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N,*N*′-Dioxide/nickel(II)-catalyzed asymmetric Diels–Alder reaction of cyclopentadiene with 2,3-dioxopyrrolidines and 2-alkenoyl pyridines†

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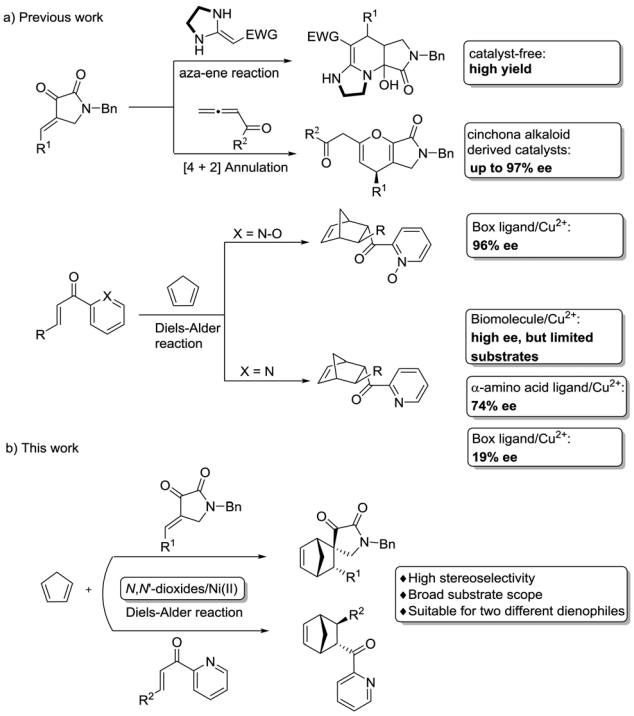
A chiral *N*,*N*′-dioxide/Ni(OTf)$_2$ complex-catalyzed asymmetric Diels–Alder reaction of cyclopentadiene with 2,3-dioxopyrrolidines and 2-alkenoyl pyridines has been achieved. The corresponding chiral bridged compounds were obtained in high yields with excellent dr and ee values (up to 97% yield, 95 : 5 dr and 97% ee).

The asymmetric Diels–Alder (DA) reactions play an important role in organic synthesis since they provide powerful C–C bond-forming transformations to obtain enantiomerically enriched cyclohexene substructures.[1] Among them, the DA reaction of cyclopentadiene is an effective method for the synthesis of bridged compounds.[2] For example, spiroindole melatonin analogues,[3] tetracyclic imine[4] and gelsemine,[5] are interesting biologically active compounds. Chiral Lewis acid-promoted-asymmetric DA reactions by activating bidentate dienophiles, such as unsaturated α-ketoesters,[6] acrylimides,[7] and *N*-hydroxy-acrylamides,[8] have been well explored. Besides, dioxopyrrolidine derivatives and 2-alkenoyl pyridine derivatives are interesting synthons. The dioxopyrrolidines can participate in a reaction as not only a monoene but also a 4π component (Scheme 1). In 2014, Lin's group[9] developed a highly efficient aza-ene reaction of heterocyclic ketene aminals (HKAs) with 2,3-dioxopyrrolidines under catalyst-free conditions to synthesize imidazo[1,2-*a*]-pyrrolo-[3,4-*e*]pyridine derivatives. Recently, Xu's group[10] reported an asymmetric inverse electron demand [4+2] annulation between allene ketones and 2,3-dioxopyrrolidines catalyzed by a cinchona alkaloid-derived amine, where 2,3-dioxopyrrolidines acted as oxa-dienes. However, the asymmetric DA reaction of cyclopentadiene with dioxopyrrolidines as dienophiles, to obtain chiral bridged spiro compounds with four adjacent stereocenters, has not been reported.

For the asymmetric DA reactions between 2-alkenoyl pyridines and cyclopentadiene, artificial metalloenzymes and DNA-based catalysts were developed and good results were obtained for the limited substrate.[11] In 1998, Engberts's group[11b] reported chiral amino acid–Cu(II) complex catalyzed DA reaction of 3-phenyl-1-(2-pyridyl)-2-propen-1-one with cyclopentadiene in water, which only gave 74% ee. In 2007, Pedro's group[11f] reported a bis(oxazoline)–Cu(II) catalytic system, which was efficient for the enantioselective DA reaction of cyclopentadiene with 2-alkenoyl pyridine *N*-oxides but not for non-oxidizing 2-alkenoyl pyridines (only 19% ee, Scheme 1).



Scheme 1 Reactions of 2,3-dioxopyrrolidines and 2-alkenoyl pyridines.

C_2-symmetric *N*,*N*′-dioxides developed by our group possess the properties of flexibility, and have been proved to be useful ligands or organocatalysts.[12] We assume that the flexible *N*,*N*′-dioxides/metal catalysts might realize the asymmetric

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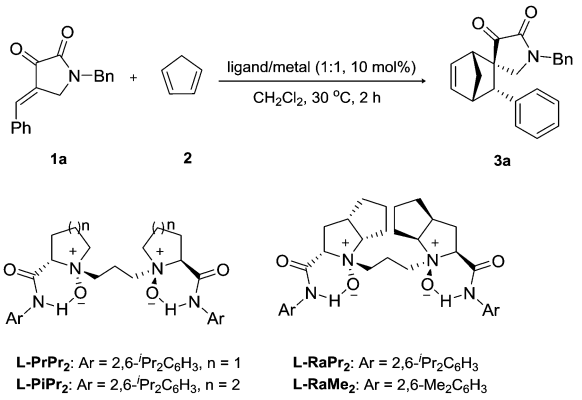
Table 1 Optimization of the reaction conditions[a]



Entry	Ligand	Metal	Yield[b] (%)	dr[c]	ee[c] (%)
1	**L-PrPr$_2$**	$Cu(OTf)_2$	96	97 : 3	29
2	**L-PrPr$_2$**	$Zn(OTf)_2$	85	97 : 3	75
3	**L-PrPr$_2$**	$Mg(OTf)_2$	88	97 : 3	81
4	**L-PrPr$_2$**	$Ni(OTf)_2$	90	97 : 3	86
5	**L-PiPr$_2$**	$Ni(OTf)_2$	90	96 : 4	74
6	**L-RaPr$_2$**	$Ni(OTf)_2$	89	94 : 6	92
7	**L-RaMe$_2$**	$Ni(OTf)_2$	91	98 : 2	39
8[d]	**L-RaPr$_2$**	$Ni(OTf)_2$	90	96 : 4 (93 : 7)[e]	97

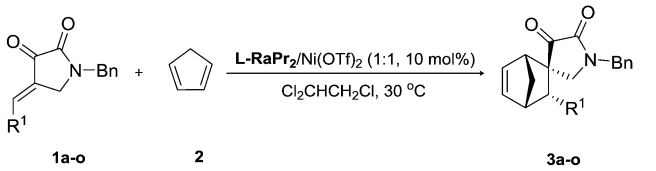
[a] Unless otherwise noted, the reactions were performed with **1a** (0.1 mmol), **2** (100 μL) and **L**/metal (1 : 1, 10 mol%) in CH_2Cl_2 (1.0 mL) at 30 °C for 2 h. [b] Isolated yield of **3a**. [c] Determined by chiral HPLC analysis. [d] Cl_2CHCH_2Cl was used. [e] Determined by ^{1}H NMR analysis.

DA reaction of cyclopentadiene with dioxopyrrolidines, and also with 2-alkenoyl pyridines. Herein, we report our efforts in developing an *N*,*N*′-dioxide/$Ni(OTf)_2$ complex system that is efficient for the asymmetric Diels–Alder reaction of cyclopentadiene with 2,3-dioxopyrrolidines and 2-alkenoyl pyridines.

In the initial study, (*E*)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **1a** and cyclopentadiene **2** were chosen as model substrates to optimize the reaction conditions. Several metal salts coordinating to the L-proline derived chiral *N*,*N*′-dioxide **L-PrPr$_2$** were tested in DCM at 30 °C (Table 1, entries 1–4). After 2 h, $Cu(OTf)_2$ showed good reactivity, but the enantioselectivity was poor (29% ee, Table 1, entry 1). $Zn(OTf)_2$ and $Mg(OTf)_2$ gave much higher ee albeit with slightly lower yields (85 and 88% yield, 97 : 3 dr, 75 and 81% ee, respectively; Table 1, entries 2 and 3). To our delight, $Ni(OTf)_2$ was more effective in promoting the reaction, and the desired product **3a** was obtained in 90% yield, 97 : 3 dr, and 86% ee (Table 1, entry 4). Exploring different chiral *N*,*N*′-dioxides revealed that **L-RaPr$_2$** derived from L-ramipril could increase the ee to 92% (Table 1, entry 6) while **L-PiPr$_2$** derived from L-piperidine acid decreased the ee to 74% (Table 1, entry 5). Decreasing the steric hindrance of the amide substituents resulted in a very poor ee though the yield and dr were still high (91% yield, 98 : 2 dr, 39% ee; Table 1, entry 7). Further exploration of solvents revealed that Cl_2CHCH_2Cl could substantially increase the enantioselectivity, and the desired product **3a** was isolated in 90% yield, 96 : 4 dr and 97% ee (Table 1, entry 8).

With the optimized reaction conditions established, we next investigated the substrate scope of the reaction by varying the 2,3-dioxopyrrolidine derivatives **1**. As summarized in Table 2,

Table 2 Substrate scope of the asymmetric DA reaction of **1** and **2**[a]



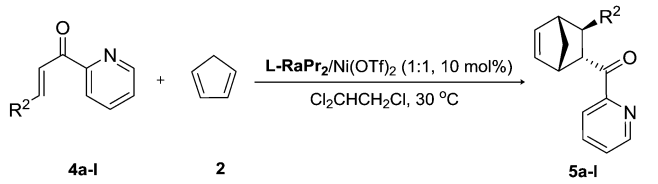
Entry	R^1	Yield[b] (%)	dr[c]	ee[d] (%)
1	Ph	90 (**3a**)	93 : 7	97 (1*R*,2*R*,3*S*,4*S*)
2	3-FC_6H_4	91 (**3b**)	93 : 7	96 (1*R*,2*R*,3*S*,4*S*)
3	4-FC_6H_4	87 (**3c**)	92 : 8	95 (1*R*,2*R*,3*S*,4*S*)
4	3-ClC_6H_4	91 (**3d**)	93 : 7	97 (1*R*,2*R*,3*S*,4*S*)
5	4-ClC_6H_4	86 (**3e**)	93 : 7	95 (1*R*,2*R*,3*S*,4*S*)
6	3-BrC_6H_4	92 (**3f**)	94 : 6	97 (1*R*,2*R*,3*S*,4*S*)
7	4-BrC_6H_4	97 (**3g**)	93 : 7	96 (1*R*,2*R*,3*S*,4*S*)
8	4-$F_3CC_6H_4$	89 (**3h**)	94 : 6	96 (1*R*,2*R*,3*S*,4*S*)
9	3,4-$Cl_2C_6H_3$	90 (**3i**)	93 : 7	97 (1*R*,2*R*,3*S*,4*S*)
10	2-MeC_6H_4	80 (**3j**)	90 : 10	75 (1*R*,2*R*,3*S*,4*S*)
11	4-MeC_6H_4	83 (**3k**)	92 : 8	93 (1*R*,2*R*,3*S*,4*S*)
12	4-$MeOC_6H_4$	85 (**3l**)	92 : 8	96 (1*R*,2*R*,3*S*,4*S*)
13	1-Naphthyl	94 (**3m**)	88 : 12	95 (1*R*,2*R*,3*S*,4*S*)
14	2-Naphthyl	85 (**3n**)	93 : 7	94 (1*R*,2*R*,3*S*,4*S*)
15		78 (**3o**)	82 : 18	92 (1*R*,2*R*,3*R*,4*S*)

[a] Unless otherwise noted, the reactions were performed with **1** (0.1 mmol), **2** (100 μL) and **L-RaPr$_2$**/$Ni(OTf)_2$ (1 : 1, 10 mol%) in Cl_2CHCH_2Cl (1.0 mL) at 30 °C for 0.5–5 h. [b] Isolated yield of **3**. [c] Determined by ^{1}H NMR analysis. [d] Determined by chiral HPLC analysis.

2,3-dioxopyrrolidine derivatives bearing different aromatic groups reacted smoothly with cyclopentadiene **2**, providing the corresponding bridged spiro products with four adjacent stereocenters in good to excellent yields with excellent diastereo- and enantioselectivities. Generally, 2,3-dioxopyrrolidines with electron-withdrawing groups on the phenyl ring achieved higher yields than those with electron-donating substituents (Table 2, entries 1–9 *vs.* entries 10–12). The *ortho*-substituted substrate **1j** yielded product **3j** in a much lower ee value (75% ee; Table 2, entry 10), which might be caused by the steric hindrance of the *ortho*-substituents with the catalyst. Furthermore, naphthyl-substituted substrates were tolerated, and the corresponding products **3m–n** were afforded in excellent results (94 and 85% yield, 88 : 12 and 93 : 7 dr, 95 and 94% ee, respectively, Table 2, entries 13 and 14). Remarkably, heteroaromatic substrate **1o** derived from thiophene-3-carbaldehyde could also be converted to the desired product in 78% yield, 82 : 18 dr value and 92% ee value (Table 2, entry 15). The absolute configuration of **3d** was determined to be (1*R*,2*R*,3*S*,4*S*) by using single-crystal X-ray diffraction analysis,[13] the others were confirmed in comparison with the Cotton effect in the CD spectra.

Encouraged by these results obtained from 2,3-dioxopyrrolidine derivatives, we attempted to broaden the reaction scope to 2-alkenoyl pyridines. To our delight, in the presence of the optimal **L-RaPr$_2$**/$Ni(OTf)_2$ complex, 2,3-dioxopyrrolidines **4a–4h** bearing either an electron-withdrawing or an electron-donating substituent on the phenyl ring converted to the corresponding chiral bridged products in high yields and stereoselectivities (74–90% yields, 90 : 10–95 : 5 dr, 88–96% ee; Table 3, entries 1–8). Remarkably, heteroaromatic substrates were also suitable. Furyl substituted **4i** and **4j** afforded the desired products **5i–j**

Table 3 Substrate scope of the asymmetric DA reaction of **2** and **4**[a]



4a-l **2** **5a-l**

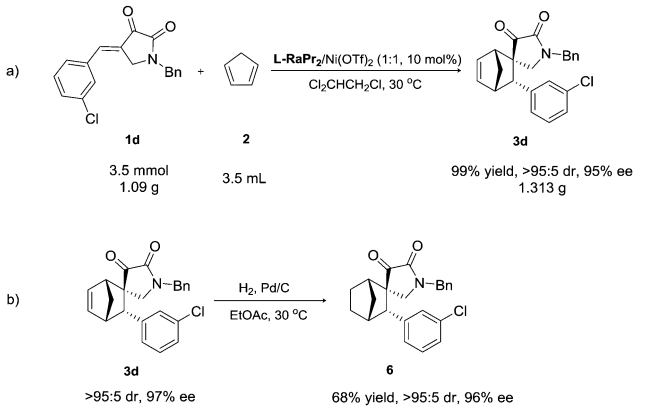
Entry	R^2	Yield[b] (%)	dr[c]	ee[d] (%)
1	Ph	89 (**5a**)	93 : 7	96 (1*S*,2*R*,3*R*,4*R*)
2	4-FC_6H_4	86 (**5b**)	93 : 7	95 (1*S*,2*R*,3*R*,4*R*)
3	4-ClC_6H_4	90 (**5c**)	92 : 8	88 (1*S*,2*R*,3*R*,4*R*)
4	2-BrC_6H_4	82 (**5d**)	92 : 8	90 (1*S*,2*R*,3*R*,4*R*)
5	3-BrC_6H_4	74 (**5e**)	90 : 10	88 (1*S*,2*R*,3*R*,4*R*)
6	4-BrC_6H_4	82 (**5f**)	91 : 9	93 (1*S*,2*R*,3*R*,4*R*)
7	4-MeC_6H_4	84 (**5g**)	94 : 6	94 (1*S*,2*R*,3*R*,4*R*)
8	4-$MeOC_6H_4$	77 (**5h**)	95 : 5	96 (1*S*,2*R*,3*R*,4*R*)
9	2-Furyl	77 (**5i**)	94 : 6	94 (1*S*,2*R*,3*R*,4*R*)
10	3-Furyl	66 (**5j**)	94 : 6	96 (1*S*,2*R*,3*R*,4*R*)
11	2-Thienyl	83 (**5k**)	94 : 6	94 (1*S*,2*R*,3*R*,4*R*)
12	3-Thienyl	75 (**5l**)	95 : 5	94 (1*S*,2*R*,3*R*,4*R*)
13	*c*-Hexyl	79 (**5m**)	77 : 23	96 (1*S*,2*R*,3*R*,4*R*)

[a] Unless otherwise noted, the reactions were performed with **4** (0.1 mmol), **2** (100 μL) and **L-RaPr$_2$**/Ni(OTf)$_2$ (1 : 1, 10 mol%) in Cl_2CHCH_2Cl (1.0 mL) at 30 °C for 11–24 h. [b] Isolated yield of **5**. [c] Determined by ^{1}H NMR analysis. [d] Determined by chiral HPLC analysis.

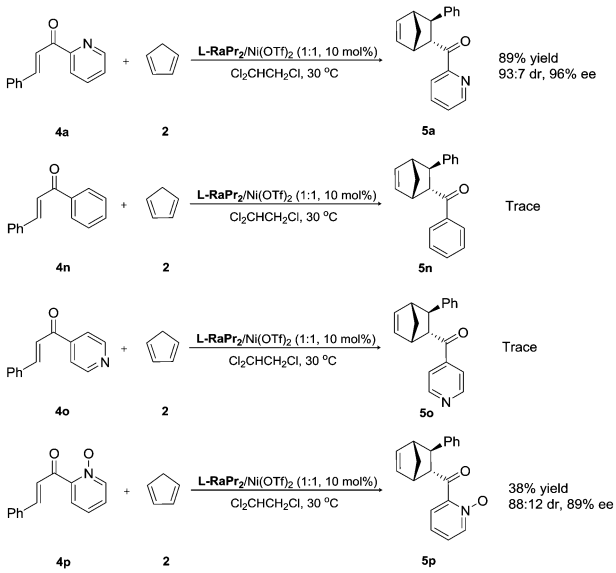
in 66–77% yields, 94 : 6 dr, 94–96% ee (Table 3, entries 9 and 10). While, thienyl substituted **4k–l** generated the products in 75–83% yields, 94 : 6–95 : 5 dr and 94% ee (Table 3, entries 11 and 12). Additionally, cyclohexyl substituted **4m** also proceed smoothly, giving the corresponding product in 79% yield, 77 : 23 dr, and 96% ee. The absolute configuration of **5a** was assigned to be (1*S*,2*R*,3*R*,4*R*) by comparing the characterization data with the literature.[14] The configuration of the other products was determined also to be (1*S*,2*R*,3*R*,4*R*) by a comparison of their CD spectra with that of **5a**.

To show the synthetic potential of the catalytic system, a gram-scale synthesis of **3d** was carried out. As shown in Scheme 2, in the presence of 10 mol% **L-RaPr$_2$**/Ni(OTf)$_2$ complex, **1d** (3.5 mmol) and **2** (3.5 mL) transformed smoothly to **3d** in 99% yield (1.313 g) with >95 : 5 dr and 95% ee (Scheme 2a). Meanwhile, product **3d** could be easily transformed to **6** in good yield (68%) without loss of stereoselectivity by simple reduction of the carbon–carbon double bond with 10% Pd/C in ethyl acetate (Scheme 2b).

It is well-known that dioxopyrrolidine **1** was readily coordinated to the catalysts by their carbonyl groups in a bidentate manner.[6,12] Then, what about the 2-alkenoyl pyridines **4**? To gain insight into the role of the pyridine group, control experiments were performed. As shown in Scheme 3, chalcone **4n** and 4-alkenoyl pyridine **4o**, whose aromatic rings have no chance to coordinate with the central metal, enabled the reaction to proceed sluggishly and only a trace amount of products was detected after 12 h, suggesting that the coordination of the nitrogen atom of pyridine to the metal center is crucial for the reaction. Furthermore, 2-alkenoyl pyridine *N*-oxide **4p**, which could also coordinate to the central metal ion in a bidentate fashion, was also synthesized and applied in the reaction under the optimized reaction conditions. To our delight, the corresponding



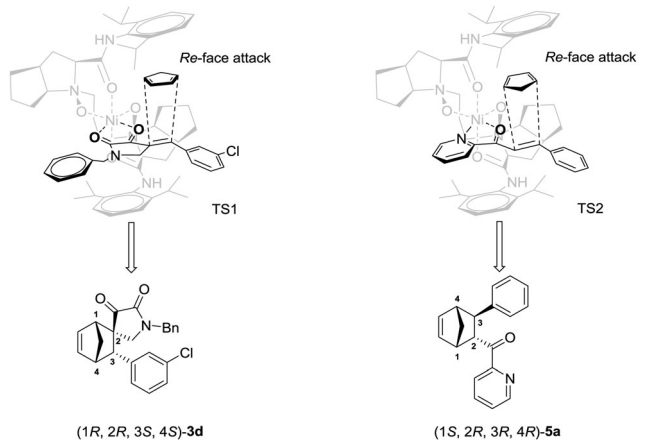
Scheme 2 (a) Gram-scale version of the reaction; (b) conversion of **3d** to **6**.



Scheme 3 Control experiments.

product **5p** was also obtained in very good stereoselectivity (88 : 12 dr and 89% ee).

To further explore the mechanism of the catalytic reaction, the catalytic composition and coordination between the substrate and the catalyst were investigated by using ESI-HRMS.[14] The spectrum of a mixture of ligand **L-RaPr$_2$**, Ni(OTf)$_2$ and **1a** in a 1 : 1 : 1 ratio in Cl_2CHCH_2Cl at 30 °C displayed an ion at *m*/*z* 907.3792 (*m*/*z* calcd for [**L-RaPr$_2$** + Ni^{2+} + OTf^-]$^+$: 907.3796), this result suggested that the ligand coordinated with the metal in a 1 : 1 ratio. A characteristic signal of [**L-RaPr$_2$** + Ni^{2+} + OTf^- + **1a**]$^+$ at *m*/*z* 1184.4904 (*m*/*z* calcd 1184.4899) was also observed, which suggested that the **L-RaPr$_2$**/Ni(OTf)$_2$ complex coordinated with **1a** in a 1 : 1 ratio. Meanwhile, the spectrum of a mixture of ligand **L-RaPr$_2$**, Ni(OTf)$_2$ and **4a** displayed ions at *m*/*z* 907.3788 (*m*/*z* calcd for [**L-RaPr$_2$** + Ni^{2+} + OTf^-]$^+$: 907.3796) and *m*/*z* 1116.4698 (*m*/*z* calcd for [**L-RaPr$_2$** + Ni^{2+} + OTf^- + **4a**]$^+$: 1116.4636), suggesting that the **L-RaPr$_2$**/Ni(OTf)$_2$ complex also coordinated with **4a** in a 1 : 1 ratio. Besides, operand IR experiments were also provided, which suggested that the reactions proceeded through a concerted pathway.[14]



Scheme 4 Proposed stereochemical model.

On the basis of the above experiments, our previous work and the absolute configuration of the products, possible transition state models were postulated. Firstly, the *N*-oxides and amide oxygens of **L-RaPr$_2$** coordinated to Ni(II) to form a six membered chelating ring. Then, 2,3-dioxopyrrolidine **1d** coordinates to the chiral catalyst **L-RaPr$_2$**/Ni(OTf)$_2$ with it's two carbonyl groups through a bidentate fashion, while **4a** coordinates with the carbonyl group and the nitrogen atom of pyridine, forming a rigid octahedral complex. The cyclopentadiene prefers to attack the dienophiles from the *Re*-face since the *Si*-face is shielded by the amide moiety, leading to the formation of product **3d** with the (1*R*,2*R*,3*S*,4*S*)-configuration (Scheme 4, TS1), and product **5a** with the (1*S*,2*R*,3*R*,4*R*)-configuration (Scheme 4, TS2).

In summary, we have developed an efficient chiral *N*,*N*′-dioxide/Ni(OTf)$_2$ complex system for the asymmetric Diels–Alder reactions of cyclopentadiene with 2,3-dioxopyrrolidines and 2-alkenoyl pyridines. Both reactions proceeded in high activities and high levels of stereocontrol. The corresponding chiral bridged compounds with four adjacent stereocenters were obtained in up to 97% yield, 95 : 5 dr and 97% ee. Furthermore, possible transition models were proposed to explain the stereochemistry. Further applications of the catalysts are underway in our laboratory.

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Notes and references

1 For selected reviews on Diels–Alder reaction, see: (*a*) D. A. Evans and J. S. Johnson, in *Comprehensive Asymmetric Catalysis*, ed. E. N. Jacobsen, A. Pfaltz and H. Yamamoto, Springer, New York, 1999, vol. 3, pp. 1177; (*b*) K. C. Nicolaou, S. A. Snyder, T. Montagnon and G. Vassilikogiannakis, *Angew. Chem., Int. Ed.*, 2002, **41**, 1668; (*c*) A. G. Doyle and E. N. Jacobsen, *Chem. Rev.*, 2007, **107**, 5713; (*d*) K. Ishihara, M. Fushimi and M. Akakura, *Acc. Chem. Res.*, 2007, **40**, 1049; (*e*) E. J. Corey, *Angew. Chem., Int. Ed.*, 2009, **48**, 2100.

2 For selected examples of asymmetric Diels–Alder reactions of cyclopentadiene, see: (*a*) S. Kobayashi and H. Ishitani, *J. Am. Chem. Soc.*, 1994, **116**, 4083; (*b*) D. A. Evans, S. J. Miller, T. Lectka and P. von Matt, *J. Am. Chem. Soc.*, 1999, **121**, 7559; (*c*) A. Sakakura, R. Kondo, Y. Matsumura, M. Akakura and K. Ishihara, *J. Am. Chem. Soc.*, 2009, **131**, 17762; (*d*) Z. L. Shen, H. L Cheong, Y. C. Lai, W. Y. Loo and T. P. Loh, *Green Chem.*, 2012, **14**, 2626; (*e*) T. F. Kang, Z. Wang, L. L. Lin, Y. T. Liao, Y. H. Zhou, X. H. Liu and X. M. Feng, *Adv. Synth. Catal.*, 2015, **357**, 2045.

3 N. A. Lozinskaya, M. S. Volkova, M. Y. Seliverstov, V. V. Temnov, S. E. Sosonyuk, M. V. Proskurnina and N. S. Zefirov, *Mendeleev Commun.*, 2014, **24**, 260.

4 (*a*) S. B. Herzon, N. A. Calandra and S. M. King, *Angew. Chem., Int. Ed.*, 2011, **50**, 8863; (*b*) S. M. King, N. A. Calandra and S. B. Herzon, *Angew. Chem., Int. Ed.*, 2013, **52**, 3642; (*c*) N. A. Calandra, S. M. King and S. B. Herzon, *J. Org. Chem.*, 2013, **78**, 10031.

5 A. Madin, C. J. O'Donnell, T. Oh, D. W. Old, L. E. Overman and M. J. Sharp, *J. Am. Chem. Soc.*, 2005, **127**, 18054.

6 G. Desimoni, G. Faita and P. Quadrelli, *Chem. Rev.*, 2013, **113**, 5924.

7 (*a*) M. P. Sibi, Z. Ma, K. Itoh, N. Prabagaran and C. P. Jasperse, *Org. Lett.*, 2005, **7**, 2349; (*b*) H. Suga, Y. Furihata, A. Sakamoto, K. Itoh, Y. Okumura, T. Tsuchida, A. Kakehi and T. Baba, *J. Org. Chem.*, 2011, **76**, 7377; (*c*) L. Dong, C. Geng and P. Jiao, *J. Org. Chem.*, 2015, **80**, 10992.

8 O. Corminboeuf and P. Renaud, *Org. Lett.*, 2002, **4**, 1735.

9 X.-B. Chen, L. Zhu, L. Fang, S.-J. Yan and J. Lin, *RSC Adv.*, 2014, **4**, 9926.

10 S. Zhang, Y.-C. Luo, X.-Q. Hu, Z.-Y. Wang, Y.-M. Liang and P.-F. Xu, *J. Org. Chem.*, 2015, **80**, 7288.

11 (*a*) S. Otto, F. Bertoncin and J. B. F. N. Engberts, *J. Am. Chem. Soc.*, 1996, **118**, 7702; (*b*) S. Otto, G. Boccaletti and J. B. F. N. Engberts, *J. Am. Chem. Soc.*, 1998, **120**, 4238; (*c*) S. Otto and J. B. F. N. Engberts, *J. Am. Chem. Soc.*, 1999, **121**, 6798; (*d*) M. T. Reetz and N. Jiao, *Angew. Chem., Int. Ed.*, 2006, **45**, 2416; (*e*) G. Roelfes, A. J. Boersma and B. L. Feringa, *Chem. Commun.*, 2006, 635; (*f*) S. Barroso, G. Blay and J. R. Pedro, *Org. Lett.*, 2007, **9**, 1983; (*g*) J. Podtetenieff, A. Taglieber, E. Bill, E. J. Reijerse and M. T. Reetz, *Angew. Chem., Int. Ed.*, 2010, **49**, 5151; (*h*) A. Livieri, M. Boiocchi, G. Desimoni and G. Faita, *Chem. – Eur. J.*, 2011, **17**, 516; (*i*) C. Wang, G. Jia, J. Zhou, Y. Li, Y. Liu, S. Lu and C. Li, *Angew. Chem., Int. Ed.*, 2012, **51**, 9352; (*j*) L. Zheng, A. Marcozzi, J. Y. Gerasimov and A. Herrmann, *Angew. Chem., Int. Ed.*, 2014, **53**, 7599; (*k*) G. Desimoni, G. Faita and P. Quadrelli, *Chem. Rev.*, 2014, **114**, 6081; (*l*) S. Park, I. Okamura, S. Sakashita, J. H. Yum, C. Acharya, L. Gao and H. Sugiyama, *ACS Catal.*, 2015, **5**, 4708.

12 For selected examples from our research group, see: (*a*) X. H. Liu, L. L. Lin and X. M. Feng, *Acc. Chem. Res.*, 2011, **44**, 574; (*b*) K. Shen, X. H. Liu, L. L. Lin and X. M. Feng, *Chem. Sci.*, 2012, **3**, 327; (*c*) K. Zheng, L. L. Lin and X. M. Feng, *Acta Chim. Sin.*, 2012, **70**, 1785; (*d*) M. S. Xie, X. X. Wu, G. Wang, L. L. Lin and X. M. Feng, *Acta Chim. Sin.*, 2014, **72**, 856; (*e*) H. F. Zheng, P. He, Y. B. Liu, Y. L. Zhang, X. H. Liu, L. L. Lin and X. M. Feng, *Chem. Commun.*, 2014, **50**, 8794; (*f*) Y. H. Zhou, Y. Zhu, L. L. Lin, Y. L. Zhang, J. F. Zheng, X. H. Liu, L. L. Lin and X. M. Feng, *Chem. – Eur. J.*, 2014, **20**, 16753; (*g*) X. H. Liu, L. L. Lin and X. M. Feng, *Org. Chem. Front.*, 2014, **1**, 298; (*h*) H. F. Zheng, X. H. Liu, C. R. Xu, Y. Xia, L. L. Lin and X. M. Feng, *Angew. Chem., Int. Ed.*, 2015, **54**, 4032; (*i*) Y. L. Zhang, N. Yang, X. H. Liu, J. Gou, X. Y. Zhang, L. L. Lin, C. W. Hu and X. M. Feng, *Chem. Commun.*, 2015, **51**, 8432; (*j*) J. F. Zheng, L. L. Lin, K. Fu, H. F. Zheng, X. H. Liu and X. M. Feng, *J. Org. Chem.*, 2015, **80**, 8836.

13 CCDC 1438596 (**3d**).

14 See the ESI† for details.

