Electronic Supplementary Information for

**A New Hierarchically Porous Pd@HSQ Monolithic Catalyst for Mizoroki-Heck Cross-Coupling Reaction**

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Fig. S1. Characterizations of the HSQ support. (a) SEM image of as-dried HSQ monolith, showing the presence of well-defined co-continuous macroporous structure. (b) Mercury porosimetry result, showing a sharp distribution of macropore size. (c) High specific surface area (800 m²/g) due to the presence of small meso- and micropores was confirmed by nitrogen adsorption desorption measurement and the BJH pore size distribution curve (inset). (d) Total preservation of highly reactive Si-H bond and high condensation degree was confirmed by ²⁹Si solid-state NMR. (e) Digital camera image of the as-prepared HSQ monolith.
**Fig. S2.** FT-IR spectra showing the decreased absorption peaks of Si-H and O-Si-H and increased absorption peaks of the Si-OH stretching vibration.

**Fig. S3.** FT-IR spectra of the Pd@HSQ monolith before and after 10-time reuses. The decrease in absorption by Si-H and O-Si-H stretching vibrations suggests slight decomposition of Si-H in the course of reuse.
1H and 13C NMR of the Products

Entry 4:

![Chemical Structure]

1H NMR (CDCl₃); δ = 7.66 (d, J = 16 Hz, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8 Hz, 2H), 6.40 (d, J = 16 Hz, 1H), 4.20 (t, J = 6.4 Hz, 2H), 2.37 (s, 3H), 1.64-1.74 (m, 2H), 1.38-1.50 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H).

13C NMR (CDCl₃); δ = 13.70, 19.24, 21.39, 30.72, 64.27, 117.19, 127.97, 129.53, 131.65, 140.54, 144.50, 167.25.

Entry 5:

![Chemical Structure]

1H NMR (CDCl₃); δ = 7.69 (d, J = 16.4 Hz, 1H), 7.50-7.57 (m, 2H), 7.36-7.43 (m, 3H), 6.45 (d, J = 16 Hz, 1H), 4.21 (t, J = 6.4 Hz, 2H), 1.65-1.75 (m, 2H), 1.38-1.50 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H).

13C NMR (CDCl₃); δ = 13.70, 19.26, 30.72, 64.25, 116.91, 127.94, 128.41, 128.52, 135.19, 144.95, 167.18.

Entry 6:

![Chemical Structure]

1H NMR (CDCl₃); δ = 7.65 (d, J = 16 Hz, 1H), 7.16-7.38 (m, 4H), 6.43 (d, J = 15.6 Hz, 1H), 4.21 (t, J = 6.8 Hz, 2H), 2.37 (s, 3H), 1.65-1.75 (m, 2H), 1.38-1.50 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H).

13C NMR (CDCl₃); δ = 13.70, 19.14, 21.24, 30.59, 64.32, 117.96, 125.18, 128.64, 128.68, 130.38, 130.99, 134.34, 138.43, 144.67, 167.12.
Entry 7:

\[
\text{MeO} \quad \begin{array}{c}
\begin{array}{c}
\text{H}
\end{array}
\end{array} \quad \begin{array}{c}
\text{O}
\end{array} \quad \begin{array}{c}
\text{O} \quad \text{Bu}
\end{array}
\]

\(^1\)H NMR (CDCl\(_3\)); \(\delta = 7.64\) (d, \(J = 16\) Hz, 1H), 7.48 (d, \(J = 7.2\) Hz, 2H), 6.91 (d, \(J = 6.8\) Hz, 2H), 6.31 (m, \(J = 16\) Hz, 1H), 4.20 (t, \(J = 6.8\) Hz, 2H), 3.84 (s, 3H), 1.64-1.74 (m, 2H), 1.38-1.50 (m, 2H), 0.97 (t, \(J = 7.6\) Hz, 3H).

\(^13\)C NMR (CDCl\(_3\)); \(\delta = 13.70, 19.14, 30.74, 55.27, 64.19, 114.21, 115.65, 127.10, 129.61, 144.14, 161.24, 167.38\).

Entry 8:

\[
\text{H}_2\text{N} \quad \begin{array}{c}
\begin{array}{c}
\text{H}
\end{array}
\end{array} \quad \begin{array}{c}
\text{O}
\end{array} \quad \begin{array}{c}
\text{O} \quad \text{Bu}
\end{array}
\]

\(^1\)H NMR (CDCl\(_3\)); \(\delta = 7.59\) (d, \(J = 16\) Hz, 1H), 7.35 (m, \(J = 8.8\) Hz, 2H), 6.65 (d, \(J = 8\) Hz, 2H), 6.24 (m, \(J = 15.6\) Hz, 1H), 4.18 (t, \(J = 7.2\) Hz, 2H), 3.94 (br, 2H), 1.62-1.72 (m, 2H), 1.38-1.49 (m, 2H), 0.96 (t, \(J = 7.2\) Hz, 3H).

\(^13\)C NMR (CDCl\(_3\)); \(\delta = 13.65, 19.08, 30.70, 63.99, 113.35, 114.64, 124.34, 129.73, 144.79, 148.74, 167.77\).

Entry 9:

\[
\text{OMe} \quad \begin{array}{c}
\begin{array}{c}
\text{H}
\end{array}
\end{array} \quad \begin{array}{c}
\text{O}
\end{array} \quad \begin{array}{c}
\text{O} \quad \text{Bu}
\end{array}
\]

\(^1\)H NMR (CDCl\(_3\)); \(\delta = 7.65\) (d, \(J = 16\) Hz, 1H), 7.30 (t, \(J = 8.4\) Hz, 1H), 7.12 (d, \(J = 7.6\) Hz, 1H), 7.05 (s, 1H), 6.94 (d, \(J = 8\) Hz, 1H), 6.43 (d, \(J = 16\) Hz, 1H), 4.21 (t, \(J = 6.8\) Hz, 2H), 3.83 (s, 3H), 1.65-1.75 (m, 2H), 1.38-1.50 (m, 2H), 0.97 (t, \(J = 7.2\) Hz, 3H).

\(^13\)C NMR (CDCl\(_3\)); \(\delta = 13.69, 19.14, 30.69, 55.20, 64.39, 112.77, 116.03, 118.47, 120.69, 129.78, 135.73, 144.41, 159.79, 166.99\).
Entry 10:

\[
\begin{align*}
&\text{O}_2\text{N} \quad \text{O} \quad \text{Bu} \\
&1^1\text{H NMR (CDCl}_3\text{); } \delta = 8.25 (d, J = 8.8 \text{ Hz}, 1\text{H}), 7.75-7.65 (m, 3\text{H}), 6.57 (m, J = 16.4 \text{ Hz}, 1\text{H}), 4.24 (t, J = 6.8 \text{ Hz}, 2\text{H}), 1.65-1.75 (m, 2\text{H}), 1.38-1.50 (m, 2\text{H}), 0.98 (t, J = 7.2 \text{ Hz}, 3\text{H}). \\
&1^3\text{C NMR (CDCl}_3\text{); } \delta = 13.67, 19.10, 30.61, 64.84, 122.52, 124.09, 128.56, 140.53, 141.37, 166.07.
\end{align*}
\]

Entry 11:

\[
\begin{align*}
&\text{Ac} \quad \text{O} \quad \text{Bu} \\
&1^1\text{H NMR (CDCl}_3\text{); } \delta = 7.97 (d, J = 8.4 \text{ Hz}, 2\text{H}), 7.70 (d, J = 8.4 \text{ Hz}, 1\text{H}), 7.61 (d, J = 8 \text{ Hz}, 2\text{H}), 6.53 (d, J = 16 \text{ Hz}, 1\text{H}), 4.23 (t, J = 6.8 \text{ Hz}, 2\text{H}), 2.61 (s, 2\text{H}), 1.65-1.75 (m, 2\text{H}), 1.38-1.50 (m, 2\text{H}), 0.97 (t, J = 7.2 \text{ Hz}, 3\text{H}). \\
&1^3\text{C NMR (CDCl}_3\text{); } \delta = 13.62, 19.05, 26.56, 30.77, 67.53, 120.68, 128.00, 130.31, 137.80, 138.66, 142.83, 166.45, 197.19.
\end{align*}
\]

Entry 12:

\[
\begin{align*}
&\text{Br} \quad \text{O} \quad \text{Bu} \\
&1^1\text{H NMR (CDCl}_3\text{); } \delta = 7.61 (d, J = 16 \text{ Hz}, 1\text{H}), 7.52 (d, J = 8.4 \text{ Hz}, 1\text{H}), 7.39 (d, J = 8.4 \text{ Hz}, 1\text{H}), 6.43 (m, J = 16 \text{ Hz}, 1\text{H}), 4.21 (t, J = 6.8 \text{ Hz}, 2\text{H}), 1.64-1.74 (m, 2\text{H}), 1.37-1.49 (m, 2\text{H}), 0.97 (t, J = 7.6 \text{ Hz}, 3\text{H}). \\
&1^3\text{C NMR (CDCl}_3\text{); } \delta = 13.68, 19.11, 30.67, 64.47, 118.90, 119.26, 124.35, 129.34, 132.02, 133.29, 143.05, 166.72.
\end{align*}
\]
Entry 13:

\[
\begin{array}{c}
\text{EtOOC-} \\
\text{O-Bu}
\end{array}
\]

\(^1\)H NMR (CDCl\(_3\)); \(\delta = 8.06 \ (d, J = 8 \text{ Hz}, 1\text{H}), 7.70 \ (d, J = 16 \text{ Hz}, 1\text{H}), 7.58 \ (d, J = 8 \text{ Hz}, 1\text{H}), 6.52 \ (m, J = 16 \text{ Hz}, 1\text{H}), 4.39 \ (d, J = 6.8 \text{ Hz}, 2\text{H}), 4.23 \ (t, J = 6.8 \text{ Hz}, 2\text{H}), 1.65-1.75 \ (m, 2\text{H}), 1.38-1.50 \ (m, 5\text{H}), 0.97 \ (t, J = 7.6 \text{ Hz}, 3\text{H}).
\]

\(^{13}\)C NMR (CDCl\(_3\)); \(\delta = 13.57, 14.13, 19.03, 30.57, 61.00, 64.43, 120.42, 127.67, 129.60, 129.87, 131.50, 138.41, 142.98, 166.41.\)