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The Nickel Catalyzed α-Allylation of Aldehydes and Tandem Aldol Condensation / Allylation Reaction with Allylic Alcohols.

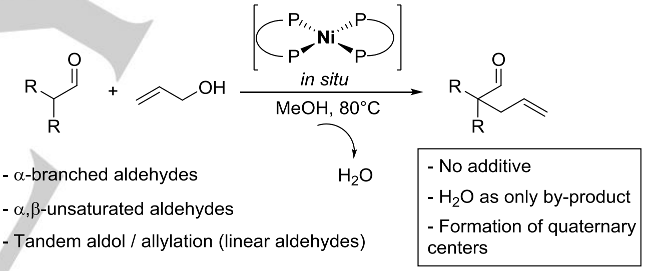
*Yann Bernhard,[a] Brodie Thomson,[a] Vincent Ferey[b] and Mathieu Sauthier[a]**

Abstract: *An additive free nickel catalyzed α-allylation of aldehydes with allyl alcohol is reported. The reaction is promoted by 1 mol % of in situ formed nickel complex in methanol and water is the sole by-product of the reaction. The experimental conditions allowed the conversion of various α-branched aldehydes and α,β-unsaturated aldehydes as nucleophiles. The same catalyst and reaction conditions allowed promoting a tandem aldol condensation of aldehyde / α-allylation reaction.*

Metal catalyzed allylic alkylation reactions represent a versatile and powerful tool for the formation of various homo- (C-C) and hetero- (C-N, C-O, C-S) bonds.[1] This family of reactions involves a nucleophile and an allylic substrate that bears a leaving group activated by a metal used in a catalytic amount. The nature of the leaving group is particularly crucial and very reactive allylic acetates, carbonates or halogens are typically used. The reaction consequently suffers from the formation of stoichiometric amounts of salts obtained from the release of the leaving group and the base commonly used to generate a reactive nucleophile. Modern organic chemistry requests the use of greener, atom economic and cheaper synthetic methods.[2] The direct use of more synthetically reliable allylic alcohols that conduce to water as side-product are in this context particularly attractive.[3] Nevertheless, that requests the use of an appropriate metal, frequently associated with an activator, to perform the initial oxidative addition. Nickel is a metal of choice in this field as it is able to rapidly perform such an oxidative step without any request of activators.[4] Moreover, this metal is attractive in comparison to the more commonly used palladium because of its low cost and wide availability.

Ni-catalyzed allylation has been conducted with several nucleophiles to form heteroatomic bonds, including amines,[4,5] phenols,[5a] amides and sulfonamides.[6] To date, the most studied class of nucleophiles that lead to C-C bond formation are activated methylene compounds (β-ketoesters, β-diketones, malonates, etc...),[5a,7] Examples of nickel catalyzed allylation reactions to form C-C bonds where outlined by Walsh's group who performed an allylation of diarylmethane pronucleophiles,[8] and Weix's group who conducted the allylation of α-amido sulfones to form protected homoallylic amines.[9]

Since recently, metal catalyzed α-allylation of aldehydes has been increasingly studied, involving principally palladium based catalysts. Most examples needed the use of additives like boron derivatives,[10] brönsted acid,[11] or in numerous cases amine to activate the aldehyde (i.e. to form *in situ* the enamine) and induce an enantioselectivity.[12] With a similar methodology, such allylations were also conducted with iridium,[13] or rhodium.[14] We now wish to report the first Nickel-catalyzed allylation of aldehyde with allyl alcohol performed in neutral conditions (Scheme 1) with a broad scope of substrates. The developed method is suitable for the allylation of various α-branched aldehydes and α,β-insaturated aldehydes. Moreover, the nickel based catalysis allows the tandem aldol condensation / allylation of linear aldehydes for the one step construction of a quaternary center. Moreover, the reaction does not request the use of additives or bases.



Scheme 1. Ni-catalyzed allylation of aldehyde with allyl alcohol.

Our study began with the optimisation of the reaction, using aldehyde **1a** and allyl alcohol **2a** as models (Table 1). The catalyst was initially generated *in situ* from the combination of 2 equivalents of 1,4-bis(diphenylphosphino)butane (dppb) and [Ni(cod)$_2$] (2 mol %). The product of allylation **3aa** was obtained with 42 % yield by reacting **1a** with 3 eq. of allyl alcohol **2a** in toluene at 80°C for 15 hours (entry 1).The PPh$_3$ ligand did not allow noticeable yield and among the diphosphines that have been evaluated, the dppf (1,1'-bis(diphenylphosphanyl) ferrocene) showed the highest efficiency (50 % GC yield, entry 7) and was thus kept for the rest of the study. The nature of the solvent used for the reaction also proved to be a crucial parameter. Apolar solvents gave rather limited yields whereas isopropanol (entry 10, see the Supporting Information) conduced to a complete GC conversion and a quantitative GC yield.[15] The use of the dppf ligand and an alcohol as solvent allowed: (1) performing the reaction with a stoichiometric amount of allyl alcohol **2a** in respect to the amount of aldehyde **1a** (92 % GC yield with 1 eq. of **2a**, entry 12); 2) reducing the catalytic charge, with 1 mol % catalyst, the yield reaches 73 % in isopropanol (entry 13) and a quantitative yield in methanol (entry 14).

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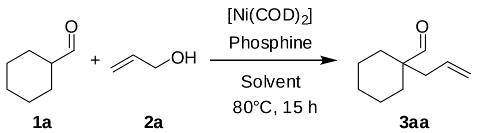
Table 1. Optimization of the nickel-catalyzed α-allylation of cyclohexane carboxaldehyde with allyl alcohol - selected conditions[a]

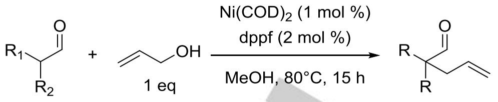


1a **2a** **3aa**

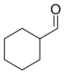
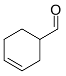
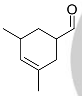
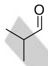
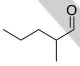
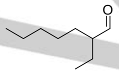
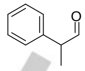
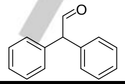
Entry	Ligand	Solvant	Eq **2a**	Cat. charge [%]	Conv **1a** [%][b]	Yield **3aa** [%][c]
1	dppb	toluene	3	2	46	42
2	PPh$_3$[d]	toluene	3	2	3	0
3	dppp	toluene	3	2	2	0
4	dpppen	toluene	3	2	22	12
5	dppmb	toluene	3	2	31	29
6	Xantphos	toluene	3	2	7	1
7	dppf	toluene	3	2	56	50
8	dppf	acetonitrile	3	2	81	78
9	dppf	THF	3	2	56	48
10	dppf	isopropanol	3	2	>99	>99
11	dppf	isopropanol	2	2	>99	96
12	dppf	isopropanol	1	2	92	92
13	dppf	isopropanol	1	1	73	73
14	dppf	methanol	1	1	>99	>99
15	dppf	allyl alcohol	10	1	52	41

[a] General reaction conditions: **1a** (1.8 mmol), **2a** (5.4 mmol, 3 equiv), Ni(cod)$_2$ (10 mg, 2 mol%), ligand (4 mol%), solvent (0.5 mL), 80°C, 15 h, in a sealed schlenk tube [b] Conversions determined by GC analysis using anisole as a internal standard. [c] Yields determined by GC analysis using anisole as a internal standard. [d] PPh$_3$ (8 mol %). cod=1,5-cyclooctadiene, THF= tetrahydrofurane, dppp= 1,4-bis(diphenylphosphino)propane, dppb= 1,4-bis(diphen-ylphosphino)butane, dppf= 1,1'- bis(diphenylphosphanyl) ferrocene.

Table 2. Scope of the Ni-catalyzed allylation of α-branched aldehydes **1** with allylic alcohols **2**.[a]

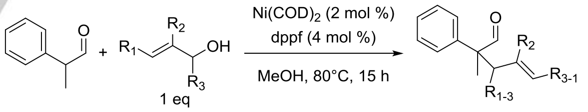


1a-h **2a** **3aa-3ha**

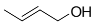
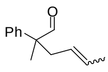
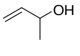
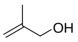
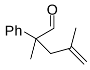
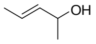
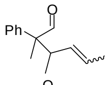
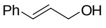
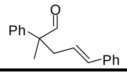
Entry	1	Product	Yield[%][b]
1	 **1a**	**3aa**	96
2	 **1b**	**3ba**	95
3	 **1c**	**3ca**	97
4[c]	 **1d**	**3da**	78
5	 **1e**	**3ea**	86
6	 **1f**	**3fa**	95
7	 **1g**	**3ga**	92
8	 **1h**	**3ha**	91

[a] Reaction conditions: **1** (1.8 mmol), **2a** (1.8 mmol), Ni(cod)$_2$ (5 mg), dppf (20 mg), MeOH (0.5 mL), 80°C, 15 h, in a sealed schlenk tube [b] Yield of product isolated after chromatographic purification. [c] Isolated as the DNPH adduct (crude mixture added to EtOH (5 mL)/ H$_2$O (1 mL)/ H$_2$SO$_4$ (1 mL)/2,4-DinitroPhenylHydrazine (0.3 g) mixture - precipitate filtered, washed (MeOH), dried.

Table 3. Scope of the Ni-catalyzed allylation of hydratropic aldehyde **1g** with various allylic alcohols.[a]



1g **2b-f** **3gb-3gf**

Entry	2	Product	Yield[%][b]
1	 **2b**	 **3gb** (Z/E 1:1)	83
2	 **2c**		61
3	 **2d**	 **3gd**	97
4	 **2e**	 **3ge** (Z/E 1:1)	65
5	 **2f**	 **3gf**	39

[a] Reaction conditions: **1g** (1.8 mmol), **2** (1.8 mmol), Ni(cod)$_2$ (10 mg), dppf (40 mg), MeOH (0.5 mL), 80°C, 15 h, in a sealed schlenk tube [b] isolated yields.

Using the optimized conditions, we first extended the scope of the Ni-catalyzed allylation with respect to the aldehyde **1** (Table 2). A complete conversion of the starting material was observed in all cases. Starting from cyclohexane carboxaldehyde **1a** and unsaturated derivatives **1b** and **1c**, the allylation method afforded compounds **3aa**, **3ba** and **3ca** with 96 %, 95 % and 97 % isolated yield, respectively (entry 1-3). We next examined the case of linear α-substituted aldehydes **1d-1f**. Because of low boiling point that prevents a simple purification procedure., A derivatization with 2,4-DiNitropPhenylHydrazine (2,4-DNPH) in acidic media was thus performed. The weight of the yellow precipitate gave the isolated yield (78 %)(entry 4). Product **3ea** and **3fa** were isolated with 86% and 95% yields, respectively (entry 5 and 6). More acidic 2-phenylpropionaldehyde **1g** gave the product with good yields (92 %, entry 7). The more sterically hindered aldehyde **1h** was also efficiently converted (91 %, entry 8).

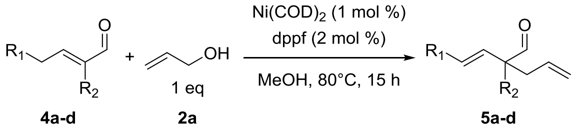
At this stage, we decided to examine the influence of the allylic source (Table 3). Compound **3gb** is obtained as unique product from crotyl alcohol **2b** and methylvinylcarbinol **2c** (entry 1 and 2).The formation of the same product from **2b** and **2c** shows that both reactants is consistent with the formation of the same (π-allyl)nickel as intermediate in the allylation reaction. The nucleophile (aldehyde) attacks preferentially the less hindered allylic carbon and yields the linear product **3gb**.

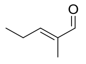
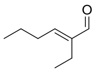
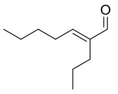
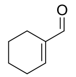
It is noteworthy that there is no selectivity between *E* and *Z* configurations, and the product is obtained as the statistical mixture, as evidenced by ^{1}H and ^{13}C NMR analysis (see the Supporting Information). A similar result was observed with (E)-pent-3-en-2-ol **2e**, yielding the product **3ge** with 65 % yield as a *Z/E* statistical mixture.

When methallyl alcohol **2d** is involved in the reaction, the product **3gd** is obtained with an excellent yield of 97 % (entry3). Lower yields are obtained starting from cinnamyl alcohol **2f** (39 %, entry 5).

In comparison to classic aldehydes, examples of metal catalyzed α-allylation of α,β-unsaturated aldehydes are rare.[10a,16] In this field, we prospected the possibility to perform such an allylation using the Ni-catalyzed procedure (Table 4).

Table 4. Scope of the Ni-catalyzed allylation of αβ-insaturated aldehydes **4** with allyl alcohol **2a**.[a]

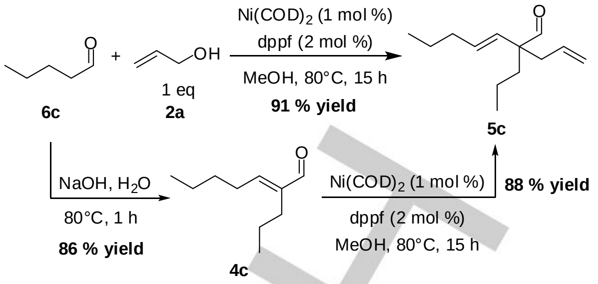


Entry	4		Product	Yield[%][b]
1		**4a**	**5a**	84
2		**4b**	**5b**	93
3		**4c**	**5c**	88
4		**4d**	**5d**	85

[a] Reaction conditions: **4** (1.8 mmol), **2a** (1.8 mmol), Ni(COD)$_2$ (5 mg), dppf (10 mg), MeOH (0.5 mL), 80°C, 15 h, in a sealed schlenk tube [b] Yield of product isolated after chromatographic purification.

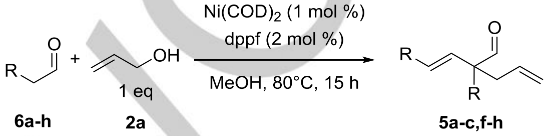
Starting from aldehydes **4a-c**, the Ni-catalyzed allylation with allyl alcohol, using the same experimental conditions as for the allylation of α-branched aldehydes, gave products **5a**, **5b** and **5c** with respectively 84 %, 93 % and 88 % yields (entries 1-3). The aldehyde **4d** with a cyclic unsaturated structure proved to be a suitable reactant and was converted in **5d** with 85 % yield.

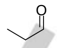
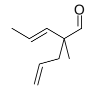
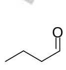
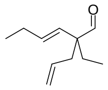
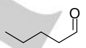
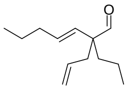
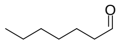
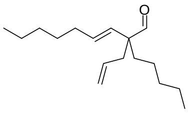
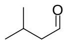
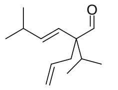
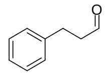
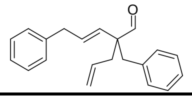
α,β-unsaturated aldehydes are typically obtained from an aldol condensation under basic conditions between two aldehydes. We thus anticipated that a tandem aldolisation / allylation reaction could be promoted by nickel catalysts. To our delight, the reaction between 2 equivalents of valeraldehyde **6c** and one equivalent of allyl alcohol straightforwardly yields **5c** with 91% yield under neutral conditions (Scheme 2). **5c** can elsewhere be obtained from a two steps procedure that involves the Aldol Condensation reaction of valeraldehyde **6c** to form **4c** (86 % yield) promoted by sodium hydroxide followed by a nickel catalyzed allylation reaction of **4c** with **2a** (**5c** was obtained with 88 % yield from the second step). The scope of this tandem reaction was extended with respect to the starting linear aldehyde **6** (Table 5). Note that for each case, the resultant ramified double bond is obtained with an *E* configuration. Starting from propionaldehyde **6a**, butyraldehyde **6b** and valeraldehyde **6c**, the products **5a**, **5b** and **5c** were respectively obtained with 82 %, 94 %and 91 % yields (entry 1-3). The reaction performed with heptanal gave after 15 hours at 80°C the product **5f** with 72 % yield (entry 4). The more sterically hindered isovaleraldehyde **6g** gave the product **5g** with 43 % yield (entry 5). Starting from hydrocinnamaldehyde **6h**, the expected product is obtained with 81 % yield (entry 6).



Scheme 2. Synthesis of aldehyde **5c**.

Table 5. Scope of the Ni-catalyzed tandem aldol condensation/α-allylation of linears aldehydes **6** with allyl alcohol **2a**.[a]

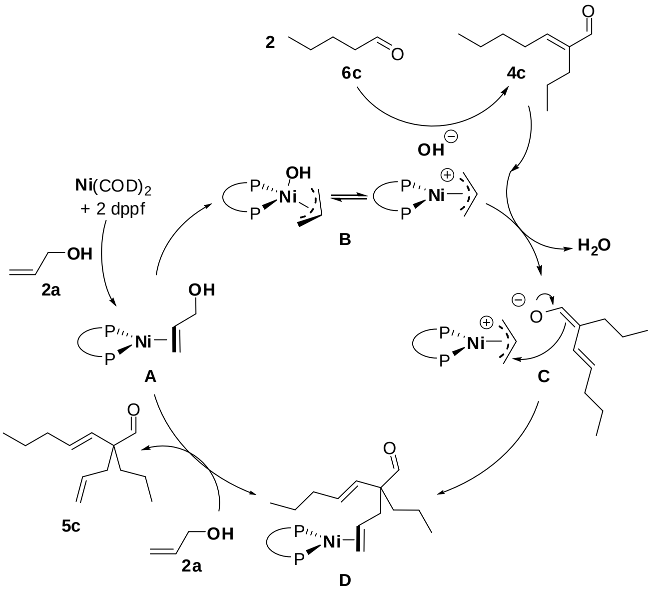


Entry	6		Product		Yield[%][b]
1		**6a**		**5a**	82
2		**6b**		**5b**	94
3		**6c**		**5c**	91
4		**6f**		**5f**	72
5		**6g**		**5g**	43
6		**6h**		**5h**	81

[a] Reaction conditions: **6** (1.8 mmol), **2a** (1.8 mmol), Ni(COD)$_2$ (5 mg), dppf (10 mg), MeOH (0.5 mL), 80°C, 15 h, in a sealed schlenk tube [b] Yield of product isolated after chromatographic purification.

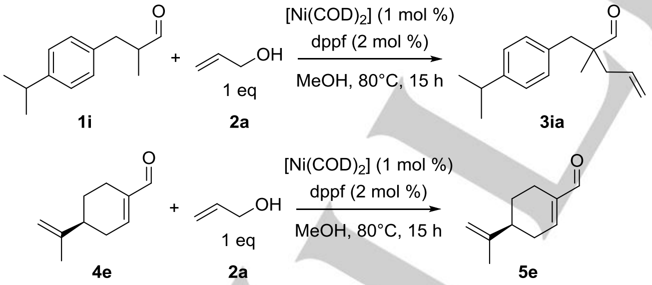
The role of the nickel in the Aldol Condensation step was assessed from a series of blank experiments (see the Supporting Information). The Aldol Condensation of **6c** is not promoted by allyl alcohol nor the precursor [Ni(cod)$_2$] / diphosphine if used separately. The combination of the nickel precursor with allyl alcohol leads to the formation of Aldol Condensation products **4c** which is then converted to the allylated product **5c**. This prompted us to propose a mechanism that involves a hydroxynickelallyl intermediate as promoter of both the Aldol Condensation and allylation steps.

The allylation of α-branched aldehydes would involve a [(dppf)Ni(0)(allyl aclohol)] complex **A** that forms the pentacoordinated complex **B** through an oxidative addition step (Scheme 4).[4,5c,6a,7c] The hydroxy ligand acts as a base and reacts with the aldehyde thus generating the enolate. The nucleophilic attack on the π-allyl ligand and coordination of the allyl alcohol to the nickel yields the product and regenerates the initial complex **A**. The nucleophile can be an alpha-substituted aldehyde or an α,β-unsaturated aldehyde. Interestingly, complex **B** is suitable to promote the aldol condensation that allows the *in situ* formation of the α,β-unsaturated aldehyde needed for the tandem reaction. Although neutral intermediates can't be completely discarded, the involvement of cationic nickel complexes is likely as a polar solvent, methanol, has been shown as the best reaction medium.



Scheme 4. Proposed mechanism for the Ni-catalyzed tandem aldol condensation plus allylation of linear aldehydes **6c**.

In comparison to the neutral forms, the ionic complex **B** with a hydroxide counter anion appears as more suitable to promote an aldol condensation.[17] Moreover, allylic fragments in cationic complexes are also well known as very reactive toward nucleophiles in palladium chemistry.[1]



Scheme 3. Synthesis of aldehyde **3i** and **5e** by Ni-catalyzed allylation of cyclamen aldehyde **1i** and (S)-perillaldehyde **4e** with allyl alcohol **2a**.

It is noteworthy that natural α-substituted aliphatic aldehyde and unsaturated aldehyde have been cleanly allylated according to this procedure (Scheme 3). Cyclamen aldehyde **1i**, which is used in the context of odorant compounds and fragrance chemistry,[18] was allylated with a good yield, thus affording aldehyde **3ia** with 94 % isolated yield. (*S*)-perilladehyde **4e**, a terpenoïd extracted from the perilla herb, used in cosmetic, fragrance chemistry and as starting material for the total synthesis of various natural products was converted in **5e** with 74 % yield.[19] The compound **5e** was obtained as a mixture of two diastereoisomers *R,R* and *R,S*, in a 45/55 ratio as highlighted by the NMR analysis of the compound (^{1}H-^{13}C-NMR spectrum, see the Supporting Information).

In summary, we have developed the first nickel catalyzed α-allylation of aldehyde with the construction of quaternary carbons. The reaction is performed under neutral conditions, without any additive and yields water as by-product. The scope of the reaction has been extended to various α-branched and α,β-unsaturated aldehydes and applied for the transformation of natural products. Moreover, the optimized conditions also allowed developing the tandem aldol-condensation /allylation of simple linear aldehydes. The proposed mechanism involves cationic allylic nickel complexes that are key intermediates in both the allylation and Aldol Condensation steps.

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Keywords: Allylation • Aldehyde • Nickel • Allyl alcohol

[1] a) J. Tsuji in *Palladium Reagents and Catalysts: New Perspectives for the 21st Century*, John Wiley & Sons, Chichester, UK, **2004**; b) B. M. Trost, D. L. Van Vranken, *Chem. Rev.* **1996**, *96*, 395–422; c) G. Consiglio, R. M. Waymouth, *Chem. Rev.* **1989**, *89*, 257–276; c) B. M. Trost, Acc. Chem. Res. **1996**, *29*, 355–364; d) B. M. Trost, *Chem. Pharm. Bull.* (Tokyo) **2002**, *50*, 1–14; e) T. Graening, H.-G. Schmalz, *Angew. Chem. Int. Ed*. **2003**, *42*, 2580–2584; f) B. M. Trost, M. L. Crawley, *Chem. Rev.* **2003**, *103*, 2921–2944; g) B. M. Trost, *J. Org. Chem.* **2004**, *69*, 5813–5837; h) B. M. Trost, M. R. Machacek, A. Aponick, *Acc. Chem. Res.* **2006**, *39*, 747–760; i) Z. Lu, S. Ma, *Angew. Chem. Int. Ed.* **2008**, *47*, 258–297; j) U. Kazmaier in *Transition Metal Catalyzed Enantioselective Allylic Substitution in Organic Synthesis*, Springer, **2011**; k) J.-M. Begouin, J. E. M. . Klein, D. Weickmann, B. Plietker, *Top Organomet. Chem.* **2012**, 38, 269–320; l) S. Olivier, A. Ewans S., *Synthesis* **2013**, 45, 3179–3198; m) A. Y. Hong, B. M. Stoltz, *Eur. J. Org. Chem.* **2013**, 14, 2745–2759.

[2] a) I. T. Horváth, P. T. Anastas, *Chem. Rev.* **2007**, *107*, 2169–2173; b) C.-J. Li, B. M. Trost, *Proc. Natl. Acad. Sci.* **2008**, *105*, 13197–13202.

[3] a) Y. Tamaru, *Eur. J. Org. Chem.* **2005**, *13*, 2647–2656; b) M. Bandini, *Angew. Chem. Int. Ed.* **2011**, 50, 994–995; c) M. Bandini, G. Cera, M. Chiarucci, *Synthesis* **2012**, *44*, 504–512; d) B. Sundararaju, M. Achard, C. Bruneau, *Chem. Soc. Rev.* **2012**, *41*, 4467–4483; e) N. A. Butt, W. Zhang, *Chem. Soc. Rev.* **2015**, *44*, 7929–7967.

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

[5] a) H. Bricout, J.-F. Carpentier, A. Mortreux, *J. Chem. Soc. Chem. Commun.***1995**, *18*, 1863–1864; b) H. Bricout, J.-F. Carpentier, A. Mortreux, *Tetrahedron* **1998**, 54, 1073–1084; c) Y. Kita, H. Sakaguchi, Y. Hoshimoto, D. Nakauchi, Y. Nakahara, J.-F. Carpentier, S. Ogoshi, K. Mashima, *Chem. – Eur. J.* **2015**, *21*, 14571–14578.

[6] a) M. S. Azizi, Y. Edder, A. Karim, M. Sauthier, *Eur. J. Org. Chem*. **2016**, *22*, 3796–3803; b) D. B. Berkowitz, M. Bose, S. Choi, *Angew. Chem.* **2002**, *114*, 1673–1677; c) D. B. Berkowitz, G. Maiti, *Org. Lett*. **2004**, *6*, 2661–2664.

[7] a) E. Alvarez, T. Cuvigny, M. Julia, *J. Organomet. Chem.***1988**, *339*, 199–212. b) R. Blieck, M. S. Azizi, A. Mifleur, M. Roger, C. Persyn, M. Sauthier, H. Bonin, *Eur. J. Org. Chem.* **2016**, *6*, 1194–1198. c) Y. Kita, R. D. Kavthe, H. Oda, K. Mashima, *Angew. Chem. Int. Ed*. **2016**, *55*, 1098-1101.

[8] S.-C. Sha, H. Jiang, J. Mao, A. Bellomo, S. A. Jeong, P. J. Walsh, *Angew. Chem. Int. Ed.* **2015**, *54*, 1–6.

[9] J. A. Caputo, M. Naodovic, D. J. Weix, *Synlett* **2015**, *26*, 323–326.

[10] a) M. Kimura, Y. Horino, R. Mukai, S. Tanaka, Y. Tamaru, J. *Am. Chem. Soc.* **2001**, 123, 10401–10402; b) M. Kimura, M. Shimizu, K. Shibata, M. Tazoe, Y. Tamaru, *Angew. Chem. Int. Ed.* **2003**, *42*, 3392–3395.

[11] G. Jiang, B. List, *Adv. Synth. Catal.* **2011**, *353*, 1667–1670.

[12] a) I. Ibrahem, A. Córdova, *Angew. Chem. Int. Ed.* **2006**, *45*, 1952–1956; b) S. Mukherjee, B. List, *J. Am. Chem. Soc.* **2007**, *129*, 11336–11337; c) G. Jiang, B. List, *Angew. Chem. Int. Ed.* **2011**, *50*, 9471–9474; d) S. Afewerki, I. Ibrahem, J. Rydfjord, P. Breistein, A. Córdova, *Chem. – Eur. J.* **2012**, *18*, 2972–2977; e) M. Yoshida, T. Terumine, E. Masaki, S. Hara, *J. Org. Chem.* **2013**, *78*, 10853–10859; f) X. Huo, G. Yang, D. Liu, Y. Liu, I. D. Gridnev, W. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 6776–6780; g) X. Huo, M. Quan, G. Yang, X. Zhao, D. Liu, Y. Liu, W. Zhang, *Org. Lett.* **2014**, *16*, 1570–1573.

[13] a) S. Krautwald, M. A. Schafroth, D. Sarlah, E. M. Carreira, *J. Am. Chem. Soc.* **2014**, *136*, 3020–3023; b) S. Krautwald, D. Sarlah, M. A. Schafroth, E. M. Carreira, *Science* **2013**, *340*, 1065–1068.

[14] T. B. Wright, P. A. Evans, *J. Am. Chem. Soc.* **2016**, *137*, 6156–6159.

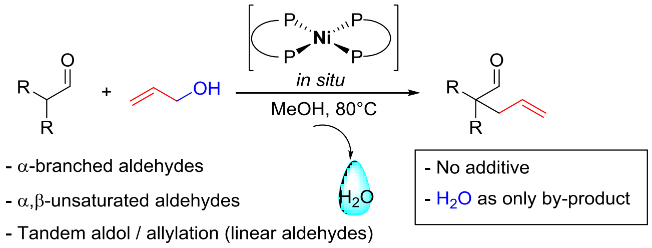
[15] Footnote: Similar results (i.e. conv. and yield > 90 %) are obtained in methanol, ethanol, *tert*-butyl alcohol or directly in allyl alcohol itself (see the Supporting Information).

[16] Y. Inoue, M. Toyofuku, M. Taguchi, S. Okada, H. Hashimoto, *Bull. Chem. Soc. Jpn.***1986**, *59*, 885–891.

[17] Footnote: sodium hydroxide is typically used as catalyst for this transformation.

[18] H. Surburg, J. Panten, *Common Fragrance and Flavor Materials*: *Preparation, Properties and Uses. 5th Edition.* Wiley-VCH, Weinheim, **2006**.

[19] a) T. Money, M. K. C. Wong, in *Stud. Nat. Prod. Chem.* (Ed.: Atta-ur-Rahman), Elsevier, **1995**, pp. 123–288. b) C. X. Zhang, F. Q. Bi, Y. L. Li, *Chin. Chem. Lett.* **2008**, *19*, 805–806. c) K. Tiefenbacher, J. Mulzer, *Angew. Chem. Int. Ed.* **2008**, *47*, 6199–6200. d) K. Mukai, D. Urabe, S. Kasuya, N. Aoki, M. Inoue, *Angew. Chem. Int. Ed.* **2013**, *52*, 5300–5304. e) K. Mukai, S. Kasuya, Y. Nakagawa, D. Urabe, M. Inoue, *Chem. Sci.* **2015**, *6*, 3383–3387. f) P. C. Roosen, C. D. Vanderwal, *Angew. Chem. Int. Ed.* **2016***, 55*, 7180–7183.



Nickel based catalysts efficiently promote the α-allylation of α-branched aldehydes and α,β-unsaturated aldehydes with allylic alcohols under additive free conditions. The reaction proceeds with high yields and water is formed as the only side product. The nickel catalysts proved to be suitable for the promotion of the tandem aldolisation/allylation reaction of simple linear aldehydes with allyl alcohol.

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