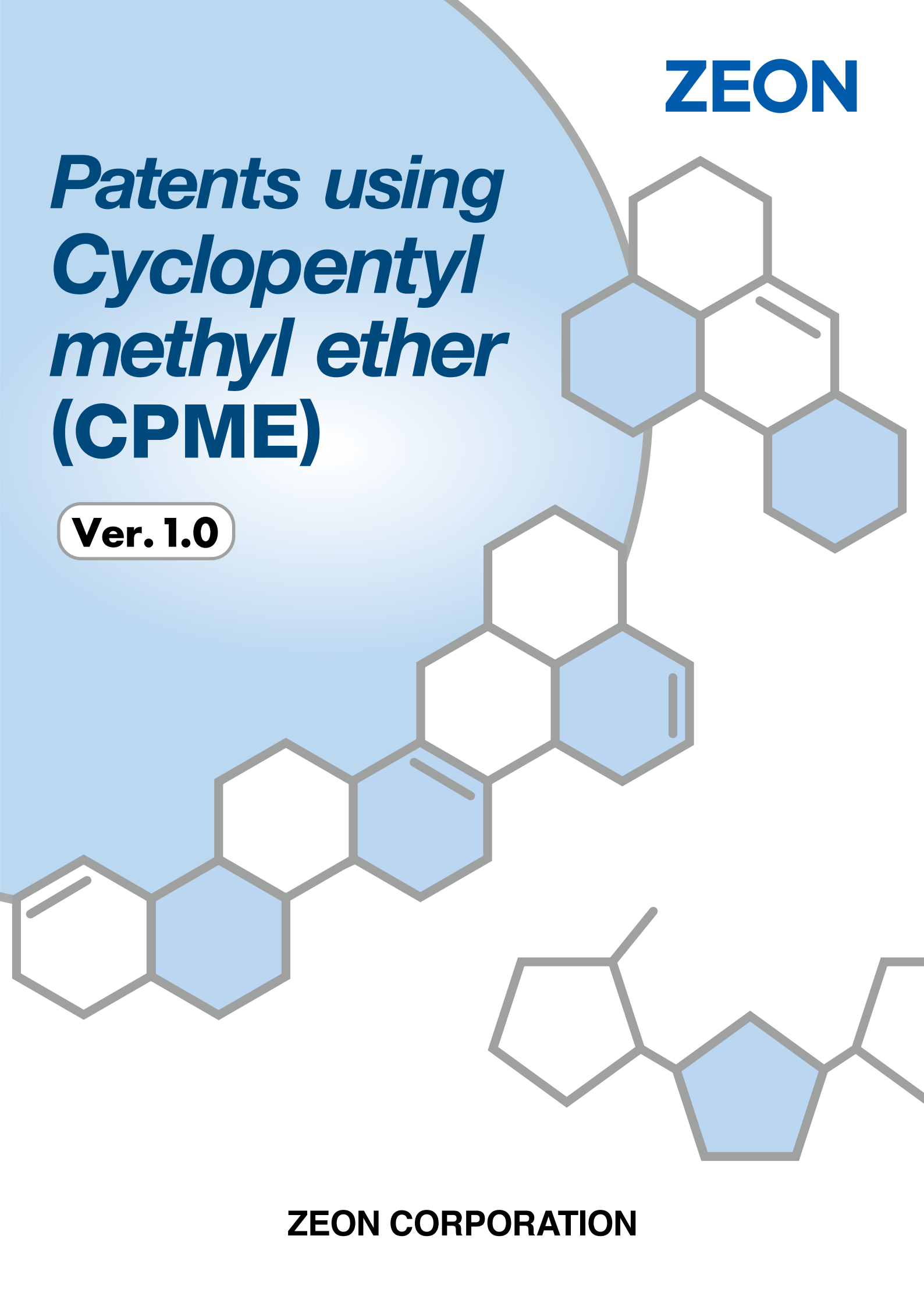


ZEON

***Patents using
Cyclopentyl
methyl ether
(CPME)***

Ver. 1.0



ZEON CORPORATION

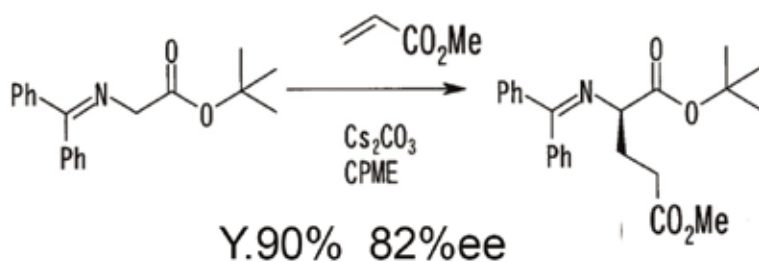
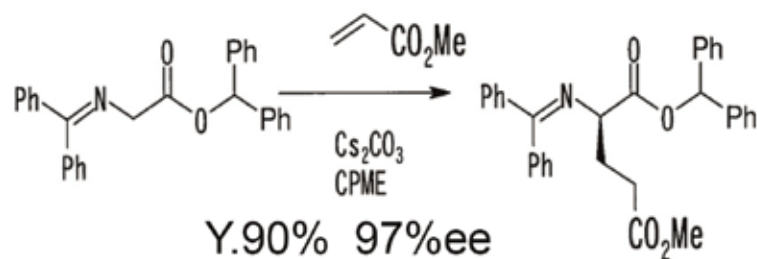
C O N T E N T S

1. Alkylation, Silylation	3
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1. Alkylation, Silylation

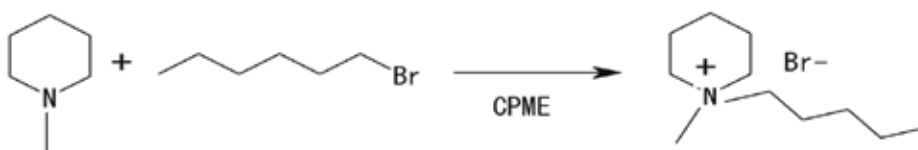
1-1 Michael Addition

Nippon Soda Co., Ltd. JP2005-225810



1-2 Ammonium salt

Nichia Corporation, JP2010-70539



1-3 Arylation

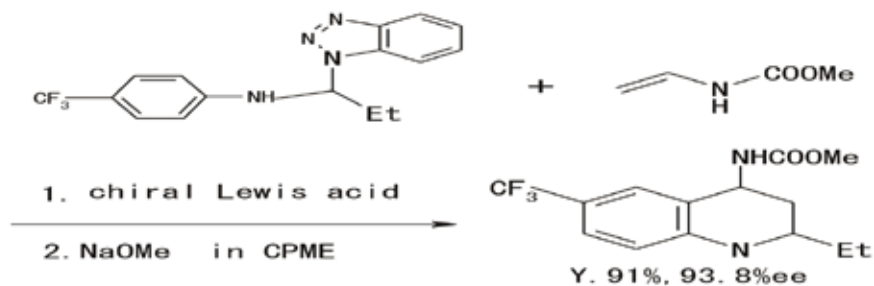
Fushimi Pharmaceutical Co., Ltd., JP2006-117637, 117638



2. Reactions under Lewis acid Conditions

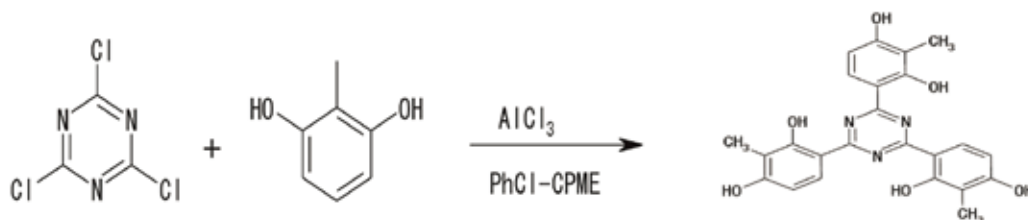
2-1 Asymmetric addition

Takasago International Corporation WO2004/078730



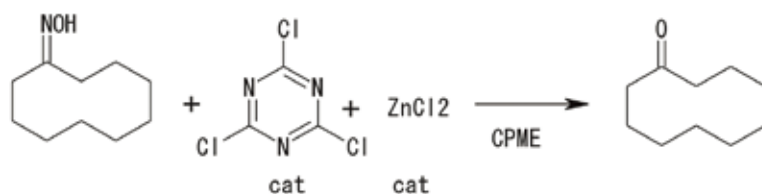
2-2 Friedel-Crafts

Adeka Corporation JP2009-292754



2-3 Beckmann rearrangement

Ube Industries Ltd. JP2010-229042

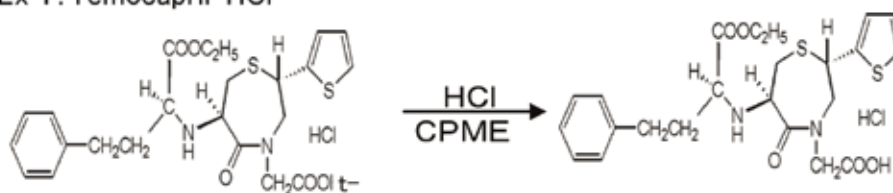


3. Reactions under Bronsted acid Conditions

3-1 Removal of t-Bu group

Daito Pharmaceutical Co., Ltd. JP2008-208068

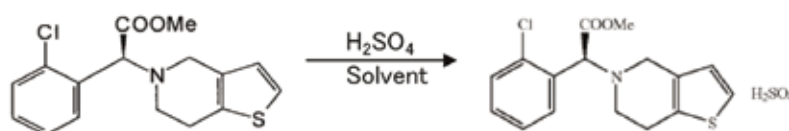
Ex 1: Temocapril•HCl



3-2 Salt formation

India-IPCA Laboratories US2008/018866

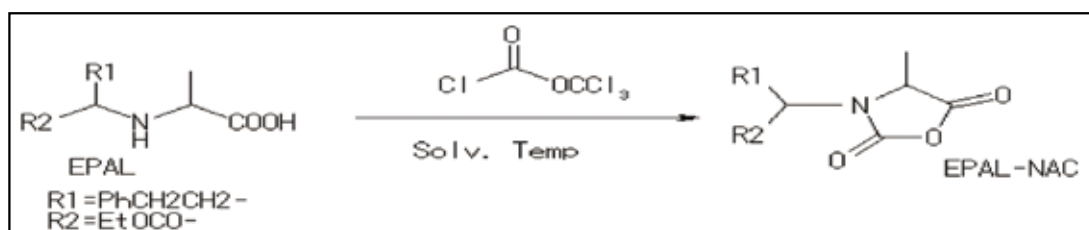
(+)-S-clopidogrel•H₂SO₄ Formula I



Ex.	Solvent	Yield(%)	free base 5.79kg / 37L Solvent used
4	MEK	60	
5	CPME	90	
12	MIPK	90	

3-3 Cyclization

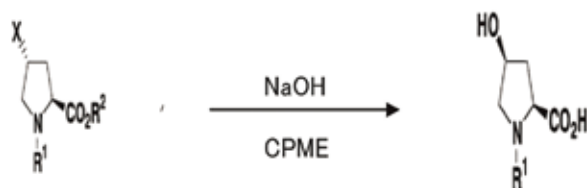
Hodogaya Chemical Co.,Ltd., JP2007-63147



4. Reaction with Base or Organometals

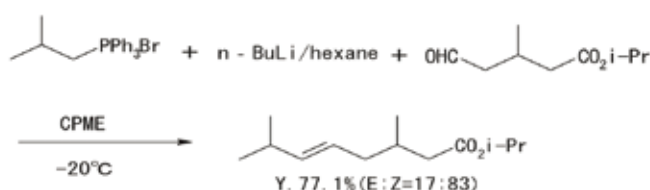
4-1 Cyclization

Toray Fine Chemicals Co., Ltd. JP2005-112761



4-2 Wittig reaction

SHIONO KORYO KAISHA, LTD. JP2007-297286



4-3 Reformatsky reagent

Takeda Pharmaceutical Co., Ltd. JP2007-182454

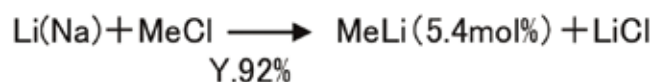


Storage Stability of BrZnCH₂CO₂Et in various Ethers(0–5°C)
purity(%) of BrZnCH₂CO₂Et

CPME(days)	THF(days)	MeTHF(days)	DME(days)
94(0)	83(0)	83(0)	90(0)
94(7)	76(30)	80(30)	84(10)
89(30)	76(60)		68(30)

4-4 MeLi

Tosoh Finechem Corporation WO2007-007697

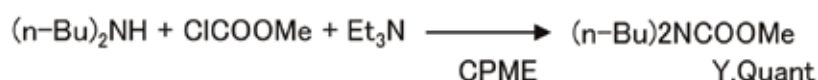


Storage Stability of MeLi in CPME (N₂, 23°C)

Time(days)	0	30	60
conc(mol%)	5.4	4.13	4.1

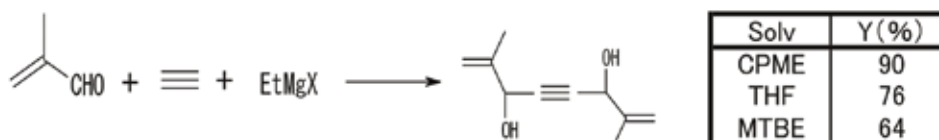
4-5 Carbamoylation

MEIJI SEIKA KAISHA, LTD. WO2006-109823



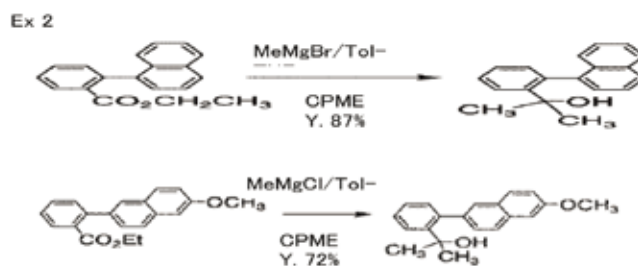
4-6 Grignard

Sumitomo Chemical Co., Ltd. WO2009-110406



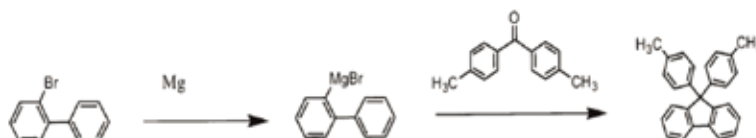
4-7 Grignard

Tosoh Finechem Corporation JP2008-231047



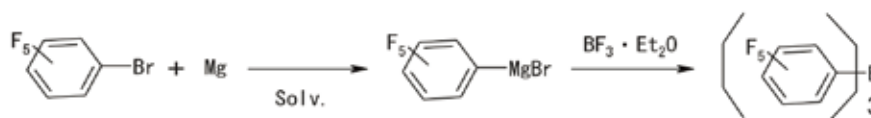
4-8 Grignard

Yamagata Prefecture JP2009-218568



4-9 Grignard

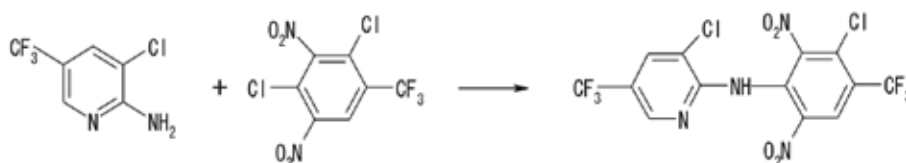
Nippon Syokubai Co., Ltd., JP2010-215569



Solvents	Y(% of Grignard reagent)	Scale Up	stability to product
CPME	97.2	easy	good
Et ₂ O	good	hard	good
THF	good	easy	bad
IPE	No Reaction	hard	good
MTBE	No Reaction	easy	good
1,2-DME	No Reaction	hard	good

4-10 N-Arylation

Ishihara Industry Co., Ltd., JP2009-242370



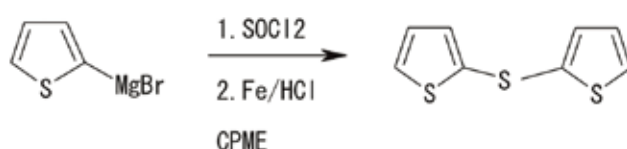
4-11 Grignard

Sumitomo Seika Chemicals Co., Ltd., JP2011-157277



4-12 Grignard

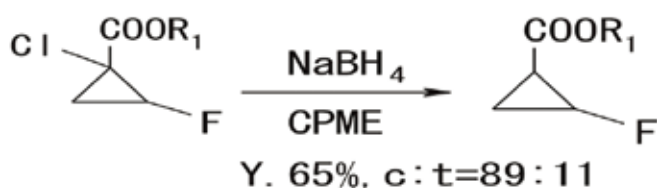
Sumitomo Seika Chemicals Co., Ltd., JP2011-157278



5. Oxidation/Reduction

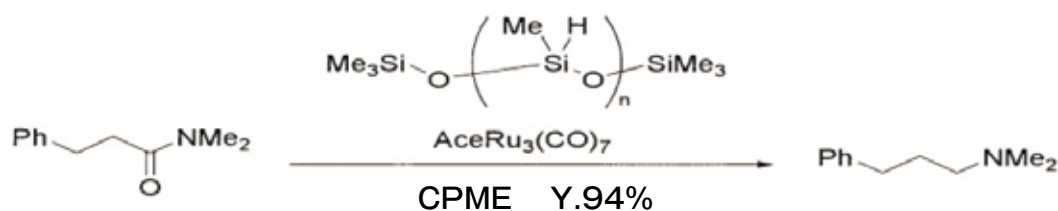
5-1 NaBH₄ reduction

Daiichi Sankyo Co., Ltd. WO2004/060851



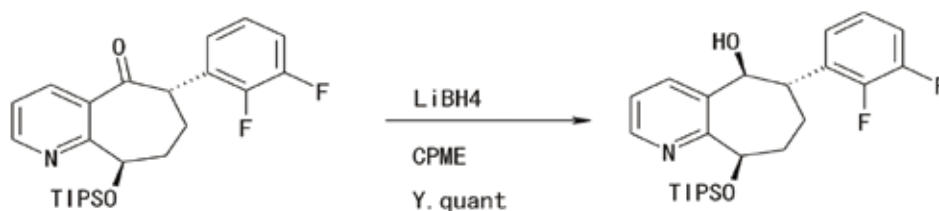
5-2 Reduction

Professor-Nagashima JP2006-282651



5-3 LiBH₄ reduction

Bristol-Myers Squibb, US2009/0258866, US8, 044, 043



5-4 LiAlH₄ reduction

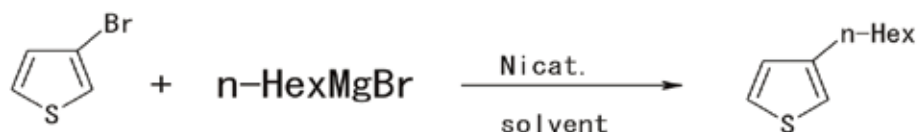
Mitsubishi Tanabe Pharma Corporation, WO2010/114179



6. Reactions with Transition Metal Catalyst

6-1 Tamao-Kumada Coupling

DE-Saltigo WO2008/151920



Lösemittel	3-(1-Methyl-pentyl)thiophen	3-Hexylthiophen	Dithiophen
Cyclopentyl-methylether	0,5	95	0,0
Cyclopentyl-methylether	0,5	90,2	0,2
Cyclopentyl-methylether	0,6	86,5	n.d.
2-Methyltetrahydrofuran	1,1	81,7	3,1
2-Methyltetrahydrofuran	1,1	93,9	n.d.

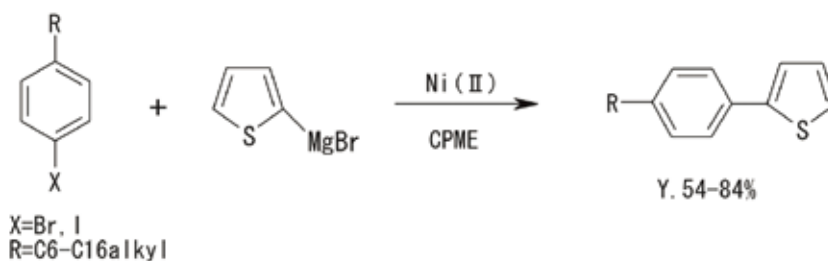
6-2 Heck Carbonylation

Tosoh F-Tech. Inc., JP2004-307488



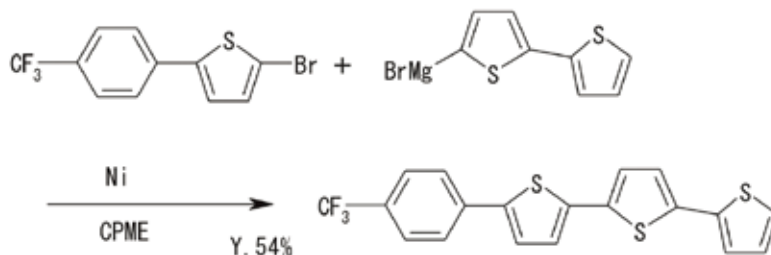
6-3 Tamao-Kumada Coupling

Sumitomo Seika Chemicals Co., Ltd., JP2009-155318



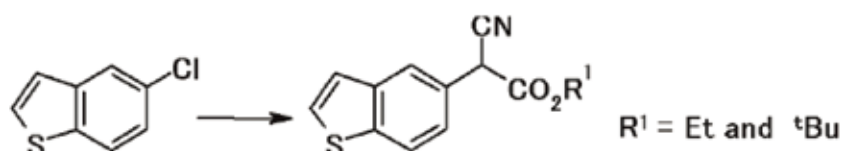
6-4 Tamao-Kumada Coupling

Sumitomo Seika Chemicals Co., Ltd., JP2010-53045



6-5 Cross-coupling

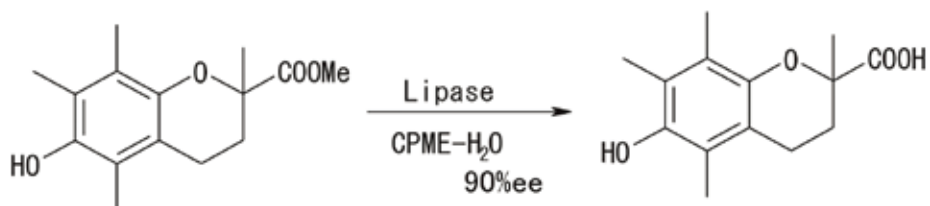
Toyama Chemical Co., Ltd., JP2011-74072



7. Reaction With Lipase

7-1 Hydrolysis

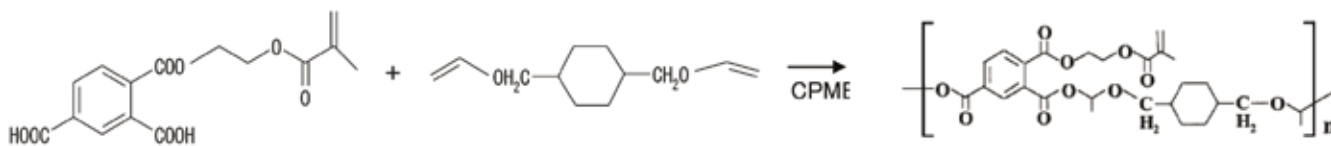
Mitsubishi Gas Chemical Co., Inc., JP2009/278930



8. Polymerisation

8-1 Co-polymer

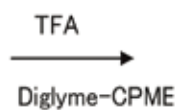
NOF Corporation, JP2008-214604



8-2 Co-polymer

AZ Electronic Materials USA Corp., US2010/119980

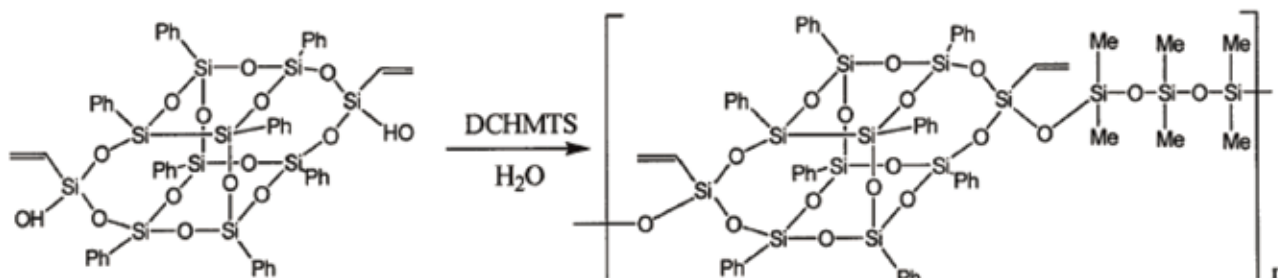
Anthracene + 1-Naphthol + Phenol + 1,3-Adamaantane diol + para formaldehyde



Poly(anthracene-co-1-naphthol-co-phenol-co-adamantane-co-methylene).

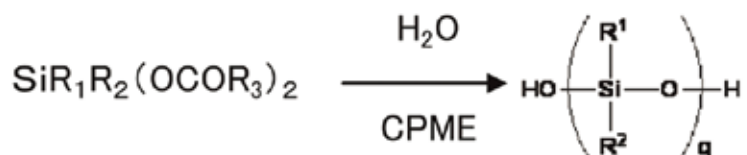
8-3 Co-polymer

JNC Corporation, JP2010-116464



8-4 Co-polymer

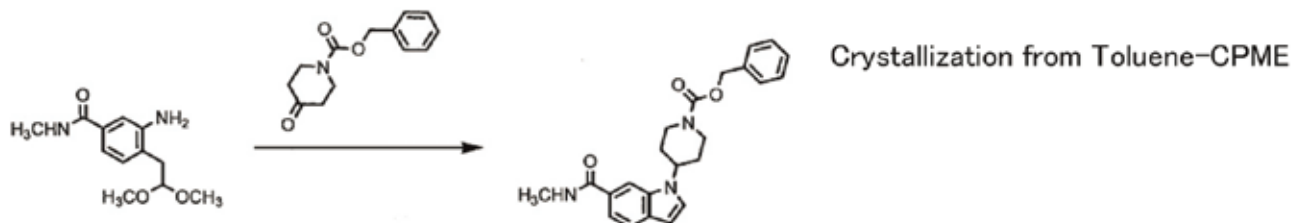
Shin-Etsu Chemical Co., Ltd., JP2011-213701



9. Extraction/Crystallization

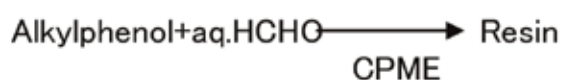
9-1 Crystallization

Eisai Co., Ltd., WO2006/121106



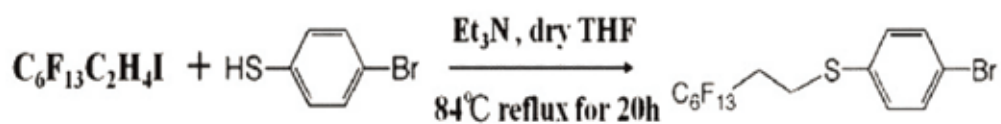
9-2 Extraction

Taaka Chemical Co., Ltd., JP2009-185187



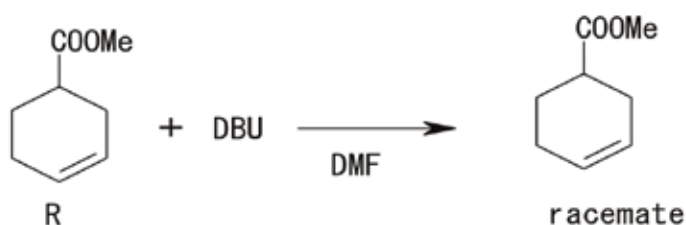
9-3 Extraction

Asahi Kasei Chemicals Corp., JP2010-229042



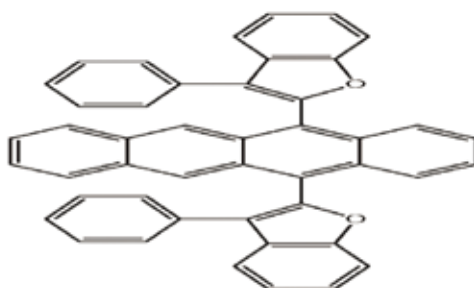
9-4 Extraction

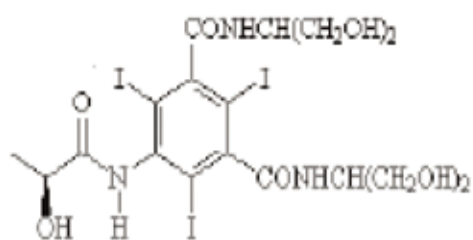
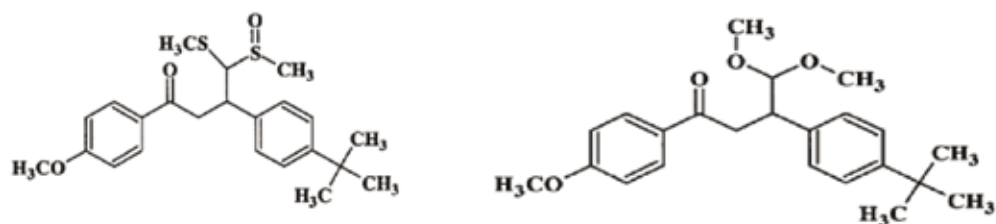
Daiichi Sankyo Co., Ltd. US2011/0257401



9-5 Crystallization

Toray Industries Inc., US2011/0272681



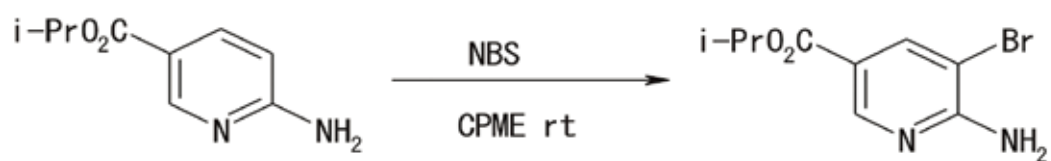


2,5-dihydroxybenzoic acid

10. Others

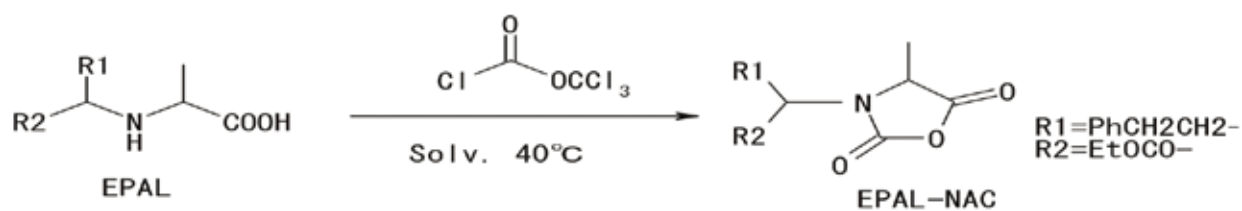
10-1 Bromination

Pfizer Inc., US2007/0219237



10-2 Cyclization

Hodogaya Chemical Co., Ltd., JP2007-63147



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Please read the Safety Data Sheet (SDS) carefully prior to handling.

This product was developed for the application in this brochure. In case of other applications, please handle under your confirmation of safety for the applications, or please talk to Zeon Corporation beforehand.

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