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exo-Selective Asymmetric Diels–Alder Reaction Catalyzed by Diamine Salts as Organocatalysts

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Abstract: An organocatalyst formed from a binaphthyl-substituted diamine and trifluoromethanesulfonic acid exhibited unprecedented levels of *exo* selectivity in the Diels–Alder reaction of α,β-unsaturated aldehydes with cyclopentadiene. A novel axially chiral diamine was also designed as an organocatalyst for an asymmetric variant of this reaction, in which the desired cycloadducts were formed with high diastereo- and enantioselectivities. The highest diastereoselectivity observed was greater than 20:1 in favor of the *exo* cycloadduct in the asymmetric Diels–Alder reaction of crotonaldehyde with cyclopentadiene.

Keywords: asymmetric catalysis · diastereoselectivity · Diels–Alder reaction · enantioselectivity · organocatalysis

Introduction

The Diels–Alder reaction remains one of the most powerful tools in synthetic organic chemistry. Its broad application in the regio- and stereochemically defined synthesis of a wide variety of natural products has led to the development of a number of enantioselective and diastereoselective Diels–Alder reactions.[1] In these stereoselective processes, the enantioselectivity is controlled by chiral reagents or catalysts, whereas the degree of diastereoselectivity depends mainly on the structure of the substrates. For example, the Diels–Alder reaction of cyclopentadiene with α,β-unsaturated carbonyl compounds, such as acrolein, methyl vinyl ketone, and methyl acrylate, is known to give predominantly the *endo* cycloadducts. This *endo* selectivity is considered to be a general attribute of the Diels–Alder family of reactions. In contrast, *exo* selectivity, in particular the catalyst-controlled *exo*-selective Diels–Alder reaction, is not enabled readily by the deliberate modification of existing methodologies, especially with simple α,β-unsaturated aldehydes and ketones.[2,3] Owing to the current importance and rapid development of organocatalytic reactions in practical organic synthesis,[4] we have been interested in the possibility of developing a hitherto difficult *exo*-selective asymmetric Diels–Alder reaction by using a chiral organocatalyst.[5–7] Herein we describe such a cycloaddition reaction catalyzed by chiral diamine salts with binaphthyl-based substituents.

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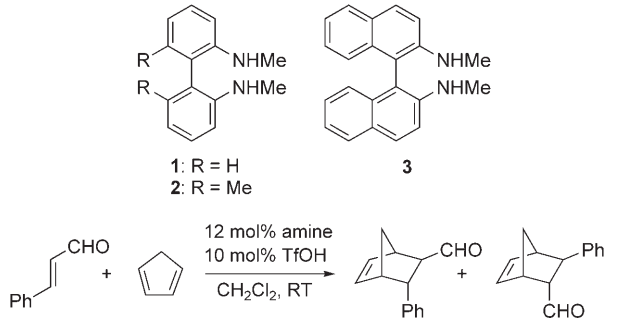
Results and Discussion

Optimization

To find an appropriate amine-salt catalyst for an *exo*-selective Diels–Alder reaction, we first examined the chemical behavior of *N*-methylaniline derivatives because of the ease of preparation and potential for further structural modification of these secondary amines. Furthermore, the presence of both electron-donating (methyl) and electron-withdrawing (phenyl) substituents on the nitrogen atom is expected to accelerate the formation and hydrolysis, respectively, of the intermediate iminium salt.[2b,d,6] Thus, the Diels–Alder reaction of cinnamaldehyde with cyclopentadiene was carried out in the presence of catalytic amounts of the secondary amine (12 mol%) and trifluoromethanesulfonic acid (10 mol%) in dichloromethane at room temperature (Table 1). With *N*-methylaniline as the catalyst, the desired *exo* adduct was obtained as the major product (*exo*/*endo* = 2.2:1) in 75% yield (Table 1, entry 1). In contrast, the parent compound aniline showed no catalytic activity (Table 1, entry 2), and the use of the aliphatic secondary amine *N*-methylbenzylamine led to the cycloadducts in only 20% yield with slightly higher *exo* selectivity (Table 1, entry 3). These findings prompted us to investigate the substituent effects of other secondary amines with an *N*-alkyl

Table 1. Survey of catalysts for the *exo*-selective Diels–Alder reaction.[a]



Entry	Amine	*t* [h]	Yield[b] [%]	*exo*/*endo*[c]
1	PhNHMe	20	75	2.2:1
2	$PhNH_2$	20	0	–
3	$PhCH_2NHMe$	20	20	2.6:1
4	2-MePhNHMe	10	30	2.8:1
5	2-*t*BuPhNHMe	10	15	2.1:1
6	2,6-Me_2PhNHMe	10	18	2.4:1
7	$PhNHCH_2CH_2NHPh$	16	47	2.3:1
8	**1**	10	86	5.8:1
9	**2**	23	83	8.0:1
10	**3**	20	99	9.2:1

[a] Reaction conditions: cinnamaldehyde (1 equiv), cyclopentadiene (3 equiv), amine (12 mol%), TfOH (10 mol%), CH_2Cl_2, room temperature. [b] Yield of the isolated cycloadducts. [c] The isomer ratio was determined by ^{1}H NMR spectroscopy. Tf = trifluoromethanesulfonyl.

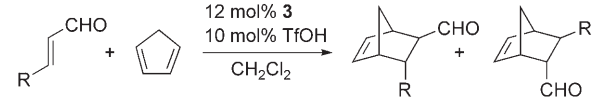
aniline core. Although neither the introduction of *ortho* substituents on the aromatic ring of *N*-methylaniline nor the use of *N*,*N*′-diphenylethylenediamine affected the diastereoselectivity significantly (Table 1, entries 4–7), improved selectivity was observed with the biphenyldiamine **1** (Table 1, entry 8). Furthermore, the axially chiral diamines **2** and **3** exhibited even higher *exo* selectivity (Table 1, entries 9 and 10). The high reactivity of the less nucleophilic diamine **3** equaled that of reported organocatalysts, such as highly nucleophilic cyclic amines with a five-membered ring and hydrazine derivatives.[2b,d,6a,d]

We then tested the generality of our system by treating a variety of α,β-unsaturated aldehydes with cyclopentadiene in the presence of diamine **3** and trifluoromethanesulfonic acid (Table 2). In the case of acrolein and β-alkyl-substituted acroleins, the Diels–Alder reaction proceeded smoothly to give the corresponding cycloadducts in good to excellent yield (>80%) with high *exo* selectivity (*exo*/*endo* ≥ 6.1:1; Table 2, entries 2–5). When a less reactive aldehyde with a furyl substituent was used, the *exo* cycloadduct was obtained predominantly, albeit in only moderate yield (Table 2, entry 6). On the other hand, the reaction of an aldehyde with an electron-withdrawing ethoxycarbonyl group proceeded to completion to give the desired cycloadduct in excellent yield with high *exo* selectivity (Table 2, entry 7).

Abstract in Japanese:

ビナフチル骨格を有するジアミン型触媒を開発し、立体選択的 Diels–Alder 反応に適用した。本触媒を用いたα,β-不飽和アルデヒドとシクロペンタジエンとの反応では、これまでにない高エキソ選択性で環化付加体が得られた。また、新規軸不斉ジアミン型触媒によって、エキソ選択的な不斉 Diels–Alder 反応が実現された。

Table 2. *exo*-Selective Diels–Alder reaction.[a]

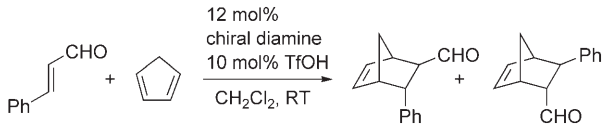


Entry	R	*T* [°C]	*t* [h]	Yield[b] [%]	*exo*/*endo*[c]
1	Ph	RT	20	99	9.2:1
2	H	−40	30	80	9.4:1
3	Me	−20	20	99	11.8:1
4	*n*Pr	0	18	83	6.1:1
5	*i*Pr	0	18	80	7.9:1
6	2-furyl	RT	96	67	7.6:1
7	CO_2Et	−40	20	93	9.2:1

[a] Reaction conditions: aldehyde (1 equiv), cyclopentadiene (3 equiv), **3** (12 mol%), TfOH (10 mol%), CH_2Cl_2. [b] Yield of the isolated cycloadducts. [c] The isomer ratio was determined by ^{1}H NMR spectroscopy.

With this information, we set out to design enantiomerically pure binaphthyldiamine catalysts for an *exo*-selective asymmetric Diels–Alder reaction. The use of enantiopure (*R*)-**3** in the Diels–Alder reaction of cinnamaldehyde with cyclopentadiene resulted in the formation of the cycloadduct with low enantioselectivity (Table 3, entry 1). We prepared a series of octahydrobinaphthyldiamine catalysts as novel chiral diamines (Scheme 1). Thus, the axially chiral diamine (*R*)-**4**[8] was converted into the *N*,*N*′-dialkyl diamines (*R*)-**5**–**7** in two steps: ethoxycarbonylation or acylation and subsequent reduction. The careful bromination of (*R*)-**5** with NBS in THF yielded (*R*)-**8**, which was treated with phenylboronic acid or 4-*tert*-butylphenylboronic acid under Suzuki–Miyaura coupling conditions to furnish (*R*)-**9** and (*R*)-**10**, respectively.

Table 3. Survey of catalysts for the *exo*-selective asymmetric Diels–Alder reaction.[a]



Entry	Chiral diamine	*t* [h]	Yield[b] [%] (*exo*/*endo*)[c]	*ee*[d] [%] (config.)[e] *exo*	*endo*
1	(*R*)-**3**	20	99 (9.2:1)	9 (*R*)	15 (*R*)
2	(*R*)-**5**	23	61 (8.2:1)	38 (*S*)	27 (*R*)
3	(*R*)-**6**	27	25 (7.3:1)	14 (*S*)	39 (*R*)
4	(*R*)-**7**	27	34 (3.3:1)	7 (*R*)	42 (*R*)
5	(*R*)-**9**	36	90 (5.6:1)	53 (*R*)	39 (*R*)
6	(*R*)-**10**	20	87 (6.5:1)	72 (*R*)	68 (*R*)

[a] Reaction conditions: cinnamaldehyde (1 equiv), cyclopentadiene (3 equiv), chiral diamine (12 mol%), TfOH (10 mol%), room temperature. [b] Yield of the isolated cycloadducts. [c] The isomer ratio was determined by ^{1}H NMR spectroscopy. [d] The *ee* values were determined by GC analysis on a chiral phase by using a capillary column. [e] The absolute configuration at the 2-position was determined by comparison of the sign of optical rotation with reported values.

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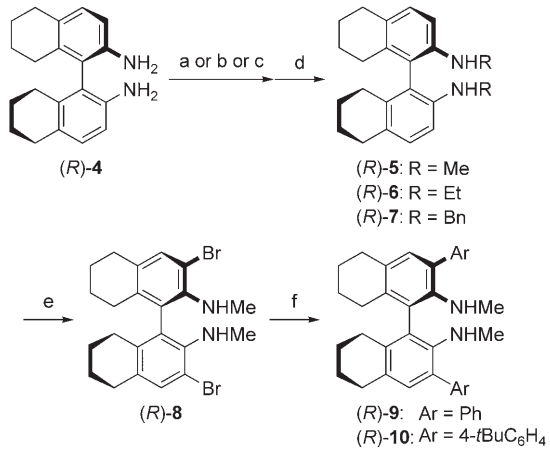


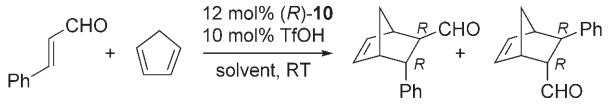
Scheme 1. Synthesis of axially chiral diamines. Reaction conditions: a) $ClCO_2Et$, pyridine, benzene; b) AcCl, pyridine, benzene; c) PhCOCl, pyridine, benzene; d) $LiAlH_4$, THF ((*R*)-**5**: 84%; (*R*)-**6**: 78%; (*R*)-**7**: 98%); e) NBS, THF (83%); f) $PhB(OH)_2$ or 4-*t*$BuC_6H_4B(OH)_2$, Pd-$(OAc)_2$, PPh_3, $Ba(OH)_2{\cdot}8H_2O$, DME/H_2O ((*R*)-**9**: 70%; (*R*)-**10**: 88%). Bn = benzyl, DME = 1,2-dimethoxyethane, NBS = *N*-bromosuccinimide.

With these new axially chiral diamines (*R*)-**5**–**7**, (*R*)-**9**, and (*R*)-**10**, we carried out the *exo*-selective asymmetric Diels–Alder reaction of cinnamaldehyde with cyclopentadiene (Table 3). Although the octahydrobinaphthyldiamine (*R*)-**5** exhibited lower reactivity than the parent binaphthyldiamine (*R*)-**3**, moderate enantioselectivity was observed (Table 3, entry 2). However, the replacement of the methyl groups in (*R*)-**5** with larger alkyl groups (Et, Bn) resulted in a decrease in both yield and stereoselectivity (Table 3, entries 3 and 4). In contrast, the introduction of phenyl groups at the 3- and 3′-positions of the octahydrobinaphthyl moiety enhanced the enantioselectivity (Table 3, entry 5), and the sterically more congested diamine (*R*)-**10** showed particularly good levels of *exo* selectivity and enantioselectivity (Table 3, entry 6).

The reaction conditions were then optimized with the (*R*)-**10**–TfOH salt as the catalyst (Table 4). We screened a variety of solvents and found that α,α,α-trifluorotoluene, which is known to be a useful alternative to CH_2Cl_2,[9] gave the best results in terms of the reaction rate and stereoselectivity (Table 4, entry 7). Furthermore, the lowering of the reaction temperature to 0°C improved both the *exo* selectivity and the enantioselectivity of the reaction (Table 4, entry 8).

We next investigated the effect of the Brønsted acid cocatalyst on the reaction (Table 5). Of several Brønsted acids examined, *p*-toluenesulfonic acid showed the highest *exo* selectivity and enantioselectivity (Table 5, entry 2). Reactions in which other Brønsted acids were used gave the cycloadduct with comparable stereoselectivities (Table 5, entries 4–6). Finally, a reaction with *p*-toluenesulfonic acid at a lower temperature (−20°C) was found to give the desired *exo* cycloadduct with excellent *exo* selectivity and enantioselectivity, although a longer reaction time was required (Table 5, entry 3).

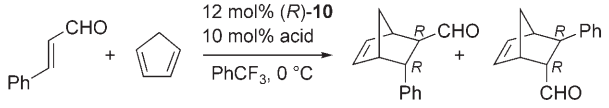
Table 4. Effect of the solvent on the *exo*-selective asymmetric Diels–Alder reaction.[a]



Entry	Solvent	*t* [h]	Yield[b] [%] (*exo*/*endo*)[c]	*ee*[d] [%] *exo*	*endo*
1	CH_2Cl_2	20	87 (6.5:1)	72	68
2	MeOH	20	97 (6.5:1)	75	64
3	DMF	20	56 (5.1:1)	60	45
4	THF	20	80 (7.1:1)	72	68
5	hexane	20	93 (4.6:1)	74	74
6	toluene	14	93 (6.4:1)	78	76
7	$PhCF_3$	9	89 (8.6:1)	79	71
8[e]	$PhCF_3$	50	80 (9.5:1)	86	79

[a] Reaction conditions: cinnamaldehyde (1 equiv), cyclopentadiene (3 equiv), (*R*)-**10** (12 mol%), TfOH (10 mol%), room temperature. [b] Yield of the isolated cycloadducts. [c] The isomer ratio was determined by ^1H NMR spectroscopy. [d] The *ee* values were determined by GC analysis on a chiral phase by using a capillary column. [e] The reaction was performed at 0°C. DMF = *N*,*N*-dimethylformamide.

Table 5. Effect of the acid cocatalyst on the *exo*-selective asymmetric Diels–Alder reaction.[a]

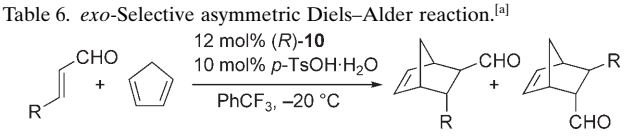


Entry	Acid	Yield[b] [%] (*exo*/*endo*)[c]	*ee*[d] [%] *exo*	*endo*
1	TfOH	80 (9.5:1)	86	79
2	*p*-$TsOH{\cdot}H_2O$	93 (11.1:1)	87	86
3[e]	*p*-$TsOH{\cdot}H_2O$	80 (12.8:1)	92	91
4	(+)-camphorsulfonic acid	57 (10.0:1)	83	80
5	$HClO_4$	97 (8.9:1)	86	80
6	3,4-dinitrobenzoic acid	30 (6.7:1)	79	69

[a] Reaction conditions: cinnamaldehyde (1 equiv), cyclopentadiene (3 equiv), (*R*)-**10** (12 mol%), acid (10 mol%), α,α,α-trifluorotoluene, 0°C, 50–60 h. [b] Yield of the isolated cycloadducts. [c] The isomer ratio was determined by ^1H NMR spectroscopy. [d] The *ee* values were determined by GC analysis on a chiral phase by using a capillary column. [e] The reaction was performed at −20°C for 160 h. More cyclopentadiene (2 equiv) was added after 48 h and again after 96 h. Ts = toluenesulfonyl.

We then applied our system to various α,β-unsaturated aldehydes. In most cases, under the appropriate reaction conditions, the corresponding cycloadducts were obtained with good to excellent *exo* and enantioselectivity (Table 6, entries 2–6 and 8). Although the use of acrolein and 2-nitrocinnamaldehyde as dienophiles resulted in a significant decrease in diastereoselectivity, the *exo* cycloadducts were still dominant (Table 6, entries 1 and 7). Unfortunately, however, this reaction system was found to be suitable only for a combination of α,β-unsaturated aldehydes with cyclopentadiene. For example, the reactions of α,β-unsaturated aldehydes with 1,3-cyclohexadiene and 1,3-pentadiene gave only traces of the corresponding cycloadducts.

Table 6. *exo*-Selective asymmetric Diels–Alder reaction.[a]



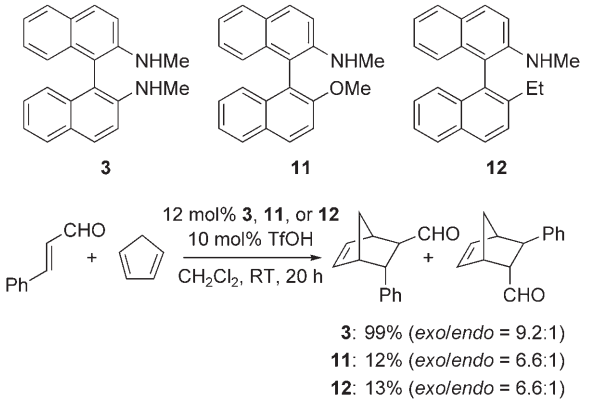
Entry	R	t [h]	Yield[b] [%] (*exo*/*endo*)[c]	*ee*[d] [%] (config.)[e] *exo*	*endo*
1	H	45	93 (1.9:1)	86	68
2	Me	160	72 (>20:1)	88 (*S*)	–
3[f]	CO_2Et	144	90 (5.5:1)	83	56
4[g]	Ph	160	80 (12.8:1)	92 (*R*)	91 (*R*)
5[h]	4-ClC_6H_4	96	99 (7.8:1)	92	96
6	4-$NO_2C_6H_4$	40	99 (7.4:1)	95	98
7[g]	2-$NO_2C_6H_4$	144	98 (1.3:1)	87	81
8[g,i]	4-*i*PrC_6H_4	144	84 (6.3:1)	82	73

[a] Reaction conditions: aldehyde (1 equiv), cyclopentadiene (3 equiv), (*R*)-**10** (12 mol%), *p*-TsOH·H_2O (10 mol%), α,α,α-trifluorotoluene, −20 °C. [b] Yield of the isolated cycloadducts. [c] The isomer ratio was determined by ^{1}H NMR spectroscopy. [d] The *ee* values were determined by GC or HPLC on a chiral phase. [e] The absolute configuration at the 2-position was determined by comparison of the sign of optical rotation with reported values. [f] The reaction was performed at −60 °C in toluene. [g] More cyclopentadiene (2 equiv) was added after 48 h and again after 96 h. [h] More cyclopentadiene (2 equiv) was added after 48 h. [i] The reaction was performed at 0 °C.

Mechanism

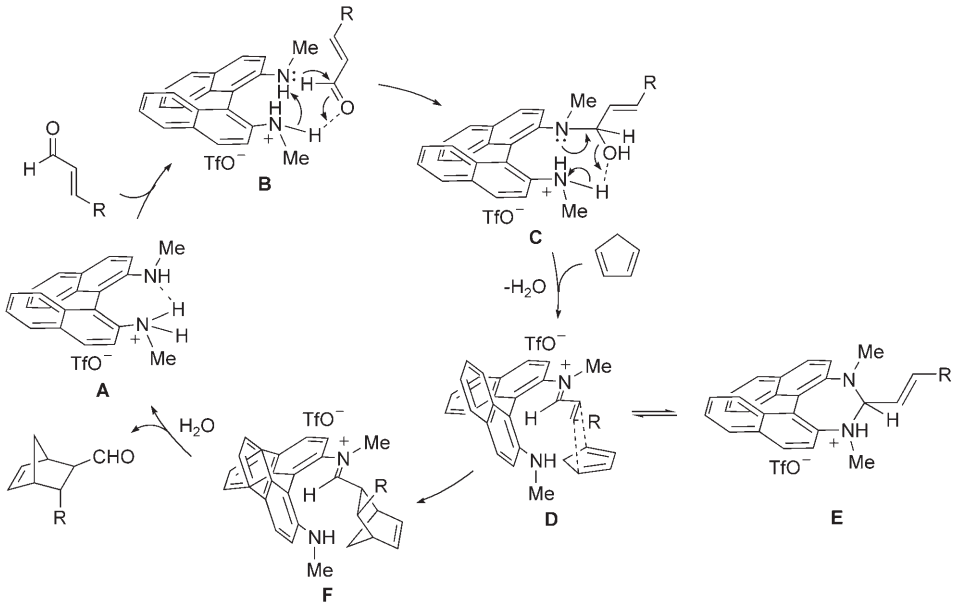
To elucidate the origin of the rate acceleration and unprecedented high *exo* selectivity observed in the biaryldiamine-salt-catalyzed Diels–Alder reaction, we prepared the binaphthyl-substituted amines **11** and **12** with a methoxy group and an ethyl group, respectively, in place of one of the methylamino groups in **3**, and used them as catalysts for the reaction between cinnamaldehyde and cyclopentadiene (Scheme 2). Both reactions proceeded slowly to give predominantly the *exo* cycloadduct, albeit in low yield. Thus, the presence of two methylamino groups in **3** was found to be essential for rate acceleration. These marked differences in reactivity were attributed to the rate of formation of an iminium intermediate on the basis of NMR spectroscopic studies. Whereas no change was observed in the chemical shift of the aldehyde hydrogen atom in an equimolar mixture of **11**, TfOH, and cinnamaldehyde even after 24 h, a substantial amount of cinnamaldehyde was consumed immediately when **3** was used instead of **11**.

On the basis of these observations and the catalytic cycle proposed by MacMillan and coworkers for reactions with iminium intermediates,[2b] we propose the following mechanism for the *exo*-selective Diels–Alder reaction (Scheme 3): Initially, the free methylamino group in the diamine–TfOH catalyst **A** reacts with the α,β-unsaturated aldehyde with the aid of the other methylamino group protonated by TfOH to form the iminium intermediate **D** and the protonated aminal **E**. The more reactive iminium intermediate **D** reacts with cyclopentadiene to give the *exo* adduct **F** under the influence of the sterically hindered binaphthyl moiety, as the binaphthyl-substituted amines **11** and **12**, which cannot form an aminal-type intermediate, also provided the *exo* adduct as the major isomer. The resulting iminium intermediate **F** is hydrolyzed to give the *exo* cycloadduct and regenerate the diamine–TfOH catalyst **A**.



Scheme 2. Comparison of the catalytic activity of **3** with that of **11** and **12**, which contain just one methylamino group.

The observed stereoselectivity in the asymmetric reaction with (*R*)-**10** can be explained by two possible transition-state models, **TS1** and **TS2** (Scheme 4). In both cases, one face of the iminium intermediate is blocked by the 4-*tert*-butylphenyl substituent, and the other face is open for the ap-



Scheme 3. Plausible mechanism for the *exo*-selective Diels–Alder reaction.

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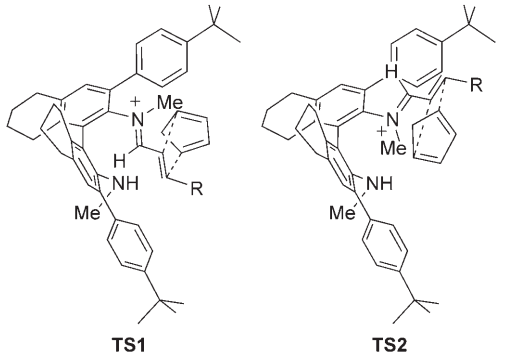

Scheme 4. Possible transition-state models for the *exo*-selective asymmetric Diels–Alder reaction.

proach of cyclopentadiene in accordance with the experimental results.

Conclusions

In summary, we have developed an *exo*-selective Diels–Alder reaction of α,β-unsaturated aldehydes with cyclopentadiene under the catalysis of diamine salts. With binaphthyl-based diamines, unprecedented levels of *exo* selectivity were observed. Furthermore, an *exo*-selective asymmetric Diels–Alder reaction was developed with a specially designed axially chiral diamine.

Experimental Section

Typical procedure for the Diels–Alder reaction with **3**: Acrolein (17 μL, 0.25 mmol) was added to a solution of the diamine **3** (9.4 mg, 0.03 mmol) and TfOH (2.2 μL, 0.025 mmol) in dichloromethane (1 mL) at −40 °C. The reaction mixture was stirred for 1–2 min, then cyclopentadiene (62 μL, 0.75 mmol) was added. Following the complete consumption of the starting material, the reaction mixture was purified directly by flash column chromatography on silica gel (pentane/ether = 20:1) to afford the desired Diels–Alder adduct (80 %; *exo*/*endo* = 9.4:1).

Typical procedure for the asymmetric Diels–Alder reaction: (*E*)-cinnamaldehyde (32 μL, 0.25 mmol) was added to a solution of the diamine (*R*)-**10** (17.4 mg, 0.03 mmol) and *p*-TsOH·H_2O (4.8 mg, 0.025 mmol) in α,α,α-trifluorotoluene (1 mL) at −20 °C. The reaction mixture was stirred for 1–2 min, then cyclopentadiene (62 μL, 0.75 mmol) was added. After 48 and 96 h, more cyclopentadiene (41 μL, 0.5 mmol) was added. Following the complete consumption of the starting material, the reaction mixture was purified directly by flash column chromatography on silica gel (hexane/ethyl acetate = 10:1) to afford the desired Diels–Alder adduct (80 %; *exo*/*endo* = 12.8:1; *exo* isomer: 92 % *ee*, *endo* isomer: 91 % *ee*).

Acknowledgements

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