Supplementary Materials for

Eight out of Eight: A Detailed Kinetic Study on the Reactivities of the Eight Hydroxyl groups of Sucrose with Phenyl Isocyanate

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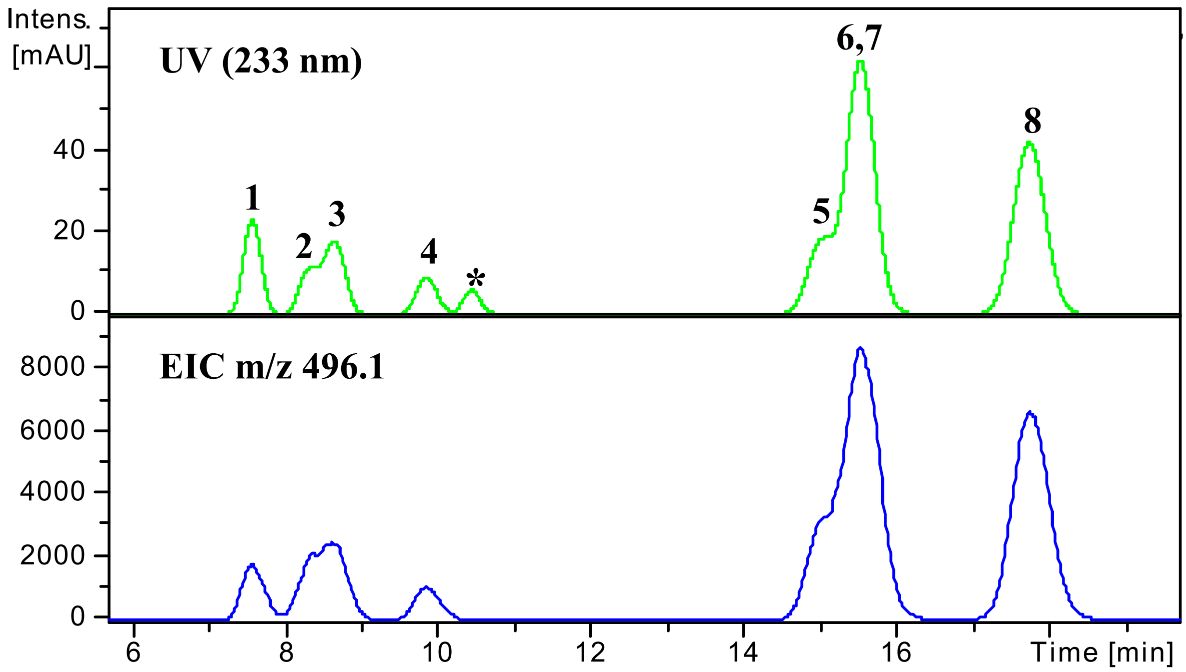

Figure S1. The HPLC-UV and the extracted ion (EIC at m/z 496.1) chromatograms

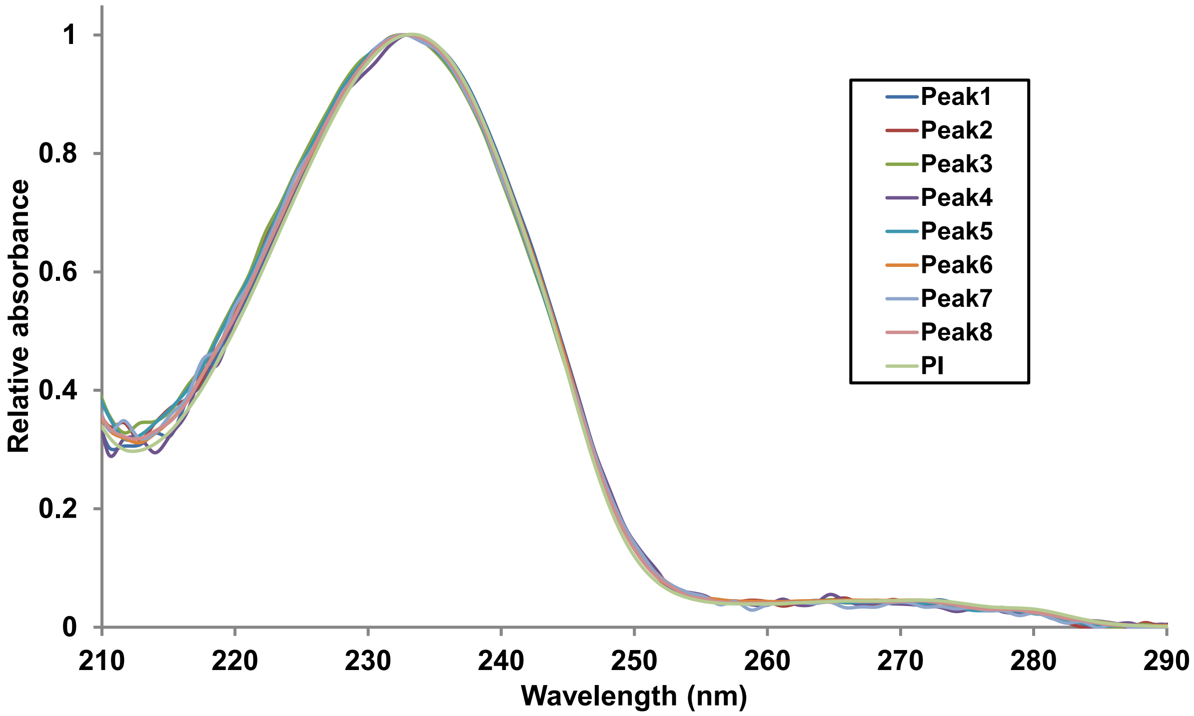

Figure S2. The normalized UV-spectra extracted at each peak from 1 to 8 together with the spectrum of methyl phenylcarbamate (PI)

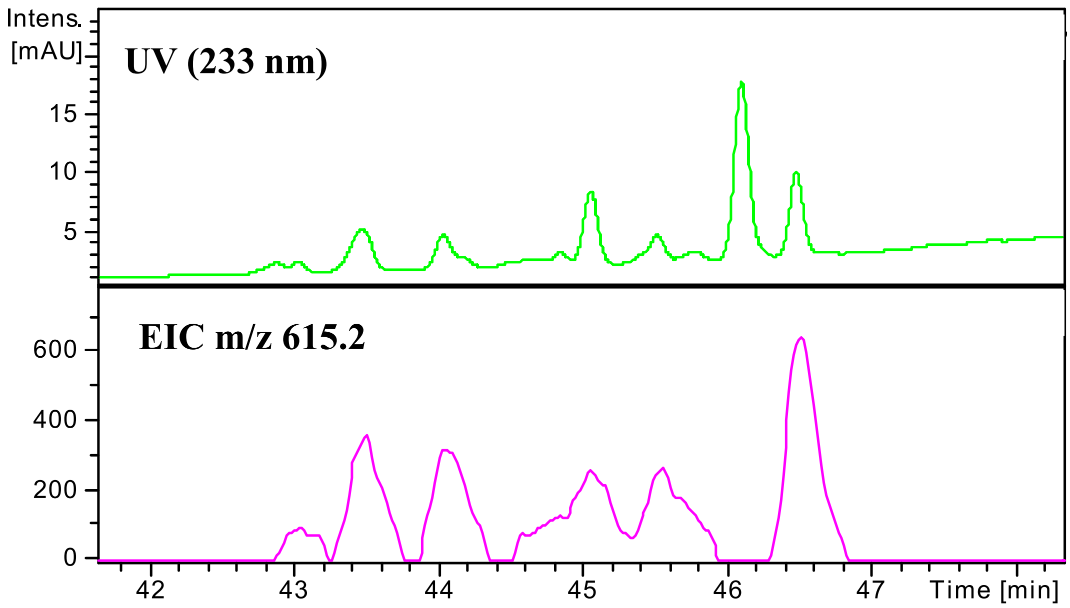

Figure S3. The HPLC-UV and the extracted ion (EIC at m/z 615.2) chromatograms
(m/z 615.2 corresponds to the chlorinated adduct of sucrose + 2 phenyl isocyanate)

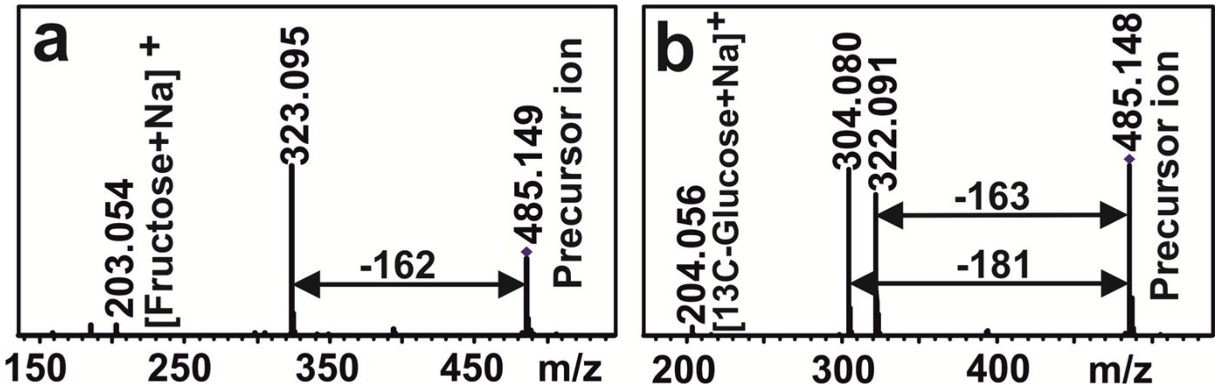

Figure S4. The MS/MS spectra for the products of ^{13}C-sucrose-phenyl isocyanate reaction at peak 6 (b) and peak 8 (a)

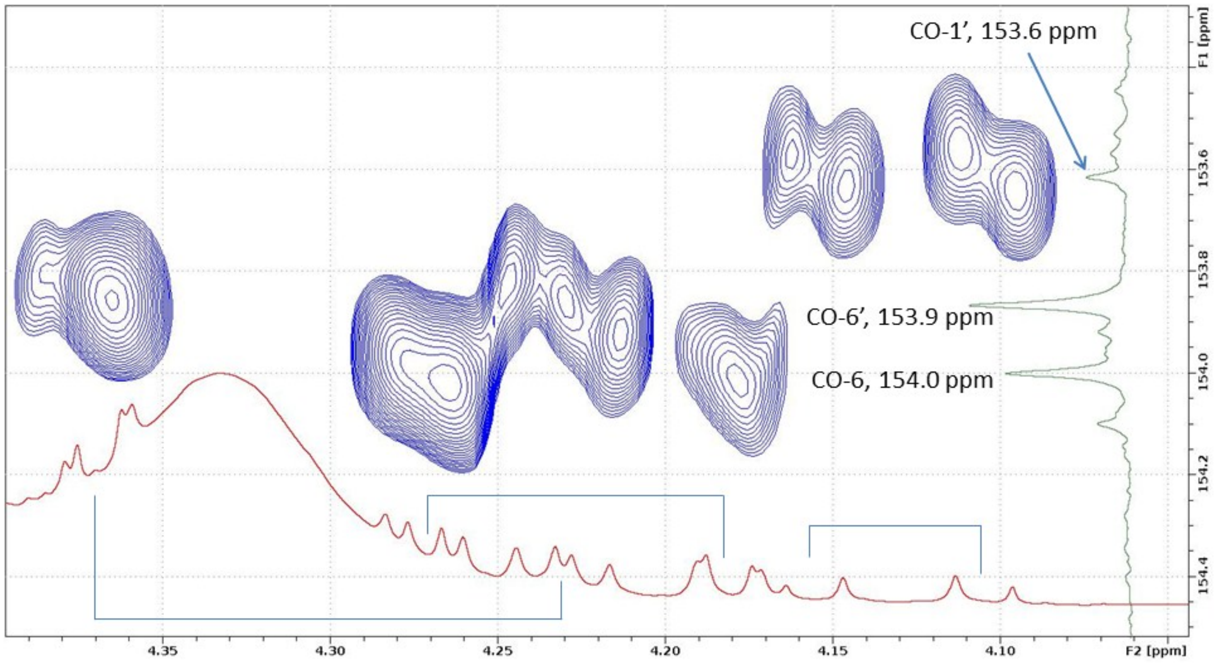

Figure S5. Partial ^{13}C-^{1}H HMBC NMR spectrum of sucrose (S) - phenyl isocyanate (PI) reaction mixture

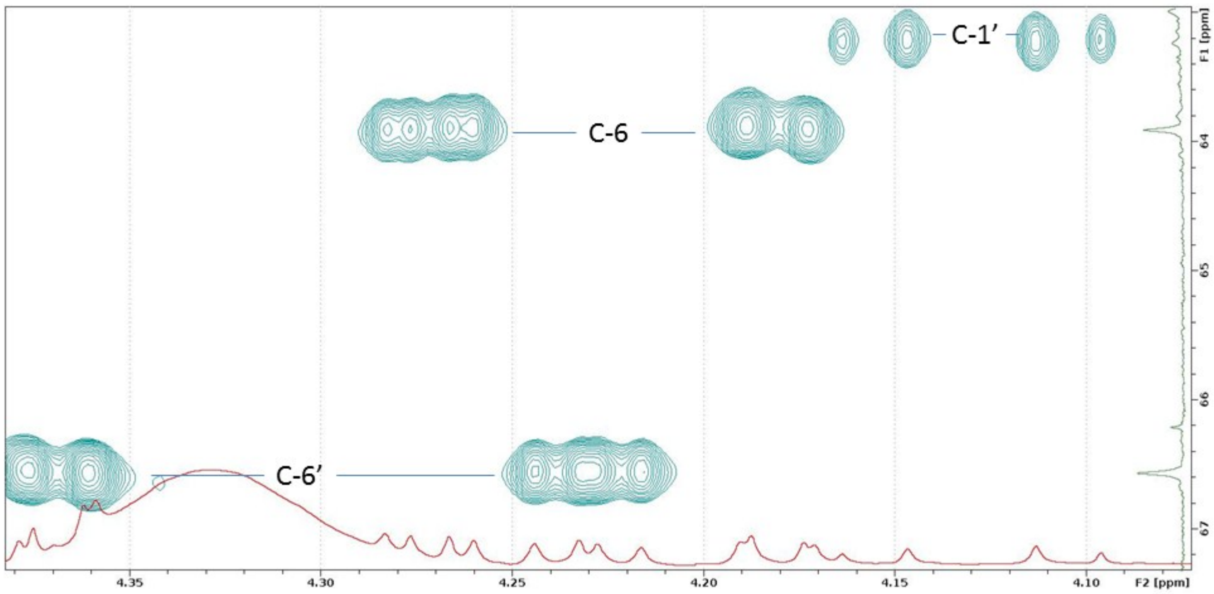

Figure S6. Excerpt from ^{13}C-^{1}H HSQC NMR spectrum of sucrose (S) - phenyl isocyanate (PI) reaction mixture. Appropriate part of the 1D ^{1}H NMR spectrum is shown at the horizontal axis. ^{1}H assignments of CH_2 groups are shown in Fig S8.

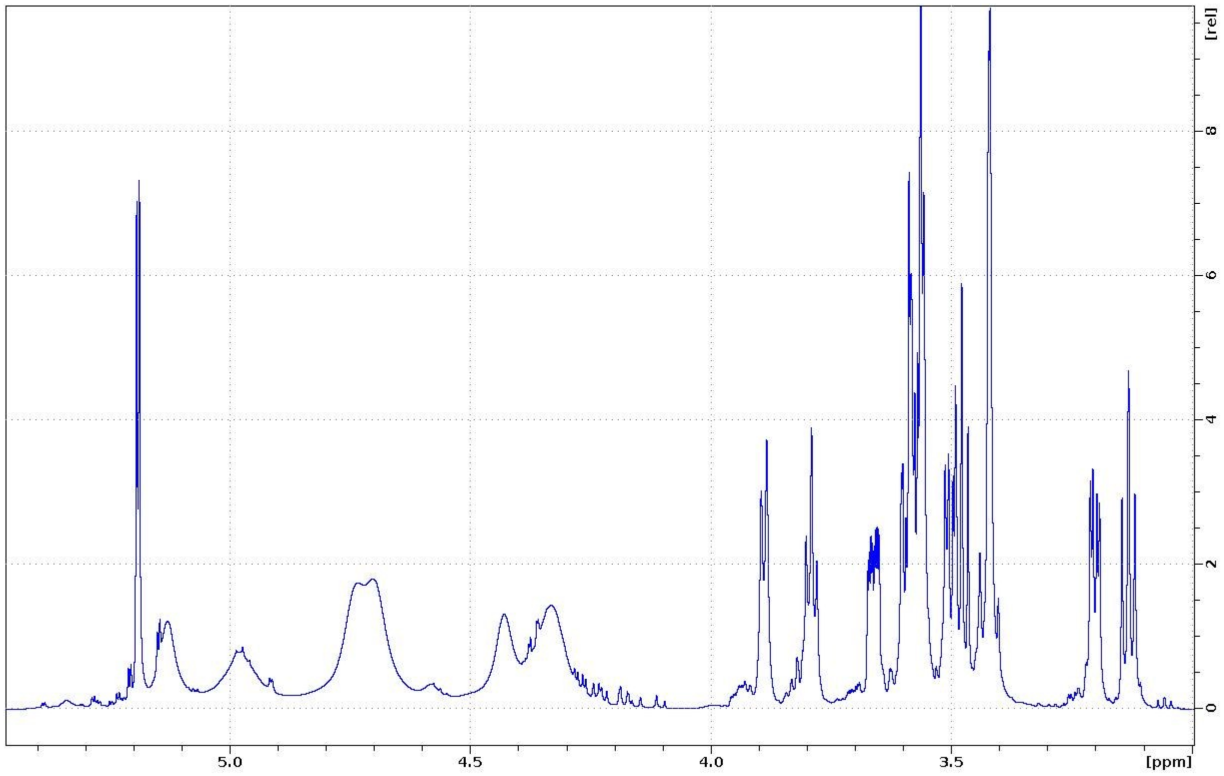

Figure S7. ^{1}H NMR spectrum of sucrose (S) - phenyl isocyanate (PI) reaction mixture with the expansion of carbohydrate region.

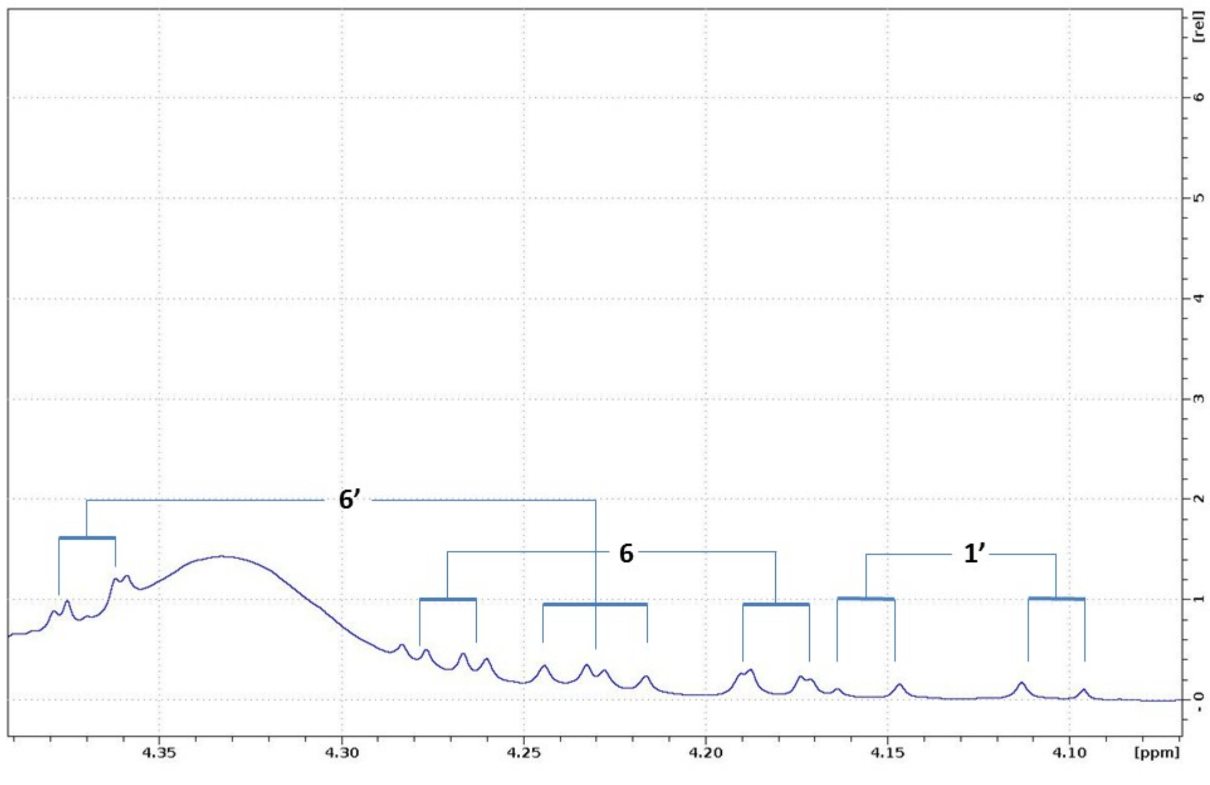

Figure S8. Expanded region of the ^{1}H NMR spectrum of sucrose (S) - phenyl isocyanate (PI) reaction mixture, showing the assigned signals of carbohydrate CH_2 groups.

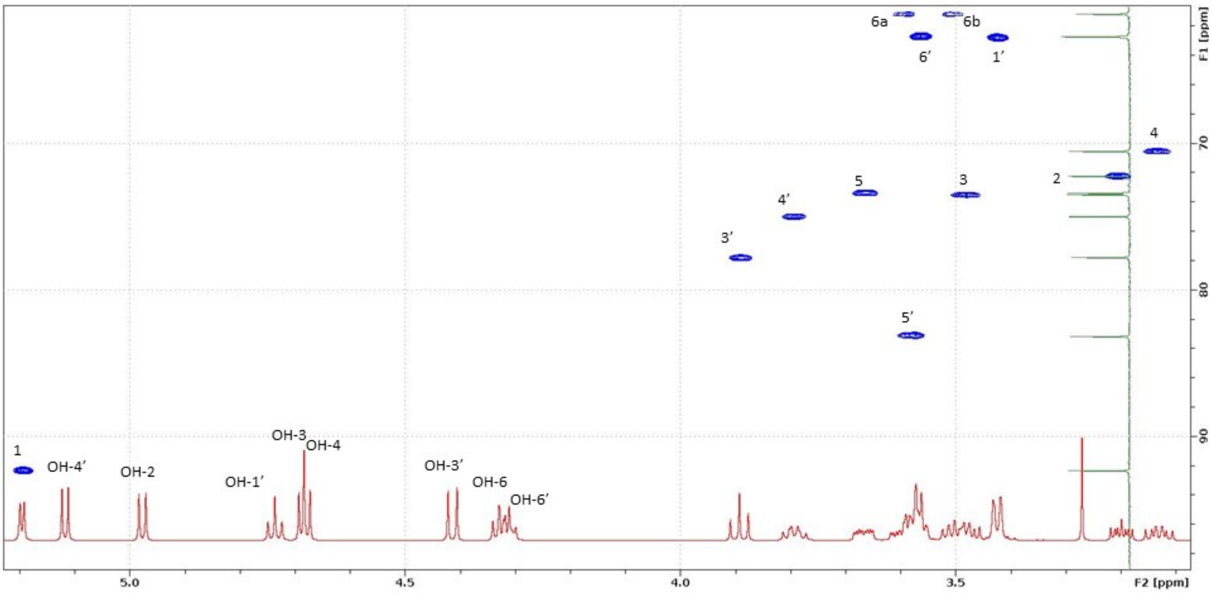

Figure S9. ^{13}C-^{1}H HSQC NMR spectral assignments of pure sucrose (S) in DMSO solution. The 1D ^{1}H NMR spectrum is shown at the horizontal axis, while ^{13}C signals are shown along the vertical axis .

Derivation of Equations 5 and 6

Dividing Equation 3 by Equation 2 one can get Equation S1 as:

$$-\frac{d[P`]}{d[S]}=1-\frac{[P`]}{2[S]} \qquad \text{(S1)}$$

Rearrangement of Equation S1 yield Equation 2:

$$\frac{d[P`]}{d[S]}-\frac{[P`]}{2[S]}=-1 \qquad \text{(S2)}$$

Equation S2 can now be solved analitically, and its solution yield Equation S3

$$[P`]=[S]^{1/2}(C_1-2[S]^{1/2}) \qquad \text{(S3)}$$

where C_1 is an integration constant.

Taking into account the initial conditions, i.e., that at [*S*] =[*S*]$_o$ --> [*P`*] = 0, $C_1$ can be determined and by substituting it into Equation 3, we get Equation S4 for the dependence of [*P`*] on [*S*] as:

$$[P`]=2[S]^{1/2}([S]_o^{1/2}-[S]^{1/2}) \qquad \text{(S4)}$$

Furthermore, dividing Equation 3 by Equation 4 one can get Equation S5 as:

$$\frac{d[P`]}{d[P]}=\frac{2[S]}{[P`]}-1 \qquad \text{(S5)}$$

Since [*S*]$_o$ >> [*I*]$_o$, the relation of 2[*S*]/[*P`*] >> 1 is also valid and then Equation S5 simplifies to Equation S6:

$$\frac{d[P`]}{d[P]}\cong\frac{2[S]}{[P`]} \qquad \text{(S6)}$$

Substituting Equation S4 into Equation S6, and after rearrangement, we obtain the following differential equation:

$$\frac{d[P]}{d[S]}\cong\frac{[S]_o+2[S]-3[S]_o^{1/2}[S]^{1/2}}{[S]} \qquad \text{(S7)}$$

After solving of Equation S7, we arrive at Equation S8.

$$[P]\cong C_1+[S]_o\ln([S])-6[S]^{1/2}[S]_o^{1/2}+2[S]) \qquad \text{(S8)}$$

where $C_1 = 4[S]_o - [S]_o \ln([S]_o)$, C_1 was obtained by considering the initial conditions, i.e., at $[S] = [S]_o$ --> $[P] = 0$.

Substitution of C_1 into Equation S8, yield Equation S9, which shows the dependence of $[P]$ on $[S]$ as:

$$[P] \cong [S]_o - [S] + [S]_o \ln\left(\frac{[S]}{[S]_o}\right) + 3\left([S]_o^{1/2} - [S]^{1/2}\right)^2 \qquad \text{(S9)}$$

Taking into account that $[S] \cong [S]_o - [I]_o$ and substituting it into Equation S4 and S9 we obtain Equations S10 and S11 which are the same as Equations 5 and 6.

$$[P`] \cong 2([S]_o - [I]_o)^{1/2}\{[S]_o^{1/2} - ([S]_o - [I]_o)^{1/2}\} \qquad \text{(S10)}$$

$$[P] \cong [I]_o + [S]_o \ln\left(1 - \frac{[I]_o}{[S]_o}\right) + 3\{[S]_o^{1/2} - ([S]_o - [I]_o)^{1/2}\}^2 \qquad \text{(S11)}$$