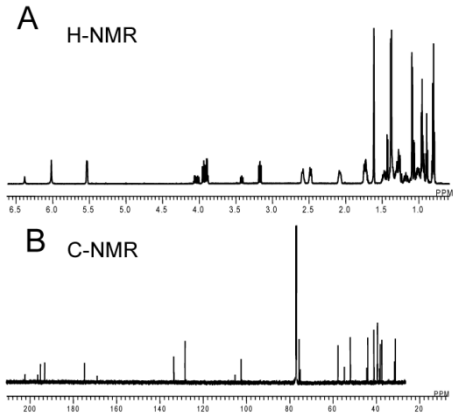

FIG. S1. 1H (a) and 13C NMR (b) spectra of signermycin B.^{1}H NMR (600 MHz, $CDCl_3$)(Fig. S1a): δ 5.93 (brs, 1H, H1'), 5.55 (brd, *J*=5.9, 1H, H9), 3.94 (dd, *J*=10.4, 11.6, 1H, H2), 3.90 (q, 7.0, 1H, H5'), 3.17 (dd, *J*=9.5, 10.7, 1H, H5), 2.59 (m, 1H, H11), 2.48 (m, 1H, H3), 2.08 (m, 1H, H8), 1.60 (s, 3H, H18), 1.38 (d, *J*=7.0, H6'), 1.36 (m, 2H, H4, 6), 1.24, 1.74 (m, m, 2H, H7), 1.17 1.47 (m, m, 2H, H12), 1.09 (d, *J*=6.3, 3H, H17), 1.00 1.30 (m, m, 2H, H13), 0.95 (t, *J*=7.2, 1H, H16), 0.94 1.72 (m, m, 2H, H15), 0.79 (t, *J*=7.3, 3H, H14); ^{13}C NMR (150 MHz, $CDCl_3$)(Fig. S1b): δ195.2 (s, C4'), 193.3 (s, C1), 174.9 (s, C2'), 133.6 (s, C10), 128.4 (d, C9), 102.5 (s, C3'), 75.7 (d, C5), 57.7 (d, C5'), 52.0 (d, C4), 43.9 (d, C11), 41.1 (d, C6), 39.5 (d, C3), 39.5 (d, C8), 38.2 (d, C2), 37.5 (t, C7), 31.2 (t, C12), 21.5 (t, C15), 20.9 (q, C18), 18.7 (q, C17), 17.7 (q, C6'), 17.0 (t, C13), 14.7 (q, C14), 13.5 (q, C16);Chemical shifts are reported as δ values relative to tetramethylsilane (TMS, 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad), coupling constant, and integration.