Asymmetric Lewis Acid–Dienophile Complexation: Secondary Attraction versus Catalyst Polarizability

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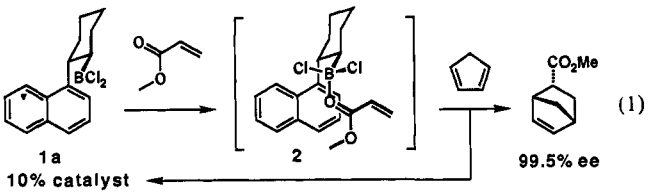
Abstract: A series of five X-ray crystal structures of chiral Lewis acid–dienophile complexes support a two-point-binding chiral recognition mechanism for these asymmetric Diels–Alder catalysts. As the arene moieties of the alkyldichloroborane Lewis acids are made more polarizable through the progression of phenyl to 3,5-dimethylphenyl to 3,5-dichlorophenyl to 3,5-dibromophenyl to naphthyl, the polar ester group of the boron-bound methyl crotonate is drawn in toward the arene of the catalyst due to an enhanced dipole–induced-dipole attraction. The catalyst with the most polarizable arene (1-naphthyl) gives higher enantioselectivity (up to 99.5% ee) in Diels–Alder reactions than the catalyst with the least polarizable arene (phenyl), demonstrating that this effect translates to the transition state.

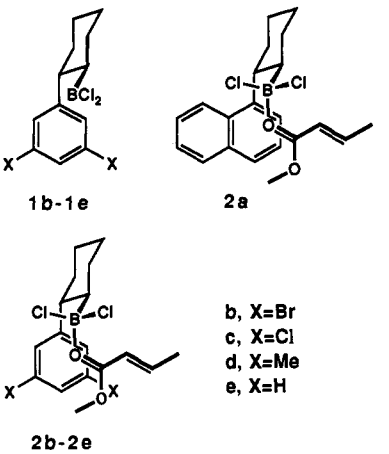
The nonempirical development of asymmetric catalysts requires a detailed understanding of chiral recognition mechanisms. We recently described asymmetric Diels–Alder catalyst **1a**, an aromatic alkyldichloroborane designed to bind and activate ester dienophiles via conformation **2**.[1,2] Catalyst **1a** gives up to 99.5% ee in Diels–Alder reactions with methyl esters (e.g. eq 1).[1,3] Active



(1)

conformation **2** was predicted by conformational analysis and supported by measurements reflecting the solid state (crystallography), solution state (selective shielding of dienophile protons by the arene), and transition state (degree and sense of asymmetric induction under Curtin–Hammett conditions).[1] A key factor favoring conformation **2** is a secondary attraction between the dienophile and the catalyst, specifically an electrostatic and dipole–induced-dipole attraction between the boron-activated carboalkoxy group of the dienophile and the electron-rich and polarizable arene of the catalyst.[1,4] Here, we provide additional evidence for this second binding interaction by reporting a series of five dienophile–catalyst crystal structures which show that the polar head group of the dienophile is drawn toward the arene of the catalyst as this arene is made more polarizable.

Boranes **1a–e** were prepared by hydroboration of the corresponding alkenes with $HBCl_2$.[5] Like **1a**,[1] **1e** could be resolved by the recrystallization of diastereomeric menthone complexes. (2*S*,5*R*)-Menthone selectively precipitates the (1*R*,2*R*)-borane in both cases.[6] Treatment of boranes **1a–e** with a slight excess



of methyl crotonate in pentane at −20 °C gave dienophile–catalyst complexes **2a–e** as white powders which yielded X-ray quality crystals by recrystallization from pentane or methylene chloride/pentane.[7-10]

The molecular geometries of **2a–e** determined by single-crystal X-ray diffraction are qualitatively the same, each possessing the basic conformation originally predicted for **2a**. That is, they each contain staggered B–C bonds, staggered B–O bonds, s-trans enone units, and binding of boron anti to the C–O bond of the ester with the CO_2Me group positioned over the arene as drawn. These features are maintained over four different crystallographic space groups for the five different arenes of **2a–e**, establishing that the structure of **2a**[1] was not fortuitous. The peri interaction in **2a** which favors positioning of the smallest benzylic substituent (H) toward the naphthalene hydrogen at C-8 is not available to phenyl compounds **2b–e**. The similarity of **2a–e** shows that this

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(1) Hawkins, J. M.; Loren, S. *J. Am. Chem. Soc.* **1991**, *113*, 7794.

(2) For a review of asymmetric Diels–Alder catalysts, see: Kagan, H. B.; Riant, O. *Chem. Rev.* **1992**, *92*, 1007.

(3) The increase in enantioselectivity for the reaction of methyl acrylate with cyclopentadiene compared to that in our original paper[1] (99.5 vs 97% ee) results from using excess cyclopentadiene.

(4) Related π-donor–acceptor interactions have been proposed in other systems: (a) Corey, E. J.; Loh, T.-P.; Roper, T. D.; Azimioara, M. D.; Noe, M. C. *J. Am. Chem. Soc.* **1992**, *114*, 8290. (b) Corey, E. J.; Loh, T.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8966. (c) Corey, E. J.; Matsumura, Y. *Tetrahedron Lett.* **1991**, *32*, 6289.

(5) Soundararajan, R.; Matteson, D. S. *J. Org. Chem.* **1990**, *55*, 2274.

(6) Borane **1d** can also be resolved with menthone, although the yield is low in this case. Boranes **1b** and **1c** give diastereomeric mixtures with menthone which do not improve with recrystallization.

(7) For a review of Lewis acid carbonyl complexes, see: Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256.

(8) For crystal structures of asymmetric Lewis acids not complexed by dienophiles, see: Corey, E. J.; Sarshar, S.; Bordner, J. *J. Am. Chem. Soc.* **1992**, *114*, 7938. Kaufmann, D.; Boese, R. *Angew, Chem., Int. Ed. Engl.* **1990**, *29*, 545. Hong, Y.; Kuntz, B. A.; Collins, S. *Organometallics* **1993**, *12*, 964.

(9) For the crystal structure of a hydrogen-bonded chiral recognition system containing strong π–π bonding, see: Pirkle, W. H.; Burke, J. A., III; Wilson, S. R. *J. Am. Chem. Soc.* **1989**, *111*, 9222.

(10) The crystalline dienophile adducts were prepared from racemic boranes. Adduct **2d** gave a chiral crystal.

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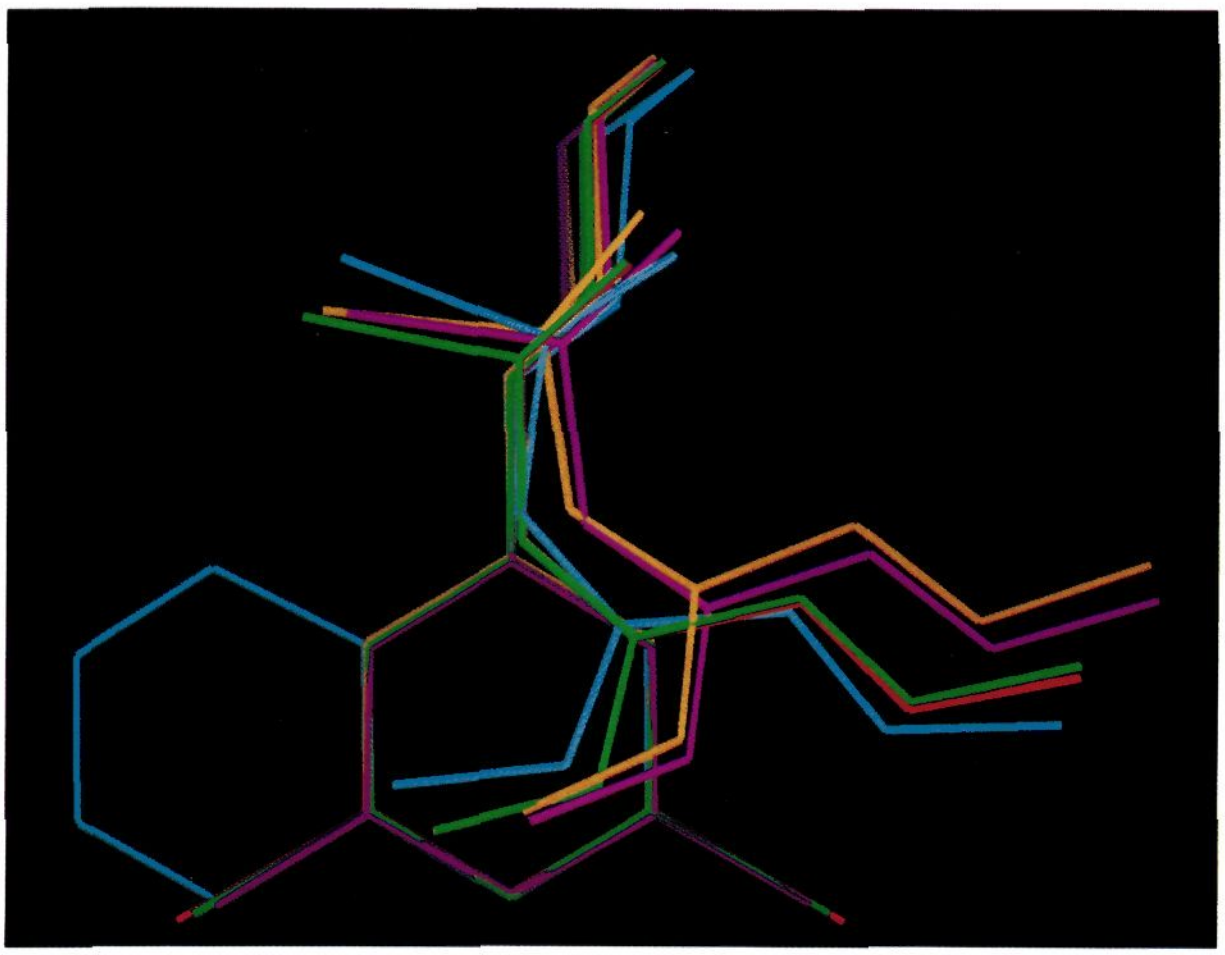


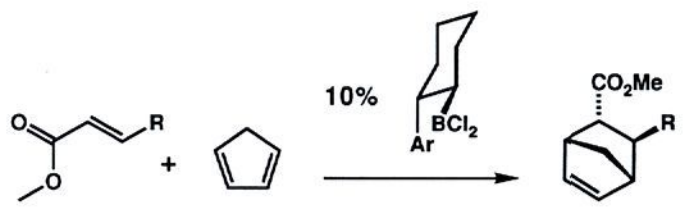
Figure 1. X-ray crystal structures of **2a** (blue), **2b** (red), **2c** (green), **2d** (purple), and **2e** (yellow) viewed above the superimposed phenyl groups of the catalysts. The CO_2Me groups of the coordinated dienophiles are above these phenyl groups with the α-, β-, and γ-carbons extending to the right.

interaction is not required for conformational control, although it may aid in preorganization[11] of the free borane **1a**.

The main differences between complexes **2a–e** are the specific positions of the CO_2Me groups with respect to the arenes. As the polarizability of the arene is increased from phenyl (**2e**) to 3,5-dimethylphenyl (**2d**) to 3,5-dichlorophenyl (**2c**) to 3,5-dibromophenyl (**2b**) to naphthyl (**2a**),[12] the CO_2Me group of the dienophile moves in toward the arene. This is most clearly seen in the top view of Figure 1, where the boron-bound methyl crotonate sweeps a trajectory from the upper right toward the lower left through this progression. From **2e** to **2a**, the distances from the center of the substituted phenyl to the carbonyl carbon, methoxy oxygen, and α-carbon decrease from 3.66 to 3.40 Å, from 3.71 to 3.53 Å, and from 4.49 to 3.96 Å, respectively. Thus, as the polarizability of the arene is increased, the dipole–induced-dipole attraction between the activated methyl crotonate and the arene is increased, drawing the dienophile in toward the catalyst.[13]

In contrast to the relative positions of the dienophiles with the arenes, the internal geometries of the methyl crotonate ligands and the binding geometries at boron are very similar for **2a–e**. Specifically, the B—O, C=O, C(carbonyl)—C(α), C=C, and C(carbonyl)—O(methoxy) bond lengths do not vary more than two standard deviations through this series of compounds. The sums of the three angles about boron in the $CBCl_2$ unit, an indication of the degree of pyramidalization at boron, also agree within two standard deviations.[14] This indicates that the movement of the dienophile toward the arene in the series **2e–a** does not involve charge transfer, or at least not different degrees of charge transfer.

The enhanced dipole–induced-dipole attraction between the substrate and the catalyst for more polarizable catalysts should translate to enhanced enantioselectivity. That is, if the transition states[15] for the exothermic reactions of the Lewis-acid-activated dienophiles of **2a–e** with dienes resemble the ground states (as expected according to the Hammond postulate), then increasing the polarizability of the arene of the catalyst should enhance reaction from conformation **2** (where the back face of the dienophile is blocked) relative to other conformations (where both faces of the dienophile are accessible) and increase the enantioselectivity of the catalyst. This was observed experimentally. Comparing **1a** (Ar = 1-naph) with **1e** (Ar = Ph), the catalyst with the more polarizable arene gives greater enantioselectivity with two different dienophiles (eq 2).[16] The diene preferentially approaches the dienophile from the top face (opposite the arene) in each case.



(2)

R=H,	Ar=1-Naph (1a)	99.5% ee
	Ar=Ph (1e)	90% ee
R=Me,	Ar=1-Naph (1a)	92% ee
	Ar=Ph (1e)	70% ee

Dipole–induced-dipole attractions between substrates and catalysts should be important for other enantioselective reactions involving polar substrate groups.

Experimental Section

All boron compounds were manipulated under an inert atmosphere using anhydrous solvents. Chiral GC analyses were performed with a J&W Cyclodex-B β-cyclodextrin column. Details of the structure determinations for **2b–e** are provided in supplementary material.

(11) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1039.

(12) The polarizabilities of benzene, *m*-xylene, 1,3-dichlorobenzene, 1,3-dibromobenzene, and naphthalene (models for the arene components of **2e**, **2d**, **2c**, **2b**, and **2a**) are 10.4, 14.2, 14.3, 16.6, and 17.6 Å^3, respectively (calculated from refractive indexes using the Clausius–Mosotti equation).

(13) For **2b** and **2c**, a dipole–dipole attraction between the carbon–halogen and C(α)–C(β) dipoles may also play a role.

(14) Average bond lengths for **2a–e** in Å (with the standard deviations of the averages in parenthesis): B–O, 1.549(7); C=O, 1.262(4); C(carbonyl)—C(α), 1.441(4); C=C, 1.32(1); C(carbonyl)—O(methoxy), 1.303(4). Average sum of the three angles about B in the $CBCl_2$ unit: 334.3(3)°. The B—O—C angles agree within three standard deviations, average 131.2(8)°.

(15) Under Curtin–Hammett conditions,[1] transition-state energies control enantioselectivity.

(16) In contrast, an analog of Narasaka's catalyst with 2-naphthyl groups gives comparable selectivity to the parent phenyl-containing catalyst, and 3,5-dimethylphenyl and 3,5-dichlorophenyl groups behave very differently in Narasaka's system.[4c]

(±)-**1a.** To a solution of 1-(1-naphthyl)cyclohexene (1.12 g, 5.4 mmol) in 25 mL of CH_2Cl_2 stirred at −78 °C was added 7.5 mL (7.5 mmol) of BCl_3 solution (1 M in CH_2Cl_2) and 0.75 g (6.5 mmol) of $HSiEt_3$. The reaction mixture was warmed to 0 °C for 12 h before removing the solvent under vacuum (**Caution**: excess hydroborating agent which may be pyrophoric is pumped off with the solvent; vacuum traps should be backfilled with argon and carefully quenched with isopropanol while still cold). The resulting clear, colorless oil (1.56 g, 99%) was used without further purification: IR (thin film) 3052, 2930, 2855, 1595, 1509, 1448, 1397, 1103, 955, 940, 914, 884, 778, 651 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 7.96 (ap d, 1H), 7.62 (ap dd, 2H), 7.4–7.1 (m, 4H), 3.40 (dt, J = 3, 11.4 Hz, 1H), 2.14 (dt, J = 3, 11.6 Hz, 1H), 2.0–1.5 (br, 8H); ^{13}C NMR ($CDCl_3$) δ 143.0, 134.5, 133.8, 133.3, 129.7, 129.5, 128.1, 127.8, 127.7, 125.7, 35.9, 33.4, 28.7, 26.5, 22.6; MS (EI) m/z (relative intensity) 206 (27.6), 165 (31.4), 128 (100).

(**1*R*,2*R*)-1a.** Crude (±)-**1a**, 1.56 g (5.36 mmol), was dissolved in 50 mL of pentane, cooled to 0 °C, and treated with 0.58 g (3.8 mmol) of *l*-menthone dropwise with rapid stirring. A white precipitate formed rapidly. The solution was stirred for 30 min and filtered. The filtrate was dried under vacuum and treated with 30 mL of methanol at 0 °C (**Caution**: HCl evolution). After 20 min, the solvent was removed under vacuum, and the resulting solid was recrystallized from pentane, yielding 0.65 (86% of the 50% theoretical maximum) of block-like crystals, mp 82–84 °C. To 0.96 g (3.4 mmol) of borinate ester prepared this way was added 8.5 mL (8.5 mmol) of BCl_3 solution (1 M in CH_2Cl_2) at 0 °C. After 12 h at 0 °C, the solvent was removed under vacuum and 8.5 mL (8.5 mmol) of additional BCl_3 solution (1 M in CH_2Cl_2) was added at 0 °C. After 12 h at 0 °C, the solvent was removed under vacuum, and the resulting oil was recrystallized from pentane (approximately 2 volumes).[17] (1*R*,2*R*)-**1a**, 0.96 g (97%), was isolated as large block-like crystals, mp 66–68.5 °C. This material was enantiomerically pure within the limits of detection by chiral stationary phase HPLC (Regis (D)-Phenylglycine Ionic Pirkle Column eluted with 0.5% DME in hexanes) analysis of the corresponding acetate prepared by oxidation (NaOH, H_2O_2) and acetylation (Ac_2O, pyridine, DMAP). The absolute configuration was determined by the crystal structure of the analogous (1*R*)-menthyl carbonate.

(±)-**1b.** The borane was prepared from the corresponding alkene as described for (±)-**1a**. (±)-**1b**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, J = 1.59 Hz, 1H), 7.26 (d, J = 1.5 Hz, 2H), 2.68 (ddd, J = 3.0, 11.4, 11.4 Hz, 1H), 1.86 (m, 5H), 1.37 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.19, 132.14, 129.24, 123.05, 46.06, 44.3, 35.52, 28.12, 26.37, 25.95.

(±)-**1c.** The borane was prepared from the corresponding alkene as described for (±)-**1a**. (±)-**1c**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, J = 1.8 Hz, 1H), 7.06 (d, J = 1.8 Hz, 2H), 2.69 (ddd, J = 3.1, 11.5, 11.5 Hz, 1H), 1.87 (m, 5H), 1.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.59, 134.97, 126.65, 125.86, 46.11, 42.9, 35.43, 28.09, 26.34, 25.95.

(±)-**1d.** The borane was prepared from the corresponding alkene as described for (±)-**1a**. (±)-**1d**: ^1H NMR (500 MHz, $CDCl_3$) δ 6.83 (s, 1H), 6.81 (s, 2H), 2.69 (ddd, J = 2.61, 11.66, 11.66 Hz, 1H), 2.30 (s, 6H), 2.06 (ddd, J = 1.94, 11.66, 11.66 Hz, 1H), 1.90 (m, 5H), 1.4 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.15 (quat), 137.83 (quat), 128.01 (CH), 125.07 (CH), 46.35 (CH), 35.89 (CH_2), 28.32 (CH_2), 26.70 (CH_2), 26.19 (CH_2), 21.34 (CH_3).

(±)-**1e.** The borane was prepared from the corresponding alkene as described for (±)-**1a**. (±)-**1e**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 2H), 7.17 (m, 3H), 2.73 (ddd, J = 3.16, 11.53, 11.53 Hz, 1H), 2.06 (ddd, J = 2.84, 11.53, 11.53 Hz, 1H), 1.86 (m, 4H), 1.38 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.12 (quat), 128.50 (CH), 127.22 (CH), 126.37 (CH), 46.50 (CH), 44.62 (CB), 35.70 (CH_2), 28.28 (CH_2), 26.61 (CH_2), 26.11 (CH_2).

(**1*R*,2*R*)-1e.** The racemic borane was resolved with *l*-menthone as described for **1a**. The *l*-menthone adduct was recrystallized to diastereomeric purity from CH_2Cl_2/pentane as determined by chiral GC analysis of the corresponding acetate prepared by oxidation (NaOH, H_2O_2) and acetylation (Ac_2O, pyridine, DMAP). The corresponding alcohol was correlated with a commercial sample of (1*R*,2*S*)-(−)-*trans*-2-phenyl-1-cyclohexanol.

(±)-**2a.** To a rapidly stirred solution of 2.04 g (7.01 mmol) of (±)-**1a** in 20 mL of pentane at −20 °C was added 0.77 g (7.1 mmol) of methyl crotonate dropwise. A white precipitate started to form after the first few drops of methyl crotonate were added. After the addition was complete, the mixture was allowed to stand for 10 min before filtering by cannula. The precipitate was dried under vacuum, yielding 2.58 g (94%) of white powder: ^1H NMR (250 MHz, $CDCl_3$) δ 8.20 (ap d, J = 8.29 Hz, 1H), 7.83 (ap d, J = 8.61 Hz, 1H), 7.67 (ap d, J = 7.67 Hz, 1H), 7.41 (m, 4H), 6.98 (dq, J = 15.53, 8.60 Hz, 1H), 5.93 (dt, J = 15.53, 1.71 Hz, 1H), 3.61 (s, 3H), 3.61 (ap dd, J = 8.52, 8.52 Hz, 1H), 2.30 (m, 1H), 2.1 (m, 2H), 1.94 (m, 1H), 1.88 (dd, J = 1.71, 8.60 Hz, 3H), 1.52 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.05, 146.33, 146.20, 143.60, 133.96, 131.27, 128.79, 126.57, 125.81, 125.52, 123.36, 122.95, 121.78, 52.20, 42.8 (CB), 40.60, 36.39, 29.00, 27.02, 26.74, 18.20. X-ray-quality crystals were grown by slowly cooling a saturated solution in pentane. Details of the structure determination for **2a** are provided in the supplementary material of ref 1.

(±)-**2b.** The methyl crotonate adduct was prepared from (±)-**1b** as described for (±)-**2a**. (±)-**2b**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (t, J = 1.6 Hz, 1H), 7.24 (d, J = 1.7 Hz, 2H), 7.17 (dq, J = 15.4, 7.0 Hz, 1H), 6.25 (dq, J = 15.5, 1.5 Hz, 1H), 3.63 (s, 3H), 2.67 (ddd, J = 3.2, 11.4, 11.4 Hz, 1H), 2.05 (m, 1H), 1.99 (dd, J = 1.5, 6.9 Hz, 3H), 1.83 (m, 2H), 1.75 (m, 1H), 1.56 (ddd, J = 3.0, 11.3, 11.3 Hz, 1H), 1.36 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.07, 151.98, 150.60, 131.44, 129.46, 122.89, 120.68, 54.06, 46.34, 41.5, 36.14, 28.59, 26.47, 26.54, 18.87. X-ray-quality crystals were obtained by recrystallization from CH_2Cl_2/pentane at −10 °C.

(±)-**2c.** The methyl crotonate adduct was prepared from (±)-**1c** as described for (±)-**2a**. (±)-**2c**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.17 (dq, J = 15.5, 7.1 Hz, 1H), 7.08 (t, J = 1.9 Hz, 1H), 7.03 (d, J = 1.8 Hz, 2H), 6.33 (dq, J = 15.6, 0.6 Hz, 1H), 3.61 (s, 3H), 2.67 (ddd, J = 3.4, 11.3, 11.3 Hz, 1H), 2.07 (m, 1H), 1.99 (dd, J = 1.3, 5.8 Hz, 3H), 1.80 (m, 2H), 1.73 (m, 1H), 1.45 (ddd, J = 2.6, 11.1, 11.1 Hz, 1H), 1.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.68, 151.71, 134.64, 126.18, 125.83, 125.78, 120.38, 54.47, 46.41, 41.0, 36.25, 28.67, 26.55, 26.48, 18.98. X-ray-quality crystals were obtained by recrystallization from CH_2Cl_2/pentane at −10 °C.

(±)-**2d.** The methyl crotonate adduct was prepared from (±)-**1d** as described for (±)-**2a**. (±)-**2d**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.03 (dq, J = 15.49, 6.92 Hz, 1H), 6.78 (ap s, 3H), 6.01 (dq, J = 15.49, 1.60 Hz, 1H), 3.65 (s, 3H), 2.65 (ddd, J = 3.48, 11.55, 11.55 Hz, 1H), 2.25 (s, 6H), 1.94 (m, 2H), 1.92 (dd, J = 1.60, 6.92 Hz, 3H), 1.83 (m, 2H), 1.38 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.89 (C=O), 146.70 (CH), 146.27 (CH), 137.76 (quat), 127.81 (CH), 125.17 (CH), 121.95 (quat), 52.18, 46.43, 43.51 (CB), 36.14 (CH_2), 28.50 (CH_2), 26.76 (CH_2), 26.35 (CH_2), 21.29, 18.19. X-ray-quality crystals were grown by slowly cooling a saturated solution in pentane.

(±)-**2e.** The methyl crotonate adduct was prepared from (±)-**1e** as described for (±)-**2a**. (±)-**2e**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (m, 2H), 7.14 (m, 3H), 7.02 (dq, J = 15.48, 6.85 Hz, 1H), 6.00 (d, J = 15.48 Hz, 1H), 3.64 (s, 3H), 2.72 (m, 1H), 1.9–1.83 (br, 8H), 1.48–1.4 (br, 4H); ^{13}C NMR (125.73 MHz, $CDCl_3$) δ 168.05, 146.77, 146.47, 128.44, 127.36, 126.16, 121.93, 52.18, 46.59, 35.97, 28.48, 26.70, 26.30, 18.21. X-ray-quality crystals were grown by slowly cooling a saturated solution in pentane.

Diels–Alder Reactions. A 100-mL Schlenk flask was charged with the borane catalyst, the flask was cooled to −78 °C, and freshly distilled CH_2Cl_2 was added slowly. Enough CH_2Cl_2 was added to establish a solvent to diene ratio of 3:1 (v/v). The diene was then added quickly, immediately followed by the dienophile. The reaction flask was sealed and allowed to warm to the reaction temperature. The reactions were quenched with 10% $NaHCO_3$(aq) and the products were isolated by flash chromatography. Enantiomeric excesses were determined by chiral GC. (1*R*)-*endo*-Methyl bicyclo[2.2.1]hept-5-ene-2-carboxylate[18] was obtained in 95% yield with 97% ee from the reaction of 0.409 g (1.41 mmol) of (1*R*,2*R*)-**1a**, 4.66 g (70.5 mmol) of cyclopentadiene, and 1.21 g (14.1 mmol) of methyl acrylate at −78 °C for 12 h. Using 10 equiv of cyclopentadiene, the enantiomeric excess was 99.5%. (1*R*)-*endo*-Methyl bicyclo[2.2.1]hept-5-ene-2-carboxylate[18] was obtained in 80% yield with 90% ee from the reaction of 49.6 mg (0.206 mmol) of (1*R*,2*R*)-**1e**, 3.4 g (51 mmol) of cyclopentadiene, and 0.44 g (5.1 mmol) of methyl acrylate at −78 °C for 12 h. (1*R*)-2-*endo*,3-*exo*-Methyl 3-methylbicyclo-[2.2.1]hept-5-ene-2-carboxylate[19] was obtained in 92% yield with 92% ee from the reaction of 0.401 g (1.38 mmol) of (1*R*,2*R*)-**1a**, 4.6 g (69 mmol) of cyclopentadiene, and 1.38 g (13.8 mmol) of methyl crotonate

(17) Recrystallization of resolved **1a** is facilitated by seed crystals. Distilled material readily solidifies providing seeds (short-path distillation, pot temperature 115 °C, 2–5 × 10^{-5} mmHg).

(18) Berson, J. A.; Walia, J. S.; Remanick, A.; Suzuki, S.; Reynolds-Warnhoff, P.; Willner, D. *J. Am. Chem. Soc.* **1961**, *83*, 3986.

(19) Berson, J. A.; Hammons, J. H.; McRowe, A. W.; Bergman, R. G.; Remanick, A.; Houston, D. *J. Am. Chem. Soc.* **1967**, *89*, 2590.

at −18 °C for 24 h and in 92% yield with 70% ee from the reaction of 0.16 g (0.67 mmol) of (1*R*,2*R*)-**1e**, 2.2 g (33 mmol) of cyclopentadiene, and 0.67 g (6.6 mmol) of methyl crotonate at −30 °C for 64 h.

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Supplementary Material Available: Details of the structure determinations for **2b–e** including ORTEP views and tables of crystal and data parameters, positional parameters and their estimated standard deviations, anisotropic thermal parameters, root-mean-square amplitudes of anisotropic displacement, and bond distances and angles (29 pages). This material is contained in many libraries in microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.