Supporting Information

Asymmetric Synthesis of γ–Chiral Borylalkanes via Sequential Reduction/Hydroboration using a Single Copper Catalyst

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General Methods

CuCl, KOtBu, pinacolborane, and other commercial reagents were purchased from Aldrich and used as received. (R)-DTBM-Segphos (L6) was purchased from TCI. 1a–1r were prepared by following literature procedures. Reactions with oxygen- and moisture-sensitive materials were carried out with the standard Schlenk technique. Toluene was purified using PureSolv solvent purification system, from Innovative Technology, Inc. Flash chromatography was performed on silica gel from Merck (70–230 mesh). All 1H NMR spectra were obtained on Bruker at 500 systems and reported in parts per million (ppm) downfield from tetramethylsilane. 13C NMR spectra are reported in ppm referenced to deuteriochloroform (77.16 ppm). Infrared spectra (IR) were obtained on Nicolet 205 FT-IR and were recorded in cm⁻¹. Optical rotation was measured with Model 343 plus polarimeter equipped with a sodium lamp (589 nm). High performance liquid chromatography (HPLC) was performed using Younglin Acme 9100 series. High resolution mass spectra (HRMS) were obtained at Korea Basic Science Institute (Cheongju, Korea) and reported in the form of m/z (intensity relative to peak = 100).

General procedure for the remote hydroboration of γ,γ-disubstituted allylic substrates

A mixture of CuCl (5 mol %, 0.025 mmol), (R)-DTBM-Segphos (5.5 mol %, 0.0275 mmol) and KOtBu (1 mmol) in anhydrous toluene (2 mL) were stirred for 5 min in a Schlenk tube under an atmosphere of nitrogen. Pinacolborane (1.5 mmol) was added to the reaction mixture and stirred for another 15 min at room temperature. Substrate 1 dissolved in toluene (1 mL) was added. The reaction mixture was sealed, stirred at 60 °C, and monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with diethyl ether (10 mL). After the aqueous layer was extracted with diethyl ether, the combined organic layers were dried over Na2SO4, and concentrated in vacuo. The product was purified by silica gel chromatography using hexanes/ethyl acetate as the eluent.
Determination of ee

![Reaction Scheme]

Sodium perborate (0.9 mmol) was added to 2 (0.3 mmol) in THF (2 mL) and water (2 mL). The reaction mixture was vigorously stirred for 4 h at room temperature. The reaction was quenched with water and then, extracted with diethyl ether. The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The product was purified by silica gel chromatography.

To 2-OH (1 equiv) in CH₂Cl₂ (3 mL) were added dicyclohexylcarbodiimide (1.05 equiv), 4-(dimethylamino)pyridine (0.25 equiv) and 2-naphthoic acid (1 equiv). The reaction mixture was stirred at room temperature and monitored by TLC. Upon completion of the reaction, the reaction mixture was purified silica gel chromatography.

Characterization of 2 (Table 1 and 2)

(R)-2-(3,7-dimethyloct-6-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: By following the general procedure, 2a was obtained in 90% yield. ¹H NMR (500 MHz, CDCl₃) δ 5.02 (t, J = 7.0 Hz, 1H), 1.94–1.84 (m, 2H), 1.60 (s, 3H), 1.52 (s, 3H), 1.40–1.33 (m, 1H), 1.30–1.23 (m, 3H), 1.17 (s, 12H), 1.06–1.02 (m, 1H), 0.78 (d, J = 6.0 Hz, 3H), 0.72–0.62 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 130.9, 125.1, 82.8, 36.7, 34.6, 31.6, 30.9, 29.7, 25.7, 25.6, 24.8, 22.7; 19.1; 17.6; 14.1; 8.5 (C–B); IR (neat) 1460, 1365, 1320, 1140, 970 cm⁻¹; HRMS (ESI) calcd for [C₁₆H₃₁BO₂⁺H⁺]: 266.2526, found: 266.2520; 99% ee were measured by chiral HPLC on AD-H column with the corresponding naphthoate derivative (iPrOH:hexane = 1:99, 0.5 mL/min); t₁ = 14.75 min (major), t₂ = 15.72 min (major).
(S)-2-(3,7-dimethyloct-6-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-
dioxaborolane: By following the general procedure, 2b was
obtained in 98% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 5.09 (t, $J = 7.5$ Hz, 1H), 2.01–1.91 (m, 2H), 1.67 (s, 3H), 1.60 (s, 3H), 1.46–
1.41 (m, 1H), 1.36–1.27 (m, 3H), 1.24 (s, 12H), 1.13–1.09 (m, 1H), 0.85 (d, $J = 6.5$ Hz, 3H), 0.81–0.71 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 130.9, 125.1, 82.8, 36.7, 34.6, 30.9, 25.7, 25.6, 24.9, 24.8, 19.1, 17.6; IR (neat) 1460, 1365, 1320, 1140, 970 cm$^{-1}$; HRMS (ESI) calcd for [C$_{16}$H$_{31}$BO$_2$+H$^+$]: 266.2526, found: 266.2520; 97% ee were measured by chiral HPLC on AD-H column with the corresponding naphthoate derivative (iPrOH:hexane = 1:99, 0.5 mL/min); $t_R$
= 14.70 min (major), $t_R$ = 16.02 min (major).
(R)-4,4,5,5-tetramethyl-2-(3-methyl-5-phenylpentyl)-1,3,2-dioxaborolane: By following the general procedure, 2c was obtained in 96% yield. The characterization data for 2c was concordant with that previously reported in the literature.\textsuperscript{2} \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.27–7.24 (m, 2H), 7.18–7.13 (m, 2H), 2.67–2.53 (m, 2H), 1.68–1.60 (m, 1H), 1.52–1.45 (m, 1H), 1.44–1.37 (m, 2H), 1.27–1.25 (m, 1H), 1.23 (s, 12H), 0.92 (d, \textit{J} = 6.0 Hz, 3H), 0.83–0.71 (m, 2H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 143.2, 128.4, 128.2, 125.5, 82.9, 38.5, 34.6, 33.5, 30.8, 24.8, 24.8, 19.1, 8.4 (C–B); >99% ee were measured by chiral HPLC on IA column with the corresponding alcohol (iPrOH:hexane = 5:95, 0.5 mL/min); \(t_R = 7.68\) min (minor), \(t_R = 11.49\) min (major).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure}
\caption{Chromatograms for 2c and 2d.}
\end{figure}

(R)-2-(6-chloro-3-methylhexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: By following the general procedure, 2d was obtained in 78% yield. The characterization data for 2d was concordant with that previously reported in the literature.\textsuperscript{3} \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 3.53 (t, \textit{J} = 7.0 Hz, 2H), 1.82–1.71 (m, 2H), 1.48–1.41 (m, 2H), 1.38–1.29 (m, 2H), 1.24 (s, 12H), 0.87 (d, \textit{J} = 6.5 Hz, 3H), 0.81–0.71 (m, 2H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 82.9, 45.5; 34.4, 33.8, 30.7, 30.3, 24.9, 24.8, 19.1; 98% ee was measured by chiral HPLC on OD-H column with the corresponding naphthoate derivative (iPrOH:hexane = 1:99, 0.5 mL/min); \(t_R = 28.26\) min (major), \(t_R = 29.18\) min (major).
(R)-2-(5-benzyloxy)-3-methylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: By following the general procedure, 2e was obtained in 77% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.34–7.33 (m, 4H), 7.28–7.24 (m, 1H), 4.49 (d, $J = 2.5$ Hz, 2H), 3.54–3.47 (m, 2H), 1.72–1.65 (m, 1H), 1.53–1.38 (m, 3H), 1.27–1.26 (m, 1H), 1.24 (s, 12H); 0.87 (d, $J = 6.5$ Hz, 3H), 0.82–0.70 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 138.8, 128.3, 127.6, 127.4, 82.9, 72.8, 68.9, 36.4, 32.0, 31.1, 24.8, 19.2, 8.7 (C−B); IR (neat) 2972, 1450, 1378, 1275, 1136 cm$^{-1}$; HRMS (ESI) calcd for [C$_{19}$H$_{31}$BO$_3$+H$^+$]: 319.2444, found: 319.2440; 98% ee was measured by chiral HPLC on AS-H column with the corresponding alcohol (iPrOH:hexane = 1:99, 0.5 mL/min); $t_b$ = 45.64 min (minor), $t_l$ = 48.69 min (major).

(R)-tert-butyl(dimethyl)((3-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)oxy)silane: By following the general procedure, 2f was obtained in 88% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 3.57 (d, $J = 7.0$ Hz, 2H), 1.57–1.42 (m, 3H), 1.35–1.31
(m, 2H), 1.24 (s, 12H), 0.89 (s, 9H), 0.85 (d, J = 6.5 Hz, 3H), 0.80–0.70 (m, 2H); 13C NMR (125 MHz, CDCl3) δ 82.8, 63.7, 34.8, 32.6, 30.9, 30.5, 26.0, 24.9, 24.8, 19.2, 18.4; IR (neat) 2987, 1444, 1285, 1140 cm−1; HRMS (ESI) calcd for [C16H18BO3Si]+: 357.2996, found: 357.2995; 98% ee was measured by chiral HPLC on OD-H column with the corresponding naphthoate derivative (iPrOH:hexane = 1.99, 1.0 mL/min); tR = 13.49 min (minor), tR = 15.89 min (major).

(R)-2-(5-(1,3-dioxolan-2-yl)-3-methylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: By following the general procedure, 2g was obtained in 70% yield. 1H NMR (500 MHz, CDCl3) δ 4.82 (t, J = 5.0 Hz, 1H), 3.97–3.92 (m, 2H), 3.87–3.82 (m, 2H), 1.71–1.62 (m, 2H), 1.26–1.21 (m, 15H), 0.87 (d, J = 6.5 Hz, 3H), 0.80–0.70 (m, 2H); 13C NMR (125 MHz, CDCl3) δ 105.0, 82.9, 64.8, 34.8, 31.5, 30.7, 30.6, 24.9, 24.8, 19.7; IR (neat) 2980, 1465, 1366, 1280, 1140 cm−1; HRMS (ESI) calcd for [C15H26BO++H]+: 285.2237, found: 285.2235; 97% ee was measured by chiral HPLC on AS-H column with the corresponding naphthoate derivative (iPrOH:hexane = 1.99, 1.0 mL/min); tR = 12.53 min (major), tR = 15.17 min (minor).
(S)-4,4,5,5-tetramethyl-2-(3-methylpentyl)-1,3,2-dioxaborolane:  By following the general procedure, 2h was obtained in 71% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 1.47–1.37 (m, 2H), 1.36–1.29 (m, 2H), 1.24 (s, 12H), 1.13–1.09 (m, 1H), 0.87–0.83 (m, 6H), 0.79–0.70 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 82.8, 36.6, 30.5, 29.0, 24.9, 24.8, 18.8, 11.5; IR (neat) 2980, 1735, 1370, 1236, 1042 cm$^{-1}$; HRMS (ESI) calcd for [C$_{12}$H$_{35}$BO$_2$+H$^+$]: 213.2025, found: 213.2030; 98% ee was measured by HPLC on OZ-H column with the corresponding naphthoate derivative (iPrOH:hexane = 1:99, 1.0 mL/min); $t_R$ = 16.37 min (minor), $t_R$ = 17.89 min (major).

[Rac]  [Chiral]

(R)-2-(3-ethynonyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:  By following the general procedure, 2i was obtained in 45% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 1.39–1.32 (m, 4H), 1.29–1.24 (m, 28H), 1.69–1.06 (m, 3H), 0.89–0.81 (m, 8H), 0.72 (t, $J$ = 8.5 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 82.8, 40.9, 32.7, 32.0, 29.8, 29.7, 27.1, 26.7, 25.37, 24.8, 22.7, 14.1, 10.9; IR (neat) 2988, 1740, 1374, 1232, 1055 cm$^{-1}$; HRMS (ESI) calcd for [C$_{11}$H$_{35}$BO$_2$+H$^+$]: 283.2808, found: 283.2810; 33% ee was measured by chiral HPLC on OJ-H column with the corresponding naphthoate derivative (iPrOH:hexane = 1:99, 0.5 mL/min); $t_R$ = 12.92 min (major), $t_R$ = 13.46 min (minor).

[Rac]  [Chiral]
(R)-2-(3-cyclohexylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: By following the general procedure, 2j was obtained in 84% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.72–7.70 (m, 2H), 1.64–1.56 (m, 3H), 1.51–1.45 (m, 1H), 1.40–1.33 (m, 1H), 1.24 (s, 12H), 1.22–1.16 (m, 4H), 1.34–0.96 (m, 3H), 0.94–0.82 (m, 1H), 0.80–0.79 (m, 3H), 0.71–0.65 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 82.8, 42.3, 40.3, 30.9, 28.5, 28.1, 27.0, 26.9, 26.8, 24.9, 24.8, 15.6, 9.3 (C–B); IR (neat) 2975, 1732, 1368, 1235, 1052 cm$^{-1}$; HRMS (ESI) calcd for [C$_{16}$H$_{31}$BO$_2$H$^+$]: 267.2495, found: 267.2495; 99% ee was measured by chiral HPLC on OD-H column with the corresponding naphthoate derivative (iPrOH:hexane = 1:99, 1.0 mL/min); $t_R = 10.08$ min (minor), $t_R = 11.17$ min (major).

(R)-4,4,5,5-tetramethyl-2-(3,4,4-trimethylpentyl)-1,3,2-dioxaborolane: By following the general procedure, 2k was obtained in 62% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.69–1.64 (m, 1H), 1.25 (s, 12H), 1.05–0.91 (m, 3H), 0.84 (s, 9H), 0.81 (d, $J = 7.0$ Hz, 3H), 0.66–0.59 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 82.8, 45.6, 33.2, 27.4, 25.6, 24.9, 24.8, 13.6; IR (neat) 2980, 1735, 1377, 1230, 1045 cm$^{-1}$; HRMS (ESI) calcd for [C$_{14}$H$_{29}$BO$_2$H$^+$]: 241.2338, found: 241.2335; 99% ee was measured by chiral HPLC on OD-H column with the corresponding naphthoate derivative (iPrOH:hexane = 1:99, 1.0 mL/min); $t_R = 16.35$ min (minor), $t_R = 17.64$ min (major).
(R)-dimethyl(phenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)silane: By following the general procedure, 2l was obtained in 74% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.51–7.47 (m, 2H), 7.34–7.32 (m, 3H), 1.70–1.64 (m, 1H), 1.23 (s, 12H), 1.21–1.17 (m, 1H), 0.95–0.90 (m, 4H), 0.82–0.77 (m, 1H), 0.73–0.67 (m, 1H), 0.25 (s, 3H), 0.24 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 139.0, 133.9, 128.6, 127.6, 82.8, 25.8, 24.9, 24.8, 21.7, 13.6, 4.6, 4.9; IR (neat) 2978, 2955, 1377, 1315, 1112 cm$^{-1}$; HRMS (ESI) calcd for [C$_{18}$H$_{31}$BO$_2$Si]+: 318.2264, found: 318.2265; >99% ee was measured by chiral HPLC on AD-H column with the corresponding alcohol (iPrOH:hexane = 1:99, 0.5 mL/min); $t_R$ = 18.48 min (major), $t_R$ = 19.38 min (minor).

(R)-4,4,5,5-tetramethyl-2-(3-phenylbutyl)-1,3,2-dioxaborolane: By following the general procedure, 2m was obtained in 79% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.28–7.25 (m, 2H), 7.18–7.14 (m, 3H), 2.65–2.58 (m, 1H), 1.69–1.64 (m, 2H), 1.24 (d, $J = 7.0$ Hz, 3H), 1.22 (s, 12H),
0.75–0.62 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 147.57, 128.2, 127.2, 125.7, 82.9, 42.2, 32.7, 24.8, 21.6; IR (neat) 1735, 1368, 1235, 1155 cm$^{-1}$; HRMS (ESI) calcd for [C$_{16}$H$_{25}$BO$_2$+H$^+$]: 261.2025, found: 261.2022; 99% ee was measured by chiral HPLC on AD-H column with the corresponding alcohol (iPrOH:hexane = 1.99, 1.0 mL/min); $t_R$ = 7.98 min (minor), $t_R$ = 9.62 min (major).

(R)-2-(3-(3-fluorophenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: By following the general procedure, 2n was obtained in 78% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.23–7.19 (m, 1H), 6.94 (d, $J$ = 7.5 Hz, 1H), 6.88–6.82 (m, 2H), 2.66–2.59 (m, 1H), 1.68–1.63 (m, 2H), 1.24–1.22 (m, 15H), 0.74–0.62 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 163.0 (d, $J$ = 242.5 Hz), 150.3 (d, $J$ = 7.5 Hz), 129.5 (d, $J$ = 7.5 Hz), 122.9 (d, $J$ = 2.5 Hz), 113.8 (d, $J$ = 21.3 Hz), 112.5 (d, $J$ = 21.3 Hz), 83.0, 42.0, 41.9, 32.5, 24.8, 21.5; 19F NMR (470 MHz, CDCl$_3$) δ -114.0; IR (neat) 2978, 2925, 1360, 1325, 1142 cm$^{-1}$; HRMS (ESI) calcd for [C$_{16}$H$_{24}$BF$_2$O$_2$+H$^+$]: 279.1931, found: 279.1932; >99% ee was measured by chiral HPLC on AD-H column with the corresponding alcohol (iPrOH:hexane = 1.99, 1.0 mL/min); $t_R$ = 11.70 min (major), $t_R$ = 12.81 min (minor).
(R)-4,4,5,5-tetramethyl-2-(3-(p-toly)butyl)-1,3,2-dioxaborolane:

By following the general procedure, 27n was obtained in 71% yield. 1H NMR (500 MHz, CDCl3) δ 7.09–7.05 (m, 4H), 2.61–2.54 (m, 1H), 2.30 (s, 3H), 1.67–1.62 (m, 2H), 1.22–1.21 (m, 15H), 0.73–0.64 (m, 2H); 13C NMR (125 MHz, CDCl3) δ 144.5, 135.1, 128.9, 127.0, 82.9, 41.7, 32.8, 24.9, 24.8, 21.7, 21.0; IR (neat) 2975, 2927, 1360, 1322, 1144 cm⁻¹; HRMS (ESI) calcd for [C17H27B2O2+H]+: 275.2182, found: 275.2185; >99% ee was measured by chiral HPLC on AS-H column with the corresponding alcohol (iPrOH:hexane = 1:99, 0.5 mL/min); tR = 27.66 min (minor), tR = 30.39 min (major).

(R)-2-(3-(4-methoxyphenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: By following the general procedure, 27o was obtained in 59% yield. The characterization data for 27o was concordant with that previously reported in the literature. 1H NMR (500 MHz, CDCl3) δ 7.13 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 3.79 (s, 3H), 3.61–3.51 (m, 2H), 2.88–2.81 (m, 1H), 1.87–1.78 (m, 2H), 1.25 (d, J = 7.0 Hz, 3H); 13C NMR (125 MHz, CDCl3) δ 127.8, 113.9, 61.3, 55.3, 41.2, 35.7, 22.6; >99% ee was measured by chiral HPLC on OD-H column with the corresponding alcohol (iPrOH:hexane = 1:99, 1.0 mL/min); tR = 13.83 min (minor), tR = 15.29 min (major).
(R)-4,4,5,5-tetramethyl-2-(3-(naphthalen-2-yl)butyl)-1,3,2-dioxaborolane: By following the general procedure, 2q was obtained in 75% yield. The characterization data for 2q was concordant with that previously reported in the literature.\textsuperscript{[2]} \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.79–7.75 (m, 3H), 7.59 (s, 1H), 7.42–7.38 (m, 2H), 7.34 (dd, \(J = 8.5\) Hz, 1.5 Hz, 1H), 2.83–2.76 (m, 1H), 1.80–1.72 (m, 2H), 1.33 (d, \(J = 7.0\) Hz, 3H), 1.21 (s, 12H), 0.77–0.65 (m, 2H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 145.0, 133.6, 132.2, 127.8, 127.6, 127.5, 126.0, 125.7, 125.4, 125.0, 82.9, 42.3, 32.6, 24.9, 24.8, 21.6, 9.6 (C–B); >99% ee was measured by chiral HPLC on OZ-H column with the corresponding alcohol (iPrOH:hexane = 1:99, 1.0 mL/min); \(t_R = 11.00\) min (minor), \(t_R = 13.31\) min (major).

\(\text{[rac]}\)

\(\text{[chiral]}\)

\((R)-4,4,5,5\text{-tetramethyl-2-(3-phenylpentyl)-1,3,2-dioxaborolane}\): By following the general procedure, 2r was obtained in 44% yield. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.27–7.24 (m, 2H), 7.17–7.14 (m, 1H), 7.13–7.11 (m, 2H), 2.35–2.30 (m, 1H), 1.77–1.54 (m, 4H), 1.21 (s, 12H), 0.76 (t, \(J = 7.5\) Hz, 3H), 0.67–0.57 (m, 2H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 145.7, 128.1, 127.9, 125.7, 82.9, 50.3, 30.8, 29.1, 24.9, 24.8, 12.3; IR (neat) 3028, 2925, 1448, 1367, 1142 cm\(^{-1}\); HRMS (ESI) calcd for [C\(_{17}\)H\(_{29}\)BO\(_2\)+H\(^+\): 275.2182, found: 275.2180; 74% ee was measured by chiral HPLC on OD-H column with the corresponding naphtholate derivative (iPrOH:hexane = 2:98, 1.0 mL/min); \(t_R = 12.32\) min (major), \(t_R = 15.21\) min (minor).
Detection of the Chiral Olefin Intermediate (Scheme 2)

A mixture of CuCl (5 mol %, 0.025 mmol), (R)-DTBM-Segphos (5.5 mol %, 0.0275 mmol) and KOtBu (1 mmol) in anhydrous toluene (2 mL) were stirred for 5 min in a Schlenk tube under an atmosphere of nitrogen. Pinacolborane (0.5 mmol) was added to the reaction mixture and stirred for another 15 min at room temperature. Substrate 1q dissolved in toluene (1 mL) was added. The reaction mixture was sealed, stirred at 60 °C and monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with diethyl ether (10 mL). After the aqueous layer was extracted with diethyl ether, the combined organic layers were dried over Na2SO4, and concentrated in vacuo. The product was purified by silica gel chromatography using hexanes/ethyl acetate as the eluent. The characterization data for 1q' was concordant with that previously reported in the literature.5 1H NMR (500 MHz, CDCl3) δ 7.84–7.78 (m, 3H), 7.66 (s, 1H), 7.48–7.35 (m, 3H), 6.15–6.00 (m, 1H), 5.12–5.05 (m, 2H), 3.70–3.61 (m, 1H), 1.47 (d, J = 7.0 Hz, 3H); 13C NMR (125 MHz, CDCl3) δ 143.3, 135.2, 133.8, 132.5, 128.0, 127.8, 127.7, 126.5, 126.0, 125.4, 113.5, 43.4, 20.8.
Determination of Absolute Configuration of 3 (Scheme 3)

Sodium perborate (0.9 mmol) was added to 2a (0.3 mmol) in THF (2 mL) and water (2 mL). The reaction mixture was stirred vigorously for 4 h at room temperature. The reaction was quenched with water and then, extracted with diethyl ether. The combined organic layers were dried over Na$_2$SO$_4$ and concentrated in vacuo. The product 3 was purified by silica gel chromatography (hexane/ethyl acetate) in 95% yield. The characterization data for 3 was concordant with that previously reported in the literature.$^5$ $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.10 (t, $J = 7.0$ Hz, 1H), 3.73–3.64 (m, 2H), 2.05–1.92 (m, 2H), 1.68 (s, 3H), 1.61–1.57 (m, 5H), 1.41–1.33 (m, 2H), 1.22–1.15 (m, 2H), 0.91 (d, $J = 6.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 131.3, 124.7, 61.2, 39.9, 37.2, 29.2, 25.7, 25.5, 19.5, 17.7; $[\alpha]_D^0 = -3.5$ (c = 1.2, CHCl$_3$) (lit.$^5$ $[\alpha]_D^0 = -4.9$ (c = 0.5, CHCl$_3$) for (S)-isomer with 99% ee); 99% ee were measured by chiral HPLC on AD-H column with the corresponding naphthoate derivative (iPrOH:hexane = 1:99, 1.0 mL/min); $t_R = 14.75$ min (minor), $t_R = 15.72$ min (major).
Suzuki-Miyaura Cross-Coupling Reaction of 2a (Scheme 3)

To a Schlenck tube, Pd₂dba₃ (2 mol%, 0.006 mmol), Ruphos (4 mol%, 0.012 mmol), 2a (0.25 mmol), bromobenzene (0.3 mmol) and NaOtfBu (3 equiv, 0.9 mmol) were added. The mixture was diluted with THF (0.5 mL) and H₂O (0.05 mL) under an atmosphere of nitrogen. The mixture was stirred for 24 h at 80 °C, and monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with diethyl ether (10 mL). After the aqueous layer was extracted with diethyl ether and the combined organic layers were dried over Na₂SO₄, and concentrated in vacuo. The product 4 was purified by silica gel chromatography (hexanes) in 82% yield. The characterization data for 4 was concordant with that previously reported in the literature.⁶ ¹H NMR (500 MHz, CDCl₃) δ 7.28–7.25 (m, 2H), 7.18–7.15 (m, 3H), 5.12–5.08 (m, 1H), 2.68–2.62 (m, 1H), 2.59–2.53 (m, 1H), 2.03–1.92 (m, 2H), 1.68 (s, 3H), 1.66–1.62 (m, 1H), 1.60 (s, 3H), 1.47–1.36 (m, 3H), 1.20–1.16 (m, 1H), 0.94 (d, J = 6.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 143.2, 131.1, 128.4, 128.3, 125.5, 124.9, 38.9, 37.0, 33.5, 32.2, 25.7, 25.5, 19.6, 17.7; 99% ee was measured by chiral HPLC on AS-H column (PrOH:hexane = 1:99, 0.5 mL/min); tᵣ = 23.60 min (minor), tᵣ = 28.71 min (major).
Amination of 2m (Scheme 3)

To a Schlenck tube, KOtBu (1.5 equiv, 0.45 mmol), MeONH₂ (1.5 equiv, 0.45 mmol), 2m (0.3 mmol), were added, and the mixture diluted with toluene (1.5 mL) under an atmosphere of nitrogen. The mixture was stirred for 16 h at 80 °C, and monitored by TLC. The reaction mixture was then cooled to room temperature and under an atmosphere of nitrogen, Boc₂O (1.5 equiv, 0.45 mmol) was added. The reaction mixture was stirred for 1 h at room temperature, and monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with ethyl acetate (10 mL). After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over Na₂SO₄, and concentrated in vacuo. The product 5 was purified by silica gel chromatography in 62% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.31–7.26 (m, 2H), 7.20–7.17 (m, 3H), 4.41 (brs, 1H), 3.06–2.97 (m, 2H), 2.87–2.71 (m, 1H), 1.81–1.73 (m, 2H), 1.43 (s, 9H), 1.26 (d, J = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 146.6, 128.5, 126.9, 126.2, 39.1, 38.3, 37.7, 29.7, 28.4, 22.3, 14.1; >99% ee was measured by chiral HPLC on AS-H column (iPrOH:hexane = 1:99, 0.5 mL/min); tᵣ = 15.59 min (major), tᵣ = 17.23 min (minor).

| RT[min] | 異性[ms/sec] | 異性比[%] |
|---------|--------------|-----------|
| 15.0730 | 37414,2250   | 43.69     |
| 17.2333 | 37880,5781   | 50.31     |

| RT[min] | 異性[ms/sec] | 異性比[%] |
|---------|--------------|-----------|
| 15.5950 | 9442,7570    | 100.00    |
Hydrolysis of Allylic Acetate

The reaction of 1m-OAc under the standard reaction conditions afforded the corresponding allylic alcohol product by hydrolysis. Proposed mechanism of hydrolysis of 1m-OAc to generate an allylic alcohol is shown in Scheme S1-b. Moreover, no hydrolysis occurred in the absence of KOtBu base (Scheme S1-c). This result indicates that KOtBu base leads to hydrolysis of the starting allylic acetate.

Scheme S1. Hydrolysis of allylic acetate
Reaction of α- or β- substituted allylic benzoate

Scheme S2. Reaction of α- or β-substituted allylic benzoate

Computational Details

To gain an insight into the origin of high enantioselectivity, we performed DFT calculations at the M06-2X/6-13G* level using a suite of Gaussian 09 programs. Images of the 3D structures were rendered using CYLView.

Figure S1. Computed energy profiles of hydrocupration of 1m-OBz.
**Figure S2.** Transition state structures of the hydrocupration step.

**Figure S3.** Evaluation of energy barriers for transition states
Cartesian Coordinates and Calculated Thermodynamic Properties of Selected Molecules

1m-OBz

Single-Point Energy: -807.531647
Thermal Correction to Enthalpy: 0.308139
Thermal Correction to Free Energy: 0.242593

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | 2.30652900 | 0.92205200 | 0.22760500 |
| C    | 1.14782200 | 0.61007100 | -0.36914300|
| H    | 1.09610100 | -0.28734700| -0.98283400|
| C    | 3.48459300 | 0.02409300 | 0.07630500 |
| C    | 4.77907200 | 0.55385200 | 0.01195200 |
| C    | 3.33373300 | -1.36656700| 0.00591400 |
| C    | 5.88419800 | -0.27592000| -0.14766500|
| H    | 4.92478200 | 1.62854000 | 0.07103500 |
| C    | 4.43731000 | -2.19745200| -0.14913200|
| H    | 2.34134300 | -1.79744300| 0.10167300 |
| C    | 5.71783200 | -1.65511200| -0.23042600|
| H    | 6.87801400 | 0.15739600 | -0.20814300|
| H    | 4.29788600 | -3.27341100| -0.19399000|
| H    | 6.58008400 | -2.30423300| -0.34801100|
| C    | -0.10970500| 1.41567600 | -0.35433000|
| H    | -0.13960000| 2.16774800 | 0.43806300 |
| H    | -0.26442000| 1.93983000 | -1.30487800|
| C    | 2.52415800 | 2.18064900 | 1.03226200 |
| H    | 3.14919600 | 1.97289700 | 1.90571800 |
| H    | 3.03889500 | 2.94422900 | 0.43713800 |
| H    | 1.58601900 | 2.61757200 | 1.37822300 |
| O    | -1.20196400| 0.50145200 | -0.16633900|
| C    | -2.42273900| 1.05503000 | -0.25398100|
| O    | -2.60102900| 2.23261900 | -0.46207800|
| C    | -3.51832800| 0.06101900 | -0.06388400|
| C    | -4.83164400| 0.52745900 | -0.14287500|
|     | x   | y   | z   |
|-----|-----|-----|-----|
| C   | -3.26341300 | -1.28852600 | 0.18546200 |
| C   | -5.89087500 | -0.35586800 | 0.02632100 |
| H   | -4.99691100 | 1.58236100  | -0.33732300 |
| C   | -4.32674100 | -2.16882200 | 0.35469700 |
| H   | -2.23784600 | -1.63675600 | 0.24559000 |
| C   | -5.63814700 | -1.70399400 | 0.27478500 |
| H   | -6.91312000 | 0.00458600  | -0.03447900 |
| H   | -4.13302500 | -3.21921100 | 0.54906400 |
| H   | -6.46536300 | -2.39517600 | 0.40729300 |

**DTBM-Segphos-CuH**

Single-Point Energy: -5803.764000
Thermal Correction to Enthalpy: 1.699458
Thermal Correction to Free Energy: 1.472397
H 2.29547300  4.13103300  2.50860700
H 2.80326000  2.60206100  0.61221800
H 1.12614800 -2.61371100  5.64024800
H -0.39147200 -1.66756600  5.94783500
H 0.17519200  1.97886900  5.86395400
H -1.33889700  2.90512000  5.48347600
C 3.35137100  0.64613000 -0.89082100
C 4.51506900  0.56855800 -0.12063600
C 3.40977200  1.21881500 -2.15170400
C 5.74534600  0.97492100 -0.62518700
H 4.44434200  0.17993900  0.88878800
C 4.60846600  1.68859100 -2.70751900
H 2.48720200  1.27547700 -2.72484700
C 5.77380700  1.46316600 -1.95825700
C 1.90964600 -1.61283500  0.24207100
C 1.28697800 -2.56955200 -0.54453000
C 2.60400500 -2.01904800  1.38350700
C 1.41103800 -3.94181000 -0.30732700
H 0.67558900 -2.22370100 -1.37575500
C 2.80318900 -3.37031200  1.65793400
H 2.97502200 -1.26113600  2.06627500
C 2.27598900 -4.31043900  0.73476100
C -3.25485900 -0.65884600 -1.01486600
C -4.44040100 -0.54545300 -0.30026500
C -3.24709400 -1.37064400 -2.21321100
C -5.64378500 -1.08191400 -0.76603400
H -4.42338100 -0.03797100  0.65967200
C -4.41540100 -1.90961900 -2.75163300
H -2.30164800 -1.46799100 -2.73771400
C -5.61569800 -1.67805700 -2.04421300
C -1.91813300  1.67795500  0.10003100
C -1.28460700  2.62827700 -0.68587400
C -2.67037300  2.09860700  1.19919400
C -1.45398200  4.00276500 -0.49354600
H -0.63001000  2.27688000 -1.48015000

S23
C  -2.91887700  3.45109000  1.42267700
H   -3.04528000  1.35104800  1.89101800
C   -2.37438700  4.37840600  0.49675300
C   -2.06658100 -2.19123000  1.33082700
C   -1.85151000 -3.01606200  2.44415100
H   -2.38948900 -3.94724100  2.57975900
H   -2.79948800 -2.50703200  0.59574800
C    0.56133500 -4.87663200 -1.19289700
C    0.53637100 -6.35923000 -0.76753000
H    0.29513900 -6.46230000  0.29291100
H   -0.24031300 -6.86152700 -1.35034500
H    1.47519600 -6.87661400 -0.95698000
C    1.02545300 -4.77196900 -2.65592300
H    0.94956100 -3.74438000 -3.02834800
H    2.06568300 -5.09509900 -2.77149900
H    0.39992200 -5.40918600 -3.29146600
C   -0.90474600 -4.39736400 -1.10957900
H   -1.28021600 -4.49738500 -0.08619200
H   -1.03252900 -3.35195700 -1.41176600
H   -1.52833400 -5.01242400 -1.76893800
C    3.49875600 -3.82161700  2.95457400
C    4.81144400 -4.57770800  2.68621400
H    5.34580000 -4.72561100  3.63183200
H    4.62639400 -5.56141900  2.25333200
H    5.46565400 -4.00742100  2.01657900
C    3.83782400 -2.61839400  3.84568600
H    4.57942600 -1.95933800  3.37951700
H    2.94878400 -2.02306900  4.07880700
H    4.26562900 -2.98221700  4.78570800
C    2.53966000 -4.73221700  3.74225200
H    2.31315100 -5.64284600  3.18435900
H    2.99651100 -5.01667500  4.69807000
H    1.59585300 -4.21617400  3.94751300
C    6.99752700  0.98826700  0.26954400
C    4.49824100  2.42836700 -4.05747600

S24
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | 5.74973600 | 3.21477800 | -4.48184000|
| H       | 5.48241900 | 3.84021100 | -5.34058000|
| H       | 6.10344800 | 3.86772900 | -3.67940800|
| H       | 6.58034300 | 2.57960900 | -4.79143600|
| C       | 3.36844100 | 3.47583100 | -3.93029700|
| H       | 2.39014700 | 3.02336000 | -3.74584700|
| H       | 3.58335900 | 4.17705800 | -3.11660800|
| H       | 3.29462200 | 4.04458900 | -4.86337200|
| C       | 4.10609400 | 1.43656100 | -5.16647100|
| H       | 4.87455300 | 0.67135500 | -4.92950800|
| H       | 3.16582900 | 0.92734200 | -3.74584700|
| C       | 7.49692900 | 2.43901600 | 0.39617700 |
| H       | 8.38519500 | 2.47229200 | 1.03790900 |
| H       | 7.75988900 | 2.85032700 | -0.58083100|
| H       | 6.72599400 | 3.07253300 | 0.84802400 |
| C       | 6.67442300 | 0.48081700 | 1.68277200 |
| H       | 5.89618200 | 1.08017900 | 2.16670300 |
| H       | 6.35279200 | -0.56732000| 1.67446200 |
| H       | 7.57584600 | 0.54721600 | 2.29991300 |
| C       | 8.13447900 | 0.10674800 | -0.27628800|
| H       | 7.77095700 | -0.89523000| -0.53063700|
| H       | 8.60220600 | 0.55165600 | -1.15475400|
| H       | 8.90894400 | -0.00361300| 0.49118400 |
| C       | -3.67957200| 3.92039500 | 2.67518100 |
| C       | -0.57849400| 4.93174700 | -1.35920900|
| C       | -0.94338800| 4.75934500 | -2.84356900|
| H       | -1.98251900| 5.04746300 | -3.03675900|
| H       | -0.29542200| 5.39093500 | -3.46200200|
| H       | -0.81536600| 3.72183700 | -3.17113300|
| C       | 0.89152100 | 4.49901300 | -1.16183100|
| H       | 1.19193700 | 4.64197800 | -0.11865300|
| H       | 1.06909900 | 3.44924700 | -1.42133300|
| H       | 1.53991200 | 5.11205700 | -1.79758700|
| C       | -0.62163200| 6.42416500 | -0.99337100|
|   |   |   |   |
|---|---|---|---|
| H | -1.56031100 | 6.91011100 | -1.26414700 |
| H | -0.45075300 | 6.58244800 | 0.07415500 |
| H | 0.17560200 | 6.93115700 | -1.54816800 |
| C | -2.76847800 | 4.86434200 | 3.48031000 |
| H | -2.53588900 | 5.76668100 | 2.91148500 |
| H | -3.26691900 | 5.16095900 | 4.41129700 |
| H | -1.82430900 | 4.36979600 | 3.73146800 |
| C | -4.99041300 | 4.64960800 | 2.33290700 |
| H | -5.56803200 | 4.80872000 | 2.91148500 |
| H | -4.80127600 | 5.62660700 | 1.88695400 |
| H | -5.60618100 | 4.05510000 | 1.64806500 |
| C | -4.03949200 | 2.73245000 | 3.57829600 |
| H | -4.74747700 | 2.05005800 | 3.09252700 |
| H | -3.15272000 | 2.15940000 | 3.86716000 |
| H | -4.51761700 | 3.10937800 | 4.48833600 |
| C | -6.84945900 | -1.02389400 | 0.19772500 |
| C | -4.35804300 | -2.79675900 | -4.00721900 |
| C | -2.91552900 | -2.93977500 | -4.51669500 |
| H | -2.49129600 | -1.98208000 | -4.83758800 |
| H | -2.25214300 | -3.36765400 | -3.75681600 |
| H | -2.91065600 | -3.61485100 | -5.37840800 |
| C | -4.86628600 | -4.20119700 | -3.63341500 |
| H | -5.89785700 | -4.16565800 | -3.27543600 |
| H | -4.82579500 | -4.85734900 | -4.51072900 |
| H | -4.23752000 | -4.64017500 | -2.85072500 |
| C | -5.20081200 | -2.24632900 | -5.17086500 |
| H | -6.26962100 | -2.35079000 | -4.97959000 |
| H | -4.96865200 | -1.19304300 | -5.36315800 |
| H | -4.97050100 | -2.81020200 | -6.08172400 |
| C | -8.06578600 | -1.87738700 | -0.20199100 |
| H | -8.76007500 | -1.89427200 | 0.64543400 |
| H | -8.61166400 | -1.48072400 | -1.05838000 |
| H | -7.77751400 | -2.90654600 | -0.42958600 |
| C | -6.38894800 | -1.57850500 | 1.56492000 |
| H | -6.03191300 | -2.60873500 | 1.46162000 |
|     |      |      |      |
|-----|------|------|------|
| H   | -5.58765800 | -0.98870400 | 2.01761200 |
| H   | -7.23310600 | -1.57677200 | 2.26270800 |
| C   | -7.29747300 | 0.43511000  | 0.38941100  |
| H   | -6.47459400 | 1.06156100  | 0.75135500  |
| H   | -7.65962900 | 0.87100200  | -0.54745500 |
| H   | -8.11095500 | 0.48495700  | 1.12225600  |
| O   | -2.77730600 | 5.69505300  | 0.59459600  |
| C   | -3.74330700 | 6.02610600  | -0.39302300 |
| H   | -3.97428500 | 7.08557300  | -0.26234100 |
| H   | -3.35381500 | 5.85678600  | -1.40275100 |
| H   | -4.65408900 | 5.42956600  | -0.26587800 |
| O   | -6.79664300 | -2.06143500 | -2.64576100 |
| O   |  7.01098200 | 1.72270900  | -2.51179900 |
| O   |  2.64220700 | -5.63271400 |  0.88794300 |
| C   |  7.42759700 | 0.69754000  | -3.40286100 |
| H   |  6.71750700 | 0.57378200  | -4.22653000 |
| H   |  8.39805100 | 1.00386600  | -3.79946200 |
| H   |  7.52690400 | -0.26048000 | -2.88066400 |
| C   |  3.64523700 | -6.01505200 | -0.04251700 |
| H   |  3.85689400 | -7.07054700 |  0.14182500 |
| H   |  3.30223900 | -5.88435700 | -1.07449000 |
| H   |  4.55748700 | -5.42419800 |  0.09925600 |
| C   | -7.48614100 | -0.95941000 | -3.21843800 |
| H   | -8.40699500 | -1.35631900 | -3.65108800 |
| H   | -7.73223500 | -0.20691700 | -2.46113100 |
| H   | -6.88427300 | -0.48334700 | -4.00013200 |
| Cu  |  0.07465700 |  0.03437200 | -1.97930200 |
| H   |  0.11019600 |  0.04995900 | -3.55286800 |

**TS1 (Favored Transition State)**

Single-Point Energy: -6611.274438
Thermal Correction to Enthalpy: 2.023527
Thermal Correction to Free Energy: 1.776289

S27
| Symbol | X    | Y    | Z    |
|--------|------|------|------|
| C      | 4.27648000 | 1.08318900 | -3.27246600 |
| C      | 2.94759600 | 1.03554800 | -2.87527000 |
| C      | 1.92059600 | 0.72444100 | -3.77863000 |
| C      | 2.28135600 | 0.46717300 | -5.10344900 |
| C      | 3.61627400 | 0.52149700 | -5.50991600 |
| C      | 4.62097900 | 0.82704100 | -4.59969800 |
| H      | 5.04027000 | 1.30984400 | -2.53216600 |
| H      | 2.70537000 | 1.24748000 | -1.89920900 |
| H      | 1.52131400 | 0.22906200 | -5.84052100 |
| H      | 3.86490800 | 0.32024400 | -6.54804200 |
| H      | 5.65885100 | 0.86033600 | -4.91746400 |
| C      | 0.48351300 | 0.68826500 | -3.30069000 |
| H      | 0.54835000 | -0.54185300 | -2.53469000 |
| C      | 0.07082400 | 1.89220200 | -2.49912700 |
| H      | 0.92621900 | 2.55719600 | -2.35653100 |
| C      | -1.09308100 | 2.67911900 | -3.03384400 |
| H      | -1.99684200 | 2.08108300 | -3.18720600 |
| H      | -0.89111400 | 3.20426400 | -3.98070600 |
| O      | -1.41409300 | 3.72191200 | -2.07615100 |
| C      | -2.32276200 | 4.61151000 | -2.49009700 |
| O      | -2.94083000 | 4.51872700 | -3.52677500 |
| C      | -0.51793600 | 0.22498800 | -4.34949300 |
| H      | -1.49522000 | 0.04216800 | -3.89378100 |
| H      | -0.64099300 | 0.98705100 | -5.12970200 |
| H      | -0.19404400 | -0.70568000 | -4.82573300 |
| Cu     | -0.01530800 | 0.39972200 | -1.06271400 |
| P      | -1.54347200 | -1.04709300 | -0.15956100 |
| P      | 1.61283300 | 0.21399100 | 0.57150200 |
| C      | -0.73952300 | -2.48330500 | 0.67554900 |
| C      | -2.70707100 | -1.80267000 | -1.34864600 |
| C      | -2.62766800 | -0.34276300 | 1.12184100 |
| C      | 0.82930600 | 0.17257000 | 2.22944300 |
| C      | 2.79710700 | 1.60711700 | 0.62196300 |
| C      | 2.69928600 | -1.24840400 | 0.49757200 |

S28
| Element | X-Coordinate | Y-Coordinate | Z-Coordinate |
|---------|--------------|--------------|--------------|
| C       | -0.00155500  | -2.26823400  | 1.87251700   |
| C       | -0.81014400  | -3.76579500  | 0.12802700   |
| C       | -4.08040700  | -1.78157600  | -1.16425400  |
| C       | -2.18888400  | -2.38237400  | -2.51200600  |
| C       | -2.76744600  | 1.03648500   | 1.13697500   |
| C       | -3.32301000  | -1.11388700  | 2.05953700   |
| C       | 0.12212100   | -0.99184400  | 2.63123200   |
| C       | 0.87258400   | 1.28962100   | 3.06566200   |
| C       | 4.16947000   | 1.41804500   | 0.79087200   |
| C       | 2.32345300   | 2.88229700   | 0.33244300   |
| C       | 2.84581700   | -1.83173300  | -0.75150700  |
| C       | 3.41956800   | -1.76370300  | 1.57949200   |
| C       | 0.56855900   | -3.38842000  | 2.44196000   |
| C       | -0.19266600  | -4.88167200  | 0.71501200   |
| H       | -1.38945900  | -3.92667600  | -0.77429000  |
| C       | -4.97339500  | -2.26751200  | -2.12924600  |
| H       | -4.47551100  | -1.36241700  | -0.24594300  |
| C       | -3.01821700  | -2.89024300  | -3.50711400  |
| H       | -1.10919300  | -2.42325200  | -2.63136700  |
| C       | -3.63922000  | 1.68779700   | 2.02029900   |
| H       | -2.17772700  | 1.62211700   | 0.43447500   |
| C       | -4.24773900  | -0.53361300  | 2.92390400   |
| H       | -3.13380100  | -2.18219200  | 2.09555600   |
| C       | -0.42566900  | -0.95714500  | 3.89726800   |
| C       | 0.27248300   | 1.30781500   | 4.33419000   |
| H       | 1.41489500   | 2.17159100   | 2.73912300   |
| C       | 5.08234000   | 2.44946800   | 0.58352100   |
| H       | 4.52672700   | 0.43219600   | 1.05594900   |
| C       | 3.18365500   | 3.97571500   | 0.16853400   |
| H       | 1.25206000   | 3.02187300   | 0.18954500   |
| C       | 3.74024100   | -2.88144000  | -0.99156000  |
| H       | 2.24063700   | -1.45580000  | -1.57219800  |
| C       | 4.37103300   | -2.76602500  | 1.39820000   |
| H       | 3.23377000   | -1.35749800  | 2.56929400   |
| C       | 0.48389400   | -4.66023700  | 1.89008300   |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| O       | 1.30196000| -3.45227100| 3.59951800|
| H       | -0.27061100| -5.87069900| 0.27875400|
| C       | -4.41503000| -2.72664300| -3.33287600|
| C       | -6.46738200| -2.28360500| -1.74050700|
| C       | -2.43437000| -3.67017000| -4.69810400|
| C       | -4.44901500| 0.86567000| 2.81828900 |
| C       | -3.57707900| 3.22666600| 2.05554700 |
| C       | -4.93840100| -1.35714500| 4.02456300 |
| C       | -0.35495400| 0.15096600| 4.73246300 |
| O       | -1.11249400| -1.95639100| 4.53986000 |
| H       | 0.32531800| 2.17760600| 4.97878300 |
| C       | 4.56342900| 3.70383400| 0.18791800 |
| C       | 6.58020700| 2.23308200| 0.86334000 |
| C       | 2.52389200| 5.36113900| 0.00999500 |
| C       | 4.57008800| -3.24807900| 0.07903300 |
| C       | 3.66924000| -3.54193700| -2.38368200|
| C       | 5.10487600| -3.39107500| 2.59696900 |
| O       | 1.15262300| -5.54618300| 2.69464600 |
| C       | 1.33283400| -4.83751300| 3.91448700 |
| O       | -5.22837800| -3.02695300| -4.40663400|
| C       | -7.37984000| -3.10260200| -2.66915400|
| C       | -6.59076700| -2.94274400| -0.34782000|
| C       | -6.99872300| -0.84321600| -1.64061000|
| C       | -0.91828200| -3.85868900| -4.54268700|
| C       | -3.06632600| -5.07431600| -4.73127600|
| C       | -2.67951100| -2.96508800| -6.04256500|
| O       | -5.48508100| 1.41281800| 3.54716200 |
| C       | -4.13696000| 3.80700300| 0.74681000 |
| C       | -2.08724100| 3.62171000| 2.18019600 |
| C       | -4.28479700| 3.88632900| 3.25067600 |
| C       | -4.58201300| -0.73178100| 5.38619600 |
| C       | -6.46850200| -1.40311300| 3.87078800 |
| C       | -4.43631400| -2.80783000| 4.02101300 |
| O       | -0.98038100| -0.14098100| 5.91773400 |
| C       | -1.08521200| -1.55902000| 5.90386000 |

S30
O  5.46224200  4.67467900  -0.20188200
C  7.01307500  3.20248200  1.97825700
C  6.85115900  0.80147400  1.35220000
C  7.46450000  2.46533600  -0.37387700
C  3.47529400  6.56809200  0.08017000
C  1.54792800  5.54310900  1.19407500
C  1.73215600  5.41853400  -1.30765000
O  5.62360100  -4.11426900  -0.13199300
C  4.43311700  -4.86911300  -2.52075000
C  4.14271000  -2.55439800  -3.46337500
C  2.18564300  -3.87749800  -2.66289500
C  6.63063100  -3.20220800  2.52799500
C  4.63422100  -2.76817300  3.91890700
H  2.30156500  -5.09067800  4.34562100
H  0.50202300  -5.07093800  4.59527900
C  -5.63973600  -1.85798400  -5.10206700
H  -8.35955100  -3.19775000  -2.18794000
H  -7.54007800  -2.63625500  -3.64174300
H  -6.98143700  -4.10662400  -2.83681900
H  -6.21016800  -3.96919200  -0.37132000
H  -6.04777600  -2.39741200  0.42951100
H  -7.64534800  -2.97436300  -0.05264400
H  -6.42820900  -0.25903100  -0.91021700
H  -6.94000500  -0.32222400  -2.60148900
H  -8.04819600  -0.85316500  -1.32430100
H  -0.37560200  -2.90753300  -4.57338300
H  -0.66532500  -4.36559900  -3.60441700
H  -0.54880700  -4.47752900  -5.36681700
H  -4.14848300  -5.02111600  -4.86206100
H  -2.64306300  -5.64979700  -5.56277500
H  -2.85103100  -5.61321700  -3.80203800
H  -3.73129400  -3.00395400  -6.32908000
H  -2.35684500  -1.91822700  -6.00300700
H  -2.10263800  -3.46588600  -6.82830300
C: -6.61963100  1.68287300  2.73716700
H: -5.18312900  3.52137300  0.59357900
H: -4.08180700  4.90180700  0.76410500
H: -3.56133300  3.45480700 -0.11609600
H: -1.65171600  3.18784800  3.08709400
H: -1.48982800  3.28753800  1.32489000
H: -2.00348200  4.71212800  2.23733800
H: -5.37303100  3.84090100  3.18963300
H: -3.97832000  3.43504300  4.19838700
H: -4.00419200  4.94549400  3.26495200
H: -5.04779600  0.24839900  5.50403000
H: -4.92483100 -1.38114800  6.20091300
H: -3.49892600 -0.59729600  5.47108400
H: -6.88253900 -2.12494800  4.58408300
H: -6.92584200 -0.43496400  4.07750000
H: -6.75624400 -1.72705200  2.86392100
H: -4.70746500 -3.32962300  3.09586000
H: -3.34997200 -2.86036400  4.14336600
H: -4.90317500 -3.34713100  4.85173400
H: -0.19725600 -1.99254100  6.38632700
H: -2.01034400 -1.86442100  6.39141700
C:  5.53516400  4.79017100 -1.61737400
H:  8.07582400  3.05875500  2.20564600
H:  6.86092200  4.24056800  1.67372000
H:  6.44014600  3.01718500  2.89307300
H:  6.29065400  0.56605100  2.26367400
H:  6.59633000  0.05345900  0.59124200
H:  7.91697300  0.69866100  1.58075200
H:  7.11104800  1.88133000 -1.23166600
H:  7.49999700  3.51961200 -0.64970000
H:  8.48874400  2.14416500 -0.15238200
H:  2.86433100  7.47420400  0.15970400
H:  4.12997700  6.51722600  0.95378500
H:  4.09959200  6.67932300 -0.80729100
H:  0.78684500  4.75889400  1.24607700
| Atoms | X         | Y         | Z         |
|-------|-----------|-----------|-----------|
| H     | 2.09488600 | 5.54328700 | 2.14341600 |
| H     | 1.03375800 | 6.50560500 | 1.09420000 |
| H     | 2.39284200 | 5.30362500 | -2.17391500 |
| H     | 0.97329100 | 4.63087100 | -1.36727500 |
| H     | 1.22105000 | 6.38476100 | -1.39630000 |
| C     | 6.73024200 | -3.46685100 | -0.74281600 |
| H     | 4.17930700 | -5.56366600 | -1.71547000 |
| H     | 4.14881500 | -5.32842500 | -3.47391600 |
| H     | 5.51707100 | -4.74633900 | -2.53184100 |
| H     | 3.52696000 | -1.64879400 | -3.47496500 |
| H     | 5.18232200 | -2.24574300 | -3.30816400 |
| H     | 4.07215400 | -3.02205600 | -4.45251000 |
| H     | 1.78665500 | -4.54846000 | -1.89423300 |
| H     | 1.55340300 | -2.98380400 | -2.69551000 |
| H     | 2.10076000 | -4.37426700 | -3.63620200 |
| H     | 7.07774500 | -3.51319200 | 3.47929300  |
| H     | 7.07909300 | -3.80682400 | 1.73926200  |
| H     | 6.89056800 | -2.14935500 | 2.36481200  |
| H     | 4.89306400 | -1.70470200 | 3.98070800  |
| H     | 3.55301500 | -2.86731100 | 4.05430100  |
| H     | 5.13425600 | -3.27803600 | 4.74890000  |
| H     | 5.20570000 | -5.41183000 | 1.77301800  |
| H     | 5.18349800 | -5.34641000 | 3.54757000  |
| H     | 3.69322700 | -5.05370000 | 2.61449300  |
| H     | -6.22544200 | -2.19321600 | -5.96071500 |
| H     | -6.25700000 | -1.21403300 | -4.46681500 |
| H     | -4.77349800 | -1.28158600 | -5.44559900 |
| H     | -7.39861400 | 2.05857300  | 3.40429600  |
| H     | -6.39492700 | 2.43726800  | 1.97597600  |
| H     | -6.96891100 | 0.77137500  | 2.23692700  |
| H     | 4.56284900  | 5.05345900  | -2.04631100 |
| H     | 6.25775500  | 5.58107100  | -1.82970500 |
| H     | 5.86911700  | 3.85009100  | -2.07076600 |
| H     | 7.50733400  | -4.22415500 | -0.86700300 |
| H     | 6.46052200  | -3.05467700 | -1.72101900 |
|     | X       | Y       | Z       |
|-----|---------|---------|---------|
| H   | 7.104537| -2.652847| -0.110607|
| C   | -2.506201| 5.741403| -1.526733|
| C   | -3.550484| 6.637210| -1.758319|
| C   | -1.685626| 5.897558| -0.410833|
| C   | -3.779011| 7.681297| -0.868322|
| H   | -4.172556| 6.491715| -2.635801|
| C   | -1.910235| 6.947677| 0.473759|
| H   | -0.890648| 5.182210| -0.233789|
| C   | -2.959404| 7.836850| 0.248869|
| H   | -4.595455| 8.374994| -1.043875|
| H   | -1.274113| 7.064157| 1.346924|
| H   | -3.138490| 8.651396| 0.944500|

**TS2 (Disfavored Transition State)**

Single-Point Energy: -6611.227501
Thermal Correction to Enthalpy: 2.023641
Thermal Correction to Free Energy: 1.776333
S35
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | 3.09153400 | -4.35957500 | 0.42785300 |
| H       | 3.10512200 | -2.56430400 | 1.61884600 |
| C       | -0.72458500 | -4.51021700 | 2.28615000 |
| O       | 0.95796800 | -3.65594900 | 3.50566800 |
| H       | -2.32754800 | -5.38700800 | 1.14878000 |
| C       | -5.77311100 | -1.16102700 | -1.81880500 |
| C       | -6.89203100 | 0.71448000  | -0.42568900 |
| C       | -4.56624600 | -2.75636700 | -3.54321200 |
| C       | -2.83098000 | 2.49508000  | 3.54477000 |
| C       | -1.39902300 | 4.30282000  | 2.27834600 |
| C       | -3.73539100 | 0.68194300  | 5.13489900 |
| C       | 1.09367200  | 0.35529300  | 4.42200800 |
| O       | -0.37525200 | -1.32099700 | 4.70401200 |
| H       | 2.47365200  | 1.99365900  | 4.20771600 |
| C       | 5.92945300  | 1.49626900  | 0.59732200 |
| C       | 7.19385100  | -0.72278100 | -0.05081700 |
| C       | 4.76856700  | 3.84955300  | -0.71614500 |
| C       | 2.62406500  | -4.90776000 | 0.79344700  |
| C       | 0.93321100  | -4.81744400 | -2.81059700 |
| C       | 3.83635500  | -5.22686000 | 1.45931700  |
| O       | -0.25704100 | -5.54053800 | 3.05998000  |
| C       | 0.53746500  | -4.89871100 | 4.05023900  |
| O       | -7.01900400 | -1.42524200 | -2.35206400 |
| C       | -8.11485100 | 0.07473400  | 0.07415300  |
| C       | -6.51448900 | 1.70875800  | 0.68426000  |
| C       | -7.29425400 | 1.53436500  | 1.66476700  |
| C       | -3.33275500 | -2.38746600 | -4.39666500 |
| C       | -4.39991400 | -4.21191200 | -3.07151600 |
| C       | -5.76170800 | -2.64282000 | -4.50479300 |
| O       | -3.37639800 | 3.43161100  | 4.39954000  |
| C       | -2.00886600 | 4.96369300  | 1.03027500  |
| C       | 0.11880400  | 4.09929800  | 2.06212900  |
| C       | -1.52644200 | 5.26163700  | 3.47342900  |
| C       | -2.83954600 | 1.20034800  | 6.27583500  |
| C       | -5.16970200 | 1.19911800  | 5.33751400  |
| Element | X         | Y           | Z         |
|---------|-----------|-------------|-----------|
| C       | -3.78348400 | -0.84964800 | 5.22987400 |
| O       | 0.74461600  | 0.37210500  | 5.74804400 |
| C       | 0.14978800  | -0.90309400 | 5.95566300 |
| O       | 7.18164500  | 2.03891700  | -0.79467300|
| C       | 7.87654400  | -0.13810500 | 1.16804900 |
| C       | 6.78259000  | -2.18031700 | 0.27761000 |
| C       | 8.09484600  | -0.75493500 | -1.25696400|
| C       | 6.05997200  | 4.51262400  | -0.20521600|
| C       | 3.63622700  | 4.38001900  | 0.19315200 |
| C       | 4.46502500  | 4.31383500  | -2.14678900|
| O       | 3.06507600  | -6.16963300 | -1.13583900|
| C       | 0.93777400  | -6.35220400 | -2.89717000|
| C       | 1.41036900  | -4.22430000 | -4.14678900|
| C       | -0.54340500 | -4.41003100 | -2.60237100|
| C       | 5.18621400  | -5.74875200 | 0.93590800 |
| C       | 4.13131000  | -4.43354400 | 2.74018800 |
| C       | 2.94262400  | -6.42339600 | 1.83383400 |
| H       | 1.41090300  | -5.51218800 | 4.27273000 |
| H       | -0.07660800 | -4.71183100 | 4.94247400 |
| C       | -7.58888600 | -2.62140200 | -1.84279000|
| H       | -8.84360900 | 0.62071700  | 0.50547900 |
| H       | -8.60932500 | -0.60743500 | -0.73847200|
| H       | -7.83253500 | -0.78996200 | 0.85495200 |
| H       | -6.25907100 | 1.19851900  | 1.62070800 |
| H       | -5.67010700 | 2.34467300  | 0.39782500 |
| H       | -7.37117600 | 2.36135700  | 0.88116600 |
| H       | -6.47735400 | 2.19876700  | -1.96662300|
| H       | -7.54999000 | 0.88238500  | -2.50361900|
| H       | -8.16580700 | 2.15753100  | -1.43166100|
| H       | -3.43132200 | -1.37829700 | -4.80202200|
| H       | -2.38788600 | -2.44053300 | -3.85071000|
| H       | -3.26297000 | -3.08964300 | -5.23546300|
| H       | -5.24691700 | -4.55239300 | -2.46717000|
| H       | -4.31215600 | -4.87918800 | -3.93697700|
| H       | -3.49211300 | -4.32252600 | -2.46633900|
H  6.35008400  4.11419500  0.77203600
H  6.90837300  4.11831900  0.77203600
H  2.64107400  4.11831900  0.77203600
H  3.74261100  4.00100800  1.21670900
H  3.68040400  5.47415400  0.22549400
H  5.28275500  4.10405300  2.84353300
H  3.57378800  3.81307900  2.53489300
H  4.28226700  5.39470000  2.16621300
H  0.68635700  6.80667500  1.93520800
H  0.18137600  6.65484000  3.62977400
H  1.89212400  6.76530000  3.22653500
H  1.33775400  3.13147400  4.14381600
H  2.45063000  4.49010000  4.36150300
H  0.78875200  4.60224800  4.96640700
H -0.91749900  4.78147500  1.64112800
H -0.67823200  3.32366800  2.61950000
H -1.15841800  4.83142900  3.40602000
H  5.73800700  6.21102500  1.76246800
H  5.05693900  6.50626800  0.16276700
H  5.80071100  6.93126800  0.54126700
H  4.82721300  3.60775600  2.55313100
H  3.22123300  4.02308700  3.18626800
H  4.60357200  5.10040000  3.46913000
H  2.80031000  7.09130900  0.98196500
H  3.40584000  6.99434300  2.64782500
H  1.95572100  6.08218100  2.16112200
H -8.58921600  2.69999700  2.27446000
H -7.00087800  3.49809900  2.13050300
H -7.66018000  2.58995200  0.75011900
H -4.89619400  4.75628100  4.58870300
H -4.25022200  4.62373800  2.92857200
H -5.28639000  3.33034600  3.57933200
H  6.94796900  3.13894700  2.55023900
H  8.56654700  2.48324000  2.20182900
|   |   |   |   |
|---|---|---|---|
| C | 7.26465000 | 1.40054100 | -2.77417900 |
| H | 4.37497700 | -7.16530100 | -2.31492500 |
| H | 3.69453600 | -5.69469700 | -3.06600100 |
| C | -1.76608300 | 0.85742200 | -4.16855200 |
| C | -2.95654700 | 1.05283400 | -3.45632300 |
| C | -1.84628400 | 0.74902400 | -5.55958400 |
| C | -4.18073600 | 1.13480500 | -4.10721900 |
| H | -2.91936700 | 1.14182800 | -2.37302300 |
| C | -3.07255500 | 0.84608100 | -6.21897200 |
| H | -0.94741900 | 0.59870100 | -6.14839500 |
| C | -4.24529600 | 1.03770800 | -5.49802400 |
| H | -5.08946900 | 1.26411500 | -3.52625800 |
| H | -3.10445400 | 0.76664500 | -7.30187900 |
| H | -5.20119000 | 1.10647700 | -6.00898400 |
| C | 0.74037200 | 0.40758400 | -4.29879700 |
| H | 1.63484800 | 0.26987000 | -3.68368600 |
| H | 0.51981500 | -0.54567100 | -4.78966400 |
| H | 0.97437100 | 1.14943500 | -5.07278300 |
| H | -1.13905600 | 2.69093700 | -2.57214000 |
| C | 1.49022900 | 6.39353900 | -1.83920200 |
| C | 0.84684800 | 6.33259900 | -0.60461500 |
| C | 2.17028400 | 7.55086200 | -2.22016800 |
| C | 0.88910400 | 7.42735100 | 0.25248600 |
| H | 0.32578500 | 5.42343600 | -0.32818300 |
| C | 2.21745300 | 8.64156800 | -1.35871000 |
| H | 2.65535800 | 7.57197500 | -3.19121600 |
| C | 1.57706700 | 8.58033000 | -0.12200400 |
| H | 0.38714800 | 7.38154000 | 1.21596000 |
| H | 2.75240900 | 9.54008900 | -1.65014300 |
| H | 1.61311700 | 9.43269100 | 0.54985700 |
References

1. (a) W. Xiong, G. Xu, X. Yu and W. Tang, *Organometallics*, 2019, **38**, 4003; (b) M. Takeda, K. Takatsu, R. Shintani and T. Hayashi, *J. Org. Chem.*, 2014, **79**, 2354.

2. D. Wang, X.-S. Xue, K. N. Houk and Z. Shi, *Angew. Chem. Int. Ed.*, 2018, **57**, 16861.

3. D. A. Gandamana, B. Wang, C. Tejo, B. Bolte, F. Gagosz and S. Chiba, *Angew. Chem. Int. Ed.*, 2018, **57**, 6181.

4. S. Movahhed, J. Westphal, M. Dindaroğlu, A. Falk and H.-G. Schmalz, *Chem. Eur. J.*, 2016, **22**, 7381.

5. Q. Wang, X. Liu, X. Liu, B. Li, H. Nie, S. Zhang and W. Chen, *Chem. Commun.*, 2014, **50**, 978.

6. A. Krasovskiy, C. Duplais and B. H. Lipshutz, *J. Am. Chem. Soc.*, 2009, **131**, 15592.

7. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr., J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford, CT, 2009.

8. C. Y. Legault, *CYLView, 1.0b*. University of Sherbrooke 2009.
