Facile One-Pot Nanocatalysts Encapsulation of Palladium-NHC Complexes for Aqueous Suzuki–Miyaura Couplings

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Table S1 X-ray crystallographic data for palladium-NHC complexes 1b, 2b and 3b

Fig. S1 Water solution of palladium-NHC loaded DSPE-PEG2000 nanoparticles

Fig. S2 Uv spectral of palladium-NHC (1b, 2b, and 3b) and the corresponding nanocatalysts (NCs) 1b-NC, 2b-NC, and 3b-NC nanoparticles, and 3b-NC after recycling from the Suzuki–Miyaura reaction mixture.

Fig. S3 Aqueous Suzuki-Miyaura coupling reaction of 4-bromotoluene with phenylboronic acid catalyzed by 3b (a), 3b-NC without TBAB (b), 3b-NC with TBAB (c)

Synthesis and characterization of 1a-3a and 1b-3b

1H and 13C NMR data of 4a-4q

1H and 13C NMR Spectrum of 1a-4q

References of the reported triphenylamine derivatives
Table S1. X-ray crystallographic data for palladium-NHC complexes 1b, 2b and 3b.

<table>
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<th>1b • CH₃CN</th>
<th>2b</th>
<th>3b</th>
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<tr>
<td>Formula</td>
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<td>( c ), Å</td>
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<td>( R ) ((I &gt; 2\sigma(I)))</td>
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Fig. S1. Water solution of 1b-NC, 2b-NC, and 3b-NC.
**Fig. S2.** Uv spectral of 1b and 1b-NC (a), 2b and 2b-NC (b), 3b and 3b-NC (c), and 3b-NC initial and after recycling from the Suzuki-Miyaura reaction mixture (d).

**Fig. S3.** Aqueous Suzuki-Miyaura coupling reaction of 4-bromotoluene and phenylboronic acid catalyzed by 0.1 mol% 3b (a), 3b-NC without TBAB (b), and 3b-NC with TBAB (c) at 60 °C for 3 h in water.
Synthesis and characterization of 1a -1b and 2a-2b

A solution of N-(2-pyridineyl)imidazole (1.45 g, 10 mmol) and benzyl chloride (1.51 g, 12 mmol) in acetonitrile (20 mL) was refluxed overnight. The solvent was removed and the residue was redissolved in water (25mL), and then a saturated NH₄PF₆ aqueous solution (20 mL) was added dropwise. The resulting precipitate was collected, washed with water and dried. Yield: 3.43 g, 90%. Anal. Calcd for C₁₅H₁₄F₆N₃P: C, 47.25; H, 3.70; N, 11.02. Found: C, 47.15; H, 3.81; N, 11.26. ¹H NMR (400 MHz, DMSO-d₆): δ 10.27 (s, imidazole acidic CH, 1H), 8.66 (dd, J = 4.8 and 2.0 Hz, pyridine CH, 1H), 8.55 (t, J = 6.0 Hz, imidazole CH, 1H), 8.22 (dt, J = 8.0 and 2.0 Hz, pyridine CH, 1H), 8.05-8.02 (m, pyridine and imidazole CH, 2H), 7.65 (dd, J = 8.0 and 4.8 Hz, pyridine CH, 1H), 7.54-7.52 (m, phenyl CH, 2H), 7.48-7.41 (m, phenyl CH, 3H), 5.55 (s, CH₂, 2H). ¹³C NMR (100 MHz, DMSO-d₆): δ 149.1, 147.2, 146.3, 145.2, 144.1, 134.2, 132.0, 131.8, 130.7, 129.4, 128.7, 128.3, 127.7, 125.6, 117.7, 116.6, 114.7, 51.0.

According to the same procedure as for 1a, 2a was obtained by the reaction of 1-(2-pyridyl)benzimidazole (1.51 g, 10 mmol) with benzyl chloride (1.51 g, 12 mmol) and a subsequently anion exchang reaction with NH₄PF₆. Yield: 3.7 g, 85%. Anal. Calcd for C₁₉H₁₆F₆N₃P: C, 52.91; H, 3.74; N, 9.74. Found: C, 52.43; H, 3.91; N, 9.62. ¹H NMR (400 MHz, DMSO-d₆): δ 10.71 (s, benzimidazole acidic CH, 1H), 8.80 (d, J = 4.0 Hz, pyridine CH, 1H), 8.49 (d, J = 7.6 Hz, benzimidazole CH, 1H), 8.32 (t, J = 6.4 Hz, pyridine CH, 1H), 8.11 (d, J = 8.0 Hz, pyridine CH, 1H), 8.01 (d, J = 7.6 Hz, benzimidazole CH, 1H), 7.78-7.83 (m, pyridine and imidazole CH, 3H), 7.66-7.64 (m, phenyl CH, 2H), 7.46-7.40 (m, phenyl CH, 3H), 5.90 (s, CH₂, 2H). ¹³C NMR (100 MHz, DMSO-d₆): δ 149.9, 147.8, 143.2, 141.0, 134.0, 131.7, 130.3, 129.4, 129.3, 128.9, 128.5, 127.7, 125.6, 117.7, 116.6, 114.7, 51.0.

3a was prepared similarly as for 1a, N-mesitylimidazole and 2-chloropyrimidine was used as
A mixture of HL1(PF₆) (381 mg, 1.0 mmol), Ag₂O (116 mg, 0.5 mmol) in 10 mL of CH₃CN was stirred at 50 °C for 4 h. After the mixture was cooled to room temperature, [Pd(CH₃CN)₂]Cl₂ (260 mg, 1.0 mmol) was added to the solution, and the solution was stirred at room temperature for another 2 h. Then, the mixture was filtered through Celite, and all volatiles were evaporated under reduced pressure. The yellow residue was dissolved in CH₃CN, and recrystallization by slow addition of Et₂O into its CH₃CN solution gave 1b as a yellow solid, 439 mg, 78%. Anal. Calcd for C₁₇H₁₆ClF₆N₄Pd: C, 36.26; H, 2.86; N, 9.95. Found: C, 36.88; H, 2.93; N, 9.88. \(^1\)H NMR (CD₃CN): 8.57 (s, pyridine CH, 1H), 8.34 (t, \(J = 7.6\) Hz, pyridine CH, 1H), 7.90 (s, imidazole CH, 1H), 7.84 (d, \(J = 7.6\) Hz, pyridine CH, 1H), 7.58 (t, \(J = 6.4\) Hz, pyridine CH, 1H), 7.42 (m, phenyl, 5H), 7.27 (s, imidazole CH, 1H), 6.34 (s, CH₂, 2H), 2.07 (s, CH₃CN, 2H). \(^{13}\)C NMR (CD₃CN-d₆): 151.3 (Pd–C), 146.7, 144.3, 136.5, 129.3, 129.0, 128.7, 128.2, 125.3, 123.9, 119.1, 113.3, 52.9, 1.7.

\[\text{[Pd(L1)(CH₃CN)Cl](PF₆)}\times 1b\]

\[\text{[Pd(L2)(CH₃CN)Cl](PF₆)}\times 2b\]

\(^2\)b was prepared by a procedure analogous to what was used for 1b and was isolated as a yellow solid. Yield: 472 mg, 77%. Anal. Calcd for C₂₁H₁₈ClF₆N₄Pd: C, 41.13; H, 2.96; N, 9.14. Found: C, 41.28; H, 2.65; N, 8.93. \(^1\)H NMR (CD₃CN-d₆): 8.59-8.55 (m, pyridine CH, 2H), 8.47-8.43 (m, pyridine and benzimidazole CH, 2H), 7.73-7.69 (m, pyridine and benzimidazole CH, 2H), 7.61 (t, \(J = 7.6\) Hz, pyridine CH, 1H), 7.56-7.48 (m, pyridine and phenyl CH, 3H), 7.38-7.29 (m, phenyl CH, 3H), 6.34 (s, CH₂, 2H), 2.07 (s, CH₃CN, 3H). \(^{13}\)C NMR (CD₃CN-d₆): 151.7 (Pd–C), 146.7, 144.3, 135.1, 133.8, 129.7, 129.0, 128.3, 127.6, 126.9, 126.4, 123.3, 118.5, 114.0, 113.0, 113.6, 50.7, 1.51.
3b was prepared by a procedure analogous to what was used for 1b and 2b and was isolated as a yellow solid. Yield: 387 mg, 65%. Anal. Calcd for C_{18}H_{19}ClF_{6}N_{5}PPd: C, 36.51; H, 3.23; N, 11.83. Found: C, 36.41; H, 3.10; N, 11.90. ^1H NMR (dms-o-d_6): 9.18 (s, pyrimidine CH, 1H), 8.73 (s, pyrimidine CH, 1H), 8.46 (s, imidazole CH, 1H), 7.79 (t, J = 5.2 Hz, pyrimidine CH, 1H), 7.69 (s, imidazole CH, 1H), 7.01 (s, Mes CH, 2H), 2.31 (s, Mes CH_3, 3H), 2.06 (s, CH_3CN, 3H), 2.05 (s, Mes CH_3, 6H), ^13C NMR (dms-o-d_6): 162.3, 156.2, 156.2 (Pd–C), 149.1, 139.3, 134.8, 134.5, 128.9, 126.5, 120.9, 119.1, 118.5, 21.1, 17.8, 1.54.

^1H and ^13C NMR data of 4a-4b

\[ \text{4a} \]

^1H NMR (400 MHz, CDCl_3): δ 7.52 (d, J = 8.8 Hz, phenyl CH, 6H), 7.47 (d, J = 8.8 Hz, phenyl CH, 6H), 7.20 (d, J = 8.8 Hz, phenyl CH, 6H), 6.97 (d, J = 8.8 Hz, phenyl CH, 6H), 3.85 (s, CH_3, 9H). ^13C NMR (100 MHz, CDCl_3): δ 158.9, 146.4, 135.2, 133.3, 127.7, 127.4, 124.4, 114.2, 55.4.

\[ \text{4b} \]

^1H NMR (400 MHz, CDCl_3): δ 7.52 (d, J = 8.8 Hz, phenyl CH, 6H), 7.34 (t, J = 8.0 Hz, phenyl CH, 3H), 7.22 (d, J = 8.8 Hz, phenyl CH, 6H), 7.18 (d, J = 8.0 Hz, phenyl CH, 3H), 7.12 (s, phenyl CH, 3H), 6.87 (d, J = 8.0 Hz, phenyl CH, 3H), 3.86 (s, CH_3, 9H). ^13C NMR (100 MHz, CDCl_3): δ 160.0, 146.9, 142.1, 135.5, 129.8, 128.0, 124.4, 119.3, 112.5, 112.3, 55.3.

\[ \text{4c} \]

^1H NMR (400 MHz, CDCl_3): δ 7.47-7.45 (m, phenyl CH, 6H), 7.36 (m, phenyl CH, 3H), 7.27-7.28 (m, phenyl CH, 3H), 7.21-7.23 (m, phenyl CH, 6H), 6.96-7.04 (m, phenyl CH, 6H), 3.83 (s, CH_3, 9H). ^13C NMR (100 MHz, CDCl_3): δ 156.5, 146.5, 132.7, 130.7, 130.3, 128.3, 123.7, 120.9, 111.2, 56.5.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.52 (t, $J = 8.8$ Hz, phenyl CH, 12H), 7.45 (d, $J = 8.8$ Hz, phenyl CH, 6H), 7.22 (d, $J = 8.8$ Hz, phenyl CH, 6H), 1.36 (s, C(CH$_3$)$_3$, 27H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.8, 146.7, 137.8, 135.4, 127.7, 126.4, 125.7, 124.4, 34.5, 31.4.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.49 (d, $J = 8.4$ Hz, phenyl CH, 12H), 7.22 (d, $J = 8.4$ Hz, phenyl CH, 6H), 7.20 (d, $J = 8.4$ Hz, phenyl CH, 6H), 2.63 (t, $J = 7.6$ Hz, CH$_2$, 6H), 1.67-1.63 (m, CH$_2$, 6H), 1.36-1.33 (m, CH$_2$CH$_2$, 12H), 0.90 (t, $J = 6.4$ Hz, CH$_3$, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.7, 141.7, 138.0, 135.6, 128.8, 127.7, 126.6, 124.4, 35.6, 31.6, 31.2, 22.6, 14.1.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.03 (d, $J = 8.4$ Hz, phenyl CH, 6H), 7.69 (d, $J = 8.4$ Hz, phenyl CH, 6H), 7.59 (d, $J = 8.4$ Hz, phenyl CH, 6H), 7.27 (d, $J = 8.4$ Hz, phenyl CH, 6H), 2.64 (s, CH$_3$, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.7, 147.3, 145.0, 135.6, 134.6, 129.0, 128.2, 126.7, 124.6, 26.7.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.05 (s, C(O)H, 3H), 7.95 (d, $J = 8.0$ Hz, phenyl CH, 6H), 7.76 (d, $J = 8.0$ Hz, phenyl CH, 6H), 7.61 (d, $J = 8.4$ Hz, phenyl CH, 6H), 7.28 (d, $J = 8.8$ Hz, phenyl CH, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.8, 147.5, 146.3, 135.0, 134.5, 130.4, 1287.4, 127.1, 124.7.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.10 (d, $J = 8.4$ Hz, phenyl CH, 6H), 7.66 (d, $J = 8.4$ Hz, phenyl CH, 6H), 7.57 (d, $J = 8.4$ Hz, phenyl CH, 6H), 7.25 (d, $J = 8.4$ Hz, phenyl CH, 6H), 3.94 (s, CH$_3$, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.0, 147.3, 144.8, 134.6, 130.2, 128.6, 128.2, 126.5, 124.6, 52.1.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.70 (q, $J = 8.8$ Hz, phenyl CH, 12H), 7.55 (d, $J = 8.8$ Hz, phenyl CH, 6H), 7.26 (d, $J = 8.8$ Hz, phenyl CH, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.5, 144.7, 134.0, 132.7, 128.3, 127.2, 124.7, 119.0, 110.6.
$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.87 (s, phenyl CH, 3H), 7.81 (d, $J$ = 8.0 Hz, phenyl CH, 3H), 7.61 (d, $J$ = 7.6 Hz, phenyl CH, 3H), 7.55 (t, $J$ = 7.6 Hz, phenyl CH, 3H), 7.51 (d, $J$ = 8.8 Hz, phenyl CH, 6H), 7.26 (d, $J$ = 8.8 Hz, phenyl CH, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.4, 141.7, 133.7, 131.0, 130.4, 130.3, 1297, 128.1, 124.7, 118.9, 113.1.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.46 (s, phenyl CH, 3H), 8.19 (d, $J$ = 8.0 Hz, phenyl CH, 3H), 7.92 (d, $J$ = 8.0 Hz, phenyl CH, 3H), 7.63-7.58 (m, phenyl CH, 9H), 7.29 (d, $J$ = 8.8 Hz, phenyl CH, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.8, 147.5, 142.1, 133.6, 132.5, 129.8, 128.3, 124.8, 121.8, 121.5.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.51 (d, $J$ = 8.8 Hz, phenyl CH, 6H), 7.42-7.35 (m, phenyl CH, 6H), 7.30-7.22 (m, phenyl CH, 9H), 7.04-6.99 (m, phenyl CH, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 163.3(d, $J$ = 245.5 Hz), 147.1, 142.8(d, $J$ = 6.8 Hz), 134.6, 130.2(d, $J$ = 7.9 Hz), 128.0, 124.5, 122.3(d, $J$ = 3.4 Hz), 113.7(d, $J$ = 20.2 Hz), 113.5(d, $J$ = 22.1 Hz).

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.51 (d, $J$ = 8.4 Hz, phenyl CH, 6H), 7.48 (d, $J$ = 8.4 Hz, phenyl CH, 6H), 7.39 (d, $J$ = 8.4 Hz, phenyl CH, 6H), 7.22 (d, $J$ = 8.4 Hz, phenyl CH, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.7, 139.0, 134.6, 133.0, 128.9, 127.9, 127.8, 124.5.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.57 (d, $J$ = 8.4 Hz, phenyl CH, 6H), 7.54 (d, $J$ = 8.4 Hz, phenyl CH, 6H), 7.48 (d, $J$ = 8.4 Hz, phenyl CH, 6H), 7.24 (d, $J$ = 8.4 Hz, phenyl CH, 6H), 6.78-6.71 (m, CH, 3H) 5.80 (d, $J$ = 17.6 Hz, CH$_2$, 3H), 5.27 (d, $J$ = 10.8 Hz, CH$_2$, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.8, 139.9, 136.5, 136.3, 135.2, 127.7, 126.7, 126.7, 124.5, 113.7.
\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.81 (d, \(J = 8.0\) Hz, phenanthrenyl CH, 3H), 8.13 (d, \(J = 8.0\) Hz, phenanthrenyl CH, 3H), 7.93 (d, \(J = 8.0\) Hz, phenanthrenyl CH, 3H), 7.79 (d, \(J = 8.0\) Hz, phenanthrenyl CH, 3H), 7.71-7.60 (m, phenanthrenyl CH, 12H), 7.57 (d, \(J = 8.4\) Hz, phenyl CH, 6H), 7.48 (d, \(J = 8.4\) Hz, phenyl CH, 6H). \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 147.0, 138.4, 135.4, 131.7, 131.2, 131.1, 130.8, 129.9, 128.6, 127.5, 127.0, 126.9, 126.5, 126.5, 126.5, 124.1, 123.0, 122.6.

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\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.50 (t, \(J = 8.4\) Hz, phenyl CH, 12H), 7.31 (d, \(J = 8.4\) Hz, phenyl CH, 6H), 7.21 (d, \(J = 8.4\) Hz, phenyl CH, 6H), 2.52 (s, CH\(_3\), 9H). \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 146.7, 137.4, 137.1, 135.0, 127.6, 127.1, 127.0, 124.5, 16.0.

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\begin{align*}
\text{S} & \quad \text{N} \\
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\text{O} \\
\text{O}
\end{array} & \quad \text{N}
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.01 (d, \(J = 8.4\) Hz, phenyl CH, 6H), 7.77 (d, \(J = 8.8\) Hz, phenyl CH, 6H), 7.58 (d, \(J = 8.8\) Hz, phenyl CH, 6H), 7.29 (d, \(J = 8.4\) Hz, phenyl CH, 6H), 3.10 (s, CH\(_3\), 9H). \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 147.6, 145.8, 138.8, 134.0, 128.5, 128.0, 127.4, 124.7, 44.6.

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\begin{align*}
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\begin{array}{c}
\text{O} \\
\text{O}
\end{array} & \quad \text{N}
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.53 (d, \(J = 8.4\) Hz, phenyl CH, 6H), 7.26-7.25 (m, thiophenyl CH, 6H), 7.15 (d, \(J = 8.0\) Hz, phenyl CH, 6H), 7.09-7.07 (m, thiophenyl CH, 3H). \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 146.5, 144.1, 129.3, 128.1, 126.9, 124.4, 124.3, 122.5.
$^1$H and $^{13}$C NMR Spectrum of 1a-4q

$^1$H NMR of [HL1](PF$_6$), 1a

$^{13}$C NMR of HL1](PF$_6$), 1a
$^1$H NMR of [HL2](PF₆), 2a

$^{13}$C NMR of [HL2](PF₆), 2a
$^1$H NMR of [HL3](PF$_6$), 3a

$^{13}$C NMR of [HL3](PF$_6$), 3a
$^1$H NMR of $[\text{Pd(L1)}(\text{CH}_3\text{CN})\text{Cl}](\text{PF}_6)$, 1b

$^{13}$C NMR of $[\text{Pd(L1)}(\text{CH}_3\text{CN})\text{Cl}](\text{PF}_6)$, 1b
$^1$H NMR of [Pd(L2) (CH$_3$CN)Cl](PF$_6$)$_2$, 2b

$^{13}$C NMR of [Pd(L2) (CH$_3$CN)Cl](PF$_6$)$_2$, 2b
$^1$H NMR of [Pd(L3) (CH$_3$CN)Cl](PF$_6$), 3b

$^{13}$C NMR of [Pd(L3) (CH$_3$CN)Cl](PF$_6$), 3b
$^{1}H$ NMR of 4a

$^{13}C$ NMR of 4a
$^1$H NMR of 4c

$^{13}$C NMR of 4c
$^{1}H$ NMR of 4e

$^{13}C$ NMR of 4e
$^1$H NMR of 4f

$^{13}$C NMR of 4f
$^1$H NMR of 4g

$^{13}$C NMR of 4g
$^1$H NMR of 4h

$^{13}$C NMR of 4h
$^1$H NMR of 4i

$^{13}$C NMR of 4i
$^1$H NMR of 4j

$^{13}$C NMR of 4j
$^1$H NMR of 4k

$^{13}$C NMR of 4k
$^1$H NMR of 4n

$^{13}$C NMR of 4n
$^1$H NMR of 4o

$^{13}$C NMR of 4o
$^1$H NMR of 4p

$^{13}$C NMR of 4p
$^1$H NMR of 4q

$^{13}$C NMR of 4q
$^1$H NMR of 4r

$^{13}$C NMR of 4r
References of the reported triphenylamine derivatives