

(19)
(12)

(KR)
(B1)

(51) 。 Int. Cl. 7
C07C 209/36

(45)
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(24)

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10 - 0331490
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(22) 1999 12 03

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(43) 2001 07 02

(73)

1가 57

(72)

152	102 701
152	105 102
152	105 1002
152	102 402

(74)

:

(54) 4,4' -

4,4' -
~100

4,4' -

가

가

4,4' -

가 .

, 4,4' -

, , ,

(nitrobenzene) , 4,4' -
 (4,4' - dinitrodiphenylamine)

(tetramethyl ammonium hydroxide; TMA(OH))
 4,4' -

4,4' - 4,4' - (4,4' - diamino diphenylamine)
 10 - 168038 (1998)

가 가 4,4' - (4,4' - diaminodiphenylamine)
 4,4' - 가 , ,

4,4' - N - (N - acetyldiphenylamine)
 (nitration) (deacetylation)

(nitrodiphenylamine)
 anate) 4,4' - 4 - (4 - chloroaniline) (alkali metal cy
 160 15 4,990,673 (1991)
 가

4 - (4 - nitroaniline)
 [, 1976, (1), p. 138 143]. 4 -

t - (t - BuOK) 2,4' -
 4,4' - 5 - () - 2,4' - (5 - Cl(B
 r) - 2,4' - dinitrodiphenyl - amine)

(nucleophilic aromatic substitution for hydrogen : NASH)
 4,4' - NASH

(amines) (amides)

(tetramethyl ammonium hydroxide; TMA(OH))

4 - (4 - nitrodiphenylamine; 4 - NDPA) 4 -
 (4 - nitrosodiphenylamine) . [J. Am. Chem. Soc., 1992, 114(2
 3), 9237 - 8, USP 5,117,063 , USP 5,252,737 , USP 5,331,099 , USP 5,453,541 , USP
 5,552,531 , USP 5,633,407]

NASH (benzamide) USP 5,436,371 , USP 5,380,407 , WO 93/24447 (N - (4 - nitrophenyl)benzamide) N - (4 -) 가 4 - N - (4 -) 가 가

NASH

4 - 4,4' - 가 가 4,4' - 4,4' - 가 가

4,4' - 4,4' - 가 가

4,4' -

TMA(OH)

4,4' - 4 - 4,4' - 4,4' - 가 4 - 가 4 - (azoxybenzene) 4,4' -

(dimethylsulfoxide, DMSO 1:1 1:16 1:4

1:8 가가 . 1:50 1:1 1:30 1:1 .
 (NaOH), (KOH), t- (t - BuOK),
 (tetramethylammoniumhydroxide; TMA(OH)) 1:1 1:20 ,
 가 가 1:12 ,
 4 60 8 4- .
 , 80 100 가 , 50 80 가 가 가
 4- 4,4' - 가 가
 가 가
 5% 가 1% 가
 6 가
 (NMR) - (GC - MSD)
 (HPLC) L - 4200 UV - VIS
 L - 6200 (intelligent pump) 254nm 1MØ
 (Hitachi) 5 18 - (Cosmosil 5C18 - AR, 4.6 × 150mm, packed column) ,
 /min. ,

[1]

(pyrene)

[1]

1g) 가 3 100Mℓ (1.2g, 20mmol), (9.6g, 240mmol), (0.
 30 DMSO 30ml (8.2ml, 80mmol) 가 .
 C 6 , 60 HPLC HPL
 4,4' - 82 mol%, 8 94 mol%

[2]

1 1

[2]

()	(h)	(mol %)	
		4 - NA ^{*1)}	DNDPA ^{*2)}
80	8	-	59
70	6	-	67
60	6	-	82
	8	-	94
50	6	8.9	55
	8	6.8	63

* 1) 4 - NA: 4 - 2) DNDPA: 4,4' -

[3]

1 2

[3]

	g(mmol)	(h)	(%)	
			4 - NA	DNDPA
	9.6(240)	8	-	94
	17.9(320)	8	9	52
t - *	4.5(40)	8	-	37
	8.6(47)	8	-	51

* t - 0.6g(10mmol)

[4]

1 3

[4]

g(mmol)	(h)	(%)	
		4 - NA	DNDPA
3.2(80)	8	14	55
6.4(160)	8	5	67
9.6(240)	8	-	94
12.8(320)	8	-	92

[5]

DMSO

1

4

[5]

DMSO (ml)	(h)	(%)	
		4 - NA	DNDPA
20	8	-	65
30	8	-	94
40	8	4	72

[6]

1

5

[6]

NB ml(mmol)	(h)	(%)	
		4 - NA	DNDPA
4.1(40)	8	7	67
8.2(80)	8	-	94
16.4(160)	8	-	75
NB :			

[7]

1

6

[7]

	(h)	(%)	
		4 - NA	DNDPA
no ^(a)	8	-	94
K ₂ CO ₃ ^(b)	8	-	73
1% ^(c)	8	-	70
5% ^(d)	8	3	58
a) 가 d) () b) 5% 가 c) 1%			

[8]

1 7 .

[8]

	(h)	(%)	
		4 - NA	DNDPA
	8	-	94
	8	2	50
	8	1	75
	8	3	56

가 가 4,4' - 가 .

(57)

1.

4,4' - , ~100
4,4' -

2.

1 , 2 10 4,4' -

3.

1 , 1 20 4,4' -

4.

1 , 1~50 4,4' -

5.

1 , 가 , , t- ,
4,4' -

6.

1 , 가 4,4' -

7.

1 , , 4,4' -