Supporting Information:

Total Synthesis of Reveromycin B

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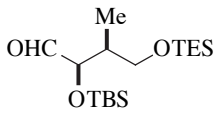
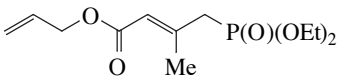
Supplementary material

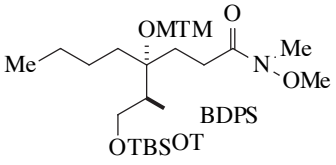
General. Optical rotations were measured on a JASCO DIP-370 polarimeter at the sodium D line (589nm) and are reported as follows: $[\alpha]_D^{t°C}$(*c* in g/100ml, solvent). Infra-red spectra were recorded on a JASCO VALOR-III FTIR spectrometer. ^{1}H nuclear magnetic resonance spectra were recorded on a JEOL JNM-ECP500 (500MHz) or a JEOL AL-300 (300MHz) spectrometer at ambient temperature using an internal deuterium lock. Chemical shifts are reported in parts per million (δ) downfield relative to tetramethylsilane (0ppm) or $CHCl_3$ (7.26ppm) and data are reported as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C nuclear magnetic resonance spectra were recorded on a JEOL JNM-ECP500 (125MHz) or a JEOL AL-300 (75MHz) spectrometer at ambient temperature using an internal deuterium lock with complete proton decoupling. Chemical shifts are reported in parts per million (δ) downfield relative to $CDCl_3$ (77.0ppm). High and low resolution mass spectra were recorded on a JEOL JMS-HX-100 spectrometer.



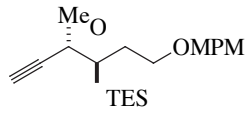
Compound 4: colorless oil; $[\alpha]_D^{25}$ +335.9 (*c* 1.5, $CHCl_3$); IR (film) ν_{max} 2936, 2879, 1737, 1463, 1252, 1091, 839; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 3 H), 0.07 (s, 3 H), 0.58 (q, *J* = 7.7 Hz, 6 H), 0.85 (d, *J* = 7.0 Hz, 3 H), 0.92 (s, 9 H), 0.95 (t, *J* = 7.7 Hz, 9 H), 2.06 (m, 1 H), 3.48 (dd, *J* = 9.9, 7.7 Hz, 1 H), 3.58 (dd, *J* = 9.9, 5.1 Hz, 1 H), 4.16 (dd, *J* = 3.7, 1.5 Hz, 1 H), 9.62 (d, *J* = 1.5 Hz, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ –5.2, –4.6, 4.4, 6.7, 10.8, 18.2, 25.7, 39.8, 63.2, 77.8, 204.8; HRMS, calcd for $C_{17}H_{38}O_3Si_2Na$ ($M+Na^+$) 369.2257, Found 369.2232.



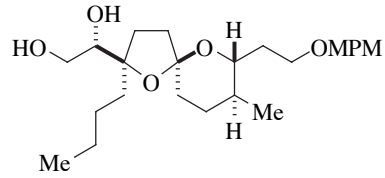
Compound 5: colorless oil; IR (film) ν_{max} 3472, 2984, 2935, 1716, 1648, 1443, 1391, 1250, 1142, 782; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.33 (t, *J* = 7.2 Hz, 6 H), 2.32 (dd, *J* = 3.3, 1.3 Hz, 3 H), 2.70 (dd, *J* = 23.5, 0.9 Hz, 2 H), 4.12 (dq, *J* = 8.1, 7.2 Hz, 4 H), 4.61 (ddd, *J* = 5.7, 1.5, 1.5 Hz, 2 H), 5.23 (ddt, *J* = 10.5, 2.8, 1.5 Hz, 1 H), 5.32 (ddt, *J* = 17.3, 2.8, 1.5 Hz, 1 H), 5.83 (br d, *J* = 5.1 Hz, 1 H), 5.94 (ddt, *J* = 17.3, 10.5, 5.7 Hz, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 16.3 (d), 20.0 (d), 38.5 (d), 62.1 (d), 64.4, 117.8, 119.5 (d), 150.2 (d), 165.4 (d); HRMS, calcd for $C_{12}H_{22}O_5P$ 277.1205 Found 277.1218.



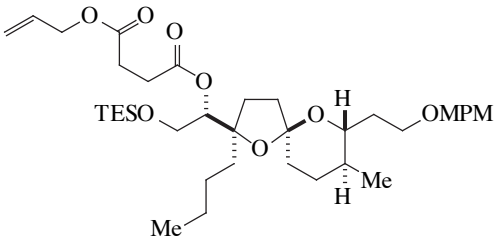
Compound 9: colorless oil; $[\alpha]_D^{21}$ +1.4 (*c* 1.3, $CHCl_3$); IR (film) ν_{max} 3072, 2957, 2932, 2858, 1742, 1672, 1472, 1252, 1112, 1079, 1047; ^{1}H-NMR (300 MHz, $CDCl_3$) δ -0.31 (s, 3 H), -0.18 (s, 3 H), 0.70 (s, 9 H), 0.87 (t, *J* = 6.6 Hz, 3 H), 1.06 (s, 9 H), 2.17 (s, 3 H), 3.13 (s, 3 H), 3.57 (s, 3 H), 3.65 (dd, *J* = 10.6, 5.0 Hz, 1 H), 3.76 (dd, *J* = 5.0, 4.0 Hz, 1 H), 3.86 (dd, *J* = 10.6, 4.0 Hz, 1 H), 4.55 (d, *J* = 10.2 Hz, 2 H), 4.63 (d, *J* = 10.2 Hz, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ –5.9, 14.0, 14.7, 18.2, 19.5, 23.4, 25.8, 25.9, 26.4, 27.2, 28.4, 32.6, 61.1, 64.9, 67.1, 78.9, 81.6, 127.2, 127.4, 129.2, 129.5 133.0, 134.9, 135.9, 136.4; HRMS, calcd for $C_{36}H_{62}NO_5SSi_2$ (M^+) 676.3888, Found 676.3876.



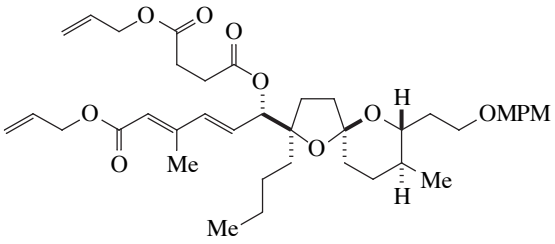
Compound 10: colorless oil; $[\alpha]_D^{24}$ +9.5 (*c* 2.3, $CHCl_3$); IR (film) ν_{max} 3310, 2956, 2877, 1614, 1514, 1459, 1248, 1098, 1039, 1010; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.59 (q, *J* = 7.6 Hz, 6 H), 0.95 (t, *J* = 7.6 Hz, 9 H), 1.16 (d, *J* = 6.9 Hz, 3 H), 1.72 (ddt, *J* = 13.9, 8.6, 6.9 Hz, 1 H), 2.00 (ddt, *J* = 13.9, 6.9, 4.0 Hz, 1 H), 2.05 (d, *J* = 2.3 Hz, 1 H), 2.60 (m, 1 H), 3.53 (t, *J* = 6.9 Hz, 2 H), 3.80 (s, 3 H), 3.91 (dt, *J* = 8.6, 4.0 Hz, 1 H), 4.43 (s, 2 H), 6.88 (d, *J* = 8.6 Hz, 2 H), 7.26 (d, *J* = 8.6 Hz, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 5.0, 6.9, 14.3, 32.3, 33.2, 55.3, 66.9, 69.9, 72.5, 86.2, 113.7, 129.3, 130.0, 159.1; HRMS, calcd for $C_{21}H_{34}O_3Si$ (M^+) 363,2356 Found 363.2355.



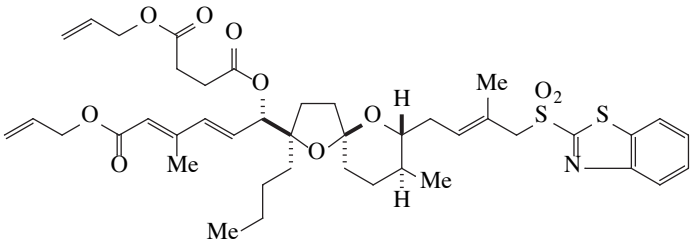
Compound 7: colorless oil; $[\alpha]_D^{25}$ +42.0 (*c* 1.1, $CHCl_3$); IR (film) ν_{max} 3439, 2954, 2933, 2872, 1740, 1613, 1514, 1460, 1249, 1093, 996; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.86 (d, *J* = 6.4 Hz, 3 H), 0.90 (t, *J* = 6.9 Hz, 3 H), 1.99 (m, 2 H), 2.30 (m, 2 H), 3.22 (br s, 1 H), 3.40 (ddd, *J* = 11.5, 8.7, 4.6 Hz, 1 H), 3.50 (ddd, *J* = 10.8, 6.2, 4.6 Hz, 1 H), 3.59 (ddd, *J* = 9.6, 9.6, 2.7 Hz, 1 H), 3.68 (m, 2 H), 3.74 (ddd, *J* = 8.2, 4.6, 1.8 Hz, 1 H), 3.80 (s, 3 H), 4.40 (d, *J* = 11.5 Hz, 1 H), 4.47 (d, *J* = 11.5 Hz, 1 H), 6.88 (d, *J* = 8.7 Hz, 2 H), 7.27 (d, *J* = 8.7 Hz, 2 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.1, 17.8, 23.3, 25.4, 28.7, 29.2, 33.0, 34.8, 35.2, 36.2, 39.3, 55.3, 63.5, 65.9, 72.3, 73.4, 75.8, 89.3, 106.2, 113.7, 129.3, 130.6, 159.2; HRMS, calcd for $C_{25}H_{40}O_6$ 437.2903 Found 437.2893.



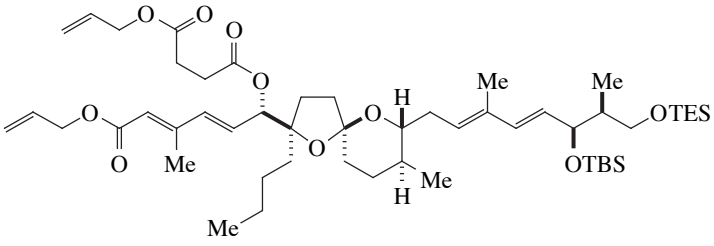
Compound 22: colorless oil; $[\alpha]_D^{25}$ +17.7 (*c* 1.3, $CHCl_3$); IR (film) ν_{max} 2946, 2877, 1742, 1613, 1514, 1460, 1379, 932; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.57 (q, *J* = 7.8 Hz, 6 H), 0.84 (d, *J* = 6.4 Hz, 3 H), 0.91 (t, *J* = 7.3 Hz, 3 H), 0.94 (t, *J* = 7.8 Hz, 9 H), 1.98 (m, 3 H), 2.67 (m, 4 H), 3.43 (ddd, *J* = 9.6, 9.6, 2.3 Hz, 1 H), 3.63 (ddd, *J* = 10.1, 10.1, 5.5 Hz, 1 H), 3.75 (dd, *J* = 10.5, 7.8 Hz, 1 H), 3.79 (s, 3 H), 3.83 (ddd, *J* = 10.1, 10.1, 5.5 Hz, 1 H), 3.98 (dd, *J* = 10.5, 2.3 Hz, 1 H), 4.46 (s, 2 H), 4.58 (ddd, *J* = 5.5, 1.4, 1.4 Hz, 2 H), 5.10 (dd, *J* = 7.8, 2.3 Hz, 1 H), 5.21 (ddt, *J* = 10.1, 2.3, 1.4 Hz, 1 H), 5.30 (ddt, *J* = 15.6, 2.3, 1.4 Hz, 1 H), 5.89 (ddt, *J* = 15.6, 10.1, 5.5 Hz, 1 H), 6.85 (d, *J* = 8.7 Hz, 2 H), 7.29 (d, *J* = 8.7 Hz, 2 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 4.4, 6.8, 14.2, 17.8, 23.3, 25.6, 29.3, 29.4, 31.9, 33.6, 34.0, 34.6, 34.8, 38.7, 55.2, 62.3, 65.3, 68.4, 72.6, 74.2, 80.7, 86.3, 106.7, 113.6, 118.2, 129.4, 131.4, 132.0, 158.9, 171.2, 171.9; HRMS, calcd for $C_{38}H_{62}O_9Si$ (M^+) 691.4242 Found 691.4224.



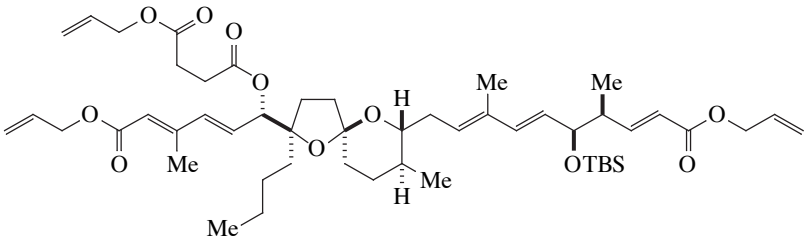
Compound 24: colorless oil; $[\alpha]_D^{25}$ –2.5 (*c* 1.2, $CHCl_3$); IR (film) ν_{max} 2954, 2862, 1740, 1716, 1614, 1514, 1248, 1151, 992; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.85 (d, *J* = 6.4 Hz, 3 H), 0.89 (t, *J* = 6.8 Hz, 3 H), 1.96 (m, 3 H), 2.25 (d, *J* = 0.9 Hz, 3 H), 2.72 (m, 4 H), 3.49 (ddd, *J* = 9.6, 9.6, 2.3 Hz, 1 H), 3.62 (t, *J* = 7.3 Hz, 2 H), 3.76 (s, 3 H), 4.38 (d, *J* = 11.5 Hz, 1 H), 4.46 (d, *J* = 11.5 Hz, 1 H), 4.58 (ddd, *J* = 6.0, 2.8, 1.4 Hz, 2 H), 4.62 (ddd, *J* = 5.5, 2.8, 1.4 Hz, 2 H), 5.22 (m, 2 H), 5.30 (ddt, *J* = 15.6, 2.8, 1.4 Hz, 1 H), 5.33 (ddt, *J* = 15.1, 2.8, 1.4 Hz, 1 H), 5.50 (d, *J* = 1.8 Hz, 1 H), 5.78 (s, 1 H), 5.92 (m, 2 H), 6.23 (s, 2 H), 6.81 (d, *J* = 8.7 Hz, 2 H), 7.23 (d, *J* = 8.7 Hz, 2 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 13.9, 14.2, 18.0, 23.2, 25.4, 29.1, 29.2, 32.1, 33.8, 34.0, 34.6, 34.8, 38.9, 55.2, 64.4, 65.4, 67.1, 72.4, 74.1, 79.6, 87.2, 107.1, 113.5, 117.8, 118.4, 119.3, 129.4, 131.1, 131.8, 131.9, 132.6, 134.2, 152.0, 158.9, 166.6, 170.9, 171.8; HRMS, calcd for $C_{40}H_{56}O_{10}Na$ ($M+Na^+$) 719.3771, Found 719.3763.



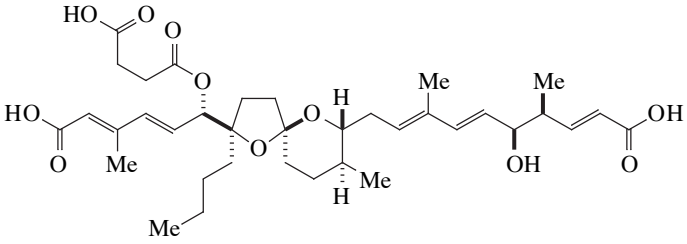
Compound 3: colorless oil; $[\alpha]_D^{25}$ –11.1 (*c* 0.1, $CHCl_3$); IR (film) ν_{max} 3024, 2955, 2873, 1737, 1716, 1614, 1379, 1331, 1234, 1155, 992; 1H-NMR (500 MHz, $CDCl_3$) δ 0.65 (d, *J* = 6.4 Hz, 3 H), 0.87 (t, *J* = 7.3 Hz, 3 H), 1.83 (s, 3 H), 2.26 (d, *J* = 0.9 Hz, 3 H), 2.66 (m, 4 H), 3.28 (ddd, *J* = 10.1, 6.9, 3.2 Hz, 1 H), 4.14 (d, *J* = 13.7 Hz, 1 H), 4.35 (d, *J* = 13.7 Hz, 1 H), 4.58 (br d, *J* = 6.0 Hz, 2 H), 4.62 (br d, *J* = 6.0 Hz, 2 H), 5.22 (br dd, *J* = 10.5, 1.4 Hz, 2 H), 5.30 (br dd, *J* = 17.1, 1.4 Hz, 1 H), 5.32 (br dd, *J* = 17.1, 1.4 Hz, 1 H), 5.34 (br s, 1 H), 5.55 (dd, *J* = 6.9, 6.9 Hz, 1 H), 5.81 (br s, 1 H), 5.89 (dt, *J* = 17.1, 10.5, 6.0 Hz, 1 H), 5.95 (dt, *J* = 17.1, 10.5, 6.0 Hz, 1 H), 6.15 (s, 2 H), 7.56 (ddd, *J* = 7.8, 7.8, 1.4 Hz, 1 H), 7.61 (ddd, *J* = 7.8, 7.8, 1.4 Hz, 1 H), 7.99 (d, *J* = 7.8 Hz, 1 H), 8.22 (d, *J* = 7.8 Hz, 1 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.0, 14.2, 17.0, 17.6, 23.2, 25.3, 28.9, 29.0, 29.1, 31.7, 31.8, 33.6, 34.6, 38.6, 64.4, 64.5, 65.5, 75.5, 79.3, 87.0, 107.0, 117.8, 118.4, 119.4, 122.8, 123.4, 125.4, 127.4, 127.7, 131.5, 132.0, 132.5, 133.9, 134.4, 137.0, 151.7, 152.8, 166.5, 171.1, 171.8; HRMS, calcd for $C_{42}H_{55}O_{10}NS_2Na$; 820.3165 Found 820.3165.



Compound 32: colorless oil; $[\alpha]_D^{25}$ –50.4 (*c* 0.8, $CHCl_3$); IR (film) ν_{max} 2956, 2877, 1791, 1742, 1716, 1615, 1461, 1251, 1233, 1150, 1006; ^{1}H-NMR (500 MHz, $CDCl_3$) δ –0.03 (s, 3 H), 0.02 (s, 3 H), 0.57 (q, *J* = 7.8 Hz, 6 H), 0.87 (s, 9 H), 0.94 (t, *J* = 7.8 Hz, 9 H), 1.71 (s, 3 H), 2.29 (s, 3 H), 2.69 (m, 4 H), 3.36 (dd, *J* = 9.6, 6.9 Hz, 1 H), 3.47 (m, 1 H), 3.61 (dd, *J* = 9.6, 6.0 Hz, 1 H), 4.19 (dd, *J* = 7.3, 3.7 Hz, 1 H), 4.59 (br d, *J* = 5.5 Hz, 1 H), 4.62 (br d, *J* = 5.5 Hz, 1 H), 5.22 (br d, *J* = 10.1 Hz, 2 H), 5.30 (m, 1 H), 5.33 (m, 1 H), 5.47 (dd, *J* = 15.6, 7.3 Hz, 1 H), 5.53 (d, *J* = 2.3 Hz, 1 H), 5.60 (dd, *J* = 6.9, 6.9 Hz, 1 H), 5.82 (br s, 1 H), 5.91 (m, 2 H), 6.18 (d, *J* = 15.6 Hz, 1 H), 6.21 (m, 2 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ –5.0, –4.0, 4.5, 6.8, 11.4, 12.7, 14.0, 14.2, 17.8, 18.2, 23.2, 25.4, 25.9, 29.1, 29.2, 31.6, 31.8, 33.6, 34.1, 34.6, 38.7, 43.2, 64.5, 65.0, 65.4, 74.3, 76.3, 79.0, 87.1, 107.2, 117.8, 118.4, 119.3, 127.7, 128.6, 131.6, 132.0, 132.5, 134.3, 134.8, 135.0, 151.9, 166.6, 170.9, 171.8; HRMS, calcd for $C_{52}H_{88}O_{10}Si_2Na$ ($M+Na^+$) 951.5814, Found 951.5811.



Compound 34: colorless oil; $[\alpha]_D^{25}$ –53.7 (*c* 0.4, $CHCl_3$); IR (film) ν_{max} 2955, 2859, 1740, 1720, 1651, 1614, 1252, 1233, 1151, 1070; ^{1}H-NMR (500 MHz, $CDCl_3$) δ –0.03 (s, 3 H), 0.01 (s, 3 H), 0.83 (d, *J* = 6.4 Hz, 3 H), 0.86 (s, 9 H), 0.88 (t, *J* = 7.3 Hz, 3 H), 0.97 (d, *J* = 6.9 Hz, 3 H), 1.69 (s, 3 H), 2.24 (m, 1 H), 2.27 (s, 3 H), 2.45 (m, 2 H), 2.68 (s, 4 H), 3.44 (ddd, *J* = 9.6, 6.9, 3.2 Hz, 1 H), 4.09 (dd, *J* = 7.8, 4.6 Hz, 1 H), 4.60 (m, 6 H), 5.21 (m, 3 H), 5.30 (m, 3 H), 5.38 (dd, *J* = 15.6, 7.8 Hz, 1 H), 5.52 (d, *J* = 2.8 Hz, 1 H), 5.66 (dd, *J* = 6.9, 6.9 Hz, 1 H), 5.78 (m, 2 H), 5.90 (m, 3 H), 6.20 (m, 2 H), 6.22 (d, *J* = 16.0 Hz, 1 H), 7.05 (dd, *J* = 16.0, 7.3 Hz, 1 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ –5.0, –4.1, 12.6, 13.8, 13.9, 14.2, 17.8, 18.1, 23.2, 25.3, 25.8, 29.0, 29.2, 29.6, 31.7, 31.9, 33.9, 34.1, 34.5, 38.7, 43.8, 64.4, 64.7, 65.4, 76.4, 77.1, 79.1, 87.1, 107.2, 117.7, 118.4, 119.3, 120.4, 126.9, 128.9, 131.6, 131.9, 132.4, 132.5, 134.0, 134.8, 136.4, 151.9, 152.4, 166.3, 166.5, 170.8, 171.7; HRMS, calcd for $C_{51}H_{78}O_{11}SiNa$ ($M+Na^+$) 917.5211 Found 917.5210.



Reveromycin B (2): white powder; $[\alpha]_D^{25}$ –51.8 (*c* 0.3, MeOH), natural[lit.1a] $[\alpha]_D^{20}$ –66 (*c* 0.1, MeOH); IR (film) ν_{max} 3429, 2957, 2931, 2874, 1738, 1695, 1647, 1418, 1375, 1253, 1162; ^{1}H-NMR (500 MHz, CD_3OD) δ 0.88 (d, *J* = 6.4 Hz, 3 H), 0.91 (t, *J* = 6.9 Hz, 3 H), 1.00 (d, *J* = 6.4 Hz, 3 H), 1.73 (s, 3 H), 2.22 (s, 3 H), 2.49 (m, 1 H), 2.55 (m, 1 H), 2.62~2.70 (m, 4 H), 3.44 (ddd, *J* = 11.0, 8.7. 2.8 Hz, 1 H), 4.07 (dd, *J* = 7.3, 5.5 Hz, 1 H), 5.46 (dd, *J* = 15.6, 7.3 Hz, 1 H), 5.56 (d, *J* = 3.7 Hz, 1 H), 5.76 (dd, *J* = 7.8, 7.8 Hz, 1 H), 5.77 (br s, 1 H) , 5.78 (d, *J* = 15.6 Hz, 1 H), 6.23 (dd, *J* = 16.0, 3.7 Hz, 1 H), 6.27 (d, *J* = 16.0 Hz, 1 H), 6.38 (d, *J* = 15.6 Hz, 1 H), 6.98 (dd, *J* = 15.6, 7.3 Hz, 1 H); ^{13}C-NMR (125 MHz, CD_3OD) δ 12.7, 14.0, 14.5, 15.1, 18.2, 24.3, 26.1, 29.9, 30.4, 30.7, 32.9, 35.3, 35.6, 35.7, 39.7, 44.0, 77.1, 78.5, 80.4, 88.8, 108.6, 121.3, 122.6, 127.2, 130.9, 132.5, 135.2, 136.1, 138.6, 152.4, 152.9, 173.1; HRMS, calcd for $C_{36}H_{52}O_{11}Na$ ($M+Na^+$) 683.3407, Found 683.3391.