Efficient and Sustainable One-pot Synthesis of alpha-Carbonyl Homoallylic Alcohols from Benzaldehyde and Allylic Alcohols Using both NHC and Nickel Catalysts

Yasmina Homrani, Bouchaib Mouhsine, Aurelien Bethegnies, Mohamed Amin El Amrani, Abdallah Karim, Isabelle Suisse, Mathieu Sauthier

▶ To cite this version:

Yasmina Homrani, Bouchaib Mouhsine, Aurelien Bethegnies, Mohamed Amin El Amrani, Abdallah Karim, et al.. Efficient and Sustainable One-pot Synthesis of alpha-Carbonyl Homoallylic Alcohols from Benzaldehyde and Allylic Alcohols Using both NHC and Nickel Catalysts. ChemCatChem, 2023, 15 (10), pp.e202300038. 10.1002/cctc.202300038 . hal-04144631

HAL Id: hal-04144631
https://hal.univ-lille.fr/hal-04144631v1

Submitted on 28 Jun 2023

ChemCatChem

Research Article
doi.org/10.1002/cctc.202300038

Chemistry Europe
European Chemical Societies Publishing

www.chemcatchem.org

Efficient and Sustainable One-pot Synthesis of α-Carbonyl Homoallylic Alcohols from Benzaldehyde and Allylic Alcohols Using both NHC and Nickel Catalysts

Yasmina Homrani,[a, b] Bouchaib Mouhsine,[b, c] Aurélien Béthegnies,[b]
Mohamed Amin El Amrani,[a] Abdallah Karim,[c] Isabelle Suisse,[b] and Mathieu Sauthier*[b]

α-carbonyl homoallylic alcohols have been synthesized in a one-pot reaction from benzaldehyde and allylic alcohols. The nickel-catalyzed allylation of α-hydroxyketones has first been studied and allowed the identification of $Ni(cod)_2$/dppf as the most suitable catalytic system. The tandem reaction that combines the benzoin condensation of aldehydes (synthesis of α-hydroxyketones) promoted by the 1,3-dimethylimidazolium chloride/DBU system and the nickel-catalyzed allylic alkylation with allylic alcohol has been realized in EtOH as green solvent. The reaction is 100% atom-economical and water is formed as sole by-product. A broad scope of different benzaldehyde derivatives as well as various allylic alcohols is also described.

Introduction

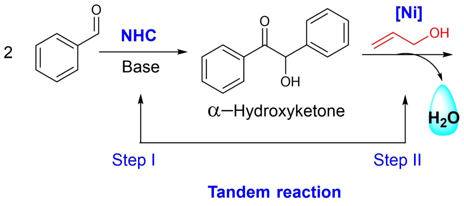
α-Hydroxyketones are important functional skeletons employed as synthetic intermediates such as acyl-type templates in catalytic asymmetric transformations[1] or as starting materials in the synthesis of dihydropyrans[2] for example. Those structural units could be synthesized starting from simple aldehydes via the benzoin condensation reaction.[3] The first example of benzoin condensation was proposed by Wöhler and Liebig[4] and the catalytic version with cyanide anion was developed shortly after.[5] Following these pioneering works, the intramolecular and intermolecular benzoin condensation was largely developed and *N*-heterocylic carbenes (NHCs) proved to be very efficient catalysts.[6] From a mechanistic point of view, the transformation allows the polarity inversion of the aldehyde through the generation of an acyl anion equivalent.[7] A nucleophilic addition to a second electrophilic aldehyde leads to the expected α-hydroxycarbonyl compounds (benzoin and derivatives).[8] The presence of an acidic C–H bond in the product of benzoin condensation makes them suitable nucleophiles for allylation reactions, one of the most fundamental and versatile step in organic chemistry,[9] thus generating α-carbonyl homoallylic alcohols. Introduction of an allyl moiety into an organic framework enhances the utility of the overall synthetic application as it opens the way to further chemical C=C transformations such as oxidation, hydroformylation or metathesis reactions. Allylation reactions are typically performed with allylation reagents such as allyl halide, acetate or carbonate. The nature of the leaving group of the allylic substrate is crucial regarding the generation of stoichiometric amounts of salts as by-products that can be potentially formed. In a context of green chemistry, allyl alcohol is particularly attractive since, with this allylation reagent, water is the sole by-product of the reaction. Moreover, it can be synthesized from vegetal raw material like glycerol.[10] However, this substrate shows much lower reactivity in comparison to the allylation reagents mentioned previously due to the poor leaving ability of the hydroxide anion. The use of appropriate metallic catalysts is then fundamental to efficiently promote allylation reactions with allylic alcohols. In our laboratory, we have developed a major interest for the clean nickel catalyzed allylation of various substrates as amides,[11] malonates,[12] aldehydes,[13] ketones,[14] dioxo compounds[15] and nitriles[16] in the presence of allylic alcohols. Nickel-based catalysts proved to be a very interesting alternative to palladium based equivalents regarding the wide availability and lower price of the metal. Hence, it has been recognized during the last two decades as a very promising organometallic catalyst in the area of allylic substitutions.[17]

From these results, we were interested to explore the use of nickel catalysts for the allylation of α-hydroxyketones and evaluate the feasibility of the one-pot benzoin condensation/allylation reaction from aromatic aldehydes and allylic alcohols leading to α-carbonyl homoallylic alcohols (Scheme 1). In literature, tandem and domino reactions are considered to be efficient and strong alternative strategies for building complex

---

[a] *Dr. Y. Homrani, Prof. M. A. El Amrani*
LOCA, FS
Abdelmalek Essaadi University
93000Tetouan (Morocco)
[b] *Dr. Y. Homrani, Dr. B. Mouhsine, Dr. A. Béthegnies, Dr. I. Suisse, Prof. M. Sauthier*
Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 – UCCS Unité de Catalyse et Chimie du Solide
F-59000 Lille (France)
E-mail: mathieu.sauthier@univ-lille.fr
[c] *Dr. B. Mouhsine, Prof. A. Karim*
Équipe de Chimie de Coordination et de Catalyse
Département de Chimie
Faculté des Sciences Semlalia
Université Cadi Ayyad
BP 2390, Marrakech (Morocco)

Supporting information for this article is available on the WWW under https://doi.org/10.1002/cctc.202300038



Scheme 1. Benzoin condensation/nickel catalyzed allylic alkylation tandem reaction.

molecular frameworks[18] and they are a versatile synthetic tool to forge C–C bonds from simple substrates in a single reaction vessel.[19] They also demonstrate a green synthetic instrument regarding the atom-economy, waste generation, time and labor loss.[20] Generally, the benzoin condensation/allylation reaction is a one-pot reaction in which the two processes are sequential with two different catalytic systems and belongs therefore to the orthogonal tandem catalysis.[21]

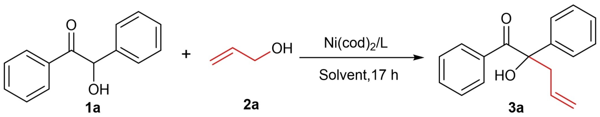
Glorious[22] and She[23] have recently reported the NHC-benzoin condensation/palladium-catalyzed allylation from aldehydes and allylic acetates as tandem catalysis. In this work, the combination of NHC-catalyzed benzoin condensation and palladium-catalyzed allylic alkylation was successful allowing a three component coupling after two successive C–C bond formations. The authors proved that NHC could be compatible with a transition metal (palladium) in a coupling reaction. Nevertheless, palladium remains a rare and expensive metal and its replacement by a more available source as nickel is an important challenge. In other hand, He *et al.* proposed the one pot condensation/allylation using NHC and nickel(II) chloride as catalysts with allyl acetate as electrophilic substrate.[24] The present work develops a sustainable Ni-catalyzed tandem reaction from benzaldehyde and allylic alcohol to produce α-carbonyl homoallylic alcohols according to an atom- and time-economical process (Scheme 1).

Results and Discussion

Before performing the tandem reaction, we started with the optimization of the nickel catalyzed allylation reaction of benzoin **1 a** with allyl alcohol **2 a**. The first test was realized in DMSO, which proved to be a good solvent for the *N*-allylation of indoles,[25] in the presence of 1.5 mol% Ni(cod)$_2$ as nickel source and dppf (diphenylphosphinoferrocene) ligand at 70 °C (Table 1 and Scheme 2). Nevertheless, the reaction did not occur (entry 1). Fortunately, as the temperature increased up to 80 °C or 90 °C, α-carbonyl homoallylic alcohol **3 a** could be produced with approximatively 60 % yield after 17 h, evidencing the feasibility of the nickel catalyzed benzoin allylation with allyl alcohol (entries 2 and 3). We then evaluated the solvent effect. The allylation yielded 75 % in MeOH (entry 4) and 82 % in EtOH. THF and toluene were also evaluated providing similar yields (84 and 95 % respectively) (entries 6 and 7) and these results showed that protic or aprotic solvents are both convenient for that reaction. We finally chose EtOH as the best solvent regarding its environmental perspectives.

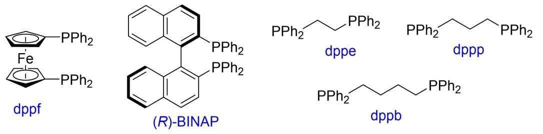
The optimization was further carried out by testing various ligands associated to the nickel precursor (Scheme 2 and Table 1). Triphenylphosphine PPh$_3$ proved to be poorly efficient with 68 % conversion (entry 9) while the diphosphines BINAP, dppb and dppp led to high conversions (entries 10, 12 and 13, 94–99 %). Dppe diphosphine led to a moderate yield, indicating the importance of the chelation cycle size (entry 11). This brief screening of reaction conditions showed that the best combination in terms of activity and yield in a context of green chemistry was the catalytic system Ni(cod)$_2$/dppf at 80 °C in EtOH as solvent.

Table 1. Optimization of reaction conditions for the allylation of benzoin **1 a**.[a]



Entry	T [°C]	Ligand L	Solvent	Conv. **1 a** [%][b]	Yield **3 a** [%][c]
1	70	dppf	DMSO	6	1
2	80	dppf	DMSO	77	61
3	90	dppf	DMSO	70	59
4	80	dppf	MeOH	96	75
5	80	dppf	EtOH	87	82
6	80	dppf	THF	> 99	84
7	80	dppf	Toluene	> 99	95
8	80	dppf	Neat	95	75
9 [d]	80	PPh$_3$	EtOH	68	28
10	80	Binap	EtOH	> 99	52
11	80	dppe	EtOH	66	39
12	80	dppb	EtOH	97	61
13	80	dppp	EtOH	94	72

[a] Reaction conditions: Benzoin **1 a** (1.8 mmol), allyl alcohol **2 a** (3.6 mmol), Ni(cod)$_2$ (1.5 mol%), ligand (3 mol%), solvent (0.5 mL) for 17 h. All reactions are run under N$_2$ in a sealed Schlenk tube. [b] Determined by GC on the crude product using anisole as internal standard. [c] Isolated yield. [d] 3 eq. of PPh$_3$ vs Ni.

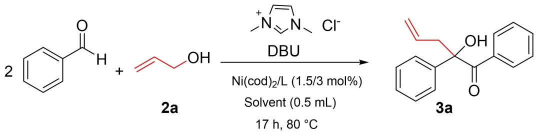


Scheme 2. Ligands evaluated in the nickel catalyzed allylation of benzoin **1 a**.

With the conditions of benzoin allylation in hand, the tandem condensation/allylation reaction was performed from benzaldehyde by adding an imidazolium salt and a base in order to generate the *N*-heterocyclic carbene (NHC) which would be able to activate the aldehyde and produce benzoin *in situ*. 1,3-dimethylimidazolium chloride as precursor of carbene and a standard base as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) were first chosen. The tandem reaction was evaluated by mixing the two catalysts and led in one step to the formation of the expected allylbenzoin **3 a**. Results are reported in Table 2. In all experiments, benzaldehyde was fully converted to benzoin **1 a** which was further allylated to **3 a** in the second step. Notably, no *O*-allylated product was observed. Ligands previously tested during the optimization of the benzoin allyllation were also screened. High conversions between 93 and 99% with satisfying yields in **3 a** (67–82%) were obtained (entries 1–4). Replacing EtOH by THF led to same results in terms of yield (compare entries 1 and 5).

A kinetic study was then carried out using the previous conditions by analyzing the composition of the reaction mixture by gas chromatography. Figure 1 presents the evolution of the products as a function of time. The curves revealed that the allylation is faster than the benzaldehyde condensation into benzoin and no accumulation of benzoin was observed in the reaction media. Less than 5 mol% of benzoin is detected. The kinetic also revealed that with the chosen reaction conditions, the process is complete after 17 hours of reaction.

Table 2. Optimization of the tandem reaction with different ligands and solvents.[a]



Entry	Solvent	Ligand	Conv. [%][b]	Yield **3 a** [%][c]
1	EtOH	dppf	93	82
2	EtOH	Binap	97	68
3	EtOH	dppb	>99	67
4	EtOH	dppp	94	72
5	THF	dppf	>99	81

[a] Reaction conditions: Benzaldehyde (1.8 mmol), allyl alcohol **2 a** (3.6 mmol), $Ni(cod)_2$ (1.5 mol%), ligand (3 mol%), imidazolium chloride (5 mol%) and DBU (1 eq), solvent (0.5 mL) for 17 h at 80 °C in a sealed Schlenk tube. [b] Benzoin conversion determined by GC. [c] Determined by ^1H NMR on the crude product using anisole as internal standard.

Using the same conditions, different α-carbonyl homoallylic alcohols were synthesized by varying the structure of the aromatic moiety of aldehydes. Results are reported in Table 3.

Except in the case of *o*-methylbenzaldehyde and 2-naphthaldehyde, conversions were in the same order to those obtained with benzaldehyde and typically range from 81% up to 99%. It is noteworthy that *o*-methylbenzaldehyde led to poor results (entry 2, conv. = 30%, yield **3 b** = 16%) probably due to the steric hindrance associated with the ortho-substituent that impedes the direct addition of the NHC to the aldehyde in the first condensation step as reported in the literature.[26] Excellent isolated yields were obtained for both products with electron-donating and withdrawing groups at the meta or para positions of the aromatic ring (entries 3, 4 and 10). A slight drop of the yield was noticed on allylated benzoins bearing longer chains (69% (**3 e**) with an ethyl group on the aromatic ring and 71% (**3 k**) with an ethoxy group, entries 5 and 11 respectively). We also compared mono and disubstituted aldehydes. With a methoxy substituent on the meta position, the allylated benzoin **3 j** was isolated with 90% yield (entry 10) whereas reacting 3,5-dimethoxybenzaldehyde gave a slightly lower yield of 80% (entry 12). As in the case of *o*-methylbenzaldehyde **3 b**, the reaction of 2-naphthaldehyde furnished the allylated product **3 m** in only 50% conversion and 28% isolated yield (entry 13). The pyridine-3-carboxaldehyde has been converted into benzoin **3 n** with 74% yield (entry 13) and allowed the introduction of a heterocyclic structure in the final product of reaction.

A range of various allylic alcohols **2 a**–**d** was also investigated using same reaction conditions (Table 4). Complete conversions of the starting materials and good yields were observed in the presence of either linear or branched alcohols. A yield of 59% (entry 2) was registered using crotyl alcohol **2 b** as linear allylic alcohol. In that case, several products corresponding to the branched and linear isomers are formed with a mixture of *Z* and *E* for linear structures. Unfortunately, due to the mixture complexity, we were unable to separate the different isomers. Nevertheless, GC and NMR analyses showed that a 74/26 ratio of linear/branched products was obtained. Reaction of benzaldehyde with 2-methylprop-2-en-1-ol **2 c** as

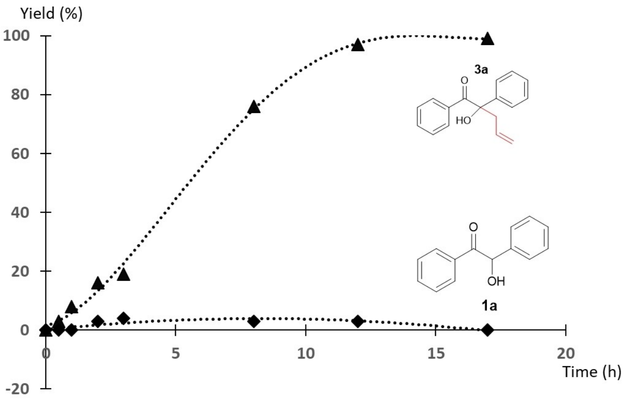
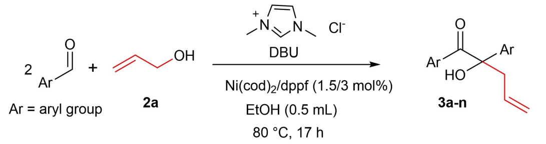
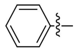
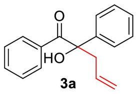
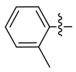
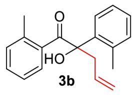
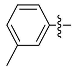
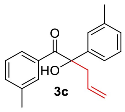
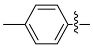
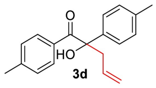
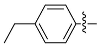
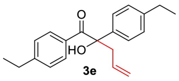
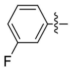
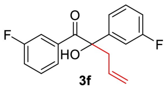
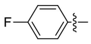
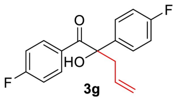
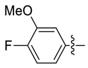
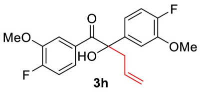
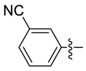
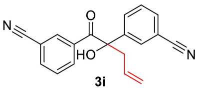
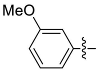
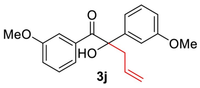
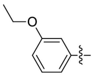
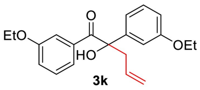
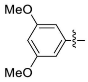
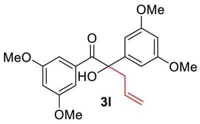
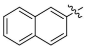
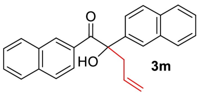
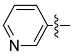
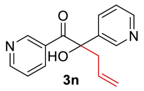


Figure 1. Evolution curve of the formation of the intermediate benzoin **1 a** and the expected allylated product **3 a**.

Table 3. Allylation of different substituted benzaldehydes.[a]



Entry	Aryl group [Ar]	Product	Conv. [%][b]	Yield [%][c]
1		 3a	>99	81
2		 3b	30	16
3		 3c	>99	93
4		 3d	98	91
5		 3e	90	69
6		 3f	89	77
7		 3g	81	71
8		 3h	94	87
9		 3i	94	78
10		 3j	>99	90
11		 3k	97	71
12		 3l	86	80
13		 3m	50	28
14		 3n	85	74

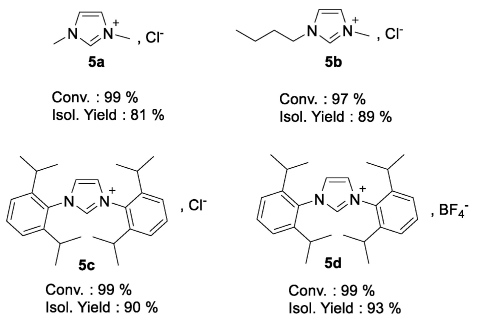
[a] Reaction conditions: aldehyde (1.8 mmol), **2a** (3.6 mmol), $Ni(cod)_2$ (1.5 mol%), dppf (3 mol%), imidazolium chloride (5 mol%)/DBU (1 eq.), EtOH (0.5 mL), T=80 °C, 17 h in a sealed Schlenk tube. [b] Benzoin conversion determined by GC. [c] Isolated yield of products after silica gel chromatography.

branched allylic alcohol led to the allylated benzoin **4c** as sole product with a yield of 78% (entry 3). In the case of secondary alcohols as but-3-en-2-ol **2d** (entry 4), an increase of the nickel catalyst amount up to 3 mol% was necessary to attain a complete conversion giving then an isolated yield of 64%. Since nickel catalysts are known to promote allyl alcohol self-etherification into diallylether,[27] diallylether **2e** as allylating reagent was also evaluated into the tandem reaction (entry 5). A slightly lower isolated yield was obtained (69%) in comparison to allyl alcohol (81%, entry 1). This result proves that allylic alcohol is more effective for the Ni-catalyzed allylic alkylation in tandem reaction of the benzaldehyde and the formation of diallylether after the self-etherification does not impact the progress of the reaction.

For further investigation, we turned our attention to the nature of carbene precursors that can be used to promote the benzoin condensation. Commercial imidazolium salts **5a**–**5d** with different *N*-substituents or counterions were evaluated using identical conditions ($Ni(cod)_2$ (1.5 mol%), dppf (3 mol%), imidazolium salt (5 mol%)/DBU (1 eq.), EtOH (0.5 mL), T=80 °C) (Scheme 3).

Alkyl (**5a** and **5b**) and aryl (**5c**) imidazolium chloride salts proved to be efficient and tolerant toward the allylation reaction with nickel catalyst giving high isolated yields into the allylated benzoin **3a** (89% with **5b** and 90% with **5c**). High yield and conversion were also obtained in the presence of the corresponding tetrafluoborate imidazolium salt **5d**. The nature of the carbene has no impact on the overall process and very similar results are obtained with imidazolium salts that bear very different steric properties. Under the chosen reaction conditions, the carbene doesn't affect the coordination sphere of nickel (0) or nickel (II) intermediates that are involved in the catalytic cycle (*vide infra*) and the two catalytic reactions occur according to an orthogonal tandem catalysis. This is very likely related to a higher reactivity of carbenes toward the aldehyde in comparison to the coordination to the nickel center.

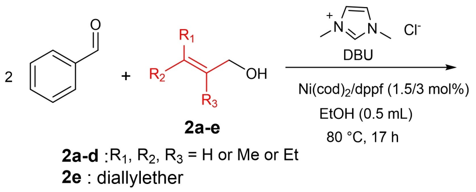
The mechanism of the reaction is based on two catalytic cycles that involve organic and organometallic catalysts (Scheme 4). The nucleophile is generated from the benzoin

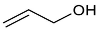
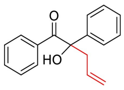
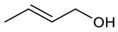
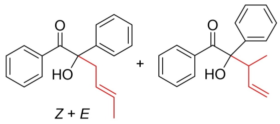
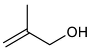
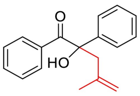
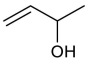
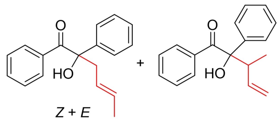
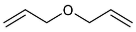
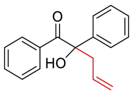


Reaction conditions: benzaldehyde (1.8 mmol), allyl alcohol (3.6 mmol), $Ni(cod)_2$ (1.5 mol%), dppf (3 mol %), imidazolium salt (5 mol%)/DBU (1 eq.), EtOH (0.5 mL), T = 80 °C in a sealed Schlenk tube.

Scheme 3. Tandem condensation/allylation reactions of benzaldehyde with allyl alcohol: influence of the imidazolium salt.

Table 4. Scope of the Ni-catalyzed condensation/allylation with various allylic alcohols **2a**–**d** and diallylether **2e**.[a]



Entry	Alcohol	Product	Yield [%][b]
1	 **2a**		81
2	 **2b**		59
3	 **2c**		78
4[c]	 **2d**		64
5	 **2e**		69

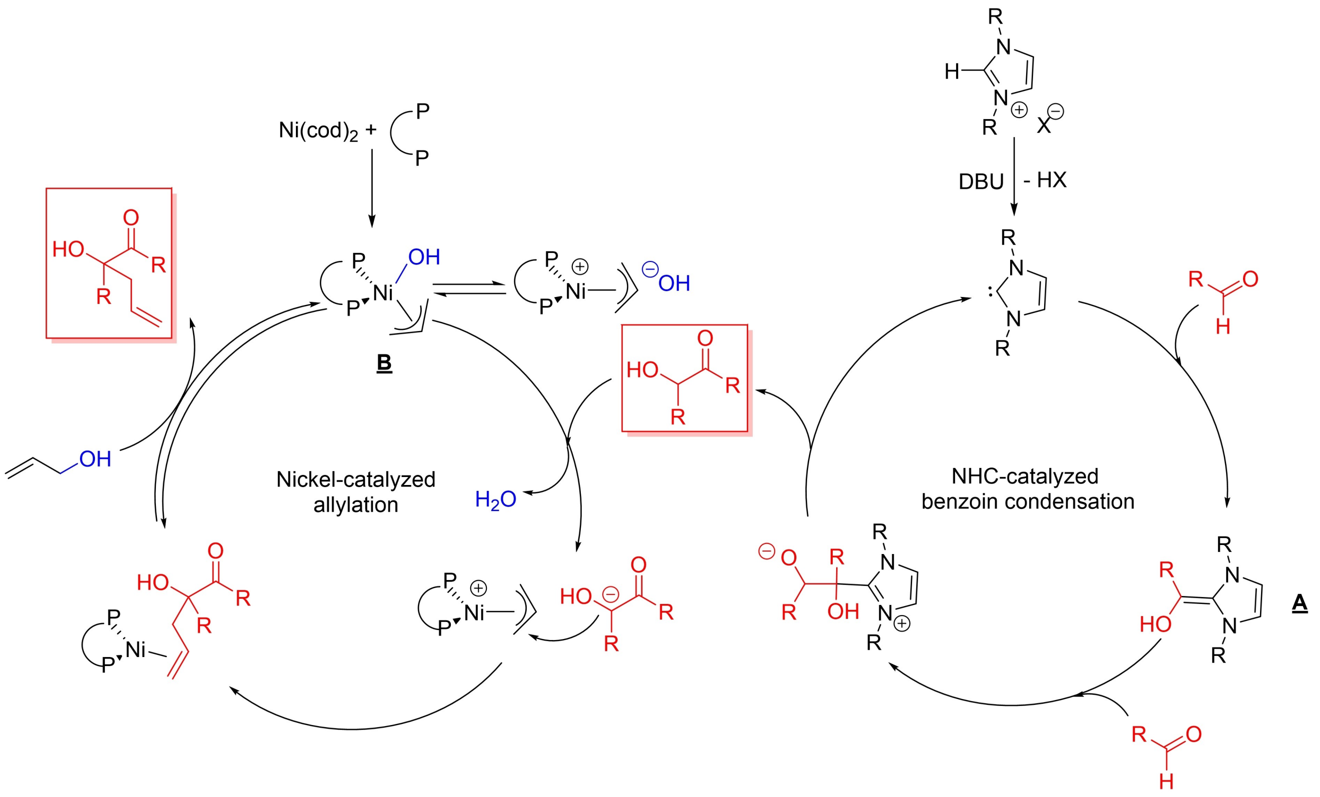
[a] Reaction conditions: benzaldehyde (2 mmol), allylic alcohol (4 mmol) or diallylether (2 mmol), Ni(cod)$_2$ (1.5 mol%), dppf (3 mol%), imidazolium chloride (5 mol%)/DBU (1 eq.), EtOH (0.5 mL), T = 80 °C in a sealed schlenk tube. [b] Isolated yield after silica gel chromatography. [c] Ni(cod)$_2$ (3 mol%) and dppf (6 mol%) were used.

condensation that involves the carbene generated from the deprotonation of an imidazolium salt by DBU (right part of scheme 4). The reaction of the carbene with one equivalent of aldehyde leads to the formation of the Breslow intermediate **A**.[28] Formally, that step allows the polarity inversion of the carbon of the carbonyl group (umpolung). The nucleophilic Breslow intermediate is involved in a nucleophilic attack on the carbonyl group of the second equivalent of aldehyde and a proton transfer accompanied with a carbene discharge leads to the *in situ* formation of the hydroxyketone. In the presence of a nickel(II) hydroxy allylic intermediate **B** obtained from the oxidative addition of allylic alcohol on a low valent nickel(0) species stabilized with the diphosphine,[29] the hydroxyketone (benzoin derivative) is readily deprotonated by the hydroxide anion and one molecule of water is released. Nucleophilic attack of the thus generated anion on the terminal carbon of the allylic moiety finally leads to the formation of the allylated hydroxyketone and regeneration of the nickel(0) precursor.

This key role of the hydroxyl anion explains that the reaction occurs under neutral conditions. 1,2-diphenylethan-1-one (benzoin without the hydroxyl group) was already known as suitable nucleophile in the nickel catalyzed allylation reaction with allyl alcohol.[30] The presence of the hydroxyl group doesn't impede the reactivity of the nucleophile as shown by the first catalytic tests performed with benzoin. Interestingly, the Breslow intermediate doesn't act as a nucleophile with the intermediate nickel allyl complexes and the corresponding product of allylation has not been observed. As the allylation step is base-free, only a catalytic amount of DBU is needed for the generation of the carbene and a control experiment showed that no reaction is observed in the absence of this base.

Conclusion

In summary, we have successfully developed a Ni-catalyzed synthesis of α-carbonyl homoallylic alcohols from aldehydes and allylic alcohols. The first step corresponds to the benzoin condensation following by an allylation step. This tandem methodology is very efficient leading in one-pot to the desired products with good to excellent yields. Moreover, in agreement with green chemistry principles, the combination of allyl alcohol as allylation reagent with water as sole co-product and EtOH as



Scheme 4. Proposed mechanism of the tandem condensation/allylation reaction.

green solvent is of great interest in the field of sustainable chemistry. This procedure will be further extended to asymmetric synthesis with chiral ligands leading to a new range of complex and chiral molecules.

Experimental Section

General procedure for the one pot benzoin condensation/allylation reaction: in a sealed Schlenk tube under nitrogen, were mixed $Ni(cod)_2$ (7.4 mg, 0.027 mmol,1.5 mol%) and dppf (29.9 mg, 0.054 mmol, 3 mol%) in EtOH (0.5 mL). After stirring for 30 min, benzaldehyde (2 mmol, 0.212 g) and allyl alcohol (4 mmol, 0.232 g), 1,3-dimethylimidazolium chloride (13.25 mg, 5 mol%) and DBU (15.22 mg, 5 mol%) were added. The mixture was heated for 17 h at 80 °C.

All experimental details and characterization data could be found in the Supporting Information.

Acknowledgements

We acknowledge the Ministère de l'Enseignement Supérieur de la Recherche et de l'Innovation (France) and the Ministère de la Recherche (Morocco) for their financial support. We would like to thank Céline Delabre for the HR-MS analyses.

Conflict of Interest

The authors declare no competing financial interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: benzoin · allylation · nickel · tandem catalysis

[1] C. Palomo, M. Oiarbide, J. M. García, *Chem. Soc. Rev.* **2012**, *41*, 4150–4164.
[2] H. Wildemann, P. Dünkelmann, M. Müller, B. Schmidt, *J. Org. Chem.* **2003**, *68*, 799–804.
[3] G. D. Yadav, A. A. Kadam, *Org. Process Res. Dev.* **2012**, *16*, 755–753.
[4] F. Wöhler, J. von Liebig, *Annal. Pharm.* **1832**, *3*, 249–282.
[5] N. Zinin, *Annal. Pharm.* **1839**, *1*, 329–332.
[6] a) M. Debiais, A. Hamoud, R. Drain, P. Barthelemy, V. Desvergnes, *RSC Adv.* **2020**, *10*, 40709–40718; b) E. G. Delany, S. J. Connon, *Org. Biomol. Chem.* **2018**, *16*, 780–786; c) P. Haghshenas, S. M. Langdon, M. Gravel, *Synlett* **2017**, *28*, 542–559; d) R. S. Menon, A. T. Biju, V. Nair, *Beilstein J. Org. Chem.* **2016**, *12*, 444–461; e) D. Enders, O. Niemeier, T. Balensiefer, *Angew. Chem. Int. Ed.* **2006**, *45*, 1463–1467; *Angew. Chem.* **2006**, *118*, 1491–1495; f) T. Ukai, R. Tanaka, T. Dokawa, *J. Pharm. Soc. Jpn.* **1943**, *63*, 296–304.
[7] a) S. Barik, A. T. Biju, *Chem. Commun.* **2020**, *56*, 15484–15494; b) X. Bugaut, F. Glorius, *Chem. Soc. Rev.* **2012**, *41*, 3511–3522.

[8] W. Zhang, Y. Wang, D. Wei, M. Tanga, X. Zhu, *Org. Biomol. Chem.* **2016**, *14*, 6577–6590.

[9] a) S. Dutta, T. Bhattacharya, D. B. Werz, D. Maiti, *Chem* **2021**, *7*, 555–605; b) J.-M. Begouin, J. E. M. Klein, D. Weickmann, B. Plietker, *Top. Organomet. Chem.* **2012**, *38*, 269–320; c) Z. Lu, S. Ma, *Angew. Chem. Int. Ed.* **2008**, *47*, 258–297; *Angew. Chem.* **2008**, *120*, 264–303; d) B. M. Trost, M. R. Machacek, A. Aponick, *Acc. Chem. Res.* **2006**, *39*, 747–760; e) B. M. Trost, D. L. Van Vranken, *Chem. Rev.* **1996**, *96*, 395–422; f) T. Graening, H.-G. Schmalz, *Angew. Chem. Int. Ed.* **2003**, *42*, 2580–2584; *Angew. Chem.* **2003**, *115*, 2684–2688; g) B. M. Trost, M. L. Crawley, *Chem. Rev.* **2003**, *103*, 2921–2944.

[10] a) Y. Nakagawa, M. Tamura, K. Tomishige, *Res. Chem. Intermed.* **2018**, *44*, 3879–3903; b) D. Sun, Y. Yamada, S. Sato, W. Ueda, *Appl. Catal. B* **2016**, *193*, 75–92.

[11] M. S. Azizi, Y. Edder, A. Karim, M. Sauthier, *Eur. J. Org. Chem.* **2016**, *22*, 3796–3803

[12] H. Bricout, J. F. Carpentier, A. Mortreux, *J. Mol. Catal. A* **1998**, *136*, 243–251.

[13] Y. Bernhard, B. Thomson, V. Ferey, M. Sauthier, *Angew. Chem. Int. Ed.* **2017**, *56*, 7460–7464; *Angew. Chem.* **2017**, *129*, 7568–7572.

[14] M. Bouchaib, A. Karim, C. Dumont, M. Sauthier, *Green Chem.* **2020**, *22*, 950–955.

[15] R. Blieck, M. S. Azizi, A. Mifleur, M. Roger, C. Persyn, M. Sauthier, H. Bonin, *Eur. J. Org. Chem.* **2016**, *6*, 1194–1198.

[16] M. Bouchaib, A. Karim, C. Dumont, I. Suisse, M. Sauthier, *Adv. Synth. Catal.* **2021**, *363*, 1457–1462.

[17] D. Ghorai, À. Cristòfol, A. W. Kleij, *Eur. J. Inorg. Chem.* **2022**, 2, e202100820.

[18] a) A. Grosmann, D. Enders, *Angew. Chem. Int. Ed.* **2012**, *51*, 314–325; *Angew. Chem.* **2012**, *124*, 320–332; b) X. Zeng, *Chem. Rev.* **2013**, *113*, 6864–6900; c) C. M. R. Volla, I. Atodiresei, M. Rueping, *Chem. Rev.* **2014**, *114*, 2390–2431; d) R. Ardkhean, D. F. J. Caputo, S. M. Morrow, H. Shi, Y. Xiong, E. A. Anderson, *Chem. Soc. Rev.* **2016**, *45*, 1557–1569.

[19] C. M. R. Volla, I. Atodiresei, M. Rueping, *Chem. Rev.* **2014**, *114*, 2390–2431.

[20] L. F. Tietze, F. Haunert, in *Stimulating Concepts in Chemistry*, (Eds: M. Shibasaki, J. F. Stoddart, F. Vögtle), Wiley-VCH, Weinheim, Germany **2000**; pp. 39–64.

[21] T. L. Lohr, T. J. Marks, *Nat. Chem.* **2015**, *7*, 477–482.

[22] R. Lebeuf, K. Hirano, F. Glorius, *Org. Lett.* **2008**, *10*, 4243–4246.

[23] J. He, S. Tang, S. Tang, J. Liu, Y. Sun, X. Pan, X. She, *Tetrahedron Lett.* **2009**, *50*, 430–433.

[24] J. He, M. Qu, Z. He, *Chinese J. Appl. Chem.* **2013**, *30*, 852–854.

[25] B. Mouhsine, A. Karim, C. Dumont, I. Suisse, M. Sauthier, *Eur. J. Org. Chem.* **2022**, 26, e202200042.

[26] K. Iwamoto, M. Hamaya, N. Hashimoto, H. Kimura, Y. Suzuki, M. Sato, *Tetrahedron Lett.* **2006**, *47*, 7175–7177.

[27] H. Bricout, J.-F. Carpentier, A. Mortreux, *J. Mol. Catal. A* **1998**, *136*, 243–251.

[28] a) J. Rehbein, S.-M. Ruser, J. Phan, *Chem. Sci.* **2015**, *6*, 6013–6018; b) M. M. Heravi, V. Zadsirjan, K. Kafshdarzadeh, Z. Amiri, *Asian J. Org. Chem.* **2020**, *9*, 1999–2034.

[29] Y. Kita, H. Sakaguchi, Y. Hoshimoto, D. Nakauchi, Y. Nakahara, J.-F. Carpentier, S. Ogoshi, K. Mashima, *Chem. Eur. J.* **2015**, *21*, 14571–14578.

[30] Unpublished experimental results.

Manuscript received: January 16, 2023
Revised manuscript received: March 22, 2023
Accepted manuscript online: March 23, 2023
Version of record online: April 26, 2023