

(72)

- 4056	14	
- 79106	148	
- 79725	14	
-		
- 68130	-	49
- 79395		2
- 4125	64	
- 4059	-	33

(74)

:

(54)

1 500 μmol 가 1

, , , ,

/

90

가

가

H₂O₂

H₂O₂

가

H₂O₂

H₂O₂

가 가

H₂O₂

1,4,7-

- 1,4,7-

Mn⁽ⁿ⁺⁾

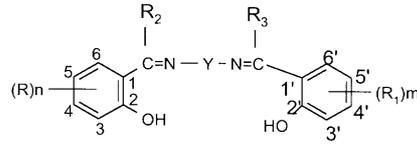
H₂O₂

가

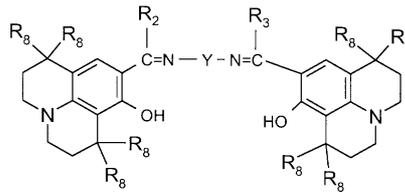
1 1 500 μmol 가

1 2

1



2



1 2 ,

n 0, 1, 2 3 ,

m 1, 2 3 ,

R₄ C₁ - C₄ ,

R₈ C₁ - C₄ ,

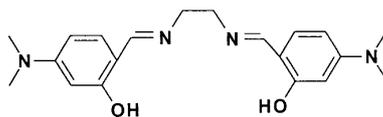
Y - [C(R₄)₂]_r - { , r 1 8 , R₄ } ,
 - CX=CX - { , X , C₁ - C₈ } (C₁ - C₈)
 - (CH₂)_q - NR₄ - (CH₂)_q - { , R₄ } , q 1, 2, 3 4 }
 { , R₉ , SO₃H, CH₂OH 1,2-CH₂NH₂ } ,

R R₁ C₁ - C₈ , , OR₄ COOR₄ { , R₄ } ,

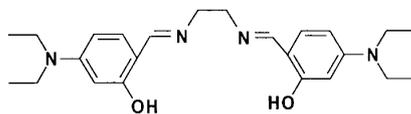
NH₂, OR₄, COOR₄ NR₅R₆ (, R₄, R₅ R₆) , NR₅R₆ { , R₅ R₆ } ,
 R₆R₇ - N R₄R₅R₆ { , R₄, R₅ R₆ } - CH₂ - N R₄

R₂ R₃ C₁ - C₄ , , O
 R₄ COOR₄ { , R₄ } , C₁ - C₄ } , C₁ - C₈ , NH
 R₅ NR₅R₆ { , R₅ R₆ } , C₁ - C₁₂ } ,
 C₁ - C₈ - R₇ { , R₇ } NH₂, OR₄, COOR₄ NR₅R₆ { , R₄, R₅ R₆ }
 } } - N R₄R₅R₆ { , R₄, R₅ R₆ } }

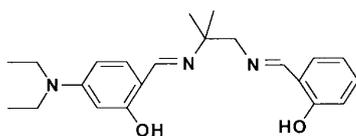
1a



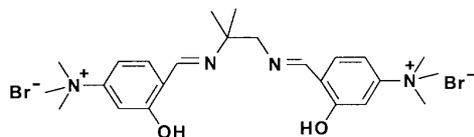
1b



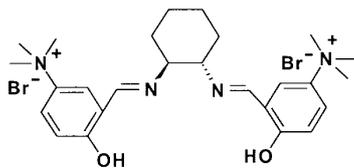
1c



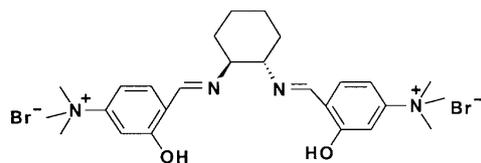
1d



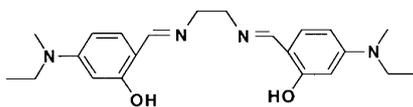
1e



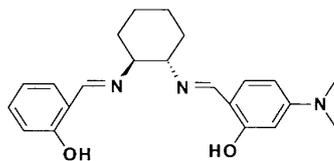
1f



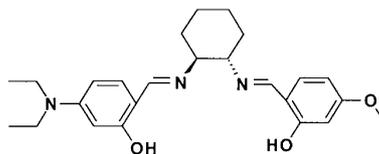
1g



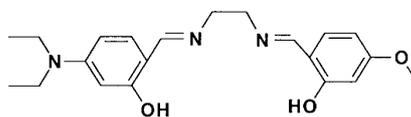
1h



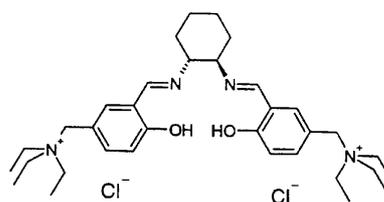
1i



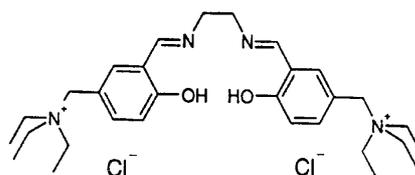
1j



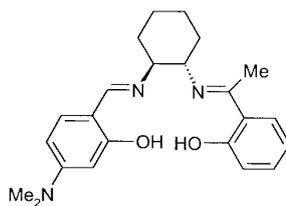
1k



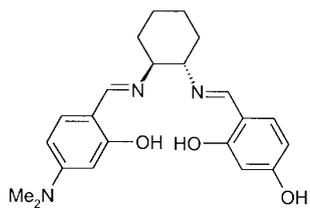
1l



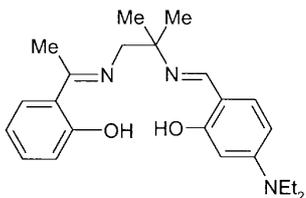
1m



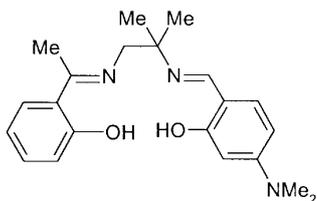
1n



1o



1p



US 1 2
5,281,578 [: Bernardo et al., Inorg. Chem. 35 (1996) 387]

1 2 1 2

1 2 , 98810870.0 , 98810289.3 가

(I) (A) / (B) 5 90%, 5 70%,

(II) (C) 5 70%, 5 50%, 5 40%,

(III) (D) 0.1 30%, 1 12%

(IV) mol 1 500 μ mol, 5 350 μ mol, 10 250 μ mol
1 2

[2]

	20 가 DY*													
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)	(n)
	0	5	16	21	14	3	15	16	21	16	10	18	13	16
* (a)	(b) H ₂ O ₂ 8.6mmol/		(c)			1.125g/		TAED 0.3g/						
	(d) H ₂ O ₂ 8.6mmol/		(A) 5 μ mol/		(e) H ₂ O ₂ 8.6mmol/			1a		100 μ mol/				
(f)	(n)	1b	1j	(e)										

3:

가
가

5

3

Kubelka - Munk)

(%)

[3]

	(%)*													
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)	(n)
(Vat Blue) 4	10	10	5	20	35	5	5	5	5	15	30	10	15	25
(Reactive Brown) 17	10	20	15	45	15	5	15	15	10	15	15	10	15	15
(Reactive Black) 5	10	10	30	45	15	10	10	10	10	10	15	10	10	10
(Vat Brown) 1	5	0	0	0	5	0	0	5	5	5	0	0	0	0
(Reactive Red) 123	10	15	15	40	5	5	5	10	5	10	10	5	5	5
(Direct Blue) 85	20	20	15	15	20	20	15	20	20	25	15	15	10	15
* 1	(a)	(n)												

4:

가

가 5

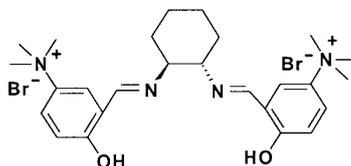
4

[4]

	(%)				
	(a)	(b)	(c)	(d)	(e)
4	5	5	5	40	5
17	0	0	5	50	0
5	0	0	0	20	0
1	10	5	20	55	5
123	5	0	5	40	5
85	10	5	0	5	10
* 1	(a)	(d).(e) H ₂ O ₂ 8.6mmol/	1b	200 μ mol/	

5: 1e

1e



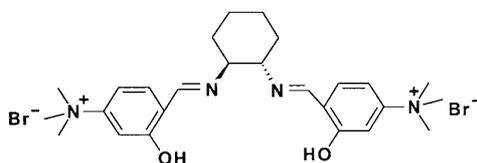
2Mℓ 3 - - 4 - [: M. Ando, S. Emo
 to, Bull. Chem. Soc. Jpn, Vol. 51 (8) 2433 (1978)] 500mg(1.92mmol) - 1,2 -
 105mg(0.915mmol) 50 가 . 80 4 .
 , , , 가 40

: 435mg(79%)

^{13}C NMR(DMSO - d_6) = 19.8, 25.5, 27.4, 29.2 (cycl. CH_2), 53.4(NCH_3), 63.6(CH_2 - CH), 118.7, 121.9, 123.1(tert aryl - C), 111.4, 131.5, 172.4(quart. aryl - C), 163.2($\text{C}=\text{N}$).

6: 1f

1f



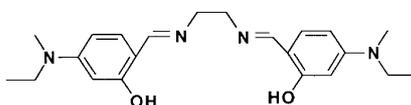
4 - - 3 - 500mg(1.92mmol) - 1,2 -
 0.105g(0.915mmol) 5 .

: 299mg(55%)

^{13}C NMR(D_2O) = 23.6, 29.5, 31.3, 33.1(cycl. CH_2), 56.8(NCH_3), 67.3(CH_2 - CH), 107.5, 112.0, 136.1 (tert aryl - C), 117.3, 152.4, 170.9(quart. aryl - C), 166.6($\text{C}=\text{N}$)

7: 1g

1g



4 - (N - - N -) 500mg(2.79mmol) 80mg(1.33mmol)
 가 , 70 4 가 . ,
 , 30 .

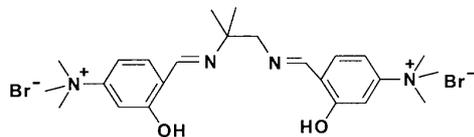
: 476mg(94%).

^1H NM_R(CDCl_3) = 1.13(m, 6H, CH_3 - CH_2), 2.9₂(s, 6H, NCH_3), 3.38(m, 4H, CH_3 - CH_2), 3.76(s, 4H, NCH_2), 6.12(m, 4H, aryl - H), 6.98(m, 2H, aryl - H), 8.08(s, 2H, $\text{CH}=\text{N}$), 13.52(s, br, 2H, OH).

¹³C N_M R(CDCl₃) = 11.7(CH₃ - C_H2), 37.4(NCH₃), 46.6(CH₃ - CH₂), 58.4(NCH₂), 68.8(NCH₂), 98.6, 103.3, 132.8(tert aryl - C), 108.6, 152.6, 165.4(quart. aryl - C), 164.6(C=N).

8: 1d

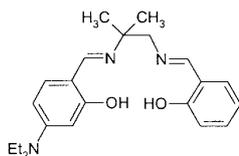
1d



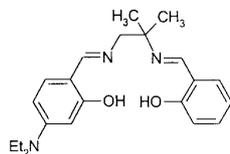
1,2- 1,2- - 2- , 6

9: 1c' 1c

1c



1c'



50ml 4- 1,2- - 2- 4.56g(0.0517mol) 5
 2 가 (DC / 9:1), 10.0g(0.0517mol) 2 가 .
 13.6g , 가 2- [(2- - 2-)- - 5- 가 .
 50ml 2- [(2- - 2-)- - 5- 13.6g(0.0517mol) 5
 0 가 , 5.5ml(6.31g, 0.0517mol) 3 가 .
 19.31g , , 1c 1c' 5
 (/ 9:1)

: 4.01g(21%)(1c'), 1.55g(8%)(1c).

NMR (1c'):

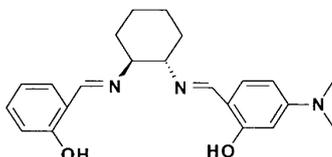
$^{13}\text{C}_{\text{NMR}}$ R(CD₃OD): = 12.2(CH₃CH₂N), 23.9((CH₃)₂C), 44.5(NCH₂CH₃), 60.1(quart.C(CH₃)₂), 62.2(=NCH₂), 99.4, 104.3, 117.0, 118.6, 132.4, 132.8, 135.6(tert aryl - C), 183.3, 119.1, 155.2, 162.2(quart. aryl - C), 162.8, 163.5(C=N).

NMR (1c):

$^{13}\text{C}_{\text{NMR}}$ R(CD₃OD): = 12.2(CH₃CH₂N), 24.7((CH₃)₂C -), 44.5(NCH₂CH₃), 57.1(quart.C(CH₃)₂), 69.3(=NH₂), 99.6, 104.1, 116.8, 118.9, 132.2, 132.8, 135.9(tert aryl - C), 108.1, 119.1, 155.4, 161.4, 177.0(quart. aryl - C), 158.0, 168.4(C=N).

10: 1h

1h



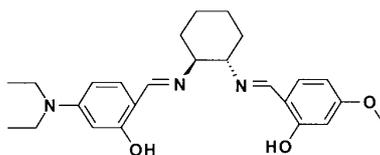
[: Tetrahedron Letters 39(1998) 4199 - 4202]
 0.5g(2.29mmol) 378mg(2.29mmol) 가 50Mℓ 60 4 가 50Mℓ 4 - ,
 829mg .
 (, / 9:1) .

: 318mg(38%).

^{13}C NMR(CDCl₃): = 24.2, 24.4, 33.2, (cycl. - CH₂), 40.0(N - CH₃), 71.1, 72.9(tert cycl. CH), 98.7, 103.4, 116.7, 118.5, 131.5, 132.0, 132.6(tert aryl - C), 108.7, 118.7, 153.6, 161.1(quart. aryl - C), 163.2, 164.7(C=N).

11: 1i

1i



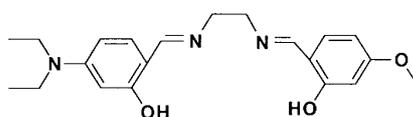
200ml 2 - [(2 - ())] - 5 - 2.5g(8.64mmol)
 200ml 4 - 1.3g(8.64mmol) 45 가 .
 60 4 가 . ,
 (/ 9:1) .

: 500mg(14%).

$^{13}\text{C}_\text{NMR}(\text{CDCl}_3)$: = 12.7($\text{CH}_3\text{CH}_2\text{N}$), 24.3, 33.2(cycl. - CH_2), 44.4($\text{CH}_3\text{CH}_2\text{N}$), 55.3(OCH_3), 70.9, 71.5, 71.6(tert cycl. CH), 98.0, 101.1, 103.0, 106.1, 106.2, 132.9(tert aryl - C), 108.2, 112.3, 151.3, 165.5(quart. aryl - C), 162.9, 163.7($\text{C}=\text{N}$)

12: 1j

1j



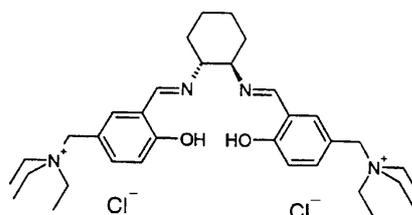
300ml 3.87g(0.0644mol) 60ml 4 -
 12.45g(0.0644mol) 가 . 2
 , 25ml 4 - 9.8g(0.0644mol) 가
 , 1 가 . , 8
 (/ 9:1)

: 4.00g(17%).

$^{13}\text{C}_\text{NMR}(\text{CDCl}_3)$: = 12.7($\text{CH}_3\text{CH}_2\text{N}$), 44.4(NCH_2CH_3), 55.3(OCH_3), 58.1, 58.7(NCH_2), 98.0, 101.2, 103.1, 106.3, 132.9, 133.0(tert aryl - C), 108.3, 112.3, 151.5, 163.5(quart. aryl - C), 164.5, 165.4($\text{C}=\text{N}$).

13: (R,R) - N,N' - (5 - ()) - 1,2 -

1k

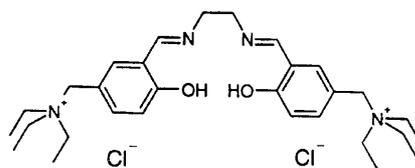


(5 -) 1.09g(4mmol) [: T. Tanaka et al., Bull. C
 hem. Soc. Jpn. 1997, 70, 615 - 629] 10Mℓ 2Mℓ 1,2 -
 0.228g(2mmol) 2 , 60 (10mbar)
 2 × 50Mℓ 가 , 90% (NM
 R) 1.22g .

¹³ C NMR(D₂O): = 7.4(CH₃), 23.8, 31.3, 52.3, 59.6(aliph. CH₂), 67.7(tert C), 115.0, 116.5(quart. aryl - C), 121.5, 138.5, 139.4(tert aryl - C), 166.9(C=N), 171.5(quart. aryl - C).

14:N,N' - (5 -) - 1,2 -

1l

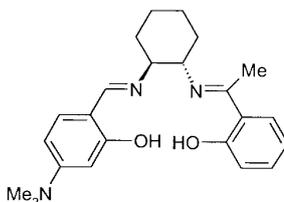


90% (NMR)

¹³ C NMR(D₂O) = 7.4(CH₃), 52.2, 53.5, 59.6(aliph. CH₂), 114.6, 116.4(quart. aryl - C), 120.5, 138.9, 139.6(tert aryl - C), 168.7(C=N), 172.3(quart. aryl - C).

15:(R,R) - N - [4 - ()] - N' - (2 -) - 1,2 -

1m



225Mℓ R,R - [4 - N - ()] - 1,2 - 2.5g(9.56mmol)
 225Mℓ 2 - 1.30g(9.56mmol) 가 , 60 8 가
 가 4 , (9:1).
 6g,) , (/ 9:1).

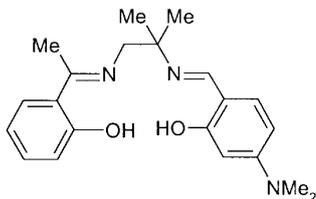
: 1.60g(44%), m.p. 129 .

¹³ C NMR(CDCl₃): = 14.7(CH₃), 24.2, 24.3, 32.4, 33.2(cycl. CH₂), 40.0(NCH₃), 62.3, 72.2(tert cycl. CH), 98.6, 103.4, 116.8, 118.6, 128.3, 132.3, 132.7(tert aryl - C), 108.6, 119.1, 153.6, 164.3, 170.9(quad. aryl - C), 163.2(C=N).

¹³C_{NM} R(CDCl₃): = 13.1(CH₃CH₂N), 15.1(CH₃), 26.0((CH₃)₂C), 44.9(CH₃CH₂N), 59.1(quart.C(CH₃)₂), 61.3(CH₂), 98.9, 103.5, 117.5, 119.0, 128.6(tert aryl - C), 108.8, 119.7, 152.2, 164.2, 167.5(quart. aryl - C), 159.6(C=N), 173.0((CH₃)C=N).

18:N - 2 - [4 -)] - N' - 1 - (2 -) - 2 - - 1,2 -

1p



- 1,2 - 500mg(2.42mmol) 4 - N - 6Mℓ N - 1 - (2 - - 2 -
 15 가 400.3mg(2.42mmol)
 (1 가 / 11:1)
 : 642mg(75%), 115 .

¹³C_{NM} R(CDCl₃): = 13.5(CH₃), 24.3((CH₃)₂C), 38.9(NCH₃), 57.8(quart.C(CH₃)₂), 59.7(CH₂), 97.9, 102.3, 106.7, 115.9, 117.4, 127.0, 131.3, 131.9(tert aryl - C), 107.8, 118.2, 152.8, 162.6, 165.1(quart. aryl - C), 158.5(C=N), 171.5((CH₃)C=N).

19:

1 . 1 : H₂O₂ 8.6mmol/ 100 μ mo
 l/ .

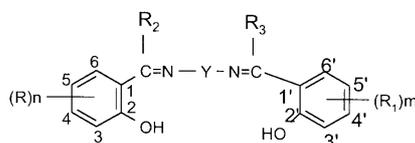
	40 가 DY					
	(1k)	(1l)	(1n)	(1m)	(1o)	(1p)
	24	22	22	23	24	23

(57)

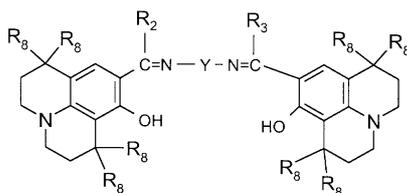
1.

mol 가 1 2 1 1 500 μ

1



2



1 2 ,

n 0, 1, 2 3 ,

m 1, 2 3 ,

R₄ C₁ - C₄ ,

R₈ C₁ - C₄ ,

Y - [C(R₄)₂]_r - { , r 1 8 , R₄ } ,
 - CX=CX - { , X , C₁ - C₈ } (C₁ - C₈)
 } - (CH₂)_q - NR₄ - (CH₂)_q - { , R₄ } , q 1, 2, 3 4 }
 { , R₉ , SO₃H, CH₂OH } ,

R R₁ C₁ - C₈ , , OR₄ COOR₄ { , R₄ } ,
 C₁ - C₈ , NR₅R₆ { , R₅ R₆ } ,
 NH₂, OR₄, COOR₄ NR₅R₆ (, R₄, R₅ R₆) } , C₁ - C₁₂ } ,
 7 - N R₄R₅R₆ { , R₄, R₅ R₆ } } - CH₂ - N R₄R₆R

R₂ R₃ C₁ - C₄ , , , OR₄
 COOR₄ { , R₄ } , C₁ - C₄ } , C₁ - C₈ , NHR₅
 NR₅R₆ { , R₅ R₆ } , C₁ - C₁₂ } ,
 C₁ - C₈ - R₇ { , R₇ } NH₂, OR₄, COOR₄ NR₅R₆ { , R₄, R₅ R₆ }
 } } - N R₄R₅R₆ { , R₄, R₅ R₆ } }

2.

1 , 1 2 1 5 350 μ mol,
 10 250 μ mol 가 .

3.

1 2 , Y가
 $C(R_4)_2 - (CH_2)_p - C(R_4)_2 - \{$, p 0 6, $-(CH_2)_r - \{$, r 1 8 }
 $C_1 - C_4$, } , 1,2- , R_4
 1,2- 1 2 .

4.

1 3 , R R₁ , OR₄, COOR₄, N(R₄)₂ N(R₄)₃ { , N(R₄)₄
 $(R_4)_2$ N(R₄)₃ R₄ , C₁ - C₄ , ,
 } 1 2 .

5.

1 4 , R₂ R₃ , , 1
 2 .

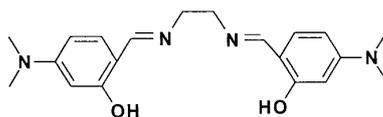
6.

1 5 , R₈ 2 .

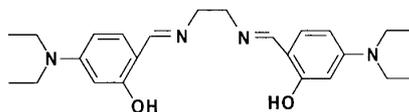
7.

1 6 , 1a, 1b, 1c, 1d, 1e, 1f, 1g, 1h, 1i, 1j, 1k, 1l, 1m, 1n, 1o
 1p .

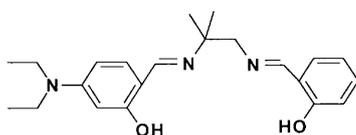
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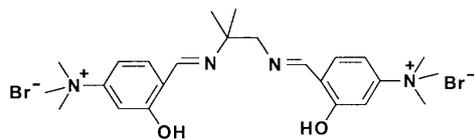
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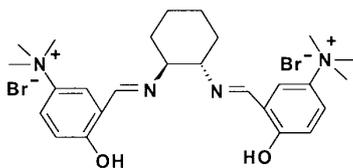
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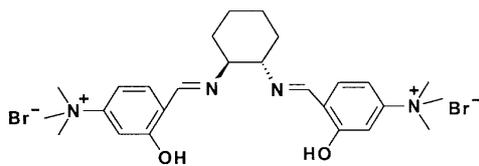
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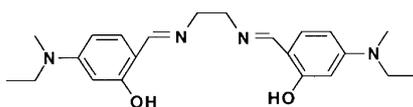
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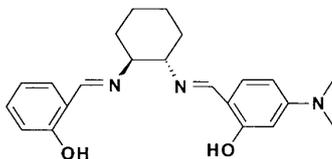
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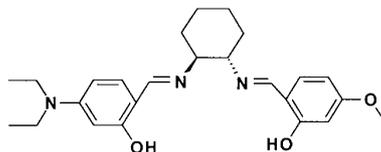
1g



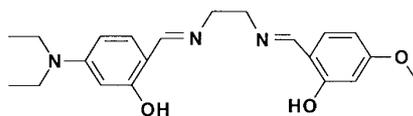
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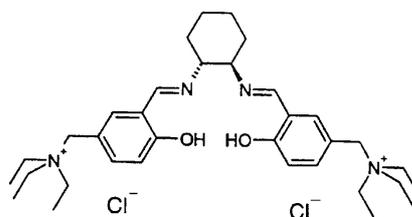
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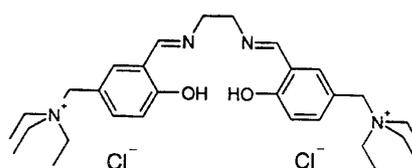
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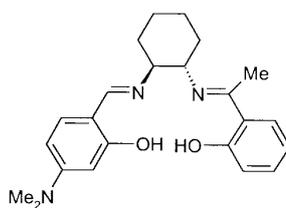
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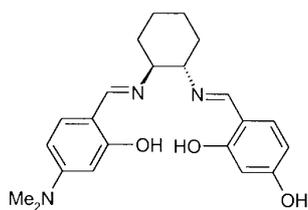
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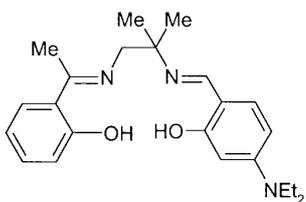
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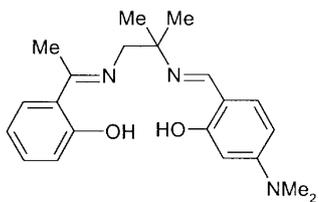
1n



1o



1p



8.

(I)	(A)	/	(B)	5	90%,	5	70%,
(II)	(C)	5	70%,	5	50%,	5	40%,
(III)	(D)	0.1	30%,	1	12%		
(IV)		1	500 μ mol,	5	350 μ mol,	10	250 μ
mol			1 2		.		

9.

8 , TAED 0.05 5 % 가 .