Supplementary Information

Oxovanadium(V)-Induced Diastereoselective Oxidative Homocoupling of Boron Enolates

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**Scheme S1.** Representative Configurations of Two Enolates for the Coupling Reaction in Chelation and Non-chelation Models

Chelation model

Non-chelation model
General. NMR spectra were recorded on a JEOL JNM-ECP 400 spectrometer. Chemical shifts in CDCl$_3$ were reported in ppm on the $\delta$ scale relative to a residual solvent ($\delta$ 7.26 for $^1$H NMR and 77.0 ppm for $^{13}$C NMR) as an internal standard. VOCl$_3$ (0.00 ppm) was used as an external standard for $^{51}$V NMR. Infrared spectra were obtained with a JASCO FT/IR-6200 spectrometer. Mass spectra were measured on a JEOL JMS-DX-303 spectrometer using fast atom bombardment (FAB) mode. Measurement for X-ray crystallography was made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite monochromated Cu-K$\alpha$ radiation.

VO(OPr-i)$_2$Cl was prepared according to the literature procedure.$^i$ VO(OPr-i)$_3$ and VO(OEt)Cl$_2$ were donated from Nichia corporation, and they were used after distillation. The dried CDCl$_3$ with MS4A was used for the reaction. The employed enones 1a,$^{ii}$ 1b,$^{ii}$ 1c,$^{iii}$ 1d,$^{ii}$ 1e,$^{i,v}$ and 1f,$^{i,v}$ are known compounds. Chalcone (1h) was purchased from WAKO Pure Chemical Industries, Ltd. 9-Borabicyclo[3,3,1]nonane (9-BBN) was purchased from Aldrich as a 0.5 M THF solution. The obtained 1,4-diones 3a,$^{viii}$ 3b,$^{ix}$ 3c,$^x$ and 3h,$^{viii}$ are known compounds.

References
Oxidative \( dl \) selective homocoupling of boron enolates

**Procedure 1:** NMR tube experiment

![Chemical structure](image)

To a CDCl\(_3\) (700 \( \mu \)L) solution of \( \alpha,\beta \)-unsaturated carbonyl compound 1 (30 \( \mu \)mol) with a portion of activated MS4A in a J-Young valve-attached NMR tube was added 0.5 M THF solution of 9-borabicyclo[3,3,1]nonane (9-BBN) (15 \( \mu \)L, 7.5 \( \mu \)mol) in \( N_2 \)-filled glove box. After the mixture was shaken at room temperature for 1 min by hand, the 9-BBN solution (15 \( \mu \)L, 7.5 \( \mu \)mol) was added again. The mixture was shaken for more 1 min by hand, followed by further addition of the 9-BBN solution (30 \( \mu \)L, 15 \( \mu \)mol). After the mixture stood at room temperature for 2 h, \(^1\)H NMR of the mixture was measured. After the formation of boron enolate 2 was confirmed, the mixture was put in refrigerator (-30 °C) for 1 h. Then, it was taken out from refrigerator. VO(OPr-i)\(_2\)Cl (17.1 \( \mu \)L, 90 \( \mu \)mol) was immediately added to the solution. The mixture was shaken for 5 sec, and then it stood in refrigerator (-30 °C) for 19 h. Then the mixture was quenched with saturated aqueous NaHCO\(_3\). The product was extracted with CH\(_2\)Cl\(_2\). The organic layer was washed with water, brine, dried over MgSO\(_4\), and evaporated \textit{in vacuo}. The residue was filtered through a short pad of silica-gel column (h = 2.5 cm, CH\(_2\)Cl\(_2\)). The mixture was evaporated \textit{in vacuo}. The yield and \( dl/meso \) ratio were determined by \(^1\)H NMR using 1,1,2,2-tetrabromoethane as an internal standard. The crude product was purified by preparative thin layer chromatography (CH\(_2\)Cl\(_2\)) to give the products. The obtained product 3 was further purified by preparative thin layer chromatography (hexane/ethylacetate = 4:1) to give the pure product.

**Procedure 2:** 100 mg scale reaction

Experiments except work-up were carried out in \( N_2 \)-filled glove box. Dry CH\(_2\)Cl\(_2\) (7 mL), 1.73M CH\(_2\)Cl\(_2\) solution of 1-phenylprop-2-en-1-one (1a) (437 \( \mu \)L, 0.76 mmol, which corresponds to 100 mg of 1a), and a portion of activated MS4A were added to a dried 50 mL round-bottomed flask. To the mixture was added 0.5 M THF solution of 9-borabicyclo[3,3,1]nonane (9-BBN) (1.66 mL, 0.83 mmol) at room temperature. After stirring at room temperature for 2 h, the mixture was cooled to -40 °C. Then, VO(OPr-i)\(_2\)Cl (431 \( \mu \)L, 2.27 mmol) was immediately added to the solution. The mixture was stirred at -40 °C for 24 h. Then, the flask was put out of glove box. The reaction
mixture was quenched with saturated aqueous NaHCO₃. The product was extracted with Et₂O twice. The combined organic layer was washed with water twice. The aqueous layer was extracted with Et₂O. The organic layer was washed with brine, dried over MgSO₄, and evaporated in vacuo. The residue was purified by silica-gel column chromatography to give 3a by eluting with hexane/CH₂Cl₂ = 1:2 to CH₂Cl₂. After evaporation and drying in vacuo, 2,3-dimethyl-1,4-diphenylbutane-1,4-dione (3a) (a dillac/meso diastereomeric mixture) was obtained as a white solid (93.2 mg, 0.350 mmol, 93% yield, dillac/meso = 86:14).

¹H NMR spectrum for 3a synthesized using procedure 2 (400 MHz, CDCl₃)
Boron enolates

(Z)-9-(1-phenylprop-1-enyloxy)-9-borabicyclo[3.3.1]nonane (2a)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.13-2.00 (m, 14H), 1.66 (d, 3H, $J = 6.9$ Hz), 5.55 (q, 1H, $J = 6.9$ Hz), 7.12-7.18 (m, 1H), 7.18-7.25 (m, 2H), 7.36-7.41 (m, 2H).

(Z)-9-(1-p-tolylprop-1-enyloxy)-9-borabicyclo[3.3.1]nonane (2b)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.07-1.91 (m, 14H), 1.59 (d, 3H, $J = 6.9$ Hz), 2.19 (s, 3H), 5.44 (q, 1H, $J = 6.9$ Hz), 6.98 (d, 2H, $J = 8.2$ Hz), 7.22 (d, 2H, $J = 8.2$ Hz).

(Z)-(4-(1-(9-borabicyclo[3.3.1]nonan-9-yloxy)prop-1-enyl)phenoxy)(tert-butyl)dime thysilane (2c)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.07 (s, 6H), 0.86 (s, 9H), 1.08-1.94 (m, 14H), 1.59 (d, 3H, $J = 6.9$ Hz), 5.36 (q, 1H, $J = 6.9$ Hz), 6.63-6.68 (m, 2H), 7.18-7.23 (m, 2H).

(Z)-9-(1-(4-fluorophenyl)prop-1-enyloxy)-9-borabicyclo[3.3.1]nonane (2d)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.08-1.93 (m, 14H), 1.61 (d, 3H, $J = 6.8$ Hz), 5.43 (q, 1H, $J = 6.9$ Hz), 6.85-6.91 (m, 2H), 7.32 (m, 2H).

(Z)-9-(1-(4-chlorophenyl)prop-1-enyloxy)-9-borabicyclo[3.3.1]nonane (2e)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.06-1.70 (m, 14H), 1.58 (d, 3H, $J = 6.9$ Hz), 5.48 (q, 1H, $J = 6.9$ Hz), 7.10-7.15 (m, 2H), 7.23-7.28 (m, 2H).
(Z)-9-(1-(4-(trifluoromethyl)phenyl)prop-1-enyloxy)-9-borabicyclo[3.3.1]nonane (2f)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.07-1.94 (m, 14H), 1.64 (d, 3H, $J$ = 6.8 Hz), 5.65 (q, 1H, $J$ = 6.9 Hz), 7.42-7.50 (m, 4H).

(Z)-9-(1-cyclohexylprop-1-enyloxy)-9-borabicyclo[3.3.1]nonane (2g)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.99-1.92 (m, 25H), 1.35 (d, 3H, $J$ = 6.9 Hz), 4.56 (q, 1H, $J$ = 6.9 Hz).

(Z)-9-(1,3-diphenylprop-1-enyloxy)-9-borabicyclo[3.3.1]nonane (2h)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.09-1.90 (m, 16H), 3.39 (d, 2H, $J$ = 7.3 Hz), 5.58 (t, 1H, $J$ = 7.3 Hz), 7.01-7.19 (m, 8H), 7.36 (m, 2H).

1,4-Diones

dl-1,4-bis(4-fluorophenyl)-2,3-dimethylbutane-1,4-dione (dl-3d)

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 1.29 (m, 6H), 3.90 (m, 2H), 7.13 (m, 2H), 8.01 (m, 2H); $^{13}$C-NMR (100 MHz, CDCl$_3$) 15.66, 43.68, 115.71 (d, $J_{C-F}$ = 22.0 Hz), 131.11 (d, $J_{C-F}$ = 9.6 Hz), 132.39 (d, $J_{C-F}$ = 2.9 Hz), 164.46, 202.81 ppm; IR(ATR) $\nu$ 2980, 2929, 1667, 1598, 1228, 1209, 1156, 971, 849 cm$^{-1}$; HRMS (FAB) calcd for C$_{18}$H$_{16}$F$_{2}$O$_2$: 302.1118, found [(M+H)$^+$]: 303.1199.

deso-1,4-bis(4-fluorophenyl)-2,3-dimethylbutane-1,4-dione (meso-3d)

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 1.12 (m, 6H), 3.98 (m, 2H), 7.18 (m, 2H), 8.08 (m, 2H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 17.42, 43.24, 115.91 (d, $J_{C-F}$ = 21.1 Hz), 131.14 (d, $J_{C-F}$ = 9.6 Hz), 133.14 (d, $J_{C-F}$ = 2.9 Hz), 164.71, 202.01; IR(ATR) $\nu$ 2977, 2937, 1668, 1595, 1225, 1191, 1159, 978, 844 cm$^{-1}$; HRMS (FAB) calcd for C$_{18}$H$_{16}$F$_{2}$O$_2$: 302.1118, found [(M+H)$^+$]: 303.1203.
**dl-1,4-bis(4-chlorophenyl)-2,3-dimethylbutane-1,4-dione (dl-3e)**

\[
\text{\textsuperscript{1}H-NMR (400 MHz, CDCl}_3\text{) } \delta \text{ 1.28 (m, 6H), 3.89 (m, 2H), 7.44 (m, 2H), 7.92 (m, 2H); }\text{\textsuperscript{13}C-NMR (100 MHz, CDCl}_3\text{) } \delta 
\]

15.58, 43.72, 128.94, 129.90, 134.32, 139.47, 203.12; IR(ATR) ν 2960, 2928, 1672, 1587, 1092, 970, 842 cm\(^{-1}\), HRMS (FAB) calced for C\(_{18}\)H\(_{16}\)Cl\(_2\)O\(_2\): 334.0527, found [(M+H)+]: 335.0604.

**meso-1,4-bis(4-chlorophenyl)-2,3-dimethylbutane-1,4-dione (meso-3e)**

\[
\text{\textsuperscript{1}H-NMR (400 MHz, CDCl}_3\text{) } \delta \text{ 1.11 (m, 6H), 3.96 (m 2H), 7.48 (m, 2H), 7.99 (m, 2H); }\text{\textsuperscript{13}C-NMR (100 MHz, CDCl}_3\text{) } \delta 
\]

17.35, 43.28, 129.14, 129.87, 135.01, 139.96, 202.30; IR(ATR) ν 2955, 2928, 1670, 1588, 1091, 977, 841 cm\(^{-1}\); HRMS (FAB) calced for C\(_{18}\)H\(_{16}\)Cl\(_2\)O\(_2\): 334.0527, found [(M+H)+]: 335.0605.

**2,3-dimethyl-1,4-bis(4-(trifluoromethyl)phenyl)butane-1,4-dione (3f)**

Major isomer: \[
\text{\textsuperscript{1}H-NMR (400 MHz, CDCl}_3\text{) } \delta \text{ 1.31 (m, 6H), 3.95 (m 2H), 7.75 (d, 2H, } J \text{ = 8.2 Hz), 8.08 (d, 2H, } J \text{ = 8.2 Hz); }\text{\textsuperscript{13}C-NMR (100 MHz, CDCl}_3\text{) } \delta 
\]

15.43, 44.16, 123.60 (q, J\(_{C,F} = 272.7 \text{ Hz})), 125.75, 128.77, 134.39 (q, J\(_{C,F} = 32.6 \text{ Hz})), 138.75, 203.42; IR(ATR) ν 2971, 2935, 1679, 1319, 1136, 1114, 973, 858 cm\(^{-1}\); HRMS (FAB) calced for C\(_{20}\)H\(_{16}\)F\(_6\)O\(_2\): 402.1054, found [(M+H)+]: 403.1127. Minor isomer: \[
\text{\textsuperscript{1}H-NMR (400 MHz, CDCl}_3\text{) } \delta \text{ 1.17 (m, 6H), 4.04 (m 2H), 7.78 (d, 2H, } J \text{ = 8.2 Hz), 8.14 (d, 2H, } J \text{ = 8.2 Hz); }\text{\textsuperscript{13}C-NMR (100 MHz, CDCl}_3\text{) } \delta 
\]

17.18, 43.61, 123.53 (q, J\(_{C,F} = 272.2 \text{ Hz})), 125.91, 128.78, 134.73 (q, J\(_{C,F} = 32.6 \text{ Hz})), 139.27, 202.41; IR(ATR) ν 2984, 2951, 1680, 1309, 1136, 1108, 974, 849 cm\(^{-1}\); HRMS (FAB) calced for C\(_{20}\)H\(_{16}\)F\(_6\)O\(_2\): 402.1054, found [(M+H)+]: 403.1128.

**1,4-dicyclohexyl-2,3-dimethylbutane-1,4-dione (3g)**

Diastereomeric mixtures. Selectivity was calculated from the integral ratio for the methyl protons. \[
\text{\textsuperscript{1}H-NMR (400 MHz, CDCl}_3\text{) } \delta \text{ 0.92-0.94 (m, } \text{-CH}_3 \text{ for minor isomer), 1.04-1.06 (m, } \text{-CH}_3 \text{ for minor isomer), 1.0-1.43 (m), 1.60-1.96 (m), 2.38-2.56 (m), 2.92-3.06 (m).} \]
X-ray structures

\textit{dl-3d}

\begin{align*}
a = & \quad 11.1477(5) \text{ Å} \\
b = & \quad 13.3381(6) \text{ Å} \\
c = & \quad 10.5647(5) \text{ Å} \\
R1 = & \quad 0.1517 \\
P2_1/c \ (\#14) & \text{ monoclinic}
\end{align*}

The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-969201.

\textit{dl-3e}

\begin{align*}
a = & \quad 15.7021(2) \text{ Å} \\
b = & \quad 9.6923(1) \text{ Å} \\
c = & \quad 10.9905(2) \text{ Å} \\
R1 = & \quad 0.0561 \\
P2_1/c \ (\#14) & \text{ monoclinic}
\end{align*}

The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-969200.
dl-1,4-bis(4-fluorophenyl)-2,3-dimethylbutane-1,4-dione (dl-3d)

$\text{dl-3d}$

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
*meso*-1,4-bis(4-fluorophenyl)-2,3-dimethylbutane-1,4-dione (*meso*-3d)

\[
\begin{align*}
\text{O} & \quad \text{F} \\
\text{F} & \quad \text{O} \\
\end{align*}
\]

*meso*-3d

\[^1\text{H}-\text{NMR} (400 \text{ MHz, CDCl}_3)\]

\[^{13}\text{C}-\text{NMR} (100 \text{ MHz, CDCl}_3)\]
**dl-1,4-bis(4-chlorophenyl)-2,3-dimethylbutane-1,4-dione (dl-3e)**

\[
\begin{array}{c}
\text{Cl} \\
| \quad | \\
\text{Cl} \\
\end{array}
\]

**dl-3e**

\[\text{H-NMR (400 MHz, CDCl}_3\text{)}\]

**13C-NMR (100 MHz, CDCl}_3\text{)**
meso-1,4-bis(4-chlorophenyl)-2,3-dimethylbutane-1,4-dione (meso-3e)

$\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{meso-3e}
\end{array}$

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)

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2,3-dimethyl-1,4-bis(4-(trifluoromethyl)phenyl)butane-1,4-dione (3f) (major isomer)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)

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2,3-dimethyl-1,4-bis(4-(trifluoromethyl)phenyl)butane-1,4-dione (3f)
(minor isomer)

$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)