Reusable magnetic Pd$_x$-Co$_y$ nanoalloys confined in mesoporous carbons for green Suzuki-Miyaura reactions

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ELECTRONIC SUPPORTING INFORMATION

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General procedure for the determination of the Pd content of C1-C4

Concentrated H$_2$SO$_4$ (3 mL) was added to a sample of C1-C4 (ca. 1 mg, precisely weighted). The mixture was brought to reflux in a fume hood. After cooling to 100 °C, fuming HNO$_3$ (2 mL) was then added and the heating resumed until disappearance of nitric fumes, complete evaporation of HNO$_3$ and beginning of the reflux of the remaining H$_2$SO$_4$. After cooling to 100 °C, fuming HNO$_3$ (2 mL) was then added, the mixture was heated until evaporation of HNO$_3$ and of most of the H$_2$SO$_4$. Concentrated HNO$_3$ (3 mL) and concentrated HCl (3 mL) were successively added and the mixture heated until evaporation of the acids. The residue was then dissolved in H$_2$O (25 mL) and the amount of Pd present in this mixture was determined by complexation following a procedure described in the literature. Two independent experiments were performed and the average value retained.

Determination of the Pd leached in the reaction medium during the Suzuki reaction

After Suzuki reaction, the catalyst C3 was magnetically recovered and washed with AcOEt (3x15 mL). The combined organic phase was evaporated under high vacuum. Concentrated H$_2$SO$_4$ (5 mL) was added to the residue and brought to reflux in a fume hood. After cooling to 100 °C fuming HNO$_3$ (5 mL) was then slowly added and the heating resumed until disappearance of the nitric fumes, complete evaporation of HNO$_3$ and beginning of the reflux of the remaining H$_2$SO$_4$. After cooling to 100 °C, fuming HNO$_3$ (5 mL) was then slowly added, the mixture was heated until evaporation of HNO$_3$ and this process was repeated twice, the heating of the sample in acids during, as a whole, 15-20 min. Most of the H$_2$SO$_4$ was then boiled off, concentrated HNO$_3$ (3 mL) and concentrated HCl (3 mL) were successively added and the mixture heated until evaporation of the acids. The residue was then dissolved in H$_2$O (25 mL) and the amount of Pd present in this mixture was determined by complexation following a procedure described in the literature. Two independent experiments were performed and the average value retained.

$^1$H and $^{13}$C-NMR Spectra of Biaryls 1a-i

1-(4-Biphenylyl)ethanone (1a): Elution with AcOEt / cyclohexane 5:95 as eluant afforded 1a as a white solid (95 mg, 97 % yield). $^1$H-NMR (300 MHz, CDCl$_3$) δ (ppm): 2.65 (s, 3H), 7.45 (m, 3H), 7.64 (d, $^3$J(H,H) = 7.0 Hz, 2H), 7.70 (d, $^3$J(H,H) = 6.7 Hz, 2H), 8.05 (d, $^3$J(H,H) = 6.7 Hz, 2H).[1] $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm): 26.6, 127.2, 128.0, 128.8, 135.8, 139.8, 145.7, 197.7.

1-(4-(4'-Methyl)biphenylyl)ethanone (1b): Elution with AcOEt / cyclohexane 5:95 afforded 1b as a white solid (104 mg, 99 % yield). $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 2.30 (s, 3H), 2.52 (s, 3H), 7.17 (d, $^3$J(H,H) = 8.1 Hz, 2H), 7.42 (d, $^3$J(H,H) = 8.1 Hz, 2H), 7.56 (d, $^3$J(H,H) = 8.3 Hz, 2H), 7.90 (d, $^3$J(H,H) = 8.3 Hz, 2H).[2] $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm): 21.0, 26.5, 126.8, 126.9, 128.8, 129.6, 136.8, 137.6, 145.6, 197.6.

1-(4-(3'-Methyl)biphenylyl)ethanone (1c): Elution with AcOEt / cyclohexane 5:95 afforded 1c as a white solid (103 mg, 98 % yield). $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 2.43 (s, 3H), 2.61 (s, 3H), 7.21
(m, 1H), 7.42 (d, m, 3H), 7.65 (d, \(3J(H,H) = 9\) Hz, 2H), 8.01 (d, \(3J(H,H) = 9\) Hz, 2H).\(^3\) \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 21.3, 26.4, 124.2, 127.0, 127.1, 128.7, 128.8, 135.6, 138.4, 139.8, 145.6, 197.4.

1-(4-(4'-Methoxy)biphenylyl)ethanone (1d): Elution with AcOEt / cyclohexane 5:95 afforded 1d as a white solid (97 mg, 86 % yield). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 2.62 (s, 3H), 3.86 (s, 3H), 7.00 (d, \(3J(H,H) = 8.8\) Hz, 2H), 7.58 (d, \(3J(H,H) = 8.8\) Hz, 2H), 7.64 (d, \(3J(H,H) = 8.3\) Hz, 2H), 8.00 (d, \(3J(H,H) = 8.3\) Hz, 2H).\(^4\) \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 26.5, 55.3, 114.3, 126.5, 128.3, 128.9, 132.1, 135.2, 145.2, 159.8, 197.6.

1-(4-(4'-chlorobiphenylyl)ethanone (1e): Elution with AcOEt / cyclohexane 5:95 afforded 1e as a white solid (114 mg, 99% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.43 (d, \(3J(H,H) = 8.7\) Hz, 2H), 7.55 (d, \(3J(H,H) = 8.7\) Hz, 2H), 7.64 (d, \(3J(H,H) = 8.1\) Hz, 2H), 8.03 (d, \(3J(H,H) = 8.1\) Hz, 2H).\(^5\) \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 26.6, 126.9, 127.0, 128.5, 129.0, 134.4, 136.1, 138.3, 144.4, 197.5.

1-(4-Biphenylyl)propanone (1f): Elution with AcOEt / cyclohexane 5:95 as eluant afforded 1f as a white solid (103 mg, 98 % yield). \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 1.26 (t, \(3J(H,H) = 9\) Hz, 3H), 3.04 (q, \(3J(H,H) = 9\) Hz, 2H), 7.45 (m, 3H), 7.67 (m, 4H), 8.04 (d, \(3J(H,H) = 9\) Hz, 2H).\(^6\) \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 8.3, 31.8, 127.2, 128.5, 128.9, 135.6, 139.9, 145.5, 200.4.

(4-Biphenylyl)phenylmethanone (1g): Elution with AcOEt / cyclohexane 5:95 as eluant afforded 1g as a white solid (86 mg, 67 % yield). \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.45 (m, 5H), 7.66 (m, 5H), 7.90 (m, 4H).\(^7\) \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 126.9, 127.0, 128.3, 128.9, 130.0, 130.7, 132.3, 136.2, 137.8, 140.0, 145.2, 196.3.

4-Biphenylcarbaldehyde (1h): Elution with AcOEt / cyclohexane 5:95 as eluant afforded 1h as a white solid (56 mg, 62 % yield). \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.45 (m, 4H), 7.63 (d, \(3J(H,H) = 8.1\) Hz, 2H), 7.75 (d, \(3J(H,H) = 8.1\) Hz, 2H), 7.95 (d, \(3J(H,H) = 8.1\) Hz, 2H), 10.06 (s, 1H).\(^7\) \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 127.1, 127.2, 127.3, 129.0, 130.7, 140.0, 146.5, 171.4, 191.9.

4-Biphenylcarbonitrile (1i): Elution with AcOEt / cyclohexane 5:95 as eluant afforded 1i as a white solid (89 mg, 99 % yield). \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.46 (m, 3H), 7.59 (d, \(3J(H,H) = 6.8\) Hz, 2H), 7.71 (m, 4H).\(^7\) \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 110.9, 118.9, 127.2, 127.7, 128.6, 129.0, 132.5, 139.1, 145.6.
Compound 1a

$^1$H-NMR, 300 MHz, CDCl$_3$
Compound 1a
$^{13}$C-NMR, 75 MHz, CDCl$_3$
Compound 1c

$^1$H-NMR, 300 MHz, CDCl$_3$
Compound 1d

$^1$H-NMR, 300 MHz, CDCl$_3$
Compound 1e

\[ ^1H\text{-NMR, 300 MHz, CDCl}_3 \]
Compound 1e

$^{13}$C-NMR, 75 MHz, CDCl$_3$
Compound 1f

$^1$H NMR, 300 MHz, CDCl$_3$
Compound 1f

$^{13}$C NMR, 75 MHz, CDCl$_3$
Compound 1g
$^1$H NMR, 300 MHz, CDCl$_3$
Compound 1g

$^{13}$C NMR, 75 MHz, CDCl$_3$
Chemical Shift (ppm)

Normalized Intensity

Compound 1h

$^1$H-NMR, 300 MHz, CDCl$_3$
Compound 1h

$^{13}$C NMR, 75 MHz, CDCl$_3$
Compound 1i

$^1$H-NMR, 300 MHz, CDCl$_3$
Compound 1i

$^{13}$C-NMR, 75 MHz, CDCl$_3$
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