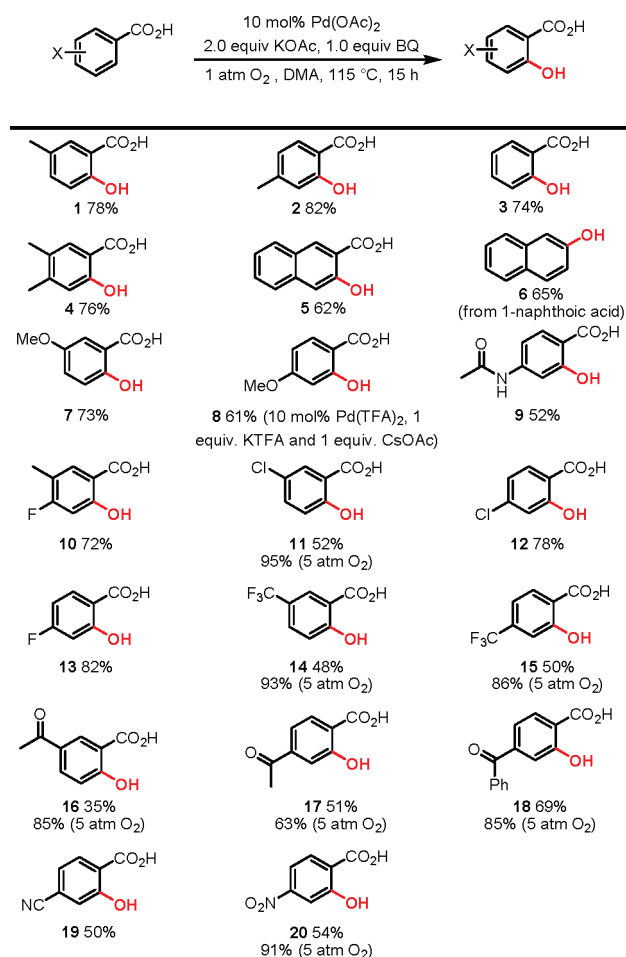
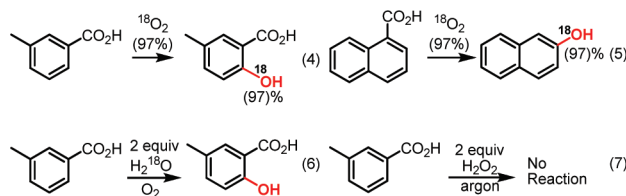




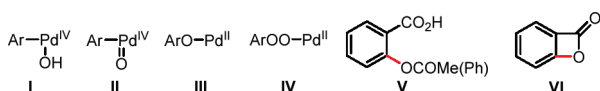
**Table 2.** Pd-Catalyzed *ortho*-Hydroxylation with O<sub>2</sub><sup>a</sup><sup>a</sup> Isolated yield.

moderate yields. In these cases, 85–95% yields can be obtained by using 5 atm of O<sub>2</sub>.

Preliminary mechanistic investigations were carried out to shed light onto this hydroxylation pathway. Our earlier studies on Pd-catalyzed C–H oxidation using peroxides<sup>7a</sup> and O<sub>2</sub> as the oxygen source were initially inspired by seminal works regarding organometallic reactions of C–Pd bonds with peroxides<sup>13</sup> and C–Pt bonds with O<sub>2</sub>.<sup>14,15</sup> These oxidants are shown to oxidize C–Pt (Pd) bonds to form Pt(IV) and Pd(IV) species **I** and **II** or directly insert oxygen atoms into C–Pt(Pd) bonds to form **III** and **IV**.<sup>7a</sup>



While no data are currently available to distinguish among these reaction pathways, labeling experiments were performed to rule out the involvement of carboxylation or lactonization intermediates **V** and **VI** (Figure 2). First, <sup>18</sup>O<sub>2</sub> was incorporated into the products with high

**Figure 2.** Possible reaction intermediates.

fidelity (eq 4). Second, the decarboxylated product showed that <sup>18</sup>O<sub>2</sub> is incorporated into the hydroxyl rather than the carboxyl group (eq 5). These observations are inconsistent with the carboxylation/hydrolysis pathway from the catalytic amount of OAc<sup>−</sup> or the benzoic acids. Finally, experiments using 2 equiv of H<sub>2</sub><sup>18</sup>O (eq 6) or H<sub>2</sub>O<sub>2</sub> (30% in H<sub>2</sub>O) (eq 7) also rule out oxygen incorporation from H<sub>2</sub>O or H<sub>2</sub>O<sub>2</sub> formed through a Pd(II)/Pd(0) catalysis.<sup>16</sup>

In summary, we have developed a versatile Pd-catalyzed *ortho*-hydroxylation of benzoic acids with 1 atm of O<sub>2</sub> or air under nonacidic conditions. Mechanistic investigations point to a direct oxygenation of the aryl-Pd species by molecular O<sub>2</sub>.

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**Supporting Information Available:** Experimental procedure and characterization of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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