Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Nanoheterogeneous Catalysis in Electrochemically Induced Olefin Perfluoroalkylation

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Ni-catalyzed electroreductive olefin perfluoroalkylation affords both monomeric and dimeric products depending on the reaction media. Recycling of the catalyst can be achieved by immobilization of (bpy)$NiBr_2$ complex on silica nanoparticles decorated with anchoring amino-groups. Switching the homogeneous and heterogeneous catalysts is found to be one more factor to control the products ratio. This catalytic technique is both green and atom economical and unites the advantages of nanoheterogeneous catalysis and electrocatalysis.

Introduction

Nowadays green and sustainable development of chemical processes requires advanced transformations and pollution abatement. Some of the more sophisticated chemical transformations involve homogeneous catalysis. In a number of instances, however, industrial application of homogeneous catalysis is complicated by difficulties in separating catalysts and products. These problems are particularly important in the case of noble or/and toxic organometallic species.[1] Converting homogeneous catalysis into heterogeneous catalysis is one approach for facilitating separations and making such transformations more environmentally friendly. Heterogenation of known catalytically active transition metal complexes, such as those based on nickel and palladium, is an attractive strategy for modern day coupling reactions, due to easy separation and recycling of the catalyst.

Traditional micrometric scale catalysts widely used in the chemical industry show lower activity and selectivity in comparison with homogeneous catalysts owing to steric and diffusion factors.[2,3] As the size of the system decreases to nanoscale the surface area of the support increases, reactions may suffer from the formation of homogeneous bulk emulsions.[3,4] Another advantage of the use of nanoparticles is that they are not porous supports and they do not exhibit difficulties in reagents and products transport to/from catalytic centres and bulk solution.

Nanocomposites have been tested in some catalytic and classical organic reactions,[1,5] cross-couplings, and photocatalysis,[6] but have never been used in electrochemical reactions. The closest electrochemical examples are systems based on polymer matrices containing organic moieties capable of coordination to transition metal ions. Such systems are obtained by electrochemical anode dissolution in the presence of polymeric ligand, although the catalytic transformation step occurs without electrochemical aid.[7]

In recent years, electrochemically generated catalysts have become increasingly important both for fine organic synthesis and for detailed studies of electron transfer, bond cleavage/breaking, substitution, addition and other reactions. One area that may benefit from the development of heterogeneous electrochemical methods is organofluorine chemistry. Organofluorine compounds are widely used in biochemistry, medical, and materials chemistry due to their unique properties.[8] Among the fluorine-containing functional groups, perfluoroalkyl groups are of special interest and new methods for their incorporation into organic substrates are needed.[9]

Recently, we developed a one-step electrocatalytic homogeneous fluoroalkylation of olefinic substrates promoted by reduced Ni complexes bearing α-diimine ligands, which led to dimeric addition-dimerization products.[10] A way to prevent the dimerization process and to obtain a monomeric product was also shown in these studies.[10e]

The present study unites the advantages of two different approaches — nanoheterogeneous catalysis (easy catalyst recycling) and electrocatalysis (generation and regeneration of the catalyst active form on the electrode surface without any additional molecular reductant) — to develop a new effective catalytic technique that is both green and atom economical. Such a technique offers exceptional control over the phase behavior and catalyst separation.

Results and discussion

The overall goal of this work is to develop a nanoheterogeneous catalyst for olefin fluoroalkylations (Table 1) and to find ways to control the product ratio (monomer/dimer) in the reactions. Moreover, it is important to compare the activity and selectivity of the heterogeneous process with the previously

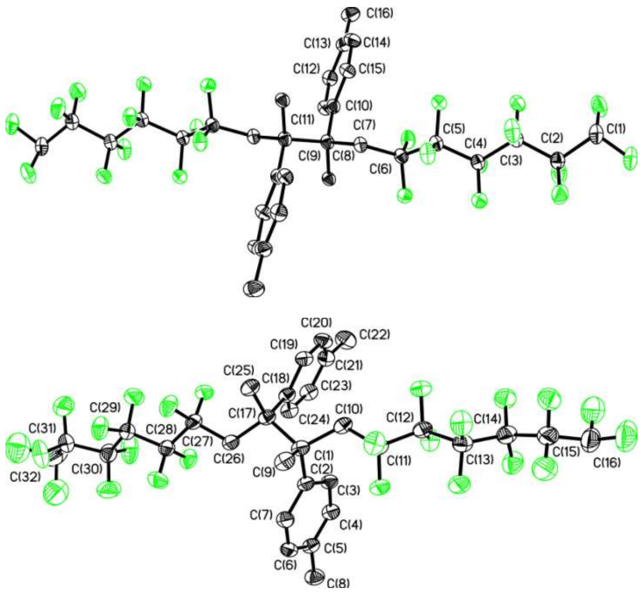
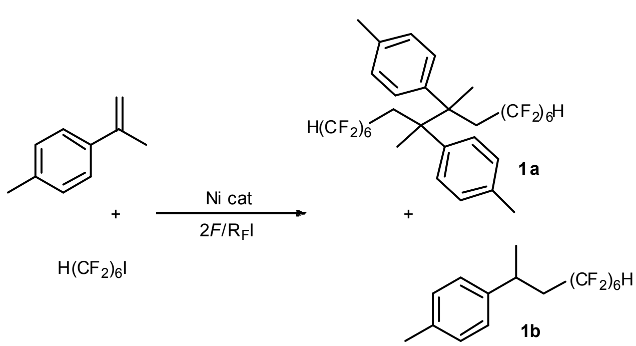


Fig. 1 ORTEP diagrams of **1a**: R,S (top) and S,S/R,R (bottom) isomers. All H atoms are omitted for clarity

studied homogeneous ones for future reaction development. The reaction described in Table 1 was investigated. Previously tested α-methylstyrene[10] and α,4-dimethylstyrene were used as the organic substrates, $H(CF_2)_6I$ was used as the perfluoroalkyl source due to its convenience for ^1H NMR analysis, [(bpy)$NiBr_2$] complex was used as the catalyst as it was previously found to be very effective for similar electrocatalytic reactions.[10] Switching homogeneous and heterogeneous catalysts is accompanied with changes in several reaction conditions. The role of the reactant stoichiometries, amount and the state of the catalyst (homogeneous or immobilized), and the presence of water (carried by silica nanoparticles synthesized in an aqueous solution) were considered in optimizations.

Table 1 Perfluoroalkylation of α,4-dimethylstyrene[a]



Entry	Solvent	Catalyst	**1a**/**1b**	Total yield [%]
1	DMF	(bpy)$NiBr_2$ (10%)	1.0 : 0.0[b]	71
2	DMF	(bpy)$NiBr_2$ (1%)	1.0 : 0.0[b]	60
3	DMF:H_2O (4:1)	(bpy)$NiBr_2$ (1%)	1.0 : 0.8	48
4	DMF:H_2O (4:1)	(bpy)$NiBr_2$ (1%) on AEPTS-SNs	1.0 : 0.45	44

[a] Reaction conditions: Substrate ratio 1:1, Q=2*F* per $H(CF_2)_6I$, -1.5V. [b] Monomeric product was observed in trace amount.

The joint electrochemical reduction of olefin and perfluoroalkyl

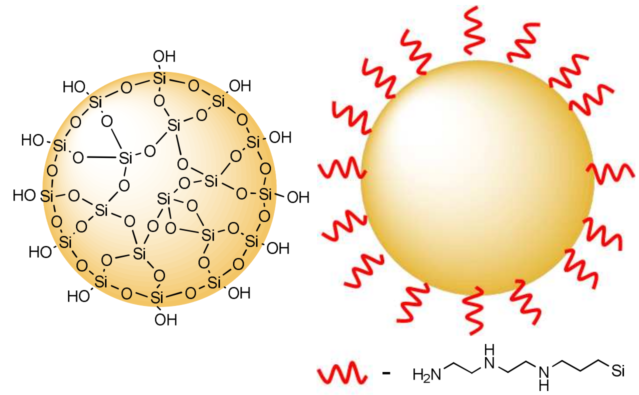


Fig. 2 Schematic representation of the AEPTS-SNs

halide (1:1) in anhydrous DMF at the potential of [(bpy)$NiBr_2$] reduction (-1.5 V) was shown to afford a dominant addition-dimerization product.[10] Thereafter joint electro-reduction of α,4-dimethylstyrene and 6-*H*-perfluorohexyl iodide in the presence of [(bpy)$NiBr_2$] (10 % mol) gave the dimeric product **1a** in 71 % yield (Entry 1). Two isolated stereoisomers of **1a** could be separated from the reaction mixture and were characterized crystallographically (Fig 1). Decreasing the catalyst amount to 1% mol resulted in a lowering of the yield by 10 % (entry 2).

Switching the reaction media to a DMF-water mixture afforded both dimeric and monomeric products in dimethylstyrene perfluoroalkylation (Table 1, entry 3). Although the general yield was lower in comparison with anhydrous DMF media, the result presented water as a more convenient, available and environmentally friendly alternative to Bu_3SnH[10e] as the hydrogen atom source in the monomeric product synthesis.

Conversion of a homogenous catalyst to a heterogeneous one results from immobilization of the Ni(II) complex on silica nanoparticles (SNs). The immobilization may be distinguished by physical and/or electrostatic adsorption of metal complexes at a silica/water interface or by inner sphere coordination of Ni(II) complexes via some anchoring groups at the silica surface. The [(bpy)$NiBr_2$] complex lacks a net positive charge, but in theory it can be fixed at the silica surface through coordination bonds with convenient anchoring groups such as amino-groups.

The SNs were obtained as 35±5 nm sized beads[11] through a well-documented water-in-oil microemulsion procedure[12] and decorated by treatment with 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilan (AEPTS)[13]. The fluorescamine-based quantitative fluorescent analysis[14] revealed the average number of NH_2-groups to be 3500 per each SN. Immobilization of the [(bpy)$NiBr_2$] complex on the SNs was performed by mixing their aqueous solutions, followed by phase separation of the SNs with further washing of the separated SNs by DMF in order to wash out water (see SI for details). The average number of the Ni(II) complex (3700) per each SN was calculated from the difference between the concentrations of the Ni(II) complex in the aqueous solution before and after the immobilization on the SNs. This number is in good agreement with the number of NH_2-groups per each SN, which suggests coordination bonds versus physical or electrostatic adsorption as the main driving force of the immobilization. Figure 2 shows schematic representation of the

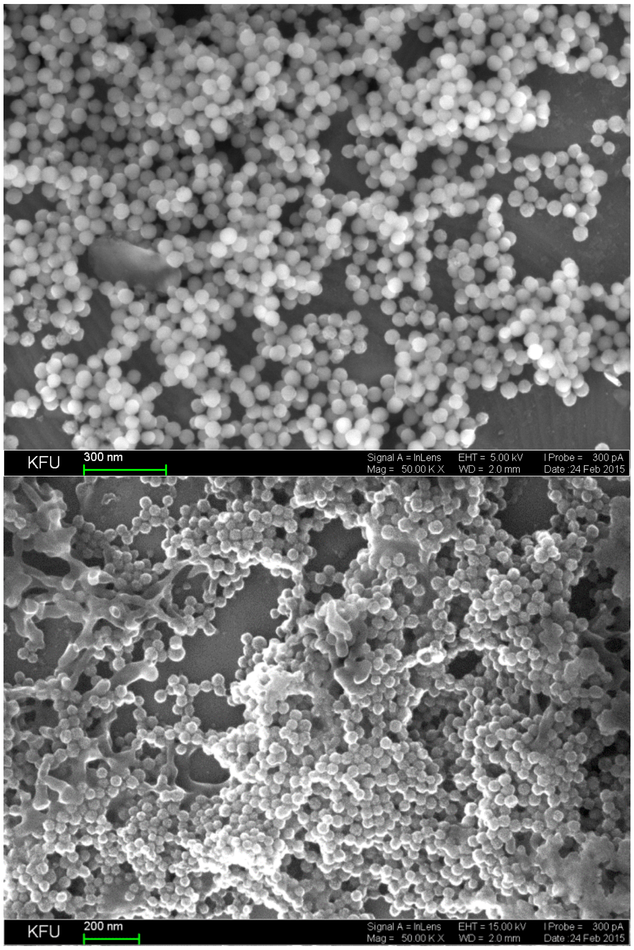


Fig. 3 SEM (scanning electron microscopy) images of the AEPTS-SNs with immobilized [(bpy)NiBr$_2$] complex before (top) and after fluoroalkylation reaction (bottom)

AEPTS-SNs. The average size of the SNs with the immobilyzed catalyst was 55±5 nm. The SEM (scanning electron microscopy) images of the AEPTS-SNs with immobilized [(bpy)NiBr$_2$] complex before and after fluoroalkylation reaction are shown in Figure 3.

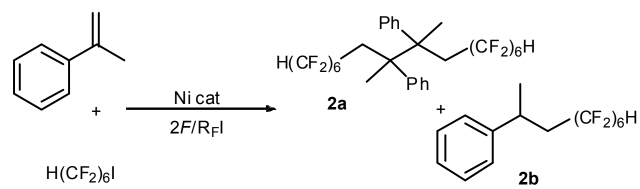
Comparison of homogeneous and heterogeneous reactions performed under the same conditions (DMF-water ratio, amount of the catalyst) shows a difference in the monomer-dimer ratio, however the total yields do not depend on the catalyst phase (Table 1, entries 3 and 4). The amount of the monomeric product was lower in reactions with immobilized catalyst. The ratio of dimers diastereomeric forms (meso and dl) did not depend on the catalyst phase and the reaction media. According to NMR spectra (^{1}H and ^{19}F) it was equal to 1:1 in reactions with α-methylstyrene and α,4-dimethylstyrene. Amount of the electricity passed was found to have no affect on the monomer-dimer ratio. The total yield did not increase by passing over 2*F* electricity per perfluoroalkyl halide.

A set of experiments with varied catalyst states and organic solvent-water ratios were carried out to determine the parameters effecting the product ratio in α-methylstyrene perfluoroalkylation (Table 2).

Water was found to promote the monomeric product formation that is illustrated in Table 2 by entries 1 and 2 with 89 and 80 % DMF and entries 3 and 4 with 80 and 67 % DMF respectively, while no transformation of the olefinic substrate was observed in pure water media (entry 5). The optimal DMF-water ratio affording to both products in good yields was found to be 4:1.

Monomeric product was obtained in a reaction with the immobilized catalyst performed in dry DMF (Table 2, entry 6), however, in lower yields than that seen in entries 1 and 2 (DMF-water mixtures) of Table 2. Reaction 3 carried out with the homogeneous catalyst and admixture of AEPTS-SNs shows the average monomer-dimer ratio between the homogeneous catalysis (entry 7) and heterogeneous catalysis (entry 2) in the same conditions. Thus the dimerization reactions are preferred when the catalyst is immobilized at the heterogeneous silica surface. Presumably, less access to water molecules near the hydrophobic AEPTS-SN surface containing immobilized and metal-containing active sites suppresses the rate of monomer formation. A model synthesis (entry 8) in dry DMF with addition of BuNH$_2$ revealed no influence of the surface amino groups on the reaction. Replacement of DMF with acetonitrile in aqueous organic media did not affect in yields and the product ratio for reactions with the immobilized catalyst (entry 9).

Table 2 Perfluoroalkylation of α–methylstyrene[a]



Entry	Solvent	Catalyst	**2a/2b**	Total yield [%]
1	DMF:H$_2$O (8:1)	(bpy)NiBr$_2$ (1%) on AEPTS-SNs	1.0 : 1.7	48
2	DMF:H$_2$O (4:1)	(bpy)NiBr$_2$ (1%) on AEPTS-SNs	1.0 : 1.4	45
3	DMF:H$_2$O (4:1)	(bpy)NiBr$_2$ (1%) + added AEPTS-SNs	1.0 : 2.7	46
4	DMF:H$_2$O (2:1)	(bpy)NiBr$_2$ (1%) + added AEPTS-SNs	1.0 : 4.1	29
5	H$_2$O	(bpy)NiBr$_2$ (10%)	No reaction	
6	DMF	(bpy)NiBr$_2$ (1%) on AEPTS-SNs	1.0 : 0.8	53
7	DMF:H$_2$O (4:1)	(bpy)NiBr$_2$ (1%)	1.0 : 3.8	44
8	DMF:H$_2$O (4:1)	(bpy)NiBr$_2$ (1%), BuNH$_2$[b]	1.0 : 3.5	48
9	CH$_3$CN:H$_2$O (4:1)	(bpy)NiBr$_2$ (1%) on AEPTS-SNs	1.0 : 1.1	41
10[c]	DMF:H$_2$O (4:1)	(bpy)NiBr$_2$ (10%)	1.0 : 1.1	94

[a] Reaction conditions: Substrate ratio 1:1, Q=2*F* per H(CF$_2$)$_6$I, -1.5V. [b] Substrates:catalyst:BuNH$_2$ ratio is 1:1:0.01:0.1. [c] α-Methylsterene:H(CF$_2$)$_6$I ratio is 1:4.

The data presented in Tables 1 and 2 reveal the immobilization of [(bpy)NiBr$_2$] on the AEPTS-SNs is one more factor affecting the monomer-dimer ratio in electrocatalytic perfluoroalkylation reactions. This tendency suggests an impact of coordination bonds versus physical and/or electrostatic adsorption in the immobilization of [(bpy)NiBr$_2$] complex on the AEPTS-SNs. Immobilization of the [(bpy)NiBr$_2$] complex through outer-sphere coordination with aminoethylaminoethylaminopropyl groups at the SNs surface is suggested to hinder access of water to coordination site that can be the reason of the aforementioned different monomer:dimer ratio. The post-catalysis picture (Figure 3, bottom) shows no signs of the catalyst reduction to metal nanoparticles. The catalytic reaction occurs at nickel centers, and noted the catalyst active form is not metal nanoparticles, but low-valent nickel species immobilized on the modified surface of silica nanoparticles.

The decrease in total yields of the isolated products in reactions carried out in aqueous organic media is likely associated with partial deactivation of the catalyst active forms by water. Such reactivity is known for nickel-catalysed electroreductive reactions in proton-donor media.[15]

Higher product yields can be achieved by increasing the amount of perfluoroalkyl halide. Thus, joint electrolysis of α-methylstyrene, 6-H-perfluorohexyl iodide (1:4 ratio), $[(bpy)NiBr_2]$ (10 mol %) led to a mixture of dimeric and monomeric products in 1.0:1.1 ratio in 94 % total yield (entry 10, Table 2).

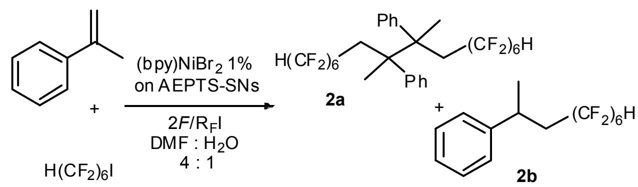
Another challenging aim of the study was to estimate the stability of the immobilized catalyst and its capability for recycling. No leakage of the Ni(II) complex immobilized on the AEPTS-SNs was detected by electrochemical analysis (the lower detection limit is 10^{-4} M) of the washing DMF solutions. The washing solutions were obtained through the phase separation of the DMF and aqueous-DMF dispersions of the AEPTS-SNs (10.9 $g{\cdot}L^{-1}$) with immobilized $[(bpy)NiBr_2]$ complex ($1.7{\cdot}10^{-3}$ M). The elemental analysis revealed the amount of nickel on the support (Ni:Si ratio) did not decrease after reaction that also confirms there is no leakage of the catalyst into the bulk solution. Moreover the Ni:Br ration after reaction was found to be 1:2, that shows the bromide likely remains coordinated to nickel during the catalytic cycle. Moreover, a catalytic test of filtrate showed it is not catalytically active, no transformation of the olefinic substrate was observed (see SI). Thus, there is no leaching of the complex from the support.

The immobilized catalyst was tested in several reaction cycles in α –methylstyrene perfluoroalkylation. The results in Table 3 demonstrate that the yields of product from reactions run with recycled catalyst do not vary, supporting a heterogeneous reaction process. After each of the rounds in Table 3, the reaction mixture was centrifuged to separate the immobilized catalyst. The nanoparticles were washed with DMF-water mixture (4:1), dispersed in water and used directly for the next synthesis. Triple use of such catalyst led only to negligible decrease in the products yield. After three reaction cycles no loss of the catalytic activity of the immobilized catalyst was observed.

Conclusions

The present work employs inner-sphere coordination of $[(bpy)NiBr_2]$ through amino-groups fixed on the surface of the amino-decorated silica nanoparticles as an efficient tool to switch from homogeneous to heterogeneous perfluoroalkylation catalysis. The introduced heterogeneous catalyst preparation provides sustained immobilization of the complex on AEPTS-SNs. The absence of leaching was confirmed by several independent techniques. After easy and quantitative separation from the reaction mixture the catalyst retains its high catalytic activity and can be reused. The results indicate that the addition of water to the reaction mixture increases the monomer/dimer

Table 3 Use of recycled $(bpy)NiBr_2$ catalyst (1 %) immobilized on



AEPTS-SNs[a]

Number of repeats	**2a/2b**	Total yield [%]
1	1.0 : 1.4	45
2	1.0 : 1.1	42
3	1.0 : 0.8	42

[a] Reaction conditions: Substrates ratio 1:1. Q=2*F* per $H(CF_2)_6I$, -1.5 V.

ratio significantly.

Although the diffusion coefficient was supposed to be an important factor for the system efficiency as the catalyst active form regeneration occur at the electrode surface, we found it to be negligible. No difference in electrosynthesis proceeding with homogeneous and heterogeneous catalysts was observed, and the electrosynthesis parameters (the cell current and potential) were the same for galvanostatic (cathodic current density from 2 to 50 mA/cm^2) and potentiostatic processes at the cathode potential equal to the first reduction wave for $[(bpy)NiBr_2]$ (-1.5 V vs. $Ag/AgNO_3$ reference electrode).

It should be mentioned that the electrocatalytic reactions reported herein generate sites of potential chirality, and we are currently exploring possibilities of enantioselective olefin perfluoroalkylations catalyzed by nickel complexes containing chiral ligands such as pybox (pybox= 2,6-bis[(4*S*)-4-phenyl-2-oxazolinyl]pyridine).

Acknowledgements

This work was supported by a RFBR grant 14-03-31774. D.A.V. thanks the Office of Basic Energy Sciences of the U. S. Department of Energy (DE-FG02-07ER15885).

Notes and references

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† Electronic Supplementary Information (ESI) available: text, Figures giving ^{1}H, ^{13}C, and ^{19}F NMR spectra. See DOI: 10.1039/b000000x/

‡ Crystal data for **1a R/S** isomer: formula $C_{32}H_{26}F_{24}$, *MW* = 866.53, *a* = 7.7287(9), *b* = 24.374(3), *c* = 9.3149(11) Å, β = 102.310(3)°, *V* = 1714.4(3)$Å^3$, ρ_{calc} = 1.679 g cm^{-3}, μ= 0.189 mm^{-1}, empirical absorption correction (0.956 ≤ T ≤ 0.970), *Z* = 2, monoclinic, space group $P2_1/n$, T = 135 K, ω scans, 27008 reflections collected (±*h*, ±*k*, ±*l*), θ_{max} = 27.90°, 4084 independent (R_{int} = 0.031) and 3237 observed reflections [$I \geq 2\,\sigma(I)$], 254 refined parameters, *R* = 0.054, wR^2 = 0.140, max. residual electron density 0.58 (-0.31) e $Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

Crystal data for **1a SS/RR** isomer: formula $C_{32}H_{26}F_{24}$, *MW* = 866.53, *a* = 27.503(2), *b* = 11.0537(9), *c* = 11.5143(9) Å, β = 99.686(2)°, *V* = 3450.5(5)Å^3, ρ_{calc} = 1.668 g cm^{-3}, μ= 0.188 mm^{-1}, empirical absorption correction (0.956 ≤ T ≤ 0.993), *Z* = 4, monoclinic, space group $P2_1/c$, T = 135 K, ω scans, 55864 reflections collected (±*h*, ±*k*, ±*l*), θ_{max} = 27.84°, 8158 independent (R_{int} = 0.054) and 4583 observed reflections [I ≥ 2 σ(*I*)], 519 refined parameters, *R* = 0.074, wR^2 = 0.200, max. residual electron density 0.42 (-0.40) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.
CCDC 1038179 (R/S) and CCDC 1038180 (SS/RR) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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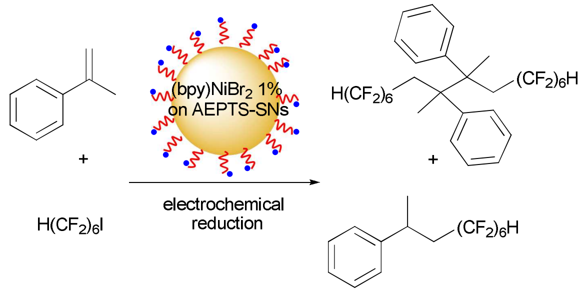

Immobilization of (bpy)$NiBr_2$ complex on silica nanoparticles decorated with anchoring amino-groups was used to perform Ni-catalyzed electroreductive olefin perfluoroalkylation.