Supplementary Materials: Suzuki-Miyaura C-C Coupling Reactions Catalyzed by Supported Pd Nanoparticles for the Preparation of Fluorinated Biphenyl Derivatives

Roghayeh Sadeghi Erami, Diana Diaz-Garcia, Sanjiv Prashar, Antonio Rodriguez-Diéguez, Mariano Fajardo, Mehdi Amirnasr and Santiago Gómez-Ruiz

Table S1. Experimental quantities of reagents for the Pd loading study.

<table>
<thead>
<tr>
<th>Final Material</th>
<th>Theoretical Pd wt %</th>
<th>G-COOH (g)</th>
<th>Pd (mg)</th>
<th>[PdCl₂(cod)] (mg)</th>
<th>Experimental Pd wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-COOH-Pd-5</td>
<td>5</td>
<td>1.0</td>
<td>52.6</td>
<td>141.2</td>
<td>3.06</td>
</tr>
<tr>
<td>G-COOH-Pd-10</td>
<td>10</td>
<td>1.0</td>
<td>111.1</td>
<td>298.1</td>
<td>7.93</td>
</tr>
<tr>
<td>G-COOH-Pd-15</td>
<td>15</td>
<td>1.0</td>
<td>176.4</td>
<td>473.4</td>
<td>11.20</td>
</tr>
</tbody>
</table>

Table S2. Adsorptive parameters of the materials G-COOH and G-COOH-Pd-10.

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface area (m²/g)</th>
<th>BJH Adsorption cumulative surface area of pores (m²/g)</th>
<th>BJH Desorption cumulative surface area of pores (m²/g)</th>
<th>BJH Adsorption cumulative volume of pores (cm³/g)</th>
<th>BJH Desorption cumulative volume of pores (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-COOH</td>
<td>7.7</td>
<td>4.874</td>
<td>7.286</td>
<td>0.0350</td>
<td>0.0357</td>
</tr>
<tr>
<td>G-COOH-Pd-10</td>
<td>4.1</td>
<td>3.838</td>
<td>6.167</td>
<td>0.0383</td>
<td>0.0385</td>
</tr>
</tbody>
</table>

Figure S1. TEM image of G-COOH showing the single layer of graphene.
**Figure S2.** TEM image of a cluster of agglomerated Pd nanoparticles.

**Figure S3.** TEM image showing the impregnation of a cluster of Pd nanoparticles at the edge of the graphene layer.
**Figure S4.** FT-IR spectrum of G-COOH-Pd-10.

**Figure S5.** Nitrogen adsorption desorption isotherm of G-COOH.
Figure S6. XRD of the material G-COOH-Pd-10

Figure S7. Comparison of the $^{19}$F NMR spectra of the reaction between 1-bromo-4-fluorobenzene and phenylboronic acid catalyzed by G-COOH-Pd-10 in the presence of a constant quantity of standard (4-fluorobenzophenone) at different reaction time periods.
Figure S8. $^{19}$F NMR spectrum of the starting solution of 1-bromo-4-fluorobenzene in the presence of a constant quantity of standard (4-fluorobenzophenone) (0 hours).

Figure S9. $^{19}$F NMR spectrum of the reaction between 1-bromo-4-fluorobenzene and phenylboronic acid catalyzed by G-COOH-Pd-10 after three hours of reaction in the presence of a constant quantity of standard (4-fluorobenzophenone).
**Figure S10.** $^{19}$F NMR spectrum of the reaction between 1-bromo-4-fluorobenzene and phenylboronic acid catalyzed by G-COOH-Pd-10 after eight hours of reaction in the presence of a constant quantity of standard (4-fluorobenzophenone).

**Figure S11.** $^{19}$F NMR spectrum of the reaction between 1-bromo-4-fluorobenzene and phenylboronic acid catalyzed by G-COOH-Pd-10 after 24 hours of reaction in the presence of a constant quantity of standard (4-fluorobenzophenone).
Figure S12. $^{19}$F NMR spectrum of the reaction between 1-bromo-4-fluorobenzene and phenylboronic acid catalyzed by G-COOH-Pd-10 after 48 hours of reaction in the presence of a constant quantity of standard (4-fluorobenzophenone).

Figure S13. Comparison of the $^{19}$F NMR spectra of the reaction between 1-bromo-2-fluorobenzene and 4-fluorophenylboronic acid catalyzed by G-COOH-Pd-10 in the presence of a constant quantity of standard (4-fluorobenzophenone) at different reaction time periods.

Spectroscopic Data ($^1$H and $^{19}$F NMR) of all the Synthesized Fluorinated Biaryl Derivatives
The spectroscopic data found for this compound are the same than those found in the literature [1]. In addition, it is a commercial compound with CAS Number: 324-74-3. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.60–7.54 (m, 4H, H2 and H3), 7.50–7.34 (m, 3H, H4, and H5), 7.20–7.12 (m, 2H, H1). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\): −116.2 (m).

The spectroscopic data found for this compound are the same than those found in the literature [2]. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.53–7.47 (m, 6H, H2, H3, and H4), 7.15–7.10 (m, 2H, H1), 6.75 (dd, \(J = 10.8, 17.6\) Hz, 1H, H5), 5.80 (d, \(J = 17.6\) Hz, 1H, H6), 5.28 (d, \(J = 11.6\) Hz, 1H, H6). \(^{19}\)F NMR (376 MHz, CD\(_3\)COCD\(_3\)): −112.2 (m).

The spectroscopic data found for this compound are the same than those found in the literature [3]. In addition, it is a commercial compound with CAS Number: 5731-10-2. \(^1\)H NMR (400 MHz, CDCl\(_3\))\(\delta\): 7.30 (t, 2H, \(J = 9.0\) Hz, H1), 7.76 (m, 4H, H2, and H3), 7.99 (d, 2H, \(J = 8.8\) Hz, H4), 12.94 (1H, br s). \(^{19}\)F NMR (376 MHz, CD\(_3\)COCD\(_3\)): −112.4 (m).

The spectroscopic data found for this compound are the same than those found in the literature [4]. In addition, it is a commercial compound with CAS Number: 398-23-2. \(^1\)H NMR (400 MHz, CDCl\(_3\))\(\delta\): 7.13 (t, 4H, \(J = 9\) Hz, H1), 7.48 (dd, 4H, \(J = 9\) and 5 Hz, H2). \(^{19}\)F NMR (376 MHz, CD\(_3\)COCD\(_3\)): −112.3 (m).

The spectroscopic data found for this compound are the same than those found in the literature [5]. \(^1\)H NMR (400 MHz, CDCl\(_3\))\(\delta\): 7.20 (m, 1H, H1), 7.37 (m, 1H, H2), 7.25 (m, 1H, H3), 7.45 (d, 1H, H4), 7.57 (m, 2H, H5), 7.18 (m, 2H, H6). \(^{19}\)F NMR (376 MHz, CD\(_3\)COCD\(_3\)): −111.1 (m), −114.8 (m).
The spectroscopic data found for this compound are the same as those found in the literature [6].$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.52 (dd, 2H, $J = 8.5, 5.0$ Hz, H5 and H8), 7.38 (td, 1H, $J = 10.0, 3.5$ Hz, H2), 7.13 (t, 2H, $J = 8.5$ Hz, H6 and H7), 7.03 (td, 1H, $J = 10.0, 2.5$ Hz, H1). $^{19}$F NMR (376 MHz, CD$_3$COCD$_3$): $-109.3$ (m), $-111.4$ (m).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26–7.21 (m, 2H, H2), 7.16–7.13 (m, 1H, H3), 7.11–7.06 (m, 2H, H1), 6.98–6.89 (m, 2H, H4 and H5), 2.22 (s, 3H, methyl group (6)). $^{19}$F NMR (376 MHz, CD$_3$COCD$_3$): $-112.3$ (m), $-112.5$ (m).

$^1$H NMR (400 MHz, CD$_3$COCD$_3$) $\delta$ 7.41–7.34 (m, 2H, H2), 7.26–7.18 (m, 2H, H3 and H4), 7.12–7.01 (m, 2H, H1), 6.94–6.99 (dd, 1H, H5), 2.20 (s, 3H, Methyl group (6)). $^{19}$F NMR (376 MHz, CD$_3$COCD$_3$): $-111.8$ (m), $-114.5$ (m).

References