Reusable polystyrene-supported Pd catalyst for Mizoroki-Heck reactions with extremely low amounts of supported Pd

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ELECTRONIC SUPPLEMENTARY INFORMATION

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General Remarks. The reagents were obtained from commercial sources and were used without further purifications. Catalysts \(1a\) and \(1b\) were prepared according to previous reports from our group.\(^1\) The syntheses of compounds \(2a-i\) were performed in dry glassware under an atmosphere of argon. The reaction mixtures were filtered on a polytetrafluoroethylene Whatman membrane (0.2 µm). \(^1\)H NMR spectra were recorded using a 400 MHz instrument in CDCl\(_3\). Chemical shifts are reported in parts per million (δ) downfield from TMS. Spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet) and m (multiplet). The \(^1\)H NMR spectra of biaryls \(2a-i\) were in accordance with literature reports (see below).

**(E)-Methyl-3-Phenylpropenoate (2a):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 1.60 g (99% yield) of a white solid; mp 37-38 °C (lit. mp 38 °C).\(^2\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 3.82 (s, 3H), 6.45 (d, \(3J = 16.0\) Hz, 1H), 7.39 (m, 3H), 7.54 (m, 2H), 7.72 (d, \(3J = 16.0\) Hz).

**(E)-Methyl-3-(4-Methylphenyl)propenoate (2b):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 1.60 g (91% yield) of a white solid; mp 58-59 °C (lit. mp 57-58 °C).\(^4\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 2.37 (s, 3H), 3.80 (s, 3H), 6.40 (d, \(3J = 16.0\) Hz, 1H), 7.18 (d, \(3J = 8.0\) Hz, 2H), 7.41 (d, \(3J = 8.0\) Hz, 2H), 7.68 (d, \(3J = 16.0\) Hz, 1H).

**(E)-Methyl-3-(3-Methylphenyl)propenoate (2c):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 1.74 g (99% yield) of a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 2.36 (s, 3H), 3.81 (s, 3H), 6.43 (d, \(3J = 16.0\) Hz, 1H), 7.27 (m, 4H), 7.38 (d, \(3J = 16.0\) Hz, 1H).

**(E)-Methyl-3-(2-Methylphenyl)propenoate (2d):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 1.74 g (99% yield) of a yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 2.28 (s, 3H), 3.66 (s, 3H), 6.22 (d, \(3J = 15.8\) Hz, 1H), 7.08 (m, 3H), 7.38 (d, \(3J = 7.8\) Hz, 1H), 7.84 (d, \(3J = 15.8\) Hz, 1H).

**(E)-Methyl-3-(4-Methoxyphenyl)propenoate (2e):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 1.85 g (96% yield) of a yellow solid; mp 87-88 °C (lit. mp 89-90 °C).\(^6\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 3.68 (s, 3H), 3.71 (s, 3H), 6.20 (d, \(3J = 16.1\) Hz, 1H), 6.78 (d, \(3J = 8.8\) Hz, 2H), 7.35 (d, \(3J = 8.8\) Hz, 2H), 7.54 (d, \(3J = 16.1\) Hz, 1H).

**(E)-Methyl-3-(2-Bromophenyl)propenoate (2f):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 2.38 g (99% yield) of a yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 3.71 (s, 3H), 6.26 (d, \(3J = 16.1\) Hz, 1H), 7.13 (m, 2H), 7.46 (m, 2H), 7.93 (d, \(3J = 16.1\) Hz, 1H).

**(E)-Methyl-3-(4-Acetylphenyl)propenoate (2g):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 2.0 g (98% yield) of a yellow solid; mp 112-114 °C (lit. mp 113-115 °C).\(^7\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 2.46 (s, 3H), 3.67 (s, 3H), 6.35 (d, \(3J = 16.1\) Hz, 1H), 7.43 (d, \(3J = 8.3\) Hz, 2H), 7.52 (d, \(3J = 16.1\) Hz, 1H), 7.80 (d, \(3J = 8.3\) Hz, 2H).

**(E)-Methyl-3-(3-Trifluoromethylphenyl)propenoate (2h):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 2.28 g (99% yield) of a yellow solid; mp 112-114 °C (lit. mp 113-115 °C).\(^4\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 3.82 (s, 3H), 6.50 (d, \(3J = 16.1\) Hz, 1H), 7.51 (m, 1H), 7.62 (m, 1H), 7.70 (m, 2H), 7.73 (d, \(3J = 16.1\) Hz, 1H).
(E)-Methyl-3-[2-Ethoxycarbonyl]phenyl]propenoate (2i): Elution with AcOEt / Cyclohexane 1 : 9 afforded 2.32 g (99% yield) of a yellow solid; mp 112-114 °C (lit. mp 113-115 °C). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 1.36 (t, ³J = 7.3 Hz, 3H), 3.76 (s, 3H), 4.34 (q, ³J = 7.3 Hz, 2H), 6.25 (d, ³J = 15.9 Hz, 1H), 7.39 (m, 3H), 7.93 (m, 1H), 8.42 (d, ³J = 15.9 Hz, 1H).
**Chemical Structure:**

![Chemical structure of compound 2a](image)

**NMR Spectroscopy:**

- **1H NMR, 400 MHz, CDCl₃**

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**Notes:**

- Supplementary Material (ESI) for Organic & Biomolecular Chemistry
- This journal is (c) The Royal Society of Chemistry 2010
$^1$H NMR, 400 MHz, CDCl$_3$
2c

$^1$H NMR, 400 MHz, CDCl$_3$
1H NMR, 400 MHz, CDCl₃

In integral

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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$^1$H NMR, 400 MHz, CDCl$_3$

**Supplementary Material (ESI) for Organic & Biomolecular Chemistry**

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Br  \( \equiv \text{CO}_2\text{Me} \)

\( 2f \)

\( ^1\text{H NMR, 400 MHz, CDCl}_3 \)


**1H NMR, 400 MHz, CDCl₃**

![NMR Spectrum](image)

**Integrals**

|------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|

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$^1$H NMR, 400 MHz, CDCl$_3$

F$_3$C

2h

$^1$H NMR, 400 MHz, CDCl$_3$
2i

$^1$H NMR, 400 MHz, CDCl$_3$
References:


