

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry
This journal is © The Royal Society of Chemistry 2012

Supporting Information

Highly Cross-Linked Imidazolium Salts Entrapped Magnetic Particles

– Preparation and Applications

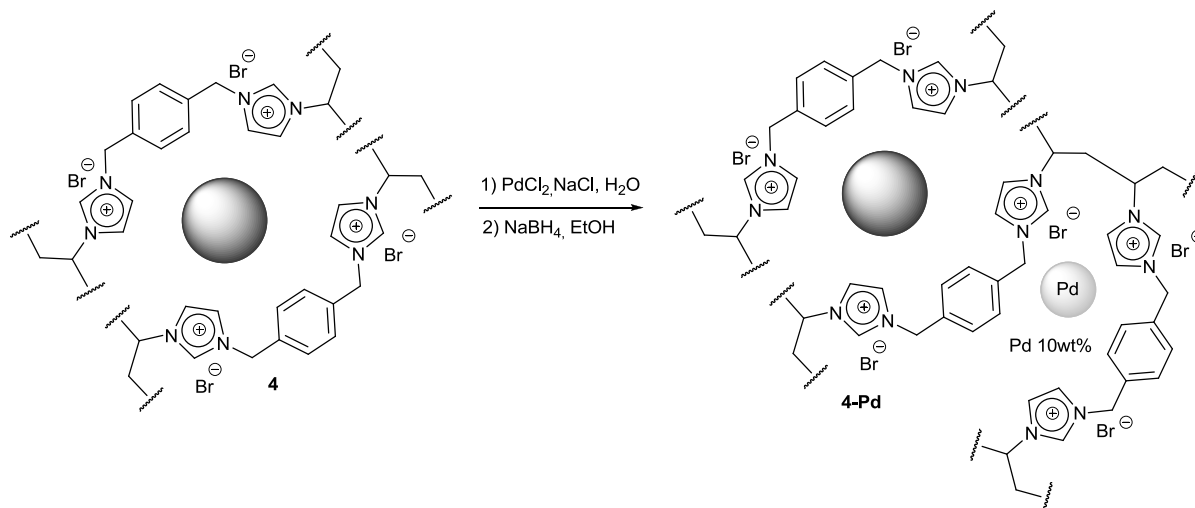
Paola Agrigento,^a Matthias Josef Beier,^b Jesper T. N. Knijnenburg,^c Alfons Baiker^b and Michelangelo Gruttadauria*^a

Contents:

1) Suzuki and Heck reactions	page S1
2) Experimental section	page S3
Figure S1. DSC of bis-vinylimidazolium salt 1 .	page S4
Figure S2. TGA of bis-vinylimidazolium salt 1 .	page S4
Figure S3. TGA of materials 4-9 .	page S5
Figure S4. TGA of material 10 .	page S5
Figure S5. FTIR spectrum of 10 .	page S6
Table S1. Experimental condition for the synthesis of materials 4-10 .	page S6
Figure S6. TEM images of material 9 (a-f), Fe ₂ O ₃ coated with SiO ₂ (23 wt%) (g-h), Fe ₂ O ₃ (i-j) and EDX of 9 (k).	page S7-S8
Figure S7. SEM images of material 9 .	page S9
Figure S8. XRD of iron oxide and 23 wt% SiO ₂ -coated iron oxide.	page S10
2a) <i>General Procedure for synthesis of carbonates</i>	page S10
2b) <i>General Procedure for the Palladium Scavenging</i>	page S11
2c) <i>General Procedure for the Supported Proline Materials</i>	page S11
2d) <i>General procedure for Aldol Reaction</i>	page S11
Figures S9-S11	page S12

1) Suzuki and Heck reactions.

In order to develop a supported metal nanoparticle species the material **4** was used for palladium immobilization. An aqueous solution of Na₂PdCl₄ was stirred with the starting material. Water was removed and Pd²⁺ reduced with NaBH₄ in ethanol (Scheme S1).



Scheme S1. Synthesis of supported palladium nanoparticles species and schematic representation of the magnetic catalytic material **4-Pd** (Pd content: 10 wt%).

Table S1. Suzuki reactions between phenylboronic acid and aryl bromides catalyzed by **4-Pd**^a

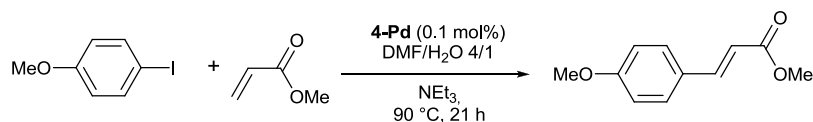
<chem>c1ccc(cc1)B(O)O + Brc1ccc(R)cc1 >> c1ccc(cc1)-c1ccc(R)cc1</chem> $\xrightarrow[\text{K}_2\text{CO}_3, \text{rt}, 15-17 \text{ h}]{\text{4-Pd (0.1 mol\%)}, \text{EtOH/H}_2\text{O}}$		
Entry	R	Isolated yield (%)
1	4-CHO	95
2 ^b	4-CHO	85
3	4-OMe	84
4	3,5-(CF ₃) ₂	65
5 ^c	4-Me	72
6 ^c	1-naphthyl	92

^a Reaction Condition: catalyst **4-Pd** (0.1 mol %), phenylboronic acid (0.5 mmol), K₂CO₃ (0.6 mmol), aryl bromide (0.55 mmol), ethanol (0.6 mL) and water (0.6 mL) ^b Reaction time of 2h. ^c reaction carried out at 50°C

The catalytic material **4-Pd** was used as catalyst (0.1 mol-%) in several Suzuki reactions at room temperature or at 50 °C in EtOH/H₂O affording biphenyls in good yields (see Table S1). It is noteworthy to stress that, because of the high loading of Pd, we needed only 1 mg of catalyst (reactions were carried out in 1 mmol scale) and this is useful for large-scale synthesis. Reaction

with 4-bromobenzaldehyde was also carried out on 10 mmol scale to give a quantitative yield of the corresponding biaryl compound.

In addition catalyst **4-Pd** was used in the Heck reaction between 4-iodoanisole and methyl acrylate in DMF/H₂O 4/1 at 90 °C using 1 mg of catalyst (0.1 mol%). The product was isolated in 98% yield (Scheme S2).



Scheme S2. Heck reaction using supported Palladium nanoparticles.

A recycling investigation on the Suzuki reaction with 4-bromobenzaldehyde was carried out and showed a drop in catalytic activity (60%). Further studies are needed in this section.

2) Experimental part

Differential Scanning Calorimetry

The measurements were carried out by using the TA Instruments DSC (2920 CE) under nitrogen flow atmosphere (flow rate = $60 \text{ cm}^3 \text{ min}^{-1}$) in the temperature range from -50 to $300 \text{ }^\circ\text{C}$ at the heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. The used pans are in aluminum and contain ca. 3 mg of the compound. DSC and TGA analysis show that salt **1** contains ca. 1 wt% of solvent and decomposes at $254 \text{ }^\circ\text{C}$.

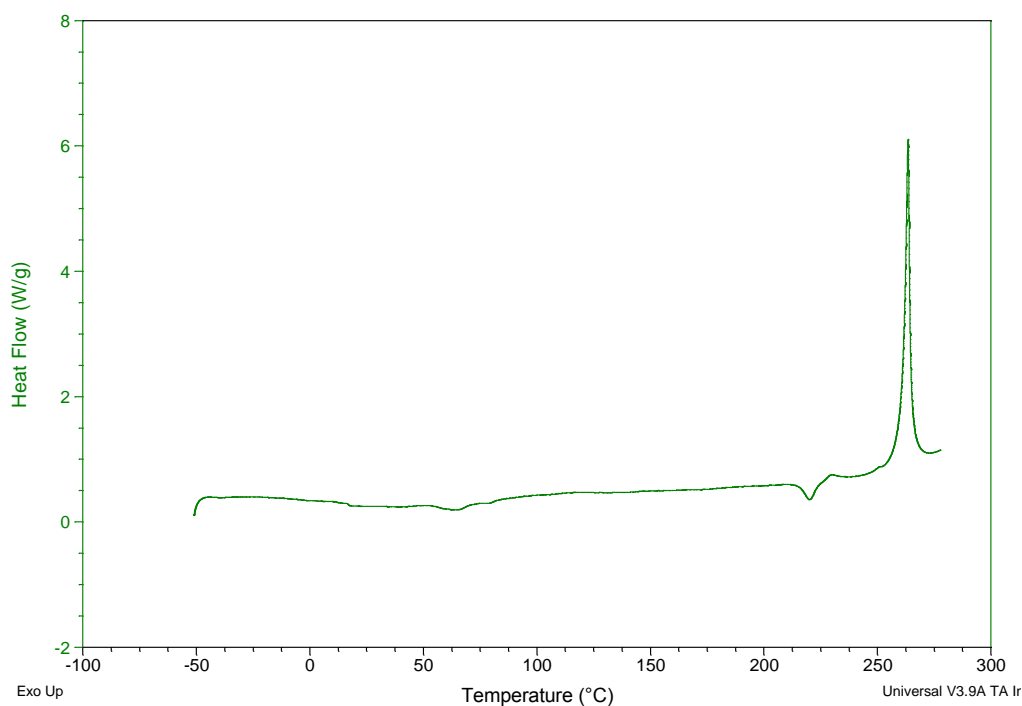


Figure S1. DSC of bis-vinylimidazolium salt **1**.

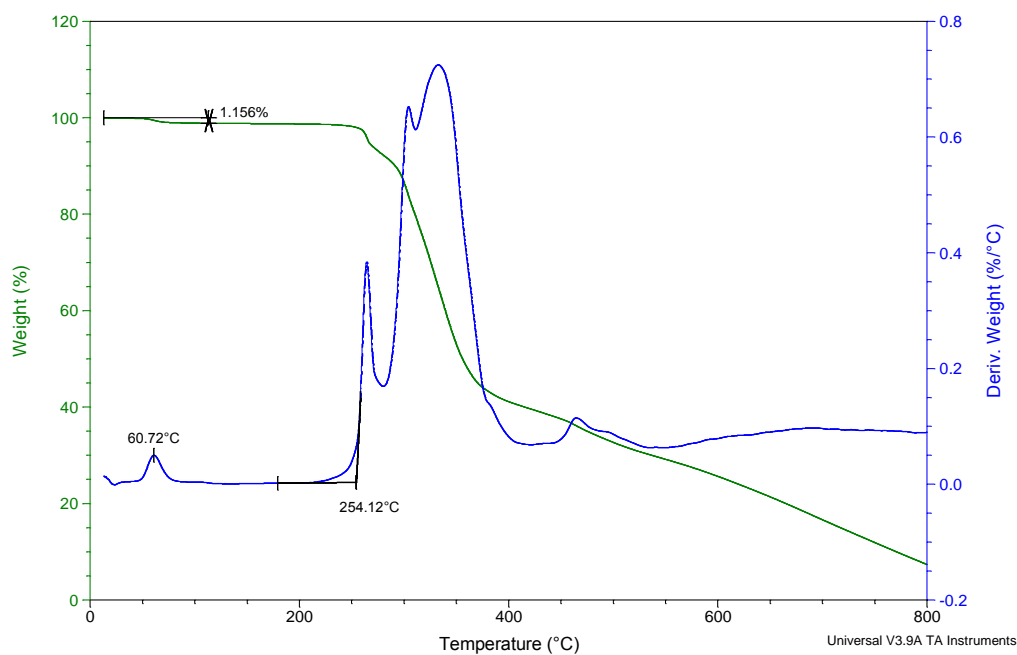


Figure S2. TGA of bis-vinylimidazolium salt **1**.

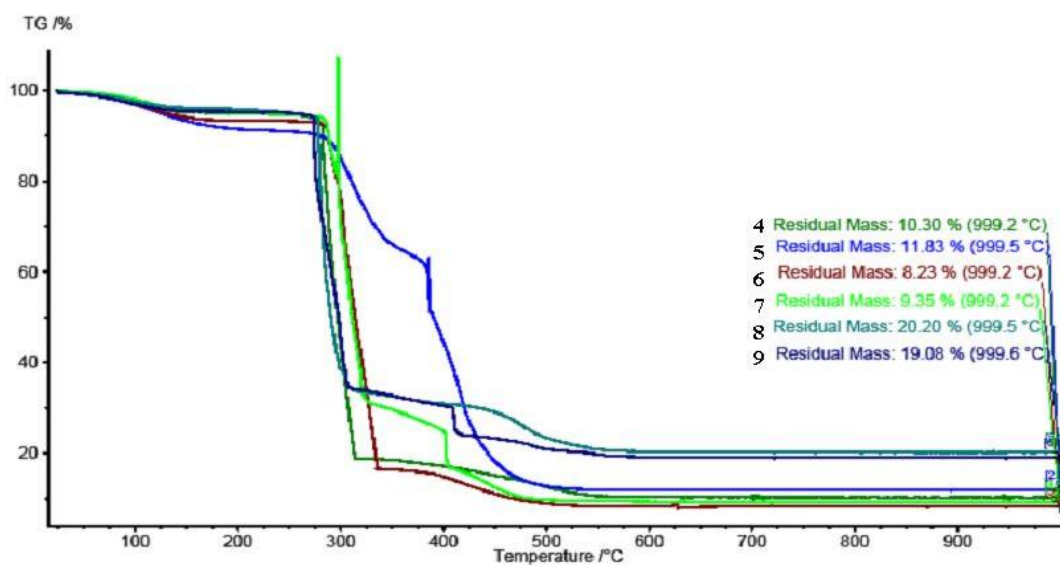


Figure S3. TGA of materials 4-9.

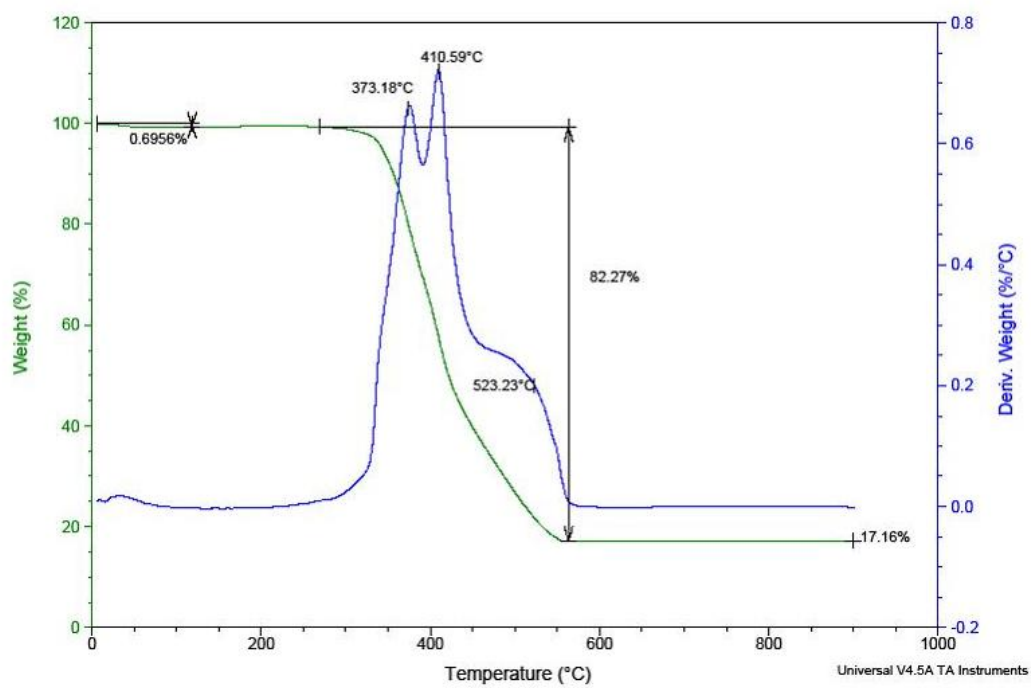


Figure S4. TGA of material 10.

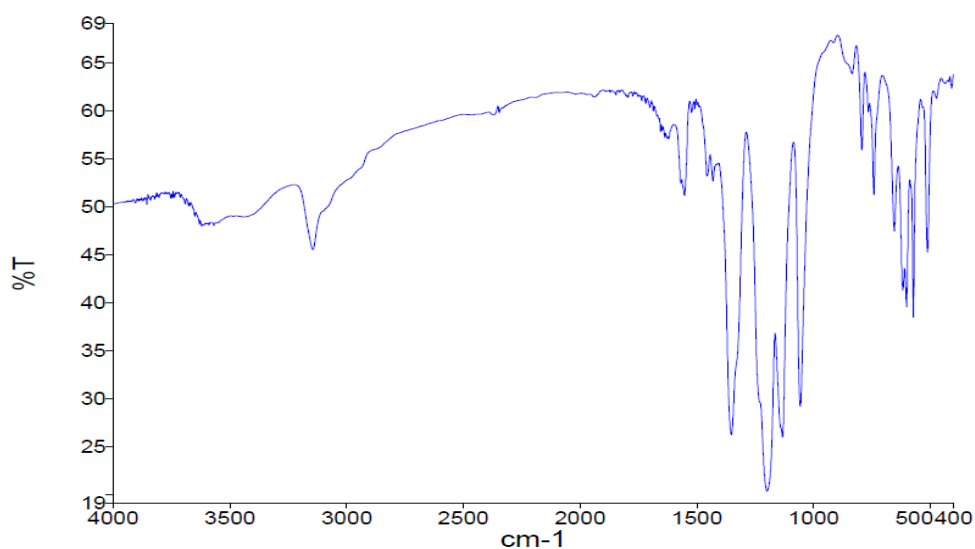
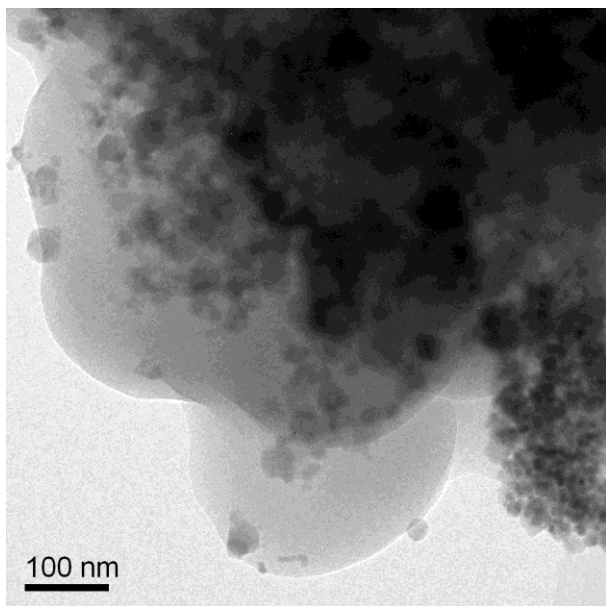


Figure S5. FTIR spectrum of **10**.

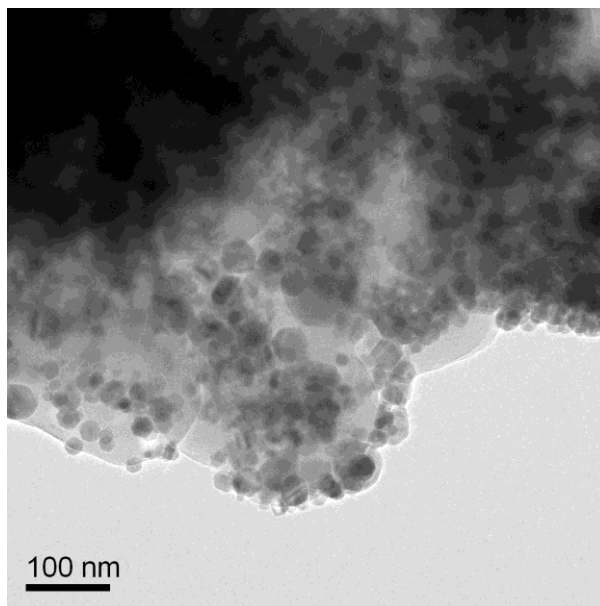
Table S1. Experimental condition for the synthesis of materials **4-9**.^a

Material	Support ^b	Support (gr)	Linker	Halide	Ethanol (mM)	Obtained amount (gr) ^c
4	Fe ₂ O ₃ 23wt% SiO ₂	0.050	<i>p</i> -CH ₂ -C ₆ H ₄ -CH ₂	Br	400	1.025
5	Fe ₂ O ₃ 23wt% SiO ₂	0.050	<i>p</i> -CH ₂ -C ₆ H ₄ -CH ₂	Cl	130	0.942
6	Fe ₂ O ₃ 23wt% SiO ₂	0.050	C ₄ H ₈	Br	130	0.890
7	Fe ₂ O ₃	0.050	C ₄ H ₈	Br	130	0.822
8	Fe ₂ O ₃	0.200	C ₄ H ₈	Br	130	1.123
9	Fe ₂ O ₃	0.200	<i>p</i> -CH ₂ -C ₆ H ₄ -CH ₂	Br	130	1.380

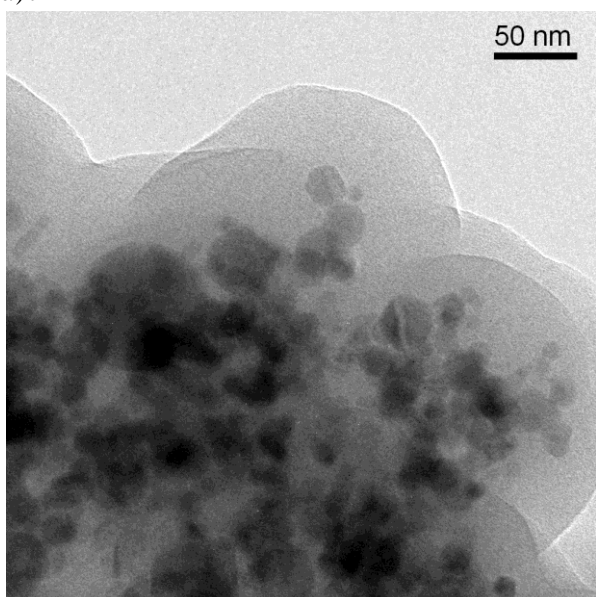
^a Reaction conditions: magnetic nanoparticles (indicated amount), the bis-vinylimidazolium salt (2.75 mmol), AIBN (40 mg) and ethanol, 78°C, 20 h. ^b The silica content in the product powder is defined as $m\text{SiO}_2 / (m\text{Fe}_2\text{O}_3 + m\text{SiO}_2)$. ^c Amount of final material after drying under vacuum for 2 hours at 40 °C.



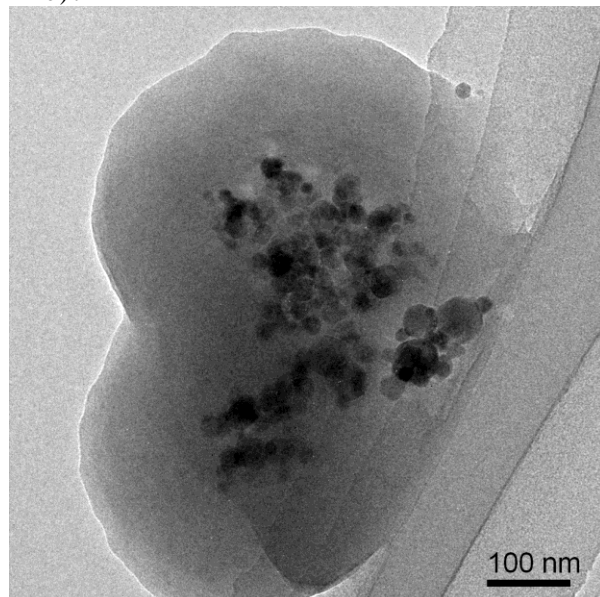
a) **9**



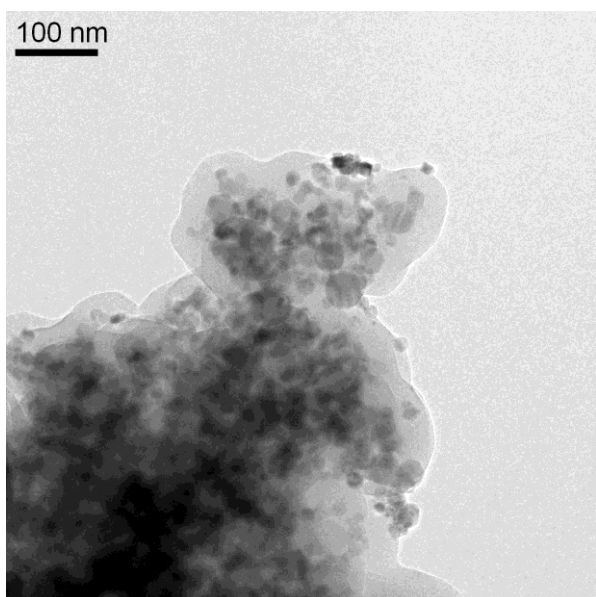
b) **9**



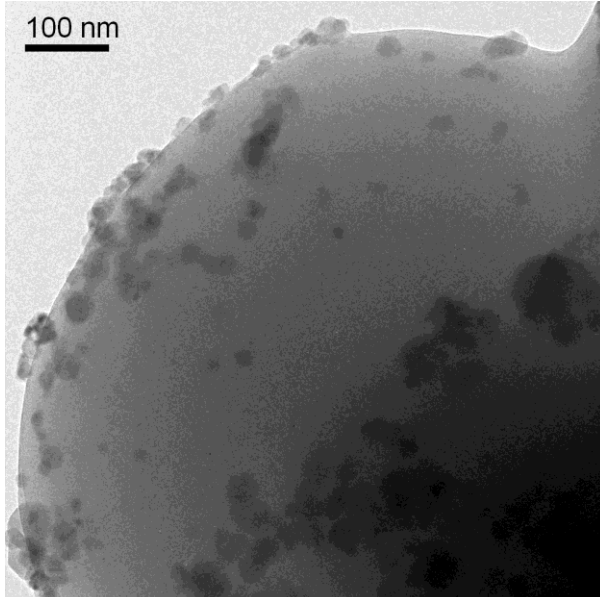
c) **9**



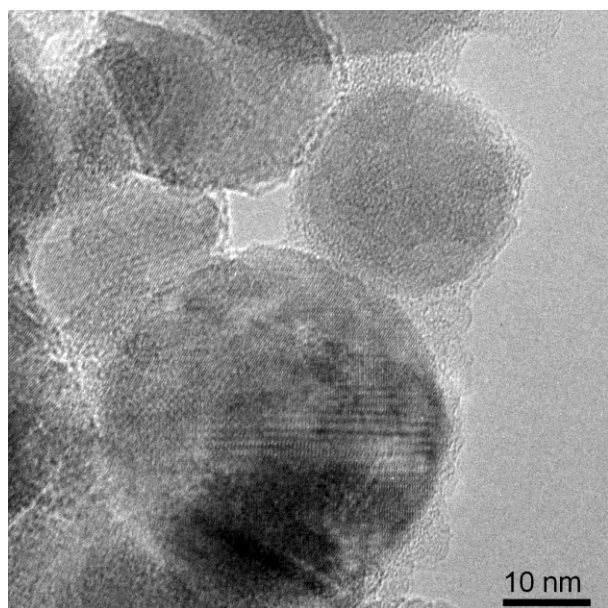
d) **9**



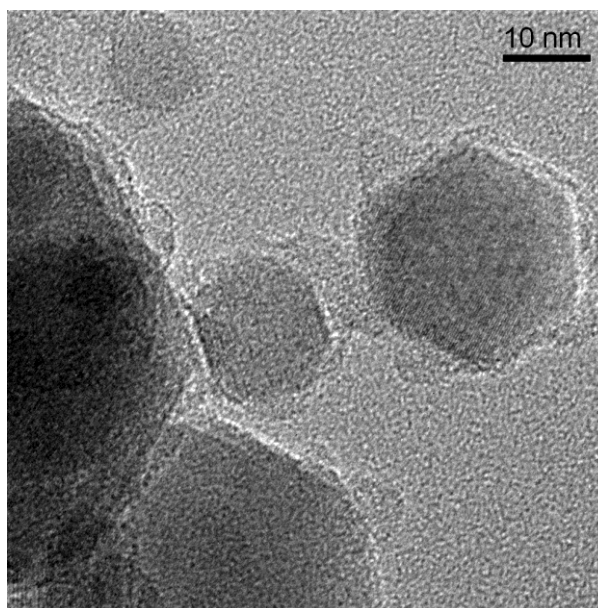
e) **9**



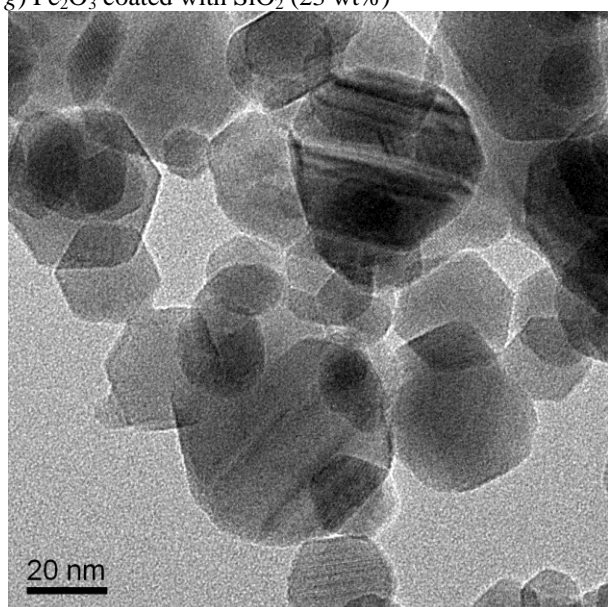
f) **9**



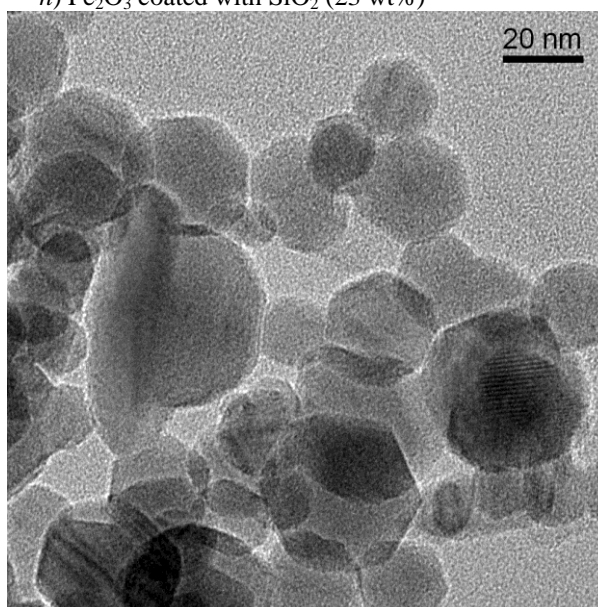
g) Fe_2O_3 coated with SiO_2 (23 wt%)



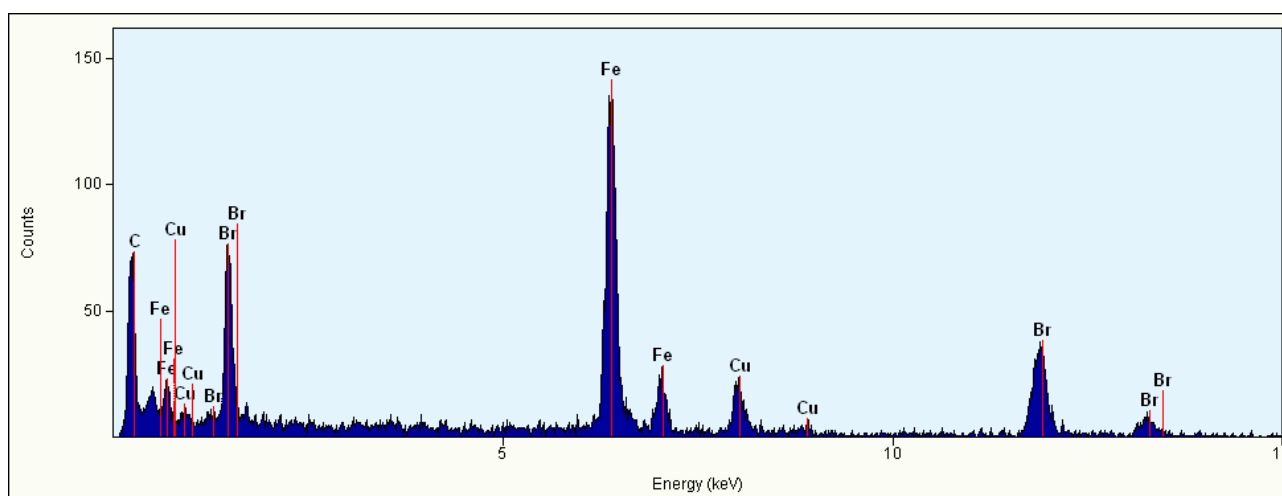
h) Fe_2O_3 coated with SiO_2 (23 wt%)



i) Fe_2O_3



j) Fe_2O_3



k) **9**

Figure S6. TEM images of material **9** (a-f), Fe_2O_3 coated with SiO_2 (23 wt%) (g-h), Fe_2O_3 (i-j) and EDX of **9** (k).

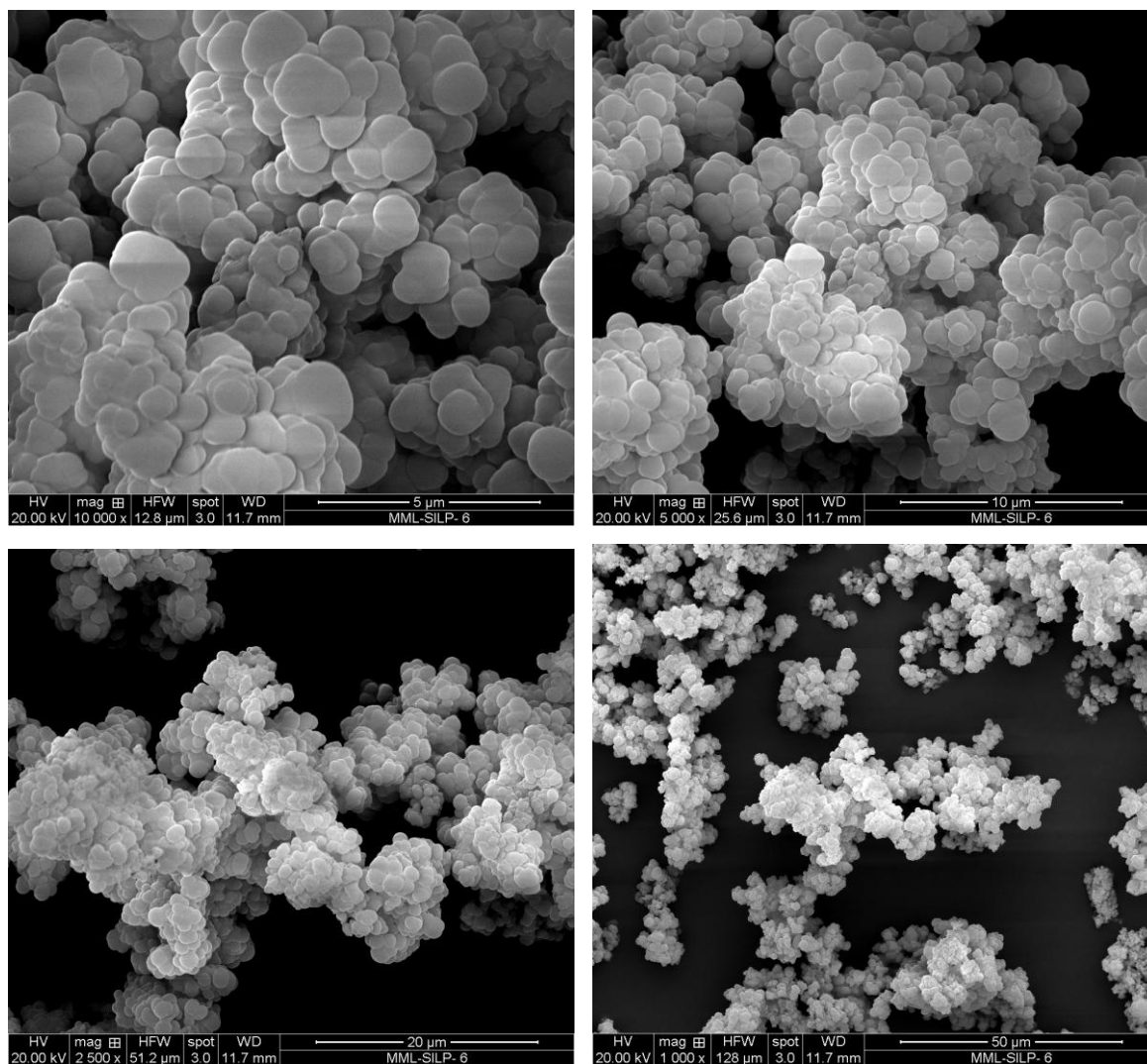


Figure S7. SEM images of material 9.

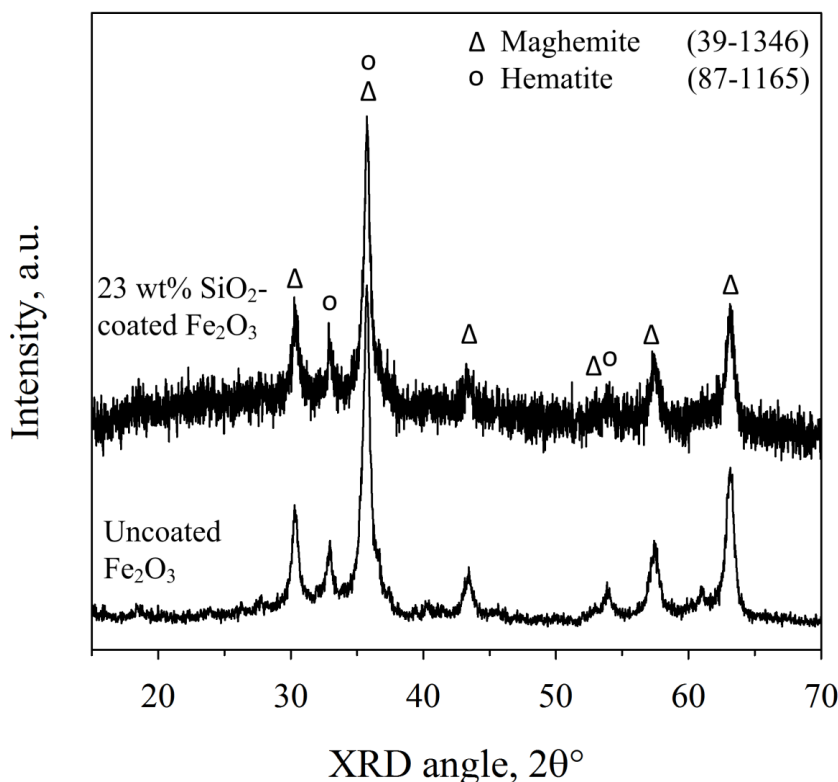


Figure S8. XRD of iron oxide and 23 wt% SiO₂-coated iron oxide.

X-ray diffraction demonstrates that both uncoated iron oxide and 23 wt% SiO₂-coated iron oxide are predominantly maghemite (γ -Fe₂O₃, PDF: 39-1346) with a small fraction of hematite (α -Fe₂O₃, PDF: 87-1165), in agreement with Teleki et al. The maghemite crystal size as obtained from the XRD patterns is 16 and 17 nm for uncoated and silica-coated iron oxide, respectively.

2a) General Procedure for synthesis of carbonates

In a typical synthesis, the 17 mL autoclave glass inset was charged with catalyst and epoxide. The autoclave was sealed and cooled with liquid N₂ to ca. -30 °C after which the atmosphere was replaced three times with CO₂. The reactor was then heated to ca. 20 °C and charged with the desired pressure of CO₂. The reaction was started by stirring and initializing reactor heating. Note that it took ca. 2 h to reach the desired reaction temperature of 120 °C (pressure was ca. 40 bar). After the desired reaction time, the reactor was removed from the heater and allowed to cool down to RT. Using liquid N₂, the reactor was cooled down to ca. -30 °C and vented slowly. The interior of the reactor and the rubber O-rings were carefully washed with acetone to extract all products and biphenyl was added to the solution as an internal standard. Product yields were determined by GC analysis (HP 6950, HP-5 column). The reaction conditions are similar to and were adapted from Zhang *et al.*¹

At the end of each cycle, the material was easily separated from the product. The remaining

magnetic nanoparticles were further washed with ethyl acetate and dried and subjected to the next run.

The results are reported in Table 4 and are the mean values of duplicate experiments. The reported yields were reproducible within $\pm 2\%$.

2b) General Procedure for the Palladium Scavenging

PdCl_2 (19 mg, 0.107 mmol), NaCl (125 mg, 2.14 mmol, 20 equiv.) and water (2.7 mL) were placed in a round-bottom flask. The flask was heated at 80 °C until PdCl_2 was dissolved. This clear reddish solution was cooled at room temperature and added to a suspension of magnetic material (100 mg) in water (2.0 mL). The suspension was stirred at room temperature for 3 h then an external magnet was applied and solution decanted.

2c) General Procedure for the Supported Proline Materials

In a round-bottom flask, L-proline (17.5 mg, 0.15 mmol) was dissolved in methanol (2 mL). To this solution the modified magnetic nanoparticle **4** (100 mg) was added. The mixture was shaken for few minutes then evaporated under reduced pressure for 25 h to give a light brown powder.

2d) General procedure for Aldol Reaction

A solution of 4-nitrobenzaldehyde (0.5 mmol) in acetone (2 mL) was added to supported proline material system (30% mol). The mixture was stirred at room temperature for 3.5 h. After this time, the reaction vessel was placed over a permanent magnet until the reaction suspension became transparent and the liquid was decanted. The liquid solution was evaporated, checked by ^1H NMR and finally purified by chromatography (light petroleum/ethyl acetate) to give the aldol product. The catalytic system was dried for a few minutes and then reused.

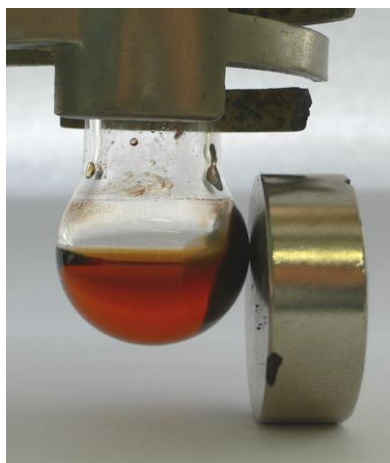


Figure S9. Application of a magnet, after 3 h, to a mixture of aqueous solution of Na_2PdCl_4 and Fe_2O_3 23wt% SiO_2 .



Figure S10. Application of a magnet to a diethyl ether suspension of **9** coated with bmimBF_4 (1:1 w/w).



Figure S11. Application of a magnet to a diethyl ether suspension of Fe_2O_3 coated with bmimBF_4 (1:1 w/w).

1. X. L. Zhang, D. F. Wang, N. Zhao, A. S. N. Al-Arifi, T. Aouak, Z. A. Al-Othman, W. Wei and Y. H. Sun, *Catal. Commun.*, 2009, **11**, 43.