Electronic Supplementary Material (ESI) for RSC Advances

Palladium Nanoparticles Supported on Ionic Liquid Modified, Magnetic Nanobeads – Recyclable, High-Capacity Catalysts for Alkene Hydrogenation

Roland Linhardt,[a] Quirin M. Kainz,[a] Robert N. Grass,[b] Wendelin J. Stark[b] and Oliver Reiser*[a]

[a] Institut für Organische Chemie, Universität Regensburg, Universitätsstr. 31, 93053 Regensburg, Germany. Fax: +49 941 943 4121; Tel: +49 941 943 4631; E-mail: oliver.reiser@chemie.uni-regensburg.de

[b] Institut für Chemie und Bioingenieurwissenschaften, Department Chemie und Angewandte Biowissenschaften, ETH Zürich, Wolfgang-Pauli-Str. 10, 8093 Zürich, Switzerland.

Supporting Information

1. **Materials and methods**
2. **Nomenclature of the nanobeads**
3. **GC data**
4. **Preparation of samples for ICP-OES analysis**
5. **IR spectra**
6. **TEM pictures**
7. **XRD measurements**
8. **NMR spectra**
9. **References**

1. Materials and methods

Carbon coated cobalt nanomagnets (Co/C, 20.5 m^2/g, mean particle size ≈ 25 nm) were purchased from Turbobeads Llc, Switzerland. Prior to use, they were washed in a concentrated HCl / water mixture (1:1) 5 times for 24 h. Acid residuals were removed by washing with millipore water (5x) and the particles were dried at 50°C in a vacuum oven.[1] All other commercially available compounds were used as received.

The magnetic nanobeads were dispersed using an ultrasound bath (Sonorex RK 255 H-R, Bandelin) and recovered with the aid of a neodymium based magnet (15 x 30 mm). They were characterized by IR-ATR spectroscopy (Biorad Excalibur FTS 3000), elemental microanalysis (LECO CHN-900), transmission electron microscopy (CM30 ST-Philips, LaB_6cathode, operated at 300 kV point resolution ~ 4 Å), x-ray powder diffraction, and inductively coupled plasma optical emission spectrometry (Spectro Analytical Instruments ICP Modula EOP).

Poly(benzylchloride)styrene coated cobalt nanoparticles **5**[2] and benzyl-alcohol functionalized cobalt nanoparticles **7**[3] were prepared on the gram scale following previously reported procedures.

$Pd_2(dba)_3 \cdot CHCl_3$ was purchased (Sigma-Aldrich) and used as received. As determined by the procedure reported by Ananikov *et al.*[4], the ratio of $Pd_2(dba)_3$:dba was 1:0.46, which reflects that 68% of the Pd content is present as $Pd_2(dba)_3$, while 32% of the Pd content are already present as Pd nanoparticles.

A solution of Na_2PdCl_4 in water (conc. 1 mg Pd per mL) was freshly prepared by mixing $PdCl_2$ (1 eq.) with NaCl (2 eq.) in H_2O using an ultrasound bath for 30 min.

NMR spectra were recorded with a Bruker AV 300 spectrometer with $CHCl_3$ as standard. Chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in Hertz (Hz). The signals in the spectra are described as d (doublet), t (triplet), and m (multiplet).

Gas chromatography was recorded on Fisons Instruments GC8000 equipped with a capillary (30 m x 250 µm x 0.25 µm) and flame ionization detector.

2. Nomenclature of the nanobeads

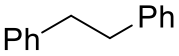
The nomenclature of the nanobeads is as follows:

Co/C	carbon coated cobalt nanoparticles
PS-IL@Co/C	poly(benzyl-methyl imidazolium chloride)styrene functionalized carbon coated cobalt nanoparticles
Bz-IL@Co/C	benzyl-methyl imidazolium chloride functionalized carbon coated cobalt nanoparticles
Spacer-IL@Co/C	benzamidopropyl-butyl-imidazolium bromide functionalized carbon coated cobalt nanoparticles
IL@Co/C	PS-IL@Co/C, Bz-IL@Co/C, and Spacer-IL@Co/C
Pd@PS-IL@Co/C	Pd NPs deposited on PS-IL@Co/C
Pd@Bz-IL@Co/C	Pd NPs deposited on Bz-IL@Co/C

Pd@Spacer-IL@Co/C	Pd NPs deposited on Spacer-IL@Co/C
Pd@IL@Co/C	Pd NPs deposited on IL@Co/C

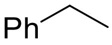
3. GC data

All products are literature-known and all spectroscopic data matched with those reported in the literature.



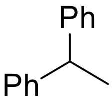
1,2-Diphenylethane[5]

1,2-Diphenylethane was prepared from *trans*-stilbene (360.5 mg, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 140 °C (3 min), 20 °C/min, 300 °C; t_R = dodecane (3.54 min), 1,2-diphenylethane (7.66 min), *trans*-stilbene (9.37 min).



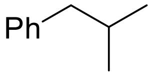
Ethylbenzene[6]

Ethylbenzene was prepared from styrene (228.9 µL, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 60 °C (3 min), 20 °C/min, 240 °C; t_R = ethylbenzene (4.29 min), styrene (4.65 min), dodecane (8.30 min).



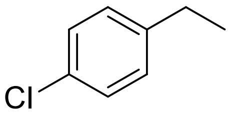
Ethane-1,1-diyldibenzene[5]

Ethane-1,1-diyldibenzene was prepared from ethane-1,1-diyldibenzene (283.0 µL, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 140 °C (3 min), 16 °C/min, 300 °C; t_R = dodecane (3.49 min), ethane-1,1-diyldibenzene (6.26 min), ethene-1,1-diyldibenzene (6.47 min).



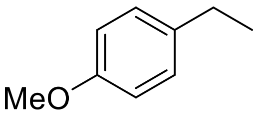
Isobutylbenzene[7]

Isobutylbenzene was prepared from (2-methylprop-1-en-1-yl)benzene (293.5 µL, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 60 °C (3 min), 24 °C/min, 300 °C; t_R = isobutylbenzene (6.01 min), (2-methylprop-1-en-1-yl)benzene (6.72 min), dodecane (7.80 min).



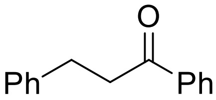
1-Chloro-4-ethylbenzene[6]

1-Chloro-4-ethylbenzene was prepared from 1-chloro-4-vinylbenzene (274.6 µL, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 100 °C (5 min), 25 °C/min, 300 °C; t_R = 1-chloro-4-ethylbenzene (4.51 min), 1-chloro-4-vinylbenzene (4.88 min), dodecane (7.12 min).



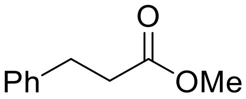
1-Ethyl-4-methoxybenzene[6]

1-Ethyl-4-methoxybenzene was prepared from 1-methoxy-4-vinylbenzene (269.2 µL, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 100 °C (5 min), 25 °C/min, 300 °C; t_R = 1-methoxy-4-vinylbenzene (4.90 min), 1-ethyl-4-methoxybenzene (5.64 min), dodecane (7.14 min).



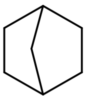
1,3-Diphenylpropan-1-one[5]

1,3-Diphenylpropan-1-one was prepared from chalcone (416.5 mg, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 140 °C (3 min), 16 °C/min, 300 °C; t_R = dodecane (3.52 min), 1,3-diphenylpropan-1-one (9.19 min), chalcone (10.22 min). The selective hydrogenation of the C=C double bond was proved by ^{1}H NMR and ^{13}C NMR: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.14 (m, 5H), 3.32 (t, *J* = 7.6 Hz, 2H), 3.09 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.3, 141.3, 136.9, 133.1, 128.7, 128.6, 128.5, 128.1, 126.2, 40.5, 30.2.



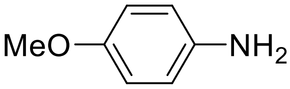
Methyl-3-phenylpropanoate[5]

Methyl-3-phenylpropanoate was prepared from methyl cinnamate (324.4 mg, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 100 °C (3 min), 20 °C/min, 300 °C; t_R = dodecane (5.95 min), methyl-3-phenylpropanoate (6.47 min), methyl cinnamate (7.43 min).



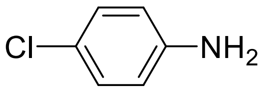
Bicyclo[2.2.1]heptanes[8]

Bicyclo[2.2.1]heptane was prepared from norbornene (188.3 mg, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 60 °C (3 min), 30 °C/min, 300 °C; t_R = norbornene (2.53 min), bicyclo[2.2.1]heptane (2.87 min), dodecane (7.27 min).



4-Methoxyaniline[9]

4-Methoxyaniline was prepared from 1-methoxy-4-nitrobenzene (306.3 mg, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 70 °C (3 min), 13 °C/min, 200 °C; t_R = 4-methoxyaniline (8.81 min), dodecane (9.01 min), 1-methoxy-4-nitrobenzene (10.92 min).



4-Chloraniline[9]
4-Chloraniline was prepared from 1-chloro-4-nitrobenzene (315.1 mg, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 50 °C (3 min), 5 °C/min, 170 °C; t_R = 4-chloroaniline (15.73 min), 1-chloro-4-nitrobenzene (16.64 min), dodecane (16.91 min).

4. Preparation of samples for ICP-OES analysis

General procedure for the preparation of Pd samples to determine the Pd amount on Pd@Co/C catalysts

5.0 mg Pd@Co/C were heated in 3.2 mL aqua regia for 30 min. Upon cooling, the mixture was diluted with H_2O (millipore grade) and after collecting the particles with an external magnet the solution was filtrated in a 10 mL measuring flask. After washing the particles for three times with H_2O with subsequent filtration the measuring flask was filled to 10 mL. The Pd concentration was then determined by ICP-OES analysis.

General procedure for the preparation of Pd and Co samples to determine the Pd and Co amount in hydrogenated products

250.0 mg 1,2-Diphenylethane was heated in 3.2 mL aqua regia for 30 min. Upon cooling, the mixture was diluted with H_2O (millipore grade) and filtrated in a 10 mL measuring flask. After washing the vial for three times with H_2O with subsequent filtration the measuring flask was filled to 10 mL. The Pd and Co concentration was then determined by ICP-OES analysis.

5. IR spectra

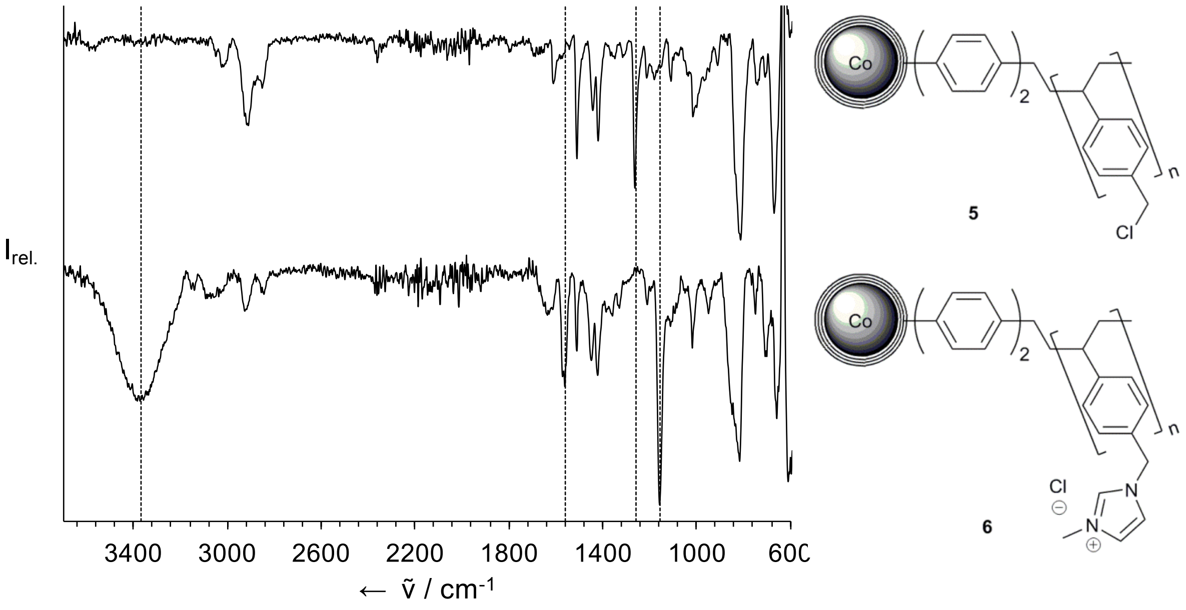


Figure S1. Example for following the reaction progress of the nanoparticle synthesis by IR spectroscopy. IR spectra of PS-Cl@Co/C **5** and PS-IL@Co/C **6** are shown.

6. TEM pictures

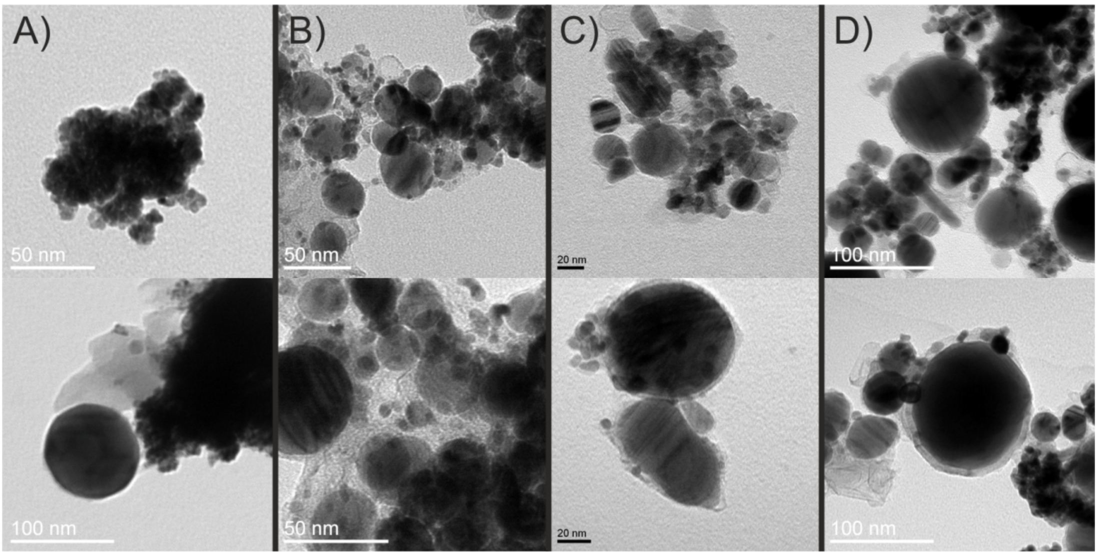


Figure S2. Transmission electron microscopy (TEM) pictures of A) Pd@PS-IL@Co/C **2b** (24 wt%), B) Pd@Bz-IL@Co/C **3b** (31 wt%), C) Pd@Spacer-IL@Co/C **4b** (34 wt%), and D) Pd@Spacer-IL@Co/C **4b** (34 wt%) after 12 cycles. Carbon coated cobalt nanopaticles have a diameter of 20-100 nm, while the Pd-NPs on the surface of the carbon coated cobalt nanoparticles have a diameter of 5-15 nm.

7. XRD measurements

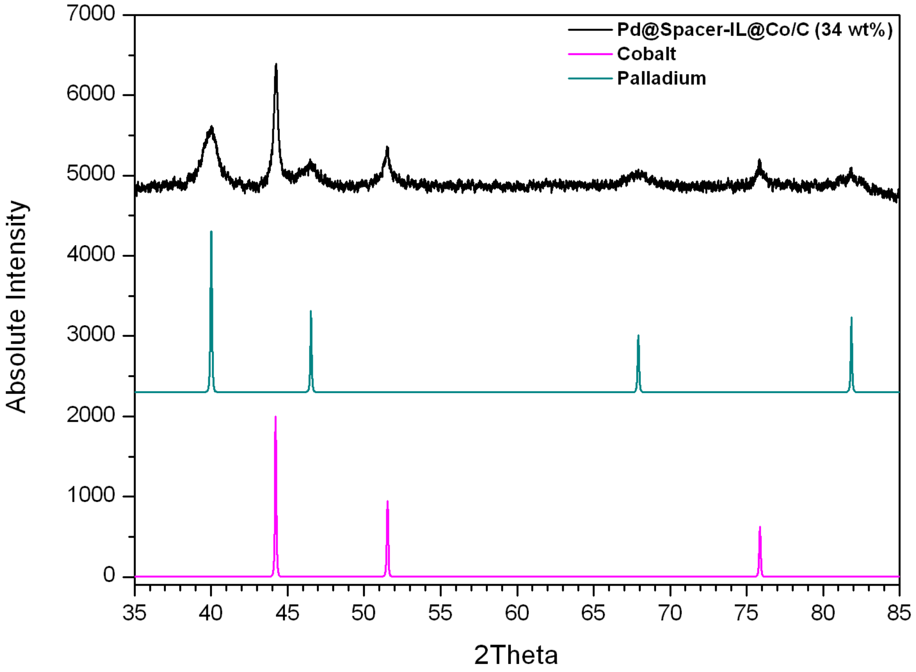
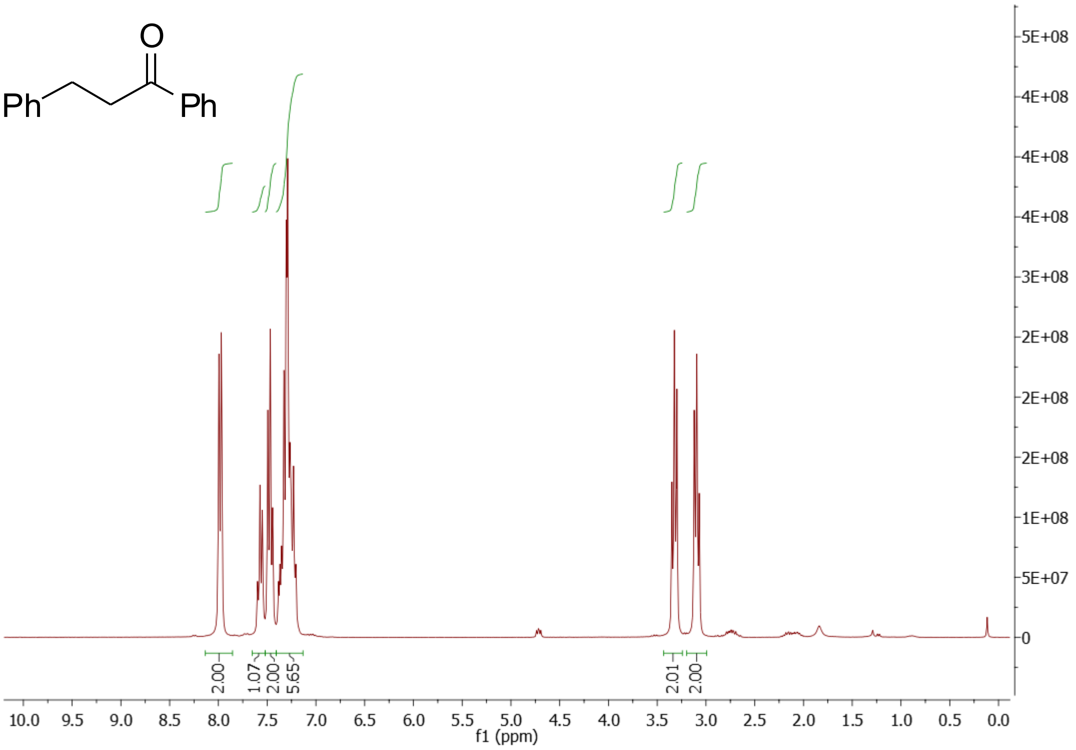
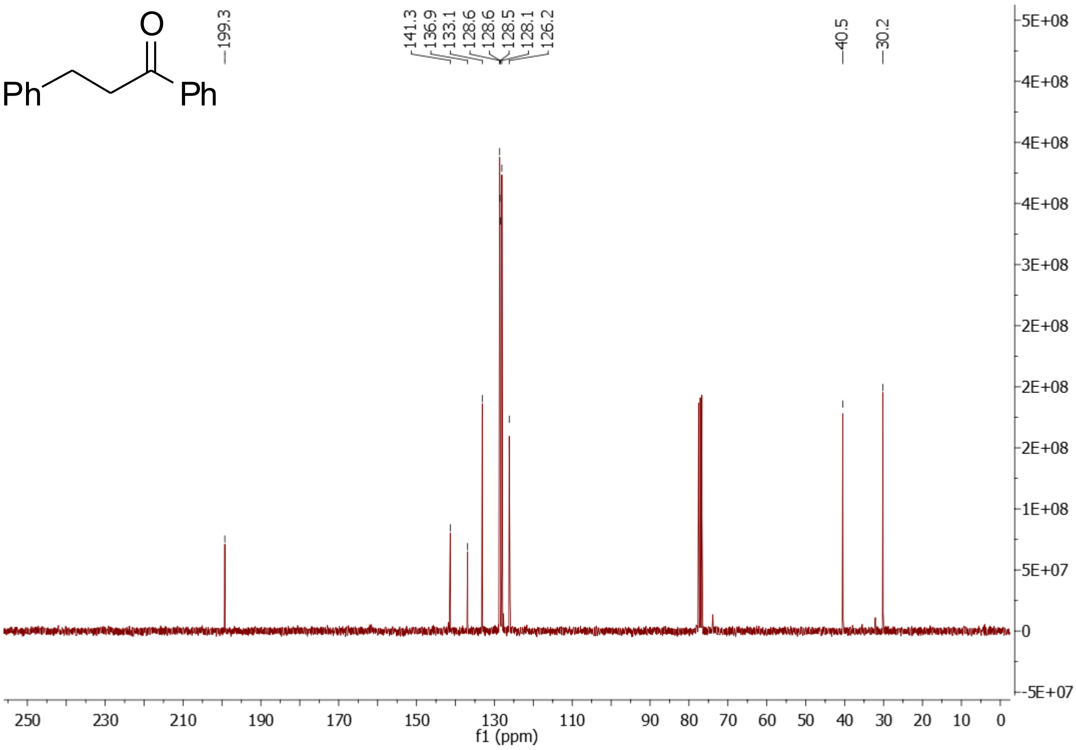


Figure S3. X-ray diffraction spectrum of Pd@Spacer-IL@Co/C **4b** with a palladium content of 34 wt%. The characteristic peaks for Co and Pd are detected.

8. NMR spectra





9. References

[1] M. Rossier, F. M. Koehler, E. K. Athanassiou, R. N. Grass, B. Aeschlimann, D. Günther and W. J. Stark, *J. Mater. Chem.*, 2009, 19(43), 8239.
[2] A. Schaetz, M. Zeltner, T. D. Michl, M. Rossier, R. Fuhrer and W. J. Stark, *Chem. Eur. J.*, 2011, 17(38), 10566.
[3] A. Schätz, R. N. Grass, W. J. Stark and O. Reiser, *Chem. Eur. J.*, 2008, 14(27), 8262.
[4] S. S. Zalesskiy and V. P. Ananikov, *Organometallics*, 2012, 31(6), 2302.
[5] F.-X. Felpin and E. Fouquet, *Chem. Eur. J.*, 2010, 16(41), 12440.
[6] D. J. Frank, L. Guiet, A. Käslin, E. Murphy and S. P. Thomas, *RSC Adv.*, 2013, 3(48), 25698.
[7] Y. S. Chun, J. Y. Shin, C. E. Song and S.-g. Lee, *Chem. Commun.*, 2008(8), 942.
[8] B. Nguyen and J. M. Brown, *Adv. Synth. Catal.*, 2009, 351(9), 1333.
[9] E. Vasilikogiannaki, C. Gryparis, V. Kotzabasaki, I. N. Lykakis and M. Stratakis, *Adv. Synth. Catal.*, 2013, 355(5), 907.