127.6, 126.0, 125.3, 125.2, 73.4, 58.9, 58.8, 48.7, 38.0, 37.2, 34.4, 31.5, 26.8. HRMS (ESI,  $m/z$ ): calcd for  $C_{25}H_{34}NO$  [MH]<sup>+</sup>: 364.2635, found 364.2628.