CN 109180406 B
2021.03.16

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2018.09.10

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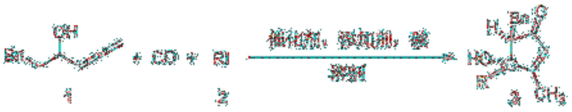
4R*,5R* -5- -4- -2- -1-



(1)

(4R*,5R*) 5 4

2 1 (2) (3) 100

(4)

CN 109180406 B

1. (4R*,5R*) 5 4 2 1
1 4,5 3 1 2
1atm CO 60 100 (4R*,5R*) 5
4 2 1 3 1 4,5 1a E~. «↑ L Ư L

(4R*,5R*) 5 4 2
1

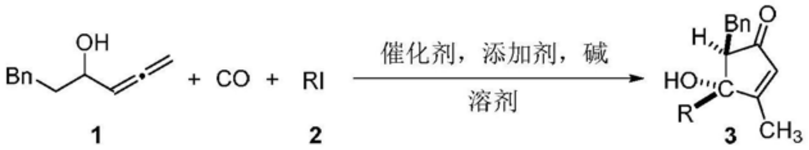
4 2 1

1,2
2,3 3 ( ) 5 (
) 4(Z) 2 1,4
N 2,3 1
4 2 1
R/S

4 2 1

(4R*,5R*) 5 4 2 1
(4R*,
5R*) 5 4 2 1

(4R*,5R*) 5 4
2 1 1 4,5 3
1 2 CO 60 100
(4R*,5R*) 5 4 2 1 3



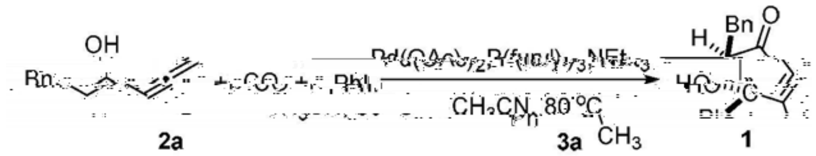
R

L

N,N 1,4
1 4,5 3 1 2
1:1 2:0.05 0.2:0.2 0.6:3 5
(1)
(2) (3) 100 (4)

(4R*,5R*) 5 4 2 1

1



25mL 1(0.3mmol,52mg) (CH_3CN,2mL) 2a(0.6mmol,67μL) ($Pd(OAc)_2$,0.03mmol,7mg) ($P(furyl)_2$, 0.12mmol,28mg) (Et_3N,1.5mmol,208μL) CO(1atm) 80 8 10mL (10 mL×3) (/ 20:1) (4R*, 5R*) 5 4 4 3 2 1 3a(63mg, 75)

^{1}H NMR(600MHz,$CDCl_3$)δ:1.86(s,3H),2.20 2.23(m, 2H),3.12 3.17(m,2H),6.14 (s,1H),6.76(d,J 7.2Hz,2H),7.12 7.15(m,5H),7.30 7.34(m, 3H).^{13}C NMR(150MHz, $CDCl_3$)δ:13.6,31.4,62.9,85.2,125.8,126.2,127.7,128.30,128.34, 128.7,129.3, 139.3,139.4,176.7,204.9.MS:m/z 277[M H]

2

25mL 1(0.3mmol,52mg) (2mL) 2a (0.3mmol,34μL) (0.03mmol,7mg) (0.12mmol,28mg) (1.5mmol,208μL) CO(1atm) 80 8 10 mL (10mL×3) (/ 20:1) 3a(44mg,53)

3

25mL 1(0.3mmol,52mg) (2mL) 2a (0.6mmol,67μL) (0.06mmol,13mg) (0.12mmol,28mg) (1.5mmol,208μL) CO(1atm) 80 8 10mL (10mL×3) (/ 20:1) 3a(58mg,70)

4

25mL 1(0.3mmol,52mg) (2mL) 2a (0.6mmol,67μL) (0.015mmol,3mg) (0.12mmol,28mg) (1.5mmol,208μL) CO(1atm) 80 8 10mL (10mL×3)

(/ 20:1) 3a(35mg,42)

5

25mL 1(0.3mmol,52mg) (2mL) 2a (0.6mmol,67μL) (0.03mmol,7mg) (0.06mmol,14mg) (1.5mmol,208μL) CO(1atm) 80 8 10 mL (10mL×3) (/ 20:1) 3a(43mg,51)

6

25mL 1(0.3mmol,52mg) (2mL) 2a (0.6mmol,67μL) (0.03mmol,7mg) (0.18mmol,42mg) (1.5mmol,208μL) CO(1atm) 80 8 10 mL (10mL×3) (/ 20:1) 3a(60mg,72)

7

25mL 1(0.3mmol,52mg) (2mL) 2a (0.6mmol,67μL) (0.03mmol,7mg) (0.12mmol,28mg) (0.9mmol,125μL) CO(1atm) 80 8 10 mL (10mL×3) (/ 20:1) 3a(50mg,60)

8

25mL 1(0.3mmol,52mg) (2mL) 2a (0.6mmol,67μL) (0.03mmol,5mg) (0.12mmol,28mg) (1.5mmol,208μL) CO(1atm) 80 8 10 mL (10mL×3) (/ 20:1) 3a(58mg,70)

9

25mL 1(0.3mmol,52mg) (2mL) 2a (0.6mmol,67μL) (0.03mmol,7mg) (0.12mmol,12mg) (1.5mmol,208μL) CO(1atm) 80 8 10mL (10mL×3) (/ 20:1) 3a(57mg,68)

10

25mL 1(0.3mmol,52mg) (2mL) 2a (0.6mmol,67μL) (0.03mmol,7mg) L (0.12mmol,14mg) (1.5mmol,208μL) CO(1atm) 80 8 10mL (10mL×3) (/ 20:1) 3a(48mg,58)

11

25mL 1(0.3mmol,52mg) (2mL) 2a

(0.6mmol,67μL) (0.03mmol,7mg) (0.12mmol,31mg) (1.5mmol, 208μL) CO(1atm) 80 8 10mL
(10mL×3)
(/ 20:1) 3a(43mg,52)

12

25mL 1(0.3mmol,52mg) (2mL) 2a (0.6mmol,67μL) (0.03mmol,7mg) (0.12mmol,28mg) (1.5mmol,207mg) CO(1atm) 80 8 10 mL
(10mL×3)
(/ 20:1) 3a(43mg,51)

13

25mL 1(0.3mmol,52mg) (2mL) 2a (0.6mmol,67μL) (0.03mmol,7mg) (0.12mmol,28mg) (1.5mmol,489mg) CO(1atm) 80 8 10 mL
(10mL×3)
(/ 20:1) 3a(35mg,42)

14

25mL 1(0.3mmol,52mg) N,N (2mL) 2a(0.6mmol,67μL) (0.03mmol,7mg) (0.12mmol, 28mg) (1.5mmol,208μL) CO(1atm) 80 8 10mL
(10mL×3)
(/ 20:1) 3a(50 mg,60)

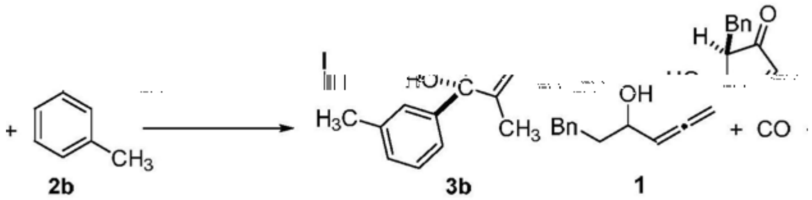
15

25mL 1(0.3mmol,52mg) 1,4 (2mL) 2a(0.6mmol,67μL) (0.03mmol,7mg) (0.12mmol,28 mg) (1.5mmol,208μL) CO(1atm) 80 8 10mL
(10mL×3)
(/ 20:1) 3a(42mg, 50)

16

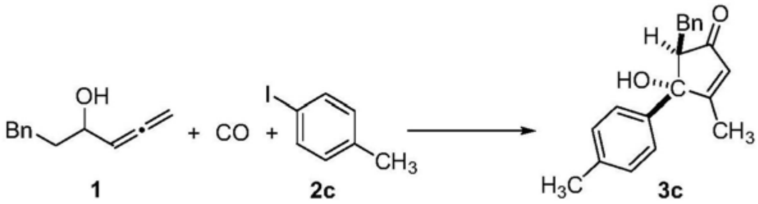
25mL 1(0.3mmol,52mg) (2mL) 2a (0.6mmol,67μL) (0.03mmol,7mg) (0.12mmol,28mg) (1.5mmol,208μL) CO(1atm) 80 8 10 mL
(10mL×3)
(/ 20:1) 3a(45mg,54)

17



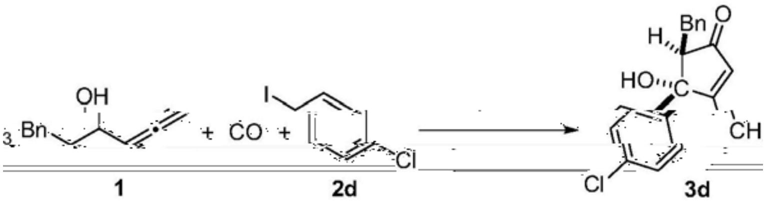
1 25mL 1(0.3mmol,52mg) (2mL) 2b(0.6mmol,77μL) (0.03mmol,7mg) (0.12mmol,28mg) (1.5mmol,208μL) CO(1atm) 80 8 10mL (10mL×3) (/ 20:1) 3b(61mg, 70) ^{1}H NMR(400MHz,$CDCl_3$)δ: 1.87(d,J 1.2Hz,3H),2.14 2.24(m,2H),2.30(s,3H),3.10 3.16(m,2H),6.14(d,J 1.6Hz, 1H),6.16 6.85(m,3H), 7.10 7.26(m,6H).^{13}C NMR(150MHz,$CDCl_3$)δ:13.7,21.6,31.5, 62.7,85.3,122.9,126.1, 128.2,128.4,128.8,129.4,139.2,139.3,176.7,205.1.MS:m/z 291 [M H]

18



1 25mL 1(0.3mmol,52mg) (2mL) 2c(0.6mmol,78μL) (0.03mmol,7mg) (0.12mmol,28mg) (1.5mmol,208μL) CO(1atm) 80 8 10mL (10mL×3) (/ 20:1) 3c(62mg, 71) ^{1}H NMR(400MHz,$CDCl_3$)δ: 1.85(d,J 1.2Hz,3H),2.18 2.24(m,1H),2.36(s,3H),2.46(br s,1H),3.05 3.13(m,2H),6.10 (d,J 1.2Hz,1H), 6.80 6.95(m,3H),7.11 7.25(m,6H).^{13}C NMR(150MHz,$CDCl_3$)δ:13.6, 21.1,31.4,62.9, 85.2,125.7,126.1,128.2,128.8,129.0,129.1,136.4,137.4,139.6,177.0,205.2. MS:m/z 291[M H]

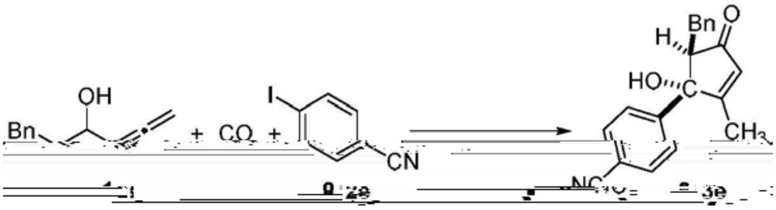
19



1 25mL 1(0.3mmol,52mg) (2mL) 2d(0.6mmol,143mg) (0.03mmol,7mg) (0.12mmol,28mg) (1.5mmol,208μL) CO(1atm) 80 8 10mL (10 mL×3)

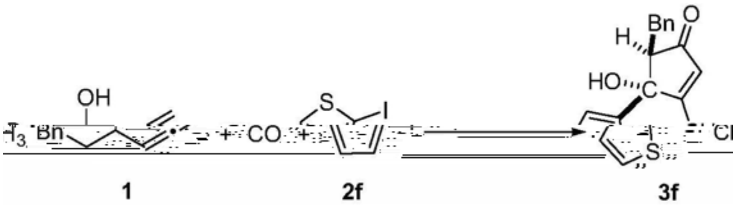
(/ 20:1) 3d(73mg, 78) ^{1}H NMR(600MHz, $CDCl_3$)δ:1.86(s,3H),2.15 2.20(m,1H),2.33(br s,1H),3.13 3.16(m,2H),6.14(s,1H),6.79 (d,J 7.2Hz,2H),7.03 7.17 (m,5H),7.29(d,J 7.8Hz,2H).^{13}C NMR(150MHz,$CDCl_3$)δ: 13.6,31.4,62.7,84.9,126.3,127.4,128.4,128.5,128.6,129.5,133.7,138.1,139.0,176.4,204.6. MS:m/z 311[M H]

20



1 25mL 1(0.3mmol,52mg) (2mL) 2e(0.6mmol,137mg) (0.03mmol,7mg) (0.12mmol,28mg) (1.5mmol,208μL) CO(1atm) 80 8 10mL (10 mL×3) (/ 20:1) 3e(75mg, 82) ^{1}H NMR(400MHz, $CDCl_3$)δ:1.85(q,J 1.2Hz,3H),2.03 (br s,1H),2.07 2.14(m,1H),3.13 3.23(m,2H),6.20 (d,J 1.2Hz,1H),6.74 6.76(m,2H),7.13 7.16(m,5H),7.59(dd,J_1 7.8Hz,J_2 1.6Hz,2H). ^{13}C NMR(150MHz,$CDCl_3$)δ: 13.7,31.5,62.4,85.0,111.6,118.5,126.4,128.4,128.5,130.2, 138.5,145.1,176.1, 204.4.MS:m/z 302[M H]

21



1 25mL 1(0.3mmol,52mg) (2mL) 2f(0.6mmol,66μL) (0.03mmol,7mg) (0.12mmol,28mg) (1.5mmol,208μL) CO(1atm) 80 8 10mL (10mL×3) (/ 20:1) 3f(52mg, 61) ^{1}H NMR(400MHz,$CDCl_3$)δ: 1.91(d,J 1.2Hz,3H),2.29 2.35(m,1H),2.69(br s,1H),3.04 3.12(m,2H),5.97(d,J 1.2 Hz,1H),6.55(dd,J_1 3.6Hz,J_2 1.2Hz,1H),6.88 6.93(m,3H),7.07 7.18(m,4H).^{13}C NMR (150MHz,$CDCl_3$)δ: 12.5,30.3,61.5,83.4,123.5,124.2,125.2,126.4,127.4,127.6,127.7, 138.5,144.2, 175.4,203.0.MS:m/z 283[M H]