Supporting Information

Total Synthesis of (+)-Benzastatin E via Diastereoselective Grignard Addition to 2-Acy lindoline

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General Information.

Unless otherwise noted, all reactions were carried out in oven-dried glassware under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from sodium metal/benzophenone ketyl. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride. All other dry solvents were purchased from Aldrich in SureSeal^{TM} containers. All other commercially obtained reagents were used as received. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian 400 or 500 spectrometer. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broadened. Infrared spectra were recorded on a JASCO FT-IR-8900 spectrometer. Mass spectra were obtained on a JEOL HX-100, a SX-102A or a JMS-AX-505H mass spectrometer. Optical rotations were measured on a JASCO P-1030 polarimeter. Analytical TLC was performed on 0.25 mm pre-coated Merck silica gel 60 F₂₅₄ plates. Flash column chromatography was performed on Merck silica gel 60 (230–400 mesh).

General procedure for the diastereoselective Grignard addition to 2-acy lindoline

To a solution of 2-acy lindoline (1.0 mmol) in THF (10 ml) was added Grignard reagent in THF (3.0 mmol) dropwise at -78°C . The mixture was stirred for 30 min at -78°C . The reaction was quenched with sat. NH_4Cl (10 ml) and extracted with AcOEt (20 ml x 2). The combined organic extracts were washed with brine (20 ml), dried over Na_2SO_4 , filtered and evaporated. The diastereoselectivity was determined by HPLC analysis. Purification by silica gel column chromatography gave the corresponding product.

7a: mp $58\text{--}60^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 1.50 (9H, br), 3.00 (1H, dd, $J = 4.5, 16.5$), 3.43 (3H, s), 3.47 (1H, br), 4.18 (2H, br), 5.03 (1H, br), 6.94 (1H, t, $J = 7.5$), 7.10 (1H, d, $J = 7.5$), 7.19 (1H, br s), 7.48 (0.4H,

br), 7.90 (0.6H, br); ^{13}C NMR (125 MHz, CDCl_3) δ 28.2, 30.9, 31.7, 59.4, 63.3, 64.0, 74.8, 75.4, 81.6, 114.7, 122.6, 124.5, 127.9, 141.7, 142.5, 151.4, 152.5, 204.8; IR (KBr) cm^{-1} : 2976, 1732, 1704, 1488, 1395, 1154, 1111, 762; HRMS calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_4\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 314.1368, found 314.1373; Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_4$: C, 65.96; H, 7.27; N, 4.81. Found: C, 65.91; H, 7.11; N, 4.84; $[\alpha]_{\text{D}}^{24} = -92.4^\circ$ (c 0.65, CHCl_3).

7b: mp 74-76 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 1.07 (3H, t, $J = 6.5$), 1.48 (9H, br), 2.53 (2H, br), 2.94 (1H, dd, $J = 5.0, 16.5$), 3.48 (1H, br), 4.83 (1H, br), 6.95 (1H, t, $J = 7.5$), 7.10 (1H, d, $J = 7.5$), 7.20 (1H, br s), 7.91 (1H, br); ^{13}C NMR (125 MHz, CDCl_3) δ 7.35, 28.2, 30.5, 31.9, 66.3, 81.5, 114.7, 122.6, 124.4, 127.9, 142.6, 151.6, 160.9, 208.7; IR (KBr) cm^{-1} : 2978, 1720, 1700, 1485, 1397, 1322, 1151, 748; HRMS calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_3$ (M) $^+$ 275.1521, found 275.1524; Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.57; H, 7.61; N, 5.13; $[\alpha]_{\text{D}}^{24} = -80.2^\circ$ (c 0.32, CHCl_3).

7c: $[\alpha]_{\text{D}}^{24} = +46.9^\circ$ (c 0.88, CHCl_3).

7d: mp 100-102 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 1.50 (9H, br), 2.15 (3H, br s), 2.97 (1H, dd, $J = 5.0, 16.5$), 3.47 (1H, br), 4.78 (1H, br), 6.95 (1H, t, $J = 7.5$), 7.12 (1H, d, $J = 7.5$), 7.20 (1H, br s), 7.49 (0.4H, br), 7.90 (0.6H, br); ^{13}C NMR (125 MHz, CDCl_3) δ 24.7, 28.2, 31.6, 66.8, 81.7, 114.8, 122.7, 124.5, 128.0, 142.5, 151.6, 206.2; IR (KBr) cm^{-1} : 2984, 1699, 1485, 1395, 1321, 1262, 1157, 752; HRMS calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3$ (M) $^+$ 261.1364, found 261.1360; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.90; H, 7.01; N, 5.40; $[\alpha]_{\text{D}}^{24} = -82.8^\circ$ (c 0.28, CHCl_3).

7e: ^1H NMR (400 MHz, CDCl_3) δ 1.48 (9H, br), 1.65 (3H, s), 1.68 (3H, s), 2.26 (2H, q, $J = 7.2$), 2.39-2.56 (2H, m), 2.91 (1H, dd, $J = 5.2, 16.8$), 3.43 (1H, br t, $J = 14.0$), 4.81 (1H, br), 5.11 (1H, dt, $J = 1.2, 7.6$), 7.20 (1H, s), 7.30 (1H, d, $J = 7.2$), 7.74 (1H, br); ^{13}C NMR (100 MHz, CDCl_3) δ 17.7, 21.9, 25.7, 28.2, 29.6, 31.3, 37.7, 42.8, 66.4, 81.9, 114.9, 116.0, 122.3, 124.6, 127.3, 130.7, 132.9, 141.8, 206.7; IR (CHCl_3) cm^{-1} : 2977, 2930, 1708, 1477, 1373, 1257, 1151; HRMS calcd for $\text{C}_{20}\text{H}_{26}\text{NO}_3\text{BrNa}$ ($\text{M} + \text{Na}$) $^+$ 430.0994, found 430.0969; $[\alpha]_D^{24} = -25.3^\circ$ (c 0.65, CHCl_3).

7f: ^1H NMR (400 MHz, CDCl_3) δ 1.49 (9H, br), 2.98 (1H, dd, $J = 4.4, 16.8$), 3.44 (3H, s), 3.48 (1H, br), 4.16 (2H, br), 5.07 (1H, br), 7.21 (1H, s), 7.31 (1.5H, br), 7.79 (1H, br); ^{13}C NMR (125 MHz, CDCl_3) δ 28.9, 31.1, 32.0, 60.3, 63.9, 64.7, 75.8, 82.7, 115.7, 116.8, 128.2, 131.5, 142.7, 151.9, 205.0; IR (CHCl_3) cm^{-1} : 2981, 1707, 1478, 1372, 1256, 1153, 1106, 1023, 909; HRMS calcd for $\text{C}_{16}\text{H}_{20}\text{NO}_4\text{Br}$ (M) $^+$ 369.0573, found 369.0567; $[\alpha]_D^{24} = -53.9^\circ$ (c 1.07, CHCl_3).

8a: ^1H NMR (500 MHz, CDCl_3) δ 0.83 (3H, t, $J = 7.0$), 1.24-1.31 (1H, m), 1.35-1.38 (1H, m), 1.57 (9H, s), 3.03 (1H, dd, $J = 2.0, 16.5$), 3.28 (1H, dd, $J = 10.5, 16.5$), 3.64 (3H, s), 3.39 (1H, d, $J = 10.0$), 3.41 (1H, d, $J = 10.0$), 4.80 (1H, d, $J = 9.5$), 6.95 (1H, t, $J = 7.5$), 7.11-7.15 (2H, m), 7.45 (1H, br); ^{13}C NMR (125 MHz, CDCl_3) δ 7.26, 24.9, 28.3, 30.1, 59.3, 64.6, 76.0, 82.1, 116.3, 122.8, 124.1, 126.9, 131.9, 142.8; IR (CHCl_3) cm^{-1} : 3373, 2981, 1667, 1484, 1382, 1331, 1287, 1165, 1115, 1015; HRMS calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_4\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 344.1838, found 344.1845; $[\alpha]_D^{24} = -62.1^\circ$ (c 0.80, CHCl_3).

8b: ^1H NMR (400 MHz, CDCl_3) δ 0.97 (3H, t, $J = 7.8$), 1.58 (9H, s), 1.61-1.70 (2H, m), 2.83 (3H, s), 3.06 (1H, d, $J = 9.0$), 3.13 (1H, dd, $J = 2.0, 16.0$), 3.16 (1H, d, $J = 9.0$), 3.25 (1H, dd, $J = 10.4, 16.0$), 4.66 (1H, dd, $J = 2.0, 10.4$), 6.96 (1H, t, $J = 7.2$), 7.12-7.21 (2H, m), 7.45 (1H, br d, $J = 6.4$); ^{13}C NMR (100 MHz, CDCl_3) δ 7.05, 27.2, 28.3, 30.4, 58.5, 65.3, 74.6, 76.2, 82.2, 114.5, 116.1, 122.8, 123.9, 126.4, 132.3, 142.0; IR (CHCl_3) cm^{-1} : 3385, 2981, 1659, 1484, 1387, 1165; HRMS calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_4\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 344.1837, found

344.1860; $[\alpha]_D^{24} = -78.5^\circ$ (c 0.43, CHCl_3).

8c: ^1H NMR (500 MHz, CDCl_3) δ 0.85 (3H, t, $J = 7.3$), 1.30 (1H, dq, $J = 7.3, 14.2$), 1.39 (1H, dq, $J = 7.3, 15.2$), 1.57 (9H, s), 3.04 (1H, d, $J = 16.6$), 3.26 (1H, dd, $J = 10.7, 16.6$), 3.35 (3H, s), 3.38 (2H, s), 4.78 (1H, br d, $J = 9.8$), 7.24 (2H, m), 7.33 (1H, br s); ^{13}C NMR (100 MHz, CDCl_3) δ 7.3, 14.1, 25.2, 28.3, 29.8, 59.3, 64.7, 75.7, 77.0, 82.3, 115.4, 117.6, 127.1, 129.8, 134.5, 142.2; IR (KBr) cm^{-1} : 3412, 2976, 2928, 1702, 1671, 1477, 1370, 1168, 1137, 1110; HRMS calcd for $\text{C}_{18}\text{H}_{26}\text{NO}_4\text{BrNa}$ ($\text{M} + \text{Na}$) $^+$ 422.0943, found 422.0927; $[\alpha]_D^{24} = +36.4^\circ$ (c 1.21, CHCl_3).

8d: ^1H NMR (500 MHz, CDCl_3) δ 1.60 (9H, s), 2.85 (1H, d, $J = 16.5$), 2.99 (1H, dd, $J = 10.0, 16.5$), 3.28 (3H, s), 3.73 (1H, d, $J = 10.0$), 3.87 (1H, d, $J = 10.0$), 4.91 (1H, br), 6.90 (1H, t, $J = 7.5$), 7.03 (1H, d, $J = 7.5$), 7.11 (1H, t, $J = 7.5$), 7.24 (1H, t, $J = 7.5$), 7.33 (2H, t, $J = 7.5$), 7.48 (3H, d, $J = 7.5$); ^{13}C NMR (125 MHz, CDCl_3) δ 28.3, 30.0, 59.4, 64.8, 77.9, 79.5, 81.4, 115.9, 122.7, 123.7, 125.6, 126.6, 127.1, 128.1, 128.2, 132.4, 142.3; IR (CHCl_3) cm^{-1} : 3549, 2981, 2932, 1685, 1602, 1484, 1381, 1282, 1258, 1166, 1135; HRMS calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_4\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 392.1838, found 392.1837; $[\alpha]_D^{24} = -41.7^\circ$ (c 0.53, CHCl_3).

8e: ^1H NMR (500 MHz, CDCl_3) δ 1.00 (3H, s), 1.22 (3H, s), 1.58 (9H, s), 2.84 (1H, d, $J = 16.5$), 3.32 (1H, dd, $J = 10.5, 16.5$), 4.51 (1H, d, $J = 10.5$), 6.95 (1H, t, $J = 7.5$), 7.12 (1H, d, $J = 7.5$), 7.15 (1H, t, $J = 7.5$), 7.47 (1H, br); ^{13}C NMR (125 MHz, CDCl_3) δ 23.3, 26.8, 28.2, 30.9, 67.5, 74.3, 82.1, 116.2, 122.9, 124.1, 127.0, 131.4, 142.5; IR (CHCl_3) cm^{-1} : 3405, 2981, 1665, 1484, 1384, 1288, 1256, 1165, 1045, 1019; HRMS calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_3\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 300.1576, found 300.1568; $[\alpha]_D^{24} = -69.7^\circ$ (c 0.69, CHCl_3).

8f: ^1H NMR (400 MHz, CDCl_3) δ 1.58 (9H, s), 3.03 (1H, dd, $J = 2.0, 16.8$), 3.27 (1H, dd, $J = 10.0, 16.8$), 3.40 (3H, s), 3.43 (1H, d, $J = 9.6$), 3.54 (1H, d, $J = 9.6$), 4.74 (1H, d, $J = 10.0$), 5.14 (1H, dd, $J = 1.2, 11.0$), 5.42 (1H, dd, $J = 1.2, 17.2$), 5.66 (1H, dd, $J = 11.0, 17.2$), 6.94 (1H, t, $J = 7.2$), 7.10-7.15 (2H, m), 7.44 (1H, br); ^{13}C NMR (125 MHz, CDCl_3) δ 28.3, 29.8, 30.0, 59.5, 63.6, 78.7, 82.0, 116.1, 116.4, 122.8, 123.9, 126.9, 131.7, 136.8, 142.7; IR (CHCl_3) cm^{-1} : 3357, 2982, 2931, 1686, 1484, 1383, 1287, 1258, 1352, 1166, 1133, 1017, 936; HRMS calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_4\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 342.1681, found 342.1682; $[\alpha]_D^{24} = -56.6^\circ$ (c 0.69, CHCl_3).

8g: ^1H NMR (500 MHz, CDCl_3) δ 1.61 (9H, s), 1.84 (3H, s), 3.08-3.16 (2H, m), 3.37 (3H, s), 3.52 (1H, d, $J = 10.0$), 3.75 (1H, d, $J = 10.0$), 4.73 (1H, br), 5.09 (1H, s), 5.22 (1H, s), 6.96 (1H, t, $J = 7.5$), 7.13-7.17 (2H, m), 7.52 (1H, br); ^{13}C NMR (125 MHz, CDCl_3) δ 19.6, 28.2, 29.3, 59.3, 61.5, 75.7, 80.6, 81.2, 113.6, 116.0, 122.7, 123.6, 126.4, 132.6, 142.9, 145.2, 153.7; IR (CHCl_3) cm^{-1} : 3559, 2980, 2930, 1685, 1484, 1373, 1285, 1166, 1135, 1014, 911; HRMS calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_4\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 356.1838, found 356.1838; $[\alpha]_D^{24} = -53.1^\circ$ (c 0.23, CHCl_3).

8h: ^1H NMR (400 MHz, CDCl_3) δ 0.89 (3H, s), 1.47-1.54 (2H, m), 1.57 (9H, s), 1.63 (3H, s), 1.69 (3H, s), 2.12-2.21 (2H, m), 2.77 (1H, d, $J = 16.8$), 3.30 (1H, dd, $J = 10.4, 16.8$), 4.60 (1H, dd, $J = 2.4, 10.4$), 5.12 (1H, t, $J = 6.4$), 7.23-7.33 (3H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 17.5, 20.9, 21.5, 25.5, 28.1, 30.5, 39.2, 66.5, 75.9, 82.7, 115.4, 117.5, 124.2, 127.1, 129.9, 131.5, 133.6, 141.8, 155.0; IR (CHCl_3) cm^{-1} : 3437, 2979, 1668, 1477, 1372, 1163, 1015; HRMS calcd for $\text{C}_{21}\text{H}_{30}\text{NO}_3\text{Br}$ (M) $^+$ 423.1409, found 423.1400; $[\alpha]_D^{24} = -72.1^\circ$ (c 0.38, CHCl_3).

8i: ^1H NMR (500 MHz, CDCl_3) δ -0.13 (9H, s), 1.58 (9H, s), 3.05 (1H, d, $J = 16.5$), 3.38 (1H, dd, $J = 10.5, 16.5$), 3.47 (3H, s), 3.54 (1H, d, $J = 10.5$), 3.66 (1H, d, $J = 10.5$), 4.90 (1H, d, $J = 10.5$), 6.95 (1H, t, $J = 7.5$), 7.11 (1H, d, $J = 7.5$), 7.13 (1H, t, $J = 7.5$), 7.42 (1H, br); ^{13}C NMR (125 MHz, CDCl_3) δ -0.55, 28.2, 31.1, 59.8, 63.5, 75.0, 82.5, 89.8, 102.7, 116.2, 122.8, 124.0, 126.7, 131.6, 142.5; IR (CHCl_3) cm^{-1} : 3317, 2981, 1664, 1484, 1383, 1251, 1165, 1135, 861, 845; HRMS calcd for $\text{C}_{21}\text{H}_{31}\text{NO}_4\text{SiNa}$ ($\text{M} + \text{Na}$) $^+$ 412.1920, found 412.1941; $[\alpha]_D^{24} = -68.8^\circ$ (c 0.35, CHCl_3).

8j: ^1H NMR (500 MHz, CDCl_3) δ 1.26 (1H, dt, $J = 5.0, 14.0$), 1.34-1.40 (1H, m), 1.53 (3H, s), 1.56 (9H, s), 1.62 (3H, s), 1.91-1.97 (1H, m), 2.01-2.07 (1H, m), 3.04 (1H, d, $J = 16.5$), 3.26 (1H, dd, $J = 10.5, 16.5$), 3.33 (3H, s), 3.38 (2H, s), 4.76 (1H, d, $J = 10.5$), 4.96 (1H, t, $J = 7.0$), 7.21-7.24 (2H, m), 7.32 (1H, br); ^{13}C NMR (125 MHz, CDCl_3) δ 17.4, 21.5, 25.5, 28.1, 29.7, 32.5, 59.2, 64.8, 76.9, 82.3, 115.3, 117.5, 124.3, 127.0, 129.6, 131.3, 134.2, 142.0, 154.4; IR (CHCl_3) cm^{-1} : 3381, 2981, 2930, 1672, 1477, 1371, 1254, 1164; HRMS calcd for $\text{C}_{22}\text{H}_{32}\text{NO}_4\text{BrNa}$ ($\text{M} + \text{Na}$) $^+$ 476.1412, found 476.1412; $[\alpha]_D^{24} = -43.5^\circ$ (c 0.93, CHCl_3).

8k: ^1H NMR (400 MHz, CDCl_3) δ 1.53 (9H, s), 2.54 (1H, dt, $J = 5.2, 11.8$), 2.67 (1H, dt, $J = 5.2, 11.8$), 3.04 (1H, d, $J = 16.9$), 3.25 (1H, dd, $J = 10.3, 16.9$), 3.32 (3H, s), 3.38 (2H, s), 4.77 (1H, d, $J = 10.3$), 7.01 (2H, d, $J = 6.6$), 7.07-7.27 (7H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 28.2, 29.3, 29.8, 34.6, 59.3, 65.0, 76.3, 76.7, 82.6, 115.5, 117.7, 125.6, 128.2, 129.8, 134.1, 141.9, 142.4, 154.6; IR (film) cm^{-1} : 3394, 2978, 2930, 1702, 1668, 1476, 1369, 1329, 1166, 1137, 757; HRMS calcd for $\text{C}_{24}\text{H}_{30}\text{NO}_4\text{BrNa}$ ($\text{M} + \text{Na}$) $^+$ 498.1256, found 498.1265; $[\alpha]_D^{24} = -37.8^\circ$ (c 1.03, CHCl_3).

8l: ^1H NMR (400 MHz, CDCl_3) δ 1.28-1.36 (1H, m), 1.38-1.46 (1H, m), 1.57 (9H, s), 1.95-2.04 (1H, m), 2.13-2.24 (1H, m), 3.04 (1H, d, $J = 16.9$), 3.26 (1H, dd, $J = 9.5, 16.9$), 3.35 (3H, s), 3.38 (2H, s), 4.77 (1H, d, $J = 10.9$), 4.87 (1H, d, $J = 10.9$), 4.92 (1H, d, $J = 19.1$), 5.66-5.76 (1H, m), 7.24-7.26 (2H, m), 7.32 (1H, br); ^{13}C NMR (125 MHz, CDCl_3) δ 27.2, 28.2, 29.8, 31.6, 59.3, 64.9, 76.0, 76.7, 82.5, 114.2, 115.4, 117.6, 127.1,

129.8, 134.2, 138.8, 142.0, 154.2; IR (film) cm^{-1} : 3401, 2977, 2928, 1703, 1670, 1477, 1369, 1167, 1015, 815; HRMS calcd for $\text{C}_{20}\text{H}_{28}\text{NO}_4\text{BrNa}$ ($\text{M} + \text{Na}$)⁺ 448.1100, found 448.1122; $[\alpha]_{\text{D}}^{24} = -50.8^\circ$ (c 1.06, CHCl_3).

Total synthesis of (+)-benzastatin E

To a solution of Carboxylic acid **3** (20.0 g, 123 mmol) in MeOH (200 ml) was added sulfuric acid (15 ml) dropwise at room temperature. The mixture was stirred for 6 h at 80 °C. The solvent was removed in vacuo. The residue was neutralized with 15% NaOH aq, then extracted with AcOEt (100 ml x 2). The combined organic extracts were washed with 1N NaOH aq (50 ml x 2), brine (50 ml), dried over Na_2SO_4 , filtered and evaporated to give methyl ester (20.3 g) as a colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 3.31 (1H, dd, $J = 6.0, 16.0$), 3.38 (1H, dd, $J = 10.0, 16.0$), 3.75 (3H, s), 4.38 (1H, dd, $J = 6.0, 10.0$), 4.43 (1H, br), 6.71 (1H, d, $J = 7.5$), 6.74 (1H, t, $J = 7.5$), 7.04 (1H, t, $J = 7.5$), 7.08 (1H, d, $J = 7.5$); ^{13}C NMR (125 MHz, CDCl_3) δ 33.6, 52.4, 59.7, 110.0, 119.4, 124.4, 126.6, 127.6, 149.9, 174.5; IR (film) cm^{-1} : 3372, 2953, 1738, 1609, 1486, 1468, 1203, 1077, 1018, 749; HRMS calcd for $\text{C}_{10}\text{H}_{11}\text{NO}_2$ (M)⁺ 177.0790, found 177.0781; $[\alpha]_{\text{D}}^{24} = +31.2^\circ$ (c 0.86, CHCl_3).

To a solution of above methyl ester (20.3 g, 114 mmol) in CH_2Cl_2 (200 ml), Boc_2O (27.5 g, 125.8 mmol) was added dropwise at room temperature. The mixture was stirred for 12 h at room temperature. The solvent was concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane-AcOEt 5:1) to give **4** (31.3 g, 92% from **3**).

4: mp 43-45 °C; ^1H NMR (500 MHz, CDCl_3) δ 1.50 (9H, br), 3.12 (1H, d, $J = 16.0$), 3.50 (1H, d, $J = 16.0$), 3.72 (3H, s), 4.87 (1H, br), 6.94 (1H, t, $J = 7.0$), 7.11 (1H, d, $J = 7.0$), 7.14-7.22 (1H, m), 7.49 (0.3H, br), 7.89 (0.7H, br); ^{13}C NMR (125 MHz, CDCl_3) δ 28.2, 31.9, 32.6, 52.2, 60.3, 81.2, 82.3, 114.6, 122.5, 124.2, 127.8, 141.6, 142.5, 151.5, 152.6, 172.4; IR (CHCl_3) cm^{-1} : 2981, 1741, 1708, 1604, 1484, 1390, 1255, 1168, 1046; HRMS calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_4$ (M)⁺ 277.1314, found 277.1305; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_4$: C, 64.97; H, 6.91; N, 5.05. Found: C, 64.76; H, 6.70; N, 5.07; $[\alpha]_{\text{D}}^{24} = -70.6^\circ$ (c 0.84, CHCl_3).

NBS (8.79 g, 49.4 mmol) was added to a solution of **4** (13.7 g, 49.4 mmol) in DMF (50 ml) at 0 °C. The mixture was stirred for 2 h at 0 °C. After addition of water (50 ml), the aqueous solution was extracted with

AcOEt (50 ml x 2). The combined organic extracts were washed with water (50 ml), brine (50 ml), dried over Na₂SO₄, filtered and evaporated. Purification by silica gel column chromatography (hexane-AcOEt 5:1 to 2:1) provided **5** (16.4 g, 93%) as a colorless oil.

5: ¹H NMR (500 MHz, CDCl₃) δ 1.49 (9H, br), 3.09 (1H, d, *J* = 16.5), 3.45-3.51 (1H, m), 3.75 (3H, s), 4.86 (1H, br), 7.22 (1H, s), 7.30 (1H, br d, *J* = 7.0), 7.77 (1H, br s); ¹³C NMR (125 MHz, CDCl₃) δ 28.1, 32.2, 52.3, 60.4, 81.6, 114.7, 115.9, 127.3, 130.1, 130.6, 141.7, 151.3, 171.9; IR (CHCl₃) cm⁻¹: 2981, 1745, 1709, 1477, 1377, 1312, 1257, 1159, 1025; HRMS calcd for C₁₅H₁₈NO₄Br (M)⁺ 355.0419, found 355.0418; [α]_D²⁴ = -31.9° (c 0.83, CHCl₃).

To a slurry of Me(MeO)NH·HCl (2.36 g, 24.3 mmol) and **5** (5.76 g, 16.2 mmol) in THF (20 ml) was added *i*-PrMgCl in THF (16.1 ml, 2.0 M) dropwise at -20°C. The mixture was stirred for 20 min at -10°C. To the reaction mixture were added Me(MeO)NH·HCl (2.36 g, 24.3 mmol) and *i*-PrMgCl in THF (16.1 ml, 2.0 M) at -20°C. After stirring for 10 min at -10°C, the reaction was quenched with sat. NH₄Cl aq (80 ml) and extracted with AcOEt (70 ml x 2). The combined organic solution was washed with brine (80 ml), dried over Na₂SO₄, filtered and evaporated. Purification by silica gel column chromatography (hexane-AcOEt 5:1 to 1:1) gave **6** (5.2 g, 83%) as a colorless solid.

6: mp 105-106 °C, ¹H NMR (400 MHz, CDCl₃) δ 1.48 (6H, br s), 1.59 (3H, br s), 2.97 (1H, d, *J* = 16.4), 3.22 (3H, s), 3.47 (1H, dd, *J* = 11.6, 16.4), 3.75 (2H, br s), 3.81 (1H, br s), 5.20 (1H, br), 7.18 (1H, s), 7.28 (1H, br s), 7.35 (0.5H, br), 7.80 (1H, br d, *J* = 8.0); ¹³C NMR (125 MHz, CDCl₃) δ 28.2, 31.6, 32.1, 32.6, 58.5, 58.9, 61.3, 81.3, 82.3, 114.5, 115.9, 127.2, 127.5, 130.5, 134.1, 142.5, 151.5, 172.0; IR (KBr) cm⁻¹: 3000, 1702, 1679, 1478, 1378, 1320, 1256, 1161, 1029, 824; HRMS calcd for C₁₆H₂₁N₂O₄BrNa (M + Na)⁺ 407.0582, found 407.0583; Anal. Calcd for C₁₆H₂₁N₂O₄Br: C, 49.88; H, 5.49; N, 7.27; Br, 20.74. Found: C, 49.99; H, 5.50; N, 7.28; Br, 20.44; [α]_D²⁴ = -89.4° (c 0.90, CHCl₃).

To a solution of MeOCH₂Sn(*n*-Bu)₃ (1.30 g, 3.90 mmol) in THF (10 ml) was added *n*-BuLi in hexane (3.90 ml, 1.6 M) dropwise at -78°C. After stirring for 10 min at -78°C, a solution of Weinreb amide **6** (500 mg, 1.30 mmol) in THF (5 ml) was added to the reaction mixture at -78°C. The mixture was stirred for 15 min at -78°C and quenched with sat. NH₄Cl aq (20 ml). The product was extracted with AcOEt (30 ml x 2) and the organic solution was washed with brine (30 ml), dried over Na₂SO₄, filtered and evaporated. Purification by silica gel

column chromatography (hexane-AcOEt 10:1 to 2:1) gave **7** (295 mg, 61%) as a colorless oil.

7: ^1H NMR (400 MHz, CDCl_3) δ 1.49 (9H, br), 2.98 (1H, dd, $J = 4.4, 16.8$), 3.44 (3H, s), 3.48 (1H, br), 4.16 (2H, br), 5.07 (1H, br), 7.21 (1H, s), 7.31 (1.5H, br), 7.79 (1H, br); ^{13}C NMR (125 MHz, CDCl_3) δ 28.9, 31.1, 32.0, 60.3, 63.9, 64.7, 75.8, 82.7, 115.7, 116.8, 128.2, 131.5, 142.7, 151.9, 205.0; IR (CHCl_3) cm^{-1} : 2981, 1707, 1478, 1372, 1256, 1153, 1106, 1023, 909; HRMS calcd for $\text{C}_{16}\text{H}_{20}\text{NO}_4\text{Br}$ (M) $^+$ 369.0573, found 369.0567; $[\alpha]_D^{24} = -53.9^\circ$ (c 1.07, CHCl_3).

To a solution of ketone **7** (282 mg, 0.761 mmol) in THF (10 ml) was added 3,4-dimethyl-3-pentenylmagnesium bromide in THF (freshly prepared from the corresponding bromide (714 mg, 0.457 mmol) and Mg (146 mg, 0.686 mmol)) dropwise at -78°C . The mixture was stirred for 15 min at -78°C . The reaction was quenched with sat. NH_4Cl aq (20 ml) and extracted with AcOEt (20 ml x 2). The combined organic extracts were washed with brine (20 ml), dried over Na_2SO_4 , filtered and evaporated. The diastereoselectivity (25 : 1) was determined by HPLC analysis (Develosil ODS-HG-5 (0.46cm ϕ x 25cm), $\text{CH}_3\text{CN}-\text{H}_2\text{O}$: 50 /50 to 90/10 for 20 min), flow rate: 1 mL/min). Purification by silica gel column chromatography (hexane-AcOEt 5:1) gave **major-8** (323 mg, 91%) as a colorless oil.

major-8: ^1H NMR (500 MHz, CDCl_3) δ 1.30 (1H, dt, $J = 5.0, 13.0$), 1.40 (1H, dt, $J = 5.0, 13.0$), 1.47 (3H, s), 1.55 (3H, s), 1.56 (3H, s), 1.56 (9H, s), 1.95-2.06 (2H, m), 3.07 (1H, dd, $J = 2.0, 17.5$), 3.27 (1H, dd, $J = 11.0, 17.5$), 3.35 (3H, s), 3.40 (2H, s), 4.74 (1H, d, $J = 9.5$), 7.25-7.33 (3H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 18.0, 19.7, 20.4, 27.9, 28.1, 29.7, 31.2, 59.2, 64.8, 76.2, 76.7, 82.2, 115.3, 117.6, 123.9, 127.0, 127.2, 129.6, 134.3, 142.0; IR (CHCl_3) cm^{-1} : 3554, 3373, 2983, 2927, 1672, 1477, 1371, 1255, 1164, 1016, 909; HRMS calcd for $\text{C}_{23}\text{H}_{34}\text{NO}_4\text{BrNa}$ ($\text{M} + \text{Na}$) $^+$ 490.1569, found 490.1571; $[\alpha]_D^{24} = -45.4^\circ$ (c 0.86, CHCl_3); HPLC: retention time = 20.40 min.

minor-8: mp $103-106^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 1.55-1.68 (2H, m), 1.58 (9H, s), 1.63 (6H, s), 1.65 (3H, s), 2.08-2.19 (2H, m), 2.98 (3H, s), 3.07 (1H, d, $J = 9.8$), 3.15 (1H, d, $J = 9.8$), 3.19-3.27 (2H, m), 4.65 (1H, dd, $J = 2.4, 10.2$), 7.25 (2H, d, $J = 9.8$), 7.31 (1H, br s); ^{13}C NMR (500 MHz, CDCl_3) δ 18.3, 19.9, 20.5, 27.5, 28.3, 30.3, 33.2, 58.6, 66.0, 75.0, 76.2, 82.9, 115.6, 117.6, 124.0, 127.2, 127.6, 129.6, 135.0, 141.5,

155.2; IR (KBr): 3447, 2984, 2921, 2908, 2887, 2860, 1665, 1481, 1379, 1369; FABMS: 468 (M + H)⁺, 368, 242, 196; HRMS calcd for C₂₃H₃₄NO₄BrNa (M + Na)⁺ 490.1569, found 490.1567; Anal. Calcd for C₂₃H₃₄BrNO₄: C, 58.97; H, 7.32; N, 2.99; Br, 17.06. Found: C, 59.26; H, 7.20; N, 2.76; Br, 16.67; [α]_D²⁴ = −77.5° (c 0.98, CHCl₃); HPLC: retention time = 21.31 min.

To a solution of major-**8** (2.29 g, 4.89 mmol) in CH₂Cl₂ (10 ml) was added formic acid (20 ml) at room temperature. After stirring for 18 h at room temperature, the reaction mixture was neutralized with 15% NaOH_{aq} and extracted with AcOEt (50 ml x 2). The combined organic extracts were washed with brine (50 ml), dried over Na₂SO₄, filtered and evaporated. Purification by silica gel column chromatography (hexane-AcOEt 5:1) yielded Boc-deprotected compound (938 mg, 52%) as a colorless oil.

¹H NMR (500 MHz, CDCl₃) δ 1.44-1.59 (2H, m), 1.64 (3H, s), 1.64 (3H, s), 1.66 (3H, s), 2.01 (1H, dt, *J* = 5.5, 12.0), 2.15 (1H, dt, *J* = 5.5, 12.0), 2.79 (1H, s), 2.90 (1H, dd, *J* = 9.0, 15.5), 3.05 (1H, dd, *J* = 10.5, 15.5), 3.39 (1H, d, *J* = 9.5), 3.40 (3H, s), 3.49 (1H, d, *J* = 9.5), 4.08 (1H, dd, *J* = 9.0, 10.5), 4.26 (1H, br s), 6.49 (1H, d, *J* = 8.5), 7.09 (1H, d, *J* = 8.5), 7.15 (1H, s); ¹³C NMR (125 MHz, CDCl₃) δ 18.2, 19.9, 20.5, 28.1, 30.3, 32.8, 59.4, 65.9, 72.7, 78.1, 110.3, 110.5, 124.2, 127.1, 127.3, 129.7, 131.0, 149.7; IR (CHCl₃) cm^{−1}: 3405, 2924, 1604, 1481, 1247, 1166, 1111; HRMS calcd for C₁₈H₂₆NO₂Br (M)⁺ 367.1147, found 367.1150; [α]_D²⁴ = −33.5° (c 0.75, CHCl₃).

To a solution of above compound (932 mg, 2.53 mmol) in CH₂Cl₂ (20 ml) was added 2,2-dimethoxypropane (3.11 ml, 25.3 ml) and pyridinium *p*-toluenesulfonate (100 mg) at room temperature. The mixture was stirred for 4 h at room temperature. The solvent was concentrated in vacuo and sat. NaHCO₃_{aq} (20 ml) was added to the residue. The product was extracted with AcOEt (20 ml x 2) and the organic extracts were washed with brine (20 ml), dried over Na₂SO₄, filtered and evaporated. Purification by silica gel column chromatography (hexane-AcOEt 10:1 to 5:1) gave major-**9** (945 mg, 91%) as a colorless oil.

major-9: ¹H NMR (400 MHz, CDCl₃) δ 1.08 (1H, dt, *J* = 4.4, 13.2), 1.50 (3H, s), 1.51 (3H, s), 1.55 (3H, s), 1.57 (3H, s), 1.57-1.62 (1H, m), 1.65 (3H, s), 1.95 (1H, dt, *J* = 4.4, 13.2), 2.05 (1H, dt, *J* = 4.4, 13.2), 2.97-3.10 (2H, m), 3.28 (1H, d, *J* = 9.6), 3.38 (3H, s), 3.52 (1H, d, *J* = 9.6), 4.34 (1H, dd, *J* = 4.4, 9.6), 6.49 (1H, d, *J* = 8.0), 7.09 (1H, dd, *J* = 2.4, 8.0), 7.12 (1H, s); ¹³C NMR (125 MHz, CDCl₃) δ 18.2, 19.8, 20.5, 25.8, 28.1, 29.0, 29.2, 31.3, 59.5, 70.3, 76.3, 82.1, 94.8, 110.7, 113.0, 124.0, 127.3, 127.5, 129.4, 134.4, 147.8; IR (CHCl₃) cm^{−1}: 2928, 1596, 1474, 1371, 1259, 1118, 969, 862; HRMS calcd for C₂₁H₃₀NO₂Br (M)⁺ 407.1460, found 407.1470; [α]_D²⁴ = +101.5° (c 1.59, CHCl₃).

minor-9: mp 68-70 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.50 (3H, s), 1.59-1.64 (1H, m), 1.63 (3H, s), 1.64 (3H, s), 1.66 (6H, s), 1.74-1.81 (1H, m), 2.04-2.17 (2H, m), 2.96 (1H, dd, $J = 10.3, 17.1$), 3.08 (1H, d, $J = 9.8$), 3.12 (1H, d, $J = 9.8$), 3.19 (3H, s), 3.39 (1H, dd, $J = 2.9, 17.1$), 4.17 (1H, dd, $J = 2.9, 10.3$), 6.55 (1H, d, $J = 7.8$), 7.12 (1H, d, $J = 7.8$), 7.16 (1H, s); ^{13}C NMR (500 MHz, CDCl_3) δ 18.4, 19.9, 20.5, 25.8, 28.2, 28.6, 31.3, 34.9, 59.01, 70.1, 73.7, 82.4, 95.1, 111.1, 113.4, 124.1, 127.4, 127.5, 129.4, 134.4, 148.2; IR (KBr) cm^{-1} : 3429, 2983, 2928, 2913, 2896, 2863, 1596, 1472, 1337, 1250, 1105; Anal. Calcd for $\text{C}_{21}\text{H}_{30}\text{BrNO}_2 \cdot 1/6\text{H}_2\text{O}$: C, 61.31; H, 7.43; N, 3.40; Br, 19.42. found: C, 61.35; H, 7.29; N, 3.41; Br, 19.42; $[\alpha]_D^{24} = +98.9^\circ$ (c 0.66, CHCl_3).

To a solution of major-**9** (919 mg, 2.25 mmol) in ether (15 ml) was added *t*-BuLi in pentane (6.0 ml, 1.5 M) dropwise at -78°C . After stirring for 15 min at -78°C , a portion of CO_2 (2.0 g) was added to the reaction mixture at -78°C . After warming up to room temperature, the reaction was quenched with sat. NH_4Cl (30 ml) and extracted with AcOEt (30 ml x 2). The combined organic extracts were washed with brine (30 ml), dried over Na_2SO_4 , filtered and evaporated. Purification by silica gel column chromatography (hexane-AcOEt 10:1 to 1:2) provided **10** (446 mg, 53%) as a colorless oil.

10: mp 210-213 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.08 (1H, dt, $J = 4.4, 13.2$), 1.49 (3H, s), 1.54 (6H, s), 1.55 (3H, s), 1.56-1.65 (1H, m), 1.73 (3H, s), 1.95 (1H, dt, $J = 4.4, 13.2$), 2.07 (1H, dt, $J = 4.4, 13.2$), 3.06-3.10 (2H, m), 3.32 (1H, d, $J = 9.6$), 3.40 (3H, s), 3.53 (1H, d, $J = 9.6$), 4.45 (1H, dd, $J = 6.0, 9.6$), 6.60 (1H, d, $J = 8.8$), 7.74 (1H, s), 7.82 (1H, dd, $J = 1.6, 8.8$); ^{13}C NMR (100 MHz, CDCl_3) δ 18.4, 20.6, 26.0, 28.0, 28.5, 28.9, 30.7, 59.6, 70.2, 75.9, 82.1, 93.9, 109.3, 118.7, 124.0, 126.5, 127.0, 130.8, 131.9, 132.5, 152.9, 171.8; IR (KBr) cm^{-1} : 2913, 1666, 1607, 1450, 1369, 1296, 1272, 1217, 1120, 827, 768; HRMS calcd for $\text{C}_{22}\text{H}_{31}\text{NO}_4$ (M^+) 373.2253, found 373.2265; $[\alpha]_D^{24} = +223.5^\circ$ (c 0.42, CHCl_3).

To a solution of **10** (103 mg, 0.276 mmol) in THF (5 ml) was added 1,1'-carbonyldiimidazole (134 mg, 0.827 mmol) at room temperature. The mixture was stirred for 30 min at room temperature.

1,1'-carbonyldiimidazole (134 mg, 0.827 mmol) was added and stirred for another 30 min at room temperature. 28% NH₃aq (5.0 ml) was added to the reaction mixture at room temperature and stirred for 12 h at this temperature. After addition of water (20 ml), the aqueous solution was extracted with AcOEt (20 ml x 2). The combined organic extracts were washed with brine (20 ml), dried over Na₂SO₄, filtered and evaporated. Purification by silica gel column chromatography (hexane-AcOEt 1:1 to AcOEt) gave **11** (76 mg, 74%) as a colorless oil.

11: ¹H NMR (400 MHz, CDCl₃) δ 1.06 (1H, dt, *J* = 5.5, 13.2), 1.48 (3H, s), 1.53 (6H, s), 1.55 (3H, s), 1.55-1.62 (1H, m), 1.71 (3H, s), 1.95 (1H, dt, *J* = 5.5, 13.2), 2.06 (1H, dt, *J* = 5.5, 13.2), 3.01-3.17 (2H, m), 3.31 (1H, d, *J* = 9.6), 3.39 (3H, s), 3.53 (1H, d, *J* = 9.6), 4.42 (1H, dd, *J* = 5.2, 8.8), 5.90 (2H, br), 6.59 (1H, d, *J* = 8.8), 7.49 (1H, dd, *J* = 2.4, 8.8), 7.52 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 18.4, 19.9, 20.6, 26.0, 28.0, 28.8, 28.9, 31.0, 59.6, 70.2, 76.0, 82.1, 94.2, 109.8, 123.0, 123.9, 124.1, 127.1, 132.1, 151.7, 169.4; IR (CHCl₃) cm⁻¹: 3534, 3417, 2928, 1663, 1609, 1492, 1444, 1370, 1272, 1118, 909; HRMS calcd for C₂₂H₃₂N₂O₃Na (M + Na)⁺ 395.2311, found 395.2313; [α]_D²⁴ = +154.2° (c 0.20, CHCl₃).

To a solution of **11** (70 mg, 0.188 mmol) in MeOH (5 ml) was added pyridinium *p*-toluenesulfonate (10 mg) at room temperature. The mixture was stirred for 3 h at room temperature. The solvent was concentrated in vacuo. The residue was purified by silica gel column chromatography (AcOEt to AcOEt-MeOH 10:1) to give **1** (40 mg, 64%) as a colorless solid.

(+)-benzastatin E (**1**): mp 171-174 °C; IR (KBr) cm⁻¹: 3416, 3312, 2918, 1645, 1606, 1441, 1380, 1262, 1112, 773; HRMS calcd for C₁₉H₂₉N₂O₃ (M + H)⁺ 333.2178, found 333.2187; Anal. Calcd for C₁₉H₂₈N₂O₃·0.3H₂O: C, 67.55; H, 8.53; N, 8.29. Found: C, 67.48; H, 8.59; N, 8.24; [α]_D²⁴ = +21.3° (c 0.10, MeOH); ¹H NMR and ¹³C NMR see table.

¹H NMR Data for Natural and Synthetic Benzastatine E (**1**) in CDCl₃

(+)-benzastatine E (**1**)

Proton	Natural 1 (600MHz)	Synthetic 1 (500MHz)
NH	4.67 (1H, br)	4.65 (1H, br)
2	7.56 (1H, br s)	7.55 (1H, s)
5	6.57 (1H, d, 7.8)	6.58 (1H, d, 7.5)
6	7.50 (1H, d, 7.8)	7.50 (1H, d, 7.5)
8	3.07 (1H, dd, 15.6, 10.1) 2.98 (1H, dd, 15.6, 8.8)	3.07 (1H, dd, 16.0, 11.0) 2.97 (1H, dd, 16.0, 8.5)
9	4.15 (1H, dd, 10.1, 8.8) 4.15 (1H, t, 9.5)	
11	1.57 (1H, ddd, 14.2, 12.7, 4.9) 1.48 (1H, ddd, 14.2, 12.7, 5.4)	1.57 (1H, ddd, 14.0, 14.0, 4.0) 1.48 (1H, ddd, 14.0, 14.0, 5.0)
12	2.15 (1H, ddd, 12.7, 12.7, 4.9) 2.01 (1H, ddd, 12.7, 12.7, 5.4)	2.15 (1H, ddd, 13.0, 13.0, 5.0) 2.01 (1H, ddd, 13.0, 13.0, 6.0)
15	1.64 (3H, s)	1.64 (3H, s)
16	3.52 (1H, d, 9.3) 3.42 (1H, d, 9.3)	3.52 (1H, d, 9.5) 3.42 (1H, d, 9.5)
17	1.64 (3H, s)	1.64 (3H, s)
18	1.66 (3H, s)	1.66 (3H, s)
CONH ₂	5.70 (1H, br) 5.48 (1H, br)	5.60 (1H, br) 5.60 (1H, br)
OCH ₃	3.42 (3H, s)	3.42 (3H, s)
OH	2.73 (1H, br. s)	2.70 (1H, br. s)

¹³C NMR Data for Natural and Synthetic Benzastatine E (**1**) in CDCl₃

(+)-benzastatine E (**1**)

Carbon		Natural 1 (150MHz)	Synthetic 1 (125MHz)
1	C	123.1	123.1
2	CH	124.1	124.1
3	C	128.8	128.6
4	C	154.5	154.5
5	CH	107.8	107.8
6	CH	127.9	128.0
7	C	169.4	169.3
8	CH ₂	30.0	30.0
9	CH	66.3	66.2
10	C	72.9	73.0
11	CH ₂	32.8	32.7
12	CH ₂	28.2	28.2
13	C	127.1	127.2
14	C	124.5	124.5
15	CH ₃	20.6	20.6
16	CH ₂	78.4	78.4
17	CH ₃	18.3	18.3
18	CH ₃	20.0	20.0
OCH ₃	CH ₃	59.6	59.6

Filename: -

at "Wed Jan 23 18:30:41 JST 2002 "
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STANDARD CARBON PARAMETERS

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 nt 1486 werr
 st 17896 wexp
 clock 48 wexp
 gain 48 wnt
 flags n
 i1 n
 in n
 dp y
 hs nm
 DISPLAY 457.3
 sp 25805.3
 wd 25805.3
 vs 0
 sc 0
 wc 250
 hzmm 103.22
 ts 500.00
 tfl 11590.0
 tlp 9679.3
 ins 100.000
 nm cdc ph