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Immobilization of MacMillan Imidazolidinone as Mac-SILC and its Catalytic Performance on Sustainable Enantioselective Diels–Alder Cycloaddition

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Abstract: MacMillan's imidazolidinone catalyst was immobilized as a supported ionic liquid catalyst (Mac-SILC) in the pores of silica gel with the aid of an ionic liquid – 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. The heterogenized organocatalyst was utilized for the enantioselective Diels–Alder reaction of cyclopentadiene and cinnamaldehyde, recovered by simple filtration and subsequent evacuation, and repeatedly used up to six times in 81% average chemical yield, 87% *ee* for *endo*- and 80% *ee* for *exo*-products. The Mac-SILC was effective for a variety of substrates.

Keywords: asymmetric catalysis; catalyst recycling; heterogeneous catalysis; ionic liquids; organocatalysis; supported catalysts

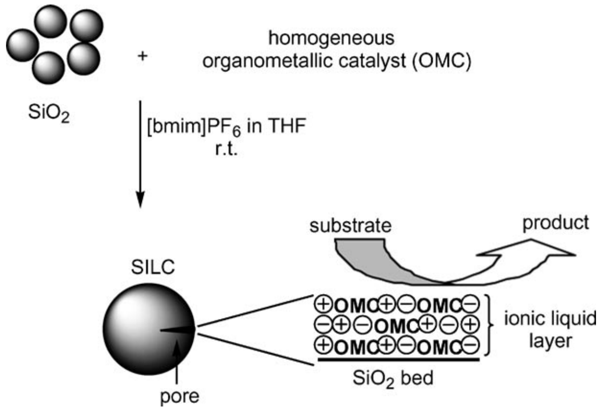
Introduction

The importance of catalytic reactions in organic synthesis is ever increasing in the context of green and sustainable chemistry. Among a variety of catalysts, organocatalysts are attracting considerable attention due to their simple design, easy reproduction and safe disposal, which is more sustainable, environmentally friendly, and cost effective and complementary to homogeneous organometallic catalysts.[1] However, homogeneous organomolecular catalysts have some drawbacks, such as low turnover number, low stability and difficulty in recycle use. One obvious way to address these issues is to immobilize the catalytic residue on a support.[2]

Dissolving organocatalysts in liquid supports, such as an ionic liquid, polyethylene glycol, fluorous solvent, or water is a very facile immobilization method that does not modify the original structure, add extra reagents, or lose the original catalytic activity, of which an ionic liquid has very special and characteristic properties, including non-lipophilicity, non-hydrophilicity and non-volatility.[3] In addition, immiscibility with other organic solvents, as well as water, should provide a good support for the immobilization of organocatalyst residues. However, the large-scale use of an ionic liquid is limited due to the high cost and tedious extraction of products from the viscous ionic liquid.

We previously confined a solution of homogeneous organometallic catalysts in an ionic liquid in the pores of an inorganic amorphous solid as a supported ionic liquid catalyst (SILC) (Scheme 1).[4,5] The procedure is simple, mild and cost-effective. The SILC was recycled by simple filtration without any pre-treatment. Palladium, copper and ruthenium were immobilized according to the SILC method, and exhibited both a sustainable nature and higher catalytic activities than their homogeneous counterparts.

The MacMillan imidazolidinone (Mac) is a very versatile organocatalyst (Figure 1),[6] which catalyzes enantioselective Diels–Alder reactions,[6a,b] 1,3-dipolar



Scheme 1. Immobilization of homogeneous organometallic catalysts as SILC.

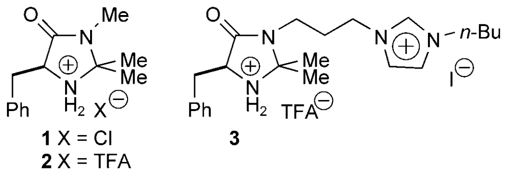
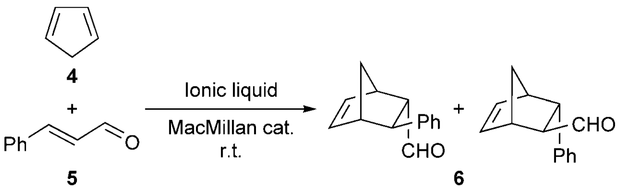


Figure 1. MacMillan catalysts.



Scheme 2. Effect of ionic liquids in the enantioselective Diels–Alder reaction.

cycloadditions,[6c] Friedel–Crafts alkylations,[6d] indole alkylations,[6e] and α-halogenations of aldehydes.[6f] The practical total synthesis of (−)-oseltamivir by Fukuyama and co-workers exemplified its catalytic value in the enantioselective Diels–Alder reaction.[7] Despite its success, the catalyst has the characteristic drawbacks of an organocatalyst. To address these issues, the MacMillan catalyst was covalently immobilized on JandaJel,[8] PEG,[9] polymer capsules,[10] liquid crystals,[11] fluorous solvent[12] or silica.[13] Alternatively, non-covalent immobilization was carried out by incorporation into dendrimers,[14] entrapment in montmorillonite[15] or ionic bonding on polymers,[16] although successful recycle use has yet to be explored in both covalent and non-covalent immobilizations.

Based on these findings, we investigated the non-covalent immobilization of the MacMillan catalyst as a Mac-SILC, and its catalytic performance in an enantioselective Diels–Alder reaction. Since the present Diels–Alder reaction proceeds *via* the iminium cation intermediate and related polar transition states, the ionic liquid in silica gel pores is expected to play the role of a sustainable reaction medium, as well as activator of the catalytic reaction.

Results and Discussion

Preparation and Optimization of Mac-SILC

MacMillan catalysts **1** and **2** (Figure 1) were easily prepared in accordance with reports in the literature.[6a,b] Although there is one precedent of a catalytic reaction in an ionic liquid,[17] the optimal ionic liquid was re-investigated prior to immobilization as Mac-SILC, using the Diels–Alder reaction of cinnamaldehyde and cyclopentadiene in an ionic liquid at room temperature for 24 h (Scheme 2). The results are shown in Table 1. Since MacMillan catalysts are not easily soluble in ionic liquids, dichloromethane was initially added to the mixture and evaporated after dissolution. Cinnamaldehyde was used directly from the bottle, after confirming its purity by NMR. The *endo*/*exo* selectivity was determined by NMR spectroscopy to be almost comparable as in the reaction in homogeneous precedents.[6a,b] The enantiomeric excess was obtained by HPLC after reduction of the Diels–Alder products by sodium borohydride. The 2*S*,3*S* absolute stereochemistries of each of the *endo*- and *exo*-products **6** were determined by a comparison of the optical rotations.[18] The Diels–Alder reaction was dependent on the counter anions of the ionic liquids, in which [bmim]PF_6 and [bmim]NTf_2 exhibited comparable chemical yields, irrespective of the counter anions of MacMillan catalysts **1** and **2** (Table 1, entries 1–3). Enantioselectivity was better in [bmim]NTf_2. Complete recovery of the starting materials in entries 4–7 has yet to be discussed.

Then, MacMillan imidazolidinone catalysts **1**–**3**[19] were immobilized with [bmim]PF_6 or [bmim]NTf_2 as Mac-SILC-**1** to Mac-SILC-**10** (Scheme 3 and Table 2). A slurry of amorphous silica gel in a dichloromethane

Table 1. Investigation of an optimal ionic liquid in enantioselective Diels–Alder reaction.

Entry[a]	Catalyst	Ionic liquid	Yield [%][b]	*endo*:*exo*[c]	*ee* [%][d]	
					endo	*exo*
1	**1**	[bmim]PF_6	62	1:1.1	73	69
2	**1**	[bmim]NTf_2	67	1:1.2	92	72
3	**2**	[bmim]NTf_2	76	1:1.3	93	90
4	**2**	[bmim]TFA	0			
5	**1**	[bmim]TFA	0			
6	**1**	[bmim]Cl	0			
7	**1**	[bmim]Br	0			

[a] Reaction was carried out with 0.1 equiv of the MacMillan catalyst at room temperature in 24 h. Cinnamaldehyde was used directly from the bottle.

[b] Isolated pure product based on the aldehyde.

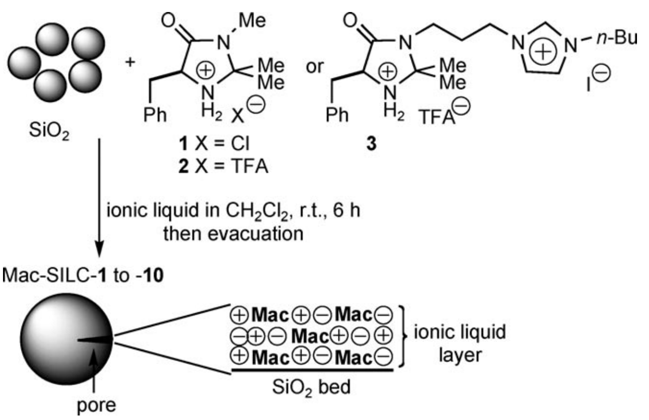
[c] Determined by ^1H NMR.

[d] Determined by HPLC of the alcohol after reduction of the formyl group.

Table 2. Immobilization of MacMillan catalysts **1**–**3** as Mac-SILC-**1** to Mac-SILC-**10**.

Entry	SILC	Catalyst	Support	Ionic liquid (wt%)	Loading [mmol g^{-1}]
1	Mac-SILC-**1**	1	silica gel-1[a]	[bmim]PF$_6$ (10)	0.148
2	Mac-SILC-**2**	1	silica gel-1[a]	[bmim]PF$_6$ (20)	0.152
3	Mac-SILC-**3**	1	silica gel-1[a]	[bmim]PF$_6$ (50)	0.135
4	Mac-SILC-**4**	1	silica gel-1[a]	[bmim]NTf$_2$ (20)	0.140
5	Mac-SILC-**5**	2	silica gel-1[a]	[bmim]NTf$_2$ (20)	0.131
6	Mac-SILC-**6**	3	silica gel-1[a]	[bmim]NTf$_2$ (20)	0.054
7	Mac-SILC-**7**	3	silica gel-1[a]	[bmim]NTf$_2$ –	0.162
8	Mac-SILC-**8**	2	silica gel-2[b]	[bmim]NTf$_2$ (20)	0.106
9	Mac-SILC-**9**	2	silica gel-3[c]	[bmim]NTf$_2$ (20)	0.021
10	Mac-SILC-**10**	2	Al$_2$O$_3$	[bmim]NTf$_2$ (20)	0.043

[a] Pore volume: 0.80–1.0 mL g^{-1}.
[b] Pore volume: 1.22 mL g^{-1}.
[c] Mercaptopropylated silica gel.



Scheme 3. Immobilization of MacMillan catalysts as Mac-SILC.

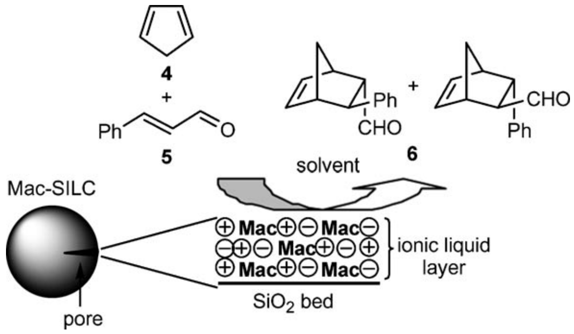
solution of the MacMillan catalyst and the ionic liquid was stirred at room temperature for 6 h, and evaporated to dryness under vacuum to give a free-flowing powder. The amount of ionic liquid did not affect the amount of catalyst loading (Table 2, entries 1–3), while the catalytic activity was dependent on the amount of ionic liquid (see Table 3, entries 1–3). On the other hand, the level of immobilization of ionic liquid tagged-catalyst **3** was not sufficient compared with imidazolidinones **1** or **2** (Table 2, entry 6), although catalyst **3** was confined sufficiently without the ionic liquid (Table 2, entry 7). Similarly, surface-modified silica gel (Table 2, entry 9) or alumina (Table 2, entry 10) was not suitable for the immobilization of a sufficient amount of MacMillan catalyst **2**.

Subsequently, an optimized Mac-SILC was investigated for the Diels–Alder reaction of cinnamaldehyde

Table 3. Investigation of an optimal Mac-SILC in the enantioselective Diels–Alder reaction.

Entry[a]	Mac-SILC	Solvent	Time [h]	Yield [%][c]	*endo*:*exo*[d	*ee* [%][e]	
						endo	*exo*
1[b]	Mac-SILC-**1**	95% EtOH	35	49	1:1.1	92	93
2	Mac-SILC-**1**	95% EtOH	47	67	1:1.1	95	92
3	Mac-SILC-**2**	95% EtOH	27	73	1:1.1	95	90
4	Mac-SILC-**2**	95% *i*-PrOH	27	69	1.1:1	96	94
5	Mac-SILC-**3**	95% *i*-PrOH	20	67	1:1	85	81
6	Mac-SILC-**2**	*t*-amylOH	22	60	1:1.2	83	77
7	Mac-SILC-**4**	*t*-amylOH	22	69	1:1.4	87	81
8	Mac-SILC-**5**	*t*-amylOH	22	74	1:1.2	92	80
9	Mac-SILC-**6**	*t*-amylOH	24	52	1:1.3	71	64
10	Mac-SILC-**7**	*t*-amylOH	22	50	nd[f]	nd[f]	nd[f]
11	Mac-SILC-**9**	*t*-amylOH	22	0			
12	Mac-SILC-**10**	*t*-amylOH	22	0			

[a] 0.1 equiv. of Mac-SILC was employed.
[b] 0.05 equiv. of Mac-SILC was employed.
[c] Isolated pure product based on aldehyde.
[d] Determined by ^{1}H NMR.
[e] Determined by HPLC of alcohol after reduction of the formyl group.
[f] Not determined.



Scheme 4. Screening of Mac-SILC in the enantioselective Diels–Alder reaction.

and cyclopentadiene at room temperature (Scheme 4). Since 0.05 equiv. of Mac-SILC was not sufficient to complete the reaction (Table 3, entry 1), 0.1 equiv. of Mac-SILC was used for further reactions. Reactions catalyzed by Mac-SILC-**2** and Mac-SILC-**3** proceeded much faster than those catalyzed by Mac-SILC-**1** (Table 3, entries 2 and 5), which indicates that 20 wt% of an ionic liquid is optimal for immobilization and the subsequent catalytic reaction. The importance of an ionic liquid as both a liquid support and a reaction medium is shown in Table 2, entries 6 and 7, and Table 3, entry 10, in which MacMillan catalyst **3**, immobilized on silica gel without an ionic liquid, exhibited unsatisfactory catalytic activity.

Mac-SILC-**2**, Mac-SILC-**4** and Mac-SILC-**5** were chosen as candidates for recycle experiments, since their catalytic performances were comparable to each other, and better than those of Mac-SILC-**1**, Mac-SILC-**3**, Mac-SILC-**6** and Mac-SILC-**7**. Mac-SILC was re-used after simple filtration and subsequent evacuation. The second use of Mac-SILC-**2** decreased the chemical yields substantially (Table 4, entries 1 and 2) in aqueous ethanol. The decrease was believed to be mainly caused by leaching and loss of the MacMillan catalyst from Mac-SILC, even though less hydrophilic [bmim]PF_6 was employed for immobilization. The MacMillan catalyst is less soluble in isopropylalcohol, and recycle use in this solvent gave no improvement (Table 4, entries 3 ~ 5). Thus, attention was focused on the more hydrophobic *t*-amyl alcohol without adding water to prevent leaching of the MacMillan catalyst; MacMillan catalysts **1** and **2** were not soluble in *t*-amyl alcohol. Although recycle use of Mac-SILC-**5** in the solvent was not improved (Table 4, entry 7), Mac-SILC-**4** could be recycled satisfactorily (Table 4, entries 8–11). This result shows the importance of the counter anion of the MacMillan catalyst, as well as the solvent in recycle use. Different from primary alcohols, formation of acetals of **6** was not observed, which is an additional aspect in favour of employing bulky *t*-amyl alcohol. The less hydrophilic *n*-heptanol did not give a satisfactory result (Table 4, entries 12 ~ 14).

Recycle Use of Mac-SILC

With the optimized reaction condition in hand (Table 4, entry 8), recycle use of the Mac-SILC-**4** (MacMillan catalyst **1** in silica gel pores with the aid of 20 wt% of [bmim]NTf_2) was newly investigated (Scheme 5) and the results are compiled in Table 5.

Table 4. Investigation on recycle use of Mac-SILC in the enantioselective Diels–Alder reaction.

Entry[a]	Mac-SILC	Solvent	Time [h]	Yield [%][b]	*endo*:*exo*[c]	*ee* [%][d] *endo*	*exo*
1	Mac-SILC-**2**	95% EtOH	27	73	1:1.1	95	90
2	Mac-SILC-**2**	95% EtOH	27	23	1:1	88	92
3	Mac-SILC-**2**	95% *i*-PrOH	27	69	1.1:1	96	94
4	Mac-SILC-**2**	95% *i*-PrOH	30	53	1:1	88	92
5	Mac-SILC-**2**	95% *i*-PrOH	40	25	1:1	86	87
6	Mac-SILC-**5**	*t*-amylOH	22	74	1:1.2	92	86
7	Mac-SILC-**5**	*t*-amylOH	25	31	1:1.1	80	79
8	Mac-SILC-**4**	*t*-amylOH	22	69	1:1.2	87	81
9	Mac-SILC-**4**	*t*-amylOH	25	67	1:1.2	88	83
10	Mac-SILC-**4**	*t*-amylOH	29	56	1:1.2	89	83
11	Mac-SILC-**4**	*t*-amylOH	41	48	1:1.2	87	83
12	Mac-SILC-**4**	*n*-heptanol	22	67	1:1.1	93	89
13	Mac-SILC-**4**	*n*-heptanol	25	63	1:1.1	90	90
14	Mac-SILC-**4**	*n*-heptanol	29	52	1:1.1	nd[e]	nd[e]

[a] 0.1 equiv. of Mac-SILC was employed, which was re-used intact after filtration and evacuation.
[b] Isolated pure product based on aldehyde.
[c] Determined by ^1H NMR.
[d] Determined by HPLC of alcohol after reduction of the product.
[e] Not determined.

Table 5. Optimized-recycle use of Mac-SILC-**4** in the enantioselective Diels–Alder reaction.

Entry[a]	Time [h]	Yield [%][b]	*endo*:*exo*[c]	*ee* [%][d]	
				endo	*exo*
0[e]	22	64	1:1.2	90	84
1[f]	22	96	1:1.2	93	89
2	25	89	1:1.1	92	88
3	29	79	1:1.1	90	88
4	39	80	1:1.1	88	86
5	45	78	1:1.1	85	84
6	56	62	1:1.1	76	77

[a] Reaction was carried out with 0.1 equiv. of Mac-SILC-**4** in *t*-amyl alcohol at room temperature. The catalyst was re-used intact after evacuation.

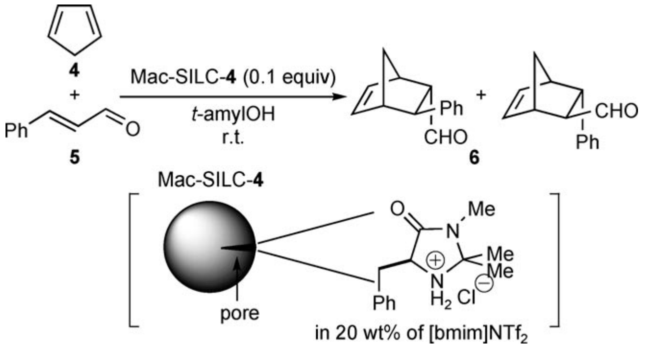
[b] Isolated pure product based on aldehyde.

[c] Determined by ^{1}H NMR.

[d] Determined by HPLC of alcohol after reduction of the formyl group.

[e] Cinnamaldehyde was used in 7 h after MPLC purification.

[f] Cinnamaldehyde was used in 3 h after MPLC purification in each recycle experiment.



Scheme 5. Optimized recycle use of Mac-SILC-**4** in the enantioselective Diels–Alder reaction.

During the course of the recycle experiments, it was found that cinnamaldehyde should be used soon after purification by medium pressure LC to allow better chemical yield (Table 5, entries 0 and 1), even though stock cinnamaldehyde was deemed pure by NMR spectroscopy. To this end, Mac-SILC-**4** was used repeatedly up to 6 times after simple filtration and subsequent evacuation in 81% average yield; 87% *ee* for *endo*- and 80% *ee* for *exo*-products. MacMillan catalyst **1** was stable at 60 °C for 6 h in a solution of [bmim]NTf$_2$ and THF. In contrast, MacMillan catalyst **1** partially leached out from Mac-SILC-**4** after 24 h stirring at room temperature in aqueous ethanol and was recovered intact. These results suggest that the gradual decrease of reactivity of Mac-SILC-**4** in the recycle use might be mainly due to leaching of MacMillan catalyst **1** from Mac-SILC **4**, not decomposition of MacMillan catalyst **1**.

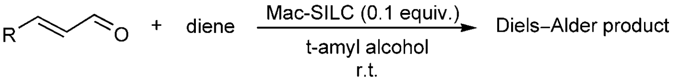
Scope of Mac-SILC-4

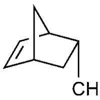
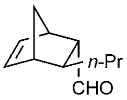
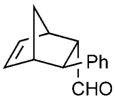
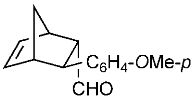
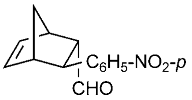
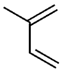
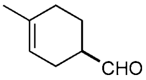
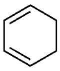
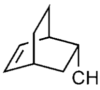
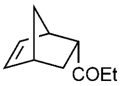
The catalytic activity of Mac-SILC-**4** was common for a variety of substrates (Table 6). The present protocol was applicable and effective for various dienes with both electron-poor and electron-rich substituents. Especially noteworthy is the reaction of electron-rich *p*-methoxycinnamaldehyde, which was not successful either by homogeneous MacMillan catalyst or conventional Lewis acid, such as trimethylaluminum, ytterbium triflate or borontrifluoride etherate (Table 6, entry 5). This result indicates that the immobilization as Mac-SILC reinforced the catalytic activity of the original MacMillan catalyst. The low *endo*-selectivity might be due to inherent steric crowding of the imidazolidinone moiety.

Conclusions

In summary, the MacMillan imidazolidinone organocatalyst was non-covalently immobilized as a Mac-SILC in the pores of silica gel with the aid of the ionic liquid [bmim]NTf$_2$, and was successfully applied to the enantioselective Diels–Alder reaction in open air at room temperature, without changing the original catalytic activity. Furthermore, it could be re-used after simple filtration up to six times in 81% average chemical yield, 87% *ee* for *endo*- and 80% *ee* for *exo*-products. Mac-SILC is more active, especially to an electron-rich dienophile, than its homogeneous counterparts, and the required reaction conditions are so mild that it might be applicable to highly functionalized but unstable substrates. The immobilization protocol is simple, practical and cost-effective without chemically modifying the original catalyst or support, and is a powerful tool as a method of soft immobilization of highly sophisticated organomolecular catalysts,

Table 6. Scope of Mac-SILC-**4** in the enantioselective Diels–Alder reaction.



Entry[a]	Dienophile R=	Diene	Product	Time [h]	Yield [%][b]	*endo*:*exo*[c]	*ee* [%][d] *endo*	*exo*
1	H (**7**)	**4** 	*endo*-**8**[8] 	22	58	3.4:1	47	–[f]
2	Me (**9**)		*endo*-**10**[6a] 	22	61	1:1	83	–
3	*n*-Pr (**11**)		*endo*-**12**[6a] 	22	78	1:1	86	72
4	Ph[f] (5)		*endo*-**6**[6a] 	22	96	1:1.2	93	89
5	*p*-MeOC$_6$H$_4$ (**13**)		*endo*-**14**[21] 	46	76	1:1.2	92	86
6	*p*-NO$_2$C$_6$H$_4$ (**15**)		*endo*-16[22] 	22	91	1:1.2	87	80
7[g]	H (**7**)	**17** 	**18**[6a] 	26	80 (87)[h]		93[i]	26
8[g]	H (**7**)	**19** 	*endo*-**20**[6a] 	48	80 (84)[h]	18:1	80[i]	–[j]
9	Ethyl vinyl ketone (**21**)	**4** 	*endo*-**22**[23] 	24	85	8:1	0	0

[a] Reaction was carried out with 0.1 equiv. of Mac-SILC-**4** in *t*-amyl alcohol at room temperature.
[b] Isolated pure product based on the aldehyde.
[c] Determined by ^{1}H NMR.
[d] Determined by HPLC of the alcohol after reduction of the formyl group.
[e] Enantiomers were not separable by HPLC of alcohol after reduction of the formyl group.
[f] Cinnamaldehydes were used soon after MPLC purification.
[g] Reaction was carried out in a sealed tube.
[h] Isolated pure product based on diene.
[i] Determined by GLC.
[j] Enantiomers were not separable by GLC.

a method that so far cannot be conducted by simple impregnation.

Experimental Section

General Remarks

MacMillan catalysts were prepared according to the literature precedent.[6a,b] Cinnamaldehyde was purified by medium pressure LC before use. Other chemicals were used directly from bottles. Silica gel for column chromatography (Kanto Chemical Co., particle size: 63–210 μm, pore size: 5.0~7.0 nm, pore volume: 0.80–1.00 mL g^{-1}) was used for immobilization after drying by microwave irradiation. Structures of products and the *exo*/*endo* ratios were determined by ^{1}H NMR spectroscopy with a JEOL EX-270 spectrometer (270 MHz). The enantiomeric excess was determined by Hitachi L-7100 high-pressure LC system employing a CHIRALCELL OJ-H column.

Preparation of the Catalyst Mac-SILC-4

A mixture of silica gel powder (4 g, dried by microwave irradiation for 5 min twice prior to use), the MacMillan imidazolidinone catalyst **1** (200 mg, 0.785 mmol), [bmim]NTf$_2$ (800 mg, 20 wt% to silica gel) in a dichloromethane solution (16 mL) was stirred for 6 h at room temperature under a nitrogen atmosphere. After evaporation of dichloromethane, the silica gel powder was rinsed with ether (15 mL) 5 times. Evaporation of the ether under vacuum left a mixture of [bmim]NTf$_2$ (38 mg) and MacMillan catalyst **1** (19 mg) by NMR analysis. Thus, the amount of loading of the MacMillan catalyst **1** as Mac-SILC-**4** was evaluated as 0.144 mmol g^{-1}.

General Procedure for the Diels–Alder Reaction

A mixture of the Mac-SILC-**4** (177 mg, 0.025 mmol, MacMillan catalyst **1** loading: 0.141 mmol g^{-1}), cyclopentadiene **4** (103 mL, 1.25 mmol), cinnamaldehyde **5** (32 mL, 0.25 mmol, used soon after purification by medium pressure liquid chromatography) in a solution of *t*-amyl alcohol (0.3 mL) was stirred at room temperature for 22 h in open air. After the addition of ether, the organic layer was removed by decantation. Evaporation of the solvent followed by medium pressure liquid chromatography (eluent: ethyl acetate:*n*-hexane = 1:9) of the residue afforded a mixture of the Diels–Alder products **6** (yield: 48 mg, 96%), in which the *exo*/*endo* ratio was determined by ^{1}H NMR.

The recovered Mac-SILC-**4** was employed for the next reaction after evacuation under vacuum.

Determination of Enantioselectivity of the Diels–Alder Products

Sodium borohydride (27 mg, 0.72 mmol) was added to a stirred solution of *endo*/*exo* mixtures of aldehydes **6** (48 mg, 0.24 mmol) in methanol (1.0 mL) at 0 °C. After the solution was stirred at room temperature for 1 h, the reaction was quenched by the addition of aqueous ammonium chloride. The product was extracted with ether and the combined organic layer was washed with water and brine. Evaporation of the solvent followed by medium pressure LC provided *exo*-alcohol (yield: 19 mg, 40%) and *endo*-alcohol (yield: 19 mg, 39%), in which the enantiomeric excess was analyzed by high pressure LC employing CHIRALCELL OJ-H column (eluent: isopropyl alcohol:*n*-hexane = 1:9.5). Retention times of *endo*-alcohols were 16.0 min for the *R* isomer and 30.66 min for the *S* isomer. Retention times of *exo*-alcohols were 40.38 min for the *R* isomer and 54.62 min for the *S* isomer.

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