NJC

PAPER

Check for updates

Cite this: DOI: 10.1039/c8nj03433h

Transfer hydrogenation and hydration of aromatic aldehydes and nitriles using heterogeneous NiO nanofibers as a catalyst[†]

S. Thenmozhi and K. Kadirvelu 🕩 *

A simple and efficient hydrogen transfer reaction of aldehydes and hydration of nitriles using nickel oxide nanofibers (NiO NFs) as a heterogeneous catalyst is reported. NiO NFs prepared by electrospinning technique was cubic (confirmed by XRD) with an average diameter of 80 nm (obtained from HR-TEM) and utilized as a nanocatalyst for heterogeneous transfer hydrogenation of aromatic aldehydes and hydration of aromatic nitriles. All the reaction products produced with minimum reaction time and maximum yield were confirmed using GC-MS with NIST library. Furthermore, heterogeneity of the catalyst was confirmed with ICP-MS analysis. The as-prepared catalyst was reused for six cycles and was found to be efficient. Hence, the present catalytic synthesis of alcohols and amides may be an economically viable process.

Received 10th July 2018, Accepted 1st August 2018

DOI: 10.1039/c8nj03433h

rsc.li/njc

1. Introduction

Aromatic alcohols and amides are functional groups present in most of the organic precursors that are mainly used for the synthesis of pharmaceuticals, agrochemicals, bio-active molecules and fine chemicals.¹ The direct and single step synthesis of these compounds in a simple manner is hydrogenation/reduction of the corresponding carbonyls.² Hydrogenation could be performed either by directly using hydrogen gas (e.g., flow reactor method) or by using a hydrogen donor, such as alcohols, formates and NH₃BH₃. Kappe et al. reported an exclusive review on the heterogeneous catalytic direct hydrogenation of carbonyl, nitrile, nitro and unsaturated compounds in a detailed manner using a hydrogen gas flow reactor method.³ In addition, Metin et al. utilized ammonia borane as a hydrogen source instead of direct hydrogen and CoPd nanoparticles as a catalyst for the hydrogenation of aromatic nitro, nitrile and carbonyl compounds.⁴ Though the direct hydrogenation reactions were well developed for this purpose, they have some drawbacks, such as use of expensive (noble) metal catalysts, safety hazards, and use of pressurised H₂.⁵ Hence, a green, safe and cost effective alternate for the reduction reaction is of major interest among researchers, due to which an eco-friendly transfer hydrogenation (TH) or borrowing hydrogen method have been developed.⁶ According to our knowledge, starting from the original Meerwein–Ponndorf– Verley (MPV) reduction, till date, the transition metal catalyst plays a dominant role in the transfer hydrogenation process.^{7,8} Particularly, nickel-based catalysts have been proven to be highly efficient towards hydrogenation reactions.⁹ However, the use of large quantities of this catalyst keeps this method away from being environmentally benign. In this regard, nanoscale materials as catalysts have attracted researchers over other materials.

The conversion of nitriles to amides was traditionally well known, for which large quantity of KOH as active surface was used to reduce the reaction time.¹⁰ Further developments were reported on hydration of nitrile using different types of catalytic systems by various researchers.¹¹ Pillai *et al.* elaborated the mechanism for hydration of nitriles using heterogeneous MnO₂ catalyst. The group reported that factors such as surface nature, polarizability, surrounding ligand and oxidation state of the metal ion play a major role in this process.¹² With this background, we prepared simple and efficient NiO nanofibers using electrospinning technique and used them as heterogeneous nanocatalysts for the transfer hydrogenation of carbonyl and hydration of nitrile compounds.

2. Experimental section

2.1. General

Analar (AR) grade ultrapure poly(vinyl pyrrolidone) (PVP), nickel acetate, organic substrates of aldehydes and nitriles were purchased from Sigma Aldrich. Solvents, such as isopropyl alcohol (IPA), ethylacetate and dichloromethane were purchased from Merck Millipore. Nanofibers were prepared using E-spin Nano (Physics



View Article Online

Defence Research and Development Organisation-Bharathiar University Centre for Life Sciences, Bharathiar University Campus, Coimbatore – 641 046, India. E-mail: kadirvelukrishna@yahoo.com; Fax: +91-0422-2425459;

Tel: +91-0422-2428156

[†] Electronic supplementary information (ESI) available: TGA curve of composite nanofibers, porosity measurement of NiO NFs and GC-MS spectra of synthesised products. See DOI: 10.1039/c8nj03433h

Paper

Equipment Pvt. Ltd, India). A small portion of the nanofibers were placed on a carbon tape for EDAX analysis and coated with gold for SEM imaging (Quanta 200, ICON analytical). HR-TEM images and selected area electron diffraction (SAED) patterns were recorded for a dispersion of nanofibers in ethanol on the copper grid. Simultaneous Thermal Analyser (STA, Perkin Elmer, Germany) was employed for the thermal analysis of nanofibers. For this analysis, a small quantity (5 mg) of fibers was taken with alumina in a sample holder. Chemical nature of the fibers was obtained using Nicolet Avatar FT-IR and powder XRD (PAN Analytical using Cu Ka radiation) instruments. Synthesis of all the hydrogenated organic products was confirmed by GC-MS (Perkin Elmer, Germany, with NIST Library) equipped with capillary column (Restek, 0.3 mm diameter & 30 m length) and mass analyser. Heterogeneity of the nanocatalyst during the transfer hydrogenation process was confirmed by inductively coupled plasma with mass spectroscopy (ICP-MS, Thermo scientific company). For ICP-MS analysis, a small portion of the organic product was acid-digested with nitric and sulphuric acid (1:1 volume ratio) for 5 hours and finely diluted for the trace level detection or leaching of metal during the reduction process. All the analytical experiments were precisely performed in triplicate.

2.2. Preparation of metal oxide nanofibers

Based on our previous report on PVP,¹³ a homogenous mixture of 15 wt% PVP in dimethyl formamide (DMF) and 0.1 mM nickel acetate in ethanol (1:1 volume ratio) was taken in a hypodermic syringe to prepare metal–polymer composite nanofibers. One end of a high voltage power supply was connected to the syringe and the other was connected to the collector surrounded by an aluminium foil. Formation of "Taylore cone" was noticed at the optimised flow rate of 0.6 mL h⁻¹, high voltage of 12 kV and distance of 11 cm from tip to collector. Electrospinning was carried out for 8 h to obtain smooth and thick metal–polymer composite nanofibers. Thus, the obtained composite nanofibers were separated from the aluminium foil and calcinated at high temperature to obtain phase pure metal oxide nanofibers (NFs).

2.3. Transfer hydrogenation of aromatic aldehydes

Initially, 1 mM of substrate was added into the solution of IPA (5 mL) containing 2 mM of KOH and loaded with NiO NFs (3.7 mg, 5 mM) (Scheme 1). The reaction mixture was refluxed at 60 $^{\circ}$ C in a round bottom flask and monitored by thin layer chromatography (TLC). The molar ratio of the substrate and the catalyst to IPA was optimised for controlled release of hydrogen by constant volume addition method. After completion, the

solution was filtered to remove the catalyst and the organic products were extracted with (3 \times 5 mL) ethyl acetate (EA). All the separated products were dissolved in ethyl acetate for GC-MS analysis. The removed catalyst was washed with water and EA for the next cycle.

2.4. Hydration of aromatic nitriles

Aromatic nitriles (0.1 mM) were taken in a round bottom flask and 5 mL IPA, 1 mM potassium hydroxide and 3.7 mg NiO NFs were added (Scheme 2). Constant temperature of 40 $^{\circ}$ C was maintained throughout the reaction with continuous stirring. At 25 min, turbidity appeared in the reaction mixture and immediately, white precipitate settled at the bottom of the flask. The reaction mixture was collected with water and centrifuged to remove the nanocatalyst. Then, the solution was extracted with ethyl acetate for GC-MS analysis and pure solid products were crystallised from the solution.

3. Results and discussion

3.1. Preparation and characterisation of nanofibers

Preparation of direct metal oxide nanofibers using electrospinning technique has some difficulties, such as low viscous nature of the precursor and high surface tension due to the presence of metal ions. Hence, the polymer (PVP) as template material was chosen to prepare metal-polymer composite nanofibers. The as-prepared electrospun metal-polymer composite nanofibers were calcinated at 500 °C (TGA given in ESI†) to remove the polymeric template and produce pure NiO NFs. The composite and pure NiO NFs were irradiated with IR to get the functional transformation upon calcination, as presented in Fig. 1(a). As expected, the FT-IR spectrum of the metal-polymer composite nanofibers showed sharp peaks at 3510 cm⁻¹ (O-H str), 1620 cm⁻¹ (C=O str), and 1188 cm⁻¹ (C-N str) corresponding to PVP,¹³ while a single sharp peak at 520 cm^{-1} in the FT-IR spectrum of pure NiO NFs correspond to Ni-O bond stretching. These results confirmed that the polymer template was completely removed from composite NFs and produced pure NiO NFs. The composite and calcinated nanofibers were then subjected to powder X-ray analysis and the results are presented in Fig. 1(b). A broad spectrum at 20° corresponding to PVP was noticed in metal-polymer composite nanofibers. In the XRD pattern of calcinated fibers, sharp peaks at 2θ equal to 37.3° , 43.5° , and 62.9° corresponding to 111, 200, and 220 planes were noticed, which correspond to pure cubic NiO NFs.¹⁴ Lack of peaks at 20°



Scheme 1 NiO NFs catalysed transfer hydrogenation of aromatic aldehydes.



Scheme 2 Synthesis of aromatic amides from aromatic nitriles using NiO NFs as catalyst.

Paper



and except cubic phase proved that the obtained NiO nanofibers were free of polymer and had good phase purity.

The SEM image of the composite nanofibers (Fig. 2(a)) show smooth surfaces, with average single fiber diameter of 140 nm. Upon calcination, the smooth composite nanofibers turned into rough NiO nanofibers (Fig. 2(b)). Then, the average diameter of single fiber was decreased to 80 nm, which was confirmed from SEM and HR-TEM results. The change in pore structure from micropores to mesopores on calcination, due to the removal of PVP content in the nanofibers, was confirmed by porosity measurements (given in ESM). A small portion of pure NiO NFs were then subjected to high resolution transmission electron microscopy imaging (Fig. 2(c)). The SAED pattern, present in Fig. 2(c), shows bright spots rather than circles, ascribed to pure NiO NFs. Hence, the calcinated NFs were highly crystalline and the *d*-spacing values further confirmed the cubic phase. The EDAX spectrum revealed that NiO NFs possess 68% of Ni and 32% of oxygen in the calcinated product. The advantage of the proposed method for the preparation of NFs was also proved from the EDAX spectrum as no trace carbon impurities were present in the final NiO NFs.



Fig. 2 (a) SEM image of composite NFs, (b) HR-TEM image, (c) SAED pattern and (d) EDAX spectrum of NiO NFs.

3.2. Catalytic activity

3.2.1. Transfer hydrogenation of aromatic aldehydes. Having successfully prepared pure NiO nanofibers as catalyst, we investigated its efficiency towards transfer hydrogenation of aromatic aldehydes. Initially, 4-bromobenzaldehyde was selected as a model substrate with different solvents, such as methanol, ethanol, IPA and 1-butanol (Table 1, entries 15–17) to understand the solvent effect on hydrogenation process. Among the solvents investigated, IPA provided better yield than others in the present catalytic system. Then, molar ratio of solvent to substrate and catalyst was screened by constant volume addition of IPA. From these screening tests, 5 mL of IPA was chosen for further study. Furthermore, reaction conditions were optimised at various time, temperature, base and catalyst loading.

Table 1 details the progress of the reaction under different environmental conditions and their corresponding yield of the product. From the first two entries of Table 1, it is well understood that there is no progress in the reaction in absence of catalyst or base. Presence of strong hydroxyl base (KOH) accelerates the reaction towards rapid formation of reduced product than weak carbonate base (Table 1, entries 8, 12 and 13). Furthermore, temperature of the reaction was varied from 25 °C to 70 °C (Table 1, entries 3-8) and the optimum thermal energy required for the conversion was found to be 60 °C (Table 1, entry 7). The minimum quantity of the catalyst required for the completion of the reaction was verified from low to high catalyst loading (Table 1, entries 8-11) and 3.7 mg (0.005 mol%) of NiO NFs was chosen as optimum. With these optimised conditions, we further extended the scope of TH to other aromatic aldehydes to verify the efficacy of our NiO nanocatalyst. Benzaldehydes substituted with various electron donating and withdrawing groups were treated with the above conditions and as expected, these substrates produced the yield of above 90%. However, significant difference in the yield was found for three different halide-substituted benzaldehyde derivatives due to their position (ortho-steric effect), size and electronegativity values (Fig. 3,

 Table 1
 Optimisation of conditions for TH of 4-bromobenzaldehyde with IPA

S. no.	Base	Catalyst quantity (mg)	Temperature (°C)	Time (min)	GC vield (%)
5. 110.	0	-1y (mg)	(-)	()	<u>j====</u> (,o)
1	_	3.7	60	60	_
2	KOH	_	60	60	—
3	KOH	3.7	25	60	25
4	KOH	3.7	30	30	30
5	KOH	3.7	40	30	50
6	KOH	3.7	50	30	68
7	КОН	3.7	60	20	96
8	KOH	3.7	70	20	95
9	KOH	1.9	60	60	45
10	KOH	5.5	60	20	96
11	KOH	7.4	60	20	99
12	Na_2CO_3	3.7	60	30	25
13	K ₂ CO ₃	3.7	60	30	30
14	NaOH	3.7	60	20	50
15	КОН	3.7	60	60	10^a
16	КОН	3.7	60	60	20^{b}
17	КОН	3.7	60	60	45^c

Note: substrate (1 mM), KOH (2 mM) in IPA (5 mL). a Reaction in methanol. b Reaction in ethanol. c Reaction in 1-butanol.



Fig. 3 Hydrogenated products using NiO nanofibers as a heterogeneous catalyst. Note: substrate (1 mM), catalyst (3.7 mg), KOH (2 mM) in IPA (5 mL) at 60 °C. TOF in (per hour).

entries 1a–g). In case of alkyl substituted benzaldehyde, methyl group (+I effect) provides more electron density than the other groups on the carbonyl group, which hampers the yield (Fig. 3(1h and 1i)). The derivative with mono and di-substituted alkoxy ($-OCH_3$) groups afforded higher yield (Fig. 3(1g–i)) due to their electron withdrawing (-I effect) nature. The excellent yield for various substitutions could be explained by the unique properties, such as narrow diameter and more active sites per unit volume of NiO NFs catalyst. GC-MS spectra of the converted products are given in electronic ESI.†

3.2.2. Hydration of aromatic nitriles. The solid product obtained from the initial investigation of hydration with benzonitrile (BN) was analysed with GC-MS to confirm the expected product. The analytical results revealed that benzamide was the major product obtained in the above conversion (given in ESI[†]). Furthermore, the scope of the reaction was extended to chloride and fluoride substituted benzonitrile, both of which are difficult to react. Interestingly, both chloro- and fluoro-substituted benzonitriles afforded higher yield of corresponding amides (Fig. 4, 2b-f) without any change in their positions. Additionally, 2-nitrobenzonitrile, an electron withdrawing group-substituted BN, also yield 98% of 2-nitrobenzamide (Fig. 4, 2g) without any change in the position of the nitro group. This conversion showed the selectivity of the catalyst towards hydration of cyano group in the bi-functional molecule. This valuable feature extends the potential of the present catalyst for major pharmaceutical applications as this catalyst can hydrate the nitrile group without affecting the nitro moiety to enable further conversions.

3.3. Proposed mechanism for transfer hydrogenation and hydration of aromatic aldehydes and nitriles

Transfer hydrogenation process in homogeneous catalysis occurs by different pathways such as, direct hydrogen transfer, hydride



Fig. 4 Hydrated products with reaction time and GC-MS yield (isolated yields in parenthesis). Note: substrate (0.1 mM), catalyst (3.7 mg), KOH (1 mM) in IPA (5 mL) at 40 $^{\circ}$ C. TOF in (per hour).

transfer or ionic pathway. Particularly, in transition metal catalysed reactions, the most preferable mechanism is the hydride route (monohydride and dihydride) due to faster ligand exchange. The monohydride route is further divided into inner-sphere or outersphere mechanism based on the type of catalyst used in the process.^{6a} The dihydride mechanism was reported by Yus et al. using Ni nanoparticles as the catalyst in TH process.^{9a} Similarly, both the direct hydrogen and hydride transfer path was also followed in heterogeneous TH process, which was detailed in a review article by Gilkey and Xu.¹⁵ The ligand exchange in the homogeneous method and surface adsorption in the heterogeneous process leads to the formation of product by either of the two routes. In this study, NiO NFs provided more active surface for the adsorption of hydrogen from IPA, thus enhancing the activity through direct hydrogen transfer method by the formation of six membered intermediate between IPA, substrate and catalyst. In the hydration process, nucleophilic attack by water (from IPA and KOH) on the electron deficient carbon of $-C \equiv N$ (in benzonitrile) followed by tautomerisation produced hydrated products. The key role of the catalyst in this process was to afford more active surface, which could adsorb the substrate

(reactant and solvent) molecules and thus provides more proximity for rapid product formation.

3.4. Heterogeneity and leach proof test

To predict the nature of catalytic process in TH, the reaction was stopped in between and the catalyst was removed by centrifugation. Then, the reaction was continued further without the catalyst and was monitored by GC-MS. The regular reaction progress with respect to substrate and product is presented in Fig. 5(a). After the removal of catalyst at 10 min (substrate 1*), there was no progress in the reaction, which was confirmed by GC-MS. This result evidenced that the catalyst followed a heterogeneous path. Furthermore, catalyst leaching was examined with small quantity of product using ICP-MS. To our delight, there was no trace Ni detected in the final product. Most of the heterogeneous catalyst usually failed this test due to the metal leaching into the solution during processing, thus adding impurities to the product.^{8a} This is the first report on leach-free transfer hydrogenation of aldehydes and hydration of nitriles using NiO NFs as a heterogeneous catalyst.

3.5. Reusability test

Reusability of a catalyst is a major concern in large scale applications and makes the process environmentally more viable. Hence, the catalyst removed from the first cycle was utilized further for six times to prove its maximum efficiency. As expected, the catalyst was unaffected by solvent treatment and gave excellent yield of 95% (by GC-MS) even in the sixth run, similar to the fresh catalyst (Fig. 5(b)) without any changes in the properties.

3.6. Advantages over other methods

The present catalytic system affords product yield of above 90% with minimum reaction time of 15–60 min. Moreover, the catalyst is obtained using very simple preparation procedures and exhibits good reusability of six cycles with high efficiency. Recently, a similar type of transfer hydrogenation was reported by Ley *et al.* using flow chemistry method, which required high pressure and difficult



Fig. 5 (a) Reaction progress monitored by GC-MS (b) re-usability test.

handling procedures.¹⁶ In our synthesis procedure, IPA acts as the hydrogen source, which eliminates the issues of processing, toxicity as well as cost.

Moreover, hydration of nitrile was also performed under similar conditions, in which hydrogen from the IPA and hydroxyl ion from KOH produce water molecule needed for the hydration process. Thus, water generated in situ in the reaction was utilized for the production of amides from nitriles. Similarly, a recent report from Hawkins et al. (the same group of Ley and co-workers) provided MnO₂ catalysed hydration of nitriles by flow chemistry process using mono and dinitriles as substrates within 15 min. However, the major problem associated with their method for large-scale synthesis was the construction of flow column, difficult handling procedures, blocking of heavy MnO2 powder on the reactor, and lack of the reuse of the reaction vessel for the next batch.¹⁷ A similar type of study using microwave irradiation at 130 °C was reported by Polshettiwar and Varma on hydration of aliphatic, aromatic and heterocyclic nitriles with nanoferrite-Ru(OH) as the heterogeneous catalyst.18

In comparison to the abovementioned reports, a single-step rapid transfer hydrogenation of aldehydes and hydration of nitriles using NiO nanofibers as a heterogeneous catalyst was superior with advantages of mild reaction conditions with minimum catalyst loading. In addition, easy separation reusability of catalyst and were the added advantages of this method for scaling.

4. Conclusion

The electrospun pure-phase cubic NiO nanofibers were prepared and studied for its catalytic efficiency towards transfer hydrogenation of aromatic aldehydes and hydration of aromatic nitriles. All the catalytic reactions proceeded well with minimum time (15–60 min) and maximum yield (above 90%). The major advantage of this method is non-leaching of the metal in the final product and reusability of the catalyst for six cycles. The use of green solvents, absence of by-products and mild reaction conditions make the catalytic system prepared in this present work advantageous over the existing catalytic systems. Hence, the present catalytic system could be upscaled for various pharmaceutical and fine chemical applications.

Conflicts of interest

Authors declare no conflict of interest.

Acknowledgements

The authors are thankful to Defence Research and Development Organisation (DRDO) for the financial support. Authors acknowledge the major scientific contribution of Dr N. Dharmaraj.

References

- (a) K. Yamaguchi, H. Kobayashi, T. Oishi and N. Mizuno, Angew. Chem., Int. Ed., 2012, 51, 544–547; (b) B. M. Trost and I. Fleming, Comprehensive Organic Synthesis., Pergamon, Oxford, UK, 1991; (c) S. K. Mohapatra, S. U. Sonavane, R. V. Jayaram and P. Selvam, Org. Lett., 2002, 4, 4297–4300.
- 2 (a) F. Kallmeier, T. Irrgang, T. Dietel and R. Kempe, Angew. Chem., Int. Ed., 2016, 55, 11806–11809; (b) N. Kalutharage and C. S. Yi, J. Am. Chem. Soc., 2015, 137, 11105–11114.
- 3 M. Irfan, T. N. Glasnov and C. O. Kappe, *ChemSusChem*, 2011, 4, 300–316.
- 4 H. Goksu, H. Can, K. Sendil, M. S. Gultekin and O. Metin, *Appl. Catal.*, *A*, 2014, **488**, 176–182.
- 5 D. Wang, C. Deraedt, J. Ruiz and D. Astruc, *J. Mol. Catal. A: Chem.*, 2015, **400**, 14–21.
- 6 (a) J. S. M. Samec, J. Backvall, P. G. Andersson and P. Brandt, *Chem. Soc. Rev.*, 2006, 35, 237–248; (b) S. K. Mohapatra, S. U. Sonavane, R. V. Jayaram and P. Selvam, *Tetrahedron Lett.*, 2002, 43, 8527–8529; (c) Z. Shao, S. Fu, M. Wei, S. Zhou and Q. Liu, *Angew. Chem., Int. Ed.*, 2016, 55, 14653–14657.
- 7 D. Wang and D. Astruc, Chem. Rev., 2015, 115, 6621-6686.
- 8 (a) V. Polshettiwar, B. Baruwati and R. S. Varma, *Green Chem.*, 2009, 11, 127–131; (b) B. Baruwati, V. Polshettiwar and R. S. Varma, *Tetrahedron Lett.*, 2009, 50, 1215–1218.
- 9 (a) F. Alonso, P. Riente and M. Yus, Acc. Chem. Res., 2011, 44, 379–391; (b) M. D. L. Page and B. R. James, Chem. Commun., 2000, 1647–1648; (c) J. A. Garduno and J. J. Garcia, ACS Omega, 2017, 2, 2337–2343; (d) N. C. Blanco, A. Arevalo and J. J. Garcia, Dalton Trans., 2016, 45, 13604–13614.
- 10 J. H. Hall and M. J. Gisler, J. Org. Chem., 1976, 41, 3769-3770.
- (a) S. Elangovan, C. Topf, S. Fischer, H. Jiao, A. Spannenberg, W. Baumann, R. Ludwig, K. Junge and M. Beller, *J. Am. Chem. Soc.*, 2016, **138**, 8809–8814; (b) S. Werkmeister, J. Neumann, K. Junge and M. Beller, *Chem. – Eur. J.*, 2015, **21**, 12226–12250.
- 12 S. C. Roy, P. Dutta, L. N. Nandy, S. K. Roy, P. Samuel, S. M. Pillai, V. K. Kaushik and M. Ravindranathan, *Appl. Catal.*, A, 2005, **290**, 175–180.
- 13 S. Thenmozhi and N. Dharmaraj, J. Nanosci. Nanotechnol., 2018, 18, 234.
- 14 S. R. Hosseini, S. Ghasemi, M. Kamali-Rousta and S. R. Nabavi, *Int. J. Hydrogen Energy*, 2017, **42**, 906–913.
- 15 M. J. Gilkey and B. Xu, ACS Catal., 2016, 6, 1420-1436.
- 16 C. Battilocchio, J. M. Hawkins and S. V. Ley, *Org. Lett.*, 2013, 15, 2278–2281.
- 17 C. Battilocchio, J. M. Hawkins and S. V. Ley, *Org. Lett.*, 2014, 16, 1060–1063.
- 18 V. Polshettiwar and R. S. Varma, *Chem. Eur. J.*, 2009, **15**, 1582–1586.