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Rhodium-complexed hyperbranched poly(ethyleneimine) and polyamidoamine and their non-covalent immobilization on magnetic nanoparticles

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ABSTRACT

We describe a synthetic strategy for the synthesis and functionalization of hyperbranched poly(-ethyleneimine) (**H-PEI**) and polyamidoamine (**H-PAMAM**) with phosphine ligands and their non-covalent immobilization on magnetic nanosupports. Treatment of these functionalized hyperbranched polymers with $Rh(COD)_2BF_4$ affords polymer-bound Rh(I) complexes that can be utilized in the hydroformylation of alkenes and in one pot hydroformylation-Knoevenagel-hydrogenation reactions. These functionalized hyperbranched polymers are linked to magnetic nanoparticles that are modified with carboxylic acid groups *via* ionic interactions resulting from the acid-base reactions, and are responsible for facilitating the separation of the polymeric catalysts. These magnetically retrievable polymeric catalysts can be reused for up to four cycles.

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1. Introduction

Over the last few decades, many intensive studies have been directed to the field of hyperbranched polymers (HBP), which became inherent in different areas and applications due to their unique properties and functions [1–8]. These polymers, as well as dendrimers, belong to a synthetic tree-like macromolecules family called dendritic polymers [9]. They are simply synthesized by a single step direct polymerization of an AB_x type monomer, based on various synthetic techniques including condensation polymerization, self-condensing vinyl polymerization and ring-opening polymerization [4,10–14]. Even though their synthesis lacks the production of a well-defined structure, and affords a broad molecular weight product rather than a monodispersed one, HBPs still possess similar properties to dendrimers, such as low viscosity, high solubility and inexhaustible functionality [15–17]. Moreover, the simplicity of their preparation in comparison to dendrimers makes them cost and time effective substitutes. Thus, in most cases, there is no need for tedious isolations and cumbersome purification steps during the synthesis of HBP. Therefore, these polymers could easily be very attractive for numerous industrial applications as favored alternative dendrimers analogues [18]. In addition, hyperbranched polymers attracted a great deal of interests in different fields including biology [19] or drug delivery [20,21], bioimaging [22] and catalysis [23–27] Due to the fact that hyperbranched polymers are capable of enhancing chemical reactivity and solubility because of their intrinsic high degree of branching (DB), which can reach up to 100% [28], these dendritic molecules have been adopted for many catalytic applications [29–32]. The judicious choice of a peripheral functionality is considered as an essential parameter for tuning their chemical properties, when being utilized as ligands for various metal catalyzed reactions [33–37], or for the stabilization of metal nanoparticles [38–43].

In recent years, dendritic catalysts immobilized on organic [44–48] or inorganic [49–52] supports have been investigated intensively, and applied to several catalytic organic transformations. These new catalytic materials are sometimes highly

Abbreviations: H-PEI, hyperbranched poly(ethyleneimine); H-PAMAM, hyperbranched polyamindoamine; HBP, hyperbranched polymers; DB, degree of branching; MNPs, magnetic nanoparticles; DCC, *N,N′*-Dicyclohexylcarbodiimide; H-PAMAM-PPh_2, phosphinated hyperbranched poly(amidoamine); H-PEI-PPh_2, phosphinated hyperbranched polyethyleneimine; TEM, transmission electron microscopy; TGA, thermogravimetric analysis; DCM, dichloromethane.

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efficient in terms of reactivity and selectivity, easily recyclable and have unusual stability [53].

In the last decade, magnetic nanoparticles (MNPs) have been investigated intensively as nanosupports of catalysts that can be isolated from the reaction medium by the application of an external magnetic field [54–60]. In this regard, magnetic nanoparticles have also been utilized in the immobilization of dendrimers *via* step-by-step divergent synthesis or grafting presynthesized dendrimers on their surfaces [32,37,52,61–63].

We report here a facile preparation of rhodium-based hyperbranched polymeric catalysts, and their non-covalent immobilization onto magnetic nanoparticles simply *via* ionic interactions. The catalytic activity of the obtained materials was evaluated in hydroformylation reactions and in one-pot hydroformylation-Knoevenagel-hydrogenation reactions. After reaction completion, the catalysts were easily retrieved by applying an external magnetic field and recycled for four consequent cycles without a significant loss in their activity.

2. Results and discussion

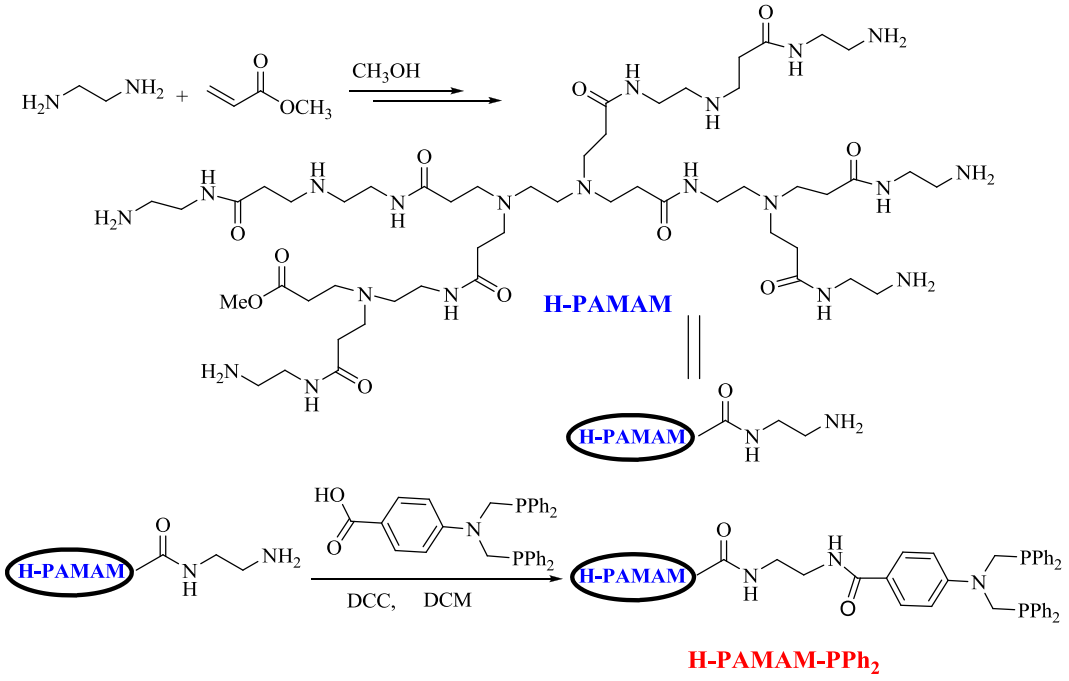
2.1. Synthesis and functionalization of hyperbranched polymers (HBP)

Hyperbranched poly(amidoamine) (**H-PAMAM**) is one of the most investigated materials in the hyperbranched polymers family. In our research, **H-PAMAM** was synthesized from methylacrylate and ethylenediamine in a one-pot reaction according to a double monomer methodology [43,64–66]. By this synthesis, Michael-type addition of methyl acrylate produces the amino propionate ester followed by amidation reaction with ethylenediamine resulting in **H-PAMAM** polymer (Scheme 1). Subsequently, the peripheral primary amino groups on the **H-PAMAM** were substituted with phosphine groups through an amidation reaction with 4-[bis[(diphenylphosphino)methyl]amino]-benzoic acid that was mediated by *N*,*N*'-dicyclohexylcarbodiimide (DCC), to afford chelate phosphines on the periphery of the hyperbranched polymer (**H-PAMAM-PPh$_2$**). By the same manner, a commercially available hyperbranched poly(ethyleneimine) (**H-PEI**) was also functionalized with phosphine groups to yield **H-PEI-PPh$_2$** (Scheme 2). The phosphinated hyperbranched polymers were treated with Rh(COD)$_2$BF$_4$ by mixing at room temperature in dry dichloromethane for 30 min, to yield rhodium complexed hyperbranched polymers **2a** and **2b** (Schemes 3 and 4).

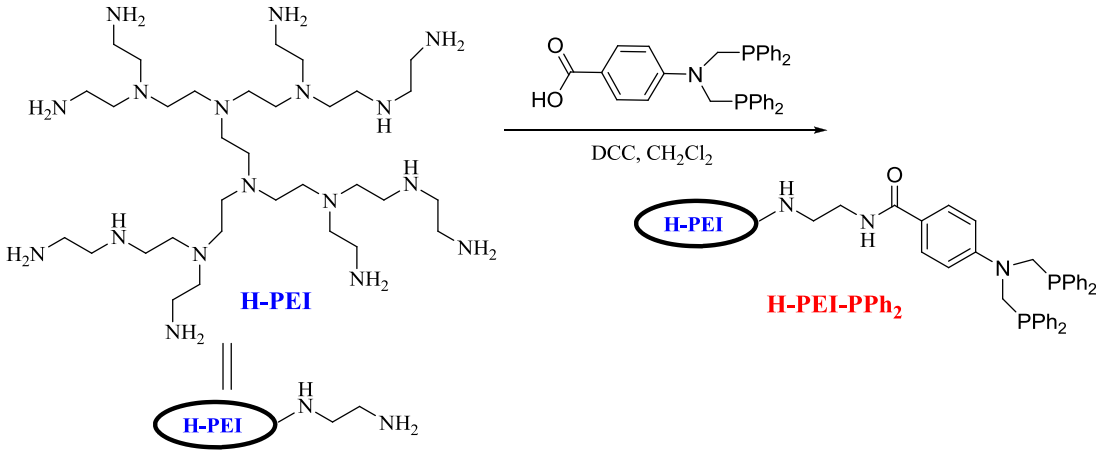
Inductively coupled plasma mass spectrometry (ICP-MS) measurements were utilized for determining the loading of the rhodium in both complexes. The homogeneously prepared **H-PEI-PPh$_2$-Rh (2a)** and **H-PAMAM-PPh$_2$-Rh (2b)** catalyst yielded a loading of 0.42 mmol/g and 0.65 mmol/g respectively. While the phosphorous content was found to be 0.916 mmol/g and 1.43 mmol/g, in a good correlation with the rhodium loading in **2a** and **2b** catalysts, respectively.

2.2. Catalysis

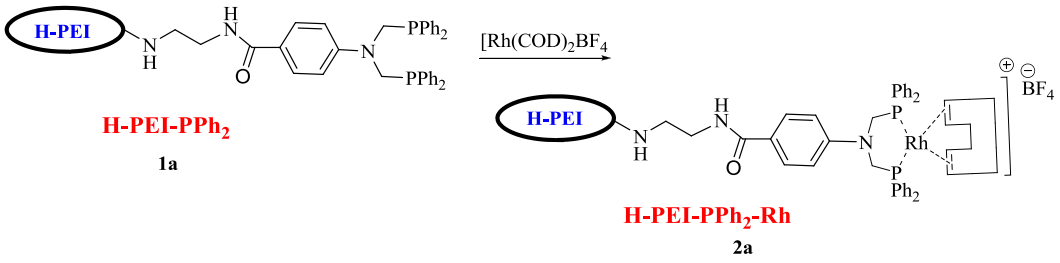
The catalytic performance of the resultant Rh(I) complexed phosphine functionalized HBPs was examined in the hydroformylation of styrene as a model reaction using a 1:1 mixture of carbon monoxide and hydrogen pressurized to 1000 psi. For initial examination, the reaction was mediated by catalyst **2a** and performed in various solvents. It was observed that the solvent polarity could highly affect the reaction progress. Thus, polar solvents could negatively affect the catalyst reactivity while nonpolar solvents could smoothly increase catalyst reactivity. Dichloromethane solvent afforded full conversion with high regioselectivity towards the branched aldehyde (B:L = 20:1) (Table 1, entry 7). The reaction in methanol was pretty slow, and was not completed probably due to the restricted solubility of the metal complex in this medium (Table 1, entry 1). Furthermore, when the polar tetrahydrofuran was used as a solvent, it showed good regioselectivity for the branched aldehyde accompanied with poor conversion, whereas at elevated temperatures the conversion of the reaction was increased and the selectivity was decreased considerably (Table 1, entries 2–3). In acetonitrile, high selectivity was obtained in spite of the low



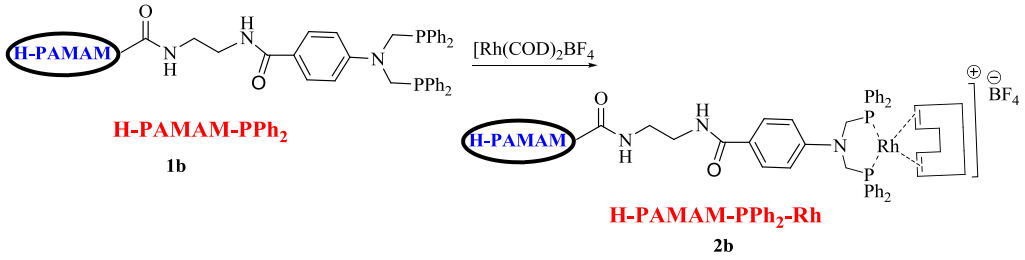
Scheme 1. Preparation of (a) hyperbranched poly(amidoamine) (**H-PAMAM**) and phosphinated hyperbranched poly(amidoamine) (**H-PAMAM-PPh$_2$**).



Scheme 2. Preparation of phosphinated hyperbranched polyethyleneimine (**H-PEI-PPh$_2$**).

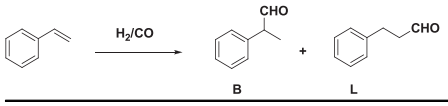


Scheme 3. Complexation of **H-PEI-PPh$_2$** with Rh(COD)$_2$BF$_4$.



Scheme 4. Complexation of **H-PAMAM-PPh$_2$** with Rh(COD)$_2$BF$_4$.

Table 1
Hydroformylation of styrene by a Rh(I)-complexed phosphine functionalized H-PEI polymer.[a]



Entry	Solvent	Temperature (°C)	Conversion (%)[b]	Selectivity (B:L ratio)[c]	TON	TOF(h^{-1})
1	MeOH	80	70	19:1	350	22
2	THF	80	19	30:1	95	6
3	THF	120	90	3:1	450	28
4	CH_3CN	80	63	32:1	315	20
5	Toluene	80	88	22:1	440	27
6	Toluene	120	82	15:1	410	26
7	CH_2Cl_2	80	100	20:1	500	31

[a] 5 mmol styrene, 2 mL solvent, 16 h, 1000 psi of 1:1 H_2:CO, 0.2% mol catalyst 2a (0.01 mmol).
[b] Determined by GC.
[c] Determined by ^{1}H NMR.

reaction conversion, which might be attributed to the poor solubility of the hyperbranched polymeric catalyst in this solvent (Table 1, entry 4). In toluene, a non-polar solvent, the reaction showed good selectivity for the branched product, but increasing

the temperature led to the decrease of the catalyst reactivity and could not enhance its selectivity (Table 1, entries 5–6).

Moreover, the catalytic performance of Rh(I) complexed to **H-PAMAM-PPh$_2$** in the hydroformylation reaction was examined. It was found, in a good agreement with the previous results, that in dichloromethane the reaction proceeds almost to completion with better regioselectivity compared to all other solvents as depicted in Table 2.

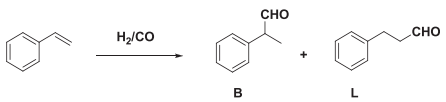
Comparison of the catalytic activity and selectivity of the two rhodium polymeric complexes revealed that the catalyst based on **H-PAMAM** polymer has better selectivity in the hydroformylation reaction of alkenes. Based on these results, a set of various substrates was tested in the hydroformylation reaction while utilizing catalyst **2b**. The reaction was carried out at 80 °C with a 1:1 mixture of carbon monoxide and hydrogen under a total pressure of 1000 psi. Obviously, the intrinsic electronic nature of the starting material could hardly affect the reactivity of the electron-donating or withdrawing group substituted styrenes (Table 3, entries 1–4). However, the highest selectivity was obtained when 3-chlorostyrene was applied in the hydroformylation reaction. In addition, 4-vinylanisole (Table 3, entry 5) was reacted completely giving a moderate regioselectivity toward the branched aldehyde. In the case of vinylbenzoate (Table 3, entry 6) the branched isomer was formed exclusively in good yields. Moreover, the lowest selectivity was observed in the case of 1-octene (Table 3, entry 7) when the linear aldehyde was attained in preference.

Furthermore, a one-pot hydroformylation-Knoevenagel-hydrogenation reaction of alkenes with malononitrile was utilized as an additional application for evaluating the catalytic performance of the Rh(I) dendritic complexes. Practically, this one-pot reaction affords first aldehydes through hydroformylation reaction, which then condense with malononitrile by the Knoevenagel reaction catalyzed by the base groups that exist in both dendritic catalysts. In the last step, the unsaturated intermediate formed from the Knoevenagel condensation turns into saturated products by the hydrogenation reaction catalyzed by the same dendritic catalysts (Scheme 5).

The reaction was mediated by **2a** and **2b** dendritic complexes. The optimization of the reaction was carried out using styrene as the model substrate at 80 °C in different solvents. From the results summarized in Table 4, it can be seen clearly that the reaction proceeds very well in THF with **H-PEI-PPh$_2$-Rh** catalyst (**2a**) (Table 4, entry 1). This result could be explained by the fact that the condensation of malononitrile with the corresponding aldehyde requires a base catalyst. The **H-PEI-PPh$_2$- Rh** polymeric catalyst contains larger number of secondary and tertiary amine groups than **H-PAMAM-PPh$_2$-Rh**, which makes it a better catalyst in the Knoevenagel reaction. The catalyst **2a** also showed moderate reactivity in other polar solvents such as methanol and acetonitrile, accompanied with a decreased selectivity (Table 4, entries 5 and 7, respectively). When the reaction was performed in toluene, an apolar solvent, moderate reactivity and good selectivity were achieved (Table 4, entry 6). The catalyst **2a** gave lower conversions and selectivity both in THF and dichloromethane (Table 4, entries 2 and 4, respectively).

Accordingly, **H-PEI-PPh$_2$-Rh** complex (**2a**) was applied in one-pot hydroformylation-Knoevenagel-hydrogenation of various vinylarenes. The reaction was performed in THF at 80 °C under pressure of 1000 psi H_2:CO (1:1). The results indicated obtaining high regioselectivity toward the branched products and good to excellent conversions (Table 5, entries 1–6). In addition, the electronic effect of the substituted vinylarenes could barely affect the attained conversion, but could certainly influence the afforded regioselectivity depending on the electronic character of the substituted group. For example, 3-chlorostyrene and 4-chlorostyrene, bearing an electron withdrawing group, gave high conversions and excellent selectivities toward the branched isomer (Table 5, entries 1–2). On the other hand, 3-methylstyrene and 4-methylstyrene showed good reactivity in the one-pot reaction, but the regioselectivity was significantly low (Table 5, entries 3–4). In the same manner, 4-methoxystyrene that contains strong electron donating group, also revealed a low selectivity for the branched product (Table 5, entry 5).

Table 2
Hydroformylation of styrene by a Rh(I)-complexed phosphine functionalized H-PAMAM polymer.[a]



Entry	Solvent	Conversion (%)[b]	Selectivity (B:L ratio)[c]	TON	TOF(h^{-1})
1	CH_2Cl_2	100	32:1	500	31
2	Toluene	85	16:1	425	27
3	CH_3CN	52	24:1	260	16
4	Methanol	35	19:1	176	11
5	THF	20	13:1	100	6

[a] 5 mmol styrene, 2 mL solvent, 16 h, 80 °C, 1000 psi of 1:1 H_2:CO, 0.2% mol catalyst 2b (0.01 mmol).
[b] Determined by GC.
[c] Determined by ^{1}H NMR.

2.3. Non-covalent immobilization of rhodium-complexed hyperbranched polymers on magnetite nanoparticles

Magnetic nanoparticles were synthesized *via* co-precipitation of iron salts Fe(II) and Fe(III) in a basic solution at 85 °C according to Massart's method [67]. To these magnetite nanoparticles, 4-oxo-4-[3-(trimethoxysilyl) propylamino] butanoic acid was anchored by a condensation reaction between the trimethoxysilane groups and the hydroxyl groups existing on the surface of the magnetite nanoparticles to yield carboxylic acid functionalized MNPs (**MNP-COOH**) as illustrated in Scheme 6. Afterwards, the phosphinated hyperbranched polymers (**1a, 1b**) were grafted onto the MNPs by ionic interaction, which resulted from the reaction of the carboxylic acid groups with the tertiary amine groups that exist in the core of the hyperbranched polymers. This non-covalent immobilization of the phosphinated HBPs provided magnetically separable HBPs (**MNP-H-PEI-PPh$_2$** and **MNP-H-PAMAM-PPh$_2$**) followed by a treatment with $Rh(COD)_2BF_4$ complex in chloroform at room temperature to give magnetic Rh(I)-bound HBP complexes (**3a** and **3b**) respectively (Scheme 6).

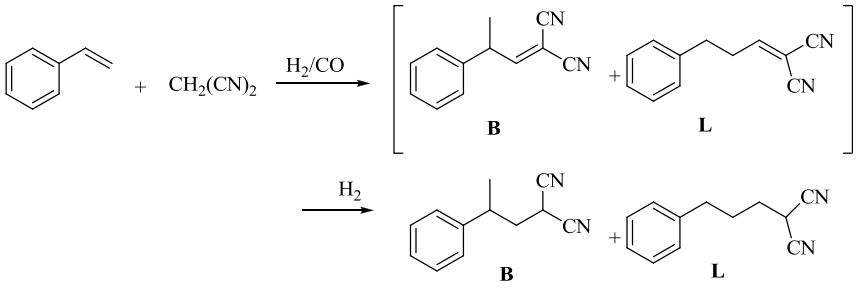
The resulting **MNP**, **MNP-COOH**, **MNP-H-PEI-PPh$_2$** and **MNP-H-PAMAM-PPh$_2$** materials were characterized by transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). The results of the TEM analysis (Fig. 1) confirmed that the magnetic nanoparticles are spherical in shape with a diameter of 5–15 nm (Fig. 1a). Moreover, functionalization with the hyperbranched polymers showed no effect on both morphologies and sizes (Fig. 1b–d).

TGA analysis (Fig. 2) showed an organic content increase when the phosphinated hyperbranched polymers were linked to the functionalized MNPs. In the case of acid-functionalized magnetite (**MNP-COOH**) (curve b), a mass loss of 19.4% was attained compared to the bare magnetite (curve a) with a slight mass loss of 3.56% ascribed to volatile adsorbed solvents. Furthermore, **MNP-H-PAMAM-PPh$_2$** exhibited a weight loss of 36.8% (curve c) compared to the **MNP-H-PEI-PPh$_2$**, which showed a mass loss of 58.7% (curve d). These results ascertain the larger number of tertiary amine groups in the **H-PEI-PPh$_2$** compared to the **H-PAMAM-PPh$_2$**, which

Table 3
Hydroformylation of various substrates by a Rh(I)-complexed phosphine functionalized H-PAMAM polymer.[a]

Entry	Substrate	Conversion (%)[b]	Selectivity (B:L ratio)[c]	TON	TOF(h^{-1})
1	3-chlorostyrene	100	32:1	500	31
2	4-chlorostyrene	100	24:1	500	31
3	4-fluorostyrene	100	19:1	500	31.2
4	4-methylstyrene	100	22:1	500	31
5	4-vinylanisole	100	10:1	500	31
6	vinylbenzoate	95	100:0	475	29.6
7	1-octene	97	1:3	485	30

[a] 5 mmol of proper substrate, 2 mL CH_2Cl_2, 16 h, 80 °C, 1000 psi of 1:1 H_2:CO, 0.2% mol catalyst 2b (0.01 mmol).
[b] Determined by GC.
[c] Determined by ^{1}H NMR.



Scheme 5. One-pot hydroformylation-Knoevenagel-hydrogenation reaction of styrene and malononitrile.

Table 4
One-pot hydroformylation-Knoevenagel-hydrogenation reaction of styrene and malononitrile by Rh(I)-complexed phosphine functionalized HBP.[a]

Entry	Solvent	Catalyst	Conversion (%)[b]	Selectivity (B:L ratio)[c]	TON	TOF(h^{-1})
1	THF	**2a**	100	24:1	500	31
2	THF	**2b**	85	12:1	425	26.5
3	CH_2Cl_2	**2a**	82	16:1	410	25.6
4	CH_2Cl_2	**2b**	95	15:1	475	29.5
5	MeOH	**2a**	76	20:1	380	23.7
6	Toluene	**2a**	88	19:1	440	27.5
7	CH_3CN	**2a**	80	15:1	400	25

[a] 5 mmol styrene, 8 mmol malononitrile, 2 mL solvent, 16 h, 1000 psi of 1:1 H_2:CO, 80 °C, 0.2% mol (0.01 mmol) catalyst **2a**, **2b**.
[b] Determined by GC.
[c] Determined by GC and ^{1}H NMR.

Table 5
One-pot hydroformylation-Knoevenagel-hydrogenation reaction of various substrates by Rh(I)-complexed phosphine functionalized H-PEI.[a]

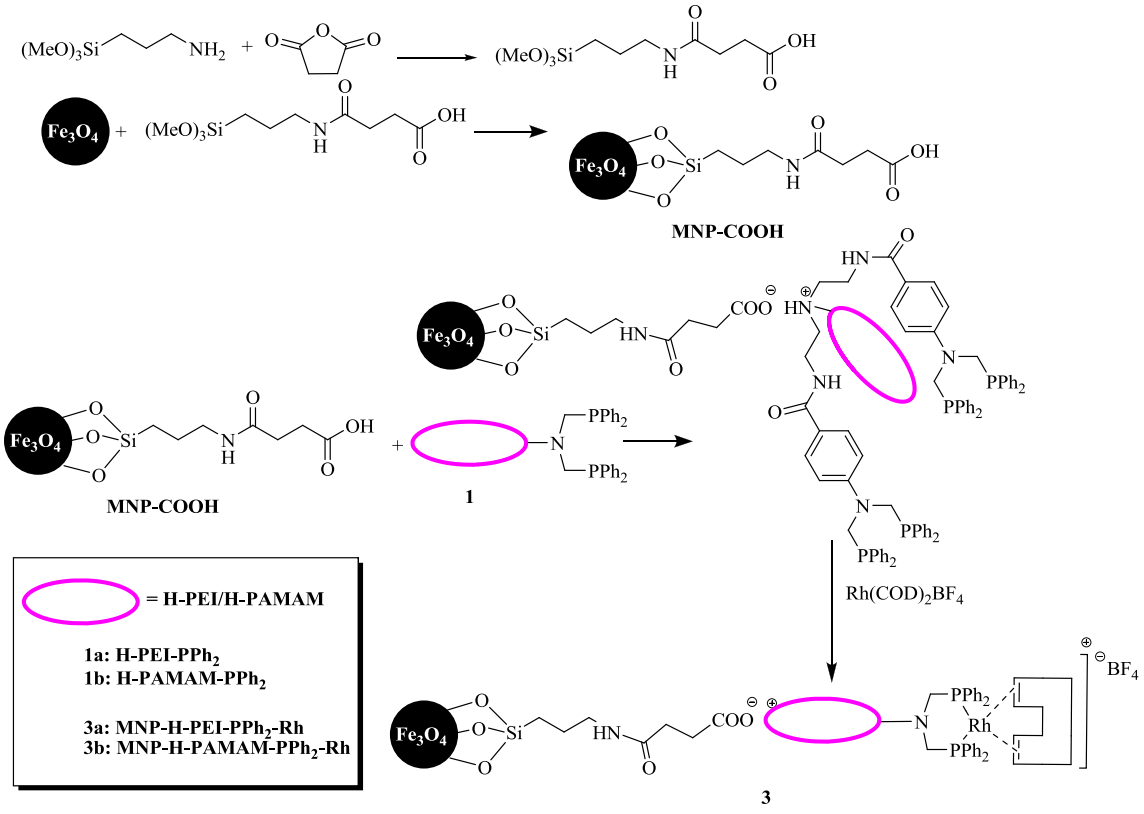
Entry	Substrate	Conversion (%)[b]	Selectivity (B:L ratio)[c]	TON	TOF(h^{-1})
1	3-chlorostyrene	>99	22:1	495	31
2	4-chlorostyrene	98	20:1	490	30.6
3	3-methylstyrene	95	14:1	475	29.6
4	4-methylstyrene	92	12:1	460	28.7
5	4-methoxystyrene	90	10:1	450	28

[a] 5 mmol of alkene, 8 mmol malononitrile, 2 mL THF, 80 °C, 1000 psi of 1:1 H_2:CO, 0.2% mol catalyst **2a** (0.01 mmol), 16 h.
[b] Determined by GC.
[c] Determined by GC and ^{1}H NMR.

makes the tethering onto the acid-modified MNPs more feasible. Inductively coupled plasma (ICP) analysis was employed to determine the loading of the phosphorous on the MNPs. This analysis revealed that **MNP-H-PEI-PPh$_2$** contains 0.36 mmolg^{-1} of phosphorous while **MNP-H-PAMAM-PPh$_2$** contains only 0.28 mmolg^{-1}. ICP analysis of the magnetically separable dendritic catalysts, obtained after coordination of the immobilized hyperbranched polymers with rhodium complex, showed a rhodium loading of 0.15 and 0.11 mmol/g in **MNP-H-PAMAM-PPh$_2$** and **MNP-H-PEI-PPh$_2$** complexes, respectively.

Grafting the phosphinated hyperbranched polymers on magnetic nanoparticles was further followed by infrared (IR) analysis. As shown in Fig. 3, successful anchoring of 4-oxo-4-[3-(trimethoxysilyl)propylamino]butanoic acid (curve a), **H-PAMAM-PPh$_2$** (curve b) and **H-PAMAM-PPh$_2$** (curve c) onto the magnetic nanoparticles was achieved. As indicated, **MNP-COOH**, **MNP-H-PAMAM-PPh$_2$** and **MNP-H-PEI-PPh$_2$** demonstrated 1701, 1642 cm^{-1} bands that are ascribed to the C=O stretching of the carbonyl groups. In addition, the interval of 3100–3653 cm^{-1} also confirmed the N-H stretching vibrations that belong to the amide and amine groups.

The synthesized **MNP-H-PAMAM-PPh$_2$-Rh** and **MNP-H-PEI-**



Scheme 6. Non-covalent immobilization of rhodium-complexed hyperbranched polymers on magnetite nanoparticles.

PPh_2-Rh complexes were applied in hydroformylation reaction of styrene (Table 6, entries 1–4) and in one-pot hydroformylation-Knoevenagel-hydrogenation reaction of styrene with malononitrile (Table 6, entries 5–8). Both catalytic systems exhibited good reactivity with enhanced regioselectivities. Catalyst **3b** showed excellent recyclability without significant decrease in its reactivity or selectivity in the hydroformylation reaction. On the other hand, catalyst **3a** kept its reactivity and selectivity for two cycles while a slight decrease in its efficacy in the third and fourth cycles was observed. ICP analysis was utilized to determine if there was a leaching of rhodium species from the magnetically separable catalysts to the reaction medium after the first cycle. In both cases, the results indicated a rhodium leaching of less than 2.6 ppm (0.5%) and 4.8 ppm (0.93%) for **MNP-H-PAMAM-PPh_2-Rh** and **MNP-H-PEI-PPh_2-Rh**, respectively. Performing the ICP analysis after the third cycle, revealed no detectable rhodium in the filtrate. A hot filtration test was also performed to confirm the ICP results. Therefore, the catalysts in the hydroformylation and one-pot reactions were magnetically separated from the hot reaction media after 2 h and then the reactions were allowed to continue for an additional 6 h. In the hydroformylation reaction of styrene a conversion of 15% was obtained after 2 h with B:L selectivity of 49:1. After continuing the reaction for an additional 6 h, the conversion was not changed. This result shows clearly that the hydroformylation reaction occurs on the surface of the magnetically separable dendritic catalyst and the very low amount of leached rhodium cannot advance the reaction. After isolation of catalyst **3a** from the one-pot hydroformylation-Knoevenagel-hydrogenation reaction of styrene and malononitrile, the reaction was allowed to proceed for an additional 6 h and no significant increase in the conversion was detected.

2.4. Conclusion

In this work, a facile method for preparation of dendritic catalysts based on hyperbranched polymers (**H-PAMAM** and **H-PEI**) was reported. The preparation method is based on the functionalization of hyperbranched polymers with 4-[bis[(diphenylphosphino)methyl]amino]-benzoic acid *via* amidation reaction with the primary amine groups that exist in the periphery of the polymers. The catalytic performance of these catalysts was tested in hydroformylation reaction and one-pot hydroformylation-Knoevenagel-hydrogenation reaction. In this regard, **H-PAMAM** based catalyst exhibited high catalytic activity and regioselectivity in hydroformylation reaction. Whereas, **H-PEI** based catalyst has proved to be an efficient and regioselective bifunctional catalyst for the one-pot hydroformylation-Knoevenagel-hydrogenation reaction. These two systems were easily immobilized on magnetic nanoparticles functionalized with carboxylic acid groups *via* ionic interactions, which resulted from the acid-base reaction of the tertiary amine groups at the core of the polymers with the carboxylic acid groups. The immobilized **H-PAMAM** based catalyst could preserve its efficacy for up to four consequent cycles, without observing any significant loss in its catalytic activity or selectivity. However, the immobilized **H-PEI** based catalyst exhibited a slight decrease in its reactivity in the one-pot hydroformylation-Knoevenagel-hydrogenation reaction after the second cycle. Moreover, convenient catalyst isolation was achieved by the application of external magnetic field. We believe that the method developed in this work for non-covalent immobilization of dendritic catalysts can be applied in various fields.

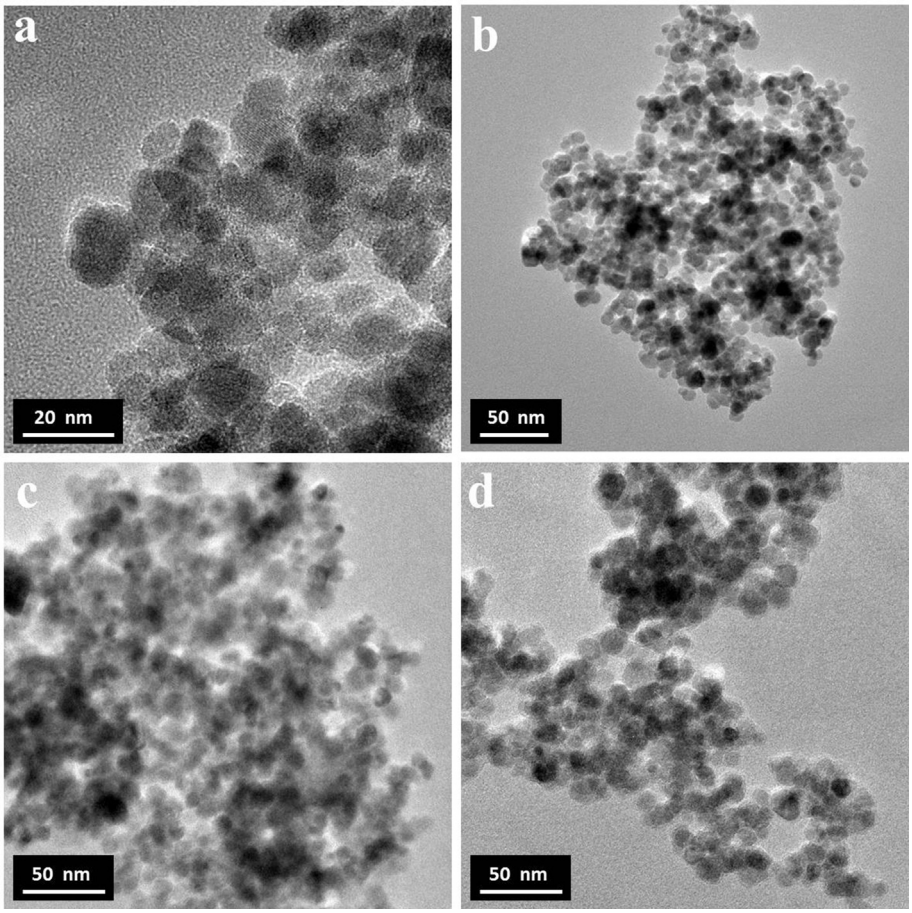


Fig. 1. TEM images of (a) **MNP**, (b) **MNP-COOH**, (c) **MNP-H-PEI-PPh$_2$** and (d) **MNP-H-PAMAM-PPh$_2$**.

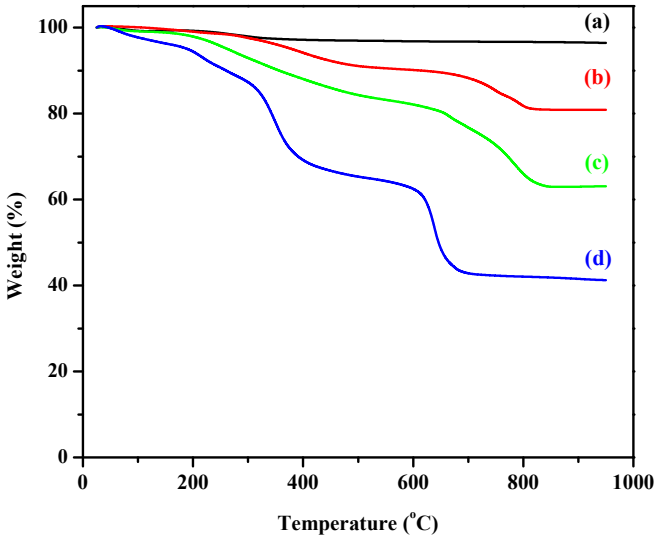


Fig. 2. TGA curves of (a) **MNP**, (b) **MNP-COOH**, (c) **MNP-H-PAMAM-PPh$_2$** and (d) **MNP-H-PEI-PPh$_2$**.

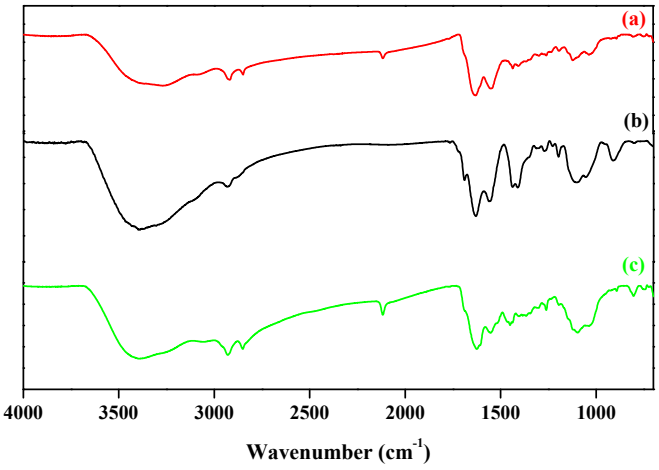


Fig. 3. IR spectra of (a) **MNP-COOH**, (b) **MNP-H-PAMAM-PPh$_2$** and (c) **MNP-H-PEI-PPh$_2$**.

3. Experimental

3.1. Materials and methods

The hyperbranched PEI (average mw~25,000), ethylenediamine (EDA) and formaldehyde were purchased from Aldrich with highest purity and used directly without further purification. Hyperbranched poly(amidoamine) (**H-PAMAM**) [64] and 4-[bis[(diphenylphosphino)methyl]amino]-benzoic acid [68] were prepared according to literature procedure. All solvents were dried and distilled prior to use. Methylacrylate (MA) was purified under reduced pressure before use.

Table 6
Recyclability of the Rh(I) complexed phosphine functionalized HBP supported on MNPs in hydroformylation reaction and one-pot hydroformylation-Knoevenagel-hydrogenation reaction.[a]

Entry	Run	Catalyst	Solvent	Conversion (%)[b]	Selectivity (B:L ratio)[c]	TON	TOF(h^{-1})
1	1	**3b**	CH_2Cl_2	100	24:1	500	31
2	2	**3b**	CH_2Cl_2	100	24:1	500	31
3	3	**3b**	CH_2Cl_2	100	24:1	500	31
4	4	**3b**	CH_2Cl_2	98	22:1	490	30.6
5[d]	1	**3a**	THF	100	20:1	500	31
6[d]	2	**3a**	THF	>99	20:1	500	31
7[d]	3	**3a**	THF	95	19:1	475	29.6
8[d]	4	**3a**	THF	90	19:1	450	28

[a] 5 mmol of styrene, 2 mL CH_2Cl_2, 80 °C, 16 h, 1000 psi of 1:1 H_2:CO, 0.2% mol (0.01 mmol) catalyst **3a** or **3b**.
[b] Determined by GC.
[c] Determined by GC and ^{1}H NMR.
[d] 8 mmol malononitrile were added to the reaction vessel.

3.2. Characterizations

The ^{1}H NMR studies were conducted on 400 MHz and 500 MHz Bruker instruments. FTIR measurements were performed on a Bruker Equinox 55 spectrometer using a Barnes analytical FTIR sealed cell (KBr 0.5 mm). Gas chromatography (GC) (Aglient Technologies, 7890A) with a capillary column (HP-5, 30 m) was used to determine the conversion of the hydroformylation and the one-pot reactions. Transmission electron microscopy (TEM) was performed with (S) TEM Tecnai F20 G2 (FEI Company, USA) operated at 200 kV. Thermogravimetric analysis (TGA) was performed on Mettler Toledo TG 50 analyzer. Measurements were carried out at temperature range that extended from 25 to 950 °C at a heating rate of 10 °C/min under nitrogen. Inductively coupled plasma mass spectrometry measurements (ICP-MS) were performed on 7500cx (Agilent Company) using an external standard calibration.

3.3. General procedure for the synthesis of phosphine end-capped hyperbranched PAMAM (***H-PAMAM-PPh$_2$***)

A mixture of 4-[bis[(diphenylphosphino)methyl]amino]-benzoic acid (18 mmol), *N,N′*-Dicyclohexylcarbodiimide (DCC) (18 mmol), triethylamine (18 mmol) in dry degassed DCM was stirred at 0 °C for 30 min under argon. 6.12 g of **H-PAMAM** (70 mmol) were dissolved in 25 mL dry dichloromethane and were added to the flask. The mixture was stirred for an additional hour at 0 °C and then was allowed to reach room temperature. The reaction mixture was stirred further for 16 h followed by refluxing for 3 h. It was cooled to room temperature, solvent was removed under reduced pressure and then 30 mL dry methanol were added. The resulting precipitate was dried under vacuum. The phosphine functionalized material was obtained as a white-yellowish solid. Yield: 8.6 g (~80%). Elementary anal. C 62.34, H 6.82, N 4.91. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.93–0.96 (br. $NHCOCH_2CH_2NH$), 1.11–1.35 (br. $NHCOCH_2CH_2NH$) 1.52–1.82 (br. $NH(CH_2)_2NH$), 2.05–2.14 (br. NCH_2), 3.49 (CH_3O), 3.88 (s, 4H), 6.70–6.72 (d, J = 8 Hz, 2H), 7.28–7.39 (m, 20H), 7.45–7.48 (d, J = 9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 24.64–26.37, 30.90–34.93, 49.59–57.28, 112.81, 124.18, 128.53–129.27, 133.06–133.28, 136.70–136.91, 149.86, 155.36, 171.61. ^{31}P NMR (161 MHz, $CDCl_3$) δ (ppm): -27.36 (s). FTIR (KBr, cm^{-1}): ν = 3075–3679, 2934, 2850, 1705, 1606, 1522, 1438, 1372, 1337, 1204, 742, 700 cm^{-1}.

3.4. General procedure for the synthesis of phosphine end-capped hyperbranched poly(ethylenimine) (***H-PEI-PPh$_2$***)

A mixture of 4-[bis[(diphenylphosphino)methyl]amino]-benzoic acid (18 mmol), *N,N′*-Dicyclohexylcarbodiimide (DCC) (18 mmol), triethylamine (18 mmol) in dry degassed DCM was stirred at 0 °C for 30 min under argon. 4.2 g of commercially available polyethylenimine (PEI) (70 mmol) (MW~ 25000, contains 31% of primary amine, 39% of secondary amine and 30% of tertiary amine group) were dissolved in 25 mL dry dichloromethane and were added to the flask. The mixture was stirred for an additional hour at 0 °C and then was allowed to reach room temperature. The reaction mixture was stirred further for 16 h followed by refluxing for 3 h. It was cooled to room temperature, the solvent was removed under reduced pressure and then 30 mL dry methanol were added. The resulting precipitate was dried under vacuum. The phosphine functionalized material was obtained as a white-yellowish solid. Yield: 8.2 g (~80%). Elementary anal. C 69.65, H 6.98, N 5.65. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.93–0.96 (br. $CONHCH_2CH_2NH$), 1.11–1.32 (br. $CONHCH_2CH_2NH$) 1.57–2.10 (br. $NH(CH_2)_2NH$), 2.6–3.2 (br. NH), 3.97 (s, 4H), 6.71–6.73 (d, J = 8 Hz, 2H), 7.30–7.45 (m, 20H), 7.46–7.48 (d, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 24.63–26.37, 30.90–34.93, 49.57–57.37, 112.79, 124.19, 128.46–129.26, 131.08–136.88, 149.86, 155.34, 171.65. ^{31}P NMR (161 MHz, $CDCl_3$) δ (ppm): -27.41 (s). FTIR (KBr, cm^{-1}): ν = 3053–3665, 2931, 2854, 1702, 1608, 1520, 1436, 1374, 1340, 1207, 1089, 745, 703 cm^{-1}.

3.5. Preparation of rhodium complexed hyperbranched polymers

4.1 mg of $Rh(COD)_2BF_4$ (0.01 mmol) were added under argon to a stirred 2 mL dichloromethane solution of the corresponding phosphinated hyperbranched polymer containing 0.01 mmol of phosphine groups. It was stirred for 30 min at room temperature. The resulting material was either used directly in the catalytic reactions or dissolved in other solvents after evaporation the dichloromethane.

3.6. Synthesis of 4-oxo-4-[3-(trimethoxysilyl)propylamino] butanoic acid

In a 100 mL round bottomed flask fitted with a reflux condenser, 5.3 mL of 3-aminopropyltrimethoxysilane (28.5 mmol) and 2.85 g of succinic anhydride (28.5 mmol) were mixed together under inert atmosphere. An exothermic reaction took place to give a viscous material in 98% yield, which was used without any further purification. Elementary anal. C 41.09, H 7.23, N 4.82. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.63–0.67 (t, J = 5.4 Hz, 2H), 1.54–1.64 (m, 2H), 2.45–2.48 (m, 2H), 2.57–2.64 (m, 2H), 3.15–3.35 (m, 2H), 3.57 (s, 9H), 9.25 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 6.38, 22.44, 29.96, 30.85, 42.07, 50.27, 172.63, 175.94. FTIR: ν = 3097–3476, 2947, 2839, 1730, 1647, 1549, 1415, 1189, 1058 cm^{-1}.

3.7. Preparation carboxylic acid modified magnetic nanoparticles (MNP-COOH)

Magnetic nanoparticles (MNP) (Fe_3O_4) were prepared in ammonia solution at 85 °C *via* co-precipitation of Fe(II) and Fe(III) ions. By this synthesis, 11.6 g of $FeCl_3$•$6H_2O$ and 4.3 g of $FeCl_2$•$4H_2O$ were taken in 400 mL degassed water, heated at 85 °C under argon followed by the addition of 18 mL ammonia solution (25%). After heating for another 30 min, the reaction was cooled to room temperature, the solution was decanted and the black particles were washed five times with 200 mL water. The particles were suspended in 500 mL ethanol and sonicated for 1 h. The suspension was stirred mechanically and 30 mmol of 4-oxo-4-[3-(trimethoxysilyl)propylamino] butanoic acid in 100 mL ethanol were added under nitrogen. After stirring for 36 h, the modified MNPs were separated by applying an external magnetic field, washed twice with ethanol and suspended in 100 mL chloroform.

3.8. Supporting functionalized hyperbranched polymers on modified magnetic nanoparticles

10 mL chloroform solution of **MNP-COOH** were sonicated for 30 min. To this solution, 20 mL of chloroform solution that contains 3 mmol of the desired functionalized hyperbranched polymer (**H-PEI-PPh$_2$** or **H-PAMAM-PPh$_2$**) were added. The resulting solution was refluxed for 48 h, cooled to room temperature, separated and washed three times with methanol. For complexation with rhodium, 0.15 g $Rh(COD)_2BF_4$ dissolved in 30 mL chloroform were added. The mixture was stirred for 1 h. Then, the resulted material was magnetically separated and washed two times with methanol.

3.9. General procedure for the hydroformylation reaction

5 mmol of the suitable substrate were mixed with the appropriate catalyst containing 0.01 mmol rhodium in 2 mL solvent. The resulting mixture was placed in 45 mL glass-lined autoclave. The autoclave was sealed, purged three times with carbon monoxide and pressurized to 1000 psi with a 1:1 mixture of carbon monoxide and hydrogen. The autoclave was placed in an oil bath preset to the desired temperature. After 16 h, the autoclave was cooled to room temperature and the gases were released. The separation of the catalyst was performed by applying an external magnetic field, in the case of using catalysts **3a** and **3b**, or by evaporation of the solvent and extracting the products with ether in the case of using catalysts **2a** and **2b**. The resulted products were analysed by ^1H NMR and GC.

3.10. General procedure for the one-pot hydroformylation-Knoevenagel-hydrogenation reaction

The one-pot reaction was performed following the same previous procedure, except that 0.5 mL (8 mmol) of malononitrile was added to the reaction vessel.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2016.05.021.

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