

(72)	2256	가	가
	2256	가	가
	2256	가	가

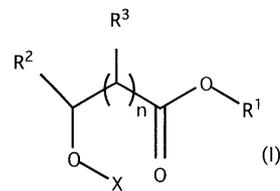
(74)

:

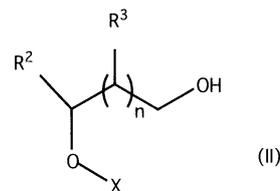
(54)

, () , ()

, ()

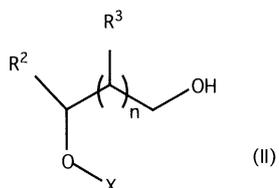


(, R^1 1 4 , R^2, R^3 , n O 1 , 1 4 , 1 , X , .) 1 , 1 , ()



(, R^2, R^3, X, n .)

()



(R) - (S) -

2 - 3 -

(2 -)

(2 -)

{ (Tetrahe
dron), 35 , 567 (1979)}, 가
{ (J. Am. Chem. Soc.), 78 ,
2582 (1956)} , {
(J. Am. Chem. Soc.), 77 , 6209 (1955)}

3 1
가 {Bull. Chem. Soc. Jpn., 57 , 1948 (1984)}, 1
{ (Synlett), 1636 (1999) : WO98/8793 },
10 - 507996 , JP10 - 507996 - A), , 1,2 -
(1 - 250369).

()

가 가 . , 가
1
가

, 1,2 - ,

, , ()

, , (R) -, (S) -, (RS) -

[]

, , ()

, ; , ,

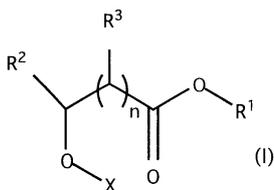
, 1 , , ()

, () 가 , 1 가

[]

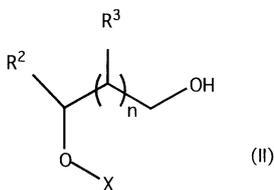
, [1], [2]

[1] (I)



(, R¹ , X 1 4 , R², R³ , n O 1 .) 1 4

1 , 1 , ()



(, R², R³, X, n .)

[2] 1 가 [1] .

, 가 () .

n- 1 4 가 () , () R¹ , n- , R¹ 1 4 , R², R³ , , , R¹ 1 4 .

(I) () X , n 0 1 , 1 가 , 가 .

, () X 가 , (R) - , (R) - , (S) - , (S) , (R) - 3 - , (S) - 3 - , (S) - 3 - -2- .

, () X 가 , (R) - , (R) - , (R) , (S) - , (S) - , (R) - 3 - , (S) - 3 - , (S) - 3 - -2- .

가 , (MOM), 2 - (MEM) , 1- , 1- (1 6) .

," 가 - 3 (Protective Groups in Organic Synthesis - 3rd ed.), John Wiley & Sons, Inc.(1999)" ,

(I) X 가 ,

(I) X 가 , (I) X 가

가 0.5 10 %, 1 3 % .

() X 가 , () X 가 , , ,

가 0.3 L()/ 2.0 L/ , 0.5 L/ 1.5 L/ .

() ()

() 가

1 , 1 .

, 1- , 4- , 2- , 2,4- ,

가 (0.3 L()/ 2.0 L/ , 0.5 L/ 1.5 L) , 1

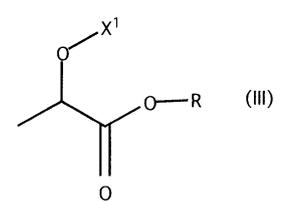
가 3 가 12 , 5 8 , 1 ()

() 1 6 , 1 3 , 1.3 2.0 ,

0 80 , 20 40 ,

() 가 () 가

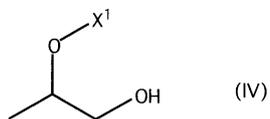
() () 가 (R) - (S) -



(, X¹ (1 6) , R R¹ .)
 () , (1 6) (R) - (S) -
 , (R) - 2 - (1 -) , (R) - 2 - (1 -)
 , (R) - 2 - (1 -)) , (R) - 2 - (1 - n -) , (R) - 2 -
 - (1 -) 가 .

() 가 , 가
 , S. Chladek and J. Smrt. Chem. Ind. (London), 1719(1964)

() , () 1,2 - ,
 , 가 .



(, X¹)
 () 1,2 - , (R) - 2 - (1 -
) - 1 - , (S) - 2 - (1 -) - 1 - , (R) - 2 - (1 - n -) - 1 - , (R)
 - 2 - (1 -) - 1 - 가 .

1
 (R) - (+) - 2 - [(- 2H - - 2 -)]
 (R) - (+) - 29.2 g(0.2) , 0.3 g , 3,4 - - 2H - 21.8 g(0.26)
 70 ml, 70 ml , 100 ml 가 70 ml,
 () 49.0 g(:92.1%) .

: 79.2 - 80.5 (106.6 - 159.9 Pa)

[]_D^{24.8} = +58 · 6 ° (c= 1.85, CHCl₃)

¹H - NMR(300 MHz, CHCl₃ - d₁): = 0.94, 0.95(d,J= 6.6Hz,6H), 1.41, 1.47(d,J= 6.9Hz,3H), 1.5 - 2.0(m, 7H), 3.4 - 3.6(m,1H), 3.8 - 4.0(m,3H), 4.22 (q,J= 6.9Hz,0.5H), 4.44(q,J= 6.9Hz,0.5H), 4.7 - 4.8(m,1H)

IR(neat) : 1751 cm⁻¹ (CO)

MS(GC - MS) m/e= 229(M⁺ - 1), 85(base)

1

(R) - (+) - 2 - [(- 2H - - 2 -)] - 1 -

1 (R) - (+) - 2 - [(- 2H - - 2 -)] 34.5 g(0.15),
 8.5 g(0.225) 100 ml , 36
 49 ml . 22 . , 50 ml 2 , 50
 ml , , , ()
) 24.2 g(: 99.8%) .

: 64.9 - 68.2 (65.3 - 73.3 Pa)

[]_D^{24.8} = +10.1 ° (c= 2.26, CHCl₃)

¹H - NMR(300 MHz, CHCl₃ - d₁): = 1.14, 1.22(d,J= 6.5Hz,3H), 1.5 - 1.9 (m,6H), 2.1 - 2.2(m,1H), 3.4 - 3.7(m,3H), 3.8 - 4.0(m,2H), 4.5 - 4.6(m,0.5H), 4.7 - 4.8(m,0.5H)

IR(neat):3439 cm⁻¹ (OH)

MS(GC - MS)m/e= 159(M⁺ - 1), 85(base)

2

(R) - (+) - 2 - (1 -)

(R) - (+) - (98.9% e.e) 20.8 g(0.2), 18.7 g(0.26)
 가 , 6 . , 100 ml 가 70 ml, 70 ml,
 70 ml . , ,
 () 49.0 g(: 97.8%) .

: 36.0 - 38.2 (46.7 - 66.6 Pa)

[]_D^{24.2} = +82.4 ° (c=10.03, CHCl₃)

¹H - NMR(300 MHz, CHCl₃ - d₁): = 1.16,1.18(t,J=7.0Hz,3H), 1.32, 1.36 (d,J= 5.4Hz,3H), 1.23,1.40(d,J = 6.9Hz,3H), 3.5 - 3.7(m,2H), 3.74(s,3H), 4.20 - 4.36(q,J= 6.9Hz,1H), 4.77(q,1H,J= 5.4Hz)

IR(neat):1754 cm⁻¹ (CO)

MS(GC - MS)m/e= 175(M⁺ - 1), 73(base)

2

(R) - (-) - 2 - (1 -) - 1 -

2 (R) - (+) - 2 - (1 -) 26.4 g (0.15), 8.5 g(0.22
 5) 70 ml , 35 14 ml
 4 , 50 ml 2 , 50 ml
 (R) - 1,2 -) 22.4 g(:99.8%)
 , 98.9% e.e (HPLC)

: 40.0 - 42.0 (65.3 - 73.3 Pa)

[α]_D^{24.0} = -40 · 6 ° (c= 2.91, CHCl₃)

¹H - NMR(300 MHz, CHCl₃ - d₁): = 0.94((d,J= 6.6Hz,6H), 1.17, 1.19 (t,J= 7.0Hz,3H), 1.31, 1.37(d,J= 5.1Hz,3H), 1.43(d,J= 6.9Hz, 3H), 1.9 - 2.0(m,1H), 3.5 - 3.7(m,2H), 3.9 - 4.0(m,2H), 4.22, 4.36(q,J= 6.9Hz,1H) , 4.79, 4.80(q,J= 5.1Hz,1H)

IR(neat):3433 cm⁻¹ (OH)

MS(GC - MS)m/e=147(M⁺ - 1), 73(base)

3

(R) - (+) - 2 - (1 -)

(R) - (+) - 32.7 g, 0.3 g , 17.2 g
 가 40 , , 200 ml 가 ,
 , , () 40.1 g(:91.8%)

: 57.0 (26.7 Pa)

[α]_D^{24.0} = +78.8 ° (c= 1.16, CHCl₃)

¹H - NMR(300 MHz, CHCl₃ - d₁): = 0.94((d,J= 6.6Hz,6H), 1.17, 1.19(t, J= 7.0Hz,3H), 1.31, 1.37(d,J= 5.1Hz,3H), 1.43(d,J= 6.9Hz,3H), 1.9 - 2.0(m,1H), 3.5 - 3.7(m,2H), 3.9 - 4.0(m,2H), 4.22, 4.36(q,J= 6.9Hz,1H) , 4.79, 4.80(q,J= 5.1 Hz,1H)

IR(neat) : 1752 cm⁻¹ (CO)

MS(GC - MS) m/e= 217(M⁺ - 1), 73(base)

3

(R) - (-) - 2 - (1 -) - 1 -

3 (R) - (+) - 2 - (1 -) 7.52 g 30 ml
 1.85 g , , 7.3 ml 가 40 ,
 , 5 , 60 ml 가 , 120 ml
 , 60 ml ,

() 4.0 g(:90.8%)

: 31.0 (53.3 Pa)

[α]_D^{24.0} = - 46.5 ° (c= 1.04,CHCl₃)

IR, NMR, MS , 2

4

(R) - (+) - 2 - (1 -)

(R) - (+) - 32.7 g, 0.3 g , 24.0 g
가 40 , , 200 ml 가

() 47.8 g(: 96.9%)

: 63.0 (40.0 Pa)

[α]_D^{24.0} = +80.7 ° (c= 1.01,CHCl₃)

¹H - NMR(300 MHz, CHCl₃ - d₁): =0.89, 0.91(d,J= 6.3Hz,6H), 0.90, 0.94(d,J= 6.6Hz,6H), 1.31, 1.36(d, J= 5.4Hz,3H), 1.40, 1.43(d,J= 6.9Hz, 3H), 1.8 - 1.9(m,1H), 1.9 - 2.0(m,1H), 3.2 - 3.4(m,2H), 3.9 - 4.0(m, 2H), 4.24, 4.38(q,J= 6.9Hz,1H), 4.78(q,J= 5.4Hz,1H)

IR(neat): 1753 cm⁻¹ (CO)

MS(GC - MS) m/e= 245(M⁺ - 1), 57(base)

4

(R) - (-) - 2 - (1 -) - 1 -

4 (R) - (+) - 2 - (1 -) 25.0 g 30 ml
5.7 g , 24 ml 가 40 ,
ml 가 , 5 , 100 ml 가 , 200
() 17.3 g(:98.0%)

: 43.0 (40.0 Pa)

[α]_D^{24.0} = - 44.5 ° (c= 1.11, CHCl₃)

¹H - NMR(300 MHz, CHCl₃ - d₁): = 0.92(d,J=6.9 Hz,6H), 1.12, 1.18(d,J = 6.3Hz, 3H), 1.33, 1.35(d,J= 5.4 Hz,3H), 1.8 - 1.9(m,1H), 2.35(dd,J= 4.5,7.8Hz,0.5H), 3.07(dd, 3.6,8.7Hz,0.5H), 3.2 - 3.3(m,2H), 3.4 - 3.6(m, 2H), 3.8 - 3.9(m,1H), 4.71, 4.79(q,J= 5.4Hz,1H)

IR(neat): 3448 cm⁻¹ (OH)

MS(GC - MS) m/e = 175(M⁺ - 1), 57(base)

5 - 12

(R) - (+) - 2 - (1 -) 7.52 g 1.85 g (1.5 eq)
 GC(가)
 1 3 , 「eq」 「h」 「 」

(R) - (-) - 2 - (1 -) - 1 - (a)

1

	1 L/	가 ()			a (%)
5		6eq		7h	99.3
6		6eq	40	5h	98.7
7		6eq	60	6h	78.2
8		3eq	40	5h	67.0
9		12eq	40	5h	92.5
10		6eq	60	6h	30.6
11		6eq		7h	94.1
12		6eq		5h	99.4

13

(R) - (-) - 2 - (1 -) - 1 -

(R) - (+) - 2 - (1 -)

12.3 g 50 ml 2.5 g 14.4 g
 가 34 , 4.5
 30 ml 가 , () 8.4 g (:96%)
 , 4

5

(R) - (+) - 2 - (1 -)

(R) - (+) - 20.8 g (0.2), 22.0 g (0.22)
 가 , 3 , 100 ml 가 100 ml, 40 ml,
 40 ml , ()
) 38.8 g (:95.1%)

:43 (53.3 Pa)

[]_D^{24.2} = +80.0 ° (c= 1.05, CHCl₃)

$^1\text{H-NMR}$ (300 MHz, $\text{CHCl}_3 - d_1$): = 0.8 - 0.9(m,6H), 1.31, 1.35(d,J= 5.4Hz,3H), 1.39, 1.42(d,J= 6.9Hz,3H), 1.7 - 1.8(m,1H), 3.2 - 3.4(m,2H), 3.74(s,3H), 4.24, 4.38(q,J= 6.9Hz,1H), 4.77(q,J= 5.4Hz,1H)

IR(neat):1755 cm^{-1} (CO)

MS(GC - MS) m/e= 203($\text{M}^+ - 1$), 59(base)

14

(R) - (-) - 2 - (1 -) - 1 -

5 (R) - (+) - 2 - (1 -) 35.8 g (0.17) 170 ml
 8.4 g(0.204) , 40.8 ml(1.02) 가
 40 , , 4 , 50 ml 가 , 0.5
 ml , 50 ml , 50 ml, 50
) 28.9 g(:98.0%) (

:47.0 (80.0 Pa)

$[\alpha]_D^{24.0} = -37.0^\circ$ (c= 1.05, CHCl_3)

IR, NMR, MS , 4 .

6

(R) - (+) - 2 - (1 - n -)

(R) - (+) - 29.2 g(0.2) , n - 22.2 g (0.22)
 가 , 4 , 100 ml 가 100 ml, 40 ml
 40 ml ,
 () 46.8 g(:94.9%) .

:67 (26.7 Pa)

$[\alpha]_D^{24.2} = +79.2^\circ$ (c= 1.04, CHCl_3)

$^1\text{H-NMR}$ (300 MHz, $\text{CHCl}_3 - d_1$): = 0.9 - 1.0(m,9H), 1.3 - 1.6(m,10H), 1.9 - 2.0(m,1H), 3.4 - 3.7(m,2H), 3.9 - 4.0(m,2H), 4.22, 4.36(q,J= 6.9Hz, 1H), 4.78(q,J= 5.4Hz,1H)

IR(neat):1753 cm^{-1} (CO)

MS(GC - MS) m/e= 245($\text{M}^+ - 1$), 101(base)

15

(R) - (-) - 2 - (1 - n -) - 1 -

6 (R) - (+) - 2 - (1 - n -) 44.1 g(0.17) 170 ml
 8.4 g(0.204) 41.3 ml(1.02)
 가 40 , 5 , 50 ml 가 , 0.
 5 , 50 ml , 50 ml,
 50 ml ()
) 27.4 g(:91.3%) .

:51.0 (53.3 Pa)

[α]_D^{24.0} = -45.8 ° (c=1.09, CHCl₃)

¹H - NMR(300 MHz, CHCl₃ - d₁): = 0.93, 0.95(t, J= 7.2Hz, 3H), 1.12, 1.17(d, J= 6.3Hz, 3H), 1.34, 1.35(d, J= 5.4Hz, 3H), 1.3 - 1.4(m, 2H), 1.5 - 1.6 (m, 2H), 2.44(dd, J= 4.5, 7.8 Hz, 0.5H), 3.17(dd, J= 3.3, 9.0 Hz, 0.5H), 3.4 - 3.7(m, 4H), 3.8 - 3.9(m, 1H), 4.71, 4.79(q, J= 5.4Hz, 1H)

IR(neat):3448 cm⁻¹ (OH)

MS(GC - MS) m/e= 175(M⁺ - 1), 59(base)

7

(R) - (+) - 2 - (1 -)

(R) - (+) - 29.2 g(0.2) , 28.0 g(0.22)
 가 , 4 , 100 ml 가 100 ml, 40 ml,
 40 ml ,
 () 54.2 g(:99.4%) .

:90 (40.0 Pa)

[α]_D^{24.2} = +100.6 ° (c= 1.34, CHCl₃)

¹H - NMR(300 MHz, CHCl₃ - d₁): = 0.95(d, J= 6.6Hz, 6H), 1.2 - 1.3(m, 6H), 1.35, 1.37(d, J= 5.1 Hz, 3H), 1.39, 1.42(d, J= 6.9Hz, 3H), 1.7 - 1.8(m, 4H), 1.9 - 2.0(m, 1H), 3.4 - 3.6(m, 1H), 3.9 - 4.0(m, 2H), 4.26, 4.38(q, J= 6.9Hz, 1H) , 4.84, 4.91(q, J= 5.1 Hz, 1H)

IR(neat):1752 cm⁻¹ (CO)

MS(GC - MS) m/e= 257, 127(base)

16

(R) - (-) - 2 - (1 -) - 1 -

7 (R) - (+) - 2 - (1 -) 47.9 g(0.17) 170 ml
 8.4 g (0.204) 41.3 ml (1.02)
 가 40 , , 7 , 50 ml 가

, 0.5 , 50 ml , 50 ml,
 50 ml () 30.5 g(:88.7%)

:76.0 (53.3 Pa)

[α]_D^{24.0} = -57.6 ° (c= 0.89, CHCl₃)

¹H - NMR(300 MHz, CHCl₃ - d₁): = 1.12, 1.16(d,J= 6.6Hz,3H), 1.2 - 1.3 (m,4H), 1.34, 1.35(d,J= 5.1 Hz, 3H), 1.5 - 1.6(m,2H), 1.7 - 1.8(m,2H), 1.8 - 1.9(m,2H), 2.78(dd,J= 4.5,8.1 Hz,0.5H), 3.21(dd,J= 3.3,9.0 Hz, 0.5H), 3.5 - 3.6(m,3H), 3.7 - 3.9(m,1H), 4.76(q,J= 5.1 Hz,0.5H), 4.89(q,J= 5.4 Hz,0.5H)

IR(neat):3448 cm⁻¹ (OH)

MS(GC - MS) m/e=187, 59(base)

17

(R) - (-) - 2 - (1 -) - 1 -

(R) - (+) - 2 - (1 -) 5.0 g(0.02) 20 ml
 1.0 g(0.024) 7.0 ml(0.12) 가 40
 , , 40 7 , 60 2
 , 20 ml 가 , 0.5 , 20 ml
 20 ml, 20 ml ,
 () 3.0 g(:84.4%)

[α]_D^{24.0} = -37.6 ° (c= 1.03, CHCl₃)

IR, MS , 4

8

(S) - 2 - - 3 - (1 -)

(S) - (+) - 3 - - 2 - 5.9 g(0.05) 가 ,
 5.5 g(0.055) 4 , 10
 0 ml 가 0.1% 50 ml, 20 ml ,
 () 10.5 g(:97.0%)

¹H - NMR(300 MHz, CHCl₃ - d₁): = 0.91(d,6H,J= 6.6 Hz), 1.18(d,3H,J= 6.9 Hz), 1.27, 1.29(d,3H,J= 5.4 Hz), 1.8 - 1.9(m,1H), 2.7 - 2.8(m,1H), 3.13, 3.17(dd,1H,J= 6.6,0.69Hz), 3.31, 3.34(dd,1H,J= 6.6,0.6 Hz), 3.69 (s,3H), 3.4 - 3.7(m,2H), 4.67, 4.69(q,1H,J=5.4 Hz)

IR (neat):1754cm⁻¹ (CO)

MS(GC - MS) m/e= 217(M⁺ - 1), 73(base)

18

(S) - 2 - 3 - (1 -) - 1 -

8 (S) - 2 - 3 - (1 -) 5.5 g(0.025), 6.0 g
 (0.15) 50 ml , 60 , 24.0 g
 , 50 ml 2 () 3.8
 g(: 80.0%) .

¹H - NMR(300 MHz, CHCl₃ - d₁): = 0.90(d,6H,J= 6.6 Hz), 0.94(d,3H,J= 6.6 Hz), 1.31(d,3H,J= 5.4Hz),
 1.8 - 1.9(m,1H), 1.9 - 2.1(m,1H), 2.57, 2.59 (d,1H,J= 11.1 Hz), 3.2 - 3.7(m,6H), 4.60,4.65(q,1H,J= 5.4 H
 z)

IR(neat):3422 cm⁻¹ (OH)MS(GC - MS) m/e= 189(M⁺ - 1), 57(base)

9

(R) - 2 - ()

60% 2.0 g 50 ml , , (R) - (+) - 7.
 3 g . 1 , 5.0 g 3 .
 50 ml, 30 ml 9.0 g(:86.6%)

¹H - NMR(300 MHz, CHCl₃ - d₁): = 0.93(d,6H,J= 6.9Hz), 1.43(d,3H,J= 6.9 Hz), 1.95(d,1H,J= 6.9 Hz),
 3.38(s,3H), 3.92(d,2H,J= 6.9 Hz), 4.24(q, 1H,J= 6.9 Hz), 4.67(d,1H,J= 10.2 Hz), 4.70(d,1H,J= 10.2 Hz)

IR(neat):1752 cm⁻¹ (CO)MS(GC - MS) m/e=189(M⁺ - 1), 89(base)

19

(R) - 2 - () - 1 -

9 (R) - 2 - () 5.2 g (0.025), 1.1 g(0.030)
 40 ml , 30 , 3.2 g
 80 ml 가 , 20 ml 2 , 10 ml 1 ,
 , 3.4 g(91.5%) .

¹H - NMR(300 MHz, CHCl₃ - d₁): = 1.15(d,3H,J= 6.3Hz), 2.85(dd,1H,J= 8.4,4.2 Hz), 3.39(s,3H), 3.4 - 3.
 6(m,2H), 3.7 - 3.8(m,1H), 4.68(d,1H,J= 11.1 Hz), 4.71(d,1H,J= 11.1 Hz)

IR(neat):3448 cm⁻¹ (OH)MS(GC - MS) m/e= 119(M⁺ - 1), 89(base)

20

(R) - (-) - 1,2 -

250 ml 61.5 g(0.42) (R) - (+) - 11.5 g(0.305)
 , 54 g(1.69) 가 40 가 ,
 2 GC 50 ml 가 , 1
 35% pH 7.3
 111 /5.3 KPa 18.3 g(78.9%) (R) - (-) - 1,2 -

[α]_D²⁶ = -21.9 ° (c= 7.5, H₂O) : [α]_D²⁵ = -20.1 ° (c= 8, H₂O) ; Synthesis, (1984)142)

NMR, IR

21

(S) - (+) - 1,2 -

250 ml 44.4 g(0.42) (S) - (-) - (98.4% e.e) 11.5 g(0.305)
 , 20 , 19.2 g(83%) (S) - (+) - 1,2 -

[α]_D²⁰ = +16.7 ° (neat)

HPLC 98.4%e.e

1(1 - 250369)

(R) - (-) - 2 - (1 -) - 1 -

(R) - (+) - 2 - (1 -) 24.9 g(0.10) 1,2 - 100 ml
 4.9 g(0.12) , 24.0 ml(0.60)
 가 40 , GC 20
 , 50 ml 가 , 0.5 , 50 ml
 , 30 ml, 30 ml ,
 () 16.3 g(:92.6%)

[α]_D^{24.0} = -37.9 ° (c= 1.07, CHCl₃)

IR, MS , 4

2()

(R) - (+) - 2 - (1 -)

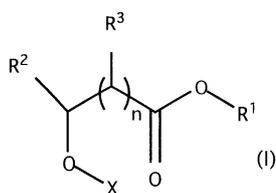
10 ml 0.5 g(0.012) , , (R) - (+) - 2 - (1

2.5 g(0.01) 가 , 6 가
 (粗製)
 가 7% ,
 92% , 2 - (1 -
 20 ml 가 , 0.5 ,
 20 ml,
 50 ml 가 , , 20 ml ,
 20 ml ,
 1.8 g . 90.8% . GC - MS 5 .

(57)

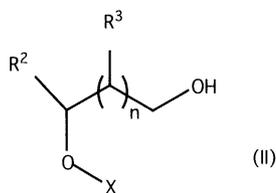
1.

()



(, R¹ , 1 4 , R² , R³ , n O 1 ,) 1 4 , X , n O 1 .)

1 , 1 , , ()



(, R² , R³ , X, n .)

2.

1 , 1 가 .