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# Dual enantioselective Diels–Alder process in the cyclization of chiral acrylamide with dienes†

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ABSTRACT: Diels–Alder cycloadditions of chiral acrylamides with cyclopentadiene or 2, 3-dimethyl butadiene proceed with high diastereofacial selectivity. Either *endo-R* or *endo-S* products have been obtained depending upon the structures of acrylamides and Lewis acids used. The *endo* form was exclusively obtained over the *exo* form. The dependence of the mechanism of formation of opposite configurations of *endo-R* or *endo-S* products on the Lewis acids is discussed. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: dual enantioselective; Diels–Alder cyclization; diastereofacial selectivity; *endo-R*; *endo-S*; Lewis acids

## INTRODUCTION

Asymmetric Diels–Alder cyclization is one of the most effective methods of creating a chiral center during the formation of six-membered rings (for reviews see Ref. 1). Various types of chiral dienophiles such as chiral esters,[1] *N*-acyloxazole derivatives,[2] *N*-acylsultams,[3] acrylates[4] and acrylamides[5] have been developed. Metal coordination is important for diastereofacial selectivity in the asymmetric synthesis. Lewis acids have been used for chelate formation in Diels–Alder cyclizations to obtain high diastereofacial selectivities.[1–5] In general, the *S*-form of the chiral dienophile (auxiliary) exclusively affords the *endo-R* adduct over the *endo-S*, and the *R*-form exclusively gives the *S*-adduct over the *endo-R*. Issues associated with this absolute stereochemical control dependence upon Lewis acids and the structures of dienophiles provide an important challenge in the area of practical Diels–Alder reaction designs.[4a,5b]

## RESULTS AND DISCUSSION

In anticipation of obtaining the opposite configuration of the *endo* adduct and understanding the mechanism, three different dienophiles **1**, **2** and **3** were prepared and reacted with dienes in the presence of various Lewis acids. Here we describe the intriguing results obtained during development of Lewis acid dependent stereocontrol toward both *endo-R* and *endo-S* configurations with high diastereofacial selectivity. We reported the preliminary results on dual enantioselective control in asymmetric Diels–Alder cyclization.[6] In order to generalize the results, the requisite dienophiles **1**–**3** were synthesized from (*S*)-indoline-2-carboxylic acid.[7] They were purified and their optical purities (>99.8% ee) were determined by HPLC (Daicel chiral OD column, i-PrOH-n-hexane, 5:95). The preliminary studies involved reaction of **1**–**3** with **4** and **5**, as shown in Fig. 1.

Extremely high levels of asymmetric induction can be achieved in Diels–Alder cycloadditions of **3** with **4**. The results obtained are summarized in Table 1.

Table 1 shows extremely high diastereoselectivities [*endo-R* (**8a**):*endo-S* (**8b**) = 99:1] in the Diels–Alder cyclizations of **3** with **4** in the presence of various Lewis acids such as $Et_2AlCl$, $EtAlCl_2$, $AlCl_3$, $BF_3{\cdot}Et_2O$, $ZnCl_2$, $TiCl_4$, $Ti(O\text{-}i\text{-}Pr)_4$, $SnCl_4$ and $ZrCl_4$. All Lewis acids resulted in the *endo*-form with the *R*-form of absolute configuration. In contrast to these results, when **1** was reacted with **4** in the presence of aluminum chlorides, $ZnCl_2$ or $BF_3{\cdot}Et_2O$, the opposite configuration of *endo-S* (**6b**) with high diastereoselectivity [*endo-R* (**6a**):*endo-S* (**6b**) = 1:>99] as shown in Table 2.

In particular, **3**, which contains a diphenyl substituted tertiary alcohol moiety, affords exceptionally high diastereofacial selectivities (**8a**:**8b** ≥ 99:1, yield ≥ 90%; Table 1) regardless of the nature of the Lewis acid. The *endo* configurations were readily ascertained by iodolactonization of **6a**–**8a** with $I_2$ in DME.[5b] The *exo* compound

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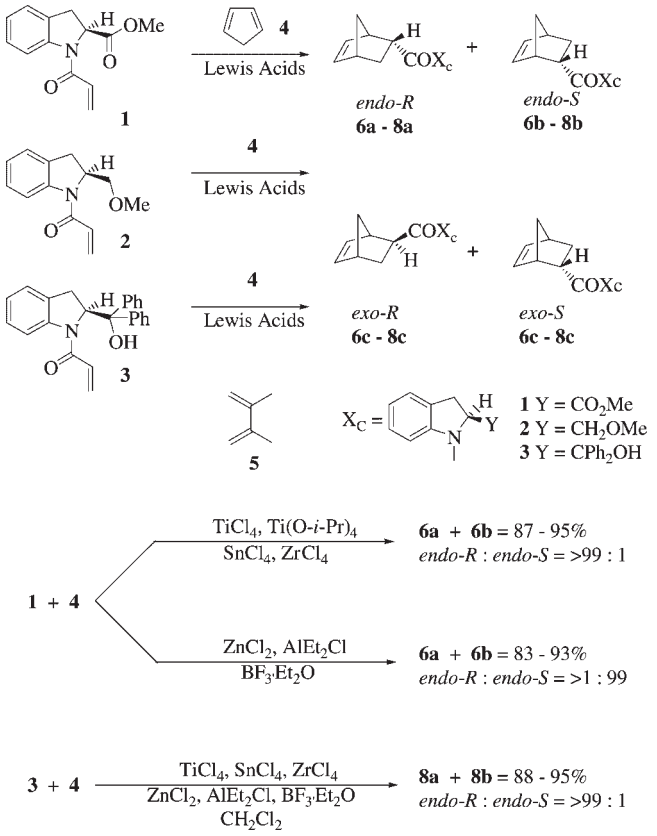


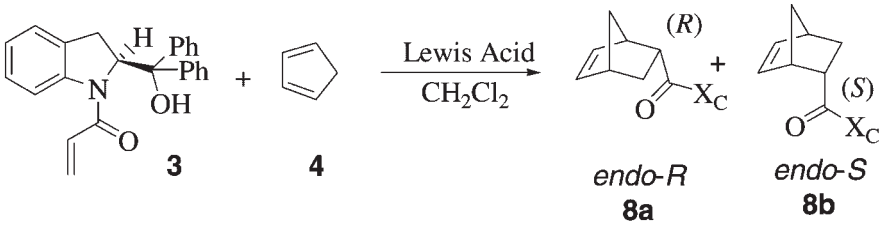

**Figure 1.** Diels–Alder cyclizations

cannot be lactonized under the same reaction conditions. The ratio of *endo-R* and *endo-S* was determined by HPLC with the crude **6a**–**8a** and **6b**–**8b** without purification. The absolute configuration of **6a**, **7b** or **8a** was determined by reductive cleavage of **6a** to the known norbornene-2-methanol and subsequent comparison of $[\alpha]_D$ values.[8]

The variously configured adducts produced can be rationalized by the intermediates formed between **1**–**3** and the metals of the Lewis acids. Compounds **1**–**3** react with **4** to favor the formation of *endo-R* species **6a** or **8a** with $TiCl_4$, $Ti(O\text{-}i\text{-}Pr)_4$, $SnCl_4$ or $ZrCl_4$ probably via formation of seven-membered ring chelates with the acryloyl moiety of **10** or **11** having a *cisoid* conformation.[4a,5b] (Fig. 2). Helmchen and co-workers reported the first evidence of formation of a seven-membered ring chelate complex.[4a] It is worth noting that even in the absence of any Lewis acid, **3** reacts with **4** to give an excellent chemical yield and high stereofacial selectivity (*endo*:*exo* $\geq$ 99:1, *endo-R*:*endo-S* $\geq$ 99:1; entry 1 in Table 1) at 25 °C after a long reaction time (48 h, in Table 1). The results can be attributed to the hydrogen bond *cisoid* conformation intermediate **11** where the hydrogen acts as a Lewis acid. On the other hand, **1** or **2** prefer *endo-S* formation **6b** or **7b** with $ZnCl_2$, $AlEtCl_2$ or $BF_3{\cdot}Et_2O$, with high diastereofacial selectivity probably resulting from intermediates **9**, as shown in Fig. 2. In contrast to Ti or Sn Lewis acids, relatively weaker Lewis acids such as Zn, Al or B may not form a seven-membered ring complex, instead forming a weak coordination with the amide carbonyl group (**9**).[4a,5b] In dienophile **2**, the same trend as for **7b** was observed, but in a less diastereoselective manner than for **1** [$Ti(O\text{-}i\text{-}Pr)_4$; 90%, *endo-R*:*endo-S* = 94:6, $SnCl_4$; 92%, *endo-R*:*endo-S* = 99:1).

Dienophile **1** and **3** also reacted with less reactive 2,3-dimehylbutadiene **5** or methylbutadiene **5′** at 25 °C, resulting in the same trend as shown in Table 3 and Figure 3.

**Table 1.** Asymmetric Diels–Alder cyclization of **3** with **4**

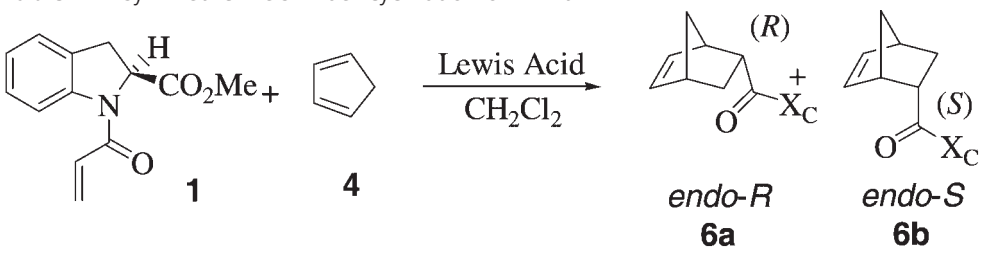



| Lewis acid | Temp. (°C) | Time (h) | Yield (%)[a] | *endo*:*exo*[b] | *endo* ds[b] | Config.[c] |
|---|---|---|---|---|---|---|
| None | rt | 48 | 92 | >99:1 | >99:1 | *R* |
| $Et_2AlCl$ | −40 | 10 | 95 | >99:1 | >99:1 | *R* |
| $EtAlCl_2$ | −78 | 7 | 94 | >99:1 | >99:1 | *R* |
| $AlCl_3$ | −40 | 8 | 88 | >99:1 | >99:1 | *R* |
| $BF_3{\cdot}Et_2O$ | −78 | 5 | 91 | >99:1 | 99:1 | *R* |
| $ZnCl_2$ | rt | 12 | 90 | >99:1 | >99:1 | *R* |
| $TiCl_4$ | rt | 7 | 90 | >99:1 | 99:1 | *R* |
| $Ti(O\text{-}i\text{-}Pr)_4$ | rt | 15 | 89 | >99:1 | >99:1 | *R* |
| $SnCl_4$ | −78 | 10 | 91 | 98:2 | 98:2 | *R* |
| $ZrCl_4$ | −40 | 5 | 93 | >99:1 | >99:1 | *R* |

[a] Isolated yield.
[b] Determined by HPLC with silica column. ds: diastereoselectivity.
[c] Confirmed by $[\alpha]_D$ of norbornene-2-methanol.

**Table 2.** Asymmetric Diels–Alder cyclization of **1** with **4**




| Lewis acid | Temp. (°C) | Time (h) | Yield (%)[a] | *endo*:*exo*[b] | *endo* ds[b] | Config.[c] |
|---|---|---|---|---|---|---|
| None | rt | 72 | 90 | 73:27 | 73:7 | *S* |
| $Et_2AlCl$ | −78 | 10 | 95 | 90:10 | >99:1 | *S* |
| $EtAlCl_2$ | −78 | 8 | 87 | 88:12 | 90:10 | *S* |
| $AlCl_3$ | −20 | 8 | 87 | 80:20 | 81:19 | *S* |
| $BF_3{\cdot}Et_2O$ | −78 | 5 | 90 | 94:6 | >99:1 | *S* |
| $ZnCl_2$ | rt | 12 | 90 | 83:17 | 99:1 | *S* |
| $TiCl_4$ | 0 | 10 | 92 | 95:5 | 99:1 | *R* |
| $Ti(O\text{-}i\text{-}Pr)_4$ | rt | 12 | 87 | 72:28 | 94:6 | *R* |
| $SnCl_4$ | −78 | 5 | 92 | 95:5 | 99:1 | *R* |
| $ZrCl_4$ | −40 | 5 | 90 | 93:7 | 94:6 | *R* |

[a] Isolated yield.
[b] Determined by HPLC with silica column.
[c] Confirmed by $[\alpha]_D$ of norbornene-2-methanol.

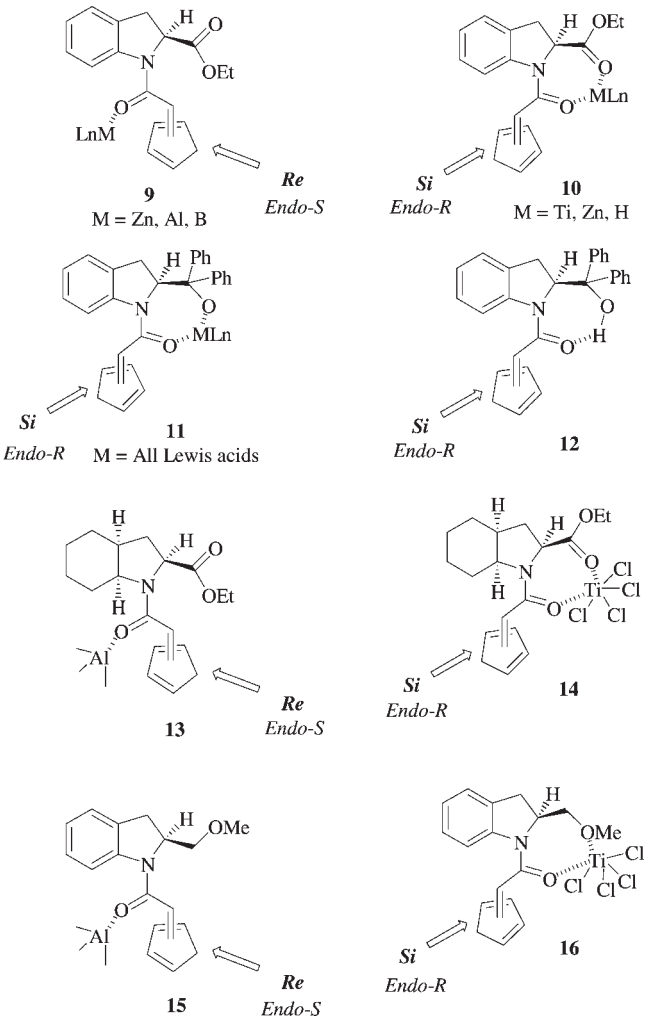



**Figure 2.** Mechanism of Diels–Alder cyclizations

In the case of Evans' model dienophile, an $\alpha,\beta$-unsaturated *S*-oxazolidinone, the *endo-R* form was obtained[2a] and explained by formation of a six-membered ring intermediate with $Et_2AlCl$, which was clarified by a $^{13}C$ NMR study[2c] (Fig. 4.) However, in contrast to a significant chemical shift change in the **1**–$SnCl_4$ chelation complex **11**, $^{13}C$ NMR measurement of the **1**–$Et_2AlCl$ mixture did not show significant changes in the chemical shifts for either of the amide or ester carbonyl peaks, *which can be explained by a weak coordination* (**9**) between **1** and $Et_2AlCl$.

Species **1** and **3** also reacted with the less reactive acyclic diene **5** at 25 °C resulting in the same trend: for **1** with $TiCl_4$ the ratio of *endo-R*:*endo-S* was 97:3, while with $EtAlCl_2$ the ratio was reversed to 3:97, which is comparable to entry 1; for **3** with both $TiCl_4$ and $Et_2AlCl$, *endo-R*:*endo-S* = 97:3 and 94:6, respectively.

However, octahydroindoline dienophile gave the similar trends through an intermediate **13** with $Et_2AlCl$ (*endo-R*:*endo-S* = 7:93) and an intermediate **14** with $TiCl_4$ (*endo-R*:*endo-S* = 93:7).

## EXPERIMENTAL

### Instruments and measurements

Melting points were taken on a Electrothermal melting point apparatus (Electrothermal Engineering). Infrared spectra were taken on a Bomen MB-100 FT-IR spectrometer. NMR spectra were determined on Brucker AC-200 and AM-300. The chemical shifts are reported in ppm relative to internal tetramethylsilane. HPLC was performed on a Waters Associates Model 44 instrument

**Table 3.** Asymmetric Diels–Alder cyclization of **1** and **3** with **5** or methylbutadiene **(5′)**

| Lewis acid | Dienophile | Diene | Temp. (°C) | Time (h) | Yield (%)[a] | ds (R:S)[b] |
|---|---|---|---|---|---|---|
| $TiCl_4$ | **1** | **5** | 0 → 25 | 8 | 85 | 97:3 |
| $EtAlCl_2$ | **1** | **5** | 0 → 25 | 10 | 80 | 97:3 |
| $TiCl_4$ | **1** | **5′** | 0 → 25 | 14 | 78 | 95:5 |
| $EtAlCl_2$ | **1** | **5′** | 0 → 25 | 18 | 76 | 10:90 |
| $TiCl_4$ | **3** | **5** | 0 → 25 | 24 | 75 | 97:3 |
| $EtAlCl_2$ | **3** | **5** | 0 → 25 | 30 | 72 | 94:6 |
| $TiCl_4$ | **3** | **5′** | 0 → 25 | 24 | 68 | 95:5 |
| $EtAlCl_2$ | **3** | **5′** | 0 → 25 | 24 | 67 | 94:6 |

[a] Isolated yield.
[b] Determined by HPLC analysis.

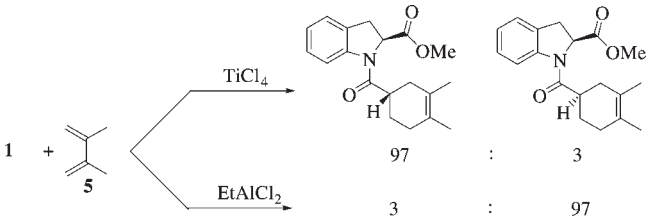



**Figure 3.** Diels–Alder cyclizations of 1 with 5

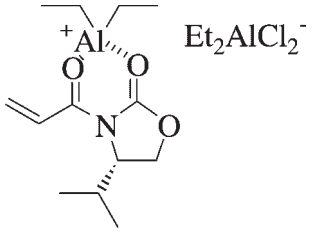



**Figure 4.** Evans' model dienophile

equipped with ultraviolet detectors. GLC analyses were performed on a Hewlett Packard 5890A gas chromatograph using a flame ionization detector and nitrogen as a carrier with a Hewlett Packard 3390A integrator. The column used for analysis was an SE-30, 10% OV101 and capillary OV-17. Mass spectra were obtained on Hewlett Packard 5980A GC/MS system using the electron impact (EI) method. Optical rotations were taken on an Autopoll III automatic polarimeter. Analytical thin layer chromatography (TLC) was performed on a glass plate (0.25 mm) coated with silica gel 60 F 254 (E. Merck). Preparative thin layer chromatography was carried out on Merck silica gel GF254, on a 20 × 20 cm glass plate of 1.0 mm thickness. The plates were activated by heating in an oven at 125 °C overnight. Also, silica gel 60 (E. Merck) was used for column chromatography.

## Materials

All the reagent grade chemicals, purchased from Aldrich, Fluka, Merck and Wako and, were used without further purification. All the organic solvents were obtained from J. T. Baker and Duksan Pharmaceutical Compound. Tetrahydrofuran and diethyl ether were refluxed over sodium and benzophenone for at least 5 h under an argon atmosphere and distilled prior to use. Methylene chloride was refluxed over calcium hydride. Some compounds were prepared by known procedures and spectral and physical data of the products were in accord with reported data.

## Synthesis of chiral dienophile 1

In an ice bath, thionyl chloride (0.1 mol) was dropped into a solution of (*S*)-indoline-2-carboxylic acid (0.1 mol) in $CH_2Cl_2$ (150 ml) and stirred for 30 min. MeOH (0.8 mol) was dropped into the solution at 0 °C for 30 min and refluxed for 1 h. The mixture was dissolved in water and neutralized with $NH_4OH$ from pH 1–2 to pH 7–8 and then extracted with $CH_2Cl_2$ three times. The organic layer was washed off with brine, dried over $MgSO_4$ and concentrated under reduced pressure to give the crude product, which was chromatographed on a silica gel column (ether:n-hexane = 1:2) to yield (*S*)-indoline-2-carboxylic acid methyl ester. This (*S*)-indoline-2-carboxylic acid methyl ester was dissolved in $CH_2Cl_2$ and cooled to 0 °C, and subsequently treated with 2 equiv. of $Et_3N$ and 2 equiv. of acryloyl chloride. The mixture was stirred for 1 h, diluted with ether, filtered thorough Celite, washed with brine and dried over $MgSO_4$ and then concentrated under reduced pressure, and chromatographed on a silica gel column to give chiral dienophile **1**.

$[\alpha]_D^{20}$ −127.85 ° (c 1.07, $CHCl_3$). $^1H$ NMR ($CDCl_3$) $\delta$3.20 (m, 1H), 3.51 (m, 1H), 3.66 (s, 3H), 5.03 (m, 1H), 5.75 (m, 1H), 6.36 (m, 2H), 6.96–7.15 (m, 4H). $^{13}C$ NMR ($CDCl_3$) $\delta$171.62, 164.22, 141.71, 139.97, 130.56, 128.64, 125.30, 117.23, 114.60, 59.69, 53.02, 32.91. IR (NaCl) 1745, 1658, 1481, 1415, 1374, 1271, 1204, 756 $cm^{-1}$. Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.66; N, 6.05. Found: C, 66.98; H, 5.74; N, 5.81.

## Synthesis of chiral dienophile 2

In a 50 ml, two necked, round-bottom flask equipped with an oil-bath, a reflux condenser with a drying tube packed with $CaCl_2$, and a stopper were placed 25 ml of

anhydrous THF and $LiAlH_4$ (591 mg, 15.6 mmol). The suspension was heated under reflux for 15 min, the heating oil-bath was switched off, and 1.63 g (10 mmol) of powdered (*S*)-indoline-2-carboxylic acid were added in small portions to the boiling mixture at such a rate to maintain reflux. The contents of the flask were kept boiling for an additional 1 h. Excess LAH was then decomposed by cautiously adding a solution of 280 mg of KOH in 1.2 ml of water (without external heating) through a syringe to the boiling mixture. Upon hydrolysis, white salts precipitate and stirring became difficult. After the addition was complete, the mixture was refluxed for 15 min and the hot solution was filtered by suction through a Buchner funnel. The precipitate was pressed dry with a beaker. Any remaining indoline was extracted from the precipitate by refluxing with 15 ml of THF for 1 h under mechanical stirring, followed again by suction filtration. The combined filters were concentrated at 30 °C under reduced pressure to yield the crude product. The crude hydroxymethyl indoline derivative, along with a magnetic stirring bar, was cooled to 0 °C. Methyl formate (5 ml, excess) was added gradually and stirring was continued overnight. Excess methyl formate was evaporated at 30 °C, which was taken up in $CH_2Cl_2$ and dried over sodium sulfate. The filtrates were concentrated under reduced pressure to yield the crude *N*-formyl derivative. This was placed in a two-necked flask in 15 ml of anhydrous THF and flushed with argon. The solution was cooled to −50 °C to −60 °C, the cooling bath was removed, and methyl iodide (4.00 mmol) was added, followed by NaH (3.7 mmol) added in one portion. The apparatus was flushed again with argon and allowed to warm to rt. During this period hydrogen gas evolved and a gray solid precipitated, which caused stirring to become difficult. At about 0 °C, the precipitate dissolves exothericmally with strong evolution of hydrogen. The solution was refluxed for 15 min, and quenched by slow addition of HCl, without external heating. THF was removed under reduced pressure to yield the crude *O*-methylated compound. To this compound, a solution of KOH (650 mg of KOH in 4 ml of water) was added and the mixture stirred overnight under an argon atmosphere. Addition of potassium carbonate (1.5 g) caused a precipitate of potassium salts to form, which were filtered off and washed with ether. The Organic layer was dried over $MgSO_4$. The solvent was evaporated on a rotary evaporator under reduced pressure. The residue was chromatographed on silica column (ether:n-hexane = 1:2) to yield (*S*)-2-methoxymethyl indoline. This indoline was treated with $Et_3N$ and acryloyl chloride as described previously to yield chiral dienophile **2**.

$[\alpha]_D^{20}$ −100.32 ° (c 1.24, $CHCl_3$). $^1H$ NMR ($CDCl_3$) $\delta$2.94 (t, 1H), 3.28 (m, 2H), 3.30 (s, 3H), 3.43 (m, 1H), 4.69 (d, 1H), 5.76 (dd, 1H), 6.74 (dd, 1H), 6.72 (dd, 1H), 6.97–8.16 (m, 4H). $^{13}C$ NMR ($CDCl_3$) $\delta$163.91, 141.77, 130.53, 129.01, 128.40, 127.16, 125.68, 123.99, 122.34, 117.72, 73.74, 58.92, 57.53, 31.57. IR (NaCl) 2894, 1655, 1615, 1480 $cm^{-1}$.

## Synthesis of chiral dienophile 3

To a THF (150 ml) solution of (*S*)-indoline-2-carboxylic acid methyl ester (21.2 mmol) and formic acid (0.88 ml, 23.3 mmol) was added DCC (4.81 g, 23.3 mmol) in THF (35 ml) at 0 °C. The mixture was stirred at 0 °C for 4 h. The precipitate was filtered off. The filtrate was concentrated under reduced pressure. The residue was chromatographed on a silica gel column (ether:n-hexane = 2:1) to yield (*S*)-*N*-formylindoline-2-carboxylic acid methyl ester. Phenyl magnesium bromide (91.02 mmol) in THF was added to a THF solution of (*S*)-*N*-formylindoline-2-carboxylic acid methyl ester at 0 °C and the mixture was stirred at 0 °C for an additional 4 h. Brine was added to quench the reaction. The mixture was extracted with $CH_2Cl_2$. The organic layer was dried and concentrated under reduced pressure and passed through a column of silica gel to give (*S*)-2-(diphenylhydroxymethyl)indoline. Again, this was treated with $Et_3N$ and acryloyl chloride as described previously and purified by column chromatography to give chiral dienophile **3**.

$[\alpha]_D^{20}$ −428.13 ° (c 0.96, $CHCl_3$). $^1H$ NMR ($CDCl_3$) $\delta$3.00 (dd, 1H), 3.55 (dd, 1H), 5.66 (d, 1H), 5.75 (m, 1H), 6.49 (d, 1H), 6.60 (m, 1H), 6.79–7.42 (m, 14H). $^{13}C$ NMR ($CDCl_3$) $\delta$167.09, 144.57, 141.47, 132.52, 129.43, 128.08, 127.68, 127.62, 127.41, 126.87, 126.66, 124.25, 124.04, 116.75. IR (NaCl) 3309, 1641, 1592, 1268 $cm^{-1}$. M.p. 167–169 °C. Anal. Calcd for $C_{24}H_{21}NO_2$: C, 81.10; H, 5.95; N, 3.94. Found: C, 81.75; H, 5.90; N, 4.00.

## General procedures for Diels–Alder cycloaddition

Lewis acid (1 equiv.) was added to a solution of chiral dienophiles **1**–**3** and **1′** in $CH_2Cl_2$ under argon at the indicated temperature. After 5 min, freshly distilled cyclopentadiene (5 equiv.) was added to the solution. The reaction mixture was stirred according to the TLC procedure, quenched with saturated aqueous $NaHCO_3$ solution and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The diastereomers were separated by preparative TLC. The ratio of diastereomers was determined by HPLC [Hibar Prepacked Column RT 250-4, LiChrosorb Si 60 (10 mM)].

## Reductive cleavage of Diels–Alder cycloadducts

$LiAlH_4$ (0.6 equiv.) was added to the Diels–Alder adduct in THF at −78 °C. The reaction mixture was stirred at −78 °C and slowly allowed to attain rt, and then quenched with water, 15% NaOH and water. The mixture was filtered and washed with ether, and the crude products were separated by chromatography on silica gel to give norbornene-2-methanol.

### Iodolactonization of cycloadducts

Iodine (1.2 equiv.) was added to a solution of cycloadduct in $H_2O$–DME (1:1) at rt and the mixture was stirred for 5 h. The resultant solution was diluted with ethyl acetate and washed with saturated $Na_2S_2O_3$ and with 0.5 mol $dm^{-3}$ HCl. The organic layer was further washed with saturated $NaHCO_3$, dried over $MgSO_4$ and concentrated. The residue was subjected to preparative TLC (ether:n-hexane = 1:1) to give iodolactone.

## CONCLUSION

Asymmetric Diels–Alder cycloadditions of **1**, or **3** with **4** proceed with absolute stereocontrolled diastereofacial selectivities in both *endo-S* and *endo-R* (up to >99% de) depending upon Lewis acids used and the structures of chiral dienophiles.

### Acknowledgement

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