Formal Total Synthesis of (–)-Apicularen A *via* Transannular Conjugate Addition

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Supporting Information

General. Unless otherwise stated, ^1H NMR and proton decoupled ^{13}C NMR spectra were recorded for deuteriochloroform solutions with residual chloroform as internal standard. Infrared spectra were run as thin films on NaCl plates. Optical rotations were recorded for 2mL solutions in a 10cm microcell. Melting points were determined on a Kofler hot stage apparatus. HRMS (ESI) mass spectra were run at Monash University, Clayton, Victoria.

Alkyne 11: colorless oil: $[\alpha]_{\text{D}} -6.4$ (c 1.14, CH_2Cl_2); IR ν_{max} (film) 3472, 3312, 3078, 2947, 2894, 2868, 2113, 1642, 1257, 1094, 999, 837 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.132 (s, 3H), 0.128 (s, 3H), 0.90 (s, 9H), 1.07-1.09 (m, 18H), 1.10-1.18 (m, 3H), 1.56 (ddd, $J = 14.2, 8.8, 8.8$ Hz, 1H), 1.77 (ddd, $J = 14.2, 4.0, 3.2$ Hz, 1H), 1.92 (ddd, $J = 13.2, 8.4, 5.8$ Hz, 1H), 2.03 (ddd, $J = 13.2, 8.4, 4.4$ Hz, 1H), 2.17-2.29 (m, 2H), 2.43 (d, $J = 2.0$ Hz, 1H), 2.93 (s, 1H), 3.85 (br m, 1H), 4.11 (m, 1H), 4.47 (ddd, $J = 8.4, 6.8, 2.0$, 1H), 5.10 (d, $J = 10.4$ Hz, 1H), 5.11 (d, $J = 16.8$ Hz, 1H), 5.84 (dddd, $J = 16.8, 10.4, 7.2, 7.2$ Hz, 1H); ^{13}C NMR (100MHz, CDCl_3) δ -4.6, -4.0, 12.3, 17.9, 18.0, 18.1, 25.8, 42.0, 42.9, 47.1, 59.9, 69.7, 69.9, 73.1, 85.1, 117.5, 134.8; HRMS (ESI) Calcd for $\text{C}_{25}\text{H}_{50}\text{O}_3\text{Si}_2\text{Na}$ [$M+\text{Na}^+$]: 477.3196, found: 477.3200.

Alkyne 12: colorless oil: $[\alpha]_{\text{D}} -8.8$ (c 1.00, CH_2Cl_2); IR ν_{max} (film) 3480, 3304, 3054, 2947, 2894, 2868, 2306, 1642, 1266, 1060, 1000, 838 cm^{-1} ; ^1H NMR (400 MHz) δ 0.11 (s, 3H), 0.12 (s, 3H), 0.90 (s, 9H), 1.07-1.09 (m, 18H), 1.10-1.18 (m, 3H), 1.64-1.74 (m, 2H), 2.03 (ddd, $J = 13.2, 8.0, 5.2$ Hz, 1H), 2.08 (ddd, $J = 13.2, 8.4, 6.0$ Hz, 1H), 2.18 (ddd, $J = 14.0, 7.2, 6.4$ Hz, 1H), 2.27 (ddd, $J = 14.0, 7.2, 6.8$ Hz, 1H), 2.43 (d, $J = 2.2$ Hz, 1H), 3.43 (s, 1H), 4.03 (br m, 1H), 4.27 (m, 1H), 4.42 (ddd, $J = 8.0, 6.0, 2.2$ Hz, 1H), 5.08 (d, $J = 10.0$ Hz, 1H), 5.10 (dd, $J = 17.2, 1.6$ Hz, 1H), 5.83 (dddd, $J = 17.2, 10.0, 7.2, 6.8$ Hz, 1H); ^{13}C NMR (100MHz) δ -4.8, -4.6, 12.3, 17.9, 18.0, 18.1, 25.8, 40.7, 42.3, 44.7, 60.0, 67.9, 68.7, 73.2, 85.0, 117.4, 134.9; HRMS (ESI) Calcd for $\text{C}_{25}\text{H}_{50}\text{O}_3\text{Si}_2\text{Na}$ [$M+\text{Na}^+$]: 477.3196, found: 477.3174.

Stannane 7: colorless oil: $[\alpha]_D -15.6$ (c 1.15, CH_2Cl_2); IR ν_{max} (film)

3507, 3078, 2958, 2930, 2868, 1642, 1255, 1062, 994, 837 cm^{-1} ; ^1H

NMR (400 MHz) δ 0.09 (s, 3H), 0.10 (s, 3H), 0.80-0.97 (m, 15H), 0.89 (s, 9H), 1.04-1.05 (m, 21H), 1.30 (sext, $J = 7.2$ Hz, 6H), 1.42-1.55 (m, 6H), 1.72-1.86 (m, 4H), 2.21 (dd, $J = 6.8, 6.4$ Hz, 2H), 3.35 (s, 1H), 3.78-3.84 (m, 2H), 5.08-5.12 (m, 2H), 5.85 (dddd, $J = 16.8, 10.4, 7.2, 6.8$ Hz, 1H), 5.87 (dd, $J = 19.2, 6.6$ Hz, 1H), 5.97 (d, $J = 19.2$ Hz, 1H); ^{13}C NMR (100MHz) δ -4.6, -3.8, 9.4, 12.3, 13.7, 17.8, 18.0, 18.1, 25.8, 27.3, 29.1, 41.8, 42.5, 47.1, 70.4, 71.1, 75.1, 117.3, 128.9, 134.9, 151.1; HRMS (ESI) Calcd for $\text{C}_{37}\text{H}_{78}\text{O}_3\text{Si}_2\text{SnNa}$ [$M+\text{Na}^+$]: 767.4409, found: 767.4407.

Stannane 8: colorless oil: $[\alpha]_D +3.7$ (c 2.52, CH_2Cl_2); IR ν_{max} (film)

3506, 3051, 2956, 2930, 1641, 1265, 1065, 995, 837 cm^{-1} ; ^1H NMR (400

MHz) δ 0.07 (s, 6H), 0.80-0.98 (m, 15H), 0.88 (s, 9H), 1.02-1.07 (m, 21H), 1.29 (sext, $J = 7.2$ Hz, 6H), 1.43-1.56 (m, 6H), 1.61-1.64 (m, 2H), 1.74 (ddd, $J = 13.6, 9.6, 4.0$ Hz, 1H), 2.05 (ddd, $J = 13.6, 10.4, 4.4$ Hz, 1H), 2.15 (ddd, $J = 13.6, 6.8, 6.8$ Hz, 1H), 2.28 (ddd, $J = 13.6, 7.2, 6.8$ Hz, 1H), 3.67 (s, 1H), 3.95-4.00 (m, 2H), 4.04 (m, 1H), 5.09 (d, $J = 10.0$ Hz, 1H), 5.10 (d, $J = 17.2$ Hz, 1H), 5.83 (dddd, $J = 17.2, 10.0, 7.2, 6.8$ Hz, 1H), 5.88 (dd, $J = 19.2, 6.8$ Hz, 1H), 6.00 (d, $J = 19.2$ Hz, 1H); ^{13}C NMR (100MHz) δ -4.9, -4.5, 9.4, 12.4, 13.7, 17.9, 18.1, 18.14, 25.8, 27.3, 29.1, 39.9, 42.3, 44.1, 67.8, 69.3, 75.0, 117.2, 129.1, 135.0, 151.0; HRMS (ESI) Calcd for $\text{C}_{37}\text{H}_{78}\text{O}_3\text{Si}_2\text{SnNa}$ [$M+\text{Na}^+$]: 767.4409, found: 767.4409.

Diene 13: colorless oil: $[\alpha]_D -17.6$ (c 1.07, CH_2Cl_2); IR ν_{max} (film) 3504, 3055,

2946, 2866, 1735, 1607, 1266, 1079, 1050, 976, 884, 838 cm^{-1} ; ^1H NMR (400

MHz) δ 0.07 (s, 6H), 0.88 (s, 9H), 1.00 (s, 21H), 1.45 (ddd, $J = 14.0, 9.2, 8.8$ Hz,

1H), 1.68 (ddd, $J = 14.0, 3.2, 2.8$ Hz, 1H), 1.70 (d, $J = 4.8$ Hz, 6H), 1.72 (ddd, $J =$

13.2, 8.8, 4.0 Hz, 1H), 1.81 (ddd, $J = 13.2, 9.6, 5.2$ Hz, 1H), 2.16 (dd, $J = 6.8, 6.4$ Hz, 2H), 3.20 (s, 1H), 3.73-3.79 (m, 2H), 3.80-3.89 (m, 2H), 4.11 (ddd, $J = 13.6, 8.4, 5.2$ Hz, 1H), 5.05-5.09 (m, 2H),

5.41 (dd, $J = 15.6, 8.0$, 1H), 5.70-5.84 (m, 2H), 6.83 (d, $J = 8.0$ Hz, 1H), 6.91 (d, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 7.8$ Hz, 1H); ^{13}C NMR (100MHz) δ -4.6, -3.9, 12.4, 17.9, 18.0, 18.1, 25.5, 25.8, 36.7, 41.8, 42.6, 47.6, 70.1, 70.8, 71.4, 105.1, 111.9, 115.7, 117.3, 125.0, 129.3, 134.7, 134.9, 135.3, 145.1, 157.1, 160.1; HRMS (ESI) Calcd for $\text{C}_{36}\text{H}_{62}\text{O}_6\text{Si}_2\text{Na}$ [$M+\text{Na}^+$]: 669.3983, found: 669.3971.

Lactone 14: colorless oil; $[\alpha]_{\text{D}}^{25} +47.9$ (c 0.75, CH_2Cl_2); IR ν_{max} (film) 3054, 2946, 2931, 2895, 2867, 1720, 1644, 1266, 1090, 982, 884, 837 cm^{-1} ; ^1H NMR (400 MHz) δ 0.01 (s, 3H), 0.02 (s, 3H), 0.86 (s, 9H), 1.02, (d, $J = 4.0$ Hz, 21H), 1.86 (dd, $J = 14.0, 2.8$ Hz, 1H), 1.88 (dd, $J = 14.0, 2.4$ Hz, 1H), 1.99-2.07 (m, 2H), 2.44-2.56 (m, 2H), 3.19 (app ddd, $J = 15.6, 2.6, 2.0$ Hz, 1H), 3.69 (dd, $J = 15.6, 8.8$ Hz, 1H), 3.79 (s, 3H), 4.10 (m, 1H), 4.53 (br m, 1H), 5.04 (m, 1H), 5.10 (dd, $J = 10.0, 1.6$ Hz, 1H), 5.13 (dd, $J = 16.8, 1.6$ Hz, 1H), 5.43 (dd, $J = 15.6, 5.2$ Hz, 1H), 5.67 (ddd, $J = 15.6, 8.8, 2.6$ Hz, 1H), 5.90 (dddd, $J = 16.8, 10.0, 7.2, 6.8$ Hz, 1H), 6.79 (d, $J = 7.2$ Hz, 1H), 6.80 (d, $J = 8.4$ Hz, 1H), 7.25 (t, $J = 8.0$ Hz, 1H); ^{13}C NMR (100MHz) δ 4.5, -4.1, 12.3, 18.0, 18.1, 18.2, 26.0, 36.8, 38.1, 39.6, 43.9, 55.6, 65.4, 69.2, 72.6, 109.5, 117.2, 122.4, 124.5, 126.4, 130.2, 134.4, 136.3, 138.7, 156.5, 168.3; HRMS (ESI) Calcd for $\text{C}_{34}\text{H}_{58}\text{O}_5\text{Si}_2\text{Na}$ [$M+\text{Na}^+$]: 625.3720, found: 625.3730

Enone 5a: colorless oil; $[\alpha]_{\text{D}}^{25} +76.0$ (c 0.49, CH_2Cl_2); IR ν_{max} (film) 3453, 3057, 3010, 2961, 2842, 1722, 1662, 1626, 1267, 988, 897 cm^{-1} ; ^1H NMR (400 MHz) δ 1.91-2.03 (m, 2H), 2.24 (d, $J = 6.0$ Hz, 1H), 2.55 (dd, $J = 6.8, 6.4$ Hz, 2H), 2.71 (dd, $J = 13.4, 7.8$ Hz, 1H), 2.92 (dd, $J = 13.4, 4.8$ Hz, 1H), 3.41 (ddd, $J = 16.8, 4.6, 2.0$ Hz, 1H), 3.82 (s, 3H), 3.93 (dd, $J = 16.8, 8.8$ Hz, 1H), 4.29 (m, 1H), 5.02 (m, 1H), 5.15 (d, $J = 10.0$ Hz, 1H), 5.17 (d, $J = 17.2$ Hz, 1H), 5.89 (dddd, $J = 17.2, 10.0, 7.2, 6.8$ Hz, 1H), 6.13 (d, $J = 16.0$ Hz, 1H), 6.76 (ddd, $J = 16.0, 8.8, 4.6$ Hz, 1H), 6.82 (d, $J = 7.6$ Hz, 1H), 6.87 (d, $J = 8.4$ Hz, 1H), 7.31 (t, $J = 8.0$ Hz, 1H); ^{13}C NMR (100MHz) δ 37.0, 38.0, 39.4, 47.4, 55.7, 65.8, 72.4, 110.1, 118.1, 122.8,

123.8, 130.8, 133.1, 133.4, 136.5, 144.5, 157.0, 168.1, 200.5; HRMS (ESI) Calcd for $C_{19}H_{22}O_5Na$ $[M+Na^+]$: 353.1365, found: 353.1365.

Diene 15: colorless oil: $[\alpha]_D^{25} +12.2$ (c 1.19, CH_2Cl_2); IR ν_{max} (film) 3477, 3055, 2945, 2893, 2866, 1737, 1607, 1267, 1076, 1052, 976, 884, 838 cm^{-1} ; 1H NMR (400 MHz) δ 0.04 (s, 3H), 0.05 (s, 3H), 0.87 (s, 9H), 1.00 (s, 21H), 1.53-1.63 (m, 2H), 1.70 (d, J = 4.0 Hz, 6H), 1.71 (ddd, J = 13.2, 9.2, 4.0 Hz, 1H), 1.99 (ddd, J = 13.2, 10.0, 4.8 Hz, 1H), 2.13 (ddd, J = 13.6, 7.2, 6.8 Hz, 1H), 2.25 (ddd, J = 13.6, 6.8, 6.8 Hz, 1H), 3.51 (s, 1H), 3.79-3.89 (m, 2H), 3.91 (m, 1H), 4.01 (br m, 1H), 4.06 (ddd, J = 13.6, 8.8, 5.2 Hz, 1H), 5.05-5.11 (m, 2H), 5.39 (dd, J = 15.6, 8.4, 1H), 5.76 (ddd, J = 15.6, 7.2, 6.4, 1H), 5.81 (dddd, J = 17.2, 10.4, 7.2, 6.8 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100MHz) δ -4.9, -4.6, 12.4, 17.9, 18.06, 18.1, 25.5, 25.8, 36.7, 40.4, 42.3, 44.9, 67.8, 68.9, 71.4, 105.1, 111.9, 115.7, 117.2, 125.1, 129.4, 134.6, 135.0, 135.3, 145.0, 157.1, 160.1; HRMS (ESI) Calcd for $C_{36}H_{62}O_6Si_2Na$ $[M+Na^+]$: 669.3983, found: 669.3969.

Lactone 16: colorless oil: $[\alpha]_D^{25} +21.9$ (c 1.90, CH_2Cl_2); IR ν_{max} (film) 3076, 3053, 2946, 2894, 2866, 1725, 1644, 1277, 1085, 975, 911, 837 cm^{-1} ; 1H NMR (400 MHz) δ 0.14 (s, 3H), 0.22 (s, 3H), 0.91 (s, 9H), 1.03 (s, 21H), 1.58 (dd, J = 15.2, 6.8 Hz, 1H), 1.70 (ddd, J = 12.8, 10.0, 3.6 Hz, 1H), 1.73 (dd, J = 15.2, 8.0 Hz, 1H), 1.84 (ddd, J = 12.8, 11.6, 5.2 Hz, 1H), 2.30 (m, 1H), 2.46 (m, 1H), 3.37 (d, J = 16.4 Hz, 1H), 3.74 (ddd, J = 16.4, 5.6, 2.4 Hz, 1H), 3.80 (s, 3H), 4.03-4.11 (m, 2H), 5.09 (dd, J = 10.0, 1.6 Hz, 1H), 5.13 (dd, J = 17.2, 1.6 Hz, 1H), 5.28 (app q, J = 7.2 Hz, 1H), 5.42-5.50 (m, 2H), 5.88 (dddd, J = 17.2, 10.0, 6.4, 6.0 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 6.81 (d, J = 8.4 Hz, 1H), 7.24 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100MHz) δ -4.5, -4.1, 12.3, 17.9, 18.0, 18.1, 25.9, 36.8, 40.0, 42.5, 44.4, 55.5, 68.8, 72.1, 74.5, 109.4, 117.2, 122.7, 124.5, 129.6, 130.0, 134.2, 135.2, 138.5, 156.6, 167.9; HRMS (ESI) Calcd for $C_{34}H_{58}O_5Si_2Na$ $[M+Na^+]$: 625.3720, found: 625.3716.

Enone 5b: colorless oil: $[\alpha]_D -18.4$ (*c* 0.91, CH₂Cl₂); IR $\nu_{\max}$ (film) 3460, 3056, 2986, 2964, 2931, 2842, 1720, 1660, 1633, 1266, 984, 896 cm⁻¹; ¹H NMR (400 MHz) δ 1.67 (ddd, *J* = 16.0, 6.8, 6.4 Hz, 1H), 1.93 (ddd, *J* = 16.0, 5.6, 2.4 Hz, 1H), 2.40-2.50 (m, 2H), 2.65 (dd, *J* = 13.2, 8.6 Hz, 1H), 2.97 (dd, *J* = 13.2, 4.0 Hz, 1H), 3.43 (ddd, *J* = 16.0, 4.0, 1.8 Hz, 1H), 3.80 (s, 3H), 3.85 (dd, *J* = 16.0, 10.0 Hz, 1H), 4.37 (m, 1H), 5.11-5.19 (m, 3H), 5.85 (dddd, *J* = 17.2, 10.0, 6.8, 6.8 Hz, 1H), 6.23 (dd, *J* = 16.0, 1.8 Hz, 1H), 6.68 (ddd, *J* = 16.0, 10.0, 4.0 Hz, 1H), 6.81-6.86 (m, 2H), 7.30 (t, *J* = 8.0 Hz, 1H); ¹³C NMR (100MHz) δ 73.0, 39.8, 41.7, 48.0, 55.7, 69.1, 73.6, 110.1, 118.4, 122.9, 124.1, 130.7, 133.0, 133.9, 136.6, 143.4, 157.0, 168.2, 200.6; HRMS (ESI) Calcd for C₁₉H₂₂O₅Na [*M*+Na⁺]: 353.1365, found: 353.1372.

Pyranone 4: colorless crystalline solid: m.p. 182-183°C (EtOAc/petrol); $[\alpha]_D +138.0$ (*c* 0.53, CHCl₃), lit.¹ (enantiomer) $[\alpha]_D -140$ (*c* 0.60, CHCl₃); IR $\nu_{\max}$ (film) 3057, 2960, 2927, 2854, 1719, 1644, 1599, 1471, 1266, 1117, 1074 cm⁻¹; ¹H NMR (400 MHz) δ 1.72 (ddd, *J* = 14.8, 3.2, 1.2 Hz, 1H), 1.83 (ddd, *J* = 14.8, 11.2, 10.0 Hz, 1H), 2.22 (dd, *J* = 17.6, 10.8 Hz, 1H), 2.37 (m, 1H), 2.43 (dd, *J* = 17.6, 3.6 Hz, 1H), 2.48 (m, 1H), 2.483 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.55 (dd, *J* = 15.2, 8.8 Hz, 1H), 2.66 (dd, *J* = 15.2, 6.4 Hz, 1H), 3.46 (dd, *J* = 14.0, 11.6 Hz, 1H), 4.25 (dddd, *J* = 15.2, 8.8, 6.4, 2.0 Hz, 1H), 4.50 (app dt, *J* = 10.0, 3.6 Hz, 1H), 5.15, (dd, *J* = 10.0, 1.6 Hz, 1H), 5.18 (dd, *J* = 16.8, 1.6 Hz, 1H), 5.63 (ddd, *J* = 11.2, 8.4, 5.2, 3.2 Hz, 1H), 5.88 (dddd, *J* = 16.8, 10.0, 7.2, 6.8 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 7.28 (dd, *J* = 8.4, 7.6 Hz, 1H); ¹³C NMR (100MHz) δ 38.9, 39.0, 40.1, 47.1, 55.8, 68.1, 72.1, 74.0, 110.0, 118.0, 122.6, 125.6, 130.5, 133.3, 147.0, 155.9, 169.8, 207.1; HRMS (ESI) Calcd for C₁₉H₂₂O₅Na [*M*+Na⁺]: 353.1365, found: 353.1372.

Alcohol 17: colorless oil: $[\alpha]_D +18.1$ (*c* 0.63, CHCl₃); IR $\nu_{\max}$ (film) 3427, 3056, 2978, 2924, 2857, 1715, 1470, 1266, 1114, 1096, 1073, 996, 897 cm⁻¹; ¹H NMR (400 MHz) δ 1.36 (ddd, *J* = 12.4, 8.0, 7.6 Hz, 1H), 1.59 (d, *J* = 6.0 Hz, 1H), 7.71

(dd, $J = 14.4, 4.0$ Hz, 1H), 1.78-1.92 (m, 4H), 2.34 (dd, $J = 14.0, 1.8$ Hz, 1H), 2.35 (m, 1H), 2.47 (ddd, $J = 14.8, 8.0, 6.8$ Hz, 1H), 3.37 (dd, $J = 14.0, 12.0$ Hz, 1H), 3.79 (s, 3H), 3.94-4.02 (m, 2H), 4.17 (m, 1H), 5.12-5.19 (m, 2H), 5.60 (m, 1H), 5.87 (dddd, $J = 17.2, 10.0, 6.8, 6.8$ Hz, 1H), 6.80 (d, $J = 7.2$ Hz, 1H), 6.81 (d, $J = 9.2$ Hz, 1H), 7.26 (dd, $J = 9.2, 7.2$ Hz, 1H); ^{13}C NMR (100MHz) δ 36.2, 37.7, 38.9, 40.6, 41.0 55.8, 65.4, 66.9, 73.1, 74.8, 109.5, 117.7, 122.7, 125.7, 130.2, 133.5, 138.6, 155.6, 170.3; HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_5\text{Na}$ [$M+\text{Na}^+$]: 355.1521, found: 355.1517.

Alcohol 18: colorless oil: $[\alpha]_{\text{D}}^{20} +10.7$ (c 0.49, CHCl_3), lit.¹ (enantiomer) $[\alpha]_{\text{D}}^{20} -10.6$ (c 1.50, CHCl_3); IR ν_{max} (film) 3427, 3056, 2942, 2924, 2841, 1716, 1470, 1266, 1115, 1095, 1072, 996, 896 cm^{-1} ; ^1H NMR (400 MHz) δ 1.51-1.59 (m, 3H), 1.78 (ddd, $J = 12.8, 6.6, 6.0$ Hz, 1H), 1.91 (ddd, $J = 14.8, 11.4, 10.8$ Hz, 1H), 1.99 (ddd, $J = 12.8, 4.4, 4.4$ Hz, 1H), 2.34 (ddd, $J = 14.4, 6.8, 5.6$ Hz, 1H), 2.45 (m, 1H), 2.46 (d, $J = 14.8$ Hz, 1H), 3.39 (dd, $J = 14.8, 10.0$ Hz, 1H), 3.97-4.08 (m, 2H), 4.32 (m, 1H), 5.10-5.18 (m, 2H), 5.59 (dddd, $J = 13.2, 10.8, 5.6, 5.6, 2.4$ Hz, 1H), 5.87 (dddd, $J = 17.2, 10.4, 7.2, 6.8$ Hz, 1H), 6.73 (d, $J = 7.6$ Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 7.22 (t, $J = 8.0$ Hz, 1H); ^{13}C NMR (100MHz) δ 38.1, 38.7, 38.9, 39.4, 39.6, 55.8, 65.1, 67.5, 72.6, 72.8, 109.4, 117.7, 122.8, 125.4, 129.9, 133.6, 138.4, 155.9, 169.1; HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_5\text{Na}$ [$M+\text{Na}^+$]: 355.1521, found: 355.1517.

Diol 3: pale yellow gum: $[\alpha]_{\text{D}}^{20} +5.6$ (c 0.41, MeOH), lit.² $[\alpha]_{\text{D}}^{20} +6.8$ (c 0.16, MeOH), lit.¹ (enantiomer) $[\alpha]_{\text{D}}^{20} -4.5$ (c 0.15, MeOH); ^1H NMR (400 MHz, d_6 -acetone) δ 1.48 (ddd, $J = 12.8, 8.4, 8.4$ Hz, 1H), 1.50 (ddd, $J = 12.8, 8.0, 4.8$ Hz, 1H), 1.57 (ddd, $J = 14.8, 2.4, 2.0$ Hz, 1H), 1.67 (ddd, $J = 12.8, 7.2, 6.8$ Hz, 1H), 1.83 (ddd, $J = 14.8, 10.8, 10.6$ Hz, 1H), 1.92 (ddd, $J = 12.8, 4.4, 4.4$ Hz, 1H), 2.29-2.41 (m, 2H), 2.43 (dd, $J = 14.8, 1.2$ Hz, 1H), 3.33 (dd, $J = 14.8, 9.6$ Hz, 1H), 3.79 (d, $J = 4.4$ Hz, 1H), 3.87 (m, 1H), 3.98 (m, 1H), 4.26 (m, 1H), 5.03 (dddd, $J = 10.2, 2.0, 1.6, 1.6$ Hz, 1H), 5.13 (dddd, $J = 17.2, 2.0, 1.6, 1.6$ Hz, 1H), 5.47 (dddd, $J = 10.6, 5.6, 5.6, 2.4$ Hz, 1H), 5.91 (dddd, $J = 17.2, 10.2, 7.2, 6.8$ Hz, 1H), 6.68 (d, $J = 7.6$

Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 7.10 (dd, $J = 8.0, 7.6$ Hz, 1H), 8.39 (s, 1H); ^{13}C NMR (100MHz, d_6 -acetone) δ 39.0, 39.7, 39.9, 40.1, 40.3, 64.8, 68.0, 73.6, 73.5, 114.3, 117.4, 122.3, 125.4, 130.2, 135.3, 140.2, 154.3, 169.2; HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_5\text{Na}$ [$M+\text{Na}^+$]: 341.1365, found: 341.1364.

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