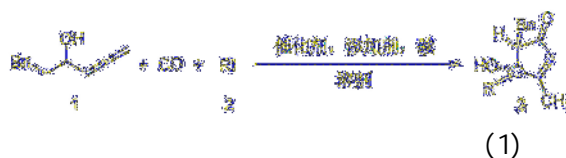




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Juntao Ye .Palladium Catalyzed Cyclization Reactions of Allenes in the	书1 书7

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



(4R*, 5R*) 5 4

2

1

(2)

(3)

100

(4)

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 c 4 š %U

1

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

4 2 1

2,3 3 () 5 (1,2

) 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

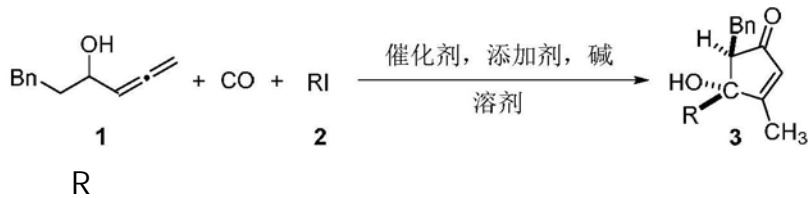
2 1

1 2

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

3 1 4,5 3

CO 60 100



L

N,N 1,4

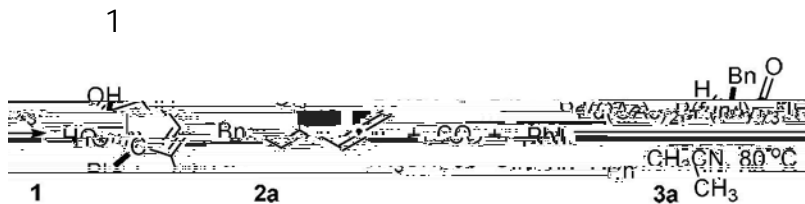
1 4,5 3 1 2

1: 1 2 0.05 0.2 0.2 0.6 3 5

(1)

(2) (3) 100 (4)

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



25mL 1(0.3mmol, 52mg) (CH₃CN, 2mL)
 2a(0.6mmol, 67μL) (Pd(OAc)₂, 0.03mmol, 7mg) (P(furyl)₂,
 0.12mmol, 28mg) (Et₃N, 1.5mmol, 208μL) CO(1atm) 80 8
 10mL (10 mL × 3)
 (/ 20:1) (4R*,
 5R*) 5 4 4 3 2 1 3a(63mg, 75)

¹H NMR(600MHz, CDCl₃) : 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). ¹³C NMR(150MHz,
 CDCl₃) : 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[MH]

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

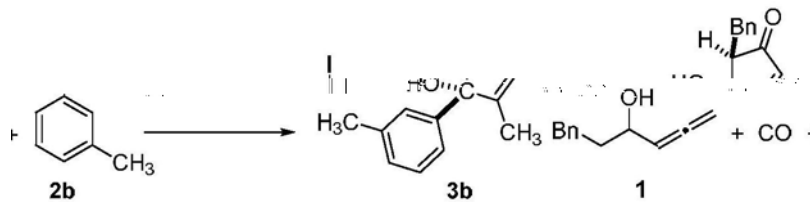
25mL 1(0.3mmol, 52mg) (2mL) 2a
 (0.6mmol, 67μL) (0.06mmol, 13mg) (0.12mmol, 28mg)
 (1.5mmol, 208μL) CO(1atm) 80 8 10mL
 (10mL × 3)
 (/ 20:1) 3a(58mg, 70)

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(35ng, 42)	
5				
25mL		1(0.3mmol , 52ng)	(2mL)	2a
(0.6mmol , 67μ L)		(0.03mmol , 7ng)	(0.06mmol , 14ng)	
(1.5mmol , 208μ L)	CO(1atn)	80	8	10 mL
		(10mL× 3)		
(/	20: 1)	3a(43ng, 51)	
6				
25mL		1(0.3mmol , 52ng)	(2mL)	2a
(0.6mmol , 67μ L)		(0.03mmol , 7ng)	(0.18mmol , 42ng)	
(1.5mmol , 208μ L)	CO(1atn)	80	8	10 mL
		(10mL× 3)		
(/	20: 1)	3a(60ng, 72)	
7				
25mL		1(0.3mmol , 52ng)	(2mL)	2a
(0.6mmol , 67μ L)		(0.03mmol , 7ng)	(0.12mmol , 28ng)	
(0.9mmol , 125μ L)	CO(1atn)	80	8	10 mL
		(10mL× 3)		
(/	20: 1)	3a(50ng, 60)	
8				
25mL		1(0.3mmol , 52ng)	(2mL)	2a
(0.6mmol , 67μ L)		(0.03mmol , 5ng)	(0.12mmol , 28ng)	
(1.5mmol , 208μ L)	CO(1atn)	80	8	10 mL
		(10mL× 3)		
(/	20: 1)	3a(58ng, 70)	
9				
25mL		1(0.3mmol , 52ng)	(2mL)	2a
(0.6mmol , 67μ L)		(0.03mmol , 7ng)	(0.12mmol , 12ng)	(1.5mmol , 208
μ L)	CO(1atn)	80	8	10mL
		(10mL× 3)		(
/		20: 1)	3a(57ng, 68)	
10				
25mL		1(0.3mmol , 52ng)	(2mL)	2a
(0.6mmol , 67μ L)		(0.03mmol , 7ng) L	(0.12mmol , 14ng)	(1.5mmol ,
208μ L)	CO(1atn)	80	8	10mL
		(10mL× 3)		
(/	20: 1)	3a(48ng, 58)	
11				
25mL		1(0.3mmol , 52ng)	(2mL)	2a

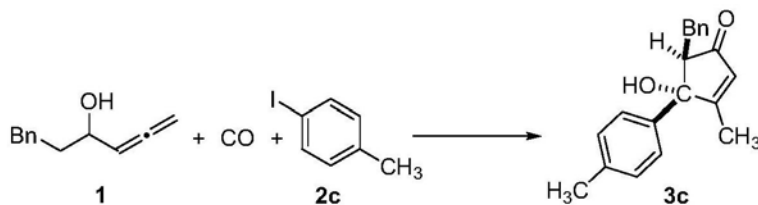
(0.6mmol, 67 μ L)	(0.03mmol, 7ng)	(0.12mmol, 31ng)	(1.5mmol, 208 μ L)	CO(1atm)	80	8	10mL	
	(10mL \times 3)							
(/)	20: 1)	3a(43ng, 52)						
12								
25mL		1(0.3mmol, 52ng)					(2mL)	2a
(0.6mmol, 67 μ L)	(0.03mmol, 7ng)						(0.12mmol, 28ng)	
(1.5mmol, 207ng)	CO(1atm)	80	8				10 mL	
	(10mL \times 3)							
(/)	20: 1)	3a(43ng, 51)						
13								
25mL		1(0.3mmol, 52ng)					(2mL)	2a
(0.6mmol, 67 μ L)	(0.03mmol, 7ng)						(0.12mmol, 28ng)	
(1.5mmol, 489ng)	CO(1atm)	80	8				10 mL	
	(10mL \times 3)							
(/)	20: 1)	3a(35ng, 42)						
14								
25mL		1(0.3mmol, 52ng)	N, N				(2mL)	
2a(0.6mmol, 67 μ L)	(0.03mmol, 7ng)						(0.12mmol, 28ng)	
(1.5mmol, 208 μ L)	CO(1atm)	80	8				10mL	
	(10mL \times 3)							
(/)	20: 1)	3a(50 ng, 60)						
15								
25mL		1(0.3mmol, 52ng)	1, 4				(2mL)	
2a(0.6mmol, 67 μ L)	(0.03mmol, 7ng)						(0.12mmol, 28 ng)	
(1.5mmol, 208 μ L)	CO(1atm)	80	8				10mL	
	(10mL \times 3)							
(/)	20: 1)	3a(42ng, 50)						
16								
25mL		1(0.3mmol, 52ng)					(2mL)	2a
(0.6mmol, 67 μ L)	(0.03mmol, 7ng)						(0.12mmol, 28ng)	
(1.5mmol, 208 μ L)	CO(1atm)	80	8				10 mL	
	(10mL \times 3)							
(/)	20: 1)	3a(45ng, 54)						
17								



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) ¹H NMR(400MHz, CDCl₃) : 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) . ¹³C NMR(150MHz, CDCl₃) : 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 [MH]

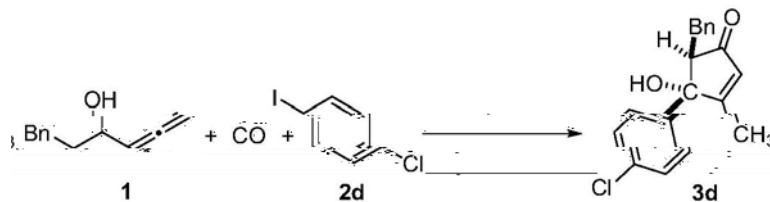
18



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) ¹H NMR(400MHz, CDCl₃) : 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) . ¹³C NMR(150MHz, CDCl₃) : 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 [MH]

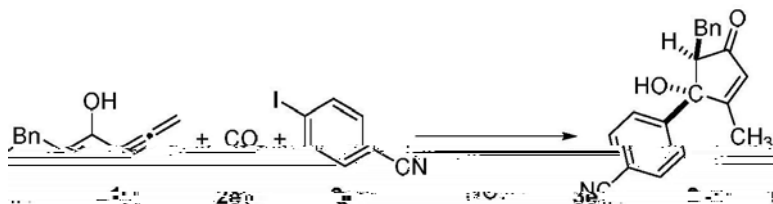
19



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)
 $^1\text{H NMR}$ (600MHz, CDCl_3) : 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). $^{13}\text{C NMR}$ (150MHz, CDCl_3) : 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[MH]

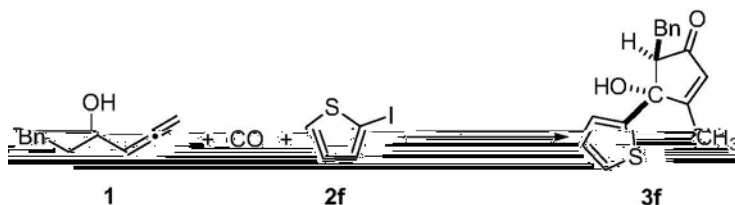
20



1 (0.12mmol, 28mg) 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)
 $^1\text{H NMR}$ (400MHz, CDCl_3) : 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, J₁ = 7.8Hz, J₂ = 1.6Hz, 2H). $^{13}\text{C NMR}$ (150MHz, CDCl_3) : 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[MH]

21



1 (0.12mmol, 28mg) 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)
 $^1\text{H NMR}$ (400MHz, CDCl_3) : 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, J₁ = 3.6Hz, J₂ = 1.2Hz, 1H), 6.88 6.93(m, 3H), 7.07 7.18(m, 4H). $^{13}\text{C NMR}$ (150MHz, CDCl_3) : 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[MH]

