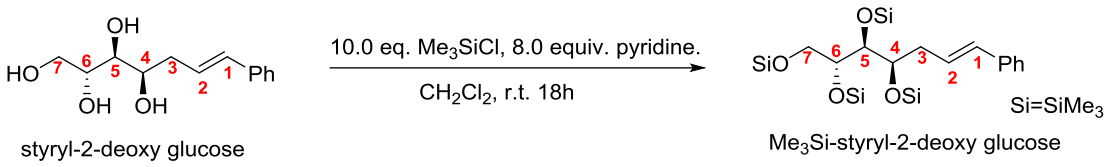
Supporting Information

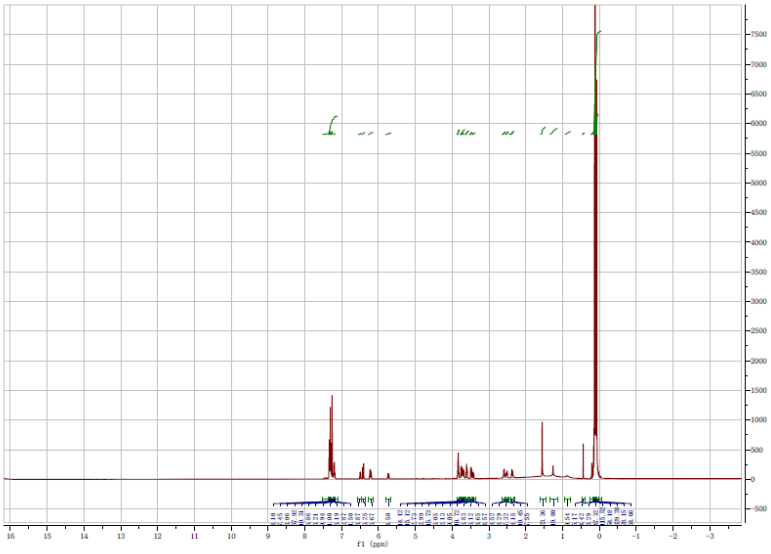
NMR characterization for previously unreported compounds:



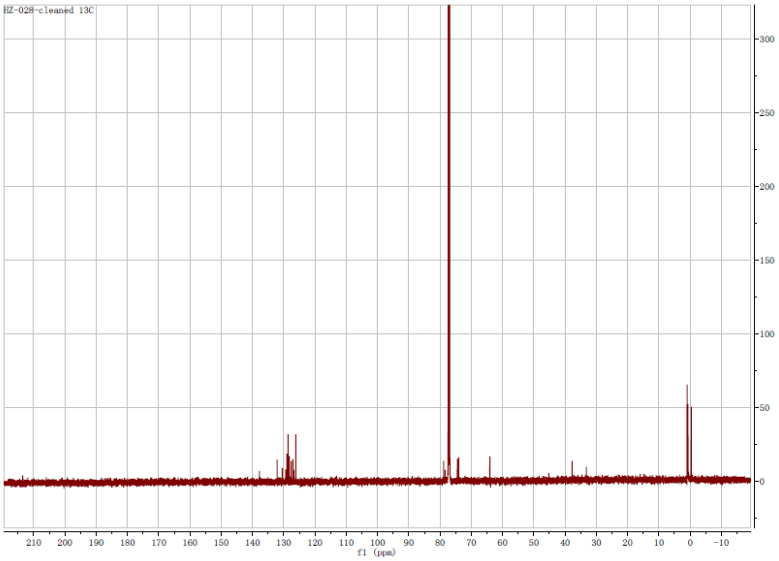
styryl-2-deoxy glucose

Me_3Si-styryl-2-deoxy glucose

^{1}H-NMR:

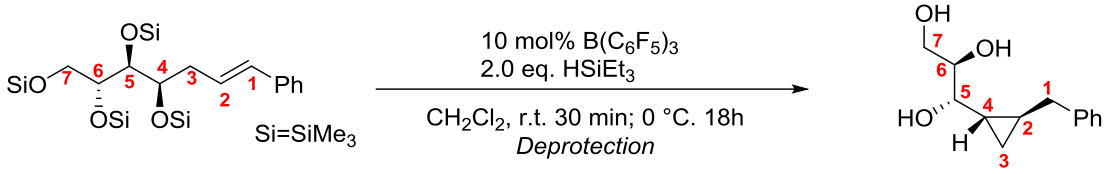


^{13}C-NMR:

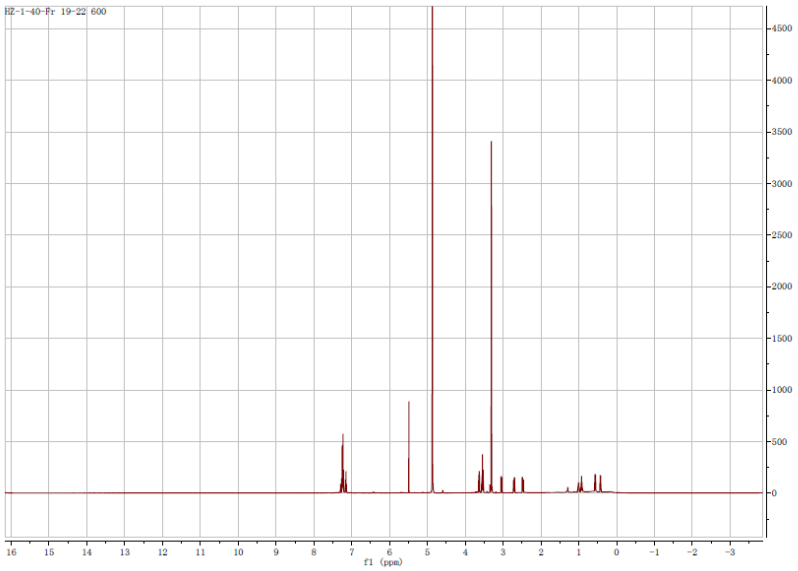


Me_3Si-Styryl-2-deoxy glucose: Prepared and used as a 61:39 *E/Z* mixture. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35–7.19 (m, 4H, Ar, *E* & *Z*), 6.49 (d, 1H, H_1, *Z*), 6.42 (d, 1H, H_1, *E*), 6.22 (ddd, $J_{H2,H1}$ = 14.4 Hz, $J_{H2,H3}$ = $J_{H2,H3'}$= 8.4 Hz, 1H, H_2, *E*), 5.73 (ddd, $J_{H2,H1}$= 14.4 Hz, $J_{H2,H3}$ = $J_{H2,H3'}$ = 7.2 Hz, 1H, H_2, *Z*), 3.85–3.81 (m, 2H, *Z*&*E*), 3.76–3.68 (m, 2H, *Z*&*E*), 3.62–3.58 (m, 1H, *Z*&*E*), 3.48 (dd, $J_{H5,H6}$ = 7.2 Hz, $J_{H5,H4}$ = 3.6 Hz, 1H, H_5, *E*), 3.43 (dd, $J_{H5,H6}$ = 6.6 Hz, $J_{H5,H4}$ = 3.6 Hz, 1H, H_5, *Z*), 2.60–2.56 (m, 2H, *Z*), 2.54–2.50 (m, 1H, *E*), 2.39–2.34 (m, 1H, *E*),

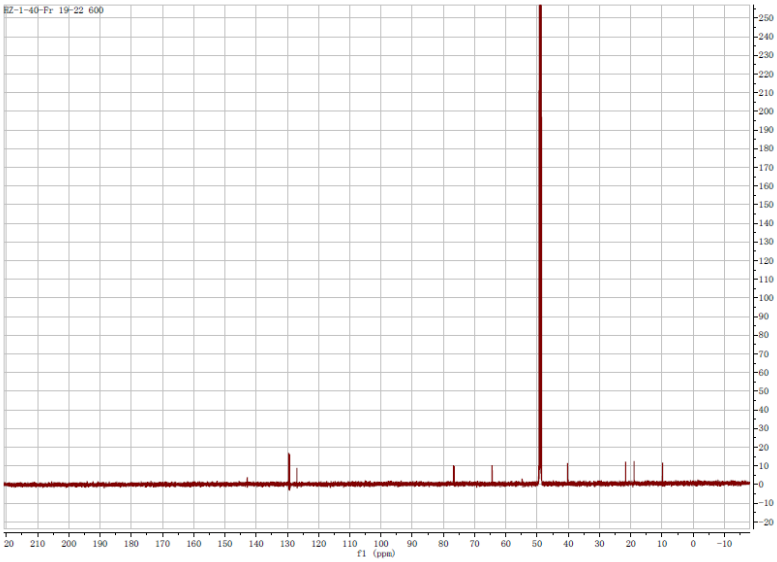
0.14 (s, 9H, -Si(CH_3)$_3$), 0.12 (s, 18H, -Si(CH_3)$_3$), 0.10 (s, 9H, -Si(CH_3)$_3$), 0.083 (s, 9H, -Si(CH_3)$_3$), 0.071 (s, 9H, -Si(CH_3)$_3$). ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ 132.1 (s), 130.4 (s), 129.4 (s), 129.0 (s), 128.6 (s), 128.3 (s), 127.6 (s), 127.1 (s), 126.7 (s), 126.1 (s), 78.9 (s), 78.4 (s), 74.5 (s), 74.4 (s), 74.0 (s), 64.1 (s), 64.0 (s), 37.8 (s), 33.2 (s), 0.98, 0.95, 0.80, 0.68, 0.64, -0.37, -0.41 (each a s, -Si(CH_3)$_3$).



^{1}H-NMR:



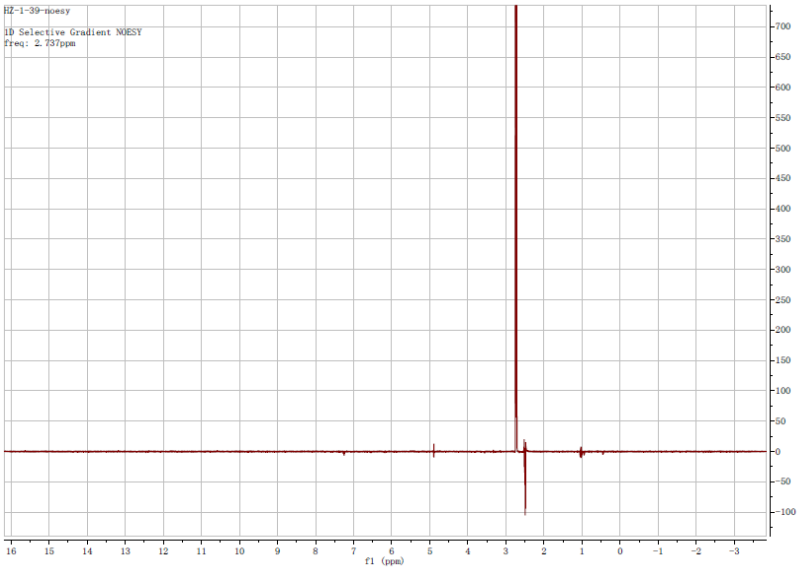
^{13}C-NMR:



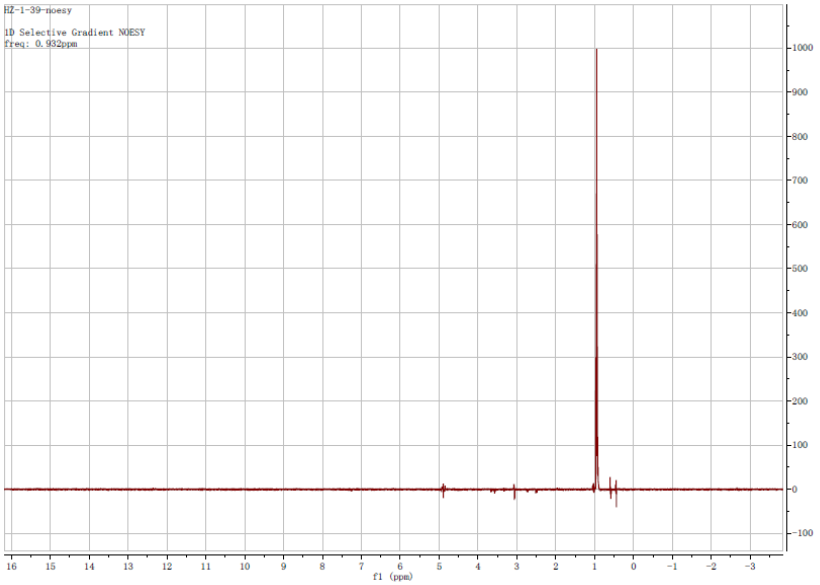
(1*R*,2*S*)-1-((1*S*,2*R*)-2-benzylcyclopropyl)propane-1,2,3-triol: ^{1}H NMR (600 MHz, CD_3OD): δ 7.27-7.22 (m, 4H, Ar), 7.17-7.14 (m, 1H, Ar), 3.66 (dd, $J_{H7,H7'}$ = 10.2 Hz, $J_{H7,H6}$ = 3.0 Hz, 1H, H_7), 3.58-3.54 (m, 2H, H_6 & $H_{7'}$), 3.07 (dd, $J_{H5,H4}$ = 7.8 Hz, $J_{H5,H6}$ = 4.2 Hz, 1H, H_5), 2.73

(dd, $J_{H1,\,H1'}$ = 14.4 Hz, $J_{H1,H2}$ = 6.0 Hz, 1H, H_1), 2.50 (dd, $J_{H1'\,H1}$ = 14.4 Hz, $J_{H1',\,H2}$ = 7.2 Hz, 1H, $H_{1'}$), 1.03 – 0.91 (m, 1H, H_2), 0.95 – 0.91 (m, 1H, H_4), 0.57 (ddd, $J_{H3,H3'}$ = 9.0 Hz, $J_{H3,H2}$ = $J_{H3,H4}$ = 4.8 Hz, 1H, H_3), 0.43 (ddd, $J_{H3',H3}$ = 9.0 Hz, $J_{H3',H2}$ = $J_{H3',H4}$ = 5.4 Hz, 1H, $H_{3'}$). ^{13}C {^1H} NMR (151 MHz, CD_3OD): δ 142.8 (s, Ph), 129.5 (s, Ph), 129.3 (s, Ph), 126.9 (s, Ph), 76.8 (s, C_5), 76.5 (s, C_6), 64.4 (s, C_7), 40.3 (s, C_1), 21.6 (s, C_4), 18.9 (s, C_2), 9.8 (s, C_3). Specific rotation: $[\alpha]^{D}_{24.9}$ -35 (c = 0.11 CH_3OH).

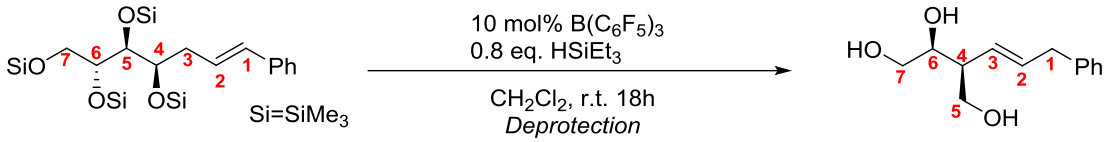
Selective 1D-gNOESY:



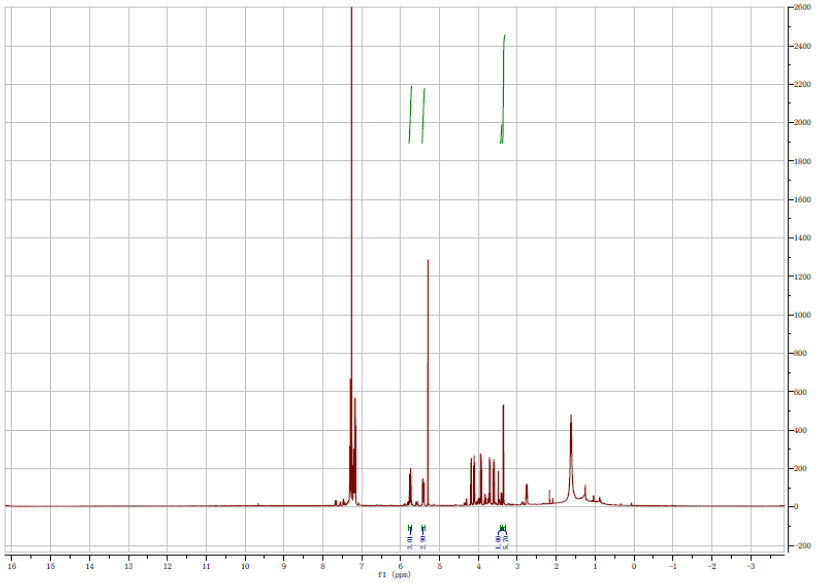
Excitation frequency: 2.73 ppm (H_1), response frequency: 2.50 (H_1').



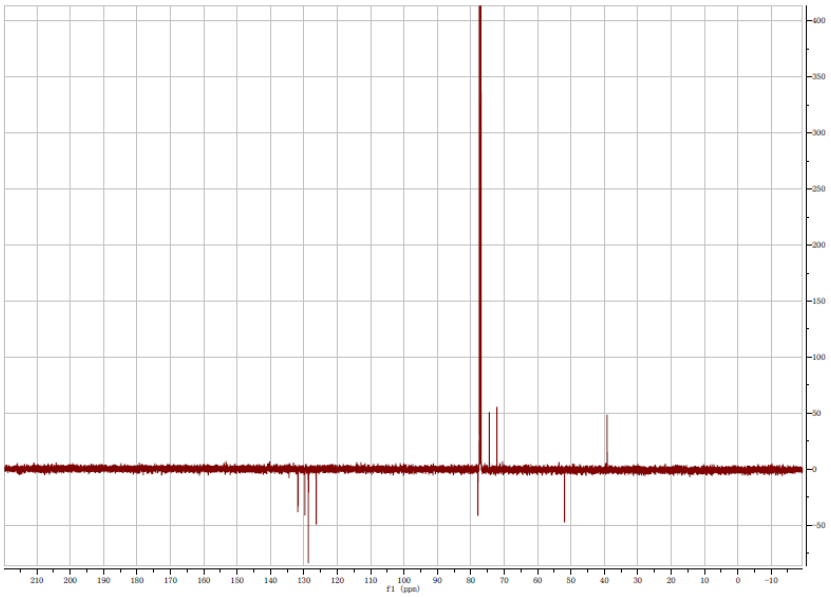
Excitation frequency: 0.932 ppm (H_4), Response frequency 0.57 (H_3) and 0.43 (H_3') ppm. No observable response signal at H_2 frequency: H_2 and H_4 have anti relation.



^{1}H-NMR:



^{13}C-APT:



(2R,3R)-3-((E)-3-phenylprop-1-en-1-yl)butane-1,2,4-triol: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31-7.16 (m, 5H, Ar), 5.75 (ddd, $J_{H2,H3}$ = 15.6 Hz, $J_{H2,H1}$ = $J_{H1',H2}$ = 6.6 Hz, 1H, H_2), 5.42 (dd, $J_{H3,H2}$ = 15.6 Hz, $J_{H3,H4}$ = 8.4Hz, 1H, H_3), 4.19 (dt, $J_{H7,H6}$ = $J_{H7',H6}$ = 3.6 Hz, $J_{H4,H6}$ = 8.4 Hz, 1H, H_6), 4.11 (dd, $J_{H4,H5}$ = 7.6 Hz, $J_{H5,H5'}$ = 9 Hz, 1H, H_5), 3.93 (dd, $J_{H6,H7}$ = 4.8 Hz, $J_{H7',H7}$ = 9.6 Hz, 1H, H_7), 3.71 (dd, $J_{H6,H7'}$ = 3.0 Hz, $J_{H7,H7'}$ = 9.6 Hz, 1H, $H_{7'}$), 3.60 (dd, $J_{H5,H5'}$ = 9 Hz, $J_{H5,H4}$ = 6Hz, 1H, H_5), 3.36 (d, $J_{H1,H2}$ = $J_{H1',H2}$ = 7.2 Hz, 2H, H_1 & $H_{1'}$), 2.76 (m, 1H, H_4). ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ 131.8

(s, C_2), 129.7 (s, C_3), 128.6 (q, Ph), 126.3 (s, Ph), 77.8 (s, C_6), 74.4 (s, C_7), 72.1 (s, C_5), 51.9 (s, C_4), 39.1 (s, C_1).