高分子固定化キラル有機分子触媒の開発と不斉反応への応用

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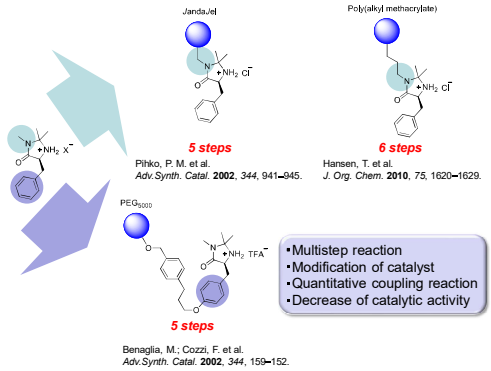
Introduction

Chiral Organocatalyst

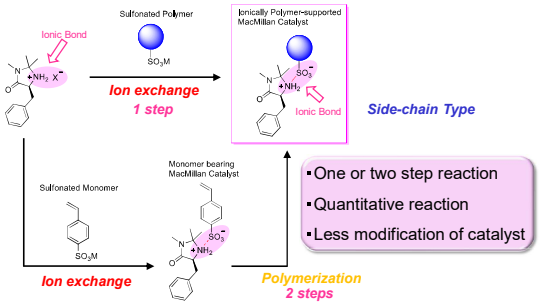
- Metal-free catalyst
- Inexpensiveness
- Stable in air and water
- Simple reaction procedure
- Mild reaction condition

Environmentally Benign Process

Polymer-supported MacMillan catalyst

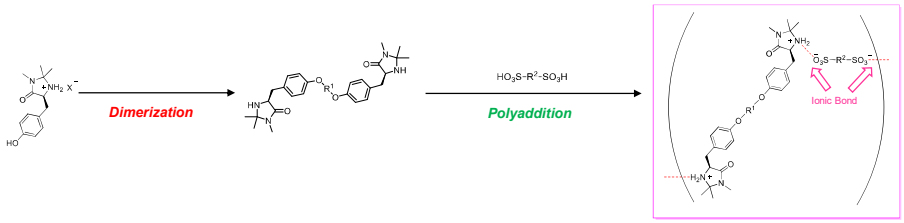


Novel Immobilization of Chiral Imidazolidinone Catalyst onto Polymer



Haraguchi, N.; Takemura, Y.; Itsuno, S. *Tetrahedron Lett.* **2010**, *51*, 1205-1208.

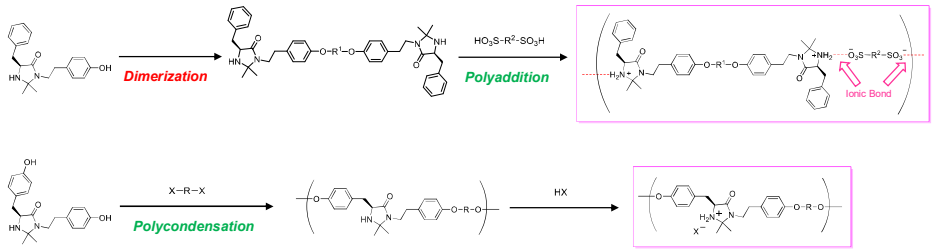
Synthesis of Main-chain Polymer of Chiral Imidazolidinone



Haraguchi, N.; Takemura, Y.; Kiyono, H.; Itsuno, S. *Chem. Commun.* **2012**, *48*, 4011-4013.

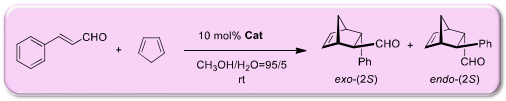
This Work

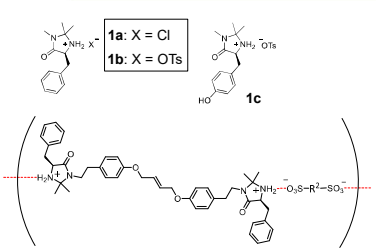
Synthesis of Novel Main-chain Polymers of Chiral Imidazolidinone

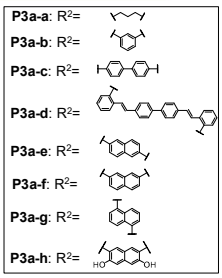


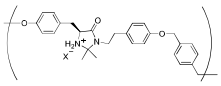
Diels-Alder Reaction

Asymmetric Diels-Alder Reaction using Main-chain Polymers of Chiral Imidazolidinone









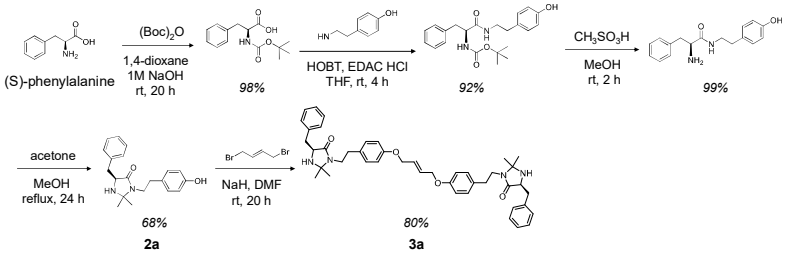
P4a: X= BF_4
P4b: X= CF_3CO_2
P4c: X= CH_3SO_3
P4d: X= CH_3PhSO_3
P4e: X= Cl
P4f: X= ClO_4

Catalyst	Time (h)	Conv. (%)[a]	*exo*:*endo*[a]	ee (*exo*) (%)[b]	ee (*endo*) (%)[b]
1a	7	>99	55:45	93	93
1b	7	>99	55:45	92	88
1c	24	>99	55:45	92	88
2a Cl	24	96	57:43	88	92
2a OTs	4	88	56:44	84	86
3a OTs	4	91	54:46	83	80
P3a-a	24	98	56:44	85	95
P3a-b	24	>99	57:43	84	93
P3a-c	24	>99	56:44	78	92
P3a-d	24	85	56:44	55	63
P3a-e	24	>99	56:44	85	98
P3a-f	24	>99	56:44	85	95
P3a-g	24	>99	56:44	84	98
P3a-h	24	>99	56:44	81	93
P4a	24	>99	54:46	80	91
P4b	24	>99	59:41	86	97
P4c	24	>99	57:43	85	96
P4d	24	64	53:47	73	77
P4e	24	>99	61:39	86	95
P4f	24	99	55:45	76	92

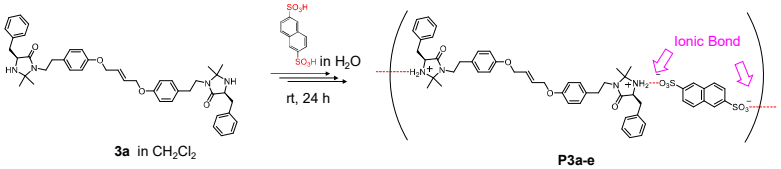
[a] by ^{1}H NMR. [b] by GC (CHIRALDEX B-PH).

Synthesis

Synthesis of Chiral Imidazolidinone Dimers



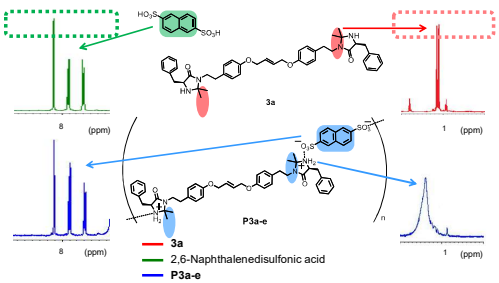
Synthesis of Ionic Polymer with MacMillan Catalyst



3a in CH_2Cl_2

P3a-e
91% yield

^{1}H NMR



Solubility Test

Monomer or Polymer	Hexane	CH_2Cl_2	CH_3OH	DMF	DMSO	H_2O
3a	−	+	+	+	+	−
Disulfonic Acid	−	−	+	+	+	+
P3a-e	−	−	−	+	+	−

+ : Soluble　- : Insoluble

Reuse of P3a-e in Asymmetric Diels-Alder Reaction

Cycle	Time (h)	Conv. (%)[a]	*exo*:*endo*[b]	ee (*exo*) (%)[b]	ee (*endo*) (%)[b]
1	8	99	58:42	93	98
2	24	86	57:43	91	91
3	48	99	56:44	93	95
4	72	81	57:43	93	92

[a] by ^{1}H NMR. [b] by GC (CHIRALDEX B-PH).