

**Supporting Information
For**

**Palladium Pincer Complexes with Reduced Bond Angle Strain: Efficient
Catalysts for the Heck Reaction**

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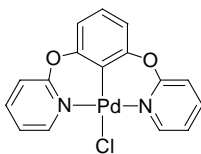
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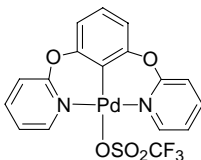
[1,3-bis(2-pyridyloxy)phenyl]palladium chloride (**3a**)



A mixture of 1,3-bis(2-pyridyloxy)benzene (0.26 g, 1.00 mmol), K_2PdCl_4 (0.33 g, 1.00 mmol), and glacial acetic acid (6 ml) was refluxed for four days. A yellow suspension was changed to a bright grey solid during the reaction. The mixture was allowed to cool to room temperature. The bright grey solid was filtered through a Büchner funnel and washed sequentially with H_2O , MeOH, and Et_2O to give pure **3a**. Yield: 0.23 g (80%). Mp: 270-272 °C. ^1H NMR (CDCl_3 , 300 MHz): δ 6.98 (d, $J = 7.8$ Hz, 2H, Py-H), 7.1 (m, 3H, Py-H), 7.29 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.86 (t, $J = 6.3$ Hz, 2H, Py-H), 9.30 (m, 2H, Py-H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 158.0, 152.3, 151.0, 141.0, 126.1, 118.6, 114.5, 113.3, 110.9. HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{11}\text{N}_2\text{O}_2\text{Pd} (\text{M}-\text{Cl})^+$ 368.9855, found 368.9860.

1,3-Bis(2-pyridyloxy)benzene was prepared from the reaction of 2-bromopyridine with resorcinol, according to the literature (ref. 7).

[1,3-bis(2-pyridyloxy)phenyl]palladium(II) trifluoromethanesulfonate (**3b**)



A mixture of **3a** (0.18 g, 0.44 mmol), silver triflate (0.11 g, 0.44 mmol), and dichloromethane (5 ml) was stirred for 7 h. The mixture was filtered through Celite to remove silver chloride and washed with dichloromethane. The solvent was evaporated to give **3b** as a pale yellow solid. Yield: 0.22 g (92%). Mp: 250-252 °C. ^1H NMR (CDCl_3 , 300 MHz): δ 6.99 (d, $J = 7.9$ Hz, 2H, Py-H), 7.23 (m, 3H, Ar-H, Py-H), 7.34 (d, $J = 8.3$ Hz, 2H, Ar-H), 7.93 (t, $J = 7.3$ Hz, 2H, Py-H), 8.75 (m, 2H, Py-H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 157.2, 150.6, 149.8, 141.5, 126.7, 121.4, 117.2 ($-\text{OSO}_2\text{CF}_3$), 119.2, 114.5, 113.6, 103.7. ^{19}F NMR (CDCl_3 , 300 MHz): δ -1.6. HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{11}\text{N}_2\text{O}_2\text{Pd} (\text{M}-\text{OTf})^+$ 368.9855, found 368.9848.

