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Hydroformylation of Terminal Alkenes with *in situ* Generation of Syngas using Schiff Base Palladium Complex under Microwave and Conventional Heating

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Hydroformylation of alkenes and alkynes without syngas is preferred for obtaining valuable aldehydes with 100% atom economy using widely available components. Regarding selectivity, atom economy and energy efficiency, microwave-promoted catalytic hydroformylation reactions are the substitutes for conventional techniques. This is compatible with an increasing demand for more environmentally friendly industrial processes. In present work, Schiff base palladium complexes were utilized as catalysts for the hydroformylation of terminal alkenes using glyoxylic acid and formaldehyde as sources of CO and H_2. Highly regio- and chemoselective olefin to aldehyde transfer hydroformylation of organic substrate in terminal unsaturated C-C bonds with microwave assistance *in situ* generation of syngas condition. Additionally, eight entries were hydroformylated to the linear aldehyde utilizing a palladium complex containing (*E*)-4-((4-nitrobenzylidene)-amino)phenol ligand under microwave and conventional heating, resulting in very high regioselectivity (l/b). Without CO and H_2 cylinders, this proposed approach produced aldehydes with a 93% yield and excellent regioselectivity. Hydroformylation of terminal alkene, when carried out with palladium catalyst using glyoxylic acid as a source of CO and H_2 and microwave-irradiated for 18-20 min at 160 ºC, led to the formation of the corresponding aldehyde without the formation of isomerized alkenes. During the hydroformylation process, the use of microwave and conventional heating techniques were compared and differentiated. The results demonstrated that microwave heating requires significantly lower temperatures and offers higher yields than traditional heating.

Keywords: Microwave assisted, Palladium Schiff base, Syngas free condition, Terminal alkenes, Conventional heating.

INTRODUCTION

The hydroformylation process catalyzed by a transition metal involves the production of an aldehyde by the interaction of an unsaturated substrate with carbon monoxide and hydrogen [1]. Using transition metal catalysts, carbon monoxide and hydrogen must be introduced to an alkene simultaneously to form two new carbon-carbon and carbon-hydrogen bonds [2]. In 1938, Otto Roelen discovered the hydroformylation reaction involving the products of cobalt Fischer-Tropsch reactions [3-6]. About 10 million tons of aldehydes are produced yearly by the hydroformylation process, catalyzed by transition metal complexes in manufacturing [7]. This reaction represents the most significant industrial application of homogeneous catalysis and has been thoroughly studied from a mechanical perspective [8]. Syngas (H_2/CO) is a feedstock because it is readily available at reasonably cost [9]. With many reaction sequences incorporating a hydroformylation step, alcohol generation is the major objective.

One of the main areas of research nowadays is the selective oxidation of internal alkenes that are less reactive than terminal alkenes when compared to linear aldehydes and alcohols [10]. The homogenous catalyst employed in the hydroformylation reaction in the past was primarily based on cobalt and rhodium. The typical oxo process, which runs at high pressures (200 to 450 bars) and temperatures between 140 and 180 ºC, uses a cobalt catalyst in solution [11]. However, recent study revealed that other transition metals, such as manganese, platinum and palladium, are also highly reactive to the hydroformylation of the organic substrates. In this context, ongoing research details a palladium Schiff base catalytic system that selectively and effectively hydroformylates terminal alkenes in moderate conditions. Palladium metal is included in this study because palladium Schiff base complexes are versatile catalyst precursors for a

range of hydroformylation processes of significant economic value [12].

Conventional heating was employed to hydroformylate the substitute at a temperature and pressure of 200-280 ºC and 200-350 bar, respectively. The alkene is hydroformylated with palladium metal to avoid this laborious procedure while heated in a microwave. Compared to the traditional heating method, the hydroformylation with microwave heating combination showed several advantages, such as a considerable decrease in reaction time and temperature and sporadic increases in selectivity [13]. Since the reaction may be carried out in small flasks, which lowers the amount of H_2 and CO lost at the end, real atom-economic hydroformylation is also feasible [14,15]. Hydroformylation has progressed with the help of syngas surrogates [15], such as formaldehyde [16], alcohols, formic acid [17] and glyoxylic acid [18].

The present study uses formaldehyde and glyoxylic acid as sources of H_2 and CO and employs Schiff base palladium complexes as catalysts for the hydroformylation of alkenes. Once the optimal reaction conditions were established, various functionalized olefins were effectively transformed into the required linear aldehydes. Highly selective and regio- and chemoselective olefine to aldehyde transfer hydroformylation of organic substrate in the unsaturated bonds, either internal or terminal, assisted by microwave and resulting in the *in situ* production of syngas. Furthermore, a palladium complex of (*E*)-4-((4-nitrobenzylidene)amino)phenol ligand was used to hydroformylate eight entry to the linear aldehyde using microwave heating, obtaining a very high regioselectivity (l/b).

EXPERIMENTAL

The chemicals and solvents purchased from a commercial suppliers were utilized after the additional purification. Derivatives like styrene, formaldehyde and glyoxylic acid were obtained from CDH (New Delhi, India). The FT-IR, GC-MS and NMR spectra were acquired at Sophisticated Analytical Instrumentation Facility (SAIF), Panjab University, Chandigarh, India and Central Instrumentation Facilities (CIF), Indian Institute of Science Education and Research (IISER), Bhopal using Bruker Avance 400 or 600 spectrometer at room temperature using TMS as internal solvent.

Synthesis of (*E*)-4-((4-nitrobenzylidene)amino)phenol: A solution of 4-nitrobenzaldehyde (0.5 g, 3.3 mmol) and 4-aminophenol (0.41 g, 3.3 mmol) in benzene (30 mL) was heated with occasional stirring and allowed to reflux for 1 h. An orange solid was recrystallized from hot benzene after removing the solvent (10 mL) [19-21]. Yield: 77% (0.61 g); m.p.: 168 ºC. Colour: orange solid; IR (ATR, cm^{-1}): 3487 (br, -OH), 2924 (m, =C-H), 1648 (m, C=N), 1592 (m, C=C), 1537 and 1346 (s), 1278.7 (C-N), 1178 (m, C-O), 854.5, 837.6, 752.3, 728.4, 691.3. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ: 6.84 (d, 3 *J* = 8.8 Hz, 2H), 7.30 (d, 3 *J* = 8.8 Hz, 2H), 8.10 (d, 3 *J* = 8.8 Hz, 2H), 8.31 (d, 3 *J* = 78.4 Hz, 2H), 8.77 (s, 1H), 9.75 (bs, 1H).

Synthesis of Schiff base complexes [$Pd_2L_2Cl_2$]: Palladium complexes were synthesized under a nitrogen atmosphere. The solvent was deoxygenated and distilled before use. The Schiff base (4.88 mmol; 0.8844 g) was added to methanolic solution of palladium chloride (2.44 mmol; 0.4330 g) while being continuously stirred at 30 ºC followed by the addition of (*E*)-4-((4-nitrobenzylidene)amino)phenol and then the mixture was thoroughly stirred for an additional hour [22]. Gradually, the greenish-yellow precipitate of palladium complex was filtered, washed thoroughly with methanol and then vacuum-dried. Yield: 81%; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ: 8.40 (d, 2H), 8.34 (d, 2H), 8.07 (d, 2H), 8.4 (s, 2H), 6.97 (d, 4H), 6.82 (d, 4H), 9.41 (bs, 2H).

Hydroformylation process

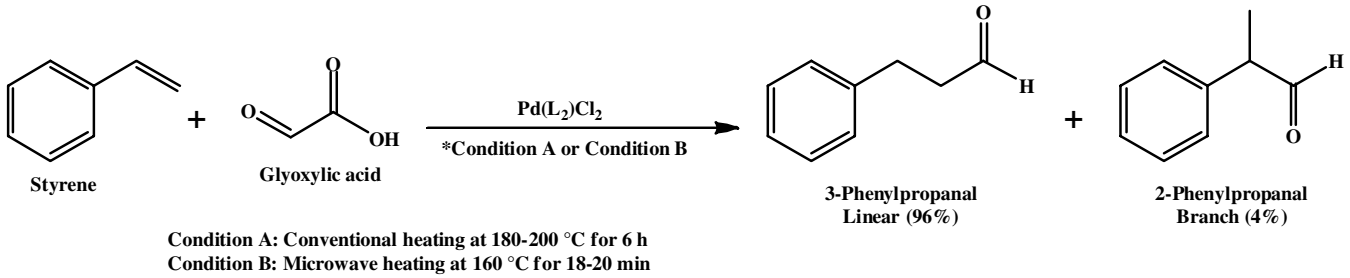
Hydroformylation reaction in conventional heating: Hydroformylation of all substrates in the glyoxylic acid medium was prepared by regularly purging and evacuating a 100 mL reaction flask with pure nitrogen. Then, conventional heating hydroformylation was performed. The palladium Schiff base complex catalyst solution in glyoxylic acid was bubbled with pure nitrogen for 10-15 min before being added to the reaction flask. In round bottom flask, carefully added 10 mL glyoxylic acid, 2 mL substrate, 1-2 drops of DMF and catalyst (0.004 g) and the setup was immediately closed. The condenser was fitted into the spherical bottle flask and a tripod stand was attached now, heat was allowed to complete the reaction.

The temperature of the reacting solution was maintained constant by vigorously swirling it with a magnetic stirrer and immersing the flask in a silicon oil bath that maintained a set temperature. The solution of palladium catalyst original yellow tint turned green or greenish brown for the first 5 to 10 min. This colour shift was observed during the reaction. The mixture was heated at 180-200 ºC for 6 h to finish the process. The reactants and products were examined by gas chromatography using an eight-fit 10% OV-17 column. Two aldehyde molecules *viz*. 2-phenyl propionaldehyde and 3-phenyl propionaldehyde were identified using GC-MS technique.

Hydroformylation reaction in microwave heating: The same reaction conditions as conventional heating were applied to the hydroformylation procedure of terminal alkene using microwave heating. Hydroformylation was carried out in glass-coated microwave ovens using Teflon chambers. After being thoroughly cleaned and drained, the Teflon chamber was stored beneath the microwave oven. After being collected in a reaction tube, the solution was kept in the Teflon chamber which contained 1 drop of DMF, 1 mL of styrene, 2 mL of glyoxylic acid and the required quantity of catalyst (0.0004 mmol). The mixture was microwaved for 18-20 min at 160 ºC to complete the process (**Scheme-I**). The crude product mixture was then analyzed using the GC-MS technique.

RESULTS AND DISCUSSION

The styrene was conventionally heated for 6 h at 180-200 ºC with 10 mL of glyoxylic acid and 0.0004 mmol of [Pd((*E*)-4-((4-nitrobenzylidene)amino)phenol)] catalyst under solvent-free condition. A 34% conversion of a linear and branched aldehyde with a ratio of 96:4 (entry-1, Table-1) was observed. The exact condition was applied for the first six entries (styrene and their derivatives). In entry 2, introduction of methoxy group



Scheme-I: Hydroformylation of styrene by palladium complex

TABLE-1
Pd-SCHIFF BASE CATALYZED HYDROFORMYLATION REACTION UNDER CONVENTIONAL HEATING

Entry	Substrate	Syngas source	[a]Products	[b]Yields (%)	[c]l/b
1	Styrene	Glyoxylic acid	3-Phenylpropanal	34	96:4
2	1-Methoxy-4-vinyl benzene	Glyoxylic acid	3-(4-Methoxyphenyl)propanal	41	95:5
3	1-Chloro-4-vinyl benzene	Glyoxylic acid	3-(4-Chlorophenyl)propanal	43	98:2
4	1-Methyl-4-vinyl benzene	Glyoxylic acid	3-(*p*-Tolyl)propanal	37	94:6
5	1,3,5-Trimethyl-2-vinyl benzene	Glyoxylic acid	3-Mesitylpropanal	32	97:3
6	2-Methylstyrene	Glyoxylic acid	3-(*o*-Tolyl)propanal	33	98:2
7	[d]Styrene	Formaldehyde	–	–	–
8	[d]1-Methoxy-4-vinyl benzene	Formaldehyde	–	–	–

Reaction condition: [a]Liner product, [b]Product yield in percentage is determined by GC-MS, [c]Branched and linear ratio and [d]Formaldehyde 10 mL (CO and H_2 source).

in the *para*-position of styrene slightly increases the aldehyde yield (41%, n/i 95;5). When comparing the eight entries, entry -3 comprising 1-chloro-4-vinylbenene (Table-1) displays the highest product yield of 43% with a ratio of 98:2. In contrast, 1,3,5-trimethyl-2-vinylbenene (entry-5) exhibited the lowest product yield of 32% due to the presence of three bulky groups in styrene decrease the reactivity but increases the selectivity (97:3, Table-1). Styrene and 1-methoxy-4-vinylbenzene (entries 7 and 8) were reacted with 10 mL of formaldehyde using catalyst [Pd(*E*)-4-((4-nitrobenzoylidene)amino)phenol]. Since formaldehyde does not breakdown into CO and H_2 under these reaction conditions, no aldehyde yield was detected.

Applying microwave heating, styrene was heated for 18 min at 160 ºC in the presence of Schiff base palladium complexes as catalyst under solvent-free conditions, it was observed that 84% yield of styrene had transformed to linear and branched aldehyde, with a ratio of 96:4 (entry 1, Table-2). In case of 1-methoxy-4-vinylbenzene and 1-chloro-4-vinylbenzene, a gradual increase in the product yields of 91% and 93% (entries 2 and 3), respectively was observed, which can be attributed due to the presence of electron-withdrawing groups (-OCH_3 and Cl groups at the *para*-position) results in the increase of the selectivity and productivity of product during hydroformylation and it was also found that with a branched/linear ratio of 98:2, entry-3 exhibits a greater yield of 93% compared to all eight entries.

Typically, the styrene undergoes hydroformylation with Rh catalysis to produce the branching chiral aldehyde as the primary product [23]. Moreover, potent π-acceptor ligands can cause an inversion of regioselectivity. Higher temperatures are necessary to convert long-chain olefins to the equivalent aldehyde efficiently. This result supports the hypothesis that styrene is inherently more reactive than alkenes. For all styrene derivatives, the Pd-Schiff base catalyst favoured the smaller substrate's higher yielding conversion. A compound possessing a functional group exhibited the highest degree of selectivity towards the substrate. The electron-withdrawing group produces an outstanding yield of 93% in entry 3, 1 chloro-4-vinylbenzene (Table-1). This group also boosts the reactivity of the substrate. These results suggest that a massive increase

TABLE-2
Pd-SCHIFF BASE CATALYZED HYDROFORMYLATION REACTION UNDER MICROWAVE HEATING

Entry	Substrate	Syngas source	[a]Products	[b]Yields (%)	[c]l/b
1	Styrene	Glyoxylic acid	3-Phenylpropanal	84	96:4
2	1-Methoxy-4-vinylbenene	Glyoxylic acid	3-(4-Methoxyphenyl)propanal	91	97:3
3	1-Chloro-4-vinylbenene	Glyoxylic acid	3-(4-Chlorophenyl)propanal	93	98:2
4	1-Methyl-4-vinylbenene	Glyoxylic acid	3-(*p*-Tolyl)propanal	87	94:6
5	1,3,5-Trimethyl-2-vinylbenene	Glyoxylic acid	3-Mesitylpropanal	82	97:3
6	2-Methyl styrene	Glyoxylic acid	3-(*o*-Tolyl)propanal	83	98:2
7	[d]Styrene	Formaldehyde	–	–	–
8	[d]1-Methoxy-4-vinylbenzene	Formaldehyde	–	–	–

Reaction condition: [a]Liner product, [b]Product yield in percentage is determined by GC-MS, [c]Branched and linear ratio and [d]Formaldehyde 2 mL (CO and H_2 source).

in reaction rate is the unique impact attributed to the microwaves during hydroformylation.

The successful high-yielding conversion of substituted styrene demonstrated the compatibility of the method with different functional groups (Table-2). The microwave effect significantly impacts the hydroformylation reaction in terms of application and effectiveness. The same reaction conditions apply to entries 7 and 8, where no product is generated when formaldehyde is utilized as syngas source. Under the identical reaction conditions and substituted styrenes with glyoxylic acid as the source of H_2 and CO at 180-200 ºC for 6-7 h, the conventional heating technique produces a much lower product yield (Table-1) than the microwave heating method (Table-2).

Table-2 illustrates the hydroformylation of aromatic olefins with remarkably high branched to linear selectivities. The range of selectivities for *p*-chloroprene and *p*-methyl styrene is 94:6 to 98:2. It was found that the linear-to-branch ratio of substituted styrenes with electron withdrawing group was smaller than that of electron-donating group. A fascinating aspect to observe is the impact of the steric effects of substrate on the regioselectivity of the hydroformylation process. When one methyl group was added to the *ortho*-position of styrene, there was a considerable increase in both the reactivity and the regioselectivity. The formation of benzylic Pd-species favour the generation of branched aldehydes, is prevented due to the presence of *ortho* substituent and the rapid reduction elimination brought on by steric interactions. Adding 2,4,6-trimethyl styrene drastically decreased the reactivity of the substrate, which may cause the substrate inability to coordinate with the metal center. A possible explanation for the significant regioselectivity seen during the hydroformylation of styrene to linear aldehyde is the steric interaction between the ligand and the substrate.

Linear and branched aldehydes are among the isomeric products produced by the reaction without alkenes and cycloalkenes as substrate. Olefins with different chain lengths are commonly employed in bulk chemical processes; however, functionalized substrates are also desirable targets. In general, internal olefins react faster than terminal bonds. The rate of hydroformylation decreases with an increase in the steric barrier of the substrate. More powerful catalysts or harsher reaction conditions are needed to branch the olefins. Functional groups may also impact the standard regioselectivity of the parent

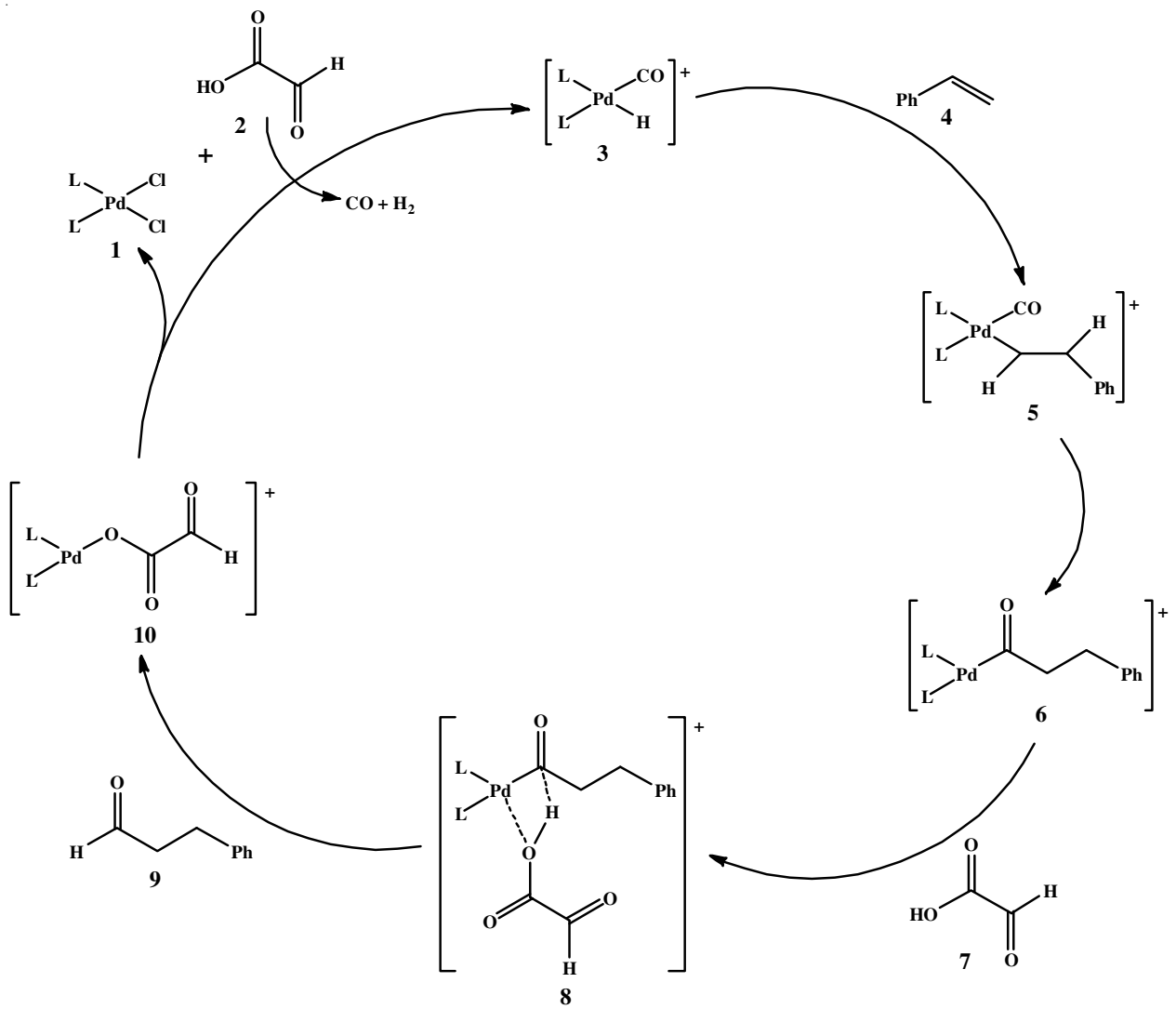


Fig. 1. Hydroformylation reaction mechanism of styrene with PdL_2 complexes (where L = 2(*E*)-4-((4-nitrobenzylidene)amino)phenol

olefin during hydroformylation. For instance, styrene is frequently utilized to create branched aldehyde. An illustration of a conversion and yield ratio is shown in Tables 1 and 2. Each olefin has a preference for bond formation at the terminal. Internal alkenes yield less than terminal alkenes due to the alkenes' tendency to branch. Pd catalysts could be helpful for the hydroformylation of alkenes and the degradation of glyoxylic acid, albeit at a lower yield than styrene. This procedure produced aldehydes with a 93% yield (entry 3, Table-1) and high *n*-regioselectivity without gaseous CO and H_2.

The reaction takes place under syngas-free conditions, using widely available glyoxylic acid as formyl source and produces a wide range of α-unsaturated aldehydes [24]. Under the experimental circumstances that are usually needed, conventional hydroformylation presents several problems, including using gaseous hydrogen and carbon monoxide at high pressure and over extended reaction times. The reaction must be carried out in a microwave oven and glyoxylic acid must be utilized as a backup source of H_2 and CO. This work uses glyoxylic acid as a solvent and hydrogen and carbon monoxide sources. This reduces the environmental impact of the reaction because no additional environmentally harmful solvents were employed after the product was separated. Alkene hydroformylation is an very effective process that usually yields a wide range of regioisomers through conjugate diene equivalent reactions.

Fig. 1 shows the mechanism of the hydroformylation reaction catalyzed by palladium as well as possible catalytic cycle. Palladium species (**10**) was first produced *via* the reaction of palladium complex (**1**) and CHOCOOH (**2**). The release of CO_2, which combines with styrene, the active cationic palladium hydride species **3**, can be created *in situ*. The insertion reaction and the creation of vinyl palladium intermediate **5** follow this. When CO is inserted into the palladium-vinyl link, acyl palladium complex (**6**) is formed. The intended aldehyde (**9**) should next be produced *via* the hydrogenolysis reaction with glyoxylic acid, which will also renew the palladium species (**10**).

Conclusion

In this work, the hydroformylation processes of olefins was carried out more efficiently and sustainably with the use of microwave irradiation, which uses less energy than conventional heating systems and delivers higher yields in shorter reaction times. Additionally, the development of palladium Schiff base catalytic systems that could particularly promote the external double bond hydroformylation (with conventional heating) or sequential hydroformylation in a microwave environment was made possible. Furthermore, employing the CO and H_2 cylinders significantly affects the catalytic activity. The glyoxylic acid, in particular, led to the higher conversions, presumably due to its improved capacity to function without a solvent under microwave irradiation. These results offer a multitude of prospects for the development of ideal reaction conditions that will enable the hydroformylation of organic substrate in internal or terminal unsaturated bonds with the assistance of microwaves.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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