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Amide Allylation

Nickel(0)-Catalyzed *N*-Allylation of Amides and *p*-Toluenesulfonamide with Allylic Alcohols under Neat and Neutral Conditions

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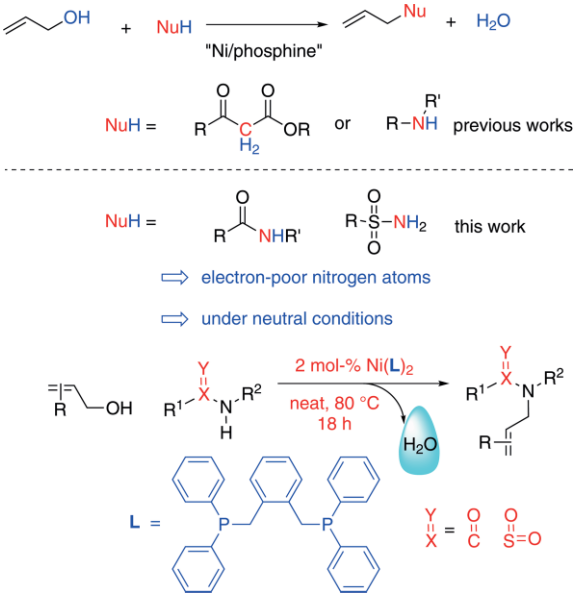
Abstract: Nickel(0)-catalyzed direct *N*-allylation of amides and *p*-toluenesulfonamide with allylic alcohols took place in the presence of Ni^0–diphosphine complexes. The corresponding *N*-allylated (and/or *N*,*N*-diallylated) products were obtained in moderate to high yields under neutral conditions.

Introduction

Direct *N*-allylation ranks among the most studied of *N*-alkylation reactions.[1] This reaction is usually performed with allyl acetates, carbonates, halides, sulfonates, or phosphonates, as substrates generating stoichiometric amounts of salt waste. Relative to these activated substrates, the use of allylic alcohols[2] has several advantages. One important feature is that, with this reagent, the reaction only releases molecules of water as easy to separate, non-toxic side products. In addition, it is noteworthy that allylic alcohols are often less expensive than alkyl halides and, in fact, are generally used to synthesize allylic substrates with good leaving groups (acetates, phosphonates). However, it is well known that the reactivity of allylic alcohols is usually lower than that of the allylic derivatives featuring good leaving groups, especially when considering the need for an oxidative addition step with a low-valent organometallic species. A key issue in developing clean allylation reactions entails the use of appropriate catalysts and reaction conditions that favor this elemental step with allylic alcohols, particularly without the use of activating additives (Scheme 1).[3]

Following the pioneering studies by Tsuji and Trost,[4] the direct amination of allylic alcohols has been frequently studied using transition-metal catalysts; a predominant focus has been on the application of palladium.[5] The *N*-allylation with allylic alcohols of electron-poor nitrogen nucleophiles has been the topic of only a few publications because of their poor nucleophilicity.[6,7] The direct *N*-protection of an amide with an allyl group is, however, an important reaction in organic synthesis, notably in total synthesis, enabling one to avoid competitive reactions.[8] On the basis of traditional procedures for *N*-allylation of amides with allyl acetates, carbonates, halides, sulfonates, and phosphonates, under neutral conditions, the use of a strong base such as sodium hydride before treatment with the allylating agent would appear to be necessary. This type of synthesis usually leads to mixtures of *N*- and *O*-allylated products.[9,6c]



Scheme 1. Nickel-catalyzed allylation reactions with allylic alcohol.

Notably, Ni^0/phosphine complexes are efficient catalysts for the reaction of various allylic alcohols with nucleophiles such as β-keto esters, β-diketones, malonates or amines under neutral conditions.[10]

Results and Discussion

To date, no nickel(0)-catalyzed direct *N*-allylation of amides and sulfonamides with allylic alcohols has been reported. Other

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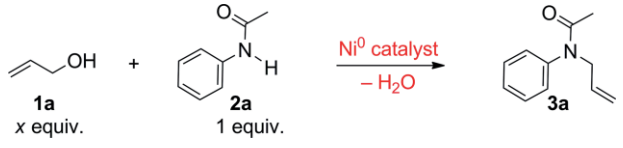
transition metals[6a–6i] or Lewis and Brønsted acids[7] have been applied such as palladium combined with strongly π-accepting diphosphines,[6a–6c] molybdenum,[6d,6e] bismuth,[6f] mercury[6g] and gold complexes.[6h–6i] Unfortunately, most such *N*-allylation reactions of amides and sulfonamides necessitate significant loading of precious metals, high reaction temperatures and require the use of additives. Lewis acids have proven to be highly efficient for the conversion of allylic alcohols substituted with aryl groups that transiently allow formation of stabilized carbocations. Allyl alcohol is typically never involved with this family of catalysts. Therefore, we present herein, the first nickel(0)-catalyzed systems for direct *N*-allylation of amides and sulfonamides using allylic alcohols and a selection of acetanilide, benzamide, benzanilide derivatives and *p*-toluenesulfonamide under neutral and additive-free conditions. The nickel(0)-catalyzed direct *N*-allylation of acetanilide (**2a**) with allyl alcohol (**1a**) was chosen as a model for the optimization of the reaction conditions (Table 1). Amide *N*-allylation with 3 equiv. of allyl alcohol in the presence of $Ni(dppmb)_2$ in toluene (as solvent) proved successful. However, after 18 h at 80 °C, the product was obtained in low yield (Table 1, Entry 1). Investigations into the use of different solvents revealed that the reaction is more efficient in more polar solvents such as THF and CH_3CN (Table 1, Entries 1–4). Interestingly, little to no product was obtained in water and methanol; these solvents very likely acted as competitive nucleophiles (Table 1, Entries 5 and 6). Worth noting is that yields of desired product further improved without use of any solvent (Table 1, Entry 7 versus Entries 1–3). Both the use of a polar medium and the high concentrations of substrate explain this improvement.

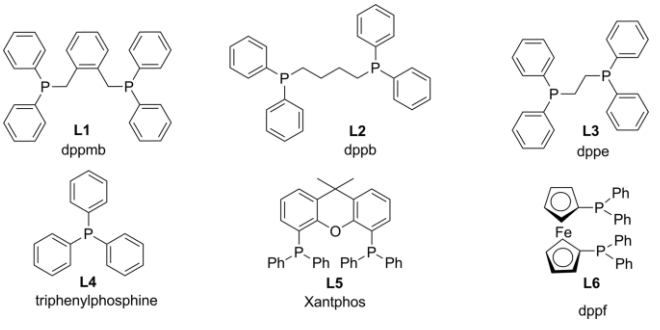
Table 1. Nickel(0)-catalyzed direct *N*-allylation of acetanilide with allyl alcohol under various conditions.[a]



Entry	Catalyst [2 mol-%]	Solvent	x[b]	T [°C]	Additive (mol-%)	Yield[c] [%]
1	$Ni(dppmb)_2$	toluene	3	80	none	4
2	$Ni(dppmb)_2$	CH_3CN	3	80	none	65
3	$Ni(dppmb)_2$	THF	3	80	none	55
4	$Ni(dppmb)_2$	Et_2O	3	80	none	0
5	$Ni(dppmb)_2$	H_2O	3	80	none	10
6	$Ni(dppmb)_2$	MeOH	3	80	none	5
7	$Ni(dppmb)_2$	neat	3	80	none	90
8	$Ni(dppb)_2$	neat	3	80	none	16
9	dppmb/$Ni(cod)_2$ (1:1)	neat	3	80	none	79
10	dppmb/$Ni(cod)_2$ (2:1)	neat	3	80	none	90
11	dppmb/$Ni(cod)_2$ (3:1)	neat	3	80	none	90
12	dppe/$Ni(cod)_2$ (2:1)	neat	3	80	none	50
13	Xantphos	neat	3	80	none	3
14	dppf	neat	3	80	none	2
15	PPh_3/$Ni(cod)_2$ (4:1)	neat	3	80	none	4
16	$Ni(dppmb)_2$	neat	3	60	none	73
17	$Ni(dppmb)_2$	neat	3	90	none	90
18	$Ni(dppmb)_2$	neat	3	100	none	67
19	$Ni(dppmb)_2$	neat	1	80	none	76
20	$Ni(dppmb)_2$	neat	2	80	none	77
21	$Ni(dppmb)_2$	neat	4	80	none	90
22[d]	$Ni(dppmb)_2$	neat	3	80	NaOH (20)	47
23	$Ni(dppmb)_2$	neat	3	80	NEt_3 (20)	14
24	$Ni(dppmb)_2$	neat	3	80	PTSA (20)	0
25	$Ni(dppmb)_2$	neat	3	80	$B(OH)_3$ (20)	0

[a] Reaction conditions: **1** (9.75 mmol, if using 3 equiv.), **2a** (3.25 mmol, 1 equiv.), if using a solvent (0.5 mL), 1–2 mol-% of $Ni(dppmb)_2$, 60–100 °C, 18 h. [b] Equiv. of allyl alcohol employed in the reaction. [c] Isolated yield. [d] Formation of aniline (yield: 2 %) and *N*-allylaniline (yield: 14 %).

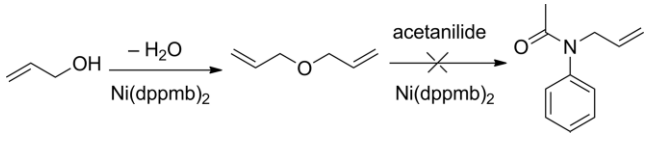
We then turned our attention to understanding the effects of phosphine ligands on the catalytic elements of *N*-allylation. For this purpose, the catalyst was obtained in situ using the combination of $Ni(cod)_2$ and the ligand (Scheme 2) with a P/Ni ratio of 4:1. 1,2-Bis[(diphenylphosphino)methyl]benzene (dppmb, **L1**) was identified as the most promising ligand compared to other monodentate and/or bidentate phosphines such as 1,4-bis(diphenylphosphino)butane (dppb, **L2**), 1,2-bis(diphenylphosphino)ethane (dppe, **L3**), triphenylphosphine (PPh_3, **L4**), Xantphos (**L5**), and 1,1′-ferrocenediylbis(diphenylphosphine) (dppf, **L6**) (Table 1, Entries 8–15). The cod ligands are easily replaced (in situ) by diphosphines; the $Ni(dppb)_2$ complex is, for example, synthesized fromby a ligand exchange reaction between 1 equiv. of $Ni(cod)_2$ and 2 equiv. of dppb.[5c] Notably, this ligand effect is a common feature in catalytic transformations that involve allylic nickel intermediates, and a similar trend has been observed in the case of diene hydroalkoxylations.[11] With dppmb, a ligand/Ni ratio of 2 or 3 is necessary to ensure stabilization of the catalytic species and the formation of **3a** with the highest yield (Table 1, Entries 9–11).



Scheme 2. Ligands used in the study.

In order to further delineate the best catalytic conditions, the effects of temperature as well as the number of allylic alcohol equivalents were studied. Temperatures higher than 90 °C lead to a loss of catalytic activity, which can be attributed to catalyst degradation (Table 1, Entries 17 and 18). At 60 °C, lower yields, as explained by insufficient catalytic activities, were obtained (Table 1, Entry 16). Although amide monoallylation was targeted in this study, it should be emphasized that 2 or 3 equiv. of allylic alcohol are necessary to achieve high yields (Table 1, Entries 19–21). This is essentially explained by the fact that, as evidenced by GC analysis of the crude mixtures, the allylic alcohol is partially converted into diallyl ether as a side product of the reaction (Scheme 3). This etherification reaction is known in nickel chemistry[12,10b] and is more commonly observed if

allylic alcohol is used in the absence of a nucleophile. The formation of this side product is in line with the rather low reactivity/nucleophilicity of amides. In order to improve our insight into the importance of this side reaction on the course of the desired reaction, diallyl ether was treated with acetanilide under the optimized reaction conditions. No product (**3a**) was formed, thus indicating that this side reaction competes with amide *N*-allylation. From a practical point of view, the formation of diallyl ether is not a major drawback as this compound is easily removed from the reaction medium during workup and evaporation of the volatiles.



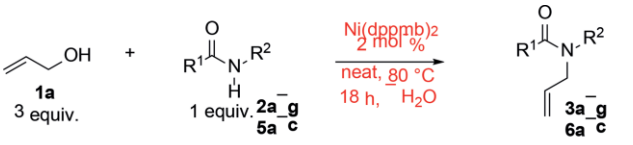
Scheme 3. Self-etherification of allylic alcohol.

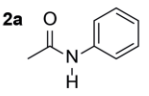
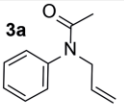
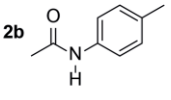
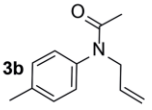
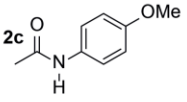
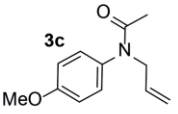
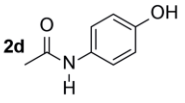
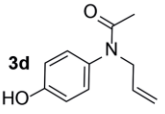
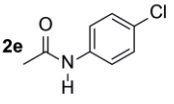
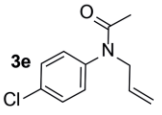
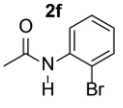
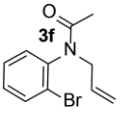
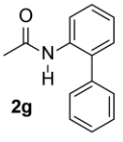
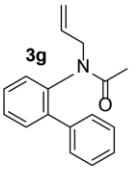
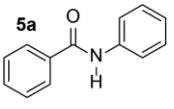
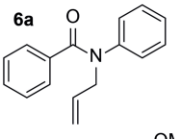
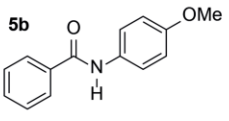
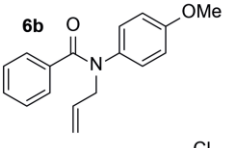
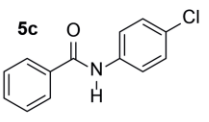
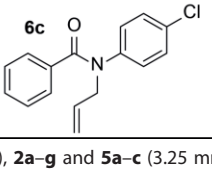
Various acids and bases that can either activate the hydroxy group of the allylic starting material or improve the nucleophilicity of the amide have been evaluated as additives. Bases were found to completely deactivate the catalyst (Table 1, Entries 22 and 23), whereas acids did not lead to any further improvements (Table 1, Entries 24 and 25). After optimization, the nickel-catalyzed reaction afforded *N*-allylated acetanilide in an isolated yield of 90 % under neutral conditions.

The reactions of various acetanilide and benzanilide derivatives were then examined. The results of the catalytic *N*-allylation are summarized in Table 2. Derivatives of acetanilide with electron-donating groups at the *para* position of the phenyl group were readily converted into the corresponding allylated derivatives (Table 2, Entries 2 and 3). The use of the *p*-hydroxy group (paracetamol, **2d**) led to a rather low product yield, although it is noteworthy that no allylation on the phenolic oxygen atom occurred (Table 2, Entry 4). This can likely be correlated to the good leaving ability of the phenoxy group in allylphenoxy substrates; these species have been used elsewhere as substrates in allylation reactions.[13] Although the oxidative addition of aryl halides to low-valent nickel species can effect substrate decomposition, *p*-chloro- and *o*-bromo-substituted acetanilides were converted into the corresponding allylated derivatives **3e** and **3f** with isolated yields of 56 % and 60 %, respectively (Table 2, Entries 5 and 6). Sterically more hindered derivative **2g**, which was prepared by acetylation of 2-phenylaniline, was very efficiently converted into **3g** (Table 2, Entry 7). Benzanilides were also evaluated as nitrogen donors, and derivatives **6a**–**c** were isolated with yields ranging from 48 % to 74 % (Table 2, Entries 8–10).

The scope of the reaction was further enlarged to other amides, and our interest focused on the conversion of primary amides (Table 3). The reaction of benzamide (**7a**) afforded a mixture of monoallylated **8a** and diallylated **8b** derivatives that were efficiently purified by silica gel column chromatography (Table 3, Entry 1). Improved selectivity for monoallylated derivatives can be achieved by using fewer equivalents of allylic alcohol. The monoallylated derivative was obtained from the reaction with *N*-methylbenzamide (**7b**) (Table 3, Entry 2). Monoallylated and diallylated derivatives were additionally obtained using substrates **7c** and **7d** (Table 3, Entries 3 and 4). The use of substrate **7d**, bearing both an amino and an amido group clearly reveals the difference in reactivity between the two nitrogen atoms. Product **8f**, allylated on the amino group, was

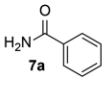
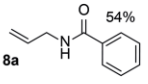
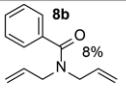
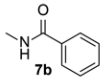
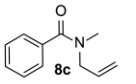
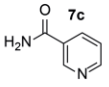
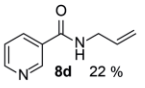
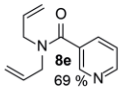
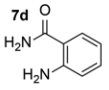
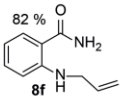
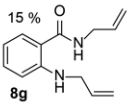
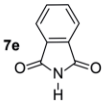
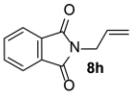
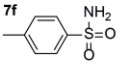
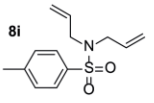
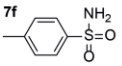
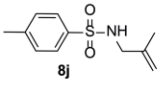
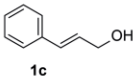
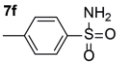
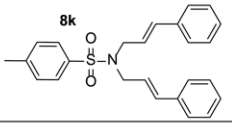
Table 2. Nickel(0)-catalyzed direct *N*-allylation of acetanilide and benzanilide derivatives.[a]



Entry	Amide	Product	Yield [%][b]
1			90
2			60[c]
3			70
4			20
5			56
6			60[c]
7			90
8			48
9			74
10			61

[a] Reaction conditions: **1** (9.75 mmol), **2a**–**g** and **5a**–**c** (3.25 mmol), 2 mol-% of Ni(dppmb)$_2$, 80 °C, 18 h. [b] Yields of isolated products. [c] Determined by GC.

Table 3. Reaction scope of the nickel(0)-catalyzed direct *N*-allylation of amides and *p*-toluenesulfonamide with allylic alcohols.[a]

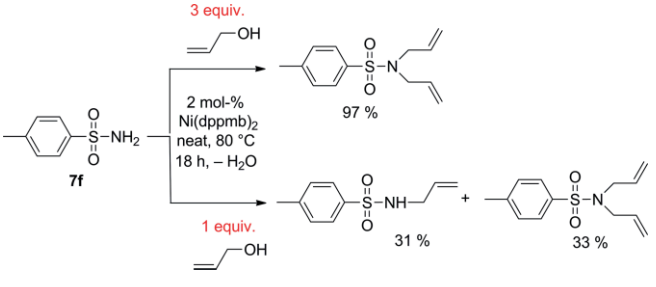
Entry	Allyl alcohol	Amide	Monoallylated product	Diallylated product	Combined yield [%][b]
1	 1a	 7a	 54% 8a	 8b 8%	62
2	 1a	 7b	 8c	–	36
3	 1a	 7c	 8d 22 %	 8e 69 %	91
4	 1a	 7d	 82 % 8f	 15 % 8g	97
5	 1a	 7e	 8h	–	33
6	 1a	 7f	–	 8i	97
7	 1b	 7f	 8j	–	62
8[c]	 1c	 7f	–	 8k	64

[a] Reaction conditions: **1a**–**c** (9.75 mmol), **7a**–**i** (3.25 mmol), cat. (2 mol-%), 80 °C, 18 h. [b] Isolated yields. [c] The reaction was carried out in CH_3CN.

obtained as a mixture with diallylated (on the amino and amido groups) compound **8g**, thus demonstrating the higher reactivity of the aniline nitrogen atom relative to that of the amide group (Table 3, Entry 4). A low yield of product was obtained using phthalimide, a widely used reactant in the chemistry of *N*-acyliminium ions (Table 3, Entry 5).[14] However, *p*-toluenesulfonamide (**7f**) was found to efficiently react with allyl alcohol yielding selectively diallylated **8i** (Table 3, Entry 6).

The reaction showed limited success with substituted allylic derivatives such as 2-methyl-2-propen-1-ol (**1b**) and cinnamyl alcohol (**1c**). Neither of these allylic alcohols reacted with acetanilide (**2a**) or nicotinamide (**7c**) under our optimized reaction conditions. However, these substituted allylic derivatives were elsewhere efficiently treated with *p*-toluenesulfonamide (**7f**). The reaction of **7f** with substituted allyl alcohol **1b** led to selective formation of monoallylated **8j** (Table 3, Entry 7); the bulkiness of this substrate very likely prevented the generation of the diallylated derivative. Conversely, the reaction of **1c** yielded selectively diallylated derivative **8k** (Table 3, Entry 8).

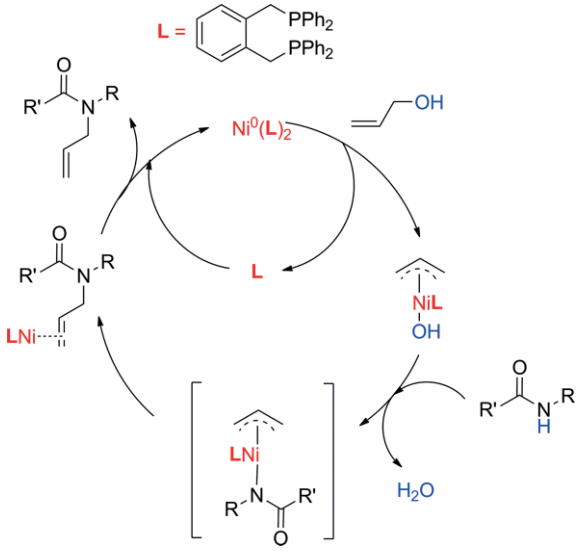
Importantly, the selectivity of the reaction could not be tuned by reducing the number of equivalents of allyl alcohol. For instance, primary sulfonamide **7f** was efficiently converted into its diallylated derivative by using 3 equiv. of allylic alcohol. However, a mixture of mono- and diallylated derivatives was obtained when using 1 equiv. allylic alcohol (Scheme 4).



Scheme 4. Allylation selectivity of **7f** as function of allyl alcohol equivalents.

The use of amides as nucleophiles in metal-catalyzed allylic alkylation reactions is rather uncommon. This is due to the poor

nucleophilicity of the nitrogen atom. This reduced reactivity relative to that of amines results from partial delocalization of the nitrogen lone pair of electrons with the carbonyl group.[15] Amide nucleophilicity can, however, be enhanced by *N*-deprotonation; this elemental step typically requires the use of strong bases.[9] In the case of the nickel-catalyzed allylation reaction, it can be expected that the nickel–hydroxy species generated from oxidative addition of allyl alcohol to an Ni^0 intermediate acts as a catalytic base[6a] assisting in the formation of an allylic nickel amide complex and subsequent release of water (see Scheme 5).



Scheme 5. Proposed mechanism for amide *N*-allylation.

A reductive elimination step leads to the formation of the *N*-allylated amide with subsequent generation of a low-valent Ni^0 precursor that can initiate a new catalytic cycle. Alternatively, an outer-sphere attack of the amide on the allylic moiety of the Ni(allyl)(hydroxy) intermediate with subsequent release of water directly affords the product along with the same Ni^0 precursor. Both pathways (inner-sphere and outer-sphere) are driven by deprotonation of the amide by the hydroxy ligand; this logic is consistent with the superior reactivity observed with acidic amides such as tosylamides.

Conclusions

We have reported that Ni^0-based catalysts stabilized with the dppmb ligand promote direct *N*-allylation of amides and *p*-toluenesulfonamide with allylic alcohols. The reaction has been shown to compete with the nickel-catalyzed self-etherification, which affords volatile diallyl ether. This synthetic pathway thus allows for clean protection of amides with an allylic moiety in an eco-friendly fashion. The reaction is performed under neutral conditions, no additive is needed to activate the allyl alcohol, and water is generated as an easily removed byproduct.

Experimental Section

General Remarks: All catalytic reactions were performed with standard Schlenk techniques under nitrogen. Solvents were dried by using an MBRAUN Solvent Purification Systems (MB-SPS-800) and degassed under nitrogen prior to use. All glass apparatus was oven-dried and cooled under vacuum before use; the dppmb ligand was prepared according to a procedure described by Li et al., from triphenylphosphine and 1,2-bis(bromomethyl)benzene in the presence of lithium[16] or potassium.[17] $Ni(dppmb)_2$ and other catalysts were prepared in a glove box (MBRAUN). Acetanilide derivatives **2a**–**g** were prepared using a classical method of acetylation of the corresponding anilines with acetic anhydride and sodium acetate in acetic acid. Benzanilide derivatives **5a**–**d** were prepared from commercially available anilines according to the Schotten–Baumann conditions[18] with benzoyl chloride. The reaction takes place in a basic medium in the presence of NaOH, and ethanol as solvent. All reactions were monitored by GC analysis using a Shimadzu GC2014 apparatus. Analytical thin layer chromatography (TLC) was performed with commercial silica gel 60 by way of fluorescent indicator UV absorbance 254 (Merck). Detection was accomplished by irradiation with a UV lamp and by an ethanolic solution of *p*-anisaldehyde. Distilled solvents were used as eluents for column chromatography. Chromatographic purifications were realized using silica gel columns (silica 60 Å, 40–63 μm) usually with a petroleum ether/ethyl acetate eluent system. Melting points were determined using a Stuart Scientific SMP 10 analyzer. ^1H and ^{13}C NMR spectra were recorded with a Bruker AC 300 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to internal Me_4Si (TMS). High-resolution mass spectra (HRMS) were measured with a Thermo Scientific Exactive spectrometer at the CUMA-Pharm. Dept., University Lille Nord de France.

General Procedure A for the Synthesis of $Ni(dppmb)_2$. Synthesis of $Ni(dppmb)_2$: In a Schlenk tube were placed dppmb (1.172 g, 2 equiv.) and a magnetic stirring bar. The Schlenk tube was then placed in a glove box to weigh the $Ni(COD)_2$ (air-sensitive reagent) (342 mg). The Schlenk tube was removed from the glovebox and connected to a vacuum/nitrogen line. Under nitrogen, toluene (20 mL) was added. The mixture was stirred at room temperature overnight, and the solvent was evaporated to give a yellow solid. For the catalytic runs, $Ni(dppmb)_2$ was weighed in air but kept stored in the Schlenck tube under nitrogen after each use.

General Procedure B for the Nickel(0)-Catalyzed *N*-Allylation of Amides and Sulfonamide with Allylic Alcohols: In a Schlenk tube were placed freshly prepared $Ni(dppmb)_2$ (2 mol-%), amide (3.25 mmol, 1 equiv.), and a magnetic stirring bar. The reagents were degassed, and then freshly distilled and degassed allyl alcohol (3 equiv.) was added. The reaction mixture was stirred without solvent at 80 °C for 18 h. At the end of the reaction, the reaction mixture was cooled to room temperature, and anisole (250 μL) was added and used as internal standard for the gas-chromatographic (GC) analysis. The reaction mixture was concentrated under reduced pressure; the residue was purified by silica gel column chromatography using ethyl acetate/petroleum ether as eluent.

Analytical Data of Products

***N*-Allyl-*N*-phenylacetamide (3a):**[19] The general procedure B was applied to amide **2a** (440 mg, 3.25 mmol, 1 equiv.) and allyl alcohol (663 μL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 75:25; yield 90 %. ^1H NMR (300 MHz, $CDCl_3$, °C): δ = 1.75 (s, 3 H), 4.20 (dt, J = 6.2, J = 1.2 Hz, 2 H), 4.97 (m, 2 H), 5.75 (m, 1 H), 7.07 (d, J = 8.4 Hz, 2 H), 7.29 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.6, 51.0, 116.7, 126.8, 127.0, 128.5, 132.1, 142.0, 169.1 ppm.

***N*-Allyl-*N*-(*p*-tolyl)acetamide (3b):**[19] The general procedure B was applied to amide **2b** (485 mg, 3.25 mmol, 1 equiv.) and allyl alcohol

(663 μL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 75:25; yield 38 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.78 (s, 3 H), 2.30 (s, 3 H), 4.20 (dt, *J* = 6.2, *J* = 1.2 Hz, 2 H), 5.00 (m, 2 H), 5.78 (m, 1 H), 6.95 (d, *J* = 8.2 Hz, 2 H), 7.11 (d, *J* = 8.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 20.0, 21.6, 51.0, 116.6, 126.8, 129.1, 132.2, 136.7, 139.4, 169.2 ppm.

***N*-Allyl-*N*-(4-methoxyphenyl)acetamide (3c):**[19] The general procedure B was applied to amide **2c** (536 mg, 3.25 mmol, 1 equiv.) and allyl alcohol (663 μL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 75:25; yield 70 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.76 (s, 3 H), 3.73 (s, 3 H), 4.17 (dt, *J* = 6.3, *J* = 1.4 Hz, 2 H), 4.99 (m, 2 H), 5.75 (m, 1 H), 6.82 (d, *J* = 8.9 Hz, 2 H), 6.98 (d, *J* = 8.9 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 22.5, 52.0, 55.3, 114.6, 117.7, 129.1, 133.2, 135.7, 158.9, 170.4 ppm.

***N*-Allyl-*N*-(4-hydroxyphenyl)acetamide (3d):**[20] The general procedure B was applied to amide **2d** (491 mg, 3.25 mmol, 1 equiv.) and allyl alcohol (663 μL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 75:25; yield 20 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.08 (s, 3 H), 4.44 (dt, *J* = 5.2, *J* = 1.4 Hz, 2 H), 5.20 (dd, *J* = 10.5, *J* = 1.3 Hz, 1 H), 5.33 (dd, *J* = 17.2, *J* = 1.5 Hz, 1 H), 5.97 (m, 1 H), 6.79 (d, *J* = 8.9 Hz, 2 H); 6.97 (s, 1 H), 7.30 (d, *J* = 9.0 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 24.1, 68.9, 115.1, 117.6, 121.8, 133.6, 143.0, 153.8, 168.1 ppm.

***N*-Allyl-*N*-(4-chlorophenyl)acetamide (3e):**[19] The general procedure B was applied to amide **2e** (551 mg, 3.25 mmol, 1 equiv.) and allyl alcohol (663 μL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 75:25; yield 56 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.79 (s, 3 H), 4.19 (dt, *J* = 6.2, *J* = 1.2 Hz, 2 H), 5.04 (m, 2 H), 5.75 (m, 1 H), 7.03 (d, *J* = 8.5 Hz, 2 H); 7.29 (d, *J* = 8.6 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 22.6, 51.9, 118.1, 129.4, 129.8, 132.8, 133.7, 141.4, 169.8 ppm.

***N*-Allyl-*N*-(2-bromophenyl)acetamide (3f):**[21] The general procedure B was applied to amide **2f** (347 mg, 1.62 mmol, 1 equiv.) and allyl alcohol (663 μL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 75:25; yield 60 % (determined by GC), NMR spectra showed that the isolated product is a mixture with the starting material [45 % of *N*-(2-bromophenyl)acetamide **2f**]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.74 (s, 3 H), 3.65 (dd, *J* = 14.7, *J* = 7.5 Hz, 1 H), 4.68 (dd, *J* = 14.7, *J* = 5.6 Hz, 1 H), 5.00 (m, 2 H), 5.80 (m, 1 H), 6.91 (m, 1 H), 7.46 (m, 1 H), 7.63 (m, 1 H), 8.25 (d, *J* = 7.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 22.4, 50.8, 118.4, 123.9, 128.4, 129.7, 131.1, 132.8, 133.8, 141.4, 170.1 ppm.

***N*-Allyl-*N*-(biphenyl-2-yl)acetamide (3g):** The general procedure B was applied to amide **3g** (171 mg, 0.810 mmol, 1 equiv.) and allyl alcohol (663 μL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 75:25. R_f = 0.56 (75:25); colorless viscous oil; yield 90 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.82 (s, 3 H), 3.07 (dd, *J* = 14.7, *J* = 7.6 Hz, 1 H), 4.53 (dd, *J* = 14.7, *J* = 5.1 Hz, 1 H), 4.89 (dd, *J* = 19.5, *J* = 7.6 Hz, 1 H), 4.94 (dd, *J* = 13.8, *J* = 1.1 Hz, 1 H), 5.57–5.79 (m, 1 H), 7.05–7.41 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 22.8, 51.4, 117.7, 127.7, 128.3, 128.41, 128.46, 128.48, 128.5, 128.7, 130.0, 131.4, 133.0, 138.7, 139.6, 140.2, 170.3 ppm. HR-MS (+ESI): calcd. for $C_{17}H_{18}NO$ $[M + H]^+$ 252.1388, found 252.1375.

***N*-Allyl-*N*-phenylbenzamide (6a):**[22] The general procedure B was applied to amide **5a** (320 mg, 1.62 mmol, 1 equiv.) and allyl alcohol (663 μL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 50:50; yield 48 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.46 (d, *J* = 6.0 Hz, 2 H), 5.11 (m, 2 H), 5.92 (m, 1 H), 6.94 (m, 2 H), 7.08 (m, 6 H), 7.26 (dd, *J* = 6.8, *J* = 1.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 53.2, 117.6, 120.2, 124.5, 126.5, 127.0, 127.5, 127.7, 128.7, 128.8, 129.0, 129.1, 129.6, 131.8, 133.2, 169.8 ppm.

***N*-Allyl-*N*-(4-methoxyphenyl)benzamide (6b):**[23] The general procedure B was applied to amide **5b** (368 mg, 1.62 mmol, 1 equiv.) and allyl alcohol (663 μL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 50:50; yield 74 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.66 (s, 3 H), 4.40 (d, *J* = 6.0 Hz, 2 H), 5.11 (m, 2 H), 5.89 (m, 1 H), 6.64 (d, *J* = 8.8 Hz, 2 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 7.17 (m, 3 H), 7.24 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 53.3, 55.3, 114.2, 117.7, 127.7, 128.6, 128.8, 129.4, 133.2, 136.2, 152.1, 158.0, 170.2 ppm.

***N*-Allyl-*N*-(4-chlorophenyl)benzamide (6c):**[23] The general procedure B was applied to amide **5c** (375 mg, 1.62 mmol, 1 equiv.) and allyl alcohol (663 μL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 50:50; yield 61 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.42 (dt, *J* = 6.0, *J* = 1.3 Hz, 2 H), 5.10 (m, 2 H), 5.87 (m, 1 H), 6.88 (d, *J* = 8.7 Hz, 2 H), 7.10 (m, 2 H), 7.15 (m, 3 H), 7.24 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 53.1, 117.8, 122.1, 122.5, 127.7, 128.6, 128.7, 128.8, 129.4, 132.1, 133.1, 131.7, 136.0, 155.1, 155.7, 165.8 ppm.

***N*-Allylbenzamide (8a):**[24] The general procedure B was applied to amide **7a** (393 mg, 3.25 mmol, 1 equiv.) and allyl alcohol (663 μL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 75:25; yield 54 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.01 (m, 2 H), 5.11 (d, *J* = 10.2 Hz, 1 H), 5.19 (d, *J* = 17.1 Hz, 1 H), 5.86 (m, 1 H), 6.22 (s, br., 1 H), 7.36 (m, 3 H), 7.71 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 41.4, 115.4, 125.9, 127.4, 130.4, 133.2, 133.4, 166.4 ppm.

***N*,*N*-Diallylbenzamide (8b):**[25] The general procedure B was applied to amide **7a** (393 mg, 3.25 mmol, 1 equiv.) and allyl alcohol (663 μL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 75:25; yield 8 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.76 (s, br., 2 H), 4.06 (s, br., 2 H), 5.13 (m, 4 H), 5.75 (m, 2 H), 7.33 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 50.2, 52.4, 117.6, 126.6, 128.3, 129.6, 136.3, 171.7 ppm.

***N*-Allyl-*N*-methylbenzamide (8c):**[26] The general procedure B was applied to amide **7b** (440 mg, 3.25 mmol, 1 equiv.) and allyl alcohol (663 μL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 75:25; yield 36 %; Existing as a 3:2 mixture of rotamers. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.84 (s, br., 3 H, minor), 2.97 (s, br., 3 H, major), 3.77 (s, br., 2 H, minor), 4.07 (s, br., 2 H, major), 5.17 (m, 2 H), 5.74 (m, 1 H), 7.31 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.1, 21.0, 29.6, 53.9, 60.3, 117.5, 126.6, 128.9, 129.5, 133.0, 136.3, 136.3, 170.5 ppm.

***N*-Allylnicotinamide (8d):**[27] The general procedure B was applied to amide **7c** (397 mg, 3.25 mmol, 1 equiv.) and allyl alcohol (663 μL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 75:25; yield 22 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.95 (tt, *J* = 7.2, *J* = 1.5 Hz, 2 H), 5.08 (m, 2 H), 5.81 (m, 1 H), 7.24 (m, 1 H), 7.59 (s, br., 1 H), 8.06 (dt, *J* = 7.9, *J* = 2.1 Hz, 2 H), 8.56 (dd, *J* = 4.8, *J* = 1.4 Hz, 2 H), 8.94 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 42.4, 116.5, 123.4, 130.2, 133.8, 135.2, 148.2, 151.8, 165.7 ppm.

***N,N*-Diallylnicotinamide (8e):**[28] The general procedure B was applied to amide **7c** (397 mg, 3.25 mmol, 1 equiv.) and allyl alcohol (663 µL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 75:25; yield 69 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.77 (s, br., 2 H), 4.06 (s, br., 2 H), 5.15 (m, 4 H), 5.72 (m, 2 H), 7.25 (ddd, *J* = 7.8, *J* = 4.8, *J* = 0.8 Hz, 1 H), 7.69 (dt, *J* = 7.8, *J* = 1.8 Hz, 1 H), 8.56 (dd, *J* = 4.8, *J* = 1.6 Hz, 1 H), 8.62 (dd, *J* = 1.4, *J* = 0.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 47.3, 50.7, 117.9, 118.1, 123.2, 132.0, 132.4, 132.6, 134.3, 147.4, 150.6, 169.1 ppm.

2-(Allylamino)benzamide (8f):[29] The general procedure B was applied to amide **7d** (442 mg, 3.25 mmol, 1 equiv.) and allyl alcohol (663 µL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 75:25; yield 82 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.75 (d, *J* = 5.1 Hz, 2 H), 5.09 (d, *J* = 10.2 Hz, 1 H), 5.22 (d, *J* = 17.1 Hz, 1 H), 5.73 (s, br., 2 H), 5.87 (m, 1 H), 6.52 (t, *J* = 8.1 Hz, 1 H), 6.63 (d, *J* = 8.4 Hz, 1 H), 7.24 (t, *J* = 7.0 Hz, 1 H), 7.31 (d, *J* = 7.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 45.5, 112.5, 113.3, 115.0, 116.1, 128.2, 133.4, 134.6, 149.8, 172.1 ppm.

***N*-Allyl-2-(allylamino)benzamide (8g):** The general procedure B was applied to amide **7e** (442 mg, 3.25 mmol, 1 equiv.) and allyl alcohol (663 µL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 75:25. R_f = 0.42 (75:25); brown viscous oil; yield 15 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.75 (dt, *J* = 5.1, 1.6 Hz, 2 H), 3.95 (tt, *J* = 5.6, *J* = 1.0 Hz, 2 H), 5.03–5.27 (m, 4 H), 5.75–5.96 (m, 2 H), 6.10 (s, br., 1 H), 6.52 (t, *J* = 7.8 Hz, 1 H), 6.61 (d, *J* = 7.8 Hz, 1 H), 7.21 (t, *J* = 1.3 Hz, 1 H), 7.28 (dd, *J* = 7.8, *J* = 1.5 Hz, 1 H), 7.78 (s, br., 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 41.0, 44.6, 111.3, 114.0, 114.2, 115.1, 115.4, 126.1, 131.7, 133.2, 133.7, 148.3, 168.5 ppm. HR-MS (+ESI): calcd. for $C_{13}H_{17}N_2O$ $[M + H]^+$ 217.1341, found 217.1330.

2-Allylisoindoline-1,3-dione (8h):[30] The general procedure B was applied to amide **7e** (478 mg, 3.25 mmol, 1 equiv.) and allyl alcohol (663 µL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 75:25; yield 33 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.22 (d, *J* = 5.6 Hz, 2 H), 5.14 (m, 2 H), 5.80 (m, 1 H), 7.65 (m, 2 H), 7.78 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 40.0, 117.7, 123.5, 131.5, 132.1, 134.2, 167.9 ppm.

***N,N*-Diallyl-4-methylbenzenesulfonamide (8i):**[31] The general procedure B was applied to the sulfonamide **7f** (556 mg, 3.25 mmol, 1 equiv.) and allyl alcohol (663 µL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 80:20; yield 97 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.39 (s, 3 H), 3.78 (d, *J* = 6.2 Hz, 4 H), 5.13 (m, 4 H), 5.60 (m, 2 H), 7.28 (d, *J* = 7.9 Hz, 2 H), 7.68 (d, *J* = 8.3 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.4, 49.3, 118.8, 127.1, 129.7, 132.7, 137.4, 143.3 ppm.

4-Methyl-*N*-(2-methylallyl)benzenesulfonamide (8j):[32] The general procedure B was applied to the sulfonamide **7f** (556 mg, 3.25 mmol, 1 equiv.) and 2-methylprop-2-en-1-ol (820 µL, 9.75 mmol, 3 equiv.). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 80:20; yield 62 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.59 (s, 3 H), 2.34 (s, 3 H), 3.39 (d, *J* = 6.2 Hz, 2 H), 4.74 (m, 3 H), 7.21 (dd, *J* = 8.5 Hz, 2 H), 7.26 (d, *J* = 8.3 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 19.0, 20.4, 47.0, 111.7, 126.1, 128.6, 136.0, 139.5, 142.3 ppm.

***N,N*-Dicinnamyl-4-methylbenzenesulfonamide (8k):**[33] The general procedure B was applied to the sulfonamide **7f** (556 mg, 3.25 mmol, 1 equiv.) and cinnamyl alcohol (1.3 g, 9.75 mmol, 3 equiv.), the reaction is carried out in CH_3CN (0.5 mL). Eluent used for the flash column chromatography: petroleum ether/ethyl acetate, 100:0 to 95:05; yield 64 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.35 (s, 3 H), 3.93 (d, *J* = 6.6 Hz, 4 H), 5.92 (m, 2 H), 6.34 (m, 2 H), 7.19 (m, 12 H), 7.68 (d, *J* = 8.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.4, 49.0, 123.9, 126.4, 127.3, 127.9, 128.6, 129.7, 134.0, 136.2, 137.6, 143.3 ppm.

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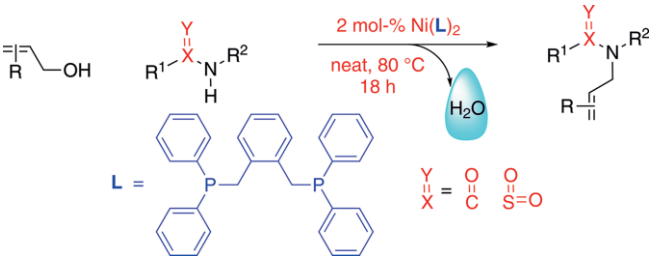
Amide Allylation



Amides and *p*-toluenesulfonamide are *N*-allylated using allyl alcohol in a catalytic fashion. The reaction is promoted by nickel-based catalysts and yields water as a byproduct. Interestingly, self-etherification of allylic alcohol is a competing side reaction that yields diallyl ether.

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