

Supporting Information for:

**Mechanism of Benzoquinone-Promoted Palladium-Catalyzed Oxidative Cross Coupling Reactions**

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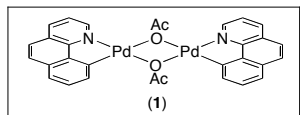
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## I. General Procedures and Materials and Methods

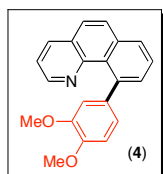
**General Procedures:** NMR spectra were obtained on a Varian Inova 500 (499.90 MHz for  $^1\text{H}$ ; 125.70 MHz for  $^{13}\text{C}$ ), a Varian Inova 400 (399.96 MHz for  $^1\text{H}$ ; 100.57 MHz for  $^{13}\text{C}$ ; 376.34 MHz for  $^{19}\text{F}$ ), or a Varian Mercury 300 (300.07 MHz for  $^1\text{H}$ ; 75.45 MHz for  $^{13}\text{C}$  NMR; 282.35 MHz for  $^{19}\text{F}$ ) spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference.  $^{19}\text{F}$  NMR spectra are referenced based on the unified scale, where the frequency of the residual solvent peak in the  $^1\text{H}$  NMR spectrum acts as the single primary reference.<sup>1</sup>  $^{19}\text{F}$  NMR spectra are proton coupled. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), doublet of quartets (dq), triplet (t), triplet of doublets (td), quartet (q), quartet of doublets (qd), and multiplet (m). Unless otherwise indicated, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at room temperature.

**Materials and Methods:** 7,8-Benzo[*h*]quinoline was obtained from Pfaltz and Bauer,  $\text{Pd}(\text{OAc})_2$  was obtained from Pressure Chemical, 1,2-dimethoxybenzene (veratrole) was obtained from Acros Chemicals, 2,6-dimethylanisole was obtained from TCI, and 2,6-dimethyl-1-nitrobenzene was obtained from Aldrich. All of these chemicals were used as received. Benzoquinone was obtained from Acros and was further purified by vacuum sublimation. Gas chromatography was carried out using a Shimadzu 17A using a Restek Rtx®-5 (Crossbond 5% diphenyl – 95% dimethyl polysiloxane; 15 m, 0.25 mmID, 0.25 mmID, 0.25  $\mu\text{m}$  df) column. All GC and isolated yields are the average of two reactions.

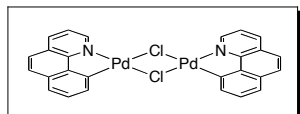
## II. Experimental Procedures



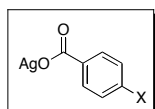
Complex **1** was synthesized as reported in the literature.<sup>2</sup> Benzo[*h*]quinoline (2.0 g, 11.2 mmol, 1 equiv) and Pd(OAc)<sub>2</sub> (2.5 g, 11.2 mmol, 1 equiv) were dissolved in MeOH (50 mL), and the resulting mixture was stirred overnight at room temperature. During the course of the reaction, a yellow solid precipitated from solution, and this solid was collected at the top of a plug of Celite and washed with Et<sub>2</sub>O (200 mL) and hexanes (200 mL). The solid was then washed through the plug of Celite with CH<sub>2</sub>Cl<sub>2</sub> (500 mL), and this solution was concentrated under vacuum. The resulting yellow solid was dissolved in a minimal quantity of CH<sub>2</sub>Cl<sub>2</sub> (~50 mL) and precipitated with hexanes (500 mL). The yellow solid was then collected, washed with hexanes (100 mL) and Et<sub>2</sub>O (100 mL), and dried under vacuum to afford **1** as a bright yellow solid (2.96 g, 77% yield). Spectroscopic data for this complex matched that reported in the literature.<sup>2</sup>



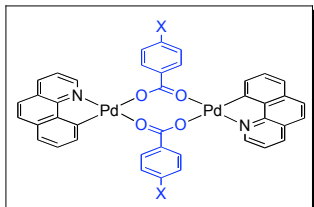
An authentic sample of product **4** was synthesized as reported in the literature.<sup>3</sup> The spectroscopic data for **4** matched that previously reported. A GC calibration curve for this compound was made using nonadecane as a standard.



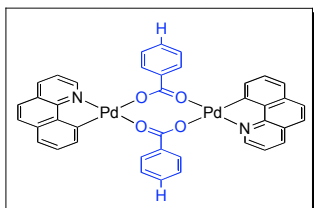
[(Bzq)PdCl]<sub>2</sub> was synthesized as reported in the literature.<sup>4</sup> [(Bzq)Pd(OAc)]<sub>2</sub> (1.0 g, 2.9 mmol, 1 equiv) and LiCl (0.80 g, 18.9 mmol, 6.5 equiv) were combined in a mixture of acetone (130 mL) and water (50 mL). The resulting suspension was stirred overnight at room temperature. The yellow/grey precipitate was then collected and dried under vacuum to afford [(Bzq)PdCl]<sub>2</sub> as a yellow solid (0.86 g, 92.6% yield). Spectroscopic data for this complex matched that reported in the literature.<sup>5</sup>



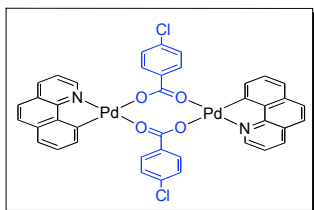
Silver benzoate derivatives were synthesized according to a literature procedure.<sup>6</sup>



**General procedure for the synthesis of [BzqPd(O<sub>2</sub>C(p-X-Ar))<sub>2</sub>]:** [(Bzq)PdCl]<sub>2</sub> (1.0 g, 1 equiv, 3.19 mmol) and Ag(O<sub>2</sub>CR)<sub>2</sub> (1 equiv, 3.22 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (350 mL). The reaction mixture was stirred at 25 °C for 3 h, during which time the solution changed color from pale yellow to bright yellow and a gray precipitate formed. The reaction mixture was filtered through a plug of Celite, and the Celite plug was washed with CH<sub>2</sub>Cl<sub>2</sub> (3 x 100 mL). The resulting yellow solution was concentrated under vacuum, and the yellow solids were redissolved in CH<sub>2</sub>Cl<sub>2</sub> (~15 mL) and then precipitated with hexanes (~100 mL). The yellow solid precipitate was collected by filtration, washed with hexanes (3 x 50 mL) and Et<sub>2</sub>O (3 x 50 mL), and dried under vacuum.

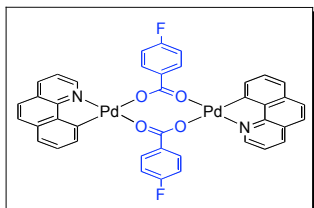


The benzoate dimer was obtained as a yellow solid (0.94 g, 74% yield). <sup>1</sup>H NMR (95% CDCl<sub>3</sub>/5% C<sub>5</sub>D<sub>5</sub>N): δ 8.68 (d, *J* = 5.2 Hz, 1H), 8.1-8.2 (m, 2H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.38-7.28 (m, 5H), 7.20 (t, *J* = 7.7 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 172.7, 154.7, 150.4, 148.3, 141.5, 137.5, 137.0, 133.0, 130.3, 129.9, 129.4, 128.6, 128.2, 127.5, 126.3, 123.1, 122.5, 121.1. IR (KBr): 1595 cm<sup>-1</sup>. Anal. Calc. for C<sub>20</sub>H<sub>13</sub>NO<sub>2</sub>Pd: C 59.20, H 3.23, N 3.45. Found C 59.21, H 3.17, N 3.53.

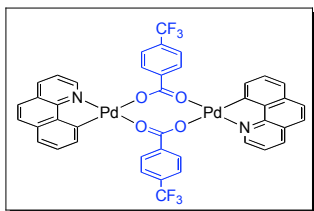


The *p*-Cl benzoate dimer was obtained as a yellow solid (0.89 g, 65% yield). <sup>1</sup>H NMR (95% CDCl<sub>3</sub>/5% C<sub>5</sub>D<sub>5</sub>N): δ 8.64 (d, *J* = 4.1 Hz, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 8.0 (d, *J* = 8.1 Hz, 2H), 7.6 (d, *J* = 8.6 Hz, 1H), 7.46 (dd, *J* = 8.4, 7.46 Hz, 2H), 7.32 (dd, *J* = 7.9, 5.2 Hz, 1H), 7.28-7.22 (m, 1H), 7.20 (t, *J* = 7.6 Hz,

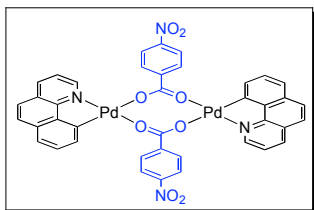
2H), 6.40 (d,  $J = 7.2$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  171.7, 154.8, 150.2, 148.3, 141.6, 137.1, 136.0, 133.1, 130.9, 130.1, 128.7, 128.2, 127.6, 126.4, 123.2, 122.6, 121.1. IR (KBr):  $1592\text{ cm}^{-1}$ . Anal. Calc. for  $\text{C}_{20}\text{H}_{12}\text{NClO}_2\text{Pd}$ : C 54.57, H 2.75, N 3.18. Found C 54.22, H 2.68, N 3.17.



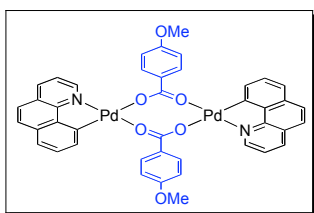
The *p*-F benzoate dimer was obtained as a yellow solid (0.86 g, 65% yield).  $^1\text{H}$  NMR (95%  $\text{CDCl}_3$ /5%  $\text{C}_5\text{D}_5\text{N}$ ):  $\delta$  8.66 (d,  $J = 5.5$  Hz, 1H), 8.18 (d,  $J = 8.6$  Hz, 1H), 8.08 (dd,  $J = 9.0, 5.9$  Hz, 2H), 7.68 (d,  $J = 8.7$  Hz, 1H), 7.50 (dd,  $J = 8.4, 5.5$  Hz, 2H), 7.34 (dd,  $J = 8.2, 5.3$  Hz, 1H), 7.22 (t,  $J = 8.2$  Hz, 1H), 6.96 (t,  $J = 8.6$  Hz, 2H), 6.40 (d,  $J = 7.6$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (95%  $\text{CD}_2\text{Cl}_2$ /5%  $\text{C}_5\text{D}_5\text{N}$ ):  $\delta$  171.6, 164.7 (d,  $^1J_{\text{C-F}} = 245.8$  Hz), 155.3, 151.1, 149.1, 142.6, 137.9, 134.9, 133.8, 132.2 (d,  $^3J_{\text{C-F}} = 8.5$  Hz), 131.2, 129.4, 128.9, 127.3, 121.9, 114.7 (d,  $^2J_{\text{C-F}} = 20.9$  Hz) (two peaks coincidently overlap with pyridine signals).  $^{19}\text{F}$  NMR (90%  $\text{CDCl}_3$ /10%  $\text{CD}_3\text{CN}$ ):  $\delta$   $-104.34$  (m, 1F). IR (KBr):  $1607\text{ cm}^{-1}$ . Anal. Calc. for  $\text{C}_{20}\text{H}_{12}\text{NFO}_2\text{Pd}$ : C 56.69, H 2.85, N 3.31. Found C 56.65, H 2.75, N 3.31.



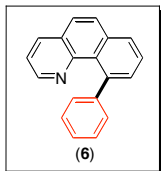
The *p*- $\text{CF}_3$  benzoate dimer was obtained as a yellow solid (1.22 g, 82% yield).  $^1\text{H}$  NMR (95%  $\text{CDCl}_3$ /5%  $\text{C}_5\text{D}_5\text{N}$ ):  $\delta$  8.60 (d,  $J = 5.0$  Hz, 1H), 8.18 (m, 2H), 7.66 (d,  $J = 8.5$  Hz, 1H), 7.60-7.50 (m, 4H), 7.36 (dd,  $J = 5.2, 7.5$  Hz, 1H), 7.26-7.10 (m, 2H), 6.42 (d,  $J = 7.3$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  171.0, 154.6, 150.0, 148.0, 141.4, 140.8, 136.9, 133.0, 131.4 (q,  $^2J_{\text{C-F}} = 30.3$  Hz), 130.1, 129.5, 128.6, 128.1, 126.3, 125.3, 124.4 (q,  $^1J_{\text{C-F}} = 275$  Hz), 123.0, 122.8, 120.9.  $^{19}\text{F}$  NMR (95%  $\text{CDCl}_3$ /5%  $\text{C}_5\text{D}_5\text{N}$ ):  $\delta$   $-62.55$  (s, 3F). IR (KBr):  $1603\text{ cm}^{-1}$ . Anal. Calc. for  $\text{C}_{21}\text{H}_{12}\text{NF}_3\text{O}_2\text{Pd}$ : C 53.24, H 2.55, N 2.96. Found C 52.90, H 2.46, N 2.97.



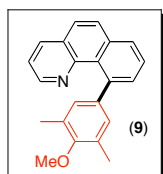
The *p*-NO<sub>2</sub> benzoate dimer was obtained as a yellow solid (0.48 g, 34% yield). <sup>1</sup>H NMR (95% CDCl<sub>3</sub>/5% C<sub>5</sub>D<sub>5</sub>N): δ 8.56 (d, *J* = 5.2 Hz, 1H), 8.24 (t, *J* = 7.6 Hz, 3H), 8.12 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.52 (t, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 5.1, 7.8 Hz, 1H), 7.18-7.22 (m, 1 H), 6.40 (d, *J* = 7.3 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 170.0, 154.4, 149.6, 148.4, 147.8, 143.3, 141.1, 136.9, 132.8, 130.0, 129.9, 128.5, 128.1, 126.2, 122.9, 122.7, 122.5, 120.9. IR (KBr): 1586 cm<sup>-1</sup>. Elemental Anal. Calc. for C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>Pd: C 53.29, H 2.68, N 6.21. Found: C 53.10, H 2.62, N 6.32.



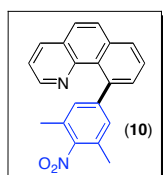
The *p*-MeO benzoate dimer was obtained as a yellow solid (1.21 g, 87% yield). <sup>1</sup>H NMR (95% CDCl<sub>3</sub>/5% C<sub>5</sub>D<sub>5</sub>N): δ 8.68 (d, *J* = 5.2 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.50 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.30 (dd, *J* = 7.7, 5.5 Hz, 1H), 7.20 (t, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 2H), 6.42 (d, *J* = 7.6 Hz, 1H), 3.8 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 172.48, 161.01, 154.67, 150.48, 148.26, 141.49, 136.89, 132.94, 131.08, 130.21, 128.55, 128.10, 126.28, 123.01, 122.46, 120.99, 112.58, 54.99 (two peaks coincidently overlap). IR (KBr): 1605 cm<sup>-1</sup>. Anal. Calc. for C<sub>21</sub>H<sub>15</sub>NO<sub>3</sub>Pd: C 57.88, H 3.47, N 3.21. Found C 57.24, H 3.43, N 3.44.



An authentic sample of product **6** was synthesized as reported in the literature.<sup>3</sup> The spectroscopic data for **6** matched that previously reported. A GC calibration curve for this compound was approximated using compound **4** and nonadecane as a standard.



An authentic sample of product **9** was synthesized as reported in the literature.<sup>3</sup> The spectroscopic data for **9** matched that previously reported. A GC calibration curve for this compound was made using nonadecane as a standard.



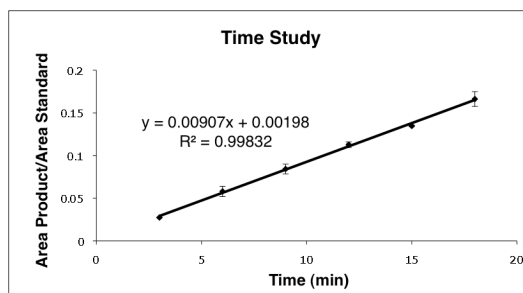
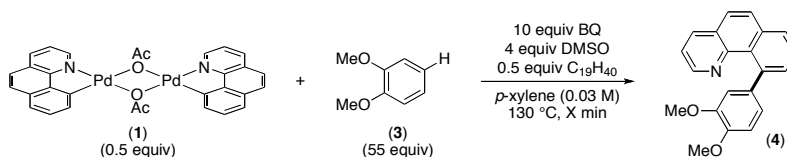
An authentic sample of product **10** was synthesized as reported in the literature.<sup>3</sup> The spectroscopic data for **4** matched that previously reported. A GC calibration curve for this compound was made using nonadecane as a standard.

### III. Mechanism Determination

**General Procedure for Kinetic Experiments.** Kinetic experiments were run in 2 dram vials sealed with Teflon-lined caps, and each data point within a kinetics run represents a reaction in an individual vial (with each vial containing a constant concentration of oxidant, catalyst, and substrate). [BzqPd(OAc)]<sub>2</sub> (**1**) was weighed into each vial, then 0.806 mL of a standard solution containing (per aliquot) benzoquinone (BQ), DMSO (5.7  $\mu$ L, 0.08 mmol, 4 equiv), nonadecane (internal standard) (2.7 mg, 0.01 mmol, 0.5 equiv), 1,2-dimethoxybenzene, and *p*-xylene (0.66 mL) was added via a 1 mL Hamilton airtight syringe. The reactions were allowed to stir at room temperature for ~30 s and were then heated at 130 °C for various amounts of time. The heating was conducted in an aluminum reaction block with stirring set at the highest rpm (IKA stirplate setting of 11). The reactions were quenched by cooling the vial to 0 °C in an ice bath, then diluting the mixture with CH<sub>2</sub>Cl<sub>2</sub> (3.2 mL). The reactions were then analyzed by GC, and the yield of **4** at each time point was determined by comparison to a calibration against the nonadecane internal standard. Importantly, we confirmed that the reactions did not progress after the quench. For example, an identical GC yield was obtained for a reaction analyzed immediately versus one analyzed after standing for 12 h.

The initial rate under each set of reaction conditions was obtained using the initial rates method. Each of the reactions was run to ~10% conversion (as determined by GC analysis), and [**4**] was plotted versus reaction time. A straight line was fitted to this plot (generally  $R^2 > 0.96$ ), and the standard deviation was determined using Excel. We chose to use the initial rates method because these reactions become heterogeneous with time (due to precipitation of Pd<sup>0</sup>), which complicates the kinetic analysis at longer time points. The reported initial rate values are the average of three unique kinetic experiments. An example of the initial rate determination is shown in Scheme S1.

**Scheme S1. Representative Kinetic Experiment**

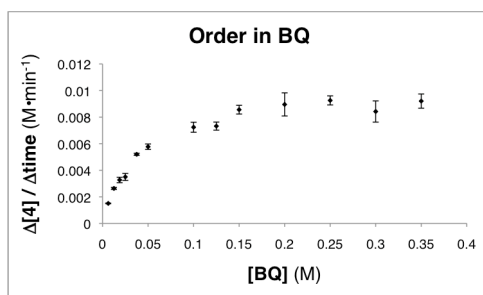
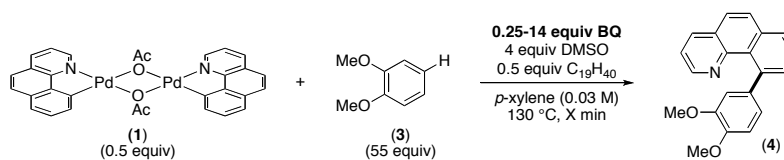




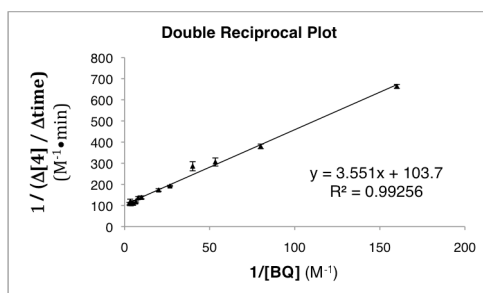
	<b>Initial rate (M/min)</b>	<b>std dev</b>
<b>Run 1</b>	0.00907	0.0002 <sub>5</sub>
<b>Run 2</b>	0.00965	0.0003 <sub>1</sub>
<b>Run 3</b>	0.00905	0.0003 <sub>5</sub>
<b>Average</b>	0.00926	0.0001 <sub>8</sub>

**Order in BQ.** The order in benzoquinone (BQ) was determined by studying the initial rate of reactions with different [BQ] (Scheme S2). The conditions used were as follows:  $[(\text{Bzq})\text{Pd}(\text{OAc})_2]$  (**1**) (6.9 mg, 0.01 mmol, 0.5 equiv (1 equiv per Pd)) was weighed into each vial, then 0.806 mL of a standard solution containing (per aliquot) benzoquinone (BQ) (0.25-14 equiv), DMSO (5.7  $\mu\text{L}$ , 0.08 mmol, 4 equiv), nonadecane (internal standard) (2.7 mg, 0.01 mmol, 0.5 equiv), 1,2-dimethoxybenzene (0.14 mL, 1.1 mmol, 55 equiv), and *p*-xylene (0.66 mL) was added. Reactions were conducted at 130  $^{\circ}\text{C}$  following the standard procedure described above. These experiments revealed that the reaction showed saturation kinetics in BQ. This was determined by plotting initial rate versus [BQ], with the [BQ] varied from 0.00625-0.35 mM (0.25-14 equiv) (Scheme S2). The double reciprocal plot of this data was also consistent with saturation kinetics, as it was linear with a non-zero intercept (Scheme S3).

**Scheme S2.** Plot of Initial Rate versus [BQ] shows Saturation Kinetics



**Scheme S3.** Double Reciprocal Plot

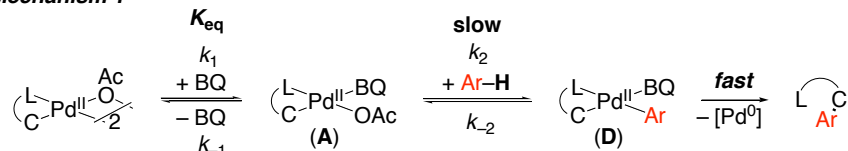


### Analysis of saturation kinetics in BQ:

There are two key experimental pieces of data from this initial order study that together provide evidence against mechanism 1:

- (1) Saturation kinetics is observed in BQ with saturation occurring at ~0.2 M BQ
- (2) Intermediate **A** is not observed by  $^1\text{H}$  NMR spectroscopy of the reaction mixture

#### Mechanism 1



Michaelis Menton kinetics should apply here; the appropriate expression is shown in eq. 1.

$$\text{Rate} = v_{\text{max}} \frac{[\text{BQ}]}{K_m + [\text{BQ}]} \quad \text{with} \quad K_m = \frac{k_{-1} + k_2[\text{Ar-H}]}{k_1} \quad (1)$$

In order to achieve saturation,  $K_m$  must be  $\ll [\text{BQ}]$  (such that the  $[\text{BQ}]$  terms cancel). Therefore, with saturation at 0.2 M BQ, we can conservatively estimate that  $K_m$  should be 10-fold less (i.e., 0.02 or smaller).

For saturation,  $K_m \ll [\text{BQ}]$ :

$$\begin{array}{ccc}
 \text{Rate} = v_{\text{max}} \frac{[\text{BQ}]}{K_m + [\text{BQ}]} & \xrightarrow{\text{reduces to}} & \text{Rate}_{\text{Sat}} = v_{\text{max}} \\
 \underbrace{K_m}_{\sim 0 \text{ (very small relative to } [\text{BQ}])} + [\text{BQ}] & & 
 \end{array} \quad (2)$$

On the basis of this equation (assuming that  $k_2[\text{Ar-H}] \ll k_1, k_{-1}$ ),  $K_{\text{eq}}$  ( $k_1/k_{-1}$ ) must be at least 50 in order to achieve saturation kinetics (eq. 3).

For saturation,  $K_m \ll [\text{BQ}]$ :

- $[\text{BQ}]_{\text{sat}} = 0.2 \text{ M}$ , so  $K_m \ll 0.2 \text{ M}$
- Also, assume  $k_2[\text{Ar-H}] \ll k_{-1}, k_1$

$$\begin{array}{c}
 \text{Assume very small} \\
 \text{(slow step)} \\
 K_m = \frac{k_{-1} + \overbrace{k_2[\text{Ar-H}]}^{\text{very small}}}{k_1} = \frac{k_{-1}}{k_1} = K_{\text{eq}}^{-1}
 \end{array}$$

$$\text{If } K_m = 0.02 \text{ M, } K_{\text{eq}} = 50$$

$$\text{If } K_m = 0.01 \text{ M, } K_{\text{eq}} = 100$$

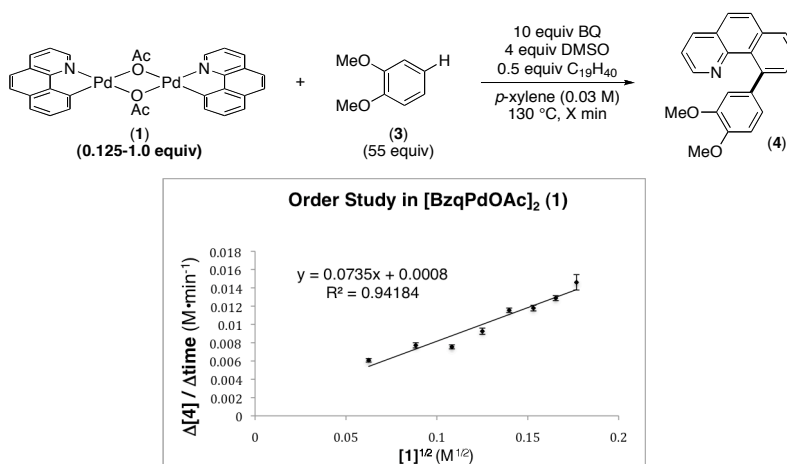
$$\text{If } K_m = 0.002 \text{ M, } K_{\text{eq}} = 500$$

(3)

With  $K_{\text{eq}} > 50$ , intermediate **A** should be observable. Since it is not detected by NMR spectroscopy, this provides quite good evidence against mechanism A. This is then further supported by several other experiments detailed in the manuscript.

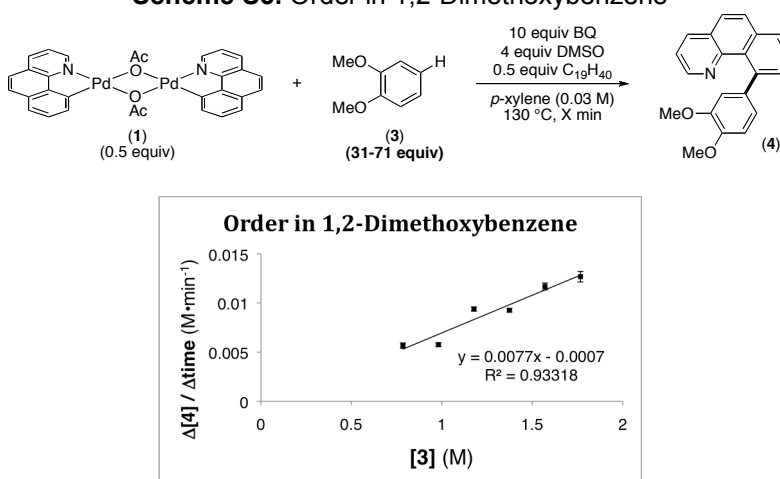
**Order in Complex 1.** The order in  $[(\text{Bzq})\text{Pd}(\text{OAc})]_2$  (**1**) was determined under flooding conditions in BQ. The conditions used were as follows:  $[(\text{Bzq})\text{Pd}(\text{OAc})]_2$  (**1**) (0.125-1 equiv) was weighed into each vial, then 0.806 mL of a standard solution containing (per aliquot) benzoquinone (BQ) (0.2 mmol, 22 mg, 10 equiv), DMSO (5.7  $\mu\text{L}$ , 0.08 mmol, 4 equiv), nonadecane (internal standard) (2.7 mg, 0.01 mmol, 0.5 equiv), 1,2-dimethoxybenzene (0.14 mL, 1.1 mmol, 55 equiv), and *p*-xylene (0.66 mL) was added. Reactions were conducted at 130 °C following the standard procedure described above. A linear correlation was obtained when initial rate was plotted against  $[\mathbf{1}]^{1/2}$  (Scheme S4).

**Scheme S4.** Order in  $[(\text{Bzq})\text{Pd}(\text{OAc})]_2$  (**1**)



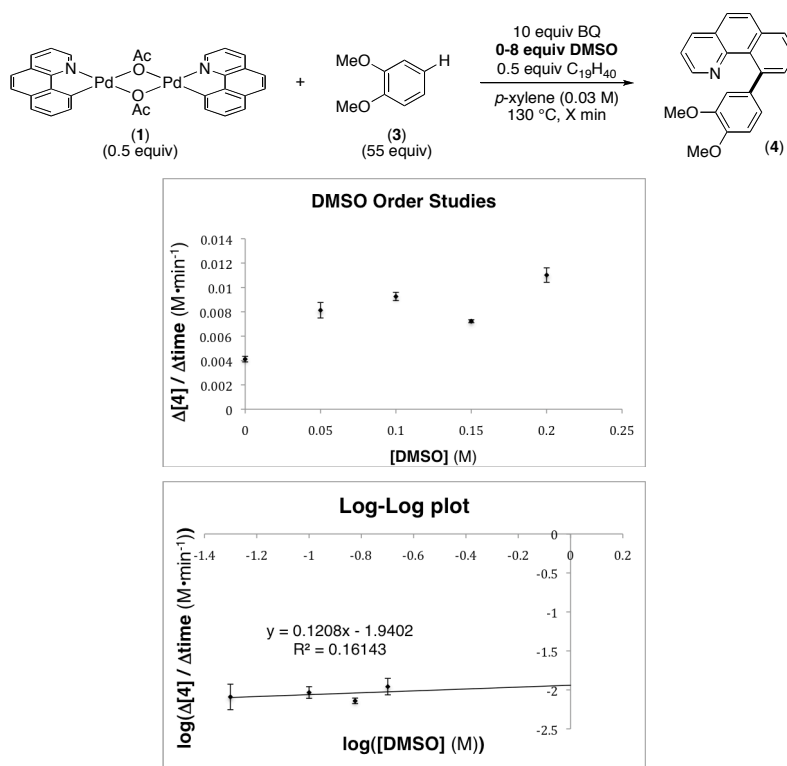
**Order in 1,2 dimethoxybenzene (3).** The order in 1,2-dimethoxybenzene (**3**) was determined under flooding conditions in BQ. The conditions used were as follows: [(Bzq)Pd(OAc)]<sub>2</sub> (**1**) (6.9 mg, 0.01 mmol, 0.5 equiv (1 equiv per Pd)) was weighed into each vial, then a standard solution containing (per aliquot) benzoquinone (BQ) (0.2 mmol, 22 mg, 10 equiv), DMSO (5.7  $\mu$ L, 0.08 mmol, 4 equiv), nonadecane (internal standard) (2.7 mg, 0.01 mmol, 0.5 equiv), 1,2-dimethoxybenzene (31-71 equiv), and *p*-xylene was added. Importantly, *p*-xylene was added or taken away in order to keep the solvent volume constant (such that volume 1,2-dimethoxybenzene + volume *p*-xylene = 0.8 mL). Reactions were conducted at 130 °C following the standard procedure described above. A linear correlation was observed when initial rate was plotted against [**3**] (Scheme S5).

**Scheme S5.** Order in 1,2-Dimethoxybenzene



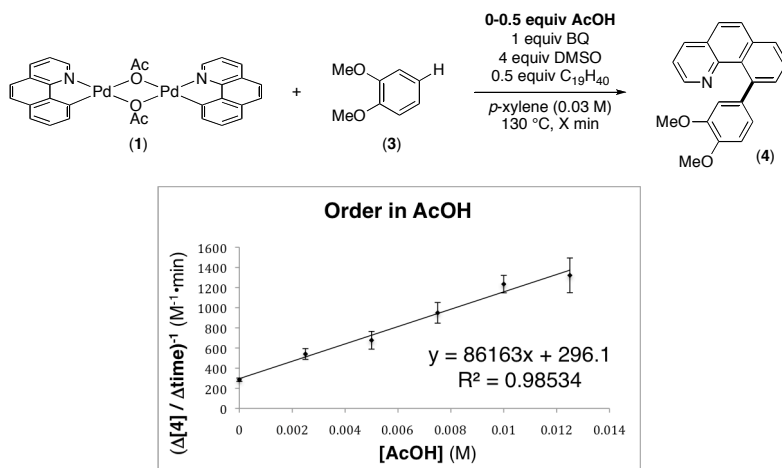
**Order in DMSO.** Order studies were also conducted with DMSO (an additive that enhanced the yields of the catalytic reactions). The conditions used were as follows: [(Bzq)PdOAc]<sub>2</sub> (**1**) (6.9 mg, 0.01 mmol, 0.5 equiv (1 equiv per Pd)) was weighed directly into a vial, then 0.806 mL of a standard solution containing (per aliquot) benzoquinone (BQ) (0.2 mmol, 22 mg, 10 equiv), DMSO (0-0.16 mmol, 0-8 equiv), nonadecane (2.7 mg, 0.01 mmol, 0.5 equiv), 1,2-dimethoxybenzene (0.14 mL, 1.1 mmol, 55 equiv), and *p*-xylene (0.66 mL) was added. Reactions were conducted at 130 °C following the standard procedure described above. As shown in Scheme S6 there was no clear order in DMSO (a log versus log plot gave an order of  $0.12 \pm 0.09$  with an  $R^2$  of 0.15, indicating no correlation). However, even small amounts of this additive did lead to a moderate rate enhancement. This may be due to an increase in the solvent polarity stabilizing the transition state.

**Scheme S6.** Order in DMSO



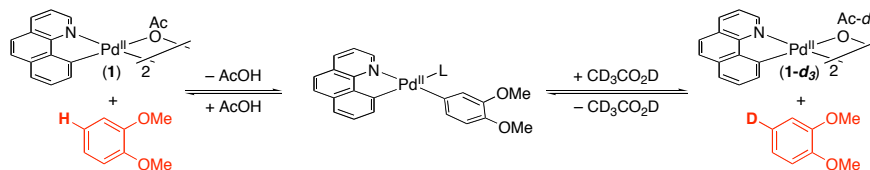
**Order in AcOH.** The conditions used were as follows: [(Bzq)Pd(OAc)]<sub>2</sub> (**1**) (6.9 mg, 0.01 mmol, 0.5 equiv (1 equiv per Pd)) was weighed directly into a vial, then 0.806 mL of a standard solution containing (per aliquot) benzoquinone (BQ) (0.02 mmol, 2.2 mg, 1 equiv), DMSO (5.7  $\mu$ L, 0.08 mmol, 4 equiv), nonadecane (2.7 mg, 0.01 mmol, 0.5 equiv), 1,2-dimethoxybenzene (0.14 mL, 1.1 mmol, 55 equiv), AcOH (0-0.01 mmol, 0-0.5 equiv), and *p*-xylene (0.66 mL) was added. Reactions were conducted at 130 °C following the standard procedure described above. A plot of (initial rate)<sup>-1</sup> versus [AcOH] showed a linear correlation as shown in Scheme S7.

**Scheme S7.** Order in AcOH

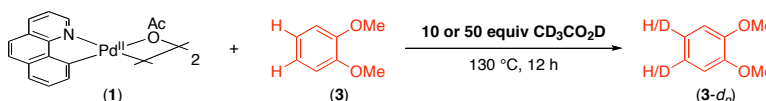


**H/D Exchange Experiments.** [(Bzq)Pd(OAc)<sub>2</sub>] (**1**) (6.9 mg, 0.02 mmol, 1 equiv), CD<sub>3</sub>CO<sub>2</sub>D (12-115  $\mu$ L, 10 or 50 equiv), and 1,2-dimethoxybenzene (0.8 mL, 6.3 mmol, 314 equiv) were heated at 130 °C for 12 h in a 2 dram vial sealed with a Teflon lined cap. DMF-*d*<sub>4</sub> (15.6  $\mu$ L, 0.2 mmol, 10 equiv) was then added as an internal standard. The % deuterium incorporation into **3** was measured using <sup>2</sup>H NMR spectroscopy by integration of the signal for 1,2-dimethoxybenzene-*d*<sub>1</sub>/*d*<sub>2</sub> versus that of DMF-*d*<sub>4</sub> (Scheme S8 and Table S1). Importantly, there was no exchange in the control reactions without added **1**.

**Scheme S8.** [(Bzq)Pd(OAc)<sub>2</sub>] Catalyzed H/D Exchange Between **3** and CD<sub>3</sub>CO<sub>2</sub>D



**Table S1.** H/D Exchange Studies.

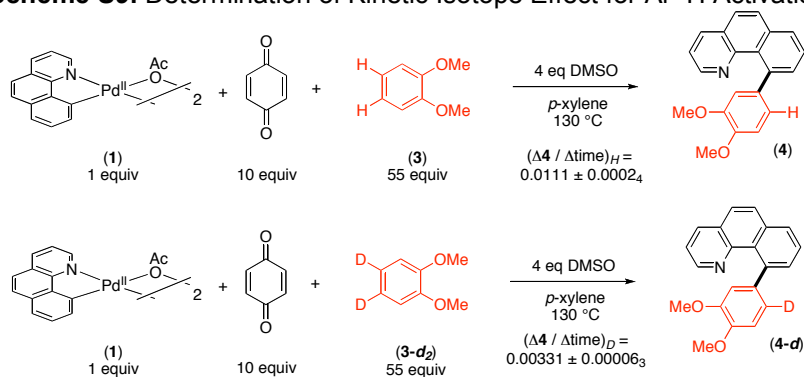


equiv CD <sub>3</sub> CO <sub>2</sub> D (mmol)	equiv <b>3</b>	mmol <b>3-d<sub>n</sub></b>	% <b>3-d</b>	TON
10 (0.20)	314	0.14	2.2	6.9
50 (1.0)	314	0.50	7.9	25



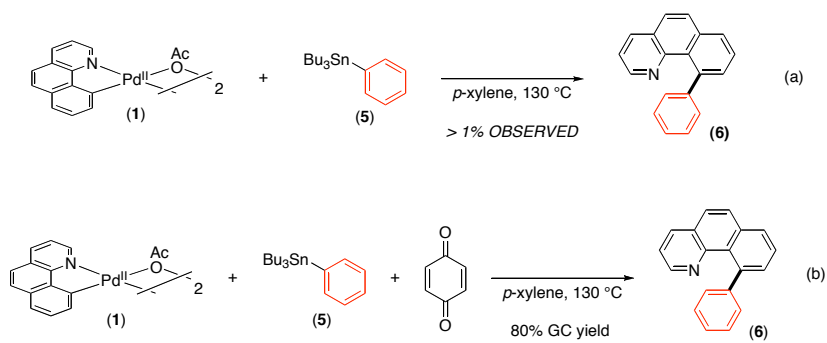
**Kinetic Isotope Effect.** We determined the kinetic isotope effect associated with this reaction by comparing the initial rate for the reaction with 1,2-dimethoxybenzene to that for the reaction with 4,5-di-deutero-1,2-dimethoxybenzene. The reaction conditions were as follows (with the reactions run at 1/3 the scale of the standard kinetic protocol):  $[(\text{Bzq})\text{Pd}(\text{OAc})]_2$  (**1**) (2.3 mg, 0.0033 mmol, 0.5 equiv (1 equiv per Pd)) was weighed directly into a vial, then 0.27 mL of a standard solution containing (per aliquot) benzoquinone (BQ) (7.2 mg, 0.067 mmol, 10 equiv), DMSO (1.9  $\mu\text{L}$ , 0.027 mmol, 4 equiv), nonadecane (0.9 mg, 0.005 mmol, 0.5 equiv), 1,2-dimethoxybenzene or 4,5-di-deutero-1,2-dimethoxybenzene (0.07 mL, 0.0033 mmol, 55 equiv), and *p*-xylene (0.22 mL) was added via a 1 mL Hamilton airtight syringe. Reactions were conducted at 130 °C following the standard procedure described above. On the basis of these experiments, the KIE was determined to be  $3.39 \pm 0.10$  (Scheme S9).

**Scheme S9.** Determination of Kinetic Isotope Effect for Ar–H Activation



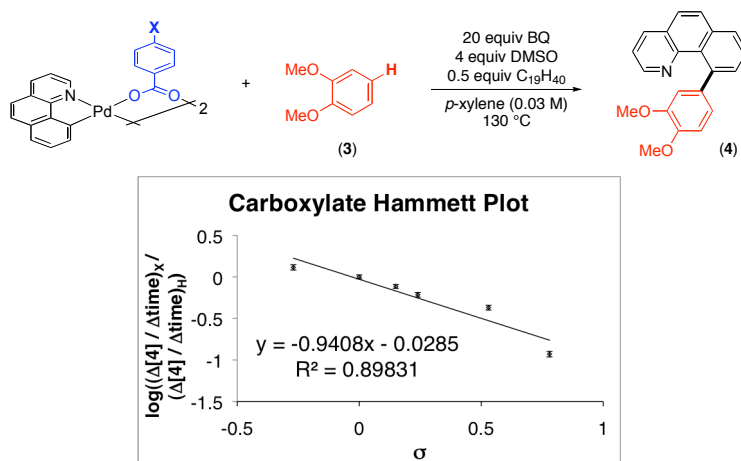
***In situ* generation of proposed intermediate B.** [(Bzq)Pd(OAc)]<sub>2</sub> (**1**) (6.9 mg, 0.01 mmol, 1 equiv (based on Pd)) tributylphenyltin (**5**) (6.5  $\mu$ L, 0.02 mmol, 1 equiv), benzoquinone (0 or 2.2 mg, 0 or 1 equiv), DMSO (5.7  $\mu$ L, 0.08 mmol, 4 equiv), and nonadecane (2.7 mg, 0.01 mmol, 0.5 equiv) were dissolved in *p*-xylene and heated to 130 °C for 12 h. The crude reaction mixtures were then analyzed by GC, and the yield of **6** was determined by comparison to the internal standard nonadecane. The reported yields represent an average of 2 runs (Scheme S10).

**Scheme S10.** *In situ* Generation of Proposed Intermediate B

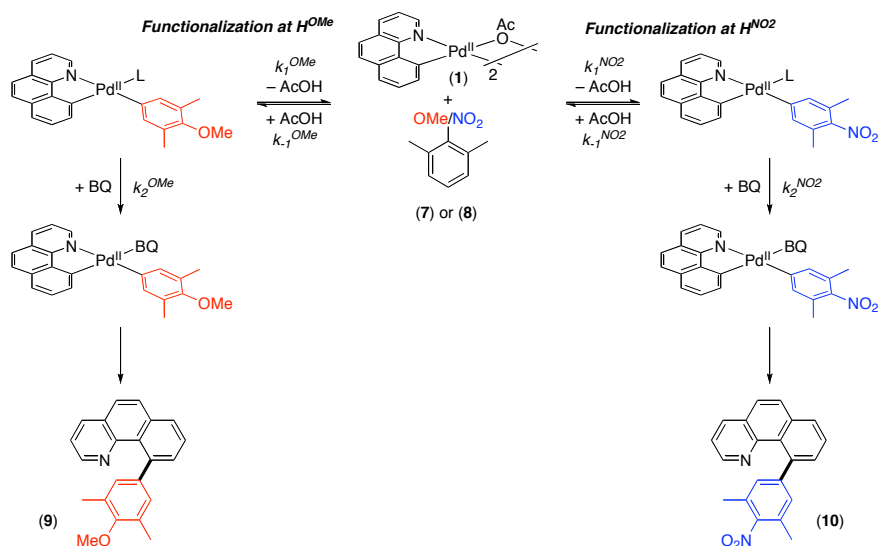


**Hammett plot for variation of the carboxylate ligand.** A Hammett plot was constructed for the reaction of various  $[\text{BzqPd}(\text{O}_2\text{C}(p\text{-X-Ar}))_2]$  derivatives under saturation conditions in BQ. The reaction conditions were as follows:  $[(\text{Bzq})\text{Pd}(\text{O}_2\text{C}(p\text{-X-Ar}))_2]$  (0.01 mmol, 0.5 equiv), 1,2-dimethoxybenzene (0.14 mL, 1.1 mmol, 55 equiv), BQ (43.2 mg, 0.4 mmol, 20 equiv), DMSO (5.6  $\mu\text{L}$ , 0.08 mmol, 4 equiv), and nonadecane (2.7 mg, 0.01 mmol, 0.5 equiv) were combined in *p*-xylene (0.66 mL). Reactions were conducted at 130 °C following the standard procedure described above. Each initial rate value represents an average of three unique kinetic experiments. A Hammett plot of this data is shown in Scheme S11.

**Scheme S11.** Hammett Plot for Reactions with Substituted Benzoates



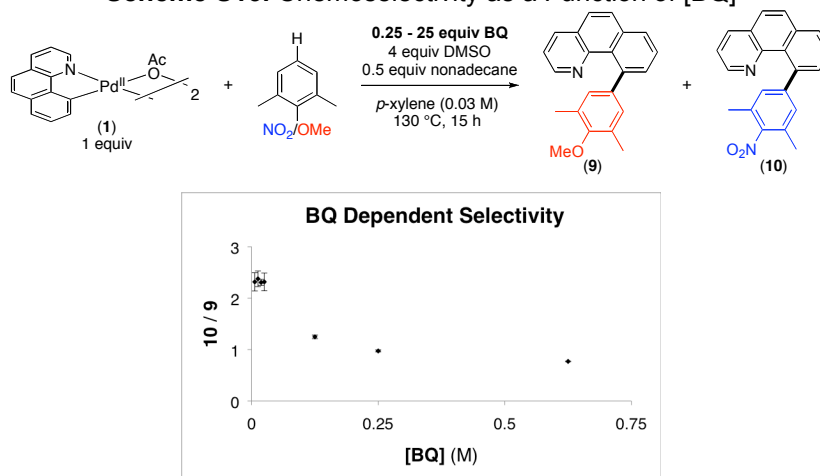
**Scheme S12.** Competition Between Electron Rich and Electron Poor Arenes



We hypothesized that changing [BQ] and/or [AcOH] would change the selectivity-determining step of the reaction. Under reaction conditions where there is a large excess of BQ, the selectivity of the reaction to form **9** vs **10** should be dictated by the relative rates associated with the C–H activation step (Scheme S12). In contrast, the addition of AcOH should lead to Curtin–Hammett conditions by establishing a pre-equilibrium for C–H activation (Scheme S12). As such, the selectivity under these conditions should reflect that of the BQ-promoted reductive elimination step. Therefore we studied the selectivity of the reaction with varying amounts of [BQ] and [AcOH].

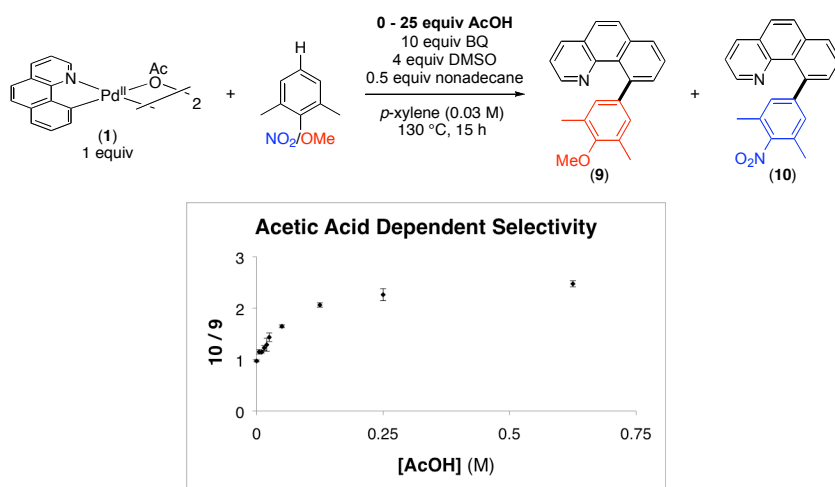
**Chemoselectivity as a Function of [Benzoquinone].** General Conditions:  $[(\text{Bzq})\text{Pd}(\text{OAc})]_2$  (**1**) (6.9 mg, 0.01 mmol, 0.5 equiv (1 equiv per Pd)) was weighed directly into a vial, then 0.806 mL of a standard solution containing (per aliquot) benzoquinone (BQ) (0.005-0.625 mmol, 0.25-25 equiv), DMSO (5.7  $\mu\text{L}$ , 0.08 mmol, 4 equiv), nonadecane (2.7 mg, 0.01 mmol, 0.5 equiv), 2,6-dimethylanisole (0.408 mL, 2.88 mmol, 144 equiv), and 2,6-dimethylnitrobenzene (0.392 mL, 2.88 mmol, 144 equiv) was added via a 1 mL Hamilton airtight syringe. The reactions were stirred at 130 °C for 15 h, then analyzed by GC. The ratio of the yield of the  $\text{NO}_2$ -product (**10**)/yield of MeO-product (**9**) was then plotted against the [BQ] (Scheme S13).

**Scheme S13.** Chemoselectivity as a Function of [BQ]



**Chemoselectivity as a Function of [AcOH].** [(Bzq)PdOAc]<sub>2</sub> (**1**) (6.9 mg, 0.01 mmol, 0.5 equiv (1 equiv per Pd)) was weighed directly into a vial, then 0.806 mL of a standard solution containing (per aliquot) benzoquinone (BQ) (0.2 mmol, 22 mg, 10 equiv), AcOH (0-0.5 mmol, 0-25 equiv), DMSO (5.7  $\mu$ L, 0.08 mmol, 4 equiv), nonadecane (internal standard) (2.7 mg, 0.01 mmol, 0.5 equiv), 2,6-dimethylanisole (0.408 mL, 2.88 mmol, 144 equiv), and 2,6-dimethylnitrobenzene (0.392 mL, 2.88 mmol, 144 equiv) was added via a 1 mL Hamilton airtight syringe. The reactions were stirred at 130 °C for 15 h, then analyzed by GC. The ratio of the yield of the NO<sub>2</sub>-product/yield of MeO-product was then plotted against the [AcOH] (Scheme S14).

**Scheme S14.** Chemoselectivity as a Function of [AcOH]



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