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2002 - 0058130  
2002 07 12

(21)  
(22)

10 - 2000 - 0085129  
2000 12 29

(71)

100

103 - 1203

(72)

100

103 - 1203

121

110 101

242 - 14

104 604

(74)

:

(54)

가 가 , .

가 , 가 , 2 - , .

가 ,

가

2 가 , 2 가

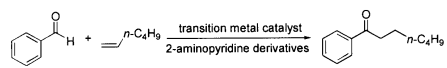
가

가

가

1 가 2 -

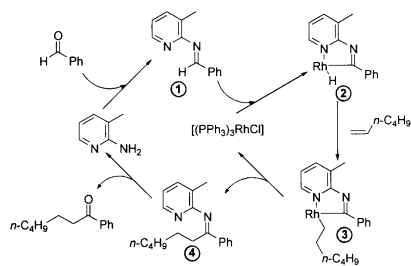
[ 1]



2 가 2 -

, 가

【반응식 2】

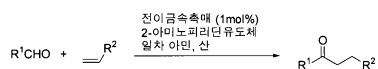


1% 2- , 10 mol% 20 mo  
 , 80% 60 가

( ) 2- 가 가

가 , 2- , 3

【반응식 3】



가 ,

,  $RhCl_3 \cdot H_2O$  (PPh<sub>3</sub>) 3가  $(PPh_3)_3 RhCl$  1가  $[Rh(C_8H_{14})_2 Cl]_2$  3가 1가

가 가 2- 가 , 2- , tert- , p

가 가 가 가

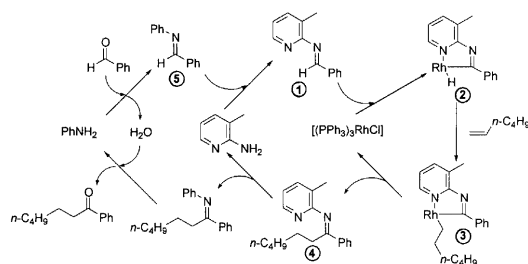
(transimination)

가 가 1- 2- -3-

2- -3- 2- -3-

2- -3- 가 가 Rh(I)

【반응식 4】



&lt; 1 &gt;

0.5 ml (0.03 mmol) 53 mg (0.5 mmol) , 28 mg (0.3 mmol) , 11 mg (0.1 mmol) 2 - - 3 - , 4 mg  
 ol) , 210 mg (2.5 mmol) 1 - 80 mg (0.87 mmol)  
 , 9.25 mg (0.01 mmol) Rh(PPh<sub>3</sub>)<sub>3</sub>Cl 가  
 130 1 가 ,  
 98% (93 mg, 0.49 mmol)

1 .

[ 1 ]

[ 1 ]

			(%)
1	1 -	1 - - 1 -	83
2	1 -	1 - - 1 -	98
3	1 -	1 - - 1 -	99
4	3,3 - - 1 -	4,4 - - 1 - - 1 -	84
5		4 - - 1 - - 1 -	95
6	2,3,4,5,6 -	3 - -	98
7		[2.2.1] - 2 - -	47
8	- -	1 - - 3 - - - 1 -	95

&lt; 2 &gt;

1 ( 0.1 mmol 2 - - 3 - , 0.03 mmol , 0.3 mmol  
 , 2.5 mmol 1 - , 0.87 mmol ) 0.5 ml ,  
 0.5 mmol 가 2 - 3 , 9.25 mg (0.01mmol)  
 Rh(PPh<sub>3</sub>)<sub>3</sub>Cl 가 130 1 ,  
 2 .

[ 2]

[ 2]

			(%)
1			98
2	- 4 -	1 - - 4 - - - 1 -	95
3	- 2 -	1 - - 2 - - - 1 -	91
4	4 - -	1 - (4 - - ) - - 1 -	79
5	4 - -	1 - (4 - - ) - - 1 -	57
6	4 - -	1 - p - - - 1 -	88
7	4 - -	1 - (4 - - ) - - 1 -	47
8	4 - -	1 - (4 - - ) - - 1 -	71
9	4 - -	1 - (4 - - ) - - 1 -	88
10	3 - -	1 - - - 3 -	71

&lt; 3&gt;

1 (0.5 mmol), 0.3 mmol, 0.03 mmol, 2.  
 5 mmol 1 -, 0.87 mmol ) 0.5 ml ,  
 3 0.1 mmol 2 - 가 . 2 - 3  
 , 0.01 mmol  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  가 . 130 1 .  
 , GC ,  
 3 .

[ 3]

[ 3]

	2 -	(%)
1	2 -	18
2	2 - - 3 -	100
3	2 - - 4 -	11
4	2 - - 5 -	12
5	2 - - 6 -	3

&lt; 4&gt;

1 (0.5 mmol), 0.1 mmol 2 - - 3 -, 0.3 mmol  
 , 2.5 mmol 1 -, 0.87 mmol ) 0.5 ml ,  
 4 0.03 mmol 가 . 2 - 3 , 0.01 mmol  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  가 .  
 130 1 .  
 GC , 4 .

[ 4]

[ 4]

		(%)
1		69
2		73
3	4 - -	82
4		100
5	4 - -	100
6	4 - -	100
7	-	95
8	p -	43
9		35

&lt; 5&gt;

1 (0.5 mmol), 0.1 mmol 2 - - 3 -, 0.03 mmol  
 , 2.5 mmol 1 - , 0.87 mmol ) 0.5 ml ,  
 5 0.3 mmol 가 . 2 - 3 , 0.01  
 mmol Rh(PPh<sub>3</sub>)<sub>3</sub>Cl 가 . 130 1 . ,  
 5 .

[ 5]

[ 5]

		(%)
1		33
2		98
3		87
4		79
5	tert -	59

&lt; 6&gt;

1 (0.5 mmol), 0.1 mmol 2 - - 3 -, 0.3 mmol  
 , 0.03mmol , 2.5 mmol 1 - , 0.87mmol ) 0.5 ml  
 가 . 2 - 3 , 0.01mmol 6  
 가 . 130 1 . ,  
 GC , 6 .

[ 6]

[ 6]

		(%)
1	$\text{Rh}(\text{PPh}_3)_3\text{Cl}$	100
2	$\text{RhCl}_3 + \text{PPh}_3$ (3equiv.)	76
3	$[\text{Rh}(\text{C}_8\text{H}_{14})_2\text{Cl}]_2 + \text{PPh}_3$ (2.5 equiv.)	100
4	$\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$	5
5	$\text{Ir}(\text{PPh}_3)_3\text{Cl}$	4
6	$\text{Ru}_3(\text{CO})_{12}$	3
7	$\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$	1

&lt; 7&gt;

1 (0.5 mmol), 0.1 mmol 2 - - 3 -, 0.3 mmol  
 , 0.03mmol , 2.5 mmol 1 - , 0.87mmol ) 0.5 ml  
 가 . 2 - 3 , 0.01 mmol  $[\text{Rh}(\text{C}_8\text{H}_{14})_2\text{Cl}]_2$  7  
 0.025 mmol 가 . 130 1 .  
 GC ,  
 7 .

[ 7]

[ 7]

			(%)
1	$\text{PPh}_3$ (30 min)	2.0 equiv.	74
2	$\text{PPh}_3$ (30 min)	2.5 equiv.	82
3	$\text{PPh}_3$ (30 min)	3.0 equiv.	75
4	$\text{PPh}_3$ ( 60 min)	2.5 equiv.	100
5	$\text{P}(\text{p}-\text{MeC}_6\text{H}_4)_3$	2.5 equiv.	99
6	$\text{P}(\text{p}-\text{MeOC}_6\text{H}_4)_3$	2.5 equiv.	99
7	$\text{P}(\text{o}-\text{MeC}_6\text{H}_4)_3$	2.5 equiv.	15
8	$\text{PCy}_3$	2.5 equiv.	25
9	$\text{PPhCy}_2$	2.5 equiv.	12
10	$\text{PBu}_3$	2.5 equiv.	10
11	DPPE	2.5 equiv.	2

&lt; 8&gt;

1 (0.5 mmol), 0.1 mmol 2 - - 3 -, 0.3 mmol  
 , 0.03mmol ) , 8 1 - 0.5 ml  
 가 . 2 - 3 , 0.01mmol  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  가 .  
 130 1 , 1 -  
 GC , 8 .

[ 8]

[ 8]

	1 -		(%)
1	1.0 mmol	0.87 mmol	42
2	1.5 mmol	0.87 mmol	66
3	2.0 mmol	0.87 mmol	93
4	2.5 mmol	0.87 mmol	100
5	2.5 mmol	0 mmol	100

&lt; 9&gt;

1 (0.5 mmol), 0.1 mmol 2 - - 3 -, 0.3 mmol  
 , 0.03mmol , 2.5 mmol 1 - , 0.87 mmol ) 0.5 ml  
 가 . 2 - 3 , 0.01mmol Rh(PPh<sub>3</sub>)<sub>3</sub>Cl 가 .  
 130 9 GC , 9 .

[ 9]

[ 9]

	(min)	(%)
1	15	52
2	30	74
3	45	89
4	60	100
5	120	100

&lt; 10&gt;

1 (0.5 mmol), 0.1 mmol 2 - - 3 -, 0.3 mmol  
 , 0.03 mmol , 2.5 mmol 1 - , 0.87 mmol ) 0.5 ml  
 가 . 2 - 3 , 0.01 mmol Rh(PPh<sub>3</sub>)<sub>3</sub>Cl 가 .  
 10 (70 130 ) 1 GC , 10 .

[ 10]

[ 10]

	( )	(%)
1	70	13
2	100	52
3	130	100
4	150	100
5	170	100
6	130 (30 min)	74
7	150 (30 min)	82
8	170 (30 min)	86

&lt; 11&gt;



2 -  
11  
1  
1  
11  
11

[ 11]

[ 11]

	(h)	2 -	2 - 가
1	0.5	8	62
2	1	9	100
3	2	12	100
4	4	16	100
5	6	19	100
6	8	20	100
7	12	24	100

,

(57)

1.

가 , 가 , 2 - ,

2.

1 , 1가 , 1가 가 , 3가 ,  
3가 , 가 , 1  
2 .

3.

, 2 -

;

- ;

;

가

.