

## Supplementary material

*Physical data for compound glucopyranosyl vinylsulfone:* Syrup;  $[\alpha]_D -9^\circ$ ,  $[\alpha]_{436} -16^\circ$  (c1, H<sub>2</sub>O); <sup>1</sup>H NMR (300 MHz, MeOH-d<sub>4</sub>): 6.97 (dd, 1H, *J* = 16.7 and 10.0 Hz), 6.43 (d, 1H, *J* = 16.7 Hz), 6.30 (d, 1H, *J* = 10.0 Hz), 4.78 (s, 3H), 4.34 (d, 1H, *J* = 9.5 Hz), 3.86 (dd, 1H, *J* = 12.5 and 2.0 Hz), 3.69 (t, 1H, *J* = 9.1 Hz), 3.68 (dd, 1H, *J* = 12.6 and 5.3 Hz), 3.45 (t, 1H, *J* = 8.8 Hz), 3.40 (ddd, 1H, *J* = 9.6, 5.5 and 2.1 Hz), 3.34 (s, 1H), 3.31 (t, 1H, *J* = 9.3 Hz); <sup>13</sup>C NMR (75 MHz, MeOH-d<sub>4</sub>): 136.2, 132.4, 92.6, 82.8, 78.8, 71.0, 70.5 and 62.4; HMRS (FAB): *m/z* calcd for C<sub>8</sub>H<sub>14</sub>O<sub>7</sub>SNa (M + Na)<sup>+</sup>, 277.0358; found (M+Na)<sup>+</sup>, 277.0356.