Supporting Information

Stereocontrolled Synthesis of Paracentrone

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General information

All reagents and solvents were purchased from either Aldrich Chemical Company, Inc., Merck & Co., Inc., Nacalai Tesque Company, Ltd., Tokyo Kasei Kogyo Co., Ltd., or Wako Pure Chemical Industries, Ltd., and used without further purification unless otherwise indicated. Dichloromethane (CH$_2$Cl$_2$) was distilled from phosphoric pentaoxide (P$_2$O$_5$). Tetrahydrofuran (THF), chloroform (CHCl$_3$) and dimethylformamide (DMF) of anhydrous grade were used. Optical rotations were taken on JASCO P-1030 polarimeter with a sodium lamp (D line). FTIR spectra were measured on a JASCO FT/IR-6200 infrared spectrophotometer. $^1$H NMR spectra were recorded on an either Bruker AVANCE 300 (300 MHz), Bruker AVANCE 400 (400 MHz) or Bruker AVANCE 600 (600 MHz) spectrometer. Chemical shifts of $^1$H NMR were reported in parts per million (ppm, $\delta$) relative to CHCl$_3$ ($\delta$= 7.26) in CDCl$_3$, C$_6$D$_5$H ($\delta$= 7.15) in C$_6$D$_6$, CD$_2$HCOCD$_3$ ($\delta$= 2.05) in d$_6$-acetone or CD$_2$HOD ($\delta$= 3.31) in CD$_3$OD. $^{13}$C NMR spectra were recorded on an either Bruker AVANCE 300 (75 MHz), Bruker AVANCE 400 (100 MHz) or Bruker AVANCE 600 (150 MHz) spectrometer. Chemical shifts of $^{13}$C NMR were reported in ppm ($\delta$) relative to CHCl$_3$ ($\delta$= 77.0) in CDCl$_3$, C$_6$D$_5$H ($\delta$= 128.0) in C$_6$D$_6$, CD$_2$HCOCD$_3$ ($\delta$= 206.0) in d$_6$-acetone or CD$_2$HOD ($\delta$= 49.0) in CD$_3$OD. High resolution mass spectra (HRMS) were obtained on a FT-ICRMS, BURUKER/solariX for atmospheric pressure chemical ionization (APCI) or FT-ICRMS, BURUKER/solariX or JEOL JMS-T100LP Accu TOF LC-plus 4G for electrospray ionization (ESI). All reactions were monitored by thin layer chromatography (TLC), which was performed with precoated plates (silica gel 60 F-254, 0.25 mm thickness, manufactured by Merck). TLC visualization was accompanied using UV lamp (254 nm) or a charring solution (ethanoic p-anisaldehyde, ethanoic phosphomolybdic acid and aqueous potassium permanganate). Daisogel IR-60 1002W (40/63 $\mu$m) was used for flash column chromatography on silica gel.
Tributyl((E)-2-methylbuta-1,3-dienyl)stannane (13)

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\text{Bu}_3\text{Sn} & \quad \equiv \\
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To a suspension of methyltriphenylphosphonium bromide (1.59 g, 4.46 mmol) in dry THF (10 mL) at –78 °C under argon was added n-BuLi (1.72 mL of a 2.65 M solution in hexane, 4.46 mmol). The mixture was warmed to 0 °C and stirred for 1 h. The mixture was cooled to –78 °C again, and a solution of 11 (1.00 g, 2.78 mmol) in THF (4 mL) was added slowly. The resulting mixture was allowed to warm to 0 °C and stirred for 40 min. The reaction was quenched by addition of saturated aqueous NH₄Cl. The mixture was extracted with Et₂O (15 mL × 3). The combined organic layers were washed with brine (15 mL × 1), dried over MgSO₄, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane only) to give 13 (838 mg, 84%) as a colorless oil. The spectral data of the resulting 13 were in good agreement with the reported data.¹)

2-(((1E,3E)-4-Iodo-3-methylbuta-1,3-dienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17)

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To a solution of 13 (40.0 mg, 112 µmol) and vinylboronic acid pinacol ester 15 (35.0 mg, 224 µmol) in dry CH₂Cl₂ (560 µL) was added Hoveyda-Grubbs 1st catalyst (10.1 mg, 16.8 µmol). The brick red solution was refluxed for 19 h. The mixture was then concentrated in vacuo to give the crude 16, which was used to the next reaction without further purification.

16: IR (neat) 2957, 2927, 2871, 2853, 1609, 1564, 1457, 1378, 1343 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.10 (d, J = 17.9 Hz, 1 H), 6.22 (s, 3JSn-H = 64.7 Hz, 1 H), 5.43 (d, J = 17.9 Hz, 1 H), 1.89 (s, 3JSn-H = 9.1 Hz, 3 H), 1.51-1.48 (m, 6 H), 1.46-1.25 (m, 6 H), 1.27 (s, 12 H), 0.95-0.85 (m, 15 H); ¹³C NMR (75 MHz, CDCl₃) δ 154.6, 151.5, 139.0, 83.1, 29.2, 27.3, 24.8, 19.8, 13.7, 10.2, [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ¹¹B nucleus]; HRMS (APCI) m/z
[M+H]$^+$ calcd for [C$_{23}$H$_{46}$BO$_2$Sn$]^+$ 485.2615, found 485.2611.

To a solution of I$_2$ (56.9 mg, 224 µmol) and Na$_2$CO$_3$ (47.5 mg, 448 µmol) in CH$_2$Cl$_2$ (1.00 mL) at 0 °C was added dropwise a solution of 16 in CH$_2$Cl$_2$ (1 mL × 3). The combined organic layers were washed with brine (1 mL × 1), dried over MgSO$_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 100 : 1) to give 17 (24.3 mg, 2 steps 68%) as a dark yellow oil: IR (neat) 3386, 2978, 2930, 1610, 1380, 1343, 1144 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.05 (d, $J$ = 18.0 Hz, 1 H), 6.62 (s, 1 H), 5.63 (d, $J$ = 18.0 Hz, 1 H), 1.96 (d, $J$ = 1.0 Hz, 3 H), 1.28 (s, 12 H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 149.2, 146.6, 88.8, 83.4, 24.7, 19.3, [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}$B nucleus]; HRMS (APCI) m/z [M+H]$^+$ calcd for [C$_{11}$H$_{19}$BIO$_2$]$^+$ 321.0519, found 321.0519.

2-((1E,3E)-4-Iodo-3-methylbuta-1,3-dienyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4)

To a solution of 17 (120 mg, 375 µmol) in (acetone/H$_2$O = 2 : 1) (3.8 mL) was added NaIO$_4$ (241 mg, 1.13 mmol) and NH$_4$OAc (86.7 mg, 1.13 mmol) at room temperature. The mixture was stirred at room temperature for 24 h, and quenched with H$_2$O. The mixture was extracted with EtOAc (5 mL × 3). The combined organic layers were washed with brine (5 mL × 1), dried over MgSO$_4$, and concentrated in vacuo. The crude boronic acid was used in the next step without any purification. Methyliminodiacetic acid (61 mg, 413 µmol) was added to a solution of crude boronic acid in (toluene/DMSO = 1 : 4) (3.8 mL). The mixture was stirred at 120 °C for 16 h and quenched with H$_2$O. The mixture was extracted with EtOAc (5 mL × 3). The combined organic layers were washed with brine (5 mL × 1), dried over MgSO$_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (EtOAc only) to give 4 (87.8 mg, 2 steps 67%) as a white solid: IR (neat) 3007,
2958, 1755, 1611, 1457, 1336, 1292, 1237, 1158, 1113, 1087, 1030, 1004, 990, 956 cm\(^{-1}\); \(^1\)H NMR (400 MHz, \(d_6\)-acetone) \(\delta\) 6.71 (d, \(J = 17.8\) Hz, 1H), 6.64 (s, 1H), 5.83 (d, \(J = 17.8\) Hz, 1H), 4.23 (d, \(J = 17.0\) Hz, 2H), 4.05 (d, \(J = 17.0\) Hz, 2H), 3.02 (s, 3H), 1.99 (s, 3H); \(^{13}\)C NMR (100 MHz, \(d_6\)-acetone) \(\delta\) 168.8, 147.2, 142.7, 85.9, 62.1, 47.2, 19.8, [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the \(^{11}\)B nucleus]; HRMS (ESI) \(m/z\) [M–H] calcd for \([C_{10}H_{12}BINO_4]\) 347.9904, found 347.9908.

Tributyl((E)-penta-2,4-dien-2-yl)stannane (14)

![Structure of 14]

To a suspension of methyltriphenylphosphonium bromide (1.59 g, 4.46 mmol) in dry THF (10 mL) at –78 °C under argon was added \(n\)-BuLi (1.72 mL of a 2.65 M solution in hexane, 4.46 mmol). The mixture was warmed to 0 °C and stirred for 1 h. The mixture was cooled to –78 °C again, and a solution of 12 (1.00 g, 2.78 mmol) in THF (4 mL) was added slowly. The resulting mixture was allowed to warm to 0 °C and stirred for 40 min. The reaction was quenched by addition of saturated aqueous NH\(_4\)Cl. The mixture was extracted with Et\(_2\)O (15 mL × 3). The combined organic layers were washed with brine (15 mL × 1), dried over Mg\(_2\)SO\(_4\), and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane only) to give 14 (864 mg, 87%) as a colorless oil: IR (neat) 2956, 2926, 2871, 1465, 1457, 1376 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 6.75 (dd, \(J = 16.9, 10.5, 10.1\) Hz, 1H), 6.19 (brd, \(J = 10.5\), \(3^3J_{Sn-H} = 76.1\) Hz, \(3^3J_{Sn-H} = 54.5\) Hz, 1H), 5.14 (dd, \(J = 16.9, 2.0\) Hz, 1H), 5.07 (dd, \(J = 10.1, 2.0\) Hz, 1H), 2.00 (d, \(J = 1.7\) Hz, \(3^3J_{Sn-H} = 46.1\) Hz, 3H), 1.52-1.44 (m, 6 H), 1.37-1.25 (sextet, \(J = 7.3\) Hz, 6 H), 0.93-0.87 (m, 15 H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 144.7, 139.5, 131.5, 115.8, 29.1, 27.4, 19.8, 13.7, 9.1; HRMS (APCI) \(m/z\) [M+H]\(^+\) calcd for \([C_{17}H_{35}Sn]\) 359.1758, found 359.1761.

2-((1E,3E)-4-Iodopenta-1,3-dienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10)
To a solution of 14 (813 mg, 2.28 mmol) and Vinylboronic acid pinacol ester 15 (702 mg, 4.56 mmol) in dry CH₂Cl₂ (11.4 mL) was added Hoveyda-Grubbs 1st catalyst (205 mg, 342 µmol). The brick red solution was refluxed for 19 h. The mixture was then concentrated in vacuo to give 18 as a dark yellow oil. A solution of the resulting 18 in CH₂Cl₂ (5.0 mL) was added dropwise to a solution of I₂ (1.16 g, 4.56 mmol) and Na₂CO₃ (966 mg, 9.12 mmol) in CH₂Cl₂ (17.8 mL) at 0 °C. The mixture was stirred at 0 °C for 15 min and quenched with saturated aqueous Na₂S₂O₃. The mixture was extracted with CH₂Cl₂ (10 mL × 3). The combined organic layers were washed with brine (20 mL × 1), dried over MgSO₄, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 100 : 1) to give 10 (426 mg, 2 steps 58%) as a dark yellow oil: IR (neat) 2978, 2929, 1614, 1379, 1357, 1328 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.07 (dd, J = 10.7, 17.4 Hz, 1 H), 6.87 (brd, J = 10.7 Hz, 1 H), 5.49 (d, J = 17.4 Hz, 1 H), 2.60 (d, J = 1.3 Hz, 3 H), 1.27 (s, 12 H); ¹³C NMR (75 MHz, CDCl₃) δ 143.1, 142.6, 103.1, 83.4, 28.7, 24.7, [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ¹¹B nucleus]; HRMS (APCI) m/z [M+H]⁺ calcd for [C₁₁H₁₉BIO₂]⁺ 321.0519, found 321.0519.

(1R,3S,6R)-1,5,5-Trimethyl-6-((3E,5E)-3-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-3,5-dien-1-ynyl)-7-oxa-bicyclo[4.1.0]heptan-3-ol (8)

To a solution of epoxyacetylene 9 (200 mg, 1.11 mmol) and vinyl iodide 10 (352 mg, 1.11 mmol) in i-Pr₂NH (5.5 mL) was added Pd(PPh₃)₄ (64.0 mg, 55.4 µmol) and cuprous iodide (21.0 mg, 110 µmol) at room temperature. The mixture was stirred at room temperature for 1 h, and quenched with saturated aqueous NH₄Cl. The mixture was extracted with EtOAc (5 mL × 3). The combined organic layers were washed with brine (5 mL × 1), dried over MgSO₄, and concentrated in vacuo. The residue was
purified by flash column chromatography on silica gel (hexane/EtOAc = 85 : 15) to give 8 (314 mg, 77%) as a yellow oil: [α]$_{D}^{20}$ $\approx$ -2.7 (c 2.00, CHCl$_3$); IR (neat) 2978, 2929, 1611, 1384, 1335 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.22 (dd, $J$ = 17.5, 11.3 Hz, 1 H), 6.42 (d, $J$=11.3 Hz, 1 H), 5.59 (d, $J$ = 17.5 Hz, 1 H), 3.83 (m, 1 H), 2.36 (ddd, $J$ = 14.2, 5.0, 1.6 Hz, 1 H), 1.97 (d, $J$ = 1.0 Hz, 3 H), 1.95-1.90 (br, 1 H), 1.64 (dd, $J$ = 14.2, 8.7 Hz, 1 H), 1.60 (m, 1 H), 1.50 (s, 3 H), 1.27 (s, 12 H), 1.23 (m, 1 H), 1.12 (s, 3 H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 143.9, 137.7, 122.0, 89.2, 87.6, 83.3, 67.2, 63.9, 63.8, 45.9, 39.9, 34.5, 29.9, 25.6, 24.7, 21.6, 17.9, [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}$B nucleus]; HRMS (ESI) m/z [M+Na]$^+$ calcd for [C$_{22}$H$_{33}$BNaO$_4$]$^+$ 395.2368, found 395.2365.

$(1R,3S,6R)$-6-((3E,5E,7E)-9-Hydroxy-3,7-dimethylnona-3,5,7-trien-1-ynyl)-1,5,5-trimethyl-7-oxa-bicyclo[4.1.0]heptan-3-ol (21)

To a solution of 8 (707 mg, 1.90 mmol) and allyl alcohol 20 (414 mg, 2.09 mmol) in DMSO (9.5 mL) was added Cs$_2$CO$_3$ (2.48 g, 7.60 mmol), Pd(OAc)$_2$ (21.3 mg, 95.0 µmol) and SPhos (78.0 mg, 190 µmol) at room temperature. The mixture was stirred at 35 ºC for 17 h, and quenched with H$_2$O. The mixture was extracted with EtOAc (5 mL x 3). The combined organic layers were washed with brine (5 mL x 1), dried over MgSO$_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 3 : 1) to give 21 (362 mg, 60%) as a yellow oil: [α]$_{D}^{25}$ $\approx$ -2.5 (c 0.50, CHCl$_3$); IR (neat) 3392, 2964, 2927, 1447, 1383, 1365, 1261, 1215, 1098, 1048, 1029 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 6.45-6.35 (m, 2H), 6.29 (dd, $J$ = 14.6, 6.5 Hz, 1H), 5.72 (t, $J$ = 6.9 Hz, 1H), 4.29 (d, $J$ = 6.9 Hz, 2H), 3.82 (m, 1H), 2.35 (ddd, $J$ = 14.4, 5.1, 1.5 Hz, 1H), 1.92 (s, 3H), 1.81 (s, 3H), 1.65-1.55 (m, 3H), 1.63 (dd, $J$ = 14.1, 8.7 Hz, 1H), 1.50 (s, 3H), 1.26 (s, 3H), 1.20 (dd, $J$ = 10.5, 2.7 Hz, 1H), 1.12 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 138.2, 136.4, 136.2, 132.0, 123.7, 117.8, 89.8, 86.3, 67.2, 64.0, 63.8, 59.4, 45.9, 39.9, 34.5, 29.9, 25.6, 21.6, 17.6, 12.5; HRMS (ESI) m/z [M+H]$^+$ calcd for [C$_{20}$H$_{29}$O$_3$]$^+$ 317.2117, found 317.2117.
(1R,3S)-1,5,5-Trimethyl-6-((3E,5E,7E,9E)-3,7-dimethyl-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-1,3,5,7,9-pentaenylidene)cyclohexane-1,3-diol (3)

To a solution of 21 (170 mg, 537 µmol) in CH₂Cl₂ (5.4 mL) was added dropwise diisobutylaluminum hydride (1.02 M in hexane, 2.6 mL, 2.69 mmol) at 0 °C. After the reaction mixture was stirred for 30 min at the same temperature, aqueous potassium sodium tartrate was added. The mixture was extracted with EtOAc (5 mL × 3). The organic layers were combined, washed with brine (5 mL × 1), dried over MgSO₄, filtered and concentrated in vacuo to give the crude allenic triol 22, which was used to the next reaction without further purification.

To a solution of 22 (120 mg, 0.38 mmol) in ethyl acetate (5.4 mL) was added MnO₂ (2.1 g, 4.0 g/mmol) at room temperature. After the reaction mixture was stirred at room temperature for 10 min, filtered and concentrated in vacuo to afford the crude aldehyde 23, which was used to the next reaction without further purification.

To a suspension of methyltriphenylphosphonium bromide (575 mg, 1.61 mmol) in dry THF (3.0 mL) at −78 °C under argon was added n-BuLi (607 µL of a 2.65 M solution in hexane, 1.56 mmol). The mixture was warmed to 0 °C and stirred for 1 h. The mixture was cooled to −78 °C again, and a solution of 23 in THF (2.4 mL) was added slowly. The resulting mixture was allowed to warm to 0 °C and stirred for 10 min. The reaction was quenched by addition of saturated aqueous NH₄Cl. The mixture was extracted with EtOAc (3 mL × 3). The combined organic layers were washed with brine (5 mL × 1), dried over MgSO₄, and concentrated in vacuo to give the crude tetraene 7, which was used to the next reaction without further purification.

To a solution of 7 and Vinylboronic acid pinacol ester 15 (120 mg, 782 µmol) in dry CH₂Cl₂ (4.0 mL) was added Grubbs 1st catalyst (16.1 mg, 19.6 µmol). The purple solution was refluxed for 3 h. The mixture was then concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5 : 1) to give 3 (71.0 mg, 4 steps 30%) as an orange oil: [α]²⁵6D −20.4 (c 0.50, CHCl₃); IR (neat): 3380, 2975, 2926, 2856, 1929, 1595, 1576, 1456, 1340, 1142, 1040 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.39 (dd, J = 17.4, 11.2 Hz, 1H), 6.62 (dd, J = 15.0, 11.2 Hz, 1H), 6.30 (d, J = 15.0 Hz, 1H), 6.17 (d, J = 11.2 Hz, 1H), 6.09 (d, J = 11.2 Hz, 1H), 6.01 (s, 1H), 5.59 (d, J = 17.4 Hz, 1H), 4.30 (m, 1H), 2.25 (m, 1H), 2.00 (s, 3H), 2.00-1.75 (m, 1H),
1.79 (s, 3H), 1.80-1.50 (m, 2H), 1.34 (s, 3H), 1.32 (s, 3H), 1.30-1.25 (m, 2H), 1.27 (s, 12H), 1.06 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.3, 145.4, 139.4, 136.8, 133.2, 132.8, 128.1, 126.3, 117.7, 103.1, 83.1, 72.9, 64.2, 49.4, 48.9, 35.8, 32.1, 31.3, 29.3, 24.7, 13.9, 13.0, [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}$B nucleus]; HRMS (ESI) $m/z$ [M+Na]$^+$ calcd for [C$_{27}$H$_{41}$BNaO$_4$]$^+$ 463.2996, found 463.2983.

2-((1E,3E,5E,7E,9E,11E)-14-((2R,4S)-2,4-Dihydroxy-2,6,6-trimethylcyclohexylidene)-3,8,12-trimethyltetradeca-1,3,5,7,9,11,13-heptaenyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (24)

To a solution of 3 (13.0 mg, 29.5 µmol) and vinyl iodide 4 (10.3 mg, 29.5 µmol) in DMSO (295 µL) was added Cs$_2$CO$_3$ (38.4 mg, 118 µmol), Pd(OAc)$_2$ (0.3 mg, 1.48 µmol) and SPhos (1.2 mg, 2.95 µmol) at room temperature. The mixture was stirred at 35 °C for 17 h, and quenched with H$_2$O. The mixture was extracted with EtOAc (2 mL $\times$ 3). The combined organic layers were washed with brine (2 mL $\times$ 1), dried over MgSO$_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (EtOAc only) to give 24 (10.0 mg, 63%) as a yellow solid: $[^{25}$D$]_{D}$ -22.9 (c 0.49, MeOH); IR (neat) 3419, 2963, 2925, 1929, 1763, 1604, 1457, 1341, 1295, 1246, 1153, 1114, 1089, 1033, 991, 958 cm$^{-1}$; $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 6.69 (d, $J = 18.0$ Hz, 1H), 6.75-6.55 (m, 3H), 6.40-6.25 (m, 3H), 6.12 (d, $J = 11.2$ Hz, 1H), 6.05 (s, 1H), 5.68 (d, $J = 18.0$ Hz, 1H), 4.20 (m, 1H), 4.15 (d, $J = 16.8$ Hz, 2H), 3.97 (d, $J = 16.8$ Hz, 2H), 2.84 (s, 3H), 2.18 (brd, $J = 12.8$ Hz, 1H), 2.00-1.75 (m, 1H), 1.96 (s, 3H), 1.95 (s, 3H), 1.82 (s, 3H), 1.40-1.20 (m, 2H), 1.33 (s, 3H), 1.31 (s, 3H), 1.06 (s, 3H); $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 203.7, 171.2, 148.4, 138.2, 137.8, 137.4, 134.6, 133.33, 133.27, 132.1, 131.0, 129.4, 126.2, 118.5, 103.8, 73.2, 64.7, 62.6, 50.6, 50.1, 47.5, 36.7, 32.9, 31.4, 29.5, 14.2, 12.8, 12.6, [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}$B nucleus]; HRMS (ESI) $m/z$ [M+Na]$^+$ calcd for [C$_{31}$H$_{42}$BNaO$_6$]$^+$ 558.3003, found 558.3002.
To a solution of 24 (10 mg, 18.7 µmol) and methyl ketone 5 (4.0 mg, 18.7 µmol) in (THF/H₂O = 5 : 1) (374 µL) was added NaOH (5.6 mg, 140 µmol), Pd(OAc)₂ (0.2 mg, 0.935 µmol) and SPhos (0.8 mg, 1.87 µmol) at room temperature. The mixture was stirred at room temperature for 20 min, and quenched with H₂O. The mixture was extracted with EtOAc (2 mL × 3). The combined organic layers were washed with brine (2 mL × 1), dried over MgSO₄, and concentrated in vacuo. The residue was purified by preparative thin layer chromatography on silica gel (hexane/EtOAc = 1 : 2) to give paracentrone 1 (6.8 mg, 65%, all-trans form) as a red solid. The spectral data of the resulting 1 were in good agreement with those of the reported data.

1 (all-trans form): mp 145–149 °C; IR (neat) 3361, 2922, 2853, 1923, 1734, 1653, 1647, 1606, 1368, 1278, 1229, 1154, 956 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.14 (d, J = 10.8 Hz, 1H), 6.75-6.55 (m, 5H), 6.39 (d, J = 11.2 Hz, 1H), 6.36 (d, J = 15.2 Hz, 1H), 6.26 (d, J = 10.8 Hz, 1H), 6.12 (d, J = 11.6 Hz, 1H), 6.03 (s, 1H), 4.32 (m, 1H), 2.36 (s, 3H), 2.26 (brd, J = 11.8 Hz, 1H), 1.992 (s, 3H), 1.985 (s, 3H), 2.00-1.95 (m, 1H), 1.94 (s, 3H), 1.81 (s, 3H), 1.55 (brs, 2H), 1.45-1.30 (m, 2H), 1.35 (s, 3H), 1.34 (s, 3H), 1.07 (s, 3H); ¹H NMR (400 MHz, C₆D₆) δ 6.94 (d, J = 12.4 Hz, 1H), 6.79-6.70 (m, 2H), 6.66-6.55 (m, 1H), 6.54-6.45 (m, 3H), 6.33 (d, J = 13.5 Hz, 1H), 6.32 (d, J = 12.6 Hz, 1H), 6.23 (d, J = 10.8 Hz, 1H), 6.05 (s, 1H), 4.22 (m, 1H), 2.14 (ddd, J = 12.8, 4.0, 2.1 Hz, 1H), 2.09 (s, 3H), 1.99 (s, 3H), 1.88 (s, 3H), 1.85-1.75 (m, 1H), 1.81 (s, 3H), 1.77 (s, 3H), 1.37 (s, 3H), 1.26-1.20 (m, 2H), 1.21 (s, 3H), 1.12 (s, 3H), 0.74 (brs, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 202.4, 199.4, 144.5, 140.0, 137.9, 137.0, 136.2, 135.6, 132.6, 132.2, 132.1, 129.4, 128.4, 125.6, 123.7, 117.7, 103.2, 73.0, 64.3, 49.5, 49.0, 35.8, 32.1, 31.4, 29.3, 25.6, 14.0, 12.9, 12.7, 11.7; HRMS (ESI) m/z [M+Na]⁺ calcd for [C₃₁H₄₂NaO₃]⁺ 485.3032, found 485.3039.

References


$\text{Bu}_3\text{SnBO}_{16}$(in CDCl$_3$)
Bu$_3$SnBO$_{16}$ (in CDCl$_3$)
(in CDCl$_3$)
I

B

17

(in CDCl₃)
4 (in d₆-acetone)
Bu$_3$Sn (in CDCl$_3$)
Bu3Sn14 (in CDCl3)
(in CDCl₃)
10 (in CDCl₃)
3 (in CDCl₃)
paracentrone (1)
in C₆D₆