NJC

PAPER

Check for updates

Cite this: *New J. Chem.*, 2026, **50**, 647

Nickel-catalyzed rearrangement of aldoximes or aldehyde into primary amides

Neelakandan Devika, *[a] Bellie Sundaram Krishnamoorthy [b] and Nandhagopal Raja *[c]

Received 28th June 2025,
Accepted 26th November 2025

DOI: 10.1039/d5nj02653a

rsc.li/njc

The synthesis of primary amides from aldehydes was carried out using the commercially available catalyst [NiCl$_2$(PPh$_3$)$_2$] without the use of any chelating agents, additives, or harsh reagents in a one-pot process. We investigated the effects of catalyst screening, reaction time, solvent, bases, and catalyst loading for this reaction. The methodology demonstrated broad substrate compatibility, proceeding efficiently with a diverse range of aldehydes. These included electron-rich, electron-deficient, halogenated, ring-extended, and aliphatic aldehydes, as well as substrates featuring extended conjugation and hetero-aromatic frameworks. A nickel catalytic system was developed, and the amides were obtained in good to excellent yields through the reaction of aldehydes and hydroxylamine hydrochloride in toluene with NaHCO$_3$. Finally, a plausible mechanism involving Ni(II)/(III) species is proposed and elucidated through DFT calculations at the BP86/Def2-TZVP level.

Introduction

The amide group is one of the most important functional groups in synthetic organic chemistry.[1] Amides are especially adaptable synthetic intermediates used in the construction of numerous pharmacological and biologically active products, drug stabilizers, detergents, lubricants, and polymers.[2] Based on traditional methods, amides can be synthesized by the activation of a carboxylic acid or carboxylic derivatives with a stoichiometric quantity of an amine. However, these methods suffer from the drawback of producing a stoichiometric amount of waste product.[3] Additionally, amides can be synthesized using enzymes or bio-catalysts as reagents, although high isolation costs and somewhat limited substrate ranges might be problematic.[4] Several synthetic strategies have been developed, including the Beckmann rearrangement,[5] Schmidt reaction,[6] Staudinger reaction,[7] reactions of alcohols with amines,[8] and hydroamination of alkynes.[9]

The Beckmann rearrangement (Scheme 1) is one of the most effective methods for preparing amides directly from ketoximes using a Lewis acid.[10] This reaction involves oximes with strong acids and hazardous reagents, often necessitating harsh conditions. The generation of by-products limits its general applicability,[11] and preparing primary amides is challenging due to the inactive migration of hydrogen from aldoximes or aldehydes.[12]

A successful modification of the standard Beckmann rearrangement conditions has been introduced using promoters such as aluminum oxide,[13] boronic acids,[14] thionyl chloride,[15] carbonyldiimidazole (CDI),[16] cyclopropenium salts,[17] propylphosphonic anhydride (T$_3$P),[18] sulfuryl fluoride,[19] tetramethyl orthosilicate (TMOS)[20] and triphenylphosphine oxide.[21] These modifications often necessitate elevated temperatures, precise catalyst loading with costly, volatile, and toxic solvents, as well as an excess of reagents to activate oximes. The introduction of transition metal catalysts in amide synthesis also opens up the possibility of starting from substrates other than carboxylic acids or their derivatives.[8]

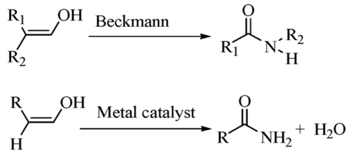
Significant efforts have been made to explore various transition metal-catalyzed one-pot syntheses of primary amides from aldehydes and hydroxylamine hydrochloride in the presence of mild bases, through the rearrangement of *in situ*-formed aldoximes (Scheme 1).[22–31] Certain ruthenium complexes, such as [RuCl$_2$(terpy)(PPh$_3$)$_2$],[32] [RuCl$_2$(DMSO)$_4$][12] (where DMSO stands for dimethyl sulfoxide), and [RuCl(CO)(PPh$_3$)(TAC)],[33] have been employed as homogeneous catalysts for the transformation using NH$_2$OH·HCl and NaHCO$_3$. Venkatachalam *et al.* recently reported that half-sandwich organometallic ruthenium complexes efficiently catalyze the rearrangement of aldoximes to amides.[34,35] In a significant advancement, Yao and coworkers have introduced an iridium catalyst for this reaction, showcasing excellent catalytic activity, mild reaction conditions, and a broad substrate scope with good-to-excellent yields through a one-pot amidation reaction of NH$_2$OH·HCl with aldehydes.[36]

---

[a] Department of Chemistry, University College of Engineering, BIT campus, Anna University, Tiruchirappalli 620024, Tamil Nadu, India. E-mail: ndevichem@aubit.edu.in

[b] Department of Chemistry (SF), PSG College of Arts and Science, Coimbatore-641014, Tamil Nadu, India

[c] Department of Chemistry, University College of Engineering, Anna University, Ariyalur 621731, Tamil Nadu, India. E-mail: nraja@auucea.edu.in



Scheme 1 Oxime to amide transformations.

In continuation of the current research on the synthesis, characterization, catalytic, and biological applications of ruthenium, rhodium, and iridium complexes,[37–41] $[NiCl_2(PPh_3)_2]$ was investigated as a catalyst for the organic transformation of aldehydes with hydroxylamine hydrochloride to primary amides in the presence of $NaHCO_3$. The main advantages of this catalyst are its commercial availability, atom-economical nature, cost-effectiveness, and ability to convert aldehydes with hydroxylamine hydrochloride to primary amides. A reaction mechanism involving the Ni(II)/(III) species is proposed and supported by DFT(BP86/Def2-TZVP) calculations. DFT computations have already been used successfully for mechanistic investigations.[42,43]

Experimental

$NiCl_2 \cdot 6H_2O$, $NiBr_2 \cdot 6H_2O$, $[NiCl_2(PPh_3)_2]$, $[NiBr_2(PPh_3)_2]$, $NaHCO_3$, $KHCO_3$, Na_2CO_3, Et_3N, 4-anisaldehyde, benzaldehyde, *trans*-cinnamaldehyde, triethylamine, hydroxylamine hydrochloride,1-naphthaldehyde, acetaldehyde and 2-thiophenecarboxaldehyde were obtained from Sigma-Aldrich, whereas 4-nitrobenzaldehyde and 4-tolylaldehyde were purchased from Fluka, and 4-bromo benzaldehyde from Acros. All reagents were of analytical grade and used as received.

General procedure for the conversion of aldehydes to amides

$[NiCl_2(PPh_3)_2]$ (0.001 mmol), the aldehyde (1 mmol), $NH_2OH \cdot HCl$ (1 mmol), and $NaHCO_3$ (1 mmol) were introduced into a dried Schlenk tube and purged with N_2. Dried and degassed toluene (2 mL) was then added to the mixture, which was stirred for about 10 minutes at room temperature before being refluxed under stirring for 6 hours. The mixture was cooled, and the products were extracted with methanol and dichloromethane, then filtered through Celite to remove the remaining catalyst and $NaHCO_3$. The crude amide was purified using column chromatography and dried under vacuum.

Computational details

DFT calculations were carried out using the software ORCA developed by Frank Neese and co-workers.[44] All calculations were performed using the BP86 density functional[45–48] and Def2-TZVP basis set included in the ORCA programme, which is free for academic use. Self-consistent field (SCF) calculations were performed using the TIGHTSCF convergence criteria. The geometry optimization was carried out and the resulting geometries are confirmed as minima through the frequency calculations. Pictures of the optimized geometries and the Frontier molecular orbitals are taken using the graphics programme Chemcraft.[49]

Results and discussion

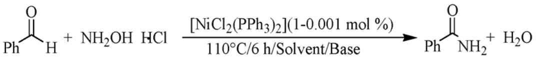
Effect of time and different nickel catalysts on amide formation

The one-pot conversion of aldehydes to amides in the presence of $NH_2OH \cdot HCl$ using various nickel complexes as catalysts was investigated under different conditions. For overall optimization, benzaldehyde was used as the test substrate. Catalyst screening was the initial optimization process. The performances of various nickel complexes or salts were compared in the reaction of benzaldehyde and hydroxylamine hydrochloride, leading to the formation of benzamide after 24 hours at 110 °C in toluene (Scheme 2). The results are summarized in Table 1. It was observed that no conversion of benzaldehyde to benzamide occurred in the absence of a base or a catalyst (entry 1).

The catalysts $[NiCl_2(PPh_3)_2]$ and $[NiBr_2(PPh_3)_2]$ proved to be excellent (entries 4 and 5) compared to other nickel salts such as $NiCl_2 \cdot 6H_2O$ and $NiBr_2 \cdot 6H_2O$ (entries 2 and 3). Thus, $[NiCl_2(PPh_3)_2]$ was identified as the best catalyst for amide formation. The next optimization involved examining the effect of time on the conversion of benzaldehyde to benzamide, ranging from 1 to 24 hours (entries 4 and 6–8). The results showed that an excellent conversion was achieved at 6 hours (entry 7), which was concluded to be the optimized time. Beyond that time, no notable improvement in the formation of benzamide was observed.

Effect of solvent, base and catalyst loading on amide formation

The choice of base was the next step in optimization. Since the base facilitates the neutralization of $NH_2OH \cdot HCl$, its effect on the formation of benzamide from benzaldehyde (Scheme 3) was investigated. Benzaldehyde was allowed to react with $[NiCl_2(PPh_3)_2]$ in the presence of different bases such as $NaHCO_3$, $KHCO_3$, Na_2CO_3, and Et_3N. Similarly, the effects of different solvents (benzene, xylene, toluene, and acetonitrile) were also investigated (Table 2). The results revealed that $NaHCO_3$ provided an excellent

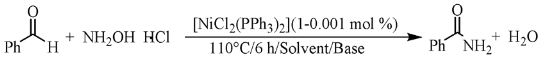


Scheme 2 Effect of time and different nickel catalysts on amide formation.

Table 1 Effect of time and different nickel catalysts on amide formation[a]

Entry	Complexes	Time (h)	Conversion[b]
1	None	24	0
2	$NiCl_2 \cdot 6H_2O$	24	35
3	$NiBr_2 \cdot 6H_2O$	24	24
4	$[NiCl_2(PPh_3)_2]$	24	95
5	$[NiBr_2(PPh_3)_2]$	24	74
6	$[NiCl_2(PPh_3)_2]$	12	95
7	$[NiCl_2(PPh_3)_2]$	6	95
8	$[NiCl_2(PPh_3)_2]$	1	85

[a] Conditions: reactions were carried out at 110 °C using 1 mmol of benzaldehyde, 1 mmol of $NH_2OH \cdot HCl$, 1 mmol of $NaHCO_3$, and 1 mol% of catalyst in 2 mL of toluene. [b] Conversions were determined using ^1H NMR (integrations of $H_{aldehyde}$ *vs.* H_{amide}).



Scheme 3 Effect of solvent, base and catalyst loading on amide formation.

Table 2 Effect of solvent, base and catalyst loading on amide formation[a]

Entry	Solvent	Base	Catalyst (mol%)	Conversion[b]
1	Benzene	$NaHCO_3$	1	55
2	Xylene	$NaHCO_3$	1	60
3	Toluene	$NaHCO_3$	1	95
4	Acetonitrile	$NaHCO_3$	1	63
5	Toluene	$KHCO_3$	1	65
6	Toluene	Na_2CO_3	1	40
7	Toluene	Et_3N	1	<20
8	Toluene	$NaHCO_3$	0.01	22
9	Toluene	$NaHCO_3$	0.1	92
10	Toluene	$NaHCO_3$	0.5	95

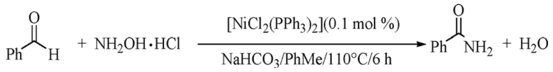
[a] Conditions: reactions were carried out at 80–110 °C using 1 mmol of benzaldehyde, 1 mmol of $NH_2OH{\cdot}HCl$, 1 mmol of base, and 1–0.001 mol % of $[NiCl_2(PPh_3)_2]$ catalyst in 2 mL of solvent. [b] Conversions were determined using ^1H NMR (integrations of $H_{aldehyde}$ *vs.* H_{amide}).

yield of amide conversion in toluene compared to other bases and solvents. $KHCO_3$ resulted in a better conversion of amide, while Na_2CO_3 and Et_3N led to moderate and poor conversion, respectively. It was found that using $NaHCO_3$ as a base with toluene as a solvent at 110 °C achieved the maximum conversion, which was concluded as the optimized condition for the reaction. Furthermore, the efficiency of catalyst activity was tested at different catalyst-to-substrate ratios in the aldehyde-to-amide formation reaction using $[NiCl_2(PPh_3)_2]$, and the results are summarized in Table 2.

Increasing the catalyst-to-substrate ratio to 0.01 or 0.02 allowed the reaction to proceed smoothly, with a moderate drop in the isolated yield. When the catalyst-to-substrate ratio was decreased to 0.05 mol%, a moderate isolated yield was obtained. The reaction proceeded with an excellent isolated yield of amide when the catalyst-to-substrate ratio was 0.1 mol%, 0.2 mol%, and 0.5 mol%. Thus, it was concluded that a catalyst-to-substrate ratio of 0.1 mol% is the best compromise, achieving optimal reaction rates in toluene with a 92% yield of amide (entry 9).

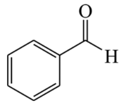
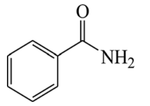
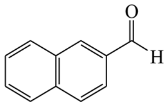
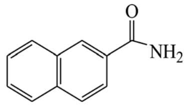
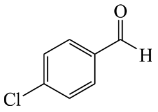
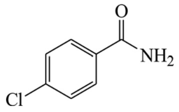
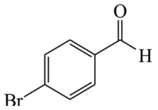
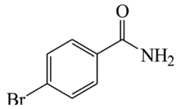
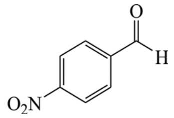
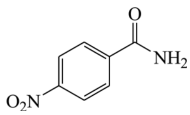
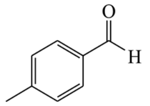
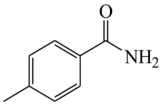
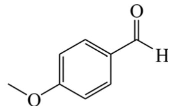
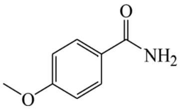
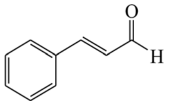
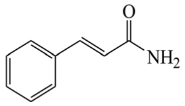
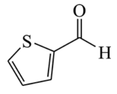
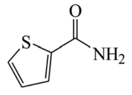
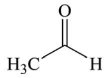
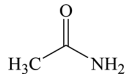
One-pot conversion of aldehydes to amides using $[NiCl_2(PPh_3)_2]$

Our catalytic system is effective for a broad range of substrates, including aromatic, extended aromatic, heterocyclic aromatic, and aliphatic aldehydes (Scheme 4), as well as those with electron-releasing and electron-withdrawing substituents. These aldehydes were converted to their corresponding amides in a one-pot process, with the results summarized in Table 3 (entries 1–10). Initially, benzaldehyde was converted to benzamide with a 92% yield (entry 1). When the aromatic ring system was extended, the yield decreased. For example, 2-naphthaldehyde was converted to 2-naphthamide with an 87% yield (entry 2). The decrease in yield from benzaldehyde (92%) to 2-naphthaldehyde (87%) is a direct result of the extended aromatic system. The larger naphthalene ring can delocalize electrons more effectively, slightly reducing the reactivity of the aldehyde group.



Scheme 4 One-pot conversion of aldehydes to amides using nickel catalysts.

Table 3 One-pot conversion of aldehydes to amides using $[NiCl_2(PPh_3)_2]$[a]

Entry	Aldehyde	Amide	Yield[b] (%)	TON[c]	TOF[d]
1			92	920	153
2			87	870	145
3			99	990	165
4			98	980	163
5			95	950	158
6			89	890	148
7			82	820	137
8			97	970	162
9			99	990	165
10			99	990	165

[a] Reaction conditions: $[NiCl_2(PPh_3)_2]$ (0.1 mol %), benzaldehyde (1 mmol), $NH_2OH{\cdot}HCl$ (1 mmol) and $NaHCO_3$ (1 mmol) in toluene (2 mL) under a N_2 atmosphere. [b] Isolated yields after column chromatography, and yields obtained by ^1H NMR (integrations of Haldehyde *vs.* Hamide). [c] TON = turnover number = ratio of moles of product formed to moles of catalyst used. [d] TOF = TON h^{-1}.

The presence of electron-withdrawing groups (–Cl, –Br, and $-NO_2$) and electron-donating groups ($-CH_3$ and $-OCH_3$) significantly influenced the conversion of the aldehyde to the amide. 4-Chlorobenzaldehyde and 4-bromobenzaldehyde were converted to their corresponding amides with 99% and 98% yields,

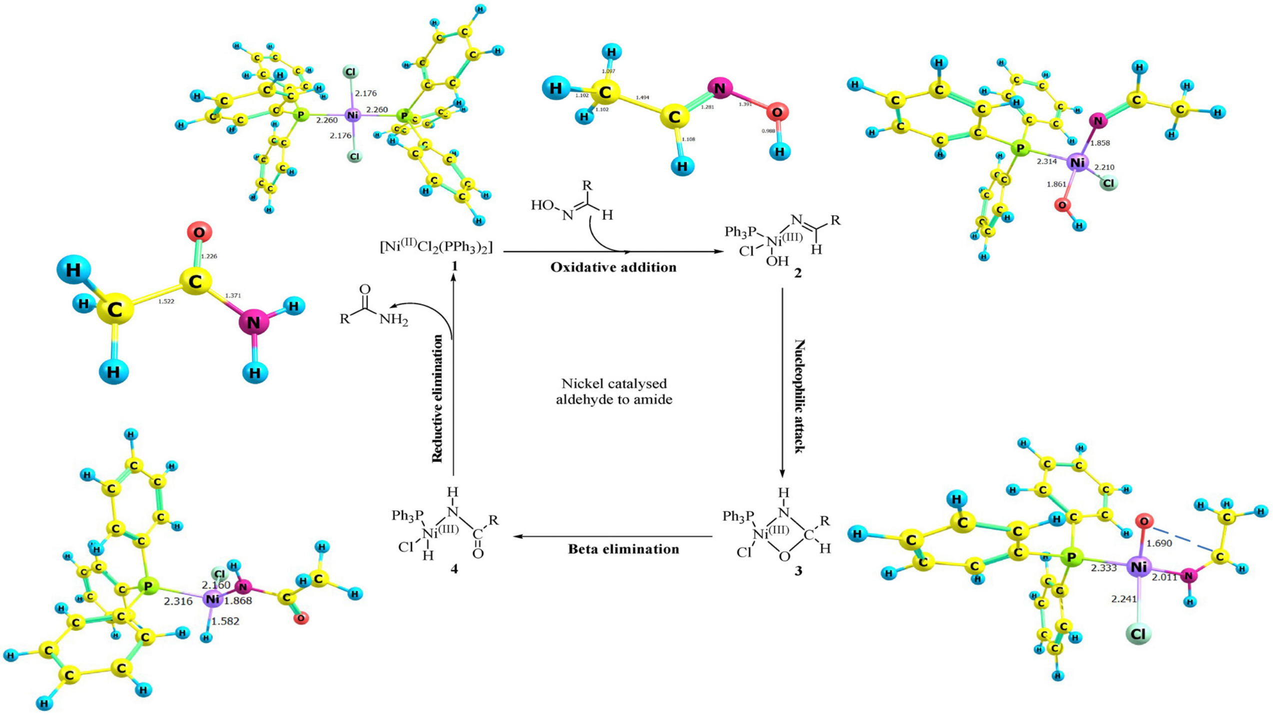


Fig. 1 Plausible mechanism for one-pot conversion of aldoxime to amide.

respectively (entries 3 and 4). Conversely, 4-nitrobenzaldehyde yielded 95% 4-nitrobenzamide (entry 5). These groups, particularly the strongly deactivating nitro group, likely make the aldehyde carbonyl carbon more electrophilic. This increased electrophilicity enhances its reactivity toward the catalytic species, ultimately leading to a more efficient conversion to the amide. In contrast, 4-methylbenzaldehyde and 4-methoxybenzaldehyde yielded their respective amides with 89% and 82% yields (entries 6 and 7). Overall, electron-withdrawing groups enhanced the yield compared to electron-releasing groups. These electron-releasing groups increase the electron density on the aromatic ring and, by extension, on the carbonyl carbon through resonance and inductive effects. This reduces the electrophilicity of the carbonyl group, making it less reactive and thus leading to a slightly diminished yield compared to the electron-withdrawing group-substituted substrates. Extended conjugation on the benzene ring also favored the yield; for instance, cinnamaldehyde yielded 97% cinnamide (entry 8). The high yield with cinnamaldehyde (97%) presents an interesting contrast, suggesting that the extended conjugation in this linear system is beneficial, possibly by stabilizing a key transition state.

The introduction of a heteroatom in the ring resulted in an excellent yield. Notably, [NiCl$_2$(PPh$_3$)$_2$] efficiently catalyzed the conversion of 2-thiophenecarboxaldehyde to the corresponding amide with a yield of >99% (entry 9). The presence of the sulfur heteroatom in the thiophene ring appears to be highly synergistic with our catalyst. This could be due to the unique electronic properties of the thiophene ring or a favorable interaction between the catalyst and the sulfur atom. Finally, when an aliphatic group was introduced, acetaldehyde gave a 99% conversion to acetamide (entry 10). We also tested formaldehyde for the amidation reaction, but unfortunately, we did not obtain formamide. The excellent conversion of acetaldehyde (99%) demonstrates that the system is not limited to aromatic compounds but is also highly effective for simple aliphatic aldehydes. This broadens the applicability of the catalyst significantly. The failure to obtain formamide from formaldehyde is an important negative.

The plausible mechanism for the present nickel-catalyzed transformation of aldehyde into amide with high yields, according to previous reports on similar metal-catalyzed reactions, is shown in Fig. 1.[12] The reaction begins with the formation of the aldoxime, which is a crucial intermediate. This occurs when the aldehyde substrate reacts with hydroxylamine hydrochloride in the presence of a sodium bicarbonate base. The bicarbonate acts to deprotonate the hydroxylamine hydrochloride, making it more nucleophilic and able to attack the carbonyl carbon of the aldehyde. The catalytic cycle itself begins when the Ni(II) pre-catalyst (**1**) undergoes an oxidative addition reaction. In this

Table 4 DFT(BP86/Def2-TZVP) computed energy values for the reactants, intermediates and products

Molecules/intermediates	Energy (Eh)
CH$_3$CHO	−20.891644
CH$_3$CHNOH	−28.150846
NiCl$_2$(PPH$_3$)$_2$ (**1**)	−373.441082
NiCl(PPh$_3$)(OH)(NCHR) (**2**)	−246.553465
NiCl(PPh$_3$)(NH-CHR)(O) (**3**)	−246.540603
NiCl(PPh$_3$)(H)(NHCOR) (**4**)	−246.559327
CH$_3$CONH$_2$	−28.233629

process, the nickel center is oxidized from its +2 to its +3 oxidation state, forming a Ni(III) species (**2**). This step is essential as it activates the nickel catalyst and prepares it for the subsequent bond formation. Next, a key step in the process is a nucleophilic attack on the coordinated imine in the Ni(III) species (**2**). This is followed by a β-elimination of the cyclometallated

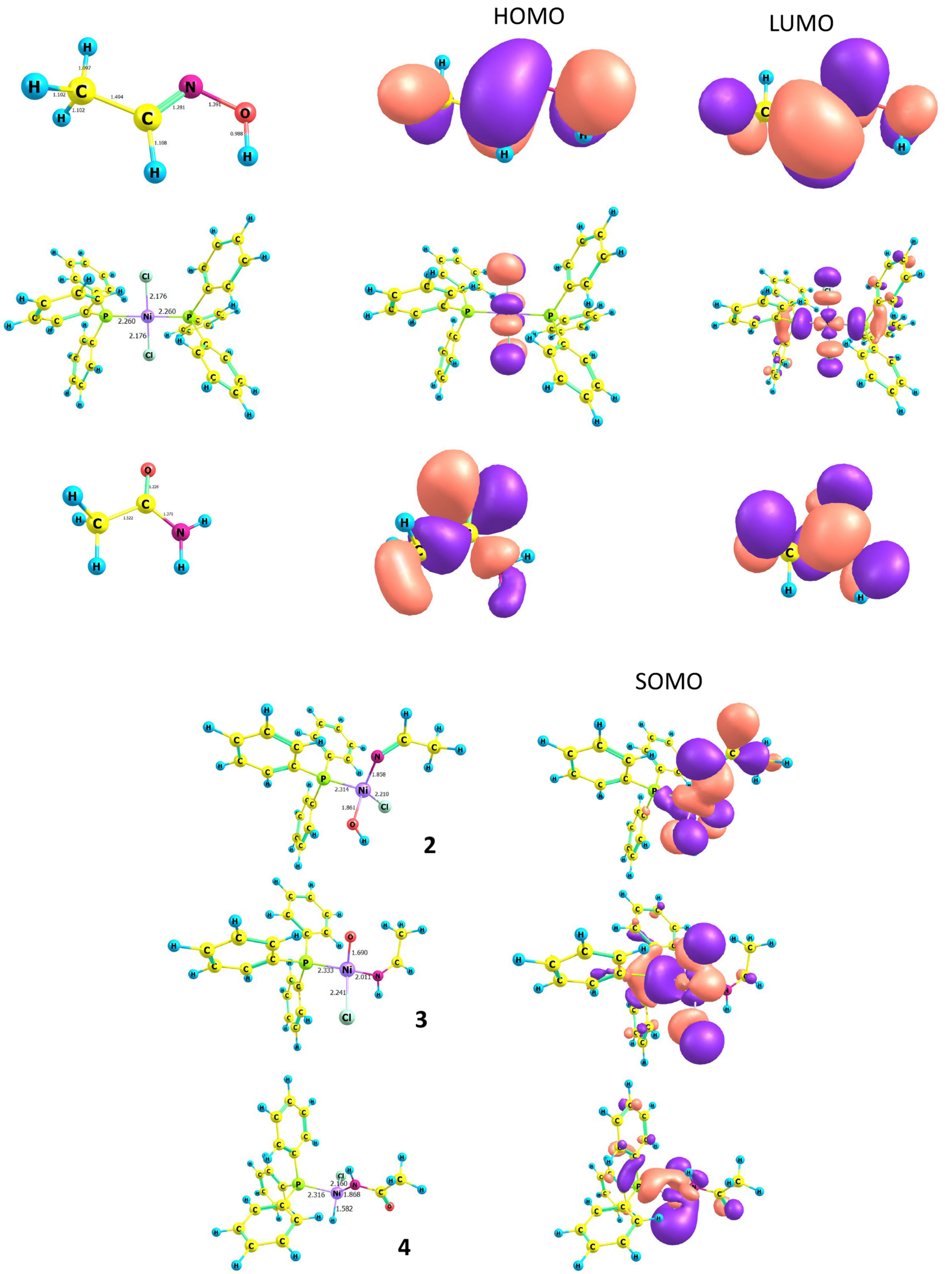


Fig. 2 Frontier molecular orbitals of the reactants, products and intermediates **2**, **3** and **4** computed from the DFT (BP86/Def2-TZVP) level.

intermediate (**3**). This process is a complex series of steps where bonds are rearranged and new species are formed, moving the reaction toward the final product. The cyclometallation refers to the formation of a ring-like structure involving the metal center. The final stage of the catalytic cycle is reductive elimination. In this step, the Ni(III) center is reduced back to its initial Ni(II) state, and the newly formed amide product is released from the catalyst. This regenerates the active Ni(II) species, allowing it to enter the cycle again and catalyze further reactions. It is important to note two key observations from this reaction. First, water was not eliminated from the intermediate (**2**), which would have led to a different product. Second, no nitrile was observed during the reaction. The absence of these byproducts confirms the specific and efficient nature of this catalytic system, which selectively produces the desired amide product. DFT(BP86/Def2-TZVP)-optimized geometries of the reactant, catalyst $NiCl_2(PPH_3)_2$, and the Ni(III) intermediates are provided in Fig. 1. The optimized geometries are found to be minima in the potential energy surface; in particular, the five-coordinated Ni(III) intermediate is also found to be a minimum. This supports the possibility that the catalytic amidation reaction can occur through the formation of Ni(III) species and the same has been proposed as a plausible mechanism. From the DFT(BP86/Def2-TZVP)-optimized geometries, the plausible intermediates (**1**), (**2**), and (**3**) in Fig. 1 show considerable stability and reasonable energy comparatively. The DFT(BP86/Def2-TZVP) computed energy of the reaction for the formation of acetamide CH_3CONH_2 from acetaldehyde is -51.95 kcal mol^{-1}, which is highly favourable (Table 4).

The proposed Ni(III) intermediates (**2**), (**3**), and (**4**) along with their energy values are provided in Table 4. Among the three intermediates of the different steps, intermediate (**4**) is -11.75 kcal mol^{-1} more stable than intermediate (**3**), but -3.68 kcal mol^{-1} more stable than intermediate (**2**). Thus, the proposed mechanism with the Ni(II)/Ni(III) species, though the Ni(III) intermediates possess a quadrate spin multiplicity, the resulting geometries are local minima in the potential energy surfaces, supporting their possible existence and involvement in the reaction. The formation of amide from the aldehyde/oxime using the $Ni(II)Cl_2(PPh_3)_2$ catalyst usually involves the following steps. (A) Activation: $NiCl_2(PPh_3)$ coordinates to the carbonyl or oxime group, increasing electrophilicity. (B) Nucleophilic attack: an amine ($R'NH_2$) attacks the activated carbonyl or imidate group. (C) Amide formation: the intermediate undergoes rearrangement and deprotonation, and the amide bond is formed with the catalyst regenerated. But the mechanism could vary depending on the particular substrates or reaction conditions. Additional factors like solvent and temperature can influence the rate of reaction and selectivity. The frontier molecular orbitals of the reactants and products along with intermediates **2**, **3**, and **4** are provided in Fig. 2a and b.

From the frontier molecular orbitals, the HOMO of $NiCL_2(PPh_3)_2$ is mainly from the d orbitals of nickel and the lone pair electrons of chlorine atoms, whereas the LUMO involves the electronic contribution from the phosphorus atoms too. Of all the three intermediates **2**, **3**, and **4**, the electronic contribution for the singly occupied molecular orbital (SOMO) is mainly from the metal nickel atom. The proposed plausible mechanism is in line with our results from DFT(BP86/Def2-TZVP) computations.

Conclusions

In summary, we have developed a novel, efficient, and cost-effective catalyst that converts aldehydes into primary amides. This catalyst exhibits excellent catalytic activity under mild conditions without requiring additives, acids, or ligands. Various aldehydes were efficiently converted into their corresponding amides in high yields. A plausible mechanism of amide formation through the Ni(III) intermediates has been proposed and supported by the DFT(BP86/Def2-TZVP) computations.

Author contributions

Neelakandan Devika – conceptualization, investigation, and writing – original draft; Nandhagopal Raja - writing – review and editing; Bellie Sundaram Krishnamoorthy – computational studies – writing – review.

Conflicts of interest

There are no conflicts to declare.

Data availability

All references include DOI hyperlinks with URLs in both the main manuscript and supplementary section.

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: materials and methods, spectral data (IR, ^1H, and ^{13}C-NMR spectra), and references. See DOI: https://doi.org/10.1039/d5nj02653a.

Acknowledgements

ND and NR thank Prof. Bruno Therrien and the University of Neuchatel for their support. ND also thanks the Vice-Chancellor, Registrar of Anna University Chennai and the Dean of the BIT campus for the permission granted to carry out her research in Switzerland.

References

1 C. L. Allen, S. Davulcu and J. M. J. Williams, *Org. Lett.*, 2010, **12**, 5096.
2 V. Froidevaux, C. Negrell, S. Caillol, J.-P. Pascault and B. Boutevin, *Chem. Rev.*, 2016, **116**, 14181.
3 V. R. Pattabiraman and J. W. Bode, *Nature*, 2011, **480**, 471.
4 M. Lubberink, W. Finnigan and S. L. Flitsch, *Green Chem.*, 2023, **25**, 2958.
5 A. B-Szafran, K. Erfurt, M. S-Kwaśny, T. Piotrowski and A. Chrobok, *ACS Sustainable Chem. Eng.*, 2022, **10**, 13568.

6 J. Liu, C. Zhang, Z. Zhang, X. Wen, X. Dou, J. Wei, X. Qiu, S. Song and N. Jiao, *Science*, 2019, **367**, 281.

7 E. Saxon, J. I. Armstrong and C. R. Bertozzi, *Org. Lett.*, 2000, **2**, 2141.

8 (*a*) C. Gunanathan, B.-D. Yehoshoa and D. Milstein, *Science*, 2007, **317**, 790; (*b*) L. U. Nordstrøm, H. Vogt and R. Madsen, *J. Am. Chem. Soc.*, 2008, **130**, 17672.

9 K. Hirano and M. Miura, *J. Am. Chem. Soc.*, 2022, **144**, 648.

10 C. H. Senanayake, L. E. Fredenburgh, R. A. Reamer, R. D. Larsen, T. R. Verhoeven and P. J. Reider, *J. Am. Chem. Soc.*, 1994, **116**, 7947.

11 R. Mocci, E. Colacino, D. L. Luca, C. Fattuoni, A. F. Porcheddu and F. Delogu, *ACS Sustainable Chem. Eng.*, 2021, **9**, 2100.

12 J. F. Hull, S. T. Hilton and R. H. Crabtree, *Inorg. Chim. Acta*, 2010, **363**, 1243.

13 Y. Uozumi and Y. M. A. Yamada, *Synfacts*, 2000, 0118.

14 R. M. Lanigan, P. Starkov and T. D. Sheppard, *J. Org. Chem.*, 2013, **78**, 4512.

15 A. Leggio, E. L. Belsito, G. De Luca, M. L. Di Gioia, V. Leotta, E. Romio, C. Siciliano and A. Liguori, *RSC Adv.*, 2016, **6**, 34468.

16 E. K. Woodman, J. G. K. Chaffey, P. A. Hopes, D. R. J. Hose and J. P. Gilday, *Org. Process Res. Dev.*, 2009, **13**, 106.

17 A. Rai and L. D. S. Yadav, *Eur. J. Org. Chem.*, 2013, 1889.

18 J. R. Dunetz, Y. Xiang, A. Baldwin and J. Ringling, *Org. Lett.*, 2011, **13**, 5048.

19 J. Gurjar and V. V. Fokin, *Chem. – Eur. J.*, 2020, **26**, 10402.

20 D. C. Braddock, P. D. Lickiss, B. C. Rowley, D. Pugh, T. Purnomo, G. Santhakumar and S. J. Fussell, *Org. Lett.*, 2018, **20**, 950.

21 J.-W. Ren, M.-N. Tong, Y.-F. Zhao and F. Ni, *Org. Lett.*, 2021, **23**, 7497.

22 D. S. Hoffenberg and C. R. Hauser, *J. Org. Chem.*, 1955, **20**, 1496.

23 L. Field, P. Barnett, S. H. Shumaker and W. S. Marshall, *J. Am. Chem. Soc.*, 1961, **83**, 1983.

24 O. Saidi, M. J. Bamford, A. J. Blacker, J. Lynch, S. P. Marsden, P. Plucinski, R. J. Watson, S. Park, Y. Choi, H. Han, S. H. Yang and S. Chang, *Chem. Commun.*, 2003, 1936.

25 N. A. Owston, A. J. Parker and J. M. J. Williams, *Org. Lett.*, 2007, **9**, 73.

26 N. A. Owston, A. J. Parker and J. M. J. Williams, *Org. Lett.*, 2007, **9**, 3599.

27 C. L. Allen, C. Burel and J. M. J. Williams, *Tetrahedron Lett.*, 2010, **51**, 2724.

28 H. Fujiwara, Y. Ogasawara, K. Yamaguchi and N. Mizuno, *Angew. Chem.*, 2007, **119**, 529.

29 C. Barfoot, G. Brooks, P. Brown, S. Dabbs, D. T. Davies, I. Giordano, A. Hennessy, G. Jones, R. Markwell, T. Miles, N. Pearson and C. A. Smethurst, *Tetrahedron Lett.*, 2010, **51**, 2685.

30 S. K. Sharma, S. D. Bishopp, C. L. Allen, R. Lawrence, M. J. Bamford, A. A. Lapkin, P. Plucinski, R. J. Watson and J. M. J. Williams, *Tetrahedron Lett.*, 2011, **52**, 4252.

31 R. R. Gowda and D. Chakraborty, *Eur. J. Org. Chem.*, 2011, **2011**, 2226–2229.

32 D. Gnanamgari and R. Crabtree, *Organometallics*, 2009, **28**, 922.

33 N. Raja, M. Ulaganatha Raja and R. Ramesh, *Inorg. Chem. Commun.*, 2012, **19**, 51.

34 M. Premkumar, P. Vijayan and G. Venkatachalam, *J. Organomet. Chem.*, 2019, **902**, 120964.

35 R. Nandhini and G. Venkatachalam, *J. Organomet. Chem.*, 2019, **895**, 15.

36 Y. Wang, W. Guo, A.-L. Guan, S. Liu and Z.-J. Yao, *Inorg. Chem.*, 2021, **60**, 11514.

37 N. Raja and B. Therrien, *J. Organomet. Chem.*, 2014, **765**, 1.

38 N. Raja, N. Devika, G. Gupta, V. L. Nayak, A. Kamal, N. Nagesh and B. Therrien, *J. Organomet. Chem.*, 2015, **794**, 104.

39 N. Devika, S. Ananthalakshmi, N. Raja, G. Gupta and B. Therrien, *J. Organomet. Chem.*, 2019, **886**, 65.

40 N. Devika, S. Ananthalakshmi and N. Raja, *Inorg. Chim. Acta*, 2024, **563**, 121907.

41 N. Devika, S. Ananthalakshmi, N. Raja, G. Gupta and B. Therrien, *J. Organomet. Chem.*, 2024, **886**, 123331.

42 W. Ding, H. Chen and H. Ji, *Ind. Eng. Chem. Res.*, 2024, **63**(16), 7064.

43 B. S. Krishnamoorthy, R. Lalitha, K. Panchanatheswaran and P. K. Chattaraj, *J. Mol. Struct. THEOCHEM*, 2006, **761**, 89.

44 F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2012, **2**, 73.

45 L. Wilk, M. Nusair and S. H. Vosko, *Can. J. Phys.*, 1981, **59**, 585.

46 A. D. Becke, *J. Chem. Phys.*, 1986, **84**, 4524.

47 J. P. Perdew, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1986, **33**, 8822.

48 C. M. Che and J. S. Huang, *Coord. Chem. Rev.*, 2002, **231**, 151.

49 *Chemcraft - graphical software for visualization of quantum chemistry computations. Version 1.8, build 682*. https://www.chemcraftprog.com.