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HETEROGENEOUS LEWIS ACID CATALYSIS WITH SELF-ORGANIZED POLYMERIC RARE EARTH ARYLSULFONATES UNDER SOLVENT-FREE CONDITIONS

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[§]Dedicated to Professor Emeritus Keiichiro Fukumoto (Tohoku University) on the occasion of the 75th anniversary of his birth.

Abstract – Polymeric rare earth arylsulfonates, easily prepared from rare earth triisopropoxides and biphenyl-4,4'-disulfonic acid (BPDSA) or 1,3,5-triphenylbenzene trisulfonic acid (TPTSA) in a self-organization manner, were found to work as an efficient heterogeneous Lewis acid catalyst for the hetero-Diels–Alder reaction of aldehydes with the Danishefsky's diene and the ring-opening reaction of epoxides with amines under solvent-free conditions. The catalysts could be quantitatively recovered and reused many times without decreasing their activities.

INTRODUCTION

Solid metal complex catalysts that can promote the reaction under heterogeneous conditions have attracted much attention from an environmental as well as a practical point of view, since they may easily be recovered from the reaction mixture by simple filtration or decantation, and then reused. In this context, a variety of heterogeneous catalysts such as inorganic materials-supported,¹ insoluble organic polymer-supported,² and dendritic metal complexes³ have so far been developed. In general, however, they show lower activities and selectivities compared to the corresponding homogeneous catalysts, and

furthermore, their preparations are often onerous. On the other hand, coordination polymer-type complexes can be easily prepared *via* self-organization process by the simple mixing of metal ions, multi-way ligands, and other components of the catalysts, in which the catalytic centers may be regularly dispersed and properly accumulated in a controlled manner by the spacers used.^{4,5}

Since the characteristic nature of rare earth metal ions, such as strong Lewis acidity, large ionic radius, and high coordination number, was expected to be advantageous for the formation of such coordination polymer catalysts,⁶ we synthesized novel self-organized polymeric rare earth arylsulfonates, $\text{RE}_2(\text{BPDS})_3$ (BPDS=biphenyl-4,4'-disulfonate) and $\text{RE}(\text{TPTS})$ (TPTS=1,3,5-triphenylbenzene trisulfonate), bearing biphenyl or triphenylbenzene moieties as a unbending spacer,^{7,8} and examined their activities and reusabilities as heterogeneous catalysts in the following two reactions: the hetero-Diels–Alder reaction of aldehydes with the Danishefsky's diene^{9,10} and the ring-opening reaction of epoxides with amines.^{11,12} The former reaction is a useful means to synthesize six-membered heterocyclic compounds in one step, and the latter provides an easy access to β -amino alcohols with 1,2-*trans* stereochemistry.

RESULTS AND DISCUSSION

The catalysts, $\text{RE}_2(\text{BPDS})_3$ and $\text{RE}(\text{TPTS})$, were conveniently prepared by the mixing of rare earth (RE) triisopropoxide with biphenyl-4,4'-disulfonic acid (BPDSA) in 2:3 ratio or with 1,3,5-triphenylbenzene trisulfonic acid (TPTSA) in 1:1 ratio, respectively, in refluxing THF (Scheme 1). Elementary analysis of these catalysts revealed that they exist as the hydrates. They are stable solids, and the SEM image of $\text{Sc}(\text{TPTS})$ is shown in Figure 1.

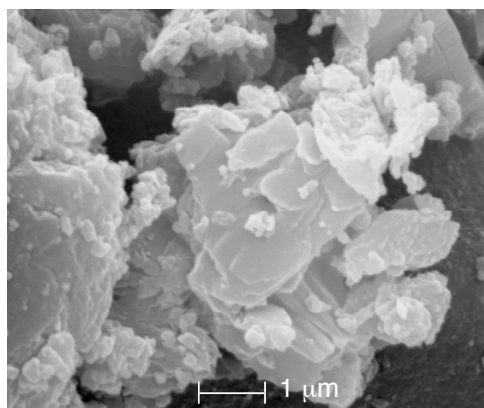
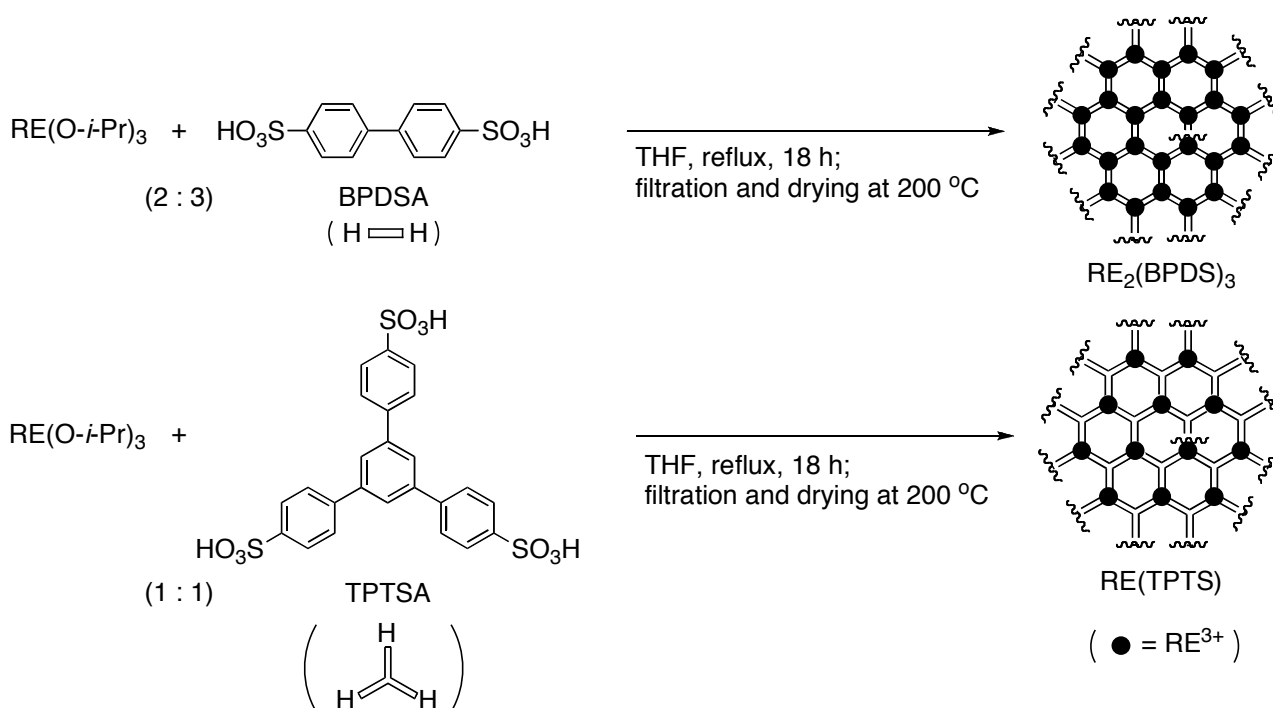


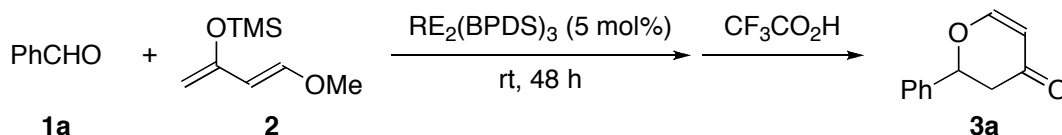
Figure 1. SEM image of $\text{Sc}(\text{TPTS})$ (Au-Pd coating, 200 Å)

For the $\text{RE}_2(\text{BPDS})_3$ (RE = Sc, Y, La, and Yb), effect of the rare earth ions on the catalytic ability was checked in the hetero-Diels–Alder reaction of benzaldehyde (**1a**) with the Danishefsky's diene (**2**) (Table 1).⁷



Scheme 1. Preparation and speculated partial structure of the catalysts

Table 1. Effect of RE metal ion and solvent on the RE₇(BPDS)₃-catalyzed hetero-Diels–Alder reaction

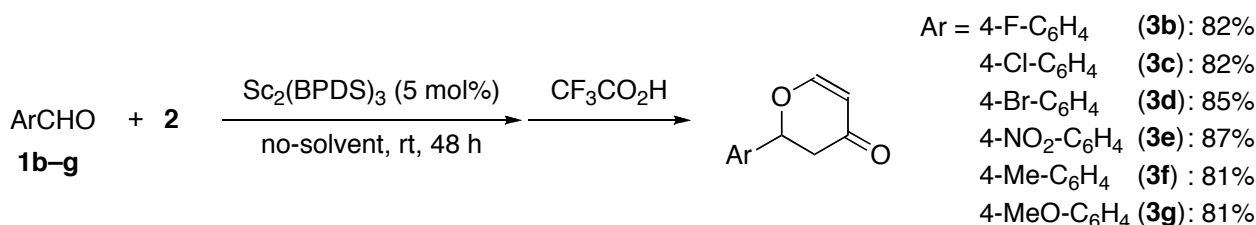


Entry	RE	Solvent	Yield (%) ^a	Entry	RE	Solvent	Yield (%) ^a
1	Sc	CH ₂ Cl ₂	61	6	Yb	none	51
2	Sc	none	90	7	Y	CH ₂ Cl ₂	18
3	Yb	CH ₂ Cl ₂	14	8	Y	none	36
4	Yb	toluene	10	9	La	CH ₂ Cl ₂	9
5	Yb	Et ₂ O	3	10	La	none	28

^a Isolated yield.

As a general trend, the complexes with smaller ionic radii, which are expected to be stronger Lewis acids, afforded better results, and the reaction performed under solvent-free conditions gave higher yields than the reactions in the presence of solvents; the best result was obtained when $\text{Sc}_2(\text{BPDS})_3$ was employed under solvent-free conditions (entry 2 in Table 1). In order to check the possibility of Brønsted acid catalysis by the sulfonic acid moiety located in the edge part of the metal complex, the reaction was carried out in the presence of BPDSA (ca. 0.6 equiv) without $\text{Sc}_2(\text{BPDS})_3$ in dichloromethane for 48 h. Only a trace amount of **3a** was produced indicating that $\text{RE}_2(\text{BPDS})_3$ worked as Lewis acid rather than Brønsted acid. Under the solvent-free conditions, various aromatic aldehydes (**1b–g**) were converted to

the corresponding dihydropyranone derivatives (**3b–g**) in good yields, regardless of the electron-withdrawing or -donating nature of the substituents (Scheme 2).



Scheme 2. Sc₂(BPDS)₃-catalyzed hetero-Diels–Alder reaction under solvent-free conditions

After completion of the reaction, a small amount of diethyl ether was added, and then the catalyst was separated from the product-containing organic compounds by centrifugation. The recovered catalyst could be successfully used for the next round of the reaction after drying in vacuo (Figure 2). Neither decrease of the catalytic ability nor leaching of the metal ion was observed even in the third round of the reaction. The use of Sc(TPTS) for this reaction in the place of Sc₂(BPDS)₃ also provided comparable results.

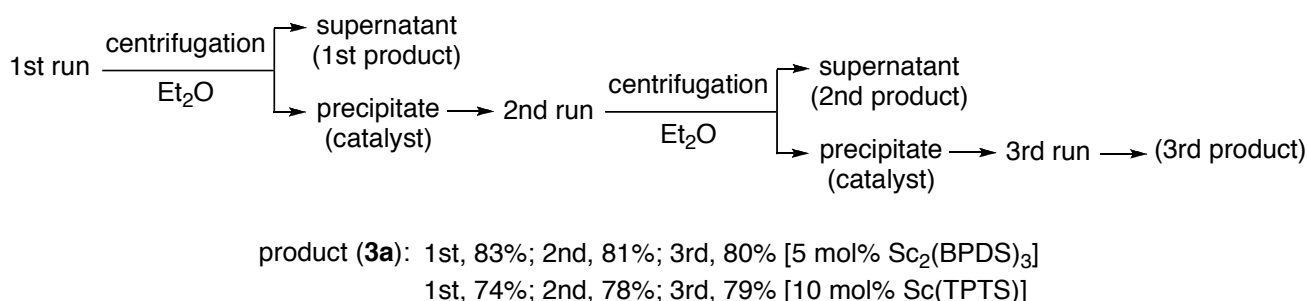
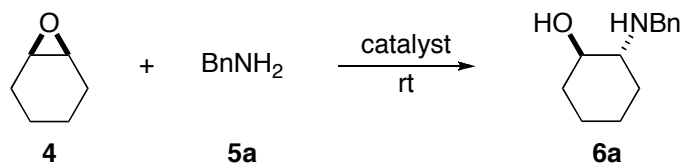


Figure 2. Recovery and reuse of the catalyst for the reaction of **1a** and **2**

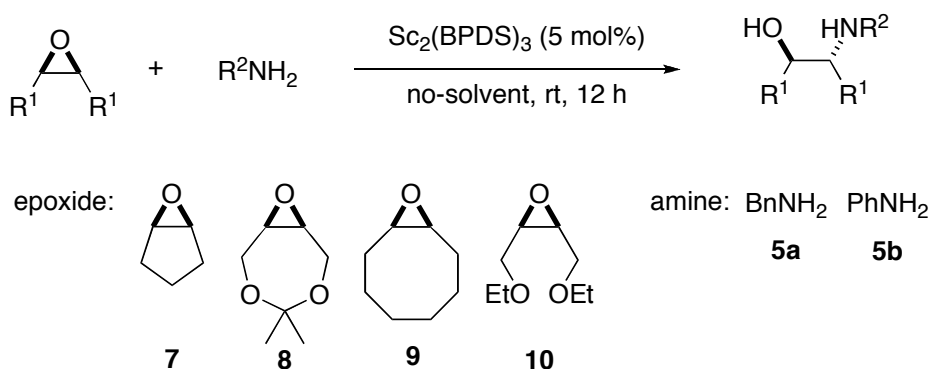
Next, we utilized several RE₂(BPDS)₃ for the catalytic ring-opening reaction of cyclohexene oxide (**4**) with benzylamine (**5a**) (Table 2).⁸ Again the use of the catalysts having relatively small ionic radii like the Sc- and the Yb-catalyst under solvent-free conditions afforded excellent results (entries 6 and 7). In the corresponding reactions performed in the presence of solvents (entries 1–5), only moderate yields of the product were obtained, even in the case where Sc₂(BPDS)₃ was used as the catalyst at 100 °C for 40 h (entry 3). As an additional observation, we found that Sc(OPf)₃ (Pf=SO₂C₈F₁₇), which was previously developed as an efficient catalyst for the hetero Diels–Alder reaction,¹³ effectively catalyzed this reaction under solvent-free conditions; only 1 mol% of the catalyst was found to be enough to complete the reaction (entry 12).

Table 2. Catalytic ring-opening reaction of cyclohexene oxide with benzylamine^a

Entry	Catalyst	Solvent	Time (h)	Yield (%) ^b
1	Sc ₂ (BPDS) ₃	CH ₂ Cl ₂	40	38
2	Sc ₂ (BPDS) ₃	toluene	40	40
3 ^c	Sc ₂ (BPDS) ₃	toluene	40	50
4	Sc ₂ (BPDS) ₃	Et ₂ O	40	21
5	Sc ₂ (BPDS) ₃	THF	40	35
6	Sc ₂ (BPDS) ₃	none	12	99 [99] ^d
7	Yb ₂ (BPDS) ₃	none	12	99
8	Y ₂ (BPDS) ₃	none	12	89
9	La ₂ (BPDS) ₃	none	12	38
10 ^e	Sc(OPf) ₃	toluene	24	30
11 ^e	Sc(OPf) ₃	none	2	99
12 ^f	Sc(OPf) ₃	none	12	99

^a The reactions were carried out by using cyclohexene oxide (1 equiv), amine (1.1 equiv), and catalyst (0.05 equiv) under argon unless otherwise stated. ^b Isolated yield.

^c The reaction carried out at 100 °C. ^d The result of the reaction in air. ^e The catalyst (0.025 equiv) was used. ^f The catalyst (0.01 equiv) was used.

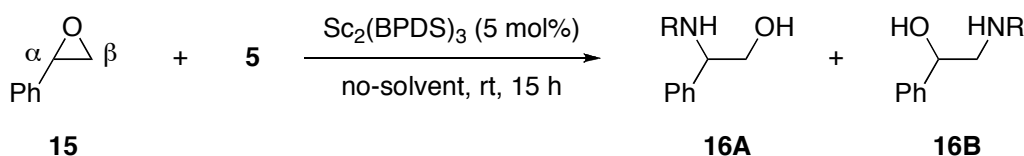
Table 3. Applicability of the Sc₂(BPDS)₃-catalyzed reaction under solvent-free conditions

Entry	Epoxide	Amine	Product	Yield (%) ^a
1	4	5b	6b	99
2	7	5a	11	72
3	8	5a	12a	97
4	8	5b	12b	>99
5	9	5a	13	NR ^b
6	10	5b	14	94

^a Isolated yield. ^b No reaction.

Some scope and limitation of the $\text{Sc}_2(\text{BPDS})_3$ -catalyzed reaction was briefly checked (Table 3 and Scheme 3). Among the *meso*-epoxides examined, five-, six-, and seven-membered ring compounds (**7**, **4**, and **8**, respectively) and an open chain epoxide (**10**) were easily reacted with benzylamine or aniline, however no reaction took place in the case of cyclooctene oxide (**9**) under the given conditions.

In the reactions of styrene oxide (**15**), the β -attacked product (**16B**) was produced preferentially when benzylamine was used, whereas the α -attacked one (**16A**) became major in the case of aniline as a nucleophile. In the latter reaction, due to the weak nucleophilicity of aniline, the transition state would become more ionic than that of the former case thus favoring the selective attack at the benzylic position.



amine **5a** (R=Bn): 90% yield (**16aA**:**16aB**=38:62)

5b (R=Ph): 86% yield (**16bA**:**16bB**=94: 6)

Scheme 3. Regioselectivity on the $\text{Sc}_2(\text{BPDS})_3$ -catalyzed ring-opening reaction of styrene

Finally, we checked the reusability of the catalysts. From the reaction mixture, $\text{Sc}_2(\text{BPDS})_3$ could be almost quantitatively recovered by the addition of diethyl ether to dissolve the product followed by centrifugation. The recovered catalyst was, after drying in vacuo at room temperature, successfully reused (e.g., 5th run, 97% for 12 h; *cf.* entry 6 in Table 2). Similarly, $\text{Sc}(\text{TPTS})$ could also be recovered and efficiently reused (e.g., 6th run, 97% for 12 h). Their original catalytic abilities could completely be regained by vacuum drying upon heating (ca. 400 °C) for five minutes by a heating gun when they dropped down leading to the formation of the desired product in less than 93% yield (e.g., 7th run). Thus, both $\text{Sc}_2(\text{BPDS})_3$ and $\text{Sc}(\text{TPTS})$ could be successfully reused ten times at least. Unfortunately, another effective catalyst, $\text{Sc}(\text{OPf})_3$, could not be effectively reused; the recovered catalyst seriously lost its activity even in the second use.

In conclusion, we succeeded in developing novel self-organized rare earth coordination polymer catalysts, $\text{RE}_2(\text{TPTS})_3$ and $\text{RE}(\text{TPTS})$, and found them as an efficient heterogeneous Lewis acid catalyst for the hetero-Diels–Alder reaction of aldehydes with the Danishefsky's diene and the ring-opening reaction of epoxides with amines under solvent-free conditions. The catalysts are highly practical as they can be prepared in one step, stored at room temperature in air, quantitatively recovered after the reaction, and effectively reused many times without decreasing their activities.

EXPERIMENTAL

IR spectra were taken with JASCO FT/IR-420. ^1H NMR spectra were recorded at 400 MHz on JEOL JMN-EX 400 and expressed as ppm down field from TMS (0 ppm) as an internal standard. Elementary analyses were accomplished at Center of Elementary, Analysis, Faculty of Sciences, Kyushu University. Scanning electron micrograph was taken on a SHIMADZU SUPERSCAN SSX-550 at the Center of Advanced Instrumental Analysis, Kyushu University. TLC was performed on 0.25 mm Merck, Kieselgel 60 F-254 silica gel plate or Fuji Silysia Chemical, NH silica gel plate. Column chromatography was conducted on silica gel 60N 70–230 mesh (Kanto Chemical Co.) or Chromatorex NH silica gel, 100–200 mesh (Fuji Silysia Chemical Co.). Rare earth triisopropoxides and diphenyl-4,4'-disulfonic acid were purchased, and 1,3,5-triphenylbenzen trisulfonic acid was prepared according to the literature.¹⁴ $\text{Sc}_2(\text{BPDS})_3$ was prepared as reported before,⁷ and all the other catalysts were prepared in a similar manner to the preparation of $\text{Sc}_2(\text{BPDS})_3$. All solvents were purified before use; THF and Et_2O were distilled over sodium 9-fluorenone ketyl,¹⁵ and dichloromethane was distilled over calcium hydride.

Discandium tris(biphenyl-4,4'-disulfonate) [$\text{Sc}_2(\text{BPDS})_3$].⁷

This compound was prepared by mixing $\text{Sc}(\text{O-}i\text{-Pr})_3$ and diphenyl-4,4'-disulfonic acid in 2:3 ratio (83% yield). Colorless solid. IR (KBr): 3399, 1599, 1388, 1279, 1161, 1112, 1048, 997, 818, 728, 610 cm^{-1} . Anal. Calcd for $\text{C}_{36}\text{H}_{24}\text{O}_{18}\text{S}_6\text{Sc}_2 \cdot 4\text{H}_2\text{O}$: C, 39.35; H, 2.94. Found: C, 39.48; H, 2.89.

Diyttrium tris(biphenyl-4,4'-disulfonate) [$\text{Y}_2(\text{BPDS})_3$].

This compound was prepared by mixing $\text{Y}(\text{O-}i\text{-Pr})_3$ and diphenyl-4,4'-disulfonic acid in 2:3 ratio (86% yield). Colorless solid. IR (KBr): 3421, 1652, 1558, 1386, 1166, 1132, 1050, 999, 819, 727, 610, 568 cm^{-1} . Anal. Calcd for $\text{C}_{36}\text{H}_{24}\text{O}_{18}\text{S}_6\text{Y}_2 \cdot 5\text{H}_2\text{O}$: C, 35.36; H, 2.97. Found: C, 35.05; H, 2.60.

Dilanthanum tris(biphenyl-4,4'-disulfonate) [$\text{La}_2(\text{BPDS})_3$].

This compound was prepared by mixing $\text{La}(\text{O-}i\text{-Pr})_3$ and diphenyl-4,4'-disulfonic acid in 2:3 ratio (>99% yield). Colorless solid. IR (KBr): 3422, 1646, 1558, 1487, 1386, 1135, 1050, 1017, 999, 820, 728, 613, 568 cm^{-1} . Anal. Calcd for $\text{C}_{36}\text{H}_{24}\text{O}_{18}\text{S}_6\text{La}_2 \cdot 5\text{H}_2\text{O}$: C, 33.14; H, 2.63. Found: C, 33.18; H, 2.53.

Diytterbium tris(biphenyl-4,4'-disulfonate) [$\text{Yb}_2(\text{BPDS})_3$].

This compound was prepared by mixing $\text{Yb}(\text{O-}i\text{-Pr})_3$ and diphenyl-4,4'-disulfonic acid in 2:3 ratio (>99% yield). Colorless solid. IR (KBr): 3392, 1647, 1558, 1487, 1386, 1168, 1132, 1045, 1018, 999, 819, 728, 611, 570 cm^{-1} . Anal. Calcd for $\text{C}_{36}\text{H}_{24}\text{O}_{18}\text{S}_6\text{Yb}_2 \cdot 5\text{H}_2\text{O}$: C, 31.92; H, 2.38. Found: C, 32.18; H, 2.69.

1,3,5-Tris(4-sulfophenyl)benzene scandium salt (scandium 1,3,5-triphenylbenzene trisulfonate) [Sc(TPTS)].

This compound was prepared by mixing $\text{Sc}(\text{O-}i\text{-Pr})_3$ and 1,3,5-triphenylbenzen trisulfonic acid in 1:1 ratio (>99% yield). Colorless solid. IR (KBr): 3400, 1595, 1487, 1385, 1264, 1157, 1126, 1035, 1006, 824, 711, 616 cm^{-1} . Anal. Calcd for $\text{C}_{24}\text{H}_{15}\text{O}_9\text{S}_3\text{Sc}\cdot 2\text{H}_2\text{O}$: C, 46.15; H, 3.07. Found: C, 45.97; H, 3.15.

Typical procedure for the hetero-Diels–Alder reaction under solvent-free conditions: synthesis of 2,3-dihydro-2-phenyl- 4*H*-pyran-4-one (3a).

To $\text{Sc}_2(\text{BPDS})_3$ (5.1 mg, 0.01 mmol) were added benzaldehyde (21.2 mg, 0.20 mmol) and the Danishefsky's diene (51.7 mg, 0.30 mmol) under argon, and the mixture was stirred at rt for 48 h. After successive treatment with three drop of trifluoroacetic acid and four drops of diisopropylamine, the resulting mixture was directly subjected to column chromatography on silica gel (AcOEt–hexane 1:9) to give the desired product **3a** (31.5 mg, 90%) as colorless oil. ^1H NMR (CDCl_3 , δ): 7.48 (d, $J = 6.10$ Hz, 1H), 7.44–7.36 (m, 5H), 5.53 (dd, $J = 6.10$, 1.22 Hz, 1H), 5.43 (dd, $J = 14.40$, 3.42 Hz, 1H), 2.91 (dd, $J = 16.85$, 14.40 Hz, 1H), 2.66 (ddd, $J = 16.85$, 3.42, 1.22 Hz, 1H). R_f (silica gel plate, ethyl acetate–hexane 3:7): 0.31. CAS registry number: 40989-96-6.

2,3-Dihydro-2-(4-fluorophenyl)-4*H*-pyran-4-one (3b).

Colorless oil. ^1H NMR (CDCl_3 , δ): 7.47 (d, $J = 6.10$ Hz, 1H), 7.41–7.37 (m, 2H), 7.13–7.08 (m, 2H), 5.53 (dd, $J = 6.10$, 1.22 Hz, 1H), 5.41 (dd, $J = 14.40$, 3.42 Hz, 1H), 2.88 (dd, $J = 16.85$, 14.40 Hz, 1H), 2.65 (ddd, $J = 16.85$, 3.42, 1.22 Hz, 1H). R_f (silica gel plate, AcOEt–hexane 3:7): 0.29. CAS registry number: 423771-15-7, 226714-93-8.

2-(4-Chlorophenyl)-2,3-dihydro-4*H*-pyran-4-one (3c).

Colorless solid. ^1H NMR (CDCl_3 , δ): 7.47 (d, $J = 6.10$ Hz, 1H), 7.40 (dt, $J = 8.55$, 1.95 Hz, 2H), 7.34 (dt, $J = 8.55$, 1.95 Hz, 2H), 5.54 (dd, $J = 6.10$, 1.22 Hz, 1H), 5.41 (dd, $J = 14.40$, 3.42 Hz, 1H), 2.86 (dd, $J = 16.85$, 14.40 Hz, 1H), 2.65 (ddd, $J = 16.85$, 3.42, 1.22 Hz, 1H). R_f (silica gel plate, AcOEt–hexane 3:7): 0.27. CAS registry number: 188116-43-0.

2-(4-Bromophenyl)-2,3-dihydro-4*H*-pyran-4-one (3d).

Colorless solid. ^1H NMR (CDCl_3 , δ): 7.57–7.54 (m, 2H), 7.47 (d, $J = 6.10$ Hz, 1H), 7.29–7.27 (m, 2H), 7.40 (dt, $J = 8.55$, 1.95 Hz, 2H), 5.53 (dd, $J = 6.10$, 1.22 Hz, 1H), 5.39 (dd, $J = 14.40$, 3.42 Hz, 1H), 2.85 (dd, $J = 16.85$, 14.40 Hz, 1H), 2.65 (ddd, $J = 16.85$, 3.42, 1.22 Hz, 1H). R_f (silica gel plate, AcOEt–hexane 3:7): 0.29. CAS registry number: 387388-81-0.

2,3-Dihydro-2-(4-nitrophenyl)-4H-pyran-4-one (3e).

Colorless solid. ^1H NMR (CDCl_3 , δ): 8.29 (d, $J = 9.03$ Hz, 2H), 7.61 (d, $J = 9.03$ Hz, 2H), 7.52 (d, $J = 6.10$ Hz, 1H), 5.58 (dd, $J = 6.10, 1.22$ Hz, 1H), 5.55 (dd, $J = 14.16, 3.91$ Hz, 1H), 2.85 (dd, $J = 16.85, 14.16$ Hz, 1H), 2.73 (ddd, $J = 16.85, 3.91, 1.22$ Hz, 1H). R_f (silica gel plate, AcOEt–hexane 1:1): 0.40. CAS registry number: 188116-44-1.

2,3-Dihydro-2-(4-tolyl)-4H-pyran-4-one (3f).

Colorless solid. ^1H NMR (CDCl_3 , δ): 7.46 (d, $J = 6.10$ Hz, 1H), 7.29 (d, $J = 8.06$ Hz, 2H), 7.23 (d, $J = 8.06$ Hz, 2H), 5.51 (dd, $J = 6.10, 1.22$ Hz, 1H), 5.39 (dd, $J = 14.40, 3.42$ Hz, 1H), 2.91 (dd, $J = 16.85, 14.40$ Hz, 1H), 2.64 (ddd, $J = 16.85, 3.42, 1.22$ Hz, 1H), 2.37 (s, 3H). R_f (silica gel plate, AcOEt–hexane 3:7): 0.35. CAS registry number: 423771-16-8, 188116-41-8.

2,3-Dihydro-2-(4-methoxyphenyl)-4H-pyran-4-one (3g).

Colorless solid. ^1H NMR (CDCl_3 , δ): 7.46 (d, $J = 6.10$ Hz, 1H), 7.33 (dt, $J = 8.55, 2.93$ Hz, 2H), 6.92 (dt, $J = 2.93, 8.55$ Hz, 2H), 5.51 (dd, $J = 6.10, 1.22$ Hz, 1H), 5.37 (dd, $J = 14.65, 3.42$ Hz, 1H), 3.83 (s, 3H), 2.93 (dd, $J = 16.85, 14.65$ Hz, 1H), 2.63 (ddd, $J = 16.85, 3.42, 1.22$ Hz, 1H). R_f (silica gel plate, AcOEt–hexane 1:1): 0.47. CAS registry number: 396134-75-1, 60380-11-2.

Typical procedure for the recovery and reuse of the catalyst in the hetero-Diels–Alder reaction.

After completion of the reaction, without treatment with trifluoroacetic acid, Et_2O (ca. 3 mL at 0.4 mmol scale) was added to the reaction mixture, and the resulting suspension was subjected to centrifugation. The supernatant was removed, and the precipitate was washed with Et_2O (three times, total 12 mL). The recovered catalyst was dried in vacuo at room temperature, and then reused for the next round of reaction. Meanwhile, the combined ethereal solution was successively treated with trifluoroacetic acid and diisopropylamine to give the desired Diels–Alder adduct.

Typical procedure for the ring-opening reaction of epoxides under solvent-free conditions: synthesis of *trans*-2-(benzylamino)cyclohexanol (6a).

A mixture of $\text{Sc}_2(\text{BPDS})_3$ (10.3 mg, 0.02 mmol), cyclohexene oxide (39.3 mg, 0.40 mmol), and benzylamine (47.2 mg, 0.44 mmol) was stirred at rt for 12 h. The resulting precipitate was collected and washed with Et_2O , and the filtrate was concentrated under reduced pressure. The concentrate was subjected to column chromatography on NH silica gel (acetone–hexane 1:9) to give the desired product **6a** (81.7 mg, 99.5%) as colorless solid. ^1H NMR (CDCl_3 , δ): 7.32–7.21 (m, 5H), 3.93 (d, $J = 12.94$ Hz, 1H), 3.66 (d, $J = 12.94$ Hz, 1H), 3.21–3.15 (m, 1H), 2.32–2.26 (m, 1H), 2.16–2.12 (m, 1H), 1.99–1.97 (m,

1H), 1.71–1.69 (m, 2H), 1.26–1.19 (m, 3H), 1.03–0.94 (m, 1H). R_f (NH silica gel plate, acetone–hexane 1:9): 0.31. CAS registry number: 40571-86-6.

***trans*-2-(Phenylamino)cyclohexanol (6b).**

Colorless solid. ^1H NMR (CDCl_3 , δ): 7.19–7.15 (m, 2H), 6.75–6.69 (m, 3H), 3.36–3.30 (m, 1H), 3.15–3.09 (m, 1H), 2.12–2.08 (m, 2H), 1.77–1.70 (m, 2H), 1.43–1.26 (m, 3H), 1.07–0.99 (m, 1H). R_f (silica gel plate, Et_2O –hexane 1:3): 0.09. CAS registry number: 75907-11-8.

***trans*-2-(Benzylamino)cyclopentanol (11).**

^1H NMR (CDCl_3 , δ): 7.32–7.20 (m, 5H), 3.86–3.78 (m, 2H), 3.70 (d, $J = 12.94$ Hz, 1H), 3.21–3.15 (m, 1H), 2.32–2.26 (m, 1H), 2.16–2.12 (m, 1H), 1.99–1.97 (m, 1H), 1.71–1.69 (m, 2H), 1.26–1.19 (m, 3H), 1.03–0.94 (m, 1H). CAS registry number: 68327-00-4.

***trans*-6-Benzylamino-2,2'-dimethyl-1,3-dioxocycloheptan-5-ol (12a).**

^1H NMR (CDCl_3 , δ): 7.32–7.22 (m, 5H), 3.90 (d, $J = 13.18$ Hz, 1H), 3.78–3.73 (m, 3H), 3.57–3.47 (m, 3H), 2.56–2.54 (br m, 1H), 2.37 (br s, 1H), 1.33 (s, 3H), 1.31 (s, 3H). CAS registry number: 232945-98-1.

***trans*-2,2'-Dimethyl-1,3-dioxo-6-(phenylamino)cycloheptan-5-ol (12b).**

^1H NMR (CDCl_3 , δ): 7.15 (t, $J = 7.32$ Hz, 2H), 6.70–6.63 (m, 3H), 4.26 (br s, 1H), 4.30 (br s, 1H), 4.03 (d, $J = 12.70$ Hz, 1H), 3.89 (d, $J = 12.94$ Hz, 1H), 3.70 (br s, 1H), 3.54 (dt, $J = 12.70$, 3.66 Hz, 2H), 3.47 (dq, $J = 7.08$, 1.22 Hz, 1H), 3.41 (br s, 1H), 1.373 (s, 3H), 1.370 (s, 3H). CAS registry number: 1027597-29-0.

***threo*-1,4-Diethoxy-3-(phenylamino)butan-2-ol (14).**

^1H NMR (CDCl_3 , δ): 7.15 (dt, $J = 7.32$, 0.73 Hz, 2H), 6.68 (dt, $J = 7.32$, 0.73 Hz, 1H), 6.63 (dd, $J = 7.32$, 0.73 Hz, 2H), 4.26 (br s, 1H), 4.18–4.15 (m, 1H), 3.64–3.59 (m, 3H), 3.53–3.45 (m, 6H), 3.23 (br s, 1H), 1.20 (t, $J = 7.08$ Hz, 3H), 1.18 (t, $J = 7.08$ Hz, 3H).

Typical procedure for the recovery and reuse of the catalyst in the ring-opening reaction of epoxides.

After completion of the reaction, Et_2O (ca. 3 mL at 0.4 mmol scale) was added to the reaction mixture, and the resulting suspension was subjected to centrifugation. The supernatant was removed, and the precipitate was washed with Et_2O (three times, total 12 mL). The recovered catalyst was dried in vacuo at rt, and then reused for the next round of reaction.

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