Efficient access to cis-decalinol frameworks: Copper(I)-catalyzed borylative cyclization of allene cyclohexanediones

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1. GENERAL INFORMATION

All solvents were dried before use following the standard procedures. Unless otherwise indicated, all starting materials purchased from commercial suppliers were used without further purification. The $^1$H and $^{13}$C NMR spectra were recorded on Bruker AV-400 MHz in the indicated solvents. Chemical shifts are reported in $\delta$ (ppm) referenced to an internal TMS standard for $^1$H NMR and CDCl$_3$ ($\delta = 77.10$ ppm) for $^{13}$C NMR. Coupling constants ($J$) are quoted in Hz. Optical rotations were measured on a JASCO P-1030 polarimeter. IR spectra were recorded on Nicolet iN 10 MX. ESI mass spectra were recorded on Agilent1200/G6100A. Microwave heating was performed on a Milestone MicroSYNTH.

2. SUBSTRATE PREPARATION

2.1 General Procedures for the Preparation of 1a-1k (except 1e, 1j) [1]

To a well-stirred solution of cyclohexane-1,3-diones 8 (10 mmol), Hantzsch ester 10 (10 mmol) and the catalyst proline (20 mol%) in DCM (50 mL) was added...

[1] 2-methylcyclohexane-1,3-dione (11a, CAS: 1193-55-1) was purchased from Energy Chemical (China)
aldehyde 9 (20 mmol) under argon atmosphere at room temperature. The resulting solution was stirred for 12–20 hours. Then the reaction mixture was diluted with water (100 mL) and extracted with DCM (50 mL × 3). The combined organic phases were washed with brine (50 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was used in the next step without any further purification.

To a well-stirred solution of the previous residue, 18-crown-6 (10 mmol) in DMF (50 mL) was added t-BuOK (10 mmol) in several portions under argon atmosphere at 0°C and allowed to stir for 30 minutes, then 5-iodine-1-pentyne (10 mmol) was added slowly in 10 min. The resulting solution was warmed to room temperature (80°C for 11g–11k) and allowed to stir for 20 hours. The reaction mixture was quenched with water (150 mL) and extracted with diethyl ether (50 mL × 3). The combined organic phases were washed with brine (50 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to afford the crude compound 12. The crude compound 12 was used in the next step without any further purification.

To a well-stirred solution of the previous crude compound 12, paraformaldehyde (15 mmol) and CuBr (1 mmol) in dioxane (25 mL) was added i-Pr₂NH (20 mmol) under argon atmosphere at room temperature. The reaction mixture was refluxed at 110°C for 2.0 h. The resulting mixture was cooled to rt, quenched with saturated aqueous NaCl (10 mL), then extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried over anhydrous MgSO₄ and concentrated in vacuo.

The residue was purified by silica gel (300–400 mesh) column chromatography to afford the desired product 1a-1k (except 1e, 1f).

2-(Hexa-4,5-dien-1-yl)-2-methylcyclohexane-1,3-dione (1a)
Pale yellow oil. 597.4 mg, 29% yield; ¹H NMR (400 MHz, CD₂OD) δ (ppm) 5.10–5.02 (m, 1H), 4.86–4.63 (m, 2H), 2.81–2.72 (m, 2H), 2.64–2.56 (m, 2H), 2.04–1.93 (m, 3H), 1.87–1.79 (m, 3H), 1.30–1.19 (m, 2H), 1.18 (s, 3H); ¹³C NMR (100 MHz, CD₂OD) δ (ppm) 212.39, 209.97, 89.94, 75.03, 66.76, 38.75, 37.94, 29.24, 25.24, 19.21, 18.80; IR (KBr) ν (cm⁻¹) 2933, 2294, 1725, 1694, 1458, 1374, 1317, 1269, 1171, 1132, 1103, 1025, 846, 557, 417; HRMS (EI) for [C₁₃H₁₈O₂]⁺: calcd. 206.1301, found: 206.1299.

2-Ethyl-2-(hexa-4,5-dien-1-yl)cyclohexane-1,3-dione (1b)
Pale yellow oil. 462.2 mg, 21% yield; ¹H NMR (400 MHz, CD₂OD) δ (ppm) 5.01–4.96 (m, 1H), 4.63–4.59 (m, 2H), 2.60–2.55 (m, 4H), 1.96–1.87 (m, 4H), 1.80–1.71 (m, 4H), 1.23–1.14 (m, 2H), 0.75–0.70 (m, 3H); ¹³C NMR (100 MHz, CD₂OD) δ (ppm) 211.19, 208.53, 89.29, 75.04, 69.22, 39.54, 35.31, 29.57, 28.52, 24.65, 16.99, 9.60; IR (KBr) ν (cm⁻¹) 2959, 2931, 2863, 1955, 1722, 1694, 1455, 1366, 1268,
1171, 1021, 847, 721, 556, 417; HRMS (EI) for [C₁₄H₂₀O₂]⁺: calcd. 220.1458, found: 220.1463.

2-(Hexa-4,5-dien-1-yl)-2-propylcyclohexane-1,3-dione (1c)

Pale yellow oil. 220.1 mg, 9.4% yield; ¹H NMR (400 MHz, CD₂OD) δ (ppm) 5.07–5.02 (m, 1H), 4.67–4.62 (m, 2H), 2.65–2.61 (m, 4H), 1.96–1.89 (m, 4H), 1.77–1.67 (m, 4H), 1.23–1.12 (m, 2H), 1.11–1.06 (m, 2H), 0.87–0.85 (m, 3H); ¹³C NMR (100 MHz, CD₂OD) δ (ppm) 212.95, 209.89, 89.98, 75.01, 70.02, 40.14, 39.54, 36.51, 29.52, 25.63, 19.38, 18.07, 14.86; IR (KBr) ν (cm⁻¹) 2960, 2932, 2873, 1955, 1723, 1693, 1458, 1317, 1258, 1211, 1031, 845, 727, 555, 418; HRMS (EI) for [C₁₅H₂₂O₂]⁺: calcd. 234.1614, found: 234.1620.

2-(Hexa-4,5-dien-1-yl)-2-isobutylcyclohexane-1,3-dione (1d)

Pale yellow oil. 134 mg, 5.4% yield; ¹H NMR (400 MHz, CD₂OD) δ (ppm) 5.06–5.02 (m, 1H), 4.66–4.62 (m, 2H), 2.73–2.60 (m, 4H), 1.98–1.88 (m, 4H), 1.76–1.71 (m, 4H), 1.56–1.52 (m, 1H), 1.22–1.17 (m, 2H), 0.81–0.78 (m, 6H); ¹³C NMR (100 MHz, CD₂OD) δ (ppm) 213.35, 209.96, 89.93, 74.96, 69.26, 46.21, 40.30, 38.15, 29.50, 26.31, 25.58, 24.48, 18.18; IR (KBr) ν (cm⁻¹) 2925, 2854, 1955, 1819, 1786, 1723, 1693, 1641, 1597, 1467, 1369, 1256, 1107, 1032, 846, 555, 411; HRMS (EI) for [C₁₆H₂₄O₂]⁺: calcd. 248.1771, found: 248.1776.

2-(Hexa-4,5-dien-1-yl)-2-(3-phenylpropyl)cyclohexane-1,3-dione (1f)

Pale yellow oil. 459.1 mg, 14.8% yield; ¹H NMR (400 MHz, CD₂OD) δ (ppm) 5.62–5.52 (m, 1H), 5.08–4.98 (m, 3H), 4.66–4.62 (m, 2H), 2.69–2.55 (m, 4H), 1.95–1.90 (m, 2H), 1.81–1.76 (m, 2H), 1.24–1.16 (m, 2H); ¹³C NMR (100 MHz, CD₂OD) δ (ppm) 212.85, 209.95, 143.00, 129.37, 129.54, 126.87, 89.95, 74.97, 70.05, 40.00, 37.04, 36.41, 36.35, 29.46, 27.94, 25.55, 18.09; IR (KBr) ν (cm⁻¹) 3285, 2957, 2872, 2112, 1755, 1725, 1691, 1459, 1332, 1250, 1203, 1147, 1096, 1052, 964, 932, 634, 590, 526, 435; HRMS (EI) for [C₁₆H₂₄O₂]⁺: calcd. 310.1927, found: 310.1933.

2-Ethyl-2-(hexa-4,5-dien-1-yl)-5,5-dimethylcyclohexane-1,3-dione (1g)

Pale yellow oil. 119.1 mg, 4.8% yield; ¹H NMR (400 MHz, CD₂OD) δ (ppm) 5.09–5.05 (m, 1H), 4.66–4.62 (m, 2H), 2.67–2.56 (m, 4H), 1.97–1.92 (m, 2H), 1.83–1.72 (m, 4H), 1.26–1.19 (m, 2H), 1.19–0.96 (m, 6H), 0.78–0.75 (m, 3H);
\[^{13}\text{C NMR}\ (100 \text{ MHz, CD}_{3}\text{OD}) \ \delta\ (\text{ppm})\ 211.72, 209.96, 90.13, 74.93, 70.18, 52.15, 34.24, 31.46, 29.53, 28.87, 28.60, 25.21, 9.42; \ \text{IR}\ (\text{KBr}) \ \nu\ (\text{cm}^{-1}) \ 3026, 2933, 2857, 1955, 1722, 1693, 1496, 1454, 1264, 1208, 1163, 1083, 1030, 847, 750, 700, 555, 457; \ \text{HRMS}\ (\text{EI})\ \text{for [C}_{16}\text{H}_{24}\text{O}_{2}^{+}:\ \text{calcd. 248.177, found: 248.1776.}}

2-(Hexa-4,5-dien-1-yl)-5,5-dimethyl-2-propylcyclohexane-1,3-dione (1h)
Pale yellow oil. 427.4 mg, 16.3% yield; \[^{1}\text{H NMR}\ (400 \text{ MHz, CD}_{3}\text{OD}) \ \delta\ (\text{ppm})\ 5.11–5.03 (1H), 4.65–4.61 (2H), 2.61–2.50 (6H), 1.95–1.91 (1H), 1.78–1.71 (4H), 1.44–1.39 (9H); \[^{13}\text{C NMR}\ (100 \text{ MHz, CD}_{3}\text{OD}) \ \delta\ (\text{ppm})\ 211.65, 209.95, 143.11, 129.40, 129.34, 126.87, 90.09, 74.96, 69.87, 52.08, 36.97, 35.08, 34.89, 31.45, 29.43, 28.76, 27.50, 25.15; \ \text{IR}\ (\text{KBr}) \ \nu\ (\text{cm}^{-1}) \ 3282, 2956, 2873, 2312, 1955, 1725, 1711, 1439, 1372, 1253, 1213, 1167, 1076, 1022, 924, 832, 656, 591, 520, 425; \ \text{HRMS}\ (\text{EI})\ \text{for [C}_{23}\text{H}_{30}\text{O}_{2}^{+}:\ \text{calcd. 338.2240, found: 338.2246.}}

2-(Hexa-4,5-dien-1-yl)-5,5-dimethyl-2-isobutyl-5,5-dimethylcyclohexane-1,3-dione (1i)
Pale yellow oil. 250.8 mg, 12.7% yield; \[^{1}\text{H NMR}\ (400 \text{ MHz, CD}_{3}\text{OD}) \ \delta\ (\text{ppm})\ 7.27–7.22 (2H), 7.17–7.12 (3H), 5.07–5.03 (1H), 4.65–4.61 (2H), 2.61–2.50 (6H), 1.95–1.91 (1H), 1.78–1.71 (4H), 1.44–1.39 (9H); \[^{13}\text{C NMR}\ (100 \text{ MHz, CD}_{3}\text{OD}) \ \delta\ (\text{ppm})\ 211.65, 209.95, 143.11, 129.40, 129.34, 126.87, 90.09, 74.96, 69.87, 52.08, 36.97, 35.08, 34.89, 31.45, 29.43, 28.76, 27.50, 25.15; \ \text{IR}\ (\text{KBr}) \ \nu\ (\text{cm}^{-1}) \ 3282, 2956, 2873, 2312, 1955, 1725, 1711, 1439, 1372, 1253, 1213, 1167, 1076, 1022, 924, 832, 656, 591, 520, 425; \ \text{HRMS}\ (\text{EI})\ \text{for [C}_{23}\text{H}_{30}\text{O}_{2}^{+}:\ \text{calcd. 338.2240, found: 338.2246.}}
2.2 Preparation of 1e, 1j

To a well-stirred solution of cyclohexane-1,3-diones 1 (10 mmol), copper powder (50 mol%) in 5% KOH (200 mL) was added allyl bromide (12 mmol), under argon atmosphere at room temperature. The resulting solution was stirred for 12 hours. Then the reaction mixture was extracted with ethyl acetate (200 mL × 3). The combined organic phases were washed with brine, dried over anhydrous MgSO$_4$ and concentrated under reduced pressure. The residue was used in the next step without any further purification. Then followed the general procedure for preparation of 1a-1k to afford the desired product 1e, 1j.

2- Allyl-2-(hexa-4,5-dien-1-yl)cyclohexane-1,3-dione (1e)
Pale yellow oil. 290.4 mg, 12.4% yield; $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ (ppm) 5.62–5.52 (m, 1H), 5.08–4.98 (m, 3H), 4.66–4.62 (m, 2H), 2.69–2.55 (m, 4H), 1.95–1.90 (m, 2H), 1.81–1.76 (m, 2H), 1.24–1.16 (m, 2H); $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ (ppm) 212.36, 209.92, 134.27, 119.22, 89.92, 75.02, 69.78, 41.30, 40.29, 36.49, 29.44, 25.51, 17.89; IR (KBr) $\nu$ (cm$^{-1}$) 2929, 1955, 1723, 1694, 1639, 1439, 1322, 1258, 1210, 1102, 1033, 999, 922, 846, 556; HRMS (EI) for C$_{15}$H$_{22}$O$_2$: calcd. 234.1458, found: 234.1459.

2- Allyl-2-(hexa-4,5-dien-1-yl)-5,5-dimethylcyclohexane-1,3-dione (1j)
Pale yellow oil. 260.2 mg, 10% yield; $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ (ppm) 5.61–5.56 (m, 1H), 5.09–4.99 (m, 3H), 4.66–4.62 (m, 2H), 2.67–2.56 (m, 4H), 2.51–2.49 (m, 2H), 1.98–1.92 (m, 2H), 1.80–1.75 (m, 2H), 1.29–1.19 (m, 2H), 0.99–0.94 (m, 6H); $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ (ppm) 211.16, 209.99, 134.31, 119.34, 90.05, 74.95, 52.32, 39.27, 35.11, 31.61, 29.38, 28.89, 28.63, 25.04; IR (KBr) $\nu$ (cm$^{-1}$) 2955, 2870, 2395, 1955, 1725, 1427, 1371, 1329, 1251, 1217, 1178, 1078, 1000, 921, 845, 588, 437; HRMS (EI) for C$_{17}$H$_{24}$O$_2$: calcd. 260.1771, found: 260.1776.
3. Scope of the Substrates in Table 2

**General Procedure:**

A dried Schlenk flask was charged with CuCl (0.01 mmol, 5 mol%), t-BuONa (0.012 mmol, 6 mol%), PPh₃ (0.024 mmol, 12 mol%), and freshly distilled dry toluene (1 mL) under argon atmosphere. The reaction mixture was stirred at room temperature for 0.5 h. Then bis(pinacolato)diboron (1 mmol, 5.0 equiv) was added and the mixture was allowed to stir for another 0.5 h under argon atmosphere at room temperature. A solution of allenes (0.2 mmol) in freshly distilled toluene (1 mL) and MeOH (16 μL, 2.0 equiv) was then added to the Schlenk flask. The mixture was allowed to stir for 120 h at room temperature under argon atmosphere. The resulting mixture was filtered and concentrated in vacuo. Then sodium perborate tetrahydrate (1 mmol, 5.0 equiv), THF (0.5 mL) and H₂O (0.5 mL) was added and the mixture was allowed to stir for 3 h at room temperature. Then quenched with saturated aqueous NaCl (2 mL), extracted with ethyl acetate (4 mL × 3). The combined organic phases were dried over anhydrous MgSO₄, filtered and concentrated in vacuo. The residue was purified by silica gel (300-400 mesh) column chromatography to afford the desired product 3.

(4aR,5R,8aR)-rel-5-Acetyl-4a-hydroxy-8a-methyloctahydronaphthalen-1(2H)-one (3a)

Colorless oil, 43.1 mg, 96% yield; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 4.28 (s, 1H), 2.64–2.55 (m, 2H), 2.28–2.14 (m, 5H), 1.94–1.86 (m, 2H), 1.78–1.70 (m, 1H), 1.67–1.64 (m, 1H), 1.59–1.48 (m, 4H), 1.24 (s, 1H), 1.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 215.67, 213.65, 75.16, 54.45, 52.69, 36.57, 32.01, 31.47, 29.16, 25.58, 22.35, 22.07, 19.87; IR (KBr) ν (cm⁻¹) 3467, 2958, 2878, 1695,
(4aR,5R,8aR)-rel-5-Acetyl-8a-ethyl-4a-hydroxyoctahydronaphthalen-1(2H)-one (3b)

Colorless oil. 43.8 mg, 92% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 4.28 (s, 1H), 2.66–2.61 (m, 1H), 2.49–2.39 (m, 1H), 2.34–2.23 (m, 1H), 2.20–2.15 (m, 4H), 1.99–1.87 (m, 2H), 1.82–1.70 (m, 2H), 1.67–1.62 (m, 3H), 1.53–1.48 (m, 1H), 1.36–1.27 (m, 3H), 0.66 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 215.89, 212.85, 75.92, 58.24, 53.06, 37.65, 31.73, 31.57, 29.79, 26.78, 25.42, 25.22, 20.16, 7.43; IR (KBr) $\nu$ (cm$^{-1}$) 3473, 2926, 2853, 2360, 1692, 1463, 1335, 1299, 1228, 1188, 1089, 1068, 1002, 968, 906, 863, 822, 668, 578; HRMS (EI) for [C$_{13}$H$_{19}$O$_3$]$^+$: calcd. 238.1563, found: 238.1568.

(4aR,5R,8aR)-rel-5-Acetyl-4a-hydroxy-8a-propyloctahydronaphthalen-1(2H)-one (3c)

Colorless oil. 46.9 mg, 93% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 4.30 (s, 1H), 2.65–2.60 (m, 1H), 2.50–2.39 (m, 1H), 2.20–2.22 (m, 2H), 2.20 (s, 3H), 2.19–2.14 (m, 1H), 1.95–1.88 (m, 1H), 1.87–1.80 (m, 1H), 1.78–1.69 (m, 2H), 1.66–1.61 (m, 4H), 1.54–1.49 (m, 1H), 1.41–1.32 (m, 1H), 1.29–1.18 (m, 2H), 0.87 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 215.89, 212.94, 75.92, 58.09, 52.96, 37.70, 36.52, 31.74, 31.57, 25.95, 25.38, 21.98, 20.21, 16.35, 14.87; IR (KBr) $\nu$ (cm$^{-1}$) 3465, 2925, 2851, 2360, 1692, 1463, 1387, 1335, 1229, 1210, 1188,1171, 1142, 1018, 968, 823, 688, 543; HRMS (ESI) for [C$_{18}$H$_{24}$O$_3$Na]$^+$: calcd. 275.1618, found: 275.1620.

(4aR,5R,8aS)-rel-5-Acetyl-4a-hydroxy-8a-isobutylloctahydronaphthalen-1(2H)-one (3d)

Colorless oil. 51.6 mg, 97% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 4.30 (s, 1H), 2.67–2.61 (m, 2H), 2.30–2.18 (m, 6H), 1.93–1.70 (m, 4H), 1.64–1.50 (m, 6H), 1.46–1.37 (m, 1H), 0.89 (d, $J = 6.8$ Hz, 3H), 0.77 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 215.85, 214.08, 76.14, 57.96, 52.78, 42.60, 37.84, 31.65, 31.55, 26.17, 25.78, 25.28, 23.57, 21.81, 20.37; IR (KBr) $\nu$ (cm$^{-1}$) 3469, 2955, 270, 1722, 1693, 1572, 1564, 1536, 1461, 1365, 1335, 1188, 1095, 1004, 973, 793, 601; HRMS (EI) for [C$_{18}$H$_{26}$O$_3$]$^+$: calcd. 266.1876, found: 266.1878.
(4aR,5R,8aS)-rel-5-Acetyl-8a-allyl-4a-hydroxyoctahydronaphthalen-1(2H)-one (3e)

Colorless oil. 51.3 mg, 94% yield; {H NMR (400 MHz, CDCl3) δ (ppm) 5.53–5.44 (m, 1H), 5.05–4.99 (m, 2H), 4.34 (s, 1H), 2.67–2.61 (m, 2H), 2.51–2.42 (m, 2H), 2.32–2.24 (m, 2H), 2.20 (br, s, 3H), 2.13–2.09 (m, 1H), 1.96–1.89 (m, 1H), 1.78–1.71 (m, 1H), 1.71–1.61 (m, 3H), 1.59–1.50 (m, 2H), 1.46–1.38 (m, 1H); 13C NMR (100 MHz, CDCl3) δ (ppm) 215.71, 211.85, 132.74, 118.21, 75.66, 58.01, 52.78, 38.93, 37.83, 31.52, 26.43, 25.44, 21.88, 20.16; IR (KBr) ν (cm⁻¹) 3204, 3075, 2925, 2872, 2377, 1690, 1639, 1460, 1335, 1314, 1206, 1187, 1169, 1095, 916, 815, 766, 652, 602; HRMS (ESI) for [C15H22O2Na]⁺: calcd. 273.1461, found: 273.1463.

(4aR,5R,8aS)-rel-5-Acetyl-4a-hydroxy-8a-(3-phenylpropyl)octahydro-naphthalen-1(2H)-one (3f)

Colorless oil. 43.1 mg, 96% yield; {H NMR (400 MHz, CDCl3) δ (ppm) 7.27–7.23 (m, 2H), 7.18–7.10 (m, 3H), 4.30 (s, 1H), 2.67–2.58 (m, 2H), 2.53–2.45 (m, 1H), 2.26–2.13 (m, 7H), 1.91–1.68 (m, 4H), 1.66–1.58 (m, 4H), 1.56–1.46 (m, 2H), 1.41–1.30 (m, 1H), 1.11–1.05 (m, 1H); 13C NMR (100 MHz, CDCl3) δ (ppm) 215.81, 212.77, 141.94, 128.48, 128.38, 125.91, 76.78, 75.89, 57.95, 52.93, 37.51, 36.22, 33.35, 31.69, 31.53, 25.89, 25.34, 24.77, 21.93, 20.11; IR (KBr) ν (cm⁻¹) 3464, 3060, 2953, 2359, 1693, 1454, 1430, 1337, 1189, 1104, 1088, 906, 812, 749, 700, 603, 543, 492; HRMS (ESI) for [C21H28O3]⁺: calcd. 328.2033, found: 328.2034.

(4aR,5R,8aR)-rel-5-Acetyl-8a-ethyl-4a-hydroxy-3,3-dimethyloctahydro-naphthalen-1(2H)-one (3g)

Colorless oil. 47.4 mg, 89% yield; {H NMR (400 MHz, CDCl3) δ (ppm) 4.65 (s, 1H), 2.73–2.70 (m, 1H), 2.46–2.42 (m, 1H), 2.29–2.25 (m, 1H), 2.18 (br, s, 3H), 2.06–2.02 (m, 1H), 2.01–1.91 (m, 1H), 1.81–1.63 (m, 6H), 1.32–1.25 (m, 2H), 1.09 (s, 3H), 1.03 (s, 3H), 0.67 (t, J = 7.6 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ (ppm) 215.77, 213.41, 109.90, 75.59, 56.63, 55.44, 50.72, 45.54, 45.77, 31.29, 30.05, 27.89, 25.66, 22.39, 7.34; IR (KBr) ν (cm⁻¹) 3566, 2924, 2853, 2349, 1991, 1749, 1698, 1615, 1464, 1387, 1337, 1296, 1179, 1018, 945, 777, 663, 592; HRMS (ESI) for [C16H24O3]⁺: calcd. 266.1876, found: 266.1878.
(4aR,5R,8aR)-rel-5-Acetyl-4a-hydroxy-3,3-dimethyl-8a-propylocta hydro-naphthalen-1(2H)-one (3h)

Colorless oil. 50.4 mg, 90% yield; 1H NMR (400 MHz, CD3OD) δ (ppm) 2.75–2.67 (m, 1H), 2.52–2.44 (m, 1H), 2.27–2.11 (m, 5H), 2.00–1.92 (m, 1H), 1.91–1.79 (m, 1H), 1.78–1.56 (m, 5H), 1.37–1.15 (m, 3H), 1.09 (s, 3H), 1.05 (s, 3H), 0.95–0.86 (m, 3H), 0.85–0.71 (m, 1H); 13C NMR (100 MHz, CD3OD) δ (ppm) 216.92, 215.46, 76.88, 57.60, 51.96, 46.30, 39.22, 35.18, 32.51, 30.31, 30.18, 27.92, 26.65, 23.51, 17.43, 15.14; IR (KBr) ν (cm⁻¹) 3466, 2957, 2870, 2369, 1868, 1699, 1578, 1506, 1489, 1471, 1419, 1397, 1337, 1292, 1180, 1074, 1021, 892, 813, 776, 592; HRMS (EI) for [C17H20O3]⁺: calcd. 280.2033, found: 280.2031.

(4aR,5R,8aS)-rel-5-Acetyl-4a-hydroxy-8a-isobutyl-3,3-dimethylocta hydro-naphthalen-1(2H)-one (3i)

Colorless oil. 48.8 mg, 83% yield; 1H NMR (400 MHz, CD3OD) δ (ppm) 2.76–2.67 (m, 2H), 2.23–2.14 (m, 5H), 2.04–1.96 (m, 1H), 1.91–1.75 (m, 2H), 1.74–1.60 (m, 4H), 1.55–1.29 (m, 3H), 1.10 (s, 3H), 1.05 (s, 3H), 0.92 (d, J = 6.4 Hz, 3H), 0.80 (d, J = 6.8 Hz, 3H); 13C NMR (100 MHz, CD3OD) δ (ppm) 216.84, 216.69, 77.02, 57.38, 52.16, 46.22, 44.79, 35.32, 32.55, 30.52, 30.08, 28.20, 26.53, 26.03, 24.93, 23.40; IR (KBr) ν (cm⁻¹) 3466, 2957, 2930, 2871, 2369, 2322, 1868, 1699, 1569, 1471, 1397, 1337, 1292, 1220, 1180, 1074, 1021, 892, 776, 592; HRMS (EI) for [C18H30O3]⁺: calcd. 294.2189, found: 294.2191.

(4aR,5R,8aS)-rel-5-Acetyl-8a-Alllyl-4a-Hydroxy-3,3-Dimethylocta hydro-naphthalen-1(2H)-one (3j)

Colorless oil. 51.2 mg, 92% yield; 1H NMR (400 MHz, CD3OD) δ (ppm) 5.56–5.43 (m, 1H), 5.12–4.97 (m, 2H), 2.79–2.64 (m, 2H), 2.60–2.51 (m, 1H), 2.47–2.36 (m, 1H), 2.27–2.17 (m, 4H), 2.15–2.06 (m, 1H), 2.03–1.96 (m, 1H), 1.75–1.66 (m, 3H), 1.65–1.54 (m, 2H), 1.42–1.22 (m, 1H), 1.11 (s, 3H), 1.06 (s, 3H); 13C NMR (100 MHz, CD3OD) δ (ppm) 216.78, 214.40, 134.16, 118.65, 76.64, 57.91, 57.48 52.19, 46.34, 41.48, 35.15, 32.52, 30.41, 28.47, 26.70, 23.41; IR (KBr) ν (cm⁻¹) 3467, 3076, 2923, 2850, 2349, 1694, 1633, 1462, 1397, 1335, 1298, 1179, 1023, 997, 917, 811, 776, 591, 562; HRMS (EI) for [C18H30O3]⁺: calcd. 278.1876, found: 278.1878.
(4aR,5R,8aS)-rel-5-Acetyl-4a-Hydroxy-3,3-Dimethyl-8a-(3-Phenylpropyl)octa-hydropaphthenal-1(2H)-one (3k)

White solid. 65.5 mg, 92% yield; Mp 120–124 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.30–7.22 (m, 2H), 7.20–7.08 (m, 3H), 4.64 (s, 1H), 2.75–2.62 (m, 2H), 2.50–2.38 (m, 1H), 2.20–2.08 (m, 5H), 2.07–1.84 (m, 2H), 1.83–1.71 (m, 2H), 1.69–1.57 (m, 6H), 1.40–1.28 (m, 1H), 1.07–0.97 (m, 1H), 0.96 (s, 3H), 0.89 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 215.91, 213.64, 141.86, 128.70, 128.39, 125.96, 75.72, 56.54, 55.46, 50.64, 45.57, 36.00, 34.75, 33.98, 31.26, 30.28, 26.58, 25.77, 24.87, 22.52; IR (KBr) \(\nu\) (cm\(^{-1}\)) 3467, 2922, 2850, 2360, 2341, 1712, 1690, 1644, 1552, 1462, 1424, 1370, 1249, 1156, 1083, 948, 748, 699, 668, 586; HRMS (EI) for [C\(_{23}\)H\(_{32}\)O\(_3\)]\(^+\): calcd. 356.2346, found: 356.2343.

### 4. Scope Of The Substrates In Table 3

\[
\begin{align*}
\text{B}_2(\text{nep})_2 (4, 2 \text{ equiv}) & \quad \text{CuCl (5 mol%), (±)-Binap (6 mol%)} \\
& \quad \text{t-BuONa (6 mol%)} \\
& \quad \text{Toluene} \\
& \quad \text{MeOH (2.0 equiv)} \\
& \quad \text{RT, 48 h}
\end{align*}
\]

For 1a to 1f, R\(^1\) = H;
- 1a: R\(^2\) = CH\(_3\)\(^-\)
- 1d: R\(^2\) = (CH\(_3\))\(_2\)CH-CH\(_2\)\(^-\)

For 1g–1k, R\(^1\) = Me.
- 1g: R\(^2\) = CH\(_3\)CH\(_2\)\(^-\)
- 1j: R\(^2\) = CH\(_2\)CH=CH-CH\(_2\)\(^-\)

**General Procedure:**

A dried Schlenk flask was charged with CuCl (0.01 mmol, 5 mol%), t-BuONa (0.012 mmol, 6 mol%), (±)-BINAP (0.012 mmol, 6 mol%), and freshly distilled dry toluene (1 mL) under argon atmosphere. The reaction mixture was stirred at room temperature for 0.5 h. Then bis(neopentyl glycolato)diboron 4 (0.4 mmol, 2.0 equiv) was added and the mixture was allowed to stir for another 0.5 h under argon atmosphere at room temperature. A solution of allenes 1 (0.2 mmol) in freshly distilled toluene (1 mL) and MeOH (16 μL, 2.0 equiv) was then added to the Schlenk flask. The mixture was allowed to stir for 48 h at room temperature under argon atmosphere. The resulting mixture was quenched with H\(_2\)O (2 mL) then extracted with ethyl acetate (4 mL \(\times\) 3). The combined organic phases were dried over anhydrous MgSO\(_4\), filtered and concentrated in vacuo. The residue was purified by silica gel (300–400 mesh) column chromatography to afford the desired product 5.
(3aS,6aR,10aR)-rel-2-Hydroxy-6a-methyl-3-methyleneoctahydro-2H-naptho[1,8-a-d][1,2]oxaborol-7(8H)-one (5a)

Colorless oil. 46.1 mg, 99% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 5.64 (br, s, 1H), 5.48 (br, s, 1H), 4.91 (br, s, 1H), 2.65–2.34 (m, 3H), 2.11–1.99 (m, 1H), 1.98–1.84 (m, 3H), 1.79–1.58 (m, 3H), 1.52–1.38 (m, 2H), 1.31–1.16 (m, 2H), 1.13 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 214.31, 120.23, 86.56, 53.68, 49.60, 37.14, 34.99, 30.39, 26.66, 21.43, 19.64, 17.97; IR (KBr) $\nu$ (cm$^{-1}$) 3358, 2921, 2851, 1841, 1659, 1632, 1582, 1470, 1376, 1011, 940, 877, 646, 582; HRMS (EI) for [C$_{13}$H$_{19}$BO$_3$]$^{+}$: calcd. 233.1464, found: 233.1467.

(3aS,6aR,10aR)-rel-6a-Ethyl-2-hydroxy-3-methyleneoctahydro-2H-naptho[1,8-a-d][1,2]oxaborol-7(8H)-one (5b)

Colorless oil. 47.5 mg, 96% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 5.62 (br, s, 1H), 5.51 (br, s, 1H), 4.38 (br, s, 1H), 2.56–2.51 (m, 1H), 2.43–2.39 (m, 2H), 2.38–2.13 (m, 2H), 1.99–1.89 (m, 1H), 1.88–1.80 (m, 1H), 1.78–1.70 (m, 1H), 1.69–1.58 (m, 2H), 1.51–1.35 (m, 4H), 1.00–0.91 (m, 1H), 0.67 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 212.28, 121.37, 86.82, 56.91, 49.07, 38.13, 34.61, 28.81, 27.48, 24.43, 19.49, 18.73, 7.81; IR (KBr) $\nu$ (cm$^{-1}$) 3361, 2935, 2877, 2360, 2341, 1693, 1461, 1317, 1291, 1228, 1144, 1018, 943, 824, 668, 544; HRMS (EI) for [C$_{14}$H$_{21}$BO$_3$]$^{+}$: calcd. 247.1620, found: 247.1623.

(3aS,6aR,10aR)-rel-2-Hydroxy-3-methylene-6a-propyloctahydro-2H-naptho[1,8-a-d][1,2]oxaborol-7(8H)-one (5c)

Colorless oil. 49.6 mg, 95% yield; $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ (ppm) 5.54 (br, s, 1H), 5.46 (br, s, 1H), 2.59–2.44 (m, 2H), 2.32–2.12 (m, 2H), 1.98–1.82 (m, 2H), 1.74–1.59 (m, 3H), 1.52–1.29 (m, 4H), 1.27–1.13 (m, 1H), 1.06–0.93 (m, 1H), 0.92–0.88 (m, 3H), 0.87–0.79 (m, 2H); $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ (ppm) 214.65, 121.02, 87.60, 58.06, 56.49, 50.28, 39.08, 38.25, 35.57, 29.82, 26.38, 20.43, 17.72, 15.06; IR (KBr) $\nu$ (cm$^{-1}$) 3334, 2926, 2870, 2375, 1701, 1455, 1402, 1286, 1186, 1144, 1074, 994, 829, 744, 672, 543; HRMS (EI) for [C$_{15}$H$_{23}$BO$_3$]$^{+}$: calcd. 261.1777, found: 261.1778.
(3\text{R},6\text{aS},10\text{aR})\text{-rel-2-Hydroxy-6a-isobutyl-3-methyleneoctahydro-2H-naphtho[1,8-a-d][1,2]oxaborol-7(8\text{H})-one (5d)}

Colorless oil. 50.1 mg, 91% yield; $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ (ppm) 5.54 (t, $J = 2.4$ Hz, 1H), 5.46 (br, s, 1H), 2.69–2.58 (m, 1H), 2.57–2.48 (m, 1H), 2.32–2.22 (m, 3H), 1.96–1.86 (m, 2H), 1.81–1.73 (m, 1H), 1.52–1.38 (m, 4H), 1.34–1.28 (m, 3H), 1.08–0.98 (m, 1H), 0.90 (d, $J = 9.6$ Hz, 3H), 0.82 (d, $J = 9.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ (ppm) 215.14, 121.18, 87.67, 58.17, 50.31, 44.87, 39.43, 35.61, 29.88, 26.75, 26.05, 24.73, 20.49, 19.96; IR (KBr) $\nu$ (cm$^{-1}$) 3371, 2925, 2869, 2375, 1848, 1699, 1455, 1286, 1198, 1144, 1029, 928, 891, 774, 672, 599; HRMS (EI) for [C$_{16}$H$_{25}$BO$_3$]$^+$: calcd. 275.1933, found: 275.1935.

(3\text{R},6\text{aS},10\text{aR})\text{-rel-6a-Allyl-2-hydroxy-3-methyleneoctahydro-2H-naphtho[1,8-a-d][1,2]oxaborol-7(8\text{H})-one (5e)}

White solid. 50.2 mg, 97% yield, Mp 97–103 °C. $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ (ppm) 5.65–5.51 (m, 2H), 5.50–5.42 (m, 1H), 2.76–2.66 (m, 1H), 2.61–2.42 (m, 3H), 2.33–2.22 (m, 2H), 2.17–2.07 (m, 1H), 1.95–1.84 (m, 1H), 1.80–1.25 (m, 8H), 1.07–1.01 (m, 1H); $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ (ppm) 213.71, 134.80, 121.05, 117.94, 87.37, 58.14, 50.37, 40.49, 39.25, 35.69, 29.52, 26.96, 20.45, 19.66; IR (KBr) $\nu$ (cm$^{-1}$) 3391, 2927, 2869, 2850, 2361, 2342, 1699, 1632, 1496, 1367, 1244, 1197, 1072, 998, 933, 882, 776, 673, 567; HRMS (EI) for [C$_{15}$H$_{21}$BO$_3$]$^+$: calcd. 259.1620, found: 259.1621.

(3\text{R},6\text{aS},10\text{aR})\text{-rel-2-Hydroxy-3-methylene-6a-(3-phenylpropyl)octahydro-2H-naphtho[1,8-a-d][1,2]oxaborol-7(8\text{H})-one (5f)}

Colorless oil. 63.4 mg, 94% yield; $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ (ppm) 7.29–7.21 (m, 2H), 7.19–7.10 (m, 3H), 5.52 (br, s, 1H), 5.43 (br, s, 1H), 2.64–2.48 (m, 3H), 2.38–2.26 (m, 1H), 2.24–2.08 (m, 3H), 1.99–1.87 (m, 1H), 1.86–1.71 (m, 2H), 1.69–1.57 (m, 2H), 1.56–1.44 (m, 2H), 1.42–1.28 (m, 2H), 1.19–1.08 (m, 1H), 1.01–0.86 (m, 2H); $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ (ppm) 214.75, 143.36, 129.49, 129.31, 126.84, 121.02, 87.62, 57.90, 50.31, 38.93, 37.10, 35.55, 34.89, 29.53, 26.45, 26.28, 20.39, 19.76; IR (KBr) $\nu$ (cm$^{-1}$) 3392, 3060, 2930, 2870, 2360, 2341, 1701, 1602, 1495, 1343, 1291, 1198, 1029, 933, 881, 747, 668, 551, 454; HRMS (EI) for [C$_{21}$H$_{37}$BO$_3$]$^+$: calcd. 337.2090, found: 337.2093.

S15
(3aR,6aR,10aR)-rel-6a-Ethyl-2-hydroxy-9,9-dimethyl-3-methyleneoctahydro-2H-naphtho[1,8a][1,2]oxaborol-7(8H)-one (5g)

Colorless oil. 52.8 mg, 96% yield; \(^1\)H NMR (400 MHz, CD\(_2\)OD) \(\delta\) (ppm) 5.53 (t, \(J = 2.8\) Hz, 1H), 5.38 (br, s, 1H), 2.63–2.55 (m, 1H), 2.48–2.27 (m, 2H), 2.12–2.05 (m, 1H), 1.87–1.67 (m, 4H), 1.56–1.28 (m, 5H), 1.12 (s, 3H), 1.01 (s, 3H), 0.73 (t, \(J = 7.6\) Hz, 3H); \(^1^3\)C NMR (100 MHz, CD\(_2\)OD) \(\delta\) (ppm) 211.91, 127.41, 73.03, 69.58, 52.18, 35.95, 35.47, 31.48, 31.20, 28.63, 25.34, 21.95, 21.62, 9.50; IR (KBr) \(\nu\) (cm\(^{-1}\)) 3353, 2936, 2878, 2361, 2344, 1701, 1401, 1317, 1229, 1172, 1144, 1090, 945, 828, 669, 544; HRMS (EI) for [C\(_{16}\)H\(_{25}\)BO\(_3\)]\(^{+}\): calcd. 275.1933, found: 275.1935.

(3aS,6aR,10aR)-rel-2-Hydroxy-9,9-dimethyl-3-methylene-6a-propyloctahydro-2H-naphtho[1,8a][1,2]oxaborol-7(8H)-one (5h)

Colorless oil. 54.4 mg, 94% yield; \(^1\)H NMR (400 MHz, CD\(_2\)OD) \(\delta\) (ppm) 5.54 (t, \(J = 2.8\) Hz, 1H), 5.43–5.34 (br, s, 1H), 2.64–2.54 (m, 1H), 2.45–2.28 (m, 2H), 2.12–2.02 (m, 1H), 1.86–1.65 (m, 4H), 1.64–1.50 (m, 2H), 1.49–1.31 (m, 4H), 1.15–1.08 (m, 4H), 1.01 (s, 3H), 0.88–0.81 (m, 3H); \(^1^3\)C NMR (100 MHz, CD\(_2\)OD) \(\delta\) (ppm) 211.89, 124.11, 73.03, 69.56, 52.15, 38.08, 36.05, 35.49, 31.50, 30.89, 28.77, 25.36, 21.62, 18.93, 14.78; IR (KBr) \(\nu\) (cm\(^{-1}\)) 3334, 2930, 2871, 2855, 2376, 2349, 1701, 1457, 1401, 1287, 1189, 1039, 930, 892, 805, 745, 665, 564; HRMS (EI) for [C\(_{17}\)H\(_{27}\)BO\(_3\)]\(^{+}\): calcd. 289.2090, found: 289.2094.

(3aR,6aS,10aR)-rel-2-Hydroxy-6a-isobutyl-9,9-dimethyl-3-methyleneoctahydro-2H-naphtho[1,8a][1,2]oxaborol-7(8H)-one (5i)

Colorless oil. 53.4 mg, 88% yield; \(^1\)H NMR (400 MHz, CD\(_2\)OD) \(\delta\) (ppm) 5.54 (t, \(J = 2.4\) Hz, 1H), 5.46–5.35 (m, 1H), 2.76–2.67 (m, 1H), 2.65–2.55 (m, 1H), 2.18–2.08 (m, 1H), 1.85–1.74 (m, 3H), 1.70–1.51 (m, 6H), 1.47–1.40 (m, 2H), 1.14 (s, 3H), 0.98 (s, 3H), 0.95–0.84 (m, 3H), 0.83–0.78 (m, 3H); \(^1^3\)C NMR (100 MHz, CD\(_2\)OD) \(\delta\) (ppm) 210.73, 125.89, 71.57, 68.83, 68.09, 50.93, 45.45, 36.64, 32.62, 30.15, 28.48, 26.36, 24.53, 23.39, 23.17; IR (KBr) \(\nu\) (cm\(^{-1}\)) 3357, 2927, 2870, 2852, 2350, 2307, 1990, 1784, 1700, 1456, 1401, 1240, 1187, 1230, 929, 892, 774, 734, 645, 598; HRMS (EI) for [C\(_{18}\)H\(_{29}\)BO\(_3\)]\(^{+}\): calcd. 303.2246, found: 303.2251.
(3aR,6aS,10aR)-rel-6a-Allyl-2-hydroxy-9,9-dimethyl-3-methyleneoctahydro-2H-naphtho[1,8a-d][1,2]oxaborol-7(8H)-one (5j)

Colorless oil. 52.8 mg, 92% yield; $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ (ppm) 5.78–5.64 (m, 1H), 5.61–5.55 (m, 1H), 5.46–5.38 (m, 1H), 4.98–4.87 (m, 2H), 2.64–2.57 (m, 1H), 2.49–2.42 (m, 2H), 2.36–2.29 (m, 1H), 2.23–2.15 (m, 2H), 1.99–1.88 (m, 1H), 1.81–1.70 (m, 2H), 1.60–1.34 (m, 4H), 1.12 (s, 3H), 1.04 (s, 3H); $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ (ppm) 216.18, 136.58, 118.12, 117.33, 88.88, 56.80, 53.22, 51.36, 37.09, 34.90, 32.00, 30.47, 30.09, 25.34, 17.90; IR (KBr) $\nu$ (cm$^{-1}$) 3371, 2925, 2862, 2382, 2350, 2017, 1869, 1844, 1771, 1540, 1436, 1396, 1286, 1086, 912, 800, 674, 663, 587; HRMS (EI) for [C$_9$H$_{25}$O$_4$B$_4$]$:^+$: calcd. 287.1933, found: 287.1934.

(3aR,6aS,10aR)-rel-2-Hydroxy-9,9-dimethyl-3-methylene-6a-(3-phenylpropyl)octahydro-2H-naphtho[1,8a-d][1,2]oxaborol-7(8H)-one (5k)

White solid. 66.5 mg, 91% yield, Mp 106–111 °C. $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ (ppm) 7.24–7.20 (m, 2H), 7.14–7.08 (m, 3H), 5.45–5.40 (m, 1H), 5.30–5.24 (m, 1H), 2.62–2.47 (m, 3H), 2.31–2.26 (m, 1H), 2.10–2.04 (m, 1H), 1.86–1.77 (m, 1H), 1.73–1.64 (m, 3H), 1.59–1.45 (m, 3H), 1.44–1.33 (m, 5H), 1.07 (s, 3H), 0.99 (s, 3H); $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ (ppm) 216.92, 143.36, 129.54, 129.27, 129.71, 118.18, 89.08, 56.55, 53.13, 51.26, 37.29, 34.68, 31.77, 30.75, 30.67, 29.52, 27.00, 25.81, 18.42; IR (KBr) $\nu$ (cm$^{-1}$) 3391, 3061, 3022, 2928, 2867, 2359, 2340, 1701, 1604, 1497, 1402, 1345, 1242, 1195, 1091, 935, 899, 882, 749, 667, 551, 435; HRMS (EI) for [C$_{25}$H$_{31}$O$_4$B$_4$]$:^+$: calcd. 365.2403, found: 365.2401.

(3aR,6aR,9aR)-rel-2-hydroxy-6a-methyl-3-methyleneoctahydroindeno[4,3a-d][1,2]oxaborol-7(2H)-one (5m)

Colorless oil. 41.6 mg, 95% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 5.71 (t, $J = 2.4$ Hz, 1H), 5.59–5.48 (m, 1H), 4.90 (br, s, 1H), 2.63–2.47 (m, 2H), 2.39–2.28 (m, 1H), 2.19–2.03 (m, 2H), 1.82–1.72 (m, 1H), 1.69–1.54 (m, 2H), 1.49–1.39 (m, 1H), 1.36–1.27 (m, 2H), 0.97 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 221.17, 120.69, 89.07, 53.52, 52.78, 48.82, 34.80, 31.59, 29.78, 25.88, 17.79, 14.21; IR (KBr) $\nu$ (cm$^{-1}$) 3361, 2932, 2857, 1847, 1664, 1637, 1593, 1477, 1382, 1009, 957, 867, 655, 573; HRMS (EI) for [C$_{12}$H$_{21}$O$_4$B$_4$]$:^+$: calcd. 219.1307, found: 219.1311.
5 Initial Evaluation of Various Chiral Ligands

5.1 Evaluation of Various Chiral Ligands for Cu-catalyzed asymmetric cyclization of allene diketone 1a using B$_2$(pin)$_2$ (2) as boron source.

1) CuCl (5 mol%), L (6 mol%), t-BuONa (6 mol%)
MeOH (2.0 equiv), Toluene
RT, 120 h

2) NaBO$_3$·4H$_2$O, THF/H$_2$O = 1:1
RT, 10 h

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<th>d.r.$^b$</th>
<th>ee (%)$^c$</th>
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a: Yield of isolated and purified product 3a.
b: Determined by $^1$H NMR
c: Determined by HPLC analysis using a chiral stationary phase
d: 12% mmol Ligand was used
L10, L18, L21, L22: purchased from Sigma-Aldrich and used as received.
L12, L14, L16, L17, L19, L20, L23, L24: purchased from Strem Chemicals Inc. and used as received.
L11, L15, L25: purchased from TCI and used as received.
L13: made by ourselves according to literatures\(^2\)

(-)-3a $[\alpha]_D^{24.2} = -26.8$ (c 0.63, CHCl$_3$) for 53% ee

5.2 Chiral Ligands (S)-DTBM-Segphos for Cu-catalyzed asymmetric cyclization of allene diketone 1a using B$_2$(nep)$_2$ (4) as boron source.

$$\begin{array}{c}
\text{CuCl (5 mol%), t-BuONa (6 mol\%)} \\
\text{(S)-DTBM-Segphos (6 mol\%)} \\
\text{B$_2$(nep)$_2$ (4, 2.0 equiv)} \\
\text{MeOH (2.0 equiv)} \\
\text{Toluene} \\
\text{RT, 48 h} \\
\end{array}$$

(-)-5a, d.r. > 20:1
80% yield, 73% ee

HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column in series with Chiracel OD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 99.5/0.5; flow = 0.5 ml/min; Retention time: 23.5 min (major), 28.9 min (minor).

HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column in series with Chiracel OD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 99/1; flow = 0.7 ml/min; Retention time: 11.4 min (major), 16.9 min (minor).
6. **TRANSFORMATIONS OF THE CYCLIZATION PRODUCTS 5b**

\[ \text{(4aR,5R,8aR)-rel-8a-Ethyl-4a-hydroxy-5-(1-phenylvinyl)octahydropaphthalen-1(2H)-one (6b) \[3\] into a 5 mL microwave reactor containing DME/H}_2\text{O (2 mL, 3:1 v/v) were added 5b (24.8 mg, 0.1 mmol), 3-methoxyphenyl iodide (24.5 mg, 0.12 mmol), K}_2\text{CO}_3 (27.6 mg, 0.2 mmol) and [Pd(PPh}_3\text{)]}_4 (5.8 mg, 0.005 mmol). The mixture was de-gassed with Ar for 10 min. The reactor was then capped and placed in the microwave oven. The temperature was ramped to 150 °C over 15 min, and kept at 150 °C for 15 min. After the reaction mixture was cooled to 25 °C, EtOAc/H}_2\text{O was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc (2 mL × 3). The combined organic phases were washed with brine, and dried over anhydrous MgSO}_4. The residue was purified by column chromatography resulting in 6b as a colorless oil (28.3 mg, 95% yield).}^{3}\text{H NMR (400 MHz, CDCl}_3 \text{) } \delta \text{ (ppm) 7.35–7.17 (m, 5H), 5.28–5.23 (m, 2H), 2.62–2.52 (m, 1H), 2.33–2.15 (m, 2H), 2.12–2.03 (m, 1H), 2.01–1.87 (m, 3H), 1.75–1.66 (m, 2H), 1.65–1.55 (m, 3H), 1.35–1.23 (m, 3H), 1.02–0.89 (m, 1H), 0.63 (t, } J = 7.6 \text{ Hz, 3H); }^{13}\text{C NMR (100 MHz, CDCl}_3 \text{) } \delta \text{ (ppm) 213.33, 151.87, 144.75, 128.53, 127.40, 126.47, 115.87, 77.37, 58.88, 47.45, 34.31, 31.42, 28.02, 25.72, 22.57, 19.10, 14.19, 7.62; IR (KBr) } \nu \text{ (cm}^{-1} \text{) 3524, 2954, 2927, 2877, 2855, 1701, 1621, 1492, 1463, 1144, 1017, 977, 906, 823, 762, 717, 702, 552, 428; HRMS (TOF-EL) for [C}_2\text{H}_2\text{O}_2\text{] }^{+}: \text{calcd. 298.1933, found 298.1930.}}^{3}

\[ \text{(3aR,6aR,10aR)-rel-6a-Ethyl-3-methyleneoctahydro-2H-naphtho[8a,1-b]furan-2, 7(8H)-dione (7b) \[3\] A dried Schlenk flask was charged with 5b (24.8 mg, 0.1 mmol), DMSO (2 mL). MeOH (1 mL) and Pd(OAc)_2 (22.5 mg, 0.1 mmol), then the reaction mixture was evacuated and filled with CO three times. The reaction mixture was stirred at 25 °C for 3 h until the brown catalyst turned to a black precipitate. The}

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mixture was poured into an Erlenmeyer flask containing 15 mL of H₂O, which was then extracted with EtOAc (3 × 10 mL). The organic phases were combined and washed with H₂O, brine, and dried over MgSO₄. The solvent was removed in vacuo and the residue was purified by column chromatography (hexane/EtOAc = 10/1) to give a white solid 7b (23.8 mg, 96% yield). Mp 124–129 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 6.23 (d, J = 2.0 Hz, 1H), 5.54 (d, J = 2.0 Hz, 1H), 2.87–2.84 (m, 1H), 2.49–2.31 (m, 3H), 2.28 (dt, J = 14.0 Hz, 4.8 Hz, 1H), 2.01–1.93 (m, 2H), 1.82–1.70 (m, 2H), 1.67–1.54 (m, 2H), 1.53–1.47 (m, 3H), 0.99–0.90 (m, 1H), 0.69 (t, J = 7.6 Hz, 3H); ¹³CNMR (100 MHz, CDCl₃) δ (ppm) 210.30, 169.44, 140.50, 121.23, 87.76, 56.19, 43.79, 37.76, 33.39, 27.42, 27.26, 23.15, 18.90, 17.16, 7.68; IR (KBr) ν (cm⁻¹) 3473, 2940, 2848, 1763, 1706, 1644, 1463, 1289, 1260, 1230, 1186, 1134, 1042, 1008, 942, 828; HRMS (TOF-EI) for [C₁₅H₂₂O₃]⁺: calcd. 248.1412, found: 248.1406.

(4aR,5R,8aR)-rel-5-Acetyl-8a-ethyl-4a-hydroxyoctahydronaphthalen-1(2H)-one (3b). A dried Schlenk flask was charged with 5b (24.8 mg, 0.1 mmol), Sodium perborate tetrahydrate (77 mg, 0.5 mmol), THF (0.5 mL) and H₂O (0.5 mL) was added and the mixture was allowed to stir for 3h at room temperature. Then quenched with saturated aqueous NaCl (2 mL), extracted with ethyl acetate (4 mL × 3). The combined organic phases were dried over anhydrous MgSO₄, filtered and concentrated in vacuo. The residue was purified by silica gel (300–400 mesh) column chromatography to afford the desired product 3b as colorless oil (21.7 mg, 91% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 4.28 (s, 1H), 2.66–2.61 (m, 1H), 2.49–2.39 (m, 1H), 2.34–2.23 (m, 1H), 2.20–2.15 (m, 4H), 1.99–1.87 (m, 2H), 1.82–1.70 (m, 2H), 1.67–1.62 (m, 3H), 1.53–1.48 (m, 1H), 1.36–1.27 (m, 3H), 0.66 (t, J = 8.0 Hz, 3H).
7. RELATIVE CONFIGURATION CONFIRMATION

7.1 Relative Configuration Confirmation of 3K
Crystal data and structure refinement for 3k.

Identification code 3k
Empirical formula C23 H32 O3
Formula weight 356.49
Temperature 296(2) K
Wavelength 1.54178 Å
Crystal system, space group Triclinic, P -1
Unit cell dimensions a = 8.0136(16) Å  alpha = 70.38(3) deg.
b = 10.278(2) Å  beta = 86.42(3) deg.
c = 13.463(3) Å  gamma = 78.55(3) deg.
 Volume 1023.7(4) Å^3
Z, Calculated density 2,  1.157 Mg/m^3
Absorption coefficient 0.586 mm^-1
F(000) 388
Crystal size 0.31 x 0.20 x 0.16 mm
Theta range for data collection 4.65 to 65.93 deg.
Limiting indices -9<=h<=9, -12<=k<=12, -14<=l<=15
Reflections collected / unique 5726 / 3136 [R(int) = 0.0163]
Completeness to theta = 65.93 88.0 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.7529 and 0.6742
Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 3136 / 0 / 236
Goodness-of-fit on F^2 1.053
Final R indices [I>2sigma(I)] R1 = 0.0441, wR2 = 0.1229
R indices (all data) R1 = 0.0459, wR2 = 0.1250
Extinction coefficient 0.0152(14)
Largest diff. peak and hole 0.178 and -0.174 e.A^-3
7.2 Relative Configuration Confirmation of 5e
Crystal data and structure refinement for 5e.

Identification code 5e
Empirical formula C15 H21 B O3
Formula weight 260.13
Temperature 296(2) K
Wavelength 1.54178 Å
Crystal system, space group Monoclinic, P 21/c
Unit cell dimensions
\[ a = 10.555(2) \text{ Å} \quad \alpha = 90 \text{ deg.} \]
\[ b = 7.2517(15) \text{ Å} \quad \beta = 101.90(3) \text{ deg.} \]
\[ c = 18.652(4) \text{ Å} \quad \gamma = 90 \text{ deg.} \]
Volume 1397.0(5) Å³
Z, Calculated density 4, 1.237 Mg/m³
Absorption coefficient 0.663 mm⁻¹
F(000) 560
Crystal size 0.32 x 0.21 x 0.15 mm
Theta range for data collection 4.85 to 67.57 deg.
Limiting indices \[-12 \leq h \leq 12, -7 \leq k \leq 8, -20 \leq l \leq 22\]
Reflections collected / unique 6044 / 2375 \( [R(\text{int}) = 0.0213] \)
Completeness to theta = 67.57 94.2 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.7529 and 0.6526
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 2375 / 0 / 173
Goodness-of-fit on F² 1.052
Final R indices \([I > 2\sigma(I)]\) R1 = 0.0398, wR2 = 0.1055
R indices (all data) R1 = 0.0405, wR2 = 0.1061
Extinction coefficient 0.0100(8)
Largest diff. peak and hole 0.184 and -0.171 e.Å⁻³

The relative configuration of 5e
8. $^1H$ NMR, $^{13}C$ NMR Copies
$\text{CHCl}_3$

$\text{^1H NMR}$

Solvent: $\text{CDCl}_3$


$^{13}$C NMR
Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CD$_3$OD
$^{13}$C NMR
Solvent: CD$_3$OD
$\text{CH}_3\text{OH}$

$\text{H}_2\text{O}$

$1^1\text{H NMR}$

Solvent: $\text{CD}_3\text{OD}$

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\(^{13}\text{C NMR}
\text{Solvent: CD}_3\text{OD}\)
\[ \text{\textsuperscript{1}H NMR} \]

Solvent: CD\textsubscript{3}OD
$^{13}$C NMR
Solvent: CD$_3$OD
$^{1}H$ NMR
Solvent: CD$_3$OD
$\text{CH}_3\text{OH}$
\[1^3C\text{ NMR}\]
Solvent: CD$_3$OD
$^{13}$C NMR
Solvent: CD$_3$OD
$\text{CH}_3\text{OH}$
$^{13}$C NMR

Solvent: CD$_3$OD
3a

$^1$H NMR
Solvent: CDCl$_3$

CHCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
$\text{CHCl}_3$

$\text{H}_2\text{O}$

$^1\text{H NMR}$

Solvent: CDCl$_3$
$\text{\textsuperscript{13}C NMR}$

Solvent: CDCl$_3$
$\text{CHCl}_3$

$\text{H}_2\text{O}$

$^1\text{H} \text{NMR}$

Solvent: CDCl$_3$
$^1$H NMR
Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
$\text{CHCl}_3$

$^{1}$H NMR
Solvent: CDCl$_3$
$^{13}\text{C} \text{NMR}$

Solvent: CDCl$_3$
$\text{CH}_3\text{OH}$

$\text{H}_2\text{O}$

$3j$

$^1\text{H NMR}$

Solvent: CD$_3$OD
$\text{CHCl}_3$

$^1\text{H NMR}$

Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
HO<sub>5c</sub>

$^{13}$C NMR

Solvent: CD<sub>3</sub>OD
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Solvent: CD$_3$OD
S82
$^{13}$C NMR

Solvent: CD$_3$OD
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$\text{CH}_3\text{OH}$
5m
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Solvent: CDCl$_3$
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$^{1}$H NMR

Solvent: CDCl$_3$