Supplementary Material (ESI) for Chemical Communications
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Supplementary Information

Suzuki cross-coupling reactions on the surface of carbon coated cobalt: expanding the applicability of core/shell nano-magnets

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A. Comparative IR Spectra and Elemental Analyses of Suzuki-coupled Products 3, 4, 5 and 6

p-benzyloxy biphenyl particles (4)

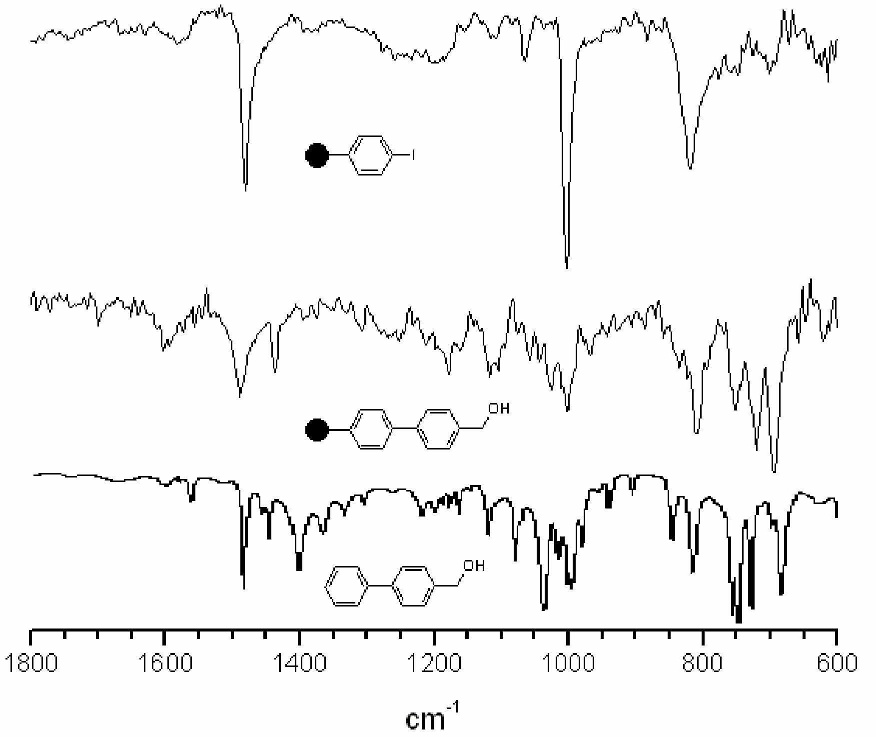

Figure S1. FTIR spectrum of iodophenyl functionalized magnetic nanoparticles **3** prior to the coupling reaction (top trace). The FTIR spectrum of **4** after the Suzuki coupling reaction (middle trace) is compared with a reference spectrum of p-benzyloxybiphenyl (bottom trace).

p-vinyl biphenyl particles (5)

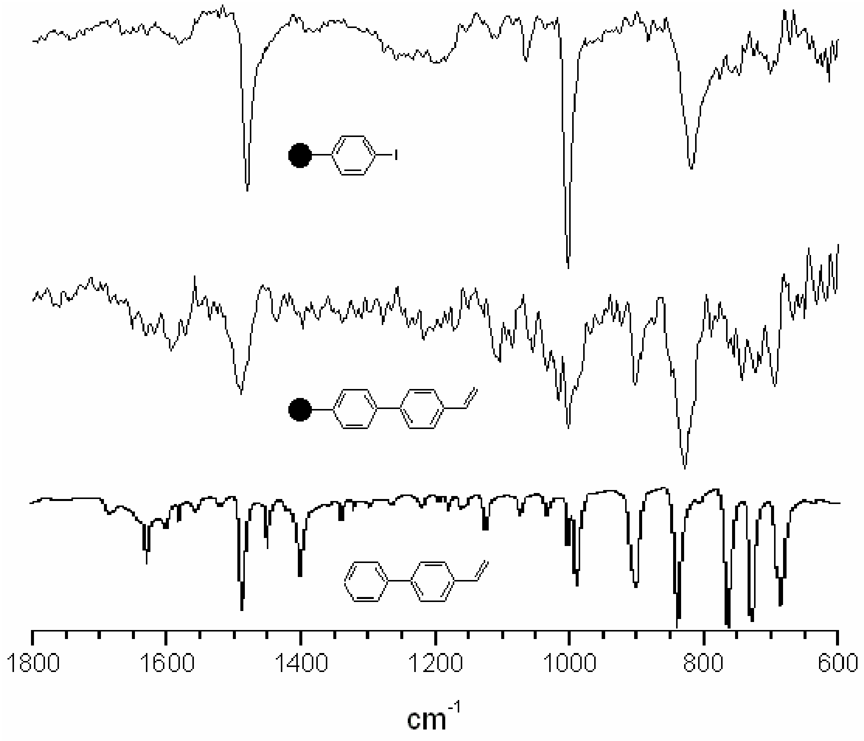

Figure S2. FTIR spectrum of iodophenyl functionalized magnetic nanoparticles **3** prior to the coupling reaction (top trace). The FTIR spectrum of **5** after the Suzuki coupling reaction (middle trace) is compared with a reference spectrum of p-vinylbiphenyl (bottom trace).

p-formyl biphenyl particles (6)

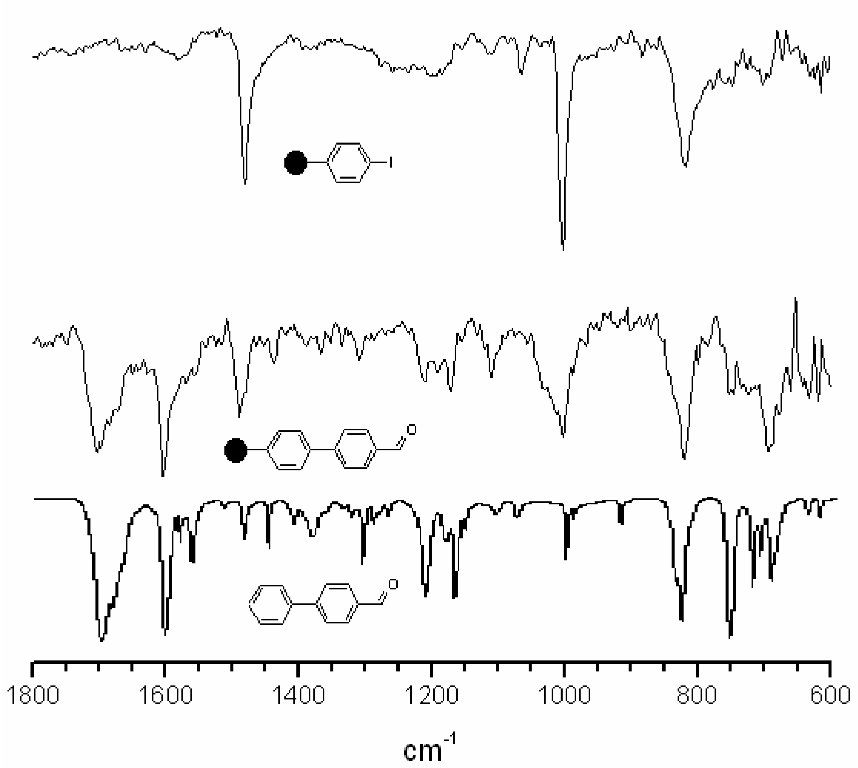

Figure S3. FTIR spectrum of iodophenyl functionalized magnetic nanoparticles **3** prior to the coupling reaction (top trace). The FTIR spectrum of **6** after the Suzuki coupling reaction (middle trace) is compared with a reference spectrum of p-formylbiphenyl (bottom trace).

p-biphenyl ethanediol particles (7)

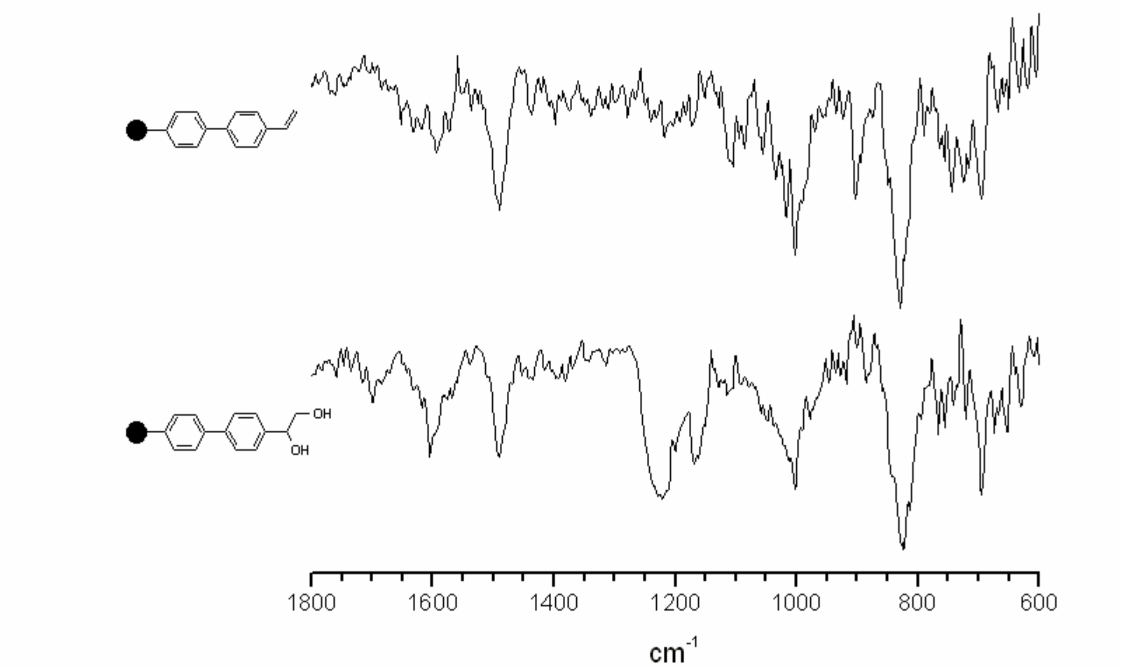

Figure S4. FTIR spectrum of **7** (bottom trace) produced by the dihydroxylation of **5** (top trace).

B. Experimental Details

Titration of Benzoate-functionalized particles (2)

A sample of 1.5 g of particles **2** was washed in 4 N HCl for 2 days to remove most of the trace Co metal, and then treated with 4 N KOH to give the benzoate. After further washing with Ultrapure water (5 x) to remove excess KOH, the particles were resuspended in Ultrapure water and titrated with 0.2 N HCl (aq.). This involved the addition of a 0.2 mL aliquot of HCl with continuous stirring of the suspension. The stable pH value (change of up to 0.02 units over 5 – 6 min) was then read and recorded. A plot of pH against volume of HCl added (Fig. S5) gave an experimental pKa value of 4.52.

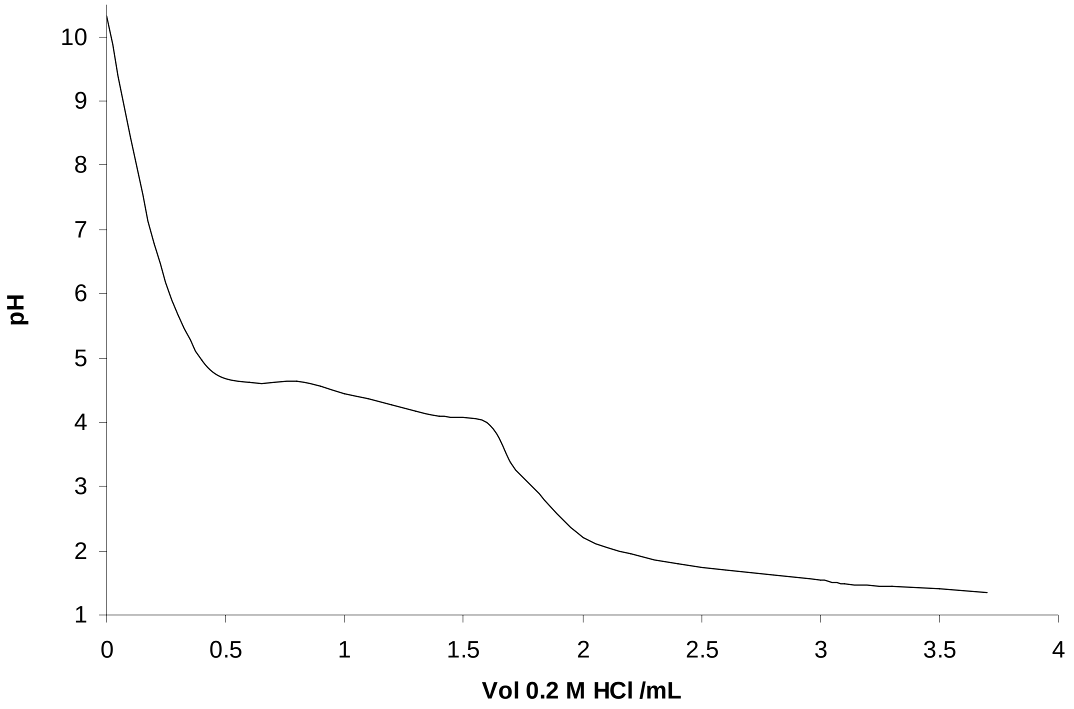

Figure S5. Plot of suspension pH against volume of 0.2 N HCl added.

General Procedure for Suzuki Coupling

Under N_2 flow, the relevant boronic acid (0.195 mmol, 8 meq.), iodophenyl-functionalised particles (120 mg), $Pd(OAc)_2$ (2.2 mg, 0.009 mmol, 5 mol%), triphenylphosphine (7.1 mg, 0.027 mmol, 3 meq. to Pd) and Na_2CO_3 (23 mg, 0.215 mmol) were added to a 10 mL Schlenk tube equipped with a stir bar. A reflux condenser was then fitted on top of the tube and the system flushed with N_2. 0.75 mL PrOH and 0.75 mL H_2O were then degassed by subjecting them to vacuum under ultrasonic agitation for 5 min. This process was repeated three times. The degassed solvents were then mixed and introduced into the tube *via* syringe. After the complete dissolution of reactants the reaction mixture was heated to 95 ºC with an oil bath and stirred at reflux overnight (~ 16-18 h). It was subsequently allowed to cool to room temperature, and then quenched with water. The stir bar was removed and the particles washed successively with water (2x), MeOH (2x), EtOAc (3x) and hexane (1x) before being dried in a vacuum oven at 60 ºC.

p-biphenyl ethanediol particles (7)

To a 5 mL round-bottomed flask equipped with a magnetic stirrer was added formylbiphenyl particles (120 mg), AD-mix-α (31 mg) and methanesulfonamide (6 mg). The flask was then flushed with N_2 three times before 0.5 mL water was added *via* syringe. The bright yellow reaction mixture was stirred for 48 h, after which the remaining brown liquid was decanted and particles washed with water, THF (3x) and EtOAc (3x) before being dried in a vacuum oven at 60 ºC.

p-biphenyl epoxide particles (8)

To a 10 mL round-bottomed flask equipped with a magnetic stirrer was added trimethyloxosulfonium iodide (105 mg, 0.48 mmol) and NaH (60 % dispersion in mineral oil, 20.4 mg, 0.50 mmol). The flask was then flushed with N_2 three times before 0.6 mL dry DMSO was added *via* syringe. The resulting white suspension was then stirred for 1 h under N_2 until it turned clear. 0.15 mL of this dimethyloxosulfonium methylide solution was then extracted by syringe and added to a prepared suspension of *p*-formylbiphenyl particles (85 mg) in DMSO (0.4 mL) in a 10 mL Schlenk tube under a N_2 atmosphere. The reaction mixture was stirred at RT for a further 1 h, then quenched with water and washed with water, THF (3x) and EtOAc (3x) before being dried in a vacuum oven at 60 ºC.

C. Characterization of the particles

The production of the carbon coated cobalt particles by reducing flame synthesis[1],[2] used throughout this work has been earlier described by Grass et al. [3] in detail. The nanoparticles were analyzed by X-ray diffraction (Stoe STADI-P2, Ge monochromator, $CuK_{\alpha 1}$, PSD detector), magnetic hysteresis susceptibility (Quantum Design, Physical Property Measurement System) as well as transmission electron microscopy (CM30 ST-Philips, LaB_6 cathode, operated at 300kV point resolution ~ 4 Å).

Phase analysis

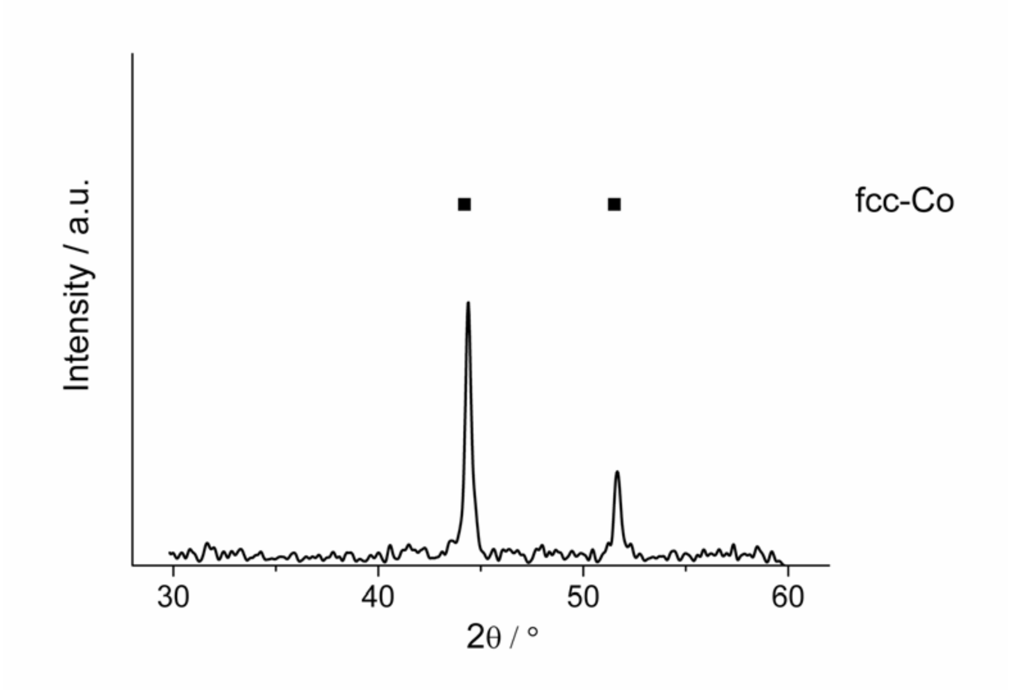

Figure S6. The X-ray diffraction pattern of the carbon coated cobalt nanoparticles shows the formation of crystalline face centred cubic (fcc) cobalt and the absence of hcp cobalt, any crystalline oxides or graphite.

Particle morphology

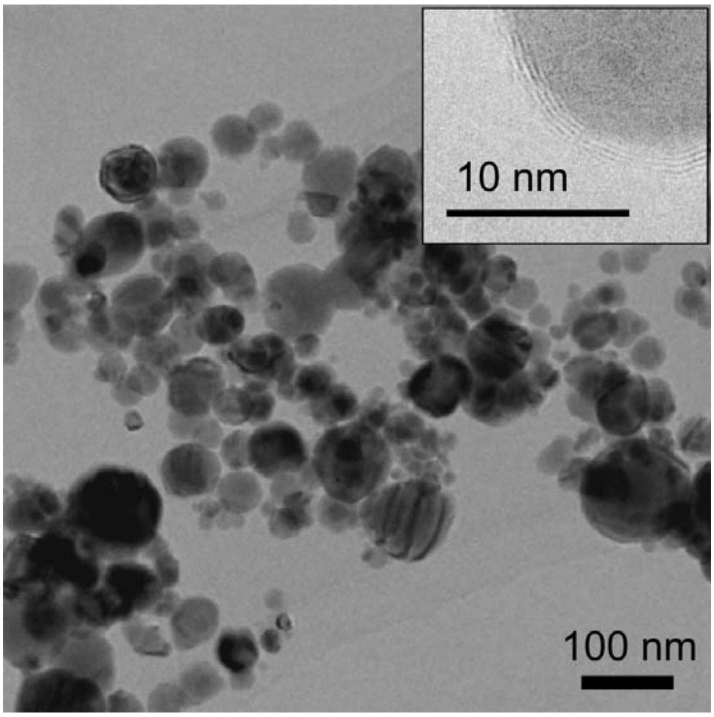

Figure S7. Transmission electron microscopy image of the as-prepared carbon coated cobalt nanoparticles. The high resolution image in the inset shows the carbon layers surrounding the individual metallic particles.

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Magnetic hysteresis

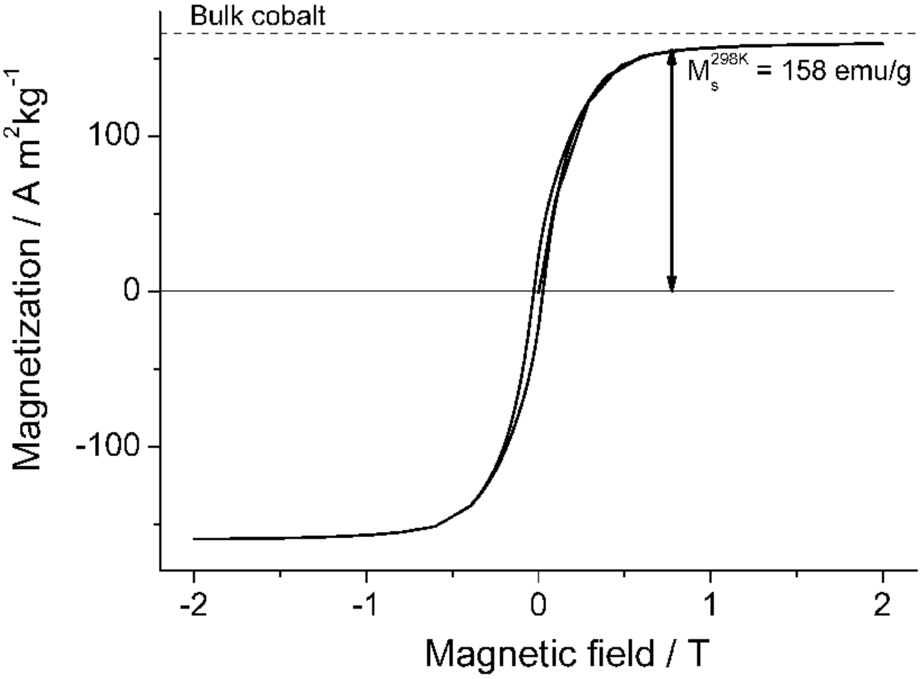

Figure S8. Magnetic hysteresis loop of the as-prepared carbon coated cobalt nanoparticles showing a ferromagnetic response with a saturation magnetization close to the saturation of bulk cobalt (166 emu/g).

References:

[1] L. Madler, H. K. Kammler, R. Mueller and S. E. Pratsinis, *J. Aerosol. Sci.* 2002, **33**, 369.
[2] R. N. Grass and W. J. Stark, *J. Mater. Chem.*, 2006**, 16**, 1825
[3] R. N. Grass, E. K. Athanassiou and W. J. Stark, *Angew. Chem. Int. Ed.*, 2007, 4909.