

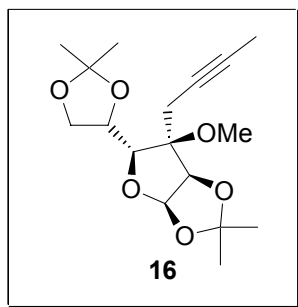
## Supporting Information

### A Facile Domino Metathetic Route to Thapsigargin Skeleton

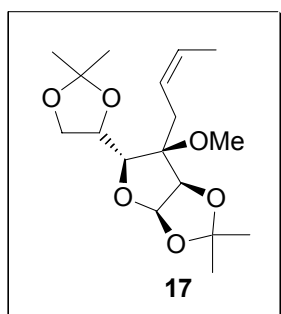
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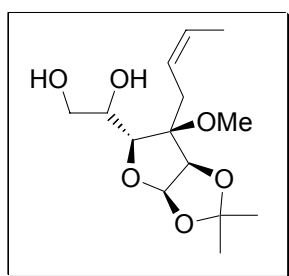
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$R_f = 0.48$  (2:1 hexane/ethyl acetate); mp 132-134 °C;  $[\alpha]_D^{25} +45.76$  (*c* 1.18, CHCl<sub>3</sub>); IR (KBr) 2238, 1469, 1377, 1240, 1077, 858 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  1.36 (s, 3H), 1.37 (s, 3H), 1.43 (s, 3H), 1.60 (s, 3H), 1.81 (t, 3H, *J* = 2.7 Hz), 2.42 (ddd, 1H, *J* = 17.1, 5.4, 2.7 Hz), 2.72 (ddd, 1H, *J* = 17.1, 5.1, 2.7 Hz), 3.53 (s, 3H), 3.55-3.96 (m, 1H), 4.02-4.17 (m, 3H), 4.64 (d, 1H, *J* = 3.6 Hz), 5.70 (d, 1H, *J* = 3.6 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  3.7, 20.7, 25.5, 26.5, 26.6, 27.1, 53.4, 68.1, 73.1, 73.4, 79.2, 82.0, 83.0, 83.7, 103.7, 109.7, 117.8; HRMS (EI) calcd. for C<sub>17</sub>H<sub>26</sub>O<sub>6</sub>Na 349.1627 *m/z*, found *m/z* 349.1625.

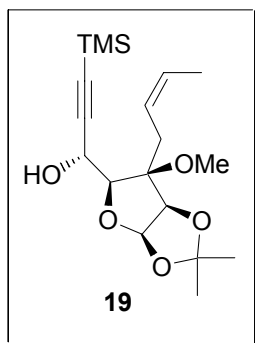


$R_f = 0.33$  (4:1 hexane/ethyl acetate);  $[\alpha]_D^{25} +44.52$  (*c* 1.46, CHCl<sub>3</sub>); IR (film) 1464, 1377, 1224, 1082, 1037 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  1.34 (s, 3H), 1.36 (s, 3H), 1.44 (s, 3H), 1.60 (s, 3H), 1.65 (d, 3H, *J* = 5.4 Hz), 2.27-2.35 (m, 1H), 2.52-2.60 (m, 1H), 3.48 (s, 3H), 3.85-3.92 (m, 1H), 4.04-4.14 (m, 3H), 4.36 (d, 1H, *J* = 3.6 Hz), 5.60 (d, 1H, *J* = 3.6 Hz), 5.63-5.71 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  13.2, 25.5, 26.5, 26.6, 27.1, 52.9, 68.6, 72.8, 82.3, 83.4, 84.0, 103.1, 109.7, 112.8, 123.7, 126.9; LRMS (EI) [M+Na]<sup>+</sup> 351.2267; HRMS (EI) calcd. for C<sub>17</sub>H<sub>28</sub>O<sub>6</sub>Na *m/z* 351.1784, found *m/z* 351.1787.

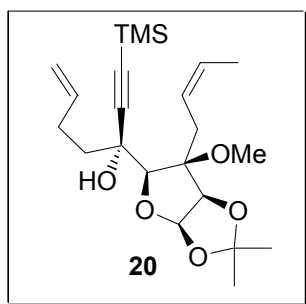


$R_f = 0.30$  (2:1 hexane/ethyl acetate);  $[\alpha]_D^{25} +51.72$  (*c* 1.16, CHCl<sub>3</sub>); IR (film) 3465, 3084, 3033, 2987, 2941, 1464, 1378, 1225, 1102 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  1.35 (s, 3H), 1.60 (s, 3H), 1.70 (d, 3H, *J* = 5.1 Hz), 2.17 (t, 1H, *J* = 6.5 Hz), 2.34-2.41 (m, 1H), 2.56-2.66 (m, 1H), 2.66 (d, 1H, *J* = 2.7 Hz), 3.48 (s, 3H), 3.61-3.65 (m, 1H), 3.66-3.87 (m, 2H), 3.99 (d, 1H,

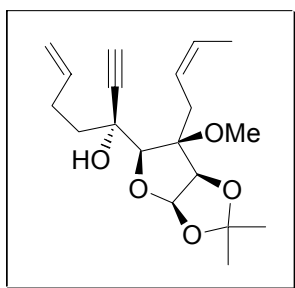
$J = 9.3$  Hz), 4.36 (d, 1H,  $J = 3.3$  Hz), 5.60-5.72 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  13.2, 26.5, 26.8, 27.2, 53.2, 64.7, 69.4, 79.0, 82.1, 85.0, 103.8, 113.0, 123.2, 127.4; HRMS (EI) calcd. for  $\text{C}_{14}\text{H}_{24}\text{O}_6\text{Na}$  311.1471  $m/z$ , found  $m/z$  311.1470.



$R_f = 0.47$  (2:1 hexane/ethyl acetate); mp 56-58 °C;  $[\alpha]_D^{25} -4.85$  ( $c$  1.03,  $\text{CHCl}_3$ ); IR (KBr) 3450, 3084, 3033, 2192, 1378, 1255, 1067  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  0.17 (s, 9H), 1.35 (s, 3H), 1.60 (s, 3H), 1.65 (d, 3H,  $J = 5.1$  Hz), 2.29-2.38 (m, 1H), 2.53-2.60 (m, 1H), 3.46 (s, 3H), 4.21 (d, 1H,  $J = 6.3$  Hz), 4.38 (d, 1H,  $J = 3.6$  Hz), 4.52 (dd, 1H,  $J = 6.3, 6.0$  Hz), 5.56-5.68 (m, 2H), 5.69 (d, 1H,  $J = 3.6$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  -0.2, 13.2, 26.7, 27.2, 27.6, 52.9, 61.8, 83.3, 83.4, 83.6, 91.6, 102.8, 103.5, 113.2, 123.9, 127.1; HRMS (EI) calcd. for  $\text{C}_{18}\text{H}_{30}\text{O}_5\text{Na}$  377.1760  $m/z$ , found  $m/z$  377.1754.

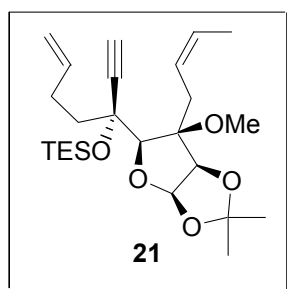


$R_f = 0.59$  (2:1 hexane/ethyl acetate);  $[\alpha]_D^{25} +15.00$  ( $c$  1.20,  $\text{CHCl}_3$ ); IR (film) 3465, 2177, 1378, 1255, 848  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  0.17 (s, 9H), 1.35 (s, 3H), 1.58 (s, 3H), 1.67 (d, 3H,  $J = 6.6$  Hz), 1.78-1.95 (m, 2H), 2.32-2.39 (m, 2H), 2.52 (dd, 1H,  $J = 15.9, 6.0$  Hz), 2.65 (s, 1H), 2.75-2.84 (m, 1H), 3.45 (s, 3H), 4.03 (s, 1H), 4.39 (d, 1H,  $J = 3.6$  Hz), 4.94-5.01 (m, 2H), 5.60-5.66 (m, 1H), 5.69 (d, 1H,  $J = 3.6$  Hz), 5.77-5.95 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  -0.2, 13.3, 26.6, 27.2, 27.7, 28.3, 39.4, 52.9, 70.2, 83.0, 84.1, 84.4, 92.5, 102.9, 104.5, 112.8, 114.6, 125.6, 127.0, 138.6; HRMS (EI) calcd. for  $\text{C}_{22}\text{H}_{36}\text{O}_5\text{Na}$  431.2230  $m/z$ , found  $m/z$  431.2233.

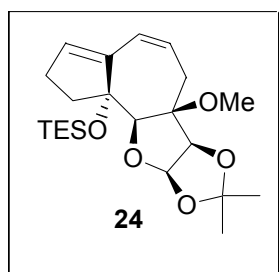


$R_f = 0.54$  (2:1 hexane/ethyl acetate); mp 68-70°C  $[\alpha]_D^{25} +30.51$  ( $c$  1.18,  $\text{CHCl}_3$ ); IR (KBr) 3470, 3271, 3043, 2126, 1648, 1393  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  1.35 (s, 3H), 1.58 (s, 3H), 1.67 (dd, 3H,  $J = 6.6, 1.8$  Hz), 1.72-1.99 (m, 2H), 2.30-2.58 (m, 3H), 2.60 (s, 1H), 2.72 (s, 1H), 2.72-2.80 (m, 1H), 3.47 (s, 3H), 4.04 (s, 1H), 4.39 (d, 1H,  $J = 3.3$  Hz), 4.96 (ddd, 1H,  $J = 10.2,$

3.3, 1.2 Hz), 5.06 (ddd, 1H,  $J = 17.2, 3.3, 1.8$  Hz), 5.63-5.73 (m, 1H), 5.71 (d, 1H,  $J = 3.3$  Hz), 5.77-5.94 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  13.3, 26.6, 27.1, 27.6, 28.1, 39.2, 53.0, 69.8, 75.8, 82.9, 83.9, 84.4, 102.8, 112.8, 114.7, 125.1, 127.4, 138.4; HRMS (EI) calcd. for  $\text{C}_{19}\text{H}_{28}\text{O}_5\text{Na}$   $m/z$  359.1834, found  $m/z$  359.1844.



$R_f = 0.63$  (4:1 hexane/ethyl acetate);  $[\alpha]_D^{25} +25.24$  ( $c$  1.03,  $\text{CHCl}_3$ ); IR (KBr) 3244, 3078, 2109, 1641, 1456, 1373, 1109, 1007  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  0.68-0.75 (m, 6H), 0.94-0.99 (m, 9H), 1.35 (s, 3H), 1.57(s, 3H), 1.65 (d, 3H,  $J = 6.3$  Hz), 1.71-1.79 (m, 1H), 1.81-2.08 (m, 1H), 2.24-2.31 (m, 2H), 2.52-2.63 (m, 1H), 2.54 (s, 1H), 2.78-2.86 (m, 1H), 3.43 (s, 3H), 4.04 (s, 1H), 4.39 (d, 1H,  $J = 3.6$  Hz), 4.96 (d, 1H,  $J = 9.9$  Hz), 5.05 (dd, 1H,  $J = 17.4, 1.8$  Hz), 5.57-5.75 (m, 2H), 5.66 (d, 1H,  $J = 3.6$  Hz), 5.79-5.91 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  6.3, 7.1, 13.1, 27.0, 28.2, 28.8, 39.7, 52.9, 72.9, 75.6, 83.2, 84.7, 85.0, 103.5, 112.9, 114.3, 125.8, 126.2, 138.7; LRMS (EI)  $[\text{M}+\text{Na}]^+$  473.2570 HRMS (EI) calcd. for  $\text{C}_{25}\text{H}_{42}\text{O}_5\text{Na}$   $m/z$  473.2699, found  $m/z$  473.2701.



$R_f = 0.47$  (9:1 hexane/ethyl acetate);  $[\alpha]_D^{25} +15.33$  ( $c$  1.50,  $\text{CHCl}_3$ ); IR (film) 3270, 3022, 1457, 1372, 1119, 1019, 741  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  0.52-0.64 (m, 6H), 0.92 (t, 9H,  $J = 7.8$  Hz), 1.40 (s, 3H), 1.56 (s, 3H), 1.99-2.06 (m, 1H), 2.32-2.49 (m, 4H), 3.13 (d, 1H,  $J = 16.0$  Hz), 3.27 (s, 3H), 3.93 (s, 1H), 4.23 (d, 1H,  $J = 4.0$  Hz), 5.49-5.54 (m, 1H), 5.75 (bs, 1H), 5.95 (d, 1H,  $J = 4.0$  Hz), 6.18 (dd, 1H,  $J = 11.2, 2.8$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  6.3, 7.1, 27.4, 27.8, 29.5, 31.5, 38.7, 52.7, 86.9, 87.4, 88.3, 91.7, 105.7, 113.5, 123.7, 126.7, 133.1, 143.9; LRMS (EI)  $[\text{M}+\text{Na}]^+$  431.2112 HRMS (EI) calcd. for  $\text{C}_{22}\text{H}_{36}\text{O}_5\text{Na}$   $m/z$  431.2230, found  $m/z$  431.2224.