Supplementary Material

A highly stable and active magnetically separable Pd nanocatalyst in aqueous phase heterogeneously catalyzed couplings

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Catalyst loading:

Table S1. Effect of different amount of catalyst on the reaction of Sonogashira cross-coupling at 80 $^{\rm 0}{\rm C}.$

| Entry ^[a] | Catalyst loading [g] | Time (min) | Isolated yield [%] $^{[b]}$ |
|----------------------|----------------------|------------|-----------------------------|
| 1 | 0.002 | 80 | 60 |
| 2 | 0.003 | 45 | 88 |
| 3 | 0.005 | 33 | 93 |
| 4 | 0.007 | 30 | 92 |
| 5 | 0.010 | 30 | 93 |
| | | | |

[a] Reaction conditions: Bromobenzene (1mmol), Phenylacetylene (1 mmol), Water (5 ml) and NaOH (1.5 mmol)

[b] Yields of purified products.

| Table S2. Effect of different amount of O-arylation of phenols at 80 ⁰ C. | | | | | |
|--|----------------------|----------|-----------------------------|--|--|
| Entry ^[a] | Catalyst loading [g] | Time (h) | Isolated yield [%] $^{[b]}$ | | |
| 1 | 0.002 | 6 | 65 | | |
| 2 | 0.003 | 3 | 80 | | |
| 3 | 0.005 | 2 | 90 | | |
| 4 | 0.007 | 1.9 | 92 | | |
| 5 | 0.010 | 1.8 | 91 | | |
| [a] Reaction conditions: Bromobenzene (1mmol), phenol (1 mmol), Water (5 ml) and NaOH (1.5 mmol) | | | | | |
| [b] Yields of purified products. | | | | | |

2 | P a g e



FTIR spectrum of catalyst:

Fig. 1. a) Fe₃O₄. b) Fe₃O₄@SiO₂. c) Fe₃O₄@SiO₂@PPh₂. d) Fe₃O₄@SiO₂@PPh₂@Pd⁰

Data of compounds:

¹H-NMR (250 MHz, CDCl₃): δ 7.15-7.26 (m, 5 H), 7.42-7.49 (m, 5H); ¹³C-NMR (CDCl₃, 62.9 MHz): δ

118.0, 123.2, 129.9 and 157.4.

¹H-NMR (250 MHz, CDCl₃): δ 6.66-8.14 (m, 12H); ¹³C-NMR (62.9 MHz, CDCl₃): δ 113.5, 118.5, 122.1, 123.1, 123.3, 125.8, 125.9, 126.6, 127.7, 129.8, 134.3, 153.1 and 157.8.

¹H-NMR (250 MHz, CDCl₃): δ 6.84-8.04 (m, 12H); ¹³C-NMR (62.9 MHz, CDCl3): δ 114.1, 119.1, 120.0, 120.8, 123.4, 123.8, 124.7, 126.5, 127.1, 127.7, 128.6, 137.2, 155.1 and 157.4.



¹H-NMR (250 MHz, CDCl₃): δ 6.87-7.00 (m, 4H), 7.11-7.17 (m, 1H), 7.29-7.35 (m, 2H), 8.06 (d, 2 H, J= 7.5 Hz,); ¹³C-NMR (62.9 MHz, CDCl₃): δ 117.0, 120.5, 125.4, 125.9, 130.3, 142.5, 154.6 and 163.3.

Me

¹H-NMR (CDCl₃, 250 MHz): δ 2.3 (s, 3H), 6.7-7.0 (m, 6H), 7.1-7.2 (m, 3H); ¹³C-NMR (CDCl₃, 62.9MHz): δ 20.7, 118.3, 119.1, 123.2, 129.6, 129.7, 130.2, 132.9, 154.7 and 157.8.

¹H NMR (CDCl₃): δ 7.23–7.29 (m, 6H), 7.43–7.47 (m, 4H); ¹³C NMR (CDCl₃): δ 89.3, 123.2, 128.3, 128.4 and 131.



¹H NMR (CDCl3): δ 3.82 (s, 3H) 6.88–6.92 (d, *J*= 8.93, 2H), 7.18–7.45 (m, 3H); ¹³C NMR (CDCl₃): δ 55.3, 113.9, 115.3, 123.5, 126.7, 127.9, 128.2, 128.8, 131.4, 133.0 and 137.



¹H NMR (CDCl₃, 250 MHz): δ 7.29-7.31 (m, 3H), 7.45-7.58 (m, 4H), 8.11 (d, J= 7.01 Hz, 2 H,); ¹³C NMR (CDCl₃, 62.9 MHz): δ 87.5, 94.7, 122.0, 123.6, 124.8, 128.5, 129.2, 130.2, 131.8, 132.2, 138.6 and 146.9.



¹H NMR (CDCl₃, 250 MHz): δ 2.27 (s, 3H), 7.048-7.442 (m, 10H); ¹³C NMR (CDCl₃, 62.9 MHz): δ 21.5, 88.7, 89.5, 123.4, 128.0, 128.3, 128.4, 129.1, 131.51, 131.55, 132.5 and 138.3.

















