

Supporting Information

Magnetically recoverable catalysts based on mono- or bis-(N-heterocyclic carbene) complexes of palladium for the Suzuki–Miyaura reaction in aqueous media: two NHC-Pd linkages are better than one

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General procedures: All reactions were performed under an argon atmosphere using standard Schlenk techniques. When required, solvents were dried using an MBraun-Solvent Purification System and deoxygenated prior to use. Unless otherwise stated, chemicals were obtained from commercial suppliers and used as received. 1-Methyl-3-(3-triethoxysilylpropyl)imidazolium bromide (**1**), and NHC complexes **2**, **3** and **4**, were prepared by modifying the reported syntheses (*vide infra*) for related azolium salts,^{1,2} PEPPSI-type complexes,^{3,4} or bis(NHC) complexes of silver⁵ and palladium,^{6,7} respectively. The handling and storage of **1–4** required the absence of moisture to prevent hydrolysis of the triethoxysilyl groups. The core-shell γ -Fe₂O₃/silica superparamagnetic nanoparticles (MNPs) used as support in this work were Silica-Adembeads (Ademtech, France): diameter = 300 nm; density \approx 2.0 g/cm³; specific surface area = 10 m²/g; iron oxide content > 70%; magnetization at saturation \approx 40 emu/g. The palladium complexes **2** and **4** were grafted onto the MNPs by combining (*vide infra*) a reported protocol in hydroalcoholic medium⁸ and the method involving nonionic surfactants described by some of us.⁹ A Bioshake iQ high-speed thermal mixer was used for operations (grafting or catalytic reactions) involving MNPs, while an Hielscher UPS200S device equipped with a sonotrode probe, or an Elmasonic S40 ultrasonic bath were used for the homogenization of their dispersions. ¹H, ¹³C, and ¹⁵N NMR spectra were recorded at room temperature using a Varian Mercury 300, Unity 300, or Unity 500 Plus spectrometer (Univ. Alcalá). Chemical shifts (δ , parts per million) are quoted relative to SiMe₄ (¹H, ¹³C) and MeNO₂ (¹⁵N), and were measured by internal referencing to the ¹³C and residual ¹H resonances of the deuterated solvents, or by the substitution method in the case of ¹⁵N. Coupling constants (*J*) are given in hertz. When required, two-dimensional NOESY, and HSQC and HMBC experiments, were performed for unequivocal assignment of resonances for the palladium complexes. The following abbreviations are used: Imz refers to imidazolic ring, and pic to γ -picoline (*i.e.*, 4-methylpyridine). IR spectra were recorded on a Perkin–Elmer Spectrum 2000 spectrophotometer, and ATR IR spectra in a Nicolet iS50 ATR spectrophotometer (ISM, Univ. Bordeaux). The Analytical Services of the Universidad de Alcalá performed the C, H, and N analyses using a LECO CHNS-932 microanalyzer, and recorded the mass spectra using an Agilent 6210 LC/MS TOF (Multimode source MM ESI/APCI) spectrometer in electrospray ionization mode. ICP-MS (inductively coupled plasma mass spectroscopy) analyses were performed in a 7700x Agilent equipment by the Center for Applied Chemistry and Biotechnology at the Universidad de Alcalá. The Suzuki reactions were followed using an Agilent GC-MS turbo system (5975-7820A

model) equipped with an autoinjector, and using a HP-5MS capillary column (30 m × 0.25 mm i.d.; 0.25 μm df; 95% dimethylpolysiloxane) under the following conditions: injector and detector temperatures: 250 °C and 230 °C, respectively; oven temperature program: 80 °C for 2.5 min, 15 °C/min ramp, 250 °C for 5 min. The catalytic runs performed in aqueous media were analyzed in a HP-5890 Series II Instrument with FID detector, a DB-WAX capillary column (30 m × 0.25 mm i.d.; 0.25 μm df; PEG), and with the followings settings: injector and detector temperatures: 250 °C and 260 °C, respectively; oven temperature program: 120 °C for 5 min, 60 °C/min ramp, 200 °C for 5 min. Transmission electron microscopy (TEM) analyses were performed at the National Center of Electronic Microscopy (Universidad Complutense-Madrid) using a JEOL JEM 2100 instrument operating at 200 kV, with samples prepared by taking microtome slices of the nanoparticles embedded in a Spurr resin. Alternatively, TEM inspections were performed in a HITACHI H7650 microscope operating at 125 kV (BIC, Univ. Bordeaux), with samples prepared by evaporation of 5-10 μL of a dispersion of the nanoparticles in water or methanol (0.25-0.5 mg/mL) onto copper grids coated with carbon (400 mesh copper grid with a lacey carbon film). EDS (Energy Dispersive X-ray Spectroscopy) was used to check the presence palladium by inspection of the characteristic emissions at 2.83 keV ($L_{\alpha 1}$) and 3.03 keV ($L_{\beta 1}$).

Synthesis of 1-methyl-3-(3-triethoxysilylpropyl)imidazolium bromide (1): (3-Bromopropyl)triethoxysilane (0.290 g, 1.02 mmol) was introduced into a glass tube equipped with a PTFE plug valve, and kept under vacuum for 10 min. Then, 1-methylimidazole (82 mg, 1.0 mmol) and dry MeCN (2 mL) were added, the tube was sealed, and the mixture stirred at 100 °C for 16 h. The volatiles were removed, and the crude washed with hexane (2 × 10 mL) and dried under vacuo to give the imidazolium salt **1** as a yellow oil. Yield: 0.33 g (90%). ^1H NMR (300 MHz, CDCl_3): δ 0.52 (t, $^3J_{\text{H-H}} = 8.5$, 2H, SiCH_2), 1.12 (t, $^3J_{\text{H-H}} = 7.0$, 9H, $\text{CH}_3\text{CH}_2\text{O}$), 1.93 (m, 2H, SiCH_2CH_2), 3.72 (q, $^3J_{\text{H-H}} = 7.0$, 6H, $\text{CH}_3\text{CH}_2\text{O}$), 4.04 (s, 3H, Imz-Me), 4.24 (t, $^3J_{\text{H-H}} = 7.2$, 2H, CH_2Imz), 7.31 and 7.57 (2 × t, $^3J_{\text{H-H}} = 1.6$, 2 × 1H, Imz- H^4 and H^5), 10.2 (broad s, 1H, Imz- H^2). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 7.0 (SiCH_2), 18.2 ($\text{CH}_3\text{CH}_2\text{O}$), 24.3 (SiCH_2CH_2), 36.6 (Imz-Me), 51.6 (CH_2Imz), 58.5 ($\text{CH}_3\text{CH}_2\text{O}$), 121.7 and 123.5 (Imz- $\text{C}^{4,5}$), 137.4 (Imz- C^2). ESI-MS (positive ion, $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_4\text{HCOO}$ 5 mM): m/z 287.1780 [$\text{M} - \text{Br}$] $^+$ (calcd 287.1791). Anal. Calc. for $\text{C}_{13}\text{H}_{27}\text{BrN}_2\text{O}_3\text{Si}$ (367.35): C, 42.50; H, 7.41; N, 7.63%. Found: C, 42.00; H, 6.85; N, 8.04%.

***trans*-Diiodido[1-methyl-3-(3-triethoxysilylpropyl)imidazol-2-ylidene](4-picoline)**

palladium(II) (2): Palladium dichloride (0.280 g, 1.58 mmol), imidazolium salt **1** (0.580 g, 1.58 mmol), and excess of potassium carbonate (1.09 g, 7.89 mmol) and of sodium iodide (1.66 g, 11.1 mmol) were placed into an ampoule equipped with a PTFE plug valve. After drying the mixture in a Büchi® glass oven under vacuum (10 mbar, 95 °C, 24 h), 4-picoline (12 mL, previously treated with molecular sieves 3 Å overnight) was added, the ampoule was sealed under argon and the resulting red suspension stirred at 80 °C for 24 h. The volatiles were then removed under vacuum and the crude extracted with CHCl₃ (3 × 5 mL). Possible impurities derived from unreacted PdCl₂ (e.g., [Pd(pic)₂I₂]) can be precipitated by adding hexane (5 mL) to the extracts. After filtration and elimination of the solvents under reduced pressure complex **2** was isolated as a yellow powder. Yield: 1.12 g (96%). ¹H NMR (300 MHz, CDCl₃): δ 0.73 (t, ³J_{H-H} = 8.0, 2H, SiCH₂), 1.21 (t, ³J_{H-H} = 7.0, 9H, CH₃CH₂O), 2.15 (m, 2H, SiCH₂CH₂), 2.35 (s, 3H, pic-Me), 3.83 (q, ³J_{H-H} = 7.0, 6H, CH₃CH₂O), 3.95 (s, 3H, Imz-Me), 4.38 (t, ³J_{H-H} = 8.0, 2H, CH₂Imz), 6.90 and 6.96 (2 × d, ³J_{H-H} = 2.0, 2 × 1H, Imz-H⁴ and H⁵), 7.09 (d, ³J_{H-H} = 5.9, 2H, *m*-pic), 8.83 (d, ³J_{H-H} = 5.9, 2H, *o*-pic). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 7.7 (SiCH₂), 18.4 (CH₃CH₂O), 21.1 (pic-Me), 23.1 (SiCH₂CH₂), 39.2 (Imz-Me), 53.7 (CH₂Imz), 58.6 (CH₃CH₂O), 121.7 and 123.0 (Imz-C^{4,5}), 125.3 (*m*-pic), 145.6 (Imz-C²), 149.4 (*p*-pic), 153.2 (*o*-pic). ¹⁵N{¹H} NMR (51 MHz, CDCl₃) and {¹H, ¹⁵N} gHMBC: δ = -143 (pic), -189 and -195 (Imz). IR (KBr): ν 3050-3120 (m, C-H), 1618 (m, C=C), 1542 (s, C=N), 1420-1470 (m, arC=C), 1080 (w, Si-O-C), 957 (w, Si-O-C), 806 (m, Si-C), 687 cm⁻¹ (m, Si-O). ESI-MS (positive ion, CH₂Cl₂/MeOH/NH₄HCOO 5 mM): *m/z* 739.9418 [M + H]⁺ (calcd 739.9494). Anal. Calc. for C₁₉H₃₃I₂N₃O₃PdSi (739.80): C, 30.85; H, 4.50; N, 5.68%. Found: C, 30.36; H, 4.40; N, 5.93%.

Bis[1-methyl-3-(3-triethoxysilylpropyl)imidazol-2-ylidene]silver(I)

dibromidoargentate(I) (3): Silver(I) oxide (0.41 g, 1.8 mmol) and imidazolium salt **1** (1.28 g, 3.48 mmol) were placed under vacuum for 10 min, before the addition of dichloromethane (10 mL). The mixture was allowed to stir at room temperature for 16 h in the absence of light, filtered through a plug of kieselguhr, and the resulting yellow solution evaporated to dryness. The residue was washed with hexane (2 × 15 mL) and dried under vacuum to give the titled complex **3** as an oily yellow solid. Yield: 1.48 g (90%). Conformer *anti*-**3**: ¹H NMR (300 MHz, CDCl₃): δ 0.56 (t, ³J_{H-H} = 7.7, 4H, SiCH₂), 1.19 (t, ³J_{H-H} = 6.9, 18H, CH₃CH₂O), 1.88 (m, 4H, SiCH₂CH₂), 3.76 (s, 6H, Imz-Me), 3.78 (q, ³J_{H-H} = 6.9, 12H, CH₃CH₂O), 4.08 (t, ³J_{H-H} = 7.7, 4H, CH₂Imz), 6.91

and 6.94 (d, $^3J_{\text{H-H}} = 1.5$, 2H, Imz-H⁴ and H⁵). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 8.7 (SiCH₂), 18.2 (CH₃CH₂O), 25.6 (SiCH₂CH₂), 38.9 (Imz-Me), 54.1 (CH₂Imz), 58.3 (CH₃CH₂O), 121.2 and 122.1 (Imz-C^{4,5}), 181.7 (Imz-C²). Conformer **syn-3**: ^1H NMR (300 MHz, CDCl_3): δ 0.55 (t, $^3J_{\text{H-H}} = 7.7$, 4H, SiCH₂), 1.18 (t, $^3J_{\text{H-H}} = 6.9$, 18H, CH₃CH₂O), 1.88 (m, 4H, SiCH₂CH₂), 3.78 (q, $^3J_{\text{H-H}} = 6.9$, 12H, CH₃CH₂O), 3.79 (s, 6H, Imz-Me), 4.06 (t, $^3J_{\text{H-H}} = 7.7$, 4H, CH₂Imz), 6.93 and 6.98 (d, $^3J_{\text{H-H}} = 1.5$, 2H, Imz-H⁴ and H⁵). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 7.3 (SiCH₂), 18.2 (CH₃CH₂O), 25.2 (SiCH₂CH₂), 38.7 (Imz-Me), 53.9 (CH₂Imz), 58.5 (CH₃CH₂O), 121.0 and 122.0 (Imz-C^{4,5}), 181.2 (Imz-C²). ESI-MS (positive ion, $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_4\text{HCOO}$ 5 mM): m/z 679.2542 [$\text{M} - \text{AgBr}_2$]⁺ (calcd 679.2476), 287.1814 [$\mathbf{1} - \text{Br}$]⁺ (calcd 287.1791). Anal. Calc. for C₂₆H₅₂Ag₂Br₂N₄O₆Si₂ (948.43): C, 32.93; H, 5.53; N, 5.91%; Found: C, 32.93; H, 5.28; N, 5.93%.

trans-Dibromido{bis[1-methyl-3-(3-triethoxysilylpropyl)imidazol-2-

ylidene]}palladium(II) (4): Silver carbene **3** (0.40 g, 0.42 mmol) and [PdBr₂(cod)] (0.16 g, 0.43 mmol, cod = 1,5-cyclooctadiene) were kept under vacuum for 5 min, dissolved in dichloromethane (10 mL), and stirred at room temperature for 1 h. After filtration of the AgBr by-product, the yellow solution was evaporated to dryness, and the resulting residue washed with hexane (2 × 15 mL) to afford **4** as a yellow powder. Yield: 0.65 g (89%). Conformer **anti-4**: ^1H NMR (300 MHz, CDCl_3): δ 0.72 (m, 4H, SiCH₂), 1.20 (t, $^3J_{\text{H-H}} = 6.9$, 18H, CH₃CH₂O), 2.20 (m, 4H, SiCH₂CH₂), 3.81 (c, $^3J_{\text{H-H}} = 6.9$, 12H, CH₃CH₂O), 4.06 (s, 6H, Imz-Me), 4.44 (m, 4H, CH₂Imz), 6.79 and 6.88 (2 × d, $^3J_{\text{H-H}} = 1.7$, 2 × 2H, Imz-H⁴ and H⁵). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 7.7 (SiCH₂), 18.3 (CH₃CH₂O), 24.4 (SiCH₂CH₂), 37.9 (Imz-Me), 53.1 (CH₂Imz), 58.6 (CH₃CH₂O), 121.1 and 121.8 (Imz-C^{4,5}), 169.2 (Imz-C²). Conformer **syn-4**: ^1H NMR (300 MHz, CDCl_3): δ 0.72 (m, 4H, SiCH₂), 1.20 (t, $^3J_{\text{H-H}} = 6.9$, 18H, CH₃CH₂O), 2.20 (m, 4H, SiCH₂CH₂), 3.81 (c, $^3J_{\text{H-H}} = 6.9$, 12H, CH₃CH₂O), 4.03 (s, 6H, Imz-Me), 4.44 (m, 4H, CH₂Imz), 6.79 and 6.86 (2 × d, $^3J_{\text{H-H}} = 1.7$, 2 × 2H, Imz-H⁴ and H⁵). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 7.5 (SiCH₂), 18.3 (CH₃CH₂O), 24.3 (SiCH₂CH₂), 37.9 (Imz-Me), 52.8 (CH₂Imz), 58.5 (CH₃CH₂O), 121.0 and 121.7 (Imz-C^{4,5}), 169.2 (Imz-C²). IR (KBr): ν 3080-3150 (m, C-H), 1525 (s, C=N), 1380-1480 (m, arC=C), 1080 (w, Si-O-C), 960 (w, Si-O-C), 720-790 (m, Si-C), 690 cm⁻¹ (m, Si-O). ESI-MS (positive ion, $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_4\text{HCOO}$ 5 mM): m/z 854.1157 [$\text{M} + \text{NH}_4$]⁺ (calcd 854.1171), 757.1635 [$\text{M} - \text{Br}$]⁺ (calcd 757.1644). Anal. Calc. for C₂₆H₅₂Br₂N₄O₆PdSi₂ (839.11): C, 37.22; H, 6.25; N, 6.68%; Found: C, 36.97; H, 6.07; N, 6.79%.

X-ray crystallographic studies

Single crystals of **2** suitable for X-ray diffraction studies were obtained by slow evaporation from CH₂Cl₂/hexane (1:1) solutions. A summary of the crystal data, data collection, and refinement parameters for the structural analysis of this compound is given in Table S1. Suitable crystals were covered with mineral oil and mounted in the N₂ stream of a Bruker-Nonius Kappa-CCD diffractometer with area detector, and equipped with an Oxford Cryostream 700 unit; data were collected using graphite monochromated Mo-*K*_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 200 K, with an exposure time of 20 s per frame (5 sets; 179 frames; phi and omega scans, 2.0° scan-width). Raw data were corrected for Lorentz and polarization effects.

CCDC-1446126 contains the supplementary crystallographic data for complex **2**.

Table S1. Crystal data and structure refinement for compound **2**.

Empirical formula	C ₁₉ H ₃₃ I ₂ N ₃ O ₃ PdSi
Formula weight	739.77
Color	orange
Temperature/K	200(2)
Wavelength (λ)/ \AA	0.71069
Crystal system, space group	triclinic, <i>P</i> -1
<i>a</i> / \AA	8.9025(13)
<i>b</i> / \AA	10.7384(10)
<i>c</i> / \AA	15.224(4)
α /°	87.238(16)
β /°	89.80(2)
γ /°	70.189(11)
Volume/ \AA^3	1367.5(4)
<i>Z</i> , Calcd. Density/ g cm ⁻³	2, 1.797
Absorption coefficient/mm ⁻¹	3.002
<i>F</i> (000)	716
Crystal size [mm]	0.45 × 0.21 × 0.21
θ range/°	3.27 to 27.50
Limiting indices	-11 ≤ <i>h</i> ≤ 11, -13 ≤ <i>k</i> ≤ 13, -19 ≤ <i>l</i> ≤ 19
Reflections collected/unique	11724/6209 [R(int) = 0.0375]
Reflections observed	3678 [<i>I</i> > 2 σ (<i>I</i>)]
Completeness to θ 27.50°	98.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.424 and 0.352
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6210/0/262
Goodness of fit on <i>F</i> ²	0.944
<i>R</i> 1/ <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0376/0.00802
<i>R</i> 1/ <i>wR</i> 2 (all data)	0.0902/0.0956
Largest diff. peak and hole [e/ \AA^3]	1.699 and -1.393

The structure was solved by direct methods, completed by subsequent difference Fourier techniques, and refined by full-matrix least-squares on *F*² with SHELXL-97.¹⁰

Anisotropic thermal parameters were used in the last cycles of refinement for the non hydrogen atoms. The hydrogen atoms were introduced in the last cycle of refinement from geometrical calculations and refined using a riding model. All the calculations were made using the WINGX program.¹¹

Grafting of the NHC complexes of palladium onto core-shell silica-maghemite MNPs:

Silica-Adembeads 300 nm nanoparticles (15 mg) were introduced into a PP Flacon™ 15 mL tube, and dispersed in 1 mL of Tx (Tx: aqueous solution 0.21wt% of Triton™ X-405; HLB = 17.9), 1 mL of ethanol, and 175 µL of ammonia solution 30wt%. The mixture was sonicated 5 min with a sonotrode probe, and placed in the shaker plate set at 25 °C and 750 rpm. Then, an ethanol solution (4.5 mL) of the palladium complex (70 (2) or 80 (4) mg, 95 µmol – optimized maximum concentration of 6.2-6.4 µmol of Pd per mg of MNPs), was added drop-wise over 2.5 h, sonicating the mixture every 15 min with the ultrasonic probe, and the tube was capped and shaken for 1 h at 40 °C and 750 rpm. The particles were trapped on the tube wall with the help of an external neodymium-iron-boron [Nd-Fe-B] magnet (Supermagnete), the solution was decanted, and the particles washed with portions of ethanol (5 mL, until colorless washings), with an aqueous solution of Pluronic® F127 0.30wt% (3 × 5 mL), and with Tx (3 × 5 mL). The MNPs functionalized with the palladium complexes were obtained as brown powders, and were stored dispersed in Tx (5 mL) at 5 °C. Figure S1 shows representative TEM micrographs, and EDS was used to check the presence palladium. The shell of the resulting particles showed an apparent increase in thickness of 2±1 nm. The Pd contents were determined by ICP-MS (Table S2).

MNP-2: ATR IR: ν 1620 (m, arC=C), 1502 (s, C=N), 1380-1480 (m, arC=C), 800 cm⁻¹ (m, Si-C). TEM: Spherical particles of 280-340 nm.

MNP-4: ATR IR: ν 3080-3150 (m, C-H), 1380-1530 (m, C=N, arC=C). TEM: Spherical particles of 260-330 nm.

Table S2. Palladium content in MNP-2 and -4.^a

	MNP-2	MNP-4
mg Pd / g MNPs	2.77	2.39
Pd wt%	0.28	0.24
mmol Pd / g MNPs	0.026	0.022
(molecules of complex/nm ²) ^b	1.6	1.3

^a Determined by ICP-MS. RSD (Relative Standard Deviations) ≤10%

^b MNPs of 300 nm with specific surface area = 10 m²/g and density = 2 g/cm³

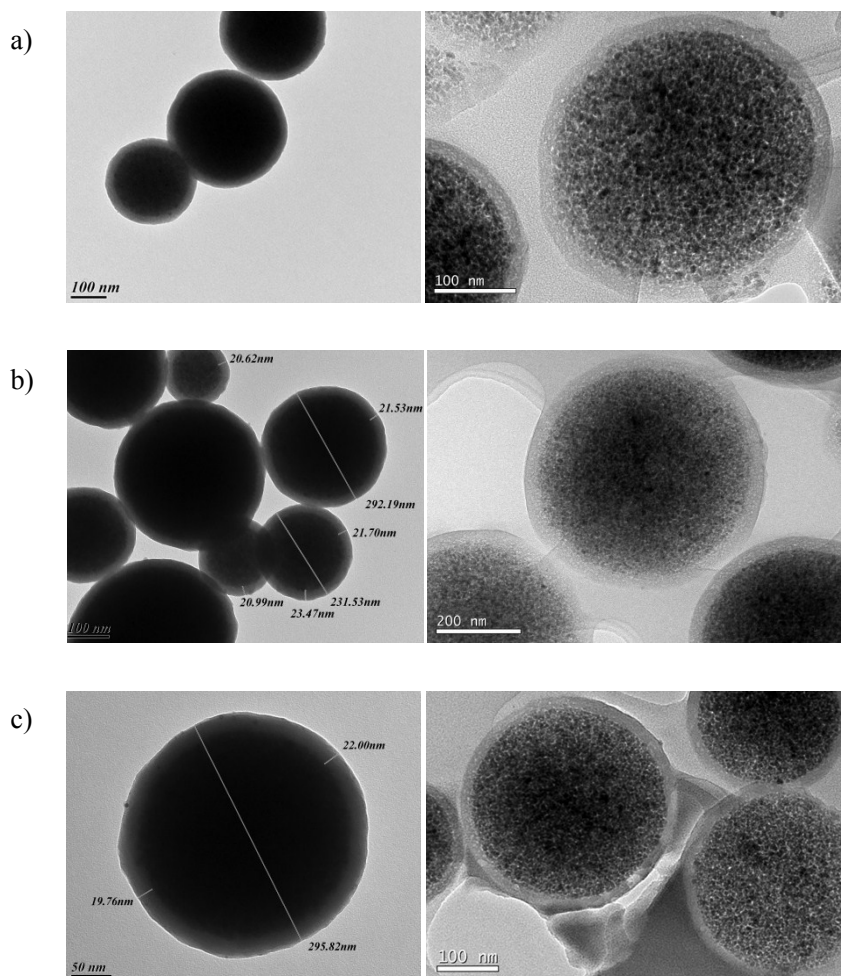


Figure S1. TEM images of the core-shell γ -Fe₂O₃/silica particles (left) and microtome slices of them (right) of: a) Starting Silica-Adembeads; b) **MNP-2**; c) **MNP-4**.

Procedure for Suzuki-Miyaura reactions: Prior to use, glassware and materials in contact with the catalytic mixtures were treated with aqua regia to remove any possible palladium residue. Reaction blanks, without catalyst or with the silica-Adembeads used as support, were performed to rule out false positives due to possible contamination by palladium from the reactants or from the starting MNPs. Different reaction conditions were tested including several solvents (CH₃CN, DMF, DMSO, dioxane, THF, EtOH, or mixtures of them with water or Tx), bases (KO^tBu, Na₂CO₃, CsCO₃, NaOH, KOH), and temperatures (up to 125 °C for **2** and **4**, or up to 90 °C for the **MNP-2** and **MNP-2**). The progress of the catalysis was followed by GC with periodic withdrawal of 1 μ L, dilution to 10 μ L in the same solvent of the reaction, and injection of 1 μ L of the resulting solution into the chromatograph. Conversions (%) were determined using naphthalene or hexadecane as internal standard and the corresponding calibration curves. All runs were performed at least in duplicate, and the reproducibility of the conversions measured is estimated at $\pm 2\%$. All catalysts were first tested with 4-bromotoluene as a

benchmark substrate, and subsequently and depending on the results, with the more reactive (iodo-) or the more challenging (chloro-) 4-halotoluene.

The catalytic assays with complexes **2** and **4** were carried out under argon in small ampoules equipped with a PTFE plug valve and a magnetic stirrer, in dioxane (2 mL), and with the following concentration (amount) of reagents: [potassium carbonate] = 0.35 M (0.7 mmol), [phenylboronic acid] = 0.30 M (0.6 mmol), [haloarene] = [naphthalene] = 0.25 M (0.5 mmol), and [Pd] = 1.25 mM or 0.5 mol% (2.5 μ mol). The ampoules were immediately placed in an oil bath thermostatted at 80 °C, with vigorous stirring, taking that instant as the starting time of the reaction. Stirring of the mixture was maintained, and the progress of the reaction monitored by GC-MS. For the reutilization experiments carried out with **2** and **4**, once the reactions were completed, the ampoules were reloaded at room temperature with the reactants and base in amounts identical to those initially added and specified above. The ampoules were then again placed in the oil bath at 80 °C taking that instant as the new starting time.

Catalysts **MNP-2** and **-4** were tested in the absence of oxygen in 2 mL PP screw thread microtubes (Deltalab) inside a 815 PGB La Petite Glove Box (Plas Labs Inc.). Mother catalytic mixtures, containing 2.5 mg/mL of particles and the reactants in the amounts indicated in Table S3 (adjusted for palladium loadings of 0.05 and 0.024 mol% for **MNP-2** and **-4**, respectively, relative to the haloarene), were prepared in Tx/THF 9:1, and homogenized briefly (1 min) in an ultrasonic bath at 37 kHz. Then, each Deltalab microtube was loaded with 1 mL of the mixture, sealed under argon with a cap with a silicon O-ring, introduced into the glove box, and placed in the plate of the thermal mixer set at 65 (4-bromotoluene) or 80 °C (4-chlorotoluene), and 750 rpm. Shaking of the vials was maintained, and the progress of the reactions monitored by GC-FID. Once the reactions were completed, the particles were trapped with an external magnet, the solutions with the products separated by decantation, and the particles washed with THF (5 \times 1 mL), and Tx (5 \times 1 mL). The recovered particles were reutilized by re-suspending them in 1 mL of Tx/THF (9:1) containing the initial amount of substrates. The palladium present in the solutions decanted with the catalytic products and in the particles recovered at the end each recycling-series, was quantified by ICP MS.

Table S3. Amount of reactants per mL used with **MNP-2** and **-4**.^a

	MNP-2	MNP-4
Pd (μ mol)	0.065	0.056
haloarene (mmol)	0.130	0.233
phenylboronic acid (mmol)	0.16	0.28
potassium carbonate (mmol)	0.39	0.70

^a Naphthalene or hexadecane (0.5 mmol) was added as internal standard.

Figure S2 shows the GC chromatogram (a) of the crude of an almost completed reaction of 4-chlorotoluene in the presence of **MNP-4**, together the mass spectra (b) registered for the trace at 13.67 min corresponding to the cross-coupling product (*i.e.*, 4-methyl-1,1'-biphenyl). The sample was prepared by extraction from the aqueous mixture with EtOAc and using hexadecane as standard reference. Traces of biphenyl ($\leq 4\%$) from the starting PhB(OH)₂ were always present in the crudes (thus, the acid was used in excess, whereas the homo-coupling product from the 4-halotoluene (*i.e.*, 4,4'-dimethylbiphenyl) was only detected in reactions with 4-chlorotoluene, and in quantities not exceeding a 2% relative to the cross-coupling product.

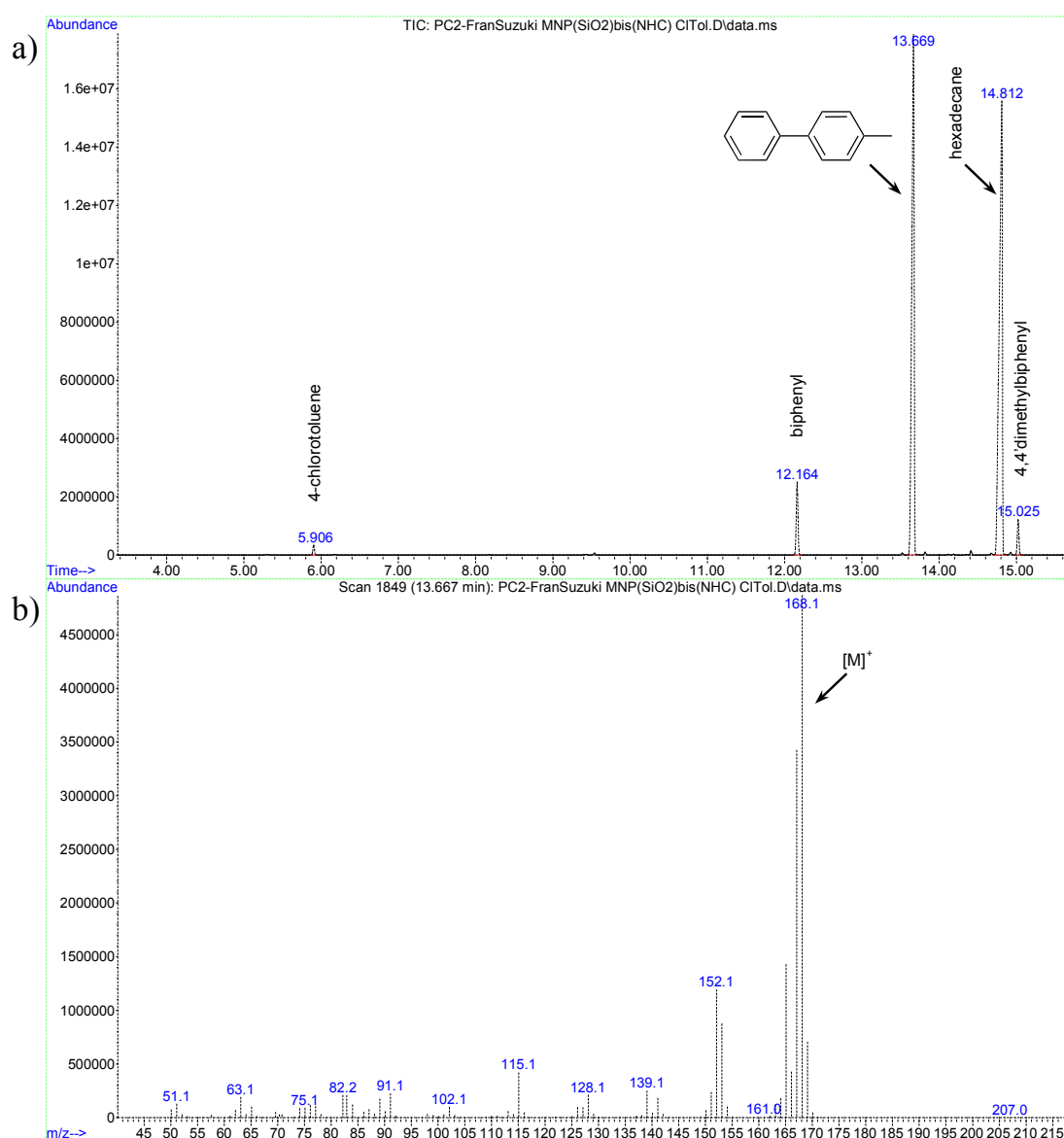


Figure S2. GC-MS of the crude of a Suzuki-Miyaura reaction of 4-chlorotoluene using **MNP-4** as catalyst: a) Chromatogram, b) Mass spectra for the trace at 13.67 min corresponding to the cross-coupling product.

Isolation of the coupling product:

In addition to monitoring the catalytic reactions and identifying the products by GC-FID or -MS, the coupling product obtained with **MNP-4** was isolated using a reported purification procedure.¹² Thus, after completion of the reaction the magnetic catalyst was separated and the aqueous mixtures of the microtubes extracted with EtOAc (3 × 2 mL), and then dried over Na₂SO₄. The solvent was removed under reduced pressure,

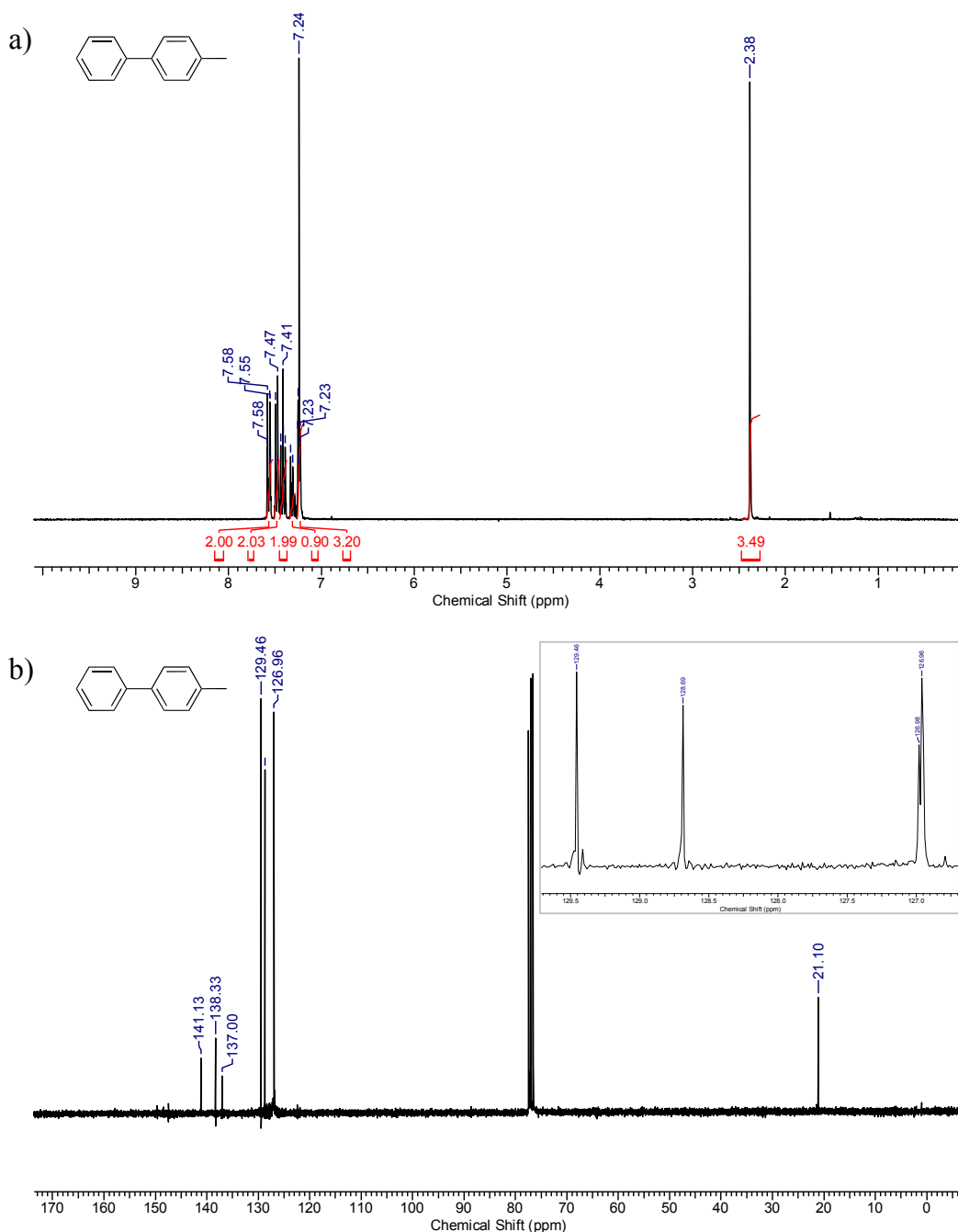


Figure S3. NMR spectra of 4-methyl-1,1'-biphenyl synthesized from 4-chlorotoluene in the presence of **MNP-4**, and isolated after purification by column chromatography: a) ¹H NMR, b) ¹³C {¹H} NMR with inset of the 130-126 ppm region.

and the resulting colorless oil was purified by silica gel column chromatography using hexane as the eluent to yield 4-methylbiphenyl as a white solid (≥ 33 mg, $\geq 84\%$ from 4-chlorotoluene; ≥ 35 mg, $\geq 89\%$ from 4-bromotoluene). Figure S3 show the NMR spectra of a product isolated and purified using this procedure. ^1H NMR (300 MHz, CDCl_3): δ 2.38 (s, 3H, *Me*), 7.22-7.25 (m, 2H, *Ar-H*), 7.31 (tt, $^3J_{\text{H-H}} = 7.3$, $^4J_{\text{H-H}} = 1.3$, 1H, *Ph-H*), 7.41 (tt, $^3J_{\text{H-H}} = 7.5$, $^4J_{\text{H-H}} = 1.3$, 2H, *Ph-H*), 7.47-7.50 (m, 2H, *Ar-H*), 7.54-7.58 (m, 2H, *Ph-H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 21.1 (*Me*), 126.9-127.0 (*o-Ph*, *o-Ar* and *p-Ph*), 128.7 (*m-Ph*), 129.5 (*m-Ar*), 137.0 (*ipso-Ar*), 138.3 (*ipso-Ar*), 141.1 (*ipso-Ph*).

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