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Catalytic Enantioselective Diboration of Cyclic Dienes. A Modified Ligand with General Utility

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Abstract

The enantioselective 1,4-diboration of cyclic dienes with a new taddol-derived phosphonite ligand occurs with excellent enantioselectivity. Oxidation delivers the derived 1,4 diol whereas homologation can be used to deliver a chiral 1,6 diol.

The enantioselective 1,4-diboration of 1,3-dienes is a reaction that provides 2-alkene-1,4-diols upon oxidative work-up.^{1,2,3} This overall reaction does not have a generally effective complement in contemporary catalytic enantioselective methodology and it is important to gain a greater understanding of the substrate scope.⁴ Previous examples from our laboratory suggested that this transformation can be realized with Pt(0) catalysis in the presence of a chiral TADDOL-derived phosphonite ligands. These studies included an example of an enantioselective 1,4-diboration of a prochiral cyclic diene (Scheme 1), a reaction that delivers a new chiral carbocyclic product with good efficiency. Using a chiral phosphonite ligand, this reaction was found to be highly selective with *n*-alkyl-substituted substrates such as **1a**. However, further study of the scope of this reaction revealed that with aryl or branched alkyl substituents on the substrate enantioselection was severely diminished (*vide infra*). In an effort to render this transformation more generally useful for asymmetric synthesis, we have undertaken a systematic survey of substituted TADDOL-derived phosphonites⁵ and report herein, that with an appropriately modified ligand structure, significantly improved generality is observed.

To identify a chiral phosphonite ligand structure that is effective with a range of substrates, 2-butyl-1,3-cyclohexadiene (**1a**) and 2-cyclohexyl-1,3-cyclohexadiene (**2a**) were chosen as representative substrates and their diboration reactions were surveyed with a range of taddol-derived phosphonite ligands. As depicted in Table 1, with the ligand described in our preliminary report (**L2**, entries 3 and 4), the diboration of *n*-butyl substituted substrate **1a** occurred with excellent enantioselectivity, however, the level of selectivity with cyclohexyl substituted substrate **2a** was markedly inferior. In an effort to ameliorate this problem, the size of the substituents on the aryl rings of the ligand backbone was modified. Previous experience showed that the *meta* positions of the aryl rings are most consequential^{1,6} and, indeed, dramatic changes in enantioselection were noticed when the methyl groups of the ligand (**R**) were replaced with either smaller (ligand **L1**) or larger substituents (ligands **L3**

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Supporting Information Available: Compound characterization (spectra). This material is available free of charge via the Internet at <http://pubs.acs.org/>.

and **L4**). As observed in Table 1, while the use of alkyl substituents on the ligand backbone did not lead to a generally effective ligand structure, use of aryl-substituted ligands was highly rewarding and offered excellent levels of enantioselection for both substrates (ligands **L5** and **L6**, entries 9–12). Comparison of ligands **L5** and **L6** showed that the more encumbered dioxolane protecting group provided a subtle enhancement in stereoselection and this ligand was chosen for further study. It is also important to note that with only 1.2 equivalents of ligand relative to platinum, reduced selectivity was observed in the diboration of **1a** (77:23 er). We attribute this outcome to incomplete precomplexation of the catalyst; precomplexation at 80 °C with 1.2 equivalents of ligand returned selectivity to higher levels.

With a more generally effective ligand in hand, the catalytic enantioselective diboration of a range of substituted cyclic dienes was examined (Table 2).^{7,8} The standard set of reaction conditions employed 6 mol% ligand **L6**, 3 mol% Pt(dba)₃, and 1.05 equivalents of B₂(pin)₂ in toluene solvent for 12 hours at 60 °C. While these conditions were effective for many substrates, it was found that for the phenyl-substituted diene in entry 3, selectivity was improved by executing the reaction at room temperature after pre-activating the catalyst at 60 °C for 20 minutes. Additionally, substrates in entries 8 and 11 reacted sluggishly under the standard conditions and required an increased catalyst loading to achieve the yields depicted in Table 2. Notable features of the substrate scope are that the reaction accommodates both aliphatic and aromatic substitution and that both small and large substituents are tolerated. The example in entry 11 suggests that seven-membered rings are processed selectively, even though these substrates require added catalyst and, even then, the cycloheptadiene provided moderated yields of reaction product. Another notable point that this substrate survey revealed is that protected alcohol and protected aldehyde functionality is well tolerated.

One attractive feature of the diboration products is that the organoboron group may be readily converted to a range of useful functional groups or used in strategic C-C bond-forming processes. While oxidation cleanly delivers hydroxylated end products as depicted in Table 1, homologation can provide other derivatives.⁹ While Matteson homologation reactions¹⁰ have previously been applied to 1,2-bis(boronates) that arise from alkene diboration,¹¹ this transformation has not been applied to 2-alkene-1,4-bis(boronates) that would arise from diene diboration. To examine the efficacy of this process, the sequence in Scheme 2 was examined. Thus, diene **6a** was subjected to catalytic diboration in the presence of the chiral catalyst and after 12 hours of reaction, the solvent was removed *in vacuo*, tetrahydrofuran was added, the mixture cooled to –78 °C and treated with chloromethylolithium (2.2 equiv). Upon oxidative work-up, this sequence delivered the 1,6-diol reaction product **12** in excellent yield and stereoselectivity.

It was also considered that the 2-alkene-1,4-bis(boronates) might engage in allylation reactions but the mode of regioselection was uncertain.¹² To learn more about this process and about the types of synthesis targets that might be accessed with these structures, the sequence in Scheme 3 was carried out. Thus, after diboration of diene **2a** in toluene at 60 °C for 12 h, isovaleraldehyde (3 equiv) was added to the reaction mixture and the concoction heated to 80 °C for 30 h. After oxidation, this reaction furnished diol **14** in excellent yield, diastereo- and enantiomeric purity.⁸ An exciting outcome of this sequence is that C-C bond formation appeared to occur by association of the aldehyde to putative intermediate allylboronate **13**, followed by progression to the product through **ts-1**.¹³ Importantly, the chair-like arrangement of the reacting array of atoms was maintained with good fidelity and furnished the product in a predictable manner. That the intermediate allylation product, prior to oxidation, maps well onto cladiellin diterpene natural products portends the use of this overall synthesis transform in complex molecule synthesis.¹⁴

In conclusion, we have described the development of a Pt-catalyzed diboration that bears general applicability to prochiral substituted cyclohexadiene substrates.

Experimental

((4R,5R)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(di([1,1':3',1''-terphenyl]-5'-yl)methanol) (15)

Prepared from 1-bromo-3,5-diphenylbenzene¹⁵ following literature procedures (495 mg, 62% yield).^{5c} ¹H NMR (500 MHz, CDCl₃): δ 1.14 (6H, s), 5.11 (2H, s), 7.32–7.40 (16H, m), 7.41–7.44 (8H, m), 7.52–7.54 (8H, m), 7.68–7.70 (10H, m), 7.76 (4H, d, *J* = 1.7 Hz), 7.83 (2H, t, *J* = 1.7 Hz), 7.97 (4H, d, *J* = 1.7 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 146.9, 143.9, 141.8, 141.4, 141.3, 141.1, 129.01, 128.96, 127.59, 127.57, 127.5, 126.6, 125.9, 125.7, 125.6, 110.3, 81.9, 78.8, 27.6; IR (neat): 3324.0 (br), 3034.5 (w), 1595.2 (m), 1497.5 (w), 1427.2 (w), 1239.8 (w), 1165.5 (w), 1049.1 (w), 879.7 (m), 759.2 (s), 742.1 (s), 696.3 (s), 614.2 (w) cm⁻¹; HRMS-(ESI+) for C₇₉H₆₂O₄Na [M+Na]: calculated: 1097.4546, found: 1097.4557; [α]_D²⁰: +37.80 (*c* = 0.84, CHCl₃, *l* = 50 mm).

((4R,5R)-2,2-diethyl-1,3-dioxolane-4,5-diyl)bis(di([1,1':3',1''-terphenyl]-5'-yl)methanol). (16)

Prepared from 1-bromo-3,5-diphenylbenzene¹⁴ following literature procedures (3.75 g, 62% yield).^{5c} ¹H NMR (500 MHz, CDCl₃): δ 0.63 (6H, t, *J* = 7.4 Hz), 1.35–1.43 (4H, m), 4.60 (2H, br), 4.88 (2H, s), 7.29–7.33 (8H, m), 7.35–7.39 (16H, m), 7.51–7.53 (8H, m), 7.62–7.64 (8H, m), 7.68–7.69 (2H, m), 7.77–7.78 (6H, m), 7.91 (4H, d, *J* = 1.7 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 147.2, 143.8, 141.8, 141.4, 141.3, 141.0, 128.93, 128.92, 127.53, 127.51, 127.48, 127.47, 126.6, 125.8, 125.7, 125.6, 113.1, 81.4, 79.0, 30.1, 8.4; IR (neat): 3203.1 (br), 3035.4 (w), 2970.8 (w), 1595.5 (m), 1497.8 (w), 1426.7 (w), 1174.6 (w), 1031.1 (w), 897.7 (w), 759.2 (s), 740.8 (s), 727.5 (m), 696.5 (s), 614.1 (w) cm⁻¹; HRMS-(MALDI +) for C₈₁H₆₆O₄Na [M+Na]: calculated: 1125.4853, found: 1125.4852; [α]_D²⁰: -22.80 (*c* = 1.01, CHCl₃, *l* = 50 mm).

(3aR,8aR)-4,4,8,8-tetra([1,1':3',1''-terphenyl]-5'-yl)-2,2-dimethyl-6-phenyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine (L5)

Prepared from **15** in direct analogy to the literature (384 mg, 70% yield).^{5c} ¹H NMR (500 MHz, CDCl₃): δ 0.34 (3H, s), 1.59 (3H, s), 5.15 (1H, d, *J* = 8.6 Hz), 6.24 (1H, dd, *J* = 8.6 Hz, 4.6 Hz), 7.30–7.31 (6H, m), 7.34–7.47 (18H, m), 7.54–7.61 (15H, m), 7.67–7.70 (5H, m), 7.72–7.74 (2H, m), 7.81–7.85 (5H, m), 8.00 (4H, s), 8.24 (2H, m); ¹³C NMR (100 MHz, CDCl₃): δ 147.9, 147.0, 146.9, 143.23, 143.22, 142.33, 142.31, 141.88, 141.82, 141.6, 141.5, 141.41, 141.40, 141.33, 141.31, 141.2, 140.9, 131.3, 130.3, 130.0, 129.1, 129.03, 128.97, 128.90, 128.83, 127.7, 127.63, 127.59, 127.54, 127.51, 127.4, 126.8, 126.2, 126.1, 125.8, 125.7, 125.6, 112.2, 84.63, 84.59, 84.0, 83.9, 83.3, 83.1, 82.90, 82.85, 28.3, 25.1; ³¹P NMR (162 MHz, CDCl₃): δ 156.7; IR (neat): 3034.2 (w), 1594.8 (m), 1497.2 (w), 1427.2 (w), 1160.3 (w), 1031.8 (m), 996.8 (m), 758.4 (s), 735.4 (s), 695.1 (s), 613.8 (w) cm⁻¹; HRMS (ESI+) for C₈₅H₆₅O₄NaP [M+Na]: calculated: 1203.4518, found: 1203.4495; [α]_D²⁰: -103.26 (*c* = 1.12, CHCl₃, *l* = 50 mm).

(3aR,8aR)-4,4,8,8-tetra([1,1':3',1''-terphenyl]-5'-yl)-2,2-diethyl-6-phenyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine (L6)

Prepared from **16** in direct analogy to the literature (494 mg, 70% yield).^{5c} ¹H NMR (400 MHz, CDCl₃): δ 0.28 (3H, t, *J* = 7.4 Hz), 0.72 (2H, q, *J* = 7.5 Hz), 0.82 (3H, t, *J* = 7.5 Hz), 1.71 (2H, q, *J* = 7.4 Hz), 5.26 (1H, d, *J* = 8.7 Hz), 6.02 (1H, dd, *J* = 8.7 Hz, 3.9 Hz), 7.28–7.43 (23H, m), 7.44–7.54 (8H, m), 7.58–7.63 (12H, m), 7.68–7.80 (6H, m), 7.89 (2H, d, *J* = 1.6 Hz), 7.93–7.98 (2H, m), 8.01 (2H, d, *J* = 1.6 Hz), 8.15 (2H, d, *J* = 1.6 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 147.8, 147.22, 147.19, 143.32, 143.30, 142.59, 142.57, 141.9, 141.6, 141.5, 141.49, 141.47, 141.4, 141.3, 141.2, 140.9, 131.3, 130.3, 130.0, 129.05, 129.04,

129.01, 128.95, 128.8, 128.7, 127.6, 127.56, 127.54, 127.50, 127.4, 127.01, 126.97, 126.05, 125.96, 125.7, 125.6, 125.4, 116.1, 84.3, 84.2, 83.79, 83.77, 83.4, 83.3, 82.6, 82.4, 30.2, 27.9, 8.7, 8.6; ^{31}P NMR (162 MHz, CDCl_3): δ 157.6; IR (neat): 3034.2 (w), 2970.8 (w), 1594.3 (w), 1426.6 (w), 1263.9 (w), 1170.4 (w), 1031.4 (w), 930.6 (m), 758.3 (m), 733.0 (s), 693.4 (s), 613.1 (m), 489.8 (w) cm^{-1} ; HRMS (ESI+) for $\text{C}_{87}\text{H}_{69}\text{O}_4\text{NaP}$ [M+Na]: calculated: 1231.4831, found: 1231.4832; $[\alpha]_{\text{D}}^{20}$: -87.30 ($c = 0.51$, CHCl_3 , $l = 50$ mm).

Preparation of cyclic dienes by Kumada coupling.⁷—Magnesium (292 mg, 12.0 mmol) and a single crystal of I_2 were diluted with diethyl ether (20 mL). Bromocyclohexane (1.23 mL, 10.0 mmol) was slowly added. The stirred reaction was heated to 40 °C for 3 h and cooled to room temperature. In a separate flask, $\text{NiCl}_2(\text{dppe})$ (16 mg, 30 mmol), cyclohexa-1,5-dien-1-yl diphenyl phosphate (1.00 g, 3.05 mmol), and Et_2O (10 mL) were cooled to 0 °C under N_2 . The Grignard reagent was then added *via* syringe. Upon complete reaction (TLC analysis; 1–2 h) saturated NH_4Cl solution (10 mL) was added. Extraction with diethyl ether (2×20 mL), drying, concentration, and purification by silica gel chromatography (100% hexanes) afforded a colorless oil (331 mg, 68% yield). A gravity column was required to separate the desired product from 1,1'-bi(cyclohexane), which can only be detected by NMR.

[1,1'-bi(cyclohexane)]-1,5-diene (2a)

(331 mg, 68% yield). ^1H NMR (500 MHz, CDCl_3): δ 1.09–1.19 (3H, m), 1.23–1.32 (2H, m), 1.66–1.77 (5H, m), 1.85 (1H, t, $J = 11.6$ Hz), 2.05–2.13 (4H, m), 5.44–5.46 (1H, m), 5.80–5.83 (1H, m), 5.88 (1H, dd, $J = 11.2$ Hz, 1.5 Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 141.3, 126.9, 126.6, 118.1, 43.7, 32.2, 26.9, 26.6, 22.8, 22.6; IR (neat): 3033.1 (w), 2921.6 (s), 2850.2 (s), 2822.3 (w), 1447.7 (m), 1425.5 (w), 1165.1 (w), 998.9 (w), 948.2 (w), 891.6 (w), 806.6 (m), 736.8 (m), 687.7 (w), 592.2 (m), 570.2 (w), 518.7 (w) cm^{-1} ; HRMS (ESI+) for $\text{C}_{12}\text{H}_{19}$ [M+H]: calculated: 163.1487, found: 163.1488; $R_f = 0.78$ (100% hexanes, stain in KMnO_4).

(cyclohexa-1,5-dien-1-ylmethyl)benzene (4a)

(2.41 g, 77% yield) ^1H NMR (500 MHz, CDCl_3): δ 2.09–2.21 (4H, m), 3.37 (2H, s), 5.51–5.54 (1H, m), 5.76–5.84 (2H, m), 7.19–7.22 (3H, m), 7.27–7.31 (2H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 140.2, 135.0, 129.1, 128.5, 127.19, 127.15, 126.2, 122.1, 42.0, 22.65, 22.58; IR (neat): 3027.6 (w), 2930.4 (w), 2872.8 (w), 2821.6 (w), 1493.7 (w), 1452.6 (w), 1425.8 (w), 1164.5 (w), 1078.5 (w), 953.9 (m), 787.9 (w), 755.2 (w), 726.8 (s), 697.0 (s), 668.0 (m), 620.0 (m), 601.4 (m), 530.8 (w), 487.5 (w), 445.7 (w) cm^{-1} ; HRMS (ESI+) for $\text{C}_{13}\text{H}_{15}$ [M+H]: calculated: 171.1174, found: 171.1168.

(2-(cyclohexa-1,5-dien-1-yl)ethyl)benzene (5a)

(234 mg, 85% yield) ^1H NMR (400 MHz, CDCl_3): δ 2.12 (4H, br), 2.34 (2H, t, $J = 8.0$ Hz), 2.70–2.74 (2H, m), 5.49 (1H, br), 5.86–5.92 (2H, m), 7.19–7.21 (3H, m), 7.27–7.31 (2H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 142.4, 135.4, 128.7, 128.4, 127.4, 127.1, 125.9, 120.8, 37.8, 35.2, 22.62, 22.57; IR (neat): 3026.9 (m), 2930.4 (m), 2871.5 (w), 2821.2 (m), 1603.2 (w), 1495.6 (m), 1453.1 (m), 1437.7 (w), 1425.9 (w), 1164.7 (w), 1030.1 (w), 939.1 (w), 805.2 (m), 745.8 (s), 696.5 (s), 593.3 (m), 566.4 (m), 544.4 (m), 491.7 (m), 462.2 (w) cm^{-1} ; HRMS (ESI+) for $\text{C}_{14}\text{H}_{17}$ [M+H]: calculated: 185.1330, found: 185.1339.

(3-(cyclohexa-1,5-dien-1-yl)propyl)benzene (6a)

(1.06 g, 58% yield) ^1H NMR (400 MHz, CDCl_3): δ 1.71–1.79 (2H, m), 2.06–2.13 (6H, m), 2.61 (2H, t, $J = 7.7$ Hz), 5.50 (1H, br), 5.84 (2H, br), 7.16–7.20 (3H, m), 7.26–7.30 (2H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 142.8, 135.7, 128.7, 128.4, 127.4, 127.0, 125.8, 120.6,

35.6, 35.3, 30.3, 22.7, 22.6; IR (neat): 3026.8 (w), 2930.2 (m), 2856.4 (w), 2821.7 (w), 1495.5 (w), 1453.1 (w), 1029.7 (w), 941.3 (w), 805.7 (w), 740.8 (s), 696.4 (s), 589.0 (w), 544.4 (w), 494.2 (w), 467.7 (w) cm^{-1} ; HRMS (ESI+) for $\text{C}_{15}\text{H}_{19}$ [M+H]: calculated: 199.1487, found: 199.1496.

2'-methyl-3,4-dihydro-1,1'-biphenyl (7a)

(225 mg, 88% yield) ^1H NMR (500 MHz, CDCl_3): δ 2.20–2.25 (2H, m), 2.29–2.35 (5H, m), 5.71–5.73 (1H, m), 5.89–5.93 (1H, m), 5.96–5.99 (1H, m), 7.12–7.18 (4H, m); ^{13}C NMR (125 MHz, CDCl_3): δ 142.2, 137.4, 135.6, 130.3, 128.8, 128.0, 127.1, 126.2, 125.9, 124.6, 22.8, 22.2, 20.3; IR (neat): 3035.2 (w), 2930.6 (w), 2822.3 (w), 1484.2 (w), 1453.7 (w), 997.5 (w), 823.7 (w), 756.3 (s), 734.4 (s), 611.0 (m), 501.2 (w), 453.5 (m) cm^{-1} ; HRMS (ESI+) for $\text{C}_{13}\text{H}_{15}$ [M+H]: calculated: 171.1174, found: 171.1174.

1-(cyclohexa-1,5-dien-1-yl)naphthalene (8a)

(243 mg, 79% yield) ^1H NMR (500 MHz, CDCl_3): δ 2.31–2.37 (2H, m), 2.41–2.46 (2H, m), 5.95 (1H, d, $J = 4.3$ Hz), 5.98 (1H, dt, $J = 9.5$ Hz, 4.4 Hz), 6.15 (1H, d, $J = 9.5$ Hz), 7.34 (1H, d, $J = 6.8$ Hz), 7.43–7.49 (3H, m), 7.78 (1H, d, $J = 8.3$ Hz), 7.84–7.88 (1H, m), 8.02–8.05 (1H, m); ^{13}C NMR (125 MHz, CDCl_3): δ 140.6, 136.5, 134.0, 131.6, 128.6, 128.5, 127.5, 126.3, 126.2, 125.9, 125.85, 125.81, 125.7, 125.6, 23.0, 22.2; IR (neat): 3035.4 (w), 2931.7 (w), 2819.5 (w), 1389.3 (w), 961.5 (w), 797.0 (m), 773.1 (s), 726.1 (m), 646.8 (m), 424.1 (w) cm^{-1} ; HRMS (ESI+) for $\text{C}_{16}\text{H}_{15}$ [M+H]: calculated: 207.1174, found: 207.1172.

2-(2-(cyclohexa-1,5-dien-1-yl)ethyl)-1,3-dioxolane (10a)

(867 mg, 55% yield) ^1H NMR (500 MHz, CDCl_3): δ 1.74–1.78 (2H, m), 2.05–2.11 (4H, m), 2.13–2.17 (2H, m), 3.82–3.89 (2H, m), 3.93–4.00 (2H, m), 4.87 (1H, t, $J = 4.5$ Hz), 5.50–5.52 (1H, m), 5.81–5.85 (2H, m); ^{13}C NMR (125 MHz, CDCl_3): δ 135.1, 127.2, 127.1, 120.5, 104.4, 65.1, 32.9, 30.1, 22.6, 22.5; IR (neat): 2929.4 (m), 2874.6 (m), 2822.5 (w), 1403.7 (m), 1131.9 (s), 1032.9 (s), 942.8 (s), 887.1 (m), 820.7 (w), 736.9 (m), 591.7 (m), 551.3 (w) cm^{-1} ; HRMS (ESI+) for $\text{C}_{11}\text{H}_{17}\text{O}_2$ [M+H]: calculated: 181.1229, found: 181.1220.

2-butylcyclohepta-1,3-diene (11a)

(325 mg, 73% yield) ^1H NMR (500 MHz, CDCl_3): δ 0.89 (3H, t, $J = 7.3$ Hz), 1.26–1.33 (2H, m), 1.35–1.41 (2H, m), 1.81–1.86 (2H, m), 2.01 (2H, t, $J = 7.1$ Hz), 2.22 (2H, dt, $J = 5.6$ Hz, 5.6 Hz), 2.28 (2H, dt, $J = 5.9$ Hz, 5.4 Hz), 5.62 (1H, t, $J = 5.9$ Hz), 5.69 (1H, d, $J = 11.7$ Hz), 5.83 (1H, dt, $J = 11.7$ Hz, 5.1 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 137.3, 133.5, 129.2, 128.6, 39.4, 31.88, 31.81, 30.1, 27.9, 22.5, 14.2; IR (neat): 2955.3 (m), 2924.5 (s), 2856.9 (m), 1437.1 (m), 1044.8 (w), 851.9 (w), 775.9 (w), 735.0 (m), 554.6 (m) cm^{-1} ; HRMS (ESI+) for $\text{C}_{11}\text{H}_{19}$ [M+H]: calculated: 151.1487, found: 151.1494.

Representative Procedure for Diene Diboration/Oxidation—In the glove box, $\text{Pt}(\text{dba})_3$ (13.5 mg, 15.0 mmol), ligand **L6** (36.3 mg, 30.0 mmol), toluene (5.0 mL, 0.1 M) were mixed. After stirring for 1 h, $\text{B}_2(\text{pin})_2$ (133.3 mg, 0.525 mmol) and [1,1'-bi(cyclohexane)]-1,5-diene (**2a**, 81.1 mg, 0.50 mmol) were added. The vessel was removed from the glovebox, and stirred at 60 °C for 12 h. The mixture was then cooled to 0 °C and slowly charged with tetrahydrofuran (3 mL), 3 M NaOH (3 mL) and 30 % H_2O_2 (1.5 mL). After stirring for 4 h at ambient temperature, the mixture was cooled to 0 °C and treated with aqueous sodium thiosulfate (3 mL, dropwise slowly). Extraction with ethyl acetate (3×20 mL), drying, concentration and purification (silica gel; hexane: ethyl acetate = 1:1 to 1:2) afforded a white solid (85.4 mg, 87% yield).

(2S,5R)-[1,1'-bi(cyclohexan)]-6-ene-2,5-diol (2b)

(85.4 mg, 87% yield) R_f = 0.17 (hexane:ethyl acetate = 1:1, stain in phosphomolybdic acid); ^1H NMR (500 MHz, CDCl_3): δ 1.01 (1H, dtd, J = 13.6 Hz, 11.9 Hz, 3.6 Hz), 1.11–1.20 (1H, m), 1.23–1.35 (3H, m), 1.61–1.82 (8H, m), 1.83–1.89 (3H, m), 2.08 (1H, tt, J = 11.5 Hz, 3.1 Hz), 4.10 (1H, br), 4.16 (1H, br), 5.53 (1H, d, J = 2.7 Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 147.8, 126.4, 67.4, 65.8, 41.3, 33.7, 31.9, 29.9, 27.7, 27.1, 26.8, 26.5; IR (neat): 3300.3 (br), 2921.8 (s), 2850.4 (s), 1446.8 (m), 1285.9 (w), 1072.4 (m), 979.9 (m), 956.6 (w) cm^{-1} ; HRMS (ESI+) for $\text{C}_{12}\text{H}_{24}\text{N}_1\text{O}_2$ [$\text{M}+\text{NH}_4$]: calculated: 214.1807, found: 214.1818; $[\alpha]_{\text{D}}^{20}$: +9.78 (c = 0.92, CHCl_3 , l = 50 mm); mp: 115.1–117.0 °C. Enantiomer ratio determined by GLC (diacetate derivative, Supelco β -dex, 180 °C, 20 psi), major enantiomer 33.27 min, minor enantiomer 33.64 min, 96:4 e.r. Absolute stereochemistry was determined by crystallography using anomalous dispersion (Flack parameter = 0.11).

(2S,5R)-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2,5-diol (3b)

(59.9 mg, 63% yield) R_f = 0.21 (hexanes: ethyl acetate = 1:2, stain in PMA); ^1H NMR (500 MHz, CDCl_3): δ 1.77–1.85 (1H, m), 1.87–1.94 (1H, m), 1.98–2.07 (2H, m), 4.35 (1H, br), 4.67 (1H, br), 6.13 (1H, dd, J = 2.9 Hz, 0.7 Hz), 7.29–7.32 (1H, m), 7.35–7.39 (2H, m), 7.49–7.52 (2H, m); ^{13}C NMR (125 MHz, CDCl_3): δ 141.2, 138.9, 130.9, 128.9, 128.1, 126.6, 67.5, 65.4, 29.3, 27.4; IR (neat): 3222.8 (br), 2938.0 (w), 1490.1 (w), 1441.9 (w), 1307.2 (w), 1047.1 (s), 969.6 (s), 950.3 (m), 760.1 (m), 697.3 (s), 508.4 (m), 485.0 (m) cm^{-1} ; HRMS (ESI+) for $\text{C}_{12}\text{H}_{13}\text{O}_1$ [$\text{M}+\text{H}-\text{H}_2\text{O}$]: calculated: 173.0966, found: 173.0966; $[\alpha]_{\text{D}}^{20}$: +64.49 (c = 0.83, CHCl_3 , l = 50 mm); mp: 137.0–139.0 °C. Enantiomer ratio determined by GLC (diacetate derivative, Supelco β -dex, 180 °C, 20 psi), major enantiomer 48.65 min, minor enantiomer 49.65 min, 93:7 e.r.

(1S,4R)-2-benzylcyclohex-2-ene-1,4-diol (4b)

(96.0 mg, 94% yield) R_f = 0.23 (hexanes: ethyl acetate = 1:2, stain in PMA); ^1H NMR (500 MHz, CDCl_3): δ 1.65–1.76 (4H, m), 1.79–1.88 (2H, m), 3.43 (1H, d, J = 15.1 Hz), 3.52 (1H, d, J = 15.1 Hz), 3.95 (1H, br), 4.18 (1H, br), 5.58 (1H, br), 7.20–7.23 (3H, m), 7.28–7.31 (2H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 142.3, 139.2, 129.7, 129.3, 128.7, 126.5, 66.9, 66.2, 40.5, 29.3, 28.0; IR (neat): 3313.5 (br), 2939.6 (m), 2867.3 (w), 1493.6 (w), 1453.1 (m), 1278.4 (w), 1070.6 (m), 1030.2 (m), 980.3 (m), 962.0 (m), 755.7 (w), 700.7 (s) cm^{-1} ; HRMS (ESI+) for $\text{C}_{13}\text{H}_{20}\text{O}_2\text{N}_1$ [$\text{M}+\text{NH}_4$]: calculated: 222.1494, found: 222.1489; $[\alpha]_{\text{D}}^{20}$: +100.80 (c = 0.92, CHCl_3 , l = 50 mm); mp: 114.8–116.6 °C. Enantiomer ratio determined by HPLC (Chiraldex OD-R, 3% iPrOH/hexanes, 1 mL/min, 220 nm), major enantiomer 45.91 min, minor enantiomer 63.95 min, 94:6 e.r.

(1R,4S)-2-phenethylcyclohex-2-ene-1,4-diol (5b)

(50.0 mg, 91% yield) R_f = 0.18 (hexanes: ethyl acetate = 1:2, stain in PMA); ^1H NMR (500 MHz, CDCl_3): δ 1.64–1.71 (1H, m), 1.74–1.80 (1H, m), 1.81–1.89 (2H, m), 2.41 (1H, ddd, J = 14.9 Hz, 10.1 Hz, 6.4 Hz), 2.48–2.54 (1H, m), 2.74 (1H, ddd, J = 13.7 Hz, 9.8 Hz, 6.4 Hz), 2.83 (1H, dd, J = 13.7 Hz, 10.1 Hz, 5.7 Hz), 4.04 (1H, br), 4.15 (1H, br), 7.17–7.20 (3H, m), 7.26–7.30 (2H, m); ^{13}C NMR (125 MHz, CDCl_3): δ 142.3, 142.0, 128.62, 128.57, 128.4, 126.2, 67.1, 66.8, 35.5, 34.6, 29.4, 28.1; IR (neat): 3300.4 (br), 2935.0 (s), 2858.3 (m), 1495.8 (w), 1453.6 (m), 1276.4 (w), 1042.3 (m), 979.1 (m), 954.8 (m), 873.4 (w), 749.0 (m), 699.3 (s) cm^{-1} ; HRMS (ESI+) for $\text{C}_{14}\text{H}_{22}\text{O}_2\text{N}_1$ [$\text{M}+\text{NH}_4$]: calculated: 236.1651, found: 236.1657; $[\alpha]_{\text{D}}^{20}$: +9.82 (c = 0.62, CHCl_3 , l = 50 mm); mp: 114.5–116.0 °C. Enantiomer ratio determined by HPLC (Chiraldex OD-R, 3% iPrOH/hexanes, 1 mL/min, 220 nm), major enantiomer 67.78 min, minor enantiomer 84.01 min, 95:5 e.r.

(1*R*,4*S*)-2-(3-phenylpropyl)cyclohex-2-ene-1,4-diol (6b)

(94.0 mg, 92% yield) R_f = 0.28 (hexanes: ethyl acetate = 1:2, stain in PMA); ^1H NMR (500 MHz, CDCl_3): δ 1.64–1.72 (1H, m), 1.73–1.81 (2H, m), 1.82–1.89 (3H, m), 2.10–2.16 (1H, m), 2.21–2.27 (1H, m), 2.58–2.68 (2H, m), 4.00–4.03 (1H, m), 4.15 (1H, br), 5.57 (1H, br), 7.17–7.19 (3H, m), 7.26–7.29 (2H, m); ^{13}C NMR (125 MHz, CDCl_3): δ 142.6, 142.5, 128.6, 128.5, 128.0, 126.0, 66.86, 66.82, 35.9, 33.4, 29.6, 29.4, 28.1; IR (neat): 3299.1 (br), 3025.2 (w), 2937.0 (s), 2859.7 (m), 1495.4 (m), 1453.1 (m), 1356.3 (w), 1287.8 (w), 1045.6 (m), 979.5 (m), 954.8 (m), 747.5 (m), 699.1 (s) cm^{-1} ; HRMS (ESI+) for $\text{C}_{15}\text{H}_{19}\text{O}_1$ [$\text{M}+\text{H}-\text{H}_2\text{O}$]: calculated: 215.1436, found: 215.1443; $[\alpha]_{\text{D}}^{20}$: +31.37 (c = 0.91, CHCl_3 , l = 50 mm); mp: 114.2–116.1 $^{\circ}\text{C}$. Enantiomer ratio determined by HPLC (diacetate derivative, Chiraldex OD-R, 1% iPrOH/hexanes, 220 nm), major enantiomer 10.96 min, minor enantiomer 9.71 min, 96:4 e.r. Absolute stereochemistry was determined by crystallography using anomalous dispersion (Flack parameter = -0.01).

(2*R*,5*S*)-2'-methyl-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2,5-diol (7b)

(76.6 mg, 75% yield) R_f = 0.26 (hexanes: ethyl acetate = 1:2, stain in PMA); ^1H NMR (500 MHz, CDCl_3): δ 1.83–1.92 (1H, m), 1.93–2.00 (3H, m), 2.30 (3H, s), 4.28–4.33 (1H, m), 4.34–4.36 (1H, m), 5.75 (1H, d, J = 3.2 Hz), 7.12–7.22 (4H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 143.3, 139.4, 136.0, 131.6, 130.6, 129.2, 127.8, 125.9, 67.5, 66.5, 28.3, 28.0, 20.1; IR (neat): 3277.4 (br), 2944.8 (m), 2899.3 (m), 1483.5 (m), 1439.7 (m), 1290.4 (w), 1269.6 (w), 1042.6 (s), 980.8 (s), 954.0 (s), 842.1 (w), 764.3 (m), 656.8 (s), 606.0 (s), 445.5 (m) cm^{-1} ; HRMS (ESI+) for $\text{C}_{13}\text{H}_{15}\text{O}_1$ [$\text{M}+\text{H}-\text{H}_2\text{O}$]: calculated: 187.1123, found: 187.1122; $[\alpha]_{\text{D}}^{20}$: +90.55 (c = 0.98, CHCl_3 , l = 50 mm); mp: 116.2–119.0 $^{\circ}\text{C}$. Enantiomer ratio determined by GLC (diacetate derivative, Supelco β -dex, 160 $^{\circ}\text{C}$, 20 psi), major enantiomer 98.20 min, minor enantiomer 99.65 min, 96:4 e.r.

(1*R*,4*S*)-2-(naphthalen-1-yl)cyclohex-2-ene-1,4-diol (8b)

(33.9 mg, 94% yield) R_f = 0.21 (hexanes: ethyl acetate = 1:2, stain in PMA); ^1H NMR (500 MHz, CDCl_3): δ 1.94–2.02 (1H, m), 2.04–2.11 (3H, m), 4.42 (1H, br), 4.52 (1H, br), 5.92 (1H, d, J = 2.9 Hz), 7.36 (1H, dd, J = 7.1 Hz, 1.0 Hz), 7.45–7.51 (3H, m), 7.82 (1H, d, J = 8.3 Hz), 7.86–7.89 (1H, m), 7.93–7.95 (1H, m); ^{13}C NMR (125 MHz, CDCl_3): δ 142.0, 137.7, 134.0, 133.4, 131.9, 128.7, 128.3, 126.4, 126.3, 126.2, 125.53, 125.51, 68.0, 66.9, 28.5, 27.9; IR (neat): 3273.1 (br), 2898.9 (m), 1440.8 (w), 1272.2 (w), 1051.3 (m), 981.8 (m), 801.8 (s), 778.3 (s), 667.5 (m), 597.4 (m) cm^{-1} ; HRMS (ESI+) for $\text{C}_{16}\text{H}_{15}\text{O}_1$ [$\text{M}+\text{H}-\text{H}_2\text{O}$]: calculated: 223.1123, found: 223.1134; $[\alpha]_{\text{D}}^{20}$: +26.13 (c = 0.15, CHCl_3 , l = 50 mm); mp: 176.5–179.2 $^{\circ}\text{C}$. Enantiomer ratio determined by HPLC (dibenzoate derivative, Chiraldex OD-R, 1% iPrOH/hexanes, 1.0 mL/min, 220 nm), major enantiomer 18.86 min, minor enantiomer 22.62 min, 96:4 e.r.

(1*R*,4*S*)-2-(2-(benzyloxy)ethyl)cyclohex-2-ene-1,4-diol (9b)

(34.3 mg, 92% yield) R_f = 0.17 (hexanes: ethyl acetate = 1:2, stain in PMA); ^1H NMR (500 MHz, CDCl_3): δ 1.69–1.76 (2H, m), 1.80–1.85 (2H, m), 2.30–2.36 (1H, m), 2.47–2.52 (1H, m), 3.56–3.60 (1H, m), 3.62–3.66 (1H, m), 3.99 (1H, br), 4.13 (1H, br), 4.52 (1H, d, J = 12.0 Hz), 4.55 (1H, d, J = 12.0 Hz), 5.59 (1H, d, J = 2.8 Hz), 7.28–7.37 (5H, m); ^{13}C NMR (125 MHz, CDCl_3): δ 141.5, 137.7, 129.8, 128.7, 128.11, 128.09, 73.5, 70.4, 66.95, 66.90, 35.3, 28.6, 28.1; IR (neat): 3343.2 (br), 2927.7 (s), 2857.1 (s), 1453.9 (m), 1360.3 (m), 1275.2 (w), 1074.6 (s), 980.3 (s), 737.7 (s), 698.2 (s), 608.1 (w); HRMS (ESI+) for $\text{C}_{15}\text{H}_{19}\text{O}_2$ [$\text{M}+\text{H}-\text{H}_2\text{O}$]: calculated: 231.1385, found: 231.1379; $[\alpha]_{\text{D}}^{20}$: -5.41 (c = 0.53, CHCl_3 , l = 50 mm). Enantiomer ratio determined by HPLC (Chiraldex OD-R, 3% iPrOH/hexanes, 1.0 mL/min, 220 nm), major enantiomer 74.35 min, minor enantiomer 67.69 min, 94:6 e.r.

(1*R*,4*S*)-2-(2-(1,3-dioxolan-2-yl)ethyl)cyclohex-2-ene-1,4-diol (10b)

(90.0 mg, 84% yield) R_f = 0.23 (100% ethyl acetate, stain in PMA); ^1H NMR (500 MHz, CDCl_3): δ 1.63–1.75 (2H, m), 1.76–1.89 (4H, m), 2.18–2.31 (2H, m), 3.81–3.87 (2H, m), 3.92–3.97 (2H, m), 3.98 (1H, br), 4.10 (1H, br), 4.87 (1H, t, J = 4.7 Hz), 5.55 (1H, br); ^{13}C NMR (125 MHz, CDCl_3): δ 141.9, 128.1, 104.4, 66.69, 66.66, 65.07, 65.04, 32.0, 29.3, 28.1, 27.9; IR (neat): 3353.7 (br), 2937.5 (w), 2878.1 (s), 1443.1 (w), 1408.9 (m), 1265.6 (w), 1135.1 (s), 1044.3 (s), 977.8 (s), 955.6 (s), 895.6 (m), 644.4 (w); HRMS (ESI+) for $\text{C}_{11}\text{H}_{17}\text{O}_3$ [$\text{M}+\text{H}-\text{H}_2\text{O}$]: calculated: 197.1178, found: 197.1169; $[\alpha]_{\text{D}}^{20}$: +15.91 (c = 0.95, CHCl_3 , l = 50 mm). Enantiomer ratio determined by HPLC (dibenzoate derivative, Chiraldex OD-R, 3% $i\text{PrOH}$ /hexanes, 1.0 mL/min, 220 nm), major enantiomer 24.53 min, minor enantiomer 14.52 min, 95:5 e.r.

(1*R*,4*S*)-2-butylcyclohept-2-ene-1,4-diol (11b)

(14.7 mg, 32% yield) R_f = 0.26 (hexanes: ethyl acetate = 3:2, stain in PMA); ^1H NMR (500 MHz, CDCl_3): δ 0.91 (3H, t, J = 7.2 Hz), 1.29–1.36 (2H, m), 1.37–1.43 (2H, m), 1.55–1.69 (3H, m), 1.84–1.93 (2H, m), 2.08 (2H, td, J = 7.6 Hz, 1.2 Hz), 2.28–2.37 (1H, m), 4.12 (1H, d, J = 6.6 Hz), 4.26 (1H, ddd, J = 6.9 Hz, 6.8 Hz, 1.5 Hz), 5.71 (1H, d, J = 6.8 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 149.7, 129.5, 72.3, 68.2, 37.9, 34.5, 33.8, 30.6, 22.6, 19.5, 14.2; IR (neat): 3315.0 (br), 2924.3 (s), 2856.1 (m), 1647.7 (w), 1453.7 (m), 1272.8 (w), 1059.3 (s), 1028.1 (s), 937.1 (m), 654.6 (w); HRMS (ESI+) for $\text{C}_{11}\text{H}_{19}\text{O}_1$ [$\text{M}+\text{H}-\text{H}_2\text{O}$]: calculated: 167.1436, found: 167.1430; $[\alpha]_{\text{D}}^{20}$: +6.28 (c = 0.53, CHCl_3 , l = 50 mm). Enantiomer ratio determined by HPLC (dibenzoate derivative, Chiraldex OD-R, 1% $i\text{PrOH}$ /hexanes, 0.25 mL/min, 220 nm), major enantiomer 28.34 min, minor enantiomer 31.49 min, 96:4 e.r.

((1*R*,4*S*)-2-(3-phenylpropyl)cyclohex-2-ene-1,4-diyl)dimethanol (12)

$\text{Pt}(\text{dba})_3$ (6.7 mg, 7.5 mmol) and phosphonite ligand (**L6**) (18.1 mg, 15.0 mmol), and toluene (2.5 mL, 0.1 M) were mixed under Ar and stirred for 1 h. Then, $\text{B}_2(\text{pin})_2$ (66.7 mg, 262.5 mmol) and (3-(cyclohexa-1,5-dien-1-yl)propyl)benzene (49.6 mg, 0.25 mmol) were added. After stirring at 60 °C for 12 h, the volatiles were removed. THF (2.5 mL) was added, the flask cooled to –78 °C, and bromochloromethane (35.7 mL, 0.55 mmol) and $n\text{-BuLi}$ (0.19 mL, 0.55 mmol) added sequentially. After 10 min, the cooling bath was removed and the contents stirred for 12 h. Then, THF (2 mL), 3 M NaOH (2 mL) and 30 % H_2O_2 (1 mL) were added, slowly, at 0 °C and allowed to stir for 4 h at ambient. After cooling to 0 °C, saturated aqueous sodium thiosulfate was added (2 mL, dropwise slowly). Extraction with ethyl acetate (3×20 mL), drying, concentration, and purification by silica gel chromatography (hexanes: ethyl acetate = 1:1) afforded a colorless oil (57.3 mg, 88% yield). R_f = 0.24 (hexanes: ethyl acetate = 1:1, stain in PMA); ^1H NMR (500 MHz, CDCl_3): δ 1.45–1.53 (1H, m), 1.59–1.76 (3H, m), 1.77–1.88 (1H, m), 1.89–1.95 (1H, m), 2.02–2.13 (2H, m), 2.23 (1H, br), 2.32 (1H, br), 2.55–2.67 (2H, m), 3.50–3.59 (3H, m), 3.66 (1H, dd, J = 10.6 Hz, 2.8 Hz), 5.49 (1H, br), 7.17–7.20 (3H, m), 7.26–7.30 (2H, m); ^{13}C NMR (125 MHz, CDCl_3): δ 142.6, 139.7, 128.6, 128.5, 125.9, 125.6, 67.3, 64.5, 39.8, 38.8, 35.9, 35.3, 30.2, 24.5, 22.0; IR (neat): 3314.4 (br), 2935.6 (w), 2862.4 (w), 1451.8 (w), 1028.7 (m), 734.2 (w), 697.4 (s), 488.5 (w) cm^{-1} ; HRMS (ESI+) for $\text{C}_{17}\text{H}_{25}\text{O}_2$ [$\text{M}+\text{H}$]: calculated: 261.1855, found: 261.1864; $[\alpha]_{\text{D}}^{20}$: +8.09 (c = 0.82, CHCl_3 , l = 50 mm). Enantiomer ratio determined by HPLC (Chiraldex AD-H, 5% $i\text{PrOH}$ /hexanes, 1.0 mL/min, 220 nm), major enantiomer 39.48 min, minor enantiomer 34.56 min, 95:5 e.r.

(2*R*,3*S*)-2-((*S*)-1-hydroxy-3-methylbutyl)-[1,1'-bi(cyclohexan)]-6-en-3-ol (14)

In a glovebox, a stir bar, $\text{Pt}(\text{dba})_3$ (13.5 mg, 15.0 mmol), phosphonite ligand (**L6**) (36.3 mg, 30.0 mmol), and toluene (5.0 mL, 0.1 M) were added to a vial. After stirring for 1 h, $\text{B}_2(\text{pin})_2$ (133.3 mg, 0.525 mmol) and [1,1'-bi(cyclohexane)]-1,5-diene (81.1 mg, 0.50

mmol) were added. The vial was sealed, removed from the glovebox, and stirred at 60 °C for 12 h. After cooling to room temperature isovaleraldehyde was added (129.2 mg, 1.50 mmol) under nitrogen atmosphere. The vial was sealed again and stirred at 80 °C for 30 h. The mixture was cooled to 0 °C and charged with THF (3 mL), 3 M NaOH (3 mL) and 30 % H₂O₂ (3 mL). The reaction was stirred for 4 h at ambient, then cooled to 0 °C and saturated aqueous sodium thiosulfate (3 mL, dropwise slowly) added dropwise. Extraction (ethyl acetate, 3×20 mL), drying, concentration, and purification on silica gel (100% dichloromethane, then hexanes : ethyl acetate = 4:1) afforded a white solid (114.6 mg, 86% yield). *R*_f = 0.18 (hexanes:ethyl acetate = 5:1, stain in PMA); ¹H NMR (500 MHz, CDCl₃): δ 0.79–0.89 (1H, m), 0.93 (3H, d, *J* = 6.6 Hz), 0.96 (3H, d, *J* = 6.6 Hz), 1.14–1.19 (1H, m), 1.23–1.34 (4H, m), 1.60–1.73 (5H, m), 1.79–1.97 (5H, m), 2.01–2.08 (1H, m), 2.25–2.33 (2H, m), 4.12 (1H, ddd, *J* = 9.0 Hz, 4.4 Hz, 4.4 Hz), 4.31 (1H, ddd, *J* = 7.3 Hz, 3.2 Hz, 3.2 Hz), 5.51 (1H, br); ¹³C NMR (100 MHz, CDCl₃): δ 141.1, 120.7, 70.4, 69.5, 45.7, 44.6, 41.9, 34.7, 31.0, 28.3, 27.2, 27.0, 26.8, 25.0, 23.9, 22.3, 21.7; IR (neat): 3311.0 (br), 2922.7 (s), 2850.4 (m), 1448.1 (m), 1261.2 (w), 1068.9 (m), 1045.3 (m), 845.9 (w), 755.2 (m), 568.4 (w); HRMS (ESI+) for C₁₇H₂₉O₁ [M+H-H₂O]: calculated: 249.2218, found: 249.2210; [α]_D²⁰: +24.83 (c = 0.60, CHCl₃, *l* = 50 mm); mp: 78.0–82.1 °C. Enantiomer ratio determined by GLC (Supelco β-dex, 150 °C, 20 psi), major enantiomer 242.57 min, minor enantiomer 246.66 min, 95:5 e.r. Absolute stereochemistry was determined by crystallography using anomalous dispersion (Flack parameter = 0.0)

Supplementary Material

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Acknowledgments

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Scheme 1.

Scheme 2.

Scheme 3.

Table 1

Evaluation of Ligands in the Pt-Catalyzed Enantioselective Diboration of **1** and **2**.^a

1a ($R_2 = n\text{-Bu}$) 2a ($R_2 = c\text{-Hex}$)		diene	ligand	R	R ¹	% yield ^b	er ^c		
1	1a	L1	L1	H	Me	31	55:45		
2	2a	L1	L1	H	Me	69	55:45		
3	1a	L2	L2	Me	Me	87	94:6		
4	2a	L2	L2	Me	Me	89	75:25		
5	1a	L3	L3	Et	Me	89	82:18		
6	2a	L3	L3	Et	Me	79	56:44		
7	1a	L4	L4	<i>i</i> -Bu	Me	60	61:39		
8	2a	L4	L4	<i>i</i> -Bu	Me	19	52:48		
9	1a	L5	L5	Ph	Me	92	94:6		
10	2a	L5	L5	Ph	Me	87	95:5		
11	1a	L6	L6	Ph	Et	97	96:4		
12	2a	L6	L6	Ph	Et	87	96:4		

^a Reaction conditions: 1.05 equiv. B₂(pin)₂, precomplexation for 1 h at room temp, reaction time = 12 h, oxidation at room temp for 4 h.

^b Yield of purified material.

^c Enantiomer ratio was determined by GC, or HPLC analysis on a chiral stationary phase.

Table 2

Catalytic Enantioselective Diboration of Cyclic Dienes.^a

entry	substrate	product ^b	% yield ^c er ^d
1			97 96:4
2			87 96:4
3			72 85:15 63 ^e 93:7
4			94 94:6
5			91 95:5
6			92 96:4

entry	substrate	product ^b	% yield ^c	er ^d
7	 R_2	 7b	75	96:4
8 ^f	 8a	 8b	94	96:4
9	 9a	 9b	92	94:6
10	 10a	 10b	84	95:5
11 ^g	 11a	 11b	32	96:4

^a Conditions: 1.05 equiv. B₂(pin)₂, precomplexation for 1 h at room temp, reaction time = 12 h, oxidation at room temp for 4 h.

^b Absolute configuration determined by x-ray crystallography for **2b** and **6b**; by comparison to the literature for **1b** (ref. 1), and assumed by analogy for others.

^c Yield of purified material. Value is an average of two experiments.

^d Enantiomer ratio was determined by GC, or HPLC, analysis on a chiral stationary phase.

^e Reaction at 60 °C for 20 min, then ambient for 48 hours.

^f Reaction employed 6 mol% Pt(dba)₃, 12 mol% ligand **L6** for 24 hours.

^g Reaction with 10 mol% Pt(dba)₃, 20 mol% ligand **16** for 48 hours