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Article

Supplemental Material

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SUPPLEMENTARY INFORMATION

Kinetics Analysis and Automated Online Screening of Aminocarbonylation of Aryl Halides in Flow

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The Supplementary information contains:

- Example reaction GC and IR spectra.
- Molar concentrations of CO at different pressures used for modeling.
- Model details, assumptions, and reaction rates.

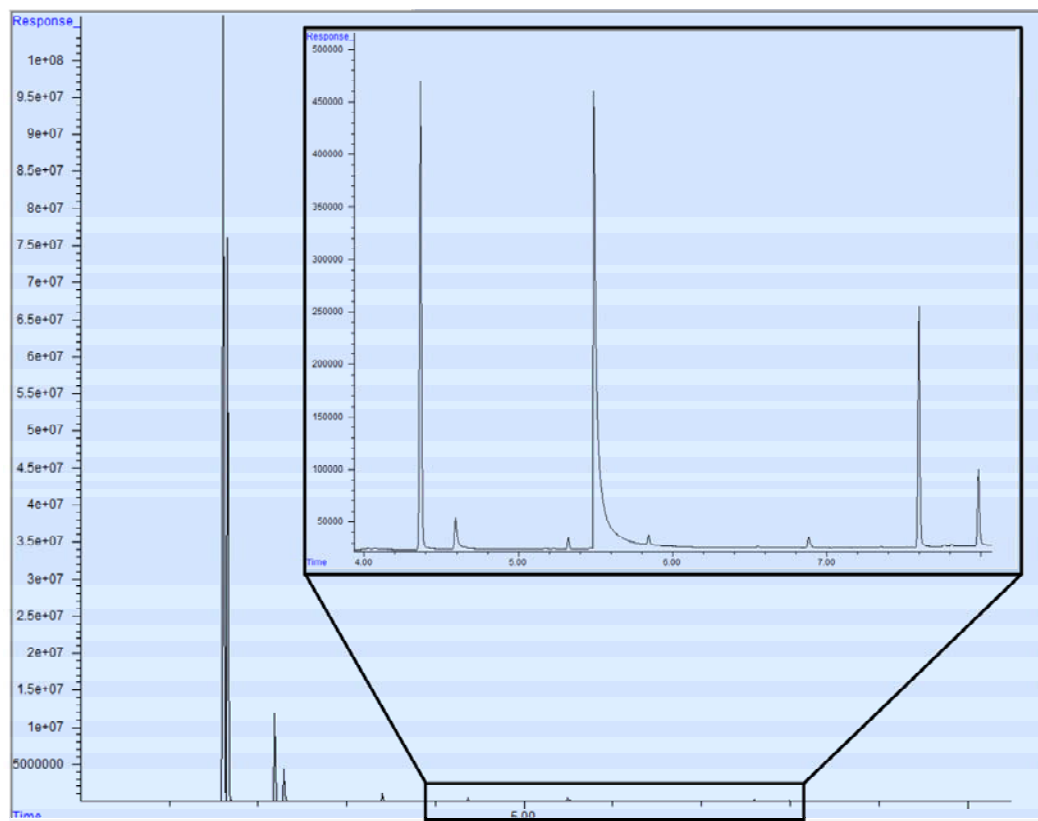


Figure S1. Example GC spectrum. Microreactor experiment at 150 °C, 8.3 bar, 2 min residence time, and 1.5% Pd.

Table S1. GC spectrum peaks in Figure S1.

Peak #	Comp	Start (min)	End (min)	Height	Area	% max	% total
1	Naphthalene	4.365	4.34	4.46×10^5	3.82×10^6	100.0	56.19
2	Starting Material	4.592	4.572	2.99×10^4	4.09×10^5	10.72	6.02
3	Mono	7.597	7.574	2.29×10^5	1.91×10^6	50.15	28.18
4	Di	7.984	7.959	7.30×10^4	6.52×10^5	17.09	9.60

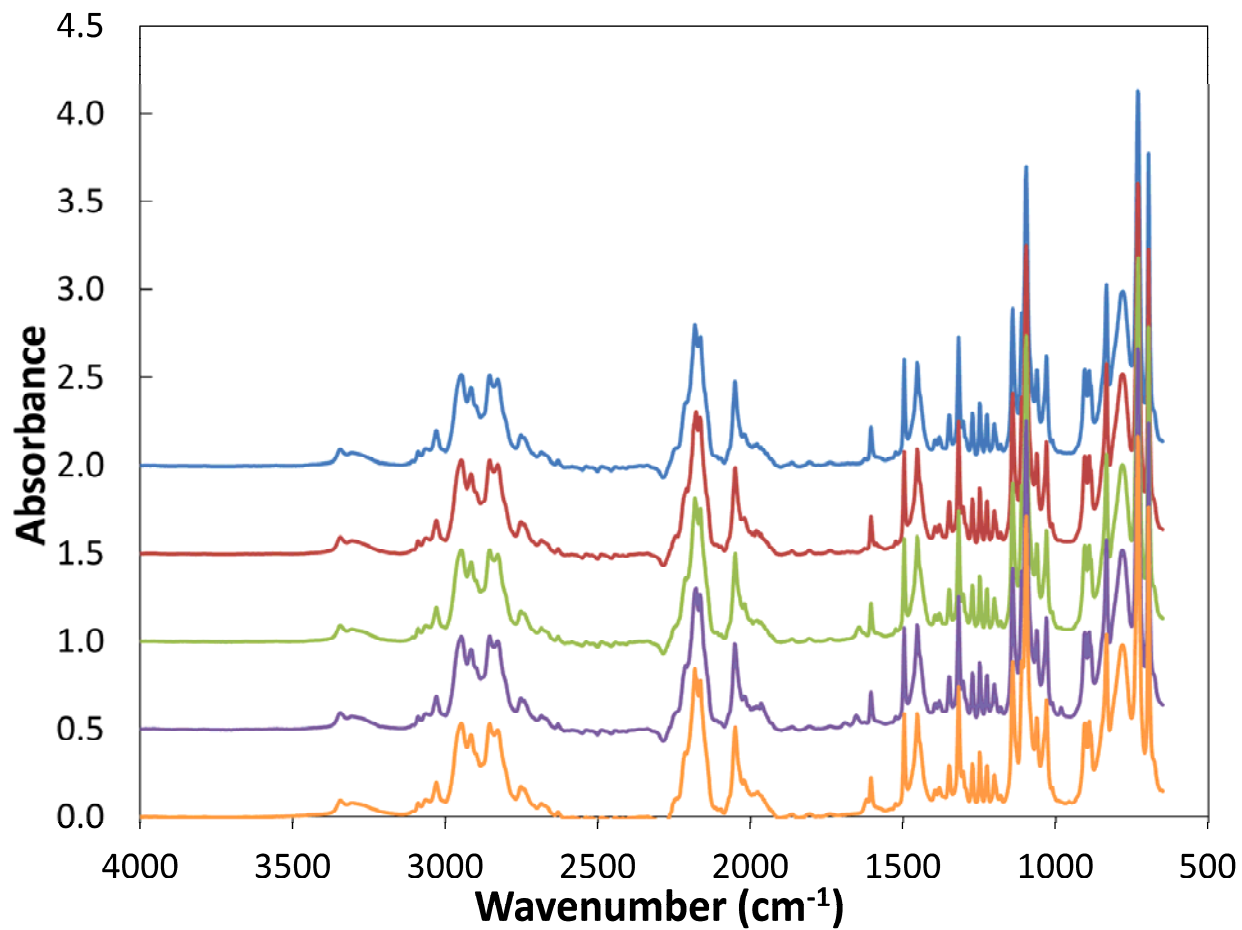


Figure S2. Example IR spectra. Top to bottom: 50 vol% morpholine and 50 vol% toluene, 0.06 M starting material, 0.06 M Mono product, 0.05 M Di product, 0.06 M DBU.

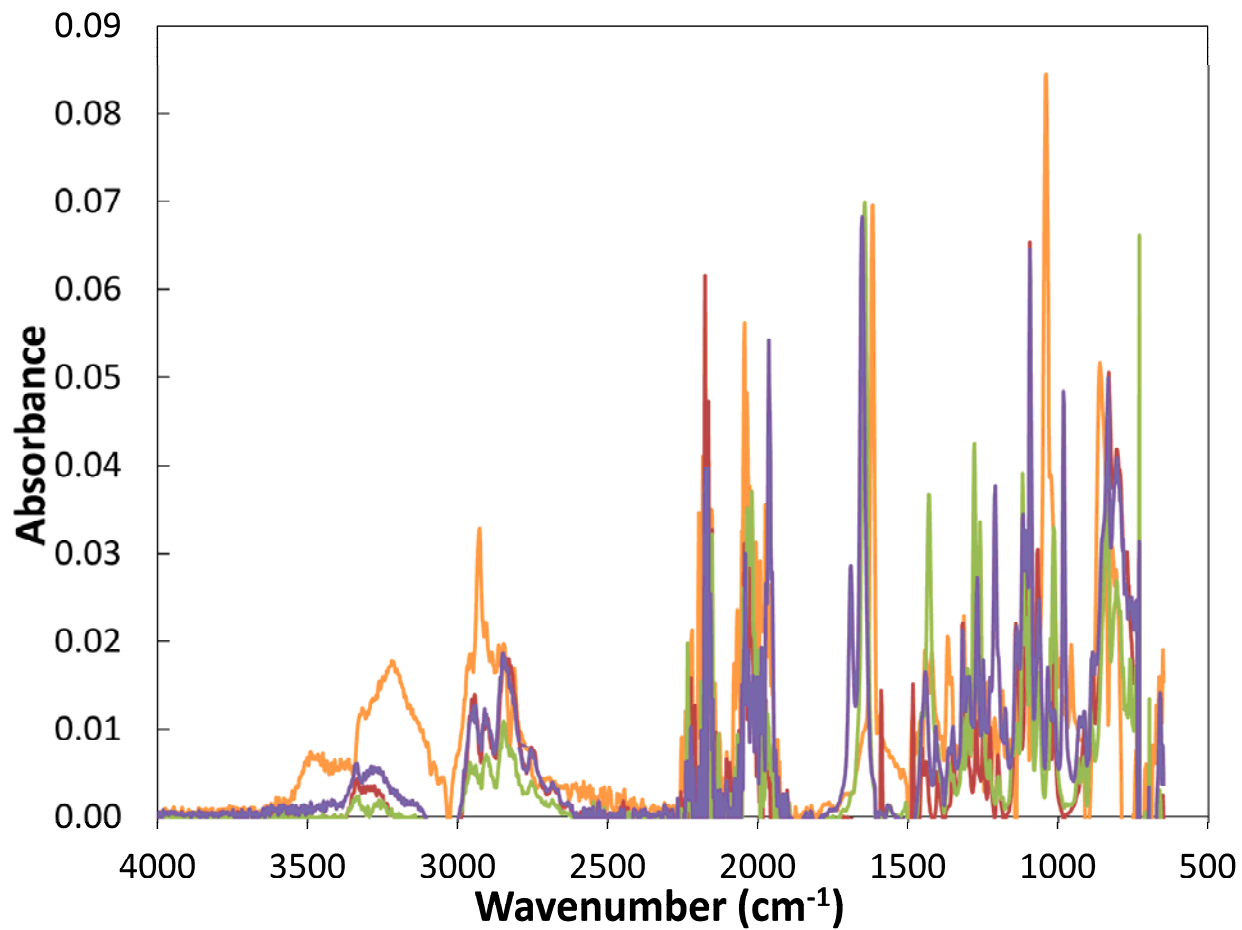


Figure S3. Example IR spectra with 50 vol% morpholine and 50 vol% toluene solvent subtracted: 0.06 M starting material (red), 0.06 M Mono product (green), 0.05 M Di product (purple), 0.06 M DBU (orange).

Table S2. Molar concentration of a gas at different pressures.

Pressure (psi)	Pressure (bar)	Concentration CO (M)
14.5	1.0	0.04
40	2.8	0.12
80	5.5	0.25
120	8.3	0.37
180	12.4	0.55

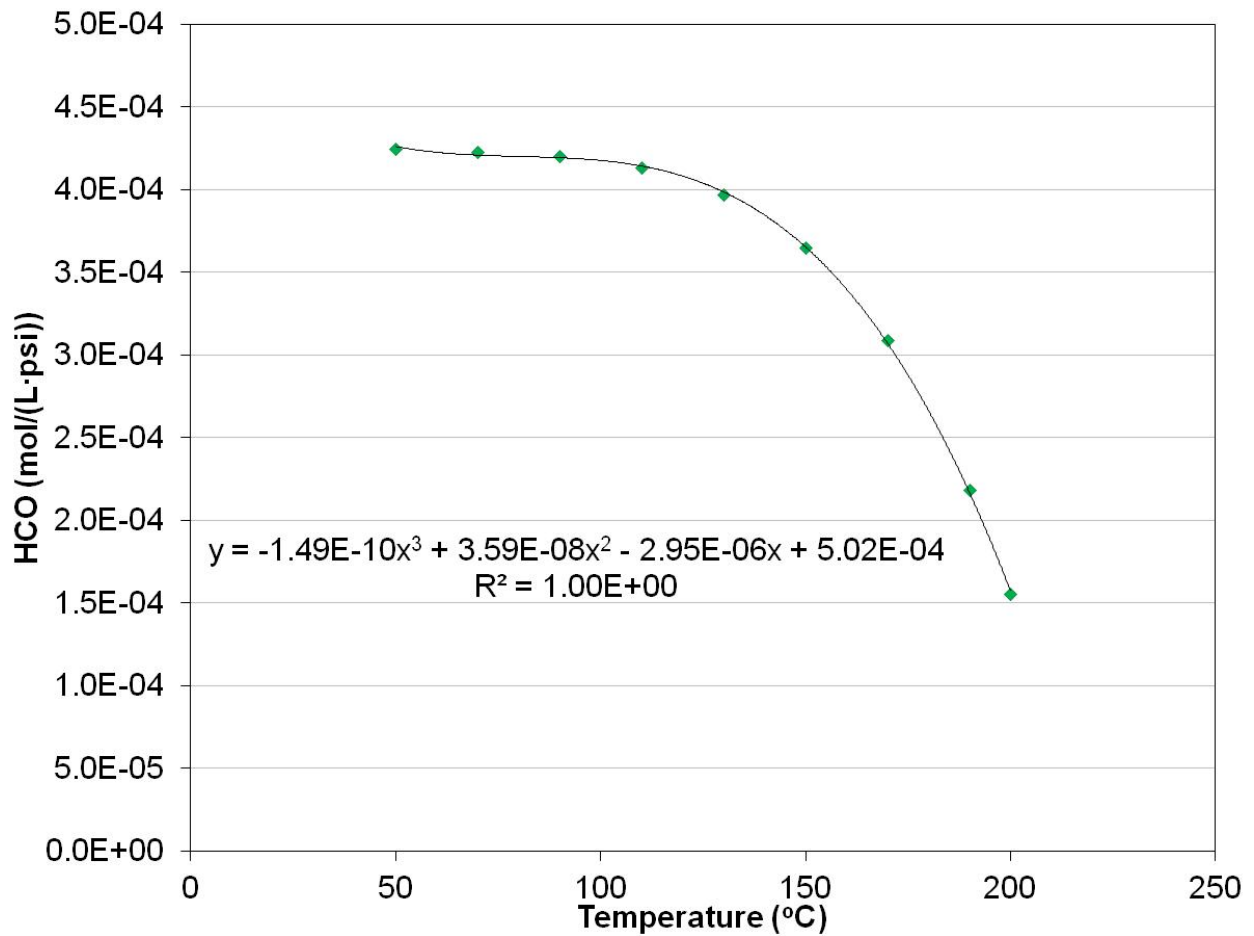


Figure S4. Carbon monoxide Henry's Law constant as a function of temperature. Polynomial was fit to data generated with Aspen Plus.

Pseudo First-Order Approximation

$$-\frac{d[ArX]}{dt} = k_1[Pd][ArX] \quad (1)$$

$$-\frac{d[ArX]}{dt} = k_1 \frac{[Pd]_0}{1 + K[CO]} [ArX]$$

$$-\frac{d[ArX]}{dt} = k_{obs}[ArX] \quad (3)$$

$$k_{obs} = \frac{k_1[Pd]_0}{1 + K[CO]}$$

Steady-State Approximation

$$[Pd] = [Pd]_0 - [Pd_{CO}]$$

$$k_f[Pd][CO] = k_r[Pd_{CO}]$$

$$[Pd_{CO}] = \frac{k_f[Pd][CO]}{k_r}$$

$$[Pd] = [Pd]_0 - \frac{k_f[Pd][CO]}{k_r}$$

$$[Pd] = \frac{[Pd]_0}{1 + K[CO]} \quad (2)$$

Arrhenius Analysis

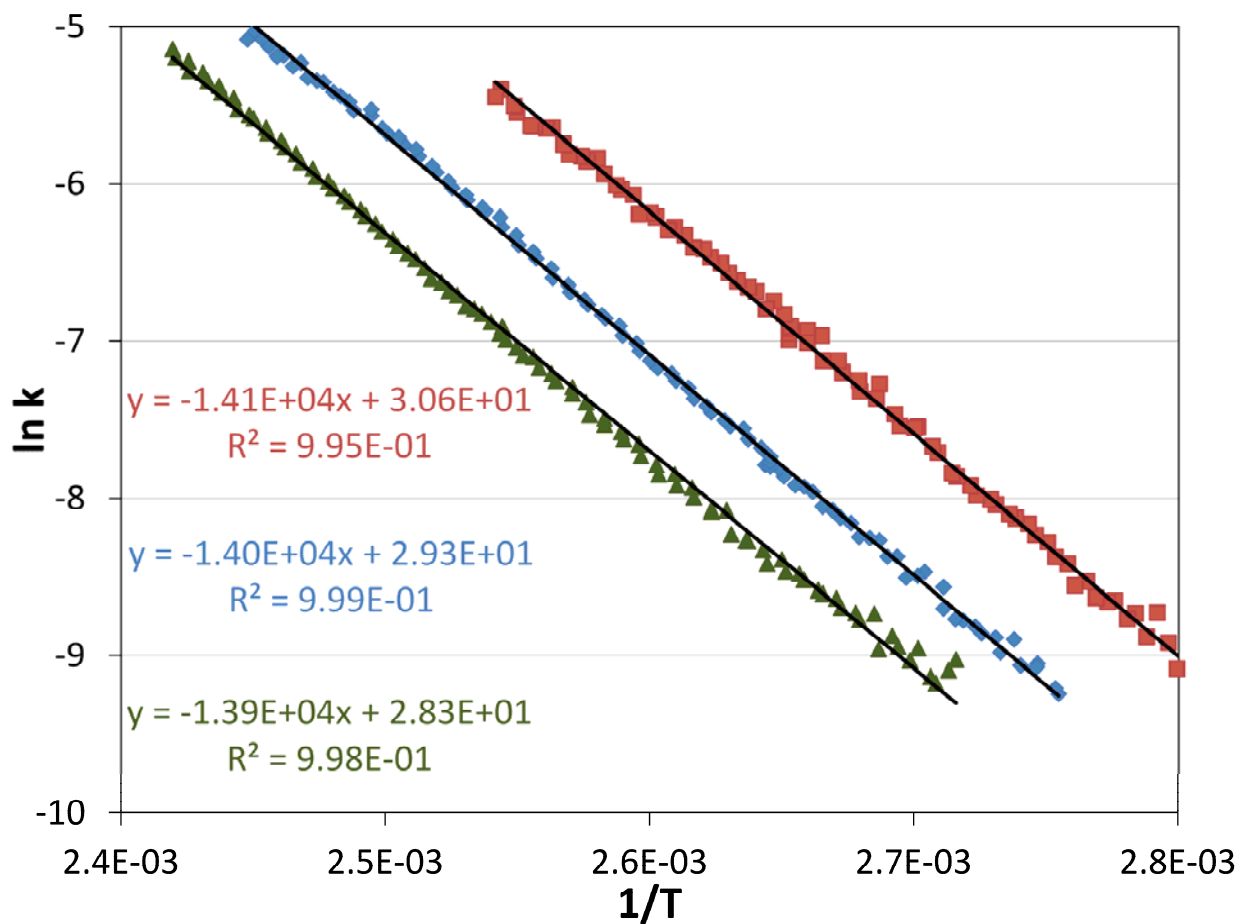
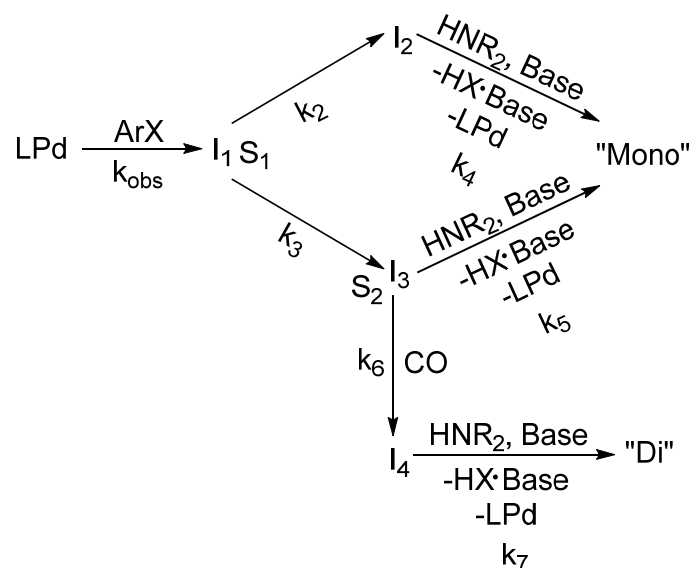


Figure S5. Arrhenius plot for the lower temperature regime of the tubular reactor temperature ramp experiments: Exp. 1 (■) at 8.3 bar CO and 2 % Pd, Exp. 2 (▲) at 13.8 bar CO and 2 % Pd, and Exp. 3 (◆) at 8.3 bar CO and 1 % Pd.

Model Details

Beginning with the full reaction scheme, several simplifications can be made based upon the pseudo-steady state assumption (PSSA). Firstly, as is discussed in the text, the reversible palladium poisoning by carbon monoxide can be lumped into an observed rate constant, k_{obs} . Additionally, as the oxidative addition is significantly slower than the carbon monoxide association, PSSA can be assumed to eliminate this intermediate step from the rate laws. For simplicity in writing the rate expressions, all intermediates have been numbered 1 through 5.



This produces the reaction rates:

$$\frac{d[ArX]}{dt} = -k_{obs}[ArX]$$

$$\frac{d[I_1]}{dt} = k_{obs}[ArX] - k_2[I_1] - k_3[I_1]$$

$$\frac{d[I_2]}{dt} = k_2[I_1] - k_4[I_2]$$

$$\frac{d[I_3]}{dt} = k_3[I_1] - k_5[I_3] - k_6[I_3]$$

$$\frac{d[I_4]}{dt} = k_6[I_3] - k_7[I_4]$$

$$\frac{d[Mono]}{dt} = k_4[I_2] + k_5[I_3]$$

$$\frac{d[Di]}{dt} = k_7[I_4]$$

Now, lumping the reaction rates at each bifurcation and using the selectivity terms modifies the equations to become:

$$\begin{aligned}
\frac{d[ArX]}{dt} &= -k_{obs}[ArX] \\
\frac{d[I_1]}{dt} &= k_{obs}[ArX] - k_{S_1}[I_1] \\
\frac{d[I_2]}{dt} &= k_{S_1}S_1[I_1] - k_4[I_2] \\
\frac{d[I_3]}{dt} &= k_{S_1}(1-S_1)[I_1] - k_{S_2}[I_3] \\
\frac{d[I_4]}{dt} &= k_{S_2}(1-S_2)[I_3] - k_7[I_4] \\
\frac{d[Mono]}{dt} &= k_4[I_2] + k_{S_2}S_2[I_3] \\
\frac{d[Di]}{dt} &= k_7[I_4]
\end{aligned}$$

Further applying PSSA to intermediates 1, 3, and 4 produces the following equalities:

$$\begin{aligned}
k_{obs}[ArX] &\approx k_{S_1}[I_1] \\
k_{S_1}(1-S_1)[I_1] &\approx k_{S_2}[I_3] \\
k_{S_2}(1-S_2)[I_3] &\approx k_7[I_4]
\end{aligned}$$

The remaining equations then become:

$$\begin{aligned}
\frac{d[ArX]}{dt} &= -k_{obs}[ArX] \\
\frac{d[I_2]}{dt} &= k_{obs}S_1[ArX] - k_4[I_2] \\
\frac{d[Mono]}{dt} &= k_4[I_2] + k_{obs}S_2(1-S_1)[ArX] \\
\frac{d[Di]}{dt} &= k_{obs}(1-S_1)(1-S_2)[ArX]
\end{aligned}$$

Additionally, the Pd balance is given by:

$$\frac{d[Pd]}{dt} = -\frac{d[ArX]}{dt} + \frac{d[Mono]}{dt} + \frac{d[Di]}{dt}$$

$$\frac{d[Pd]}{dt} = -k_{obs}[ArX] + k_4[I_2] + k_{obs}S_2(1-S_1)[ArX] + k_{obs}(1-S_1)(1-S_2)[ArX]$$

$$\frac{d[Pd]}{dt} = k_4[I_2] - k_{obs}S_1[ArX]$$

This set of equations was modeled in Matlab using the following differential code and fitted parameters:

```

k = ([1.3334, 1.1147, 1.0712, 2.4226, 3.8659, 2.0095]);
k = [k(1)*1E17,116.4,k(2)*1E6,55.6,k(3)*1E2,k(4)*1E-13,k(5)*1E1,k(6)*1E-4];
% [(k0,[1]), (EA,[1]), (k0,[4]), (EA,[4]), (EA,[2]-EA,[3]), (k0,[3]/k0,[2]), (EA,[5]-EA,[6]),
(k0,[6]/k0,[5])]

function der = ODEFun(~,C,T,pCO,Pd0,k)
% C = [ArX, I2, M, D, Pd]

HCO = -1.49E-10*T^3+3.59E-8*T^2-2.95E-6*T+5.02E-4;
k1 = k(1)*exp(-k(2)*1E3/(8.314*(273+T)));
k4 = k(3)*exp(-k(4)*1E3/(8.314*(273+T)));

kobs = k1*(C(5)*Pd0/(HCO*pCO));
S1 = 1/(1+k(6)*exp(k(5)*1E3/(8.314*(273+T))));
S2 = 1/(1+k(8)*exp(k(7)*1E3/(8.314*(273+T)))*HCO*pCO);

der(1,1) = -kobs*C(1); %d[ArX]/dt
der(2,1) = S1*kobs*C(1)-k4*C(2); %d[I2]/dt
der(3,1) = k4*C(2)+(1-S1)*kobs*C(1)*S2; %d[M]/dt
der(4,1) = (1-S1)*kobs*C(1)*(1-S2); %d[D]/dt
der(5,1) = k4*C(2)-S1*kobs*C(1); %d[Pd]/dt

```