Supporting Information

Solid supported palladium (0) nano/microparcles catalyzed ultrasound induced continuous flow technique for large scale Suzuki reaction

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(1) **Table 1.** Optimization table for SS-Pd catalysed ultrasound mediated Suzuki cross coupling reaction in a continuous flow process

![Reaction Scheme]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Flow rate (ml/min.)</th>
<th>Amplitude (%)</th>
<th>Catalyst loading (mol% Pd)</th>
<th>Time (h)</th>
<th>%Yield(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>88</td>
<td>30</td>
<td>3</td>
<td>2.5</td>
<td>72</td>
</tr>
<tr>
<td>2</td>
<td>127</td>
<td>30</td>
<td>3</td>
<td>3</td>
<td>85</td>
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<td>3</td>
<td>136</td>
<td>30</td>
<td>3</td>
<td>3.5</td>
<td>84</td>
</tr>
<tr>
<td>4</td>
<td>127</td>
<td>20</td>
<td>2</td>
<td>4</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>136</td>
<td>30</td>
<td>5</td>
<td>3</td>
<td>82</td>
</tr>
</tbody>
</table>

\(^a\)Isolated yields
(2) Typical experimental procedure for the Suzuki coupling reaction under continuous flow technique.

![Diagram](image)

**Fig. 1** Schematic outline of continuous flow technique

**4-Methoxybiphenyl (2b) (Table 1, entry 2)**

![Structure](image)

A mixture of 4-iodoanisole 1b (5 gm., 0.021 mol), phenylboronic acid (3.12 gm., 0.025 mol), potassium carbonate (5.80 gm., 0.042 mol) were taken in an oven dried 250 ml round bottomed flask and 200 ml of MeOH : H₂O (2:3) was added into it. The resulting mixture was homogenized by stirring at room temperature. The SS-Pd (14 gm., 0.0006 mol Pd) catalyst was charged in the reaction vessel having cotton plug at outlet, and attached to the probe holder with a screw. The previously prepared reaction mixture was poured (through b) into the reservoir. The stopcock c was opened and the pump was also turned on to circulate the reaction mixture through reaction vessel. After approximately one cycle the ultrasonicator was turned on and the circulation of the reaction mixture was continued through c→e→f→b path. The progress of reaction was monitored by TLC by taking out small amount of
reaction mixture from stopcock d. On completion, the whole reaction mixture was drained out through stopcock d and concentrated on rotary evaporator. The concentrated reaction mixture was extracted with ethyl acetate (3×20 ml). The combined organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The crude residue was purified by silica gel (mesh 230-400) column chromatography using hexane:EtOAc (98:2) as eluent to afford 2b as crystalline white solid (3.55 gm., 92%); mp 87-89 °C; ¹H NMR (300 MHz; CDCl₃) δ = 3.87 (s, 3H), 7.00 (d, J = 9 Hz, 2H), 7.31-7.36 (m, 1H), 7.42-7.47 (m, 2H), 7.55-7.60 (m, 4H); ¹³C NMR (75 MHz; CDCl₃) δ = 55.49, 114.37 (2C), 126.83, 126.91 (2C), 128.32 (2C), 128.89 (2C), 133.76, 141.00, 159.32.

2. Synthesis and characterization data for the products 2c-2m

3-Methoxybiphenyl (2c) (Table 1, entry 3)

Prepared as described for 2b, starting from 1c (1 gm, 0.004 mol) gave, after purification with silica gel column chromatography (Hexane 100%) 2c as colourless oily liquid (0.668 gm, 85%); ¹H NMR (300 MHz; CDCl₃) δ = 3.88 (s, 3H), 6.90-6.94 (m, 1H), 7.15-7.22 (m, 1H), 7.35-7.40 (m, 2H), 7.43-7.48 (m, 2H), 7.63 (d, J = 7.8 Hz, 2H); ¹³C NMR (75 MHz; CDCl₃) δ = 55.24, 112.64, 112.87, 119.64, 127.15 (2C), 127.36, 128.68 (2C), 129.70, 141.07, 142.74, 159.91.

1-Phenylnaphthalene (2d) (Table 1, entry 4)

Prepared as described for 2b, starting from 1d (1 gm, 0.003 mmol) gave, after purification with silica gel column chromatography (Hexane 100%) 2d as colourless viscous liquid (0.714 mg, 89%); ¹H NMR (300
MHz; CDCl₃ δ = 7.49-7.63 (m, 9H), 7.93-8.03 (m, 3H); ¹³C NMR (75 MHz; CDCl₃) δ = 125.32, 125.70, 125.98 (2C), 126.87, 127.17, 127.58, 128.20 (3C), 130.03 (2C), 131.62, 134.79, 140.24, 140.75.

2-Nitrobiphenyl (2e) (Table 1, entry 5)

![2-Nitrobiphenyl](image)

Prepared as described for 2b, starting from 1e (5 gm., 0.02 mol) gave, after purification with silica gel column chromatography (Hexane:EtOAc::98:2) 2e as yellow viscous liquid (3.66 gm., 92%); ¹H NMR (300 MHz; CDCl₃) δ = 7.32-7.35 (m, 2H), 7.41-7.51 (m, 5H), 7.60-7.65 (m, 1H), 7.86 (d, J = 9 Hz, 1H); ¹³C NMR (75 MHz; CDCl₃) δ = 123.98, 127.82 (2C), 128.10, 128.15, 128.61 (2C), 131.88, 132.20, 136.25, 137.33, 149.25.

4-Nitrobiphenyl (2f) (Table 1, entry 6)

![4-Nitrobiphenyl](image)

Prepared as described for 2b, starting from 1f (5 gm., 0.02 mol) gave, after purification with silica gel column chromatography (Hexane: EtOAc::95:5) 2f as light yellow crystalline solid (3.54 gm., 89%); mp 113-116 °C; ¹H NMR (300 MHz; CDCl₃) δ = 7.42-7.53 (m, 3H), 7.65 (d, 2H, J = 6 Hz), 7.73 (d, 2H, J = 9 Hz), 8.29 (d, 2H, J = 9 Hz); ¹³C NMR (75 MHz; CDCl₃) δ = 124.04, 127.33, 127.73, 128.86, 129.10, 138.71, 147.06, 147.56.

4-Methoxybiphenyl (2g) (Table 1, entry 7) Prepared as described for 2b, starting from 1g (5 gm., 0.021 mol) gave, after purification with silica gel column chromatography using hexane to afford 2g as white crystalline solid (2.74 gm., 71%); melting point and NMR data are same as Table 1, entry 2.
1,4-Diphenylbenzene (2h) (Table 1, entry 8)

![Structure of 1,4-Diphenylbenzene](image)

Prepared as described for 2b, starting from 1h (5 gm, 0.021 mol) gave, after purification with silica gel column chromatography (Hexane: EtOAc::95:5) 2h as white crystalline solid (2.20 gm., 60%); mp 209-213 °C; $^1$H NMR (300 MHz; CDCl$_3$) $\delta$ = 7.37-7.42 (m, 2H), 7.47-7.52 (m, 4H), 7.67-7.74 (m, 8H); $^{13}$C NMR (75 MHz; CDCl$_3$) $\delta$ = 127.04 (4C), 127.33 (2C), 127.49 (4C), 128.80 (4C), 140.14 (2C), 140.73 (2C).

4-Bromobiphenyl (2h′) (Table 1, entry 8)

![Structure of 4-Bromobiphenyl](image)

2h′ was formed with 2h, starting from 1h gave, after purification with silica gel column chromatography using hexane to afford 2h′ as colourless oily liquid (0.93 gm., 25%); $^1$H NMR (300 MHz; CDCl$_3$) $\delta$ = 7.36-7.39 (m, 1H), 7.42-7.47 (m, 4H), 7.54-7.62 (m, 4H); $^{13}$C NMR (300 MHz; CDCl$_3$) $\delta$ = 121.51, 126.92, 127.15, 127.62, 128.73 (2C), 128.88, 131.84 (2C), 133.12, 139.98, 140.11.

4-Nitrobiphenyl (2i) (Table 1, entry 9) Prepared as described for 2b, starting from 1i (5 gm., 0.024 mol) gave, after purification with silica gel column chromatography (Hexane:EtOAc::95:5) 2i as light yellow crystalline solid (0.807 gm, 82%); melting point and NMR data are same as 2f (Table 1, entry 6).
**2,4-Dinitrobiphenyl (2j) (Table 1, entry 10)**

\[
\begin{array}{c}
\text{NO}_2 \\
\text{O} \\
\text{NO}_2 \\
\end{array}
\]

Prepared as described for 2b, starting from 1j (5 gm., 0.024 mol) gave, after purification with silica gel column chromatography (Hexane:EtOAc::95:5) 2j as yellow crystalline solid (3.10 gm., 53%); mp 76-78 °C; \(^1\)H NMR (300 MHz; CDCl\(_3\)) \(\delta = 7.32-7.39\) (m, 2H), 7.42-7.57 (m, 3H), 7.68 (d, \(J = 8.7\) Hz, 1H), 8.47 (q, \(J = 2.1\) Hz, 1H), 8.69 (d, \(J = 2.1\) Hz, 1H); \(^{13}\)C NMR (300 MHz; CDCl\(_3\)) \(\delta = 119.69, 126.41, 127.63\) (2C), 129.04 (2C), 129.52, 133.17, 135.16, 142.22, 146.83, 149.06.

**2-Nitrobiphenyl (2k) (Table 1, entry 11)** Prepared as described for 2b, starting from 1k (5 gm., 0.031 mol) gave, after purification with silica gel column chromatography (Hexane:EtOAc::98:2) 2k as yellow viscous liquid (3.82 gm., 62%); NMR data are same as 2e (Table 2, entry 4).

**4-Nitrobiphenyl (2l) (Table 1, entry 12)** Prepared as described for 2b, starting from 1l (1 gm., 0.006 mol) gave, after purification with silica gel column chromatography (Hexane:EtOAc::95:5) 2l as light yellow crystalline solid (1.102 gm, 87%); melting point and NMR data are same as 2f (Table 2, entry 5).

**4-Methoxybiphenyl (2m) (Table 1, entry 13)** Prepared as described for 2b, starting from 1m (5 gm., 0.035 mol) gave, after purification with silica gel column chromatography (Hexane:EtOAc::98:2) 2m as white crystalline solid (1.67 gm, 26%); melting point and NMR data are same as 2a.

**3. \(^1\)H and \(^{13}\)C NMR spectra of products**

4-Methylbiphenyl (2a) (\(^1\)H NMR in CDCl\(_3\))
4-Methylbiphenyl (2a) ($^{13}$C NMR in CDCl$_3$)
4-Methoxybiphenyl (2b) (\(^1\)H NMR in CDCl\(_3\))
4-Methoxybiphenyl (2b) ($^{13}$C NMR in CDCl$_3$)
3-Methoxybiphenyl (2c) (1H NMR in CDCl₃)
3-Methoxybiphenyl (2c) ($^{13}$C NMR in CDCl$_3$)
1-Phenylnaphthalene (2d) ($^1$H NMR in CDCl$_3$)
1-Phenylnapthalene (2d) (\(^{13}\text{C NMR in CDCl}_3\))
2-Nitrobiphenyl (2e) (¹H NMR in CDCl₃)
2-Nitrobiphenyl (2e) ($^{13}$C NMR in CDCl$_3$)
4-Nitrobiphenyl (2f) ($^1$H NMR in CDCl$_3$)
4-Nitrobiphenyl (2f) \(^{13}\text{C} \text{NMR in CDCl}_3\)
1,4-Diphenylbenzene (2h) \((^1\text{H NMR in CDCl}_3)\)
1,4-Diphenylbenzene (2h) ($^{13}$C NMR in CDCl$_3$)
4-Bromobiphenyl (2i) ($^1$H NMR in CDCl$_3$)
4-Bromobiphenyl (2i) ($^{13}$C NMR in CDCl$_3$)
2,4-Dinitrobiphenyl (2k) (1H NMR in CDCl₃)
2,4-Dinitrobiphenyl (2k) ($^{13}$C NMR in CDCl$_3$)
(2) Powder XRD analysis data of SS-Pd: The powdered SS-Pd was prepared by grinding SS-Pd. The XRD pattern of both fresh as well as used (after 5th cycle) shows a hump at 2θ = 40 which indicates the presence of Pd(0).  

Fig 2. (A) Powder XRD pattern of freshly prepared powdered SS-Pd; (B) Powder XRD pattern of SS-Pd after 5th cycle.

Reference