Microwave-Assisted Palladium-Catalyzed Allylation of β-Enaminones

Imen Erray,[a,b,c] Farhat Rezgui,[a] Julie Oble,*[b,c] Giovanni Poli*[b,c]

[a] Laboratoire de Chimie Organique Structurale et Macromoléculaire, Faculté des Sciences Campus Universitaire, Université de Tunis El Manar, 2092 Tunis, Tunisia

[b] Sorbonne Universités, UPMC Univ Paris 06, UMR 8232, Institut Parisien de Chimie Moléculaire, FR2769 Institut de Chimie Moléculaire, 75005, Paris, France
Fax +33(1)44274287; E-mail: giovanni.poli@upmc.fr, julie.oble@upmc.fr

[c] CNRS, UMR 8232, Institut Parisien de Chimie Moléculaire, 75005, Paris, France

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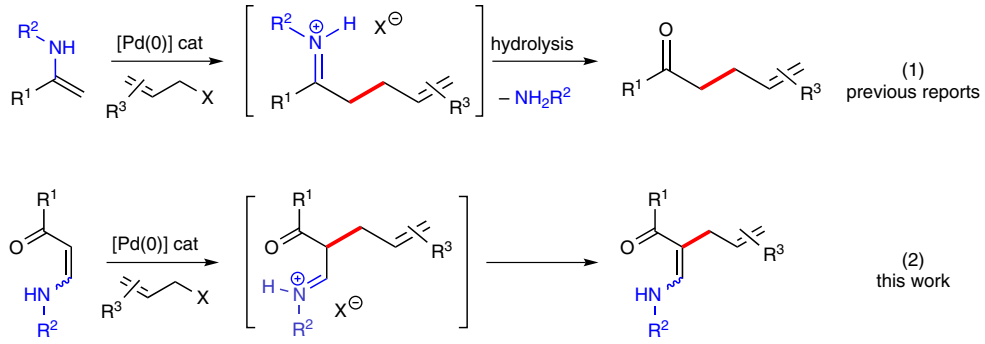
Abstract: A new palladium-catalyzed approach for the C-allylation of β-enaminones under microwave irradiation is reported. This methodology provides an easy access to a variety of α-allylated enaminones. The reaction takes place with the preservation of the enamine function, which is poised for further transformations towards nitrogen-containing heterocycles.

Key words: enaminone, palladium, allylation, allyl acetate, microwave irradiation

Palladium-catalyzed transformations have gained an important place in the toolbox of synthetic chemists.[1] During the last 30 years, the Tsuji–Trost allylation arose as a versatile method for the functionalization of a wide array of scaffolds.[2,3] In particular, enamines have been amongst the first nucleophiles shown to smoothly react with a η^3-allylpalladium complex, as reported by Tsuji et al. in their seminal paper.[4] Indeed, such structures can be efficiently allylated at carbon, leading to the corresponding γ,δ-unsaturated carbonyls after hydrolysis of the iminium ion intermediate (Scheme 1, eq. 1).[5] On the other hand, C-allylation of enamines with conservation of the nitrogen atom is a hitherto unsolved and challenging transformation,[6] of high potential interest for the synthesis of nitrogen-containing frameworks. To reach this goal, and in keeping with our ongoing interest in η^3-allylpalladium chemistry,[7] we herein report a new protocol of allylation of β-enaminones,[8] wherein the enamine function is preserved (Scheme 1, eq. 2).

Due to their particular reactivity, combining the nucleophilicity of enamines with the electrophilicity of enones, β-enamino carbonyl scaffolds are versatile nitrogen-containing building blocks,[9] which have been employed for transition-metal-catalyzed syntheses of various heterocyclic derivatives.[10] We thought that such structures could keep the conventional carbonucleophilic reactivity toward transiently generated η^3-allylpalladium complexes, yet, derailing from the classical reactivity in the subsequent evolution of the iminium ion generated. Indeed, due to the increased acidity of the newly allylated carbon atom, elimination to regenerate the enamine function can be predicted (Scheme 2, right) instead of the classical iminium ion hydrolysis (Scheme 2, left).

With this idea in mind, we undertook an investigation of the palladium-catalyzed allylation using β-enaminone **1a**, [readily prepared from 4-(trimethylsilyl)-3-butyn-2-one and benzylamine and isolated in *E*/*Z* ratio of 1:1.3][11] as the model substrate. As recent studies showed that the combination of $Pd(OAc)_2$ with a phosphinoferrocene ligand in a molecular ratio of 1:1.1 allows efficient allylations of enamines,[5c,g,h] we decided to carry out our first reaction with 10 mol% of $Pd(OAc)_2$, 11 mol% of dppf [1,1′-bis(diphenylphosphino)ferrocene] and one equivalent of allyl phosphate in toluene at 60 °C or 40 °C. Pleasantly, the desired allylated enaminone **2a** could be obtained in 31% or 30% NMR yields[12] after 18 hours at 60 °C or 65 hours at 40 °C, respectively (Table 1, entries 1 and 2).[13]



Scheme 1 Pd-mediated allylation of enamine derivatives

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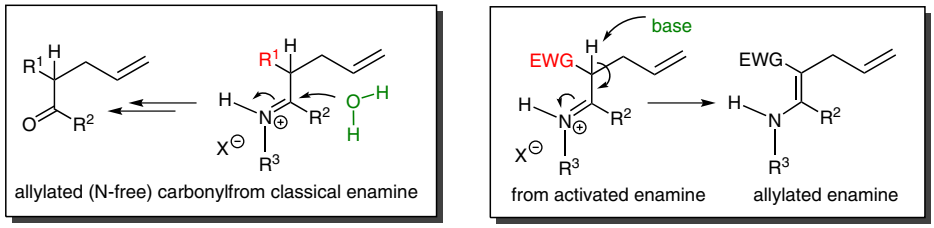
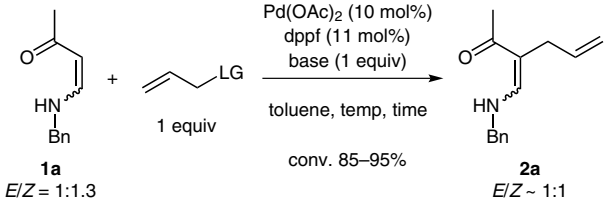


Scheme 2 Concept: expected different evolution in the allylation of classical vs. EWG-activated enamines

Table 1 Allylation of Enaminone **1a** under Thermal Conditions[a]



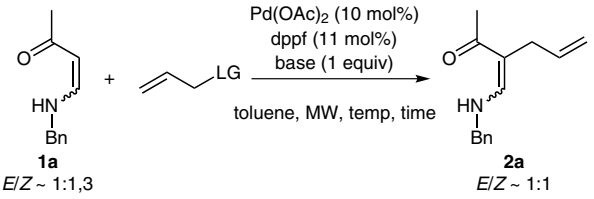
Entry	LG	Base	Temp (°C)	Time (h)	Yield (%)[b]
1	$OP(O)(OEt)_2$	–	60	18	31
2	$OP(O)(OEt)_2$	–	40	65	30
3	$OP(O)(OEt)_2$	proton sponge	60	18	52[c]
4	$OP(O)(OEt)_2$	lutidine	60	18	50
5	OAc	–	40	65	33
6	OAc	proton sponge	40	65	63

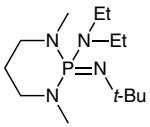
[a] Unless otherwise noted, all reactions were conducted in sealed tube under argon atmosphere at 0.5 M concentration with **1a** (1 equiv), allylic partner (1 equiv), $Pd(OAc)_2$ (10 mol%), dppf (11 mol%), and base (1 equiv) in toluene.
[b] Spectroscopic (^{1}H NMR) yields using an internal standard (1,3,5-trimethoxybenzene).
[c] The same yield was obtained in the presence of the following additives: i) 4 Å MS; ii) H_2O (10 equiv).

However, we noticed some degradation, likely due to the hydrolysis of the iminium intermediate. Therefore, we hypothesized that the use of additives such as non-nucleophilic amine bases could favor the regeneration of the enamine moiety by deprotonation at the α-position of the carbonyl (Scheme 2, right), and thus improve the efficiency of this transformation. Indeed, adding proton sponge [1,8-bis(dimethylamino)naphthalene] or lutidine (2,6-dimethylpyridine) demonstrated a beneficial effect, and allylated enaminone **2a** was formed in 52% and 50% NMR yields, respectively, after 18 hours at 60 °C (Table 1, entries 3 and 4). The same effect was observed in the presence of 1 equivalent of proton sponge with allyl acetate as the allylic partner, in which case an improved 63% NMR yield was obtained after 65 hours at 40 °C (Table 1, compare entries 5 vs. 6). Finally, experiment of entry 6 (Table 1), when run in the presence of 4 Å molecular sieves, led to the same yield as when run without, demonstrating that traces of water do not play a role in the degradation process (Table 1, entry 3).

Despite the yield improvement, the prolonged reaction time remained a drawback. Hence, in order to speed up the reaction, we decided to test microwave irradiation (Table 2).[14]

Table 2 Allylation of Enaminone **1a** under Microwave Irradiation[a]



Entry	LG (equiv)	Base	Temp (°C)	Time (min)	Yield (%)[b]
1	$OP(O)(OEt)_2$ (1)	proton sponge	100	60	–[c]
2	OAc (1)	proton sponge	100	60	68
3	**OAc (2)**	**proton sponge**	**100**	60	**72 (60)[d]**
4	OAc (2)	proton sponge	100	90	71
5	OAc (2)	proton sponge	130	60	41
6	OAc (2)	lutidine	100	60	31
7	OAc (2)		100	60	47
8	OAc (2)	DBU	100	60	42

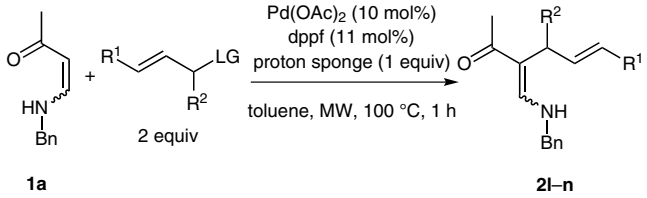
[a] Unless otherwise noted, all reactions were conducted in sealed tube under argon atmosphere and microwave irradiation at 0.5 M concentration with **1a** (1 equiv), allylic partner (1 or 2 equiv), $Pd(OAc)_2$ (10 mol%), dppf (11 mol%), and base (1 equiv) in toluene.
[b] Spectroscopic (^{1}H NMR) yields using an internal standard (1,3,5-trimethoxybenzene).
[c] Degradation.
[d] Isolated yield in parentheses.

While allyl phosphate only gave degradation after one hour at 100 °C under microwave irradiation (Table 2, entry 1), allyl acetate afforded the desired allylated enaminone **2a** in 68% NMR yield (Table 2, entry 2). An improved (72% ^{1}H NMR) yield was obtained when two equivalents of allylic partner were used (Table 2, entry 3).

The time (Table 2, entry 4), the temperature (Table 2, entry 5), and the nature of the base (Table 2, entries 5–8) were also screened, and the best result was obtained with one equivalent of proton sponge after one hour of microwave irradiation at 100 °C. An investigation of the influence of the solvent (toluene, dioxane, DMF, EtOH, DMSO, THF) and the nature of both the palladium catalyst and the ligand was also undertaken.[15] We found the optimal yield for allylation of enaminone **1a** (^{1}H NMR yield 72%, isolated yield 60%) was obtained in the presence of two equivalents of allyl acetate with 10 mol% of $Pd(OAc)_2$, 11 mol% of dppf, and one equivalent of proton sponge in toluene after one hour, under microwave heating at 100 °C (Table 2, entry 3).[16,17]

With these optimized conditions in hand, we began to explore the scope of the allylation with allyl acetate on a series of β-enaminones (Scheme 3). Benzyl (**2a**–**c**), allyl (**2d**), and alkyl groups (**2e**–**g**) on the secondary amine moiety were well tolerated and provided the target allylated enaminones in good to moderate yields. A less nucleophilic enaminone, such as *N*-tosyl-enaminone **1h** only gave 13% of N-allylated product **3h**, which proved that the electron-richness of the nitrogen atom is crucial for the reaction at the carbon atom. Moreover, the tertiary enaminone **1i** was unreactive. The presence of a methyl substituent at the C3-position was also investigated, in which case a 23% yield (53% ^{1}H NMR yield) was obtained for the allylated enaminone **2j**. Finally, a β-enamino ester could be used, leading to **2k** in a low yield (20%). We speculate that in this case the weakly acidic character of the α-proton favors degradation of the iminium intermediate over enamine regeneration.

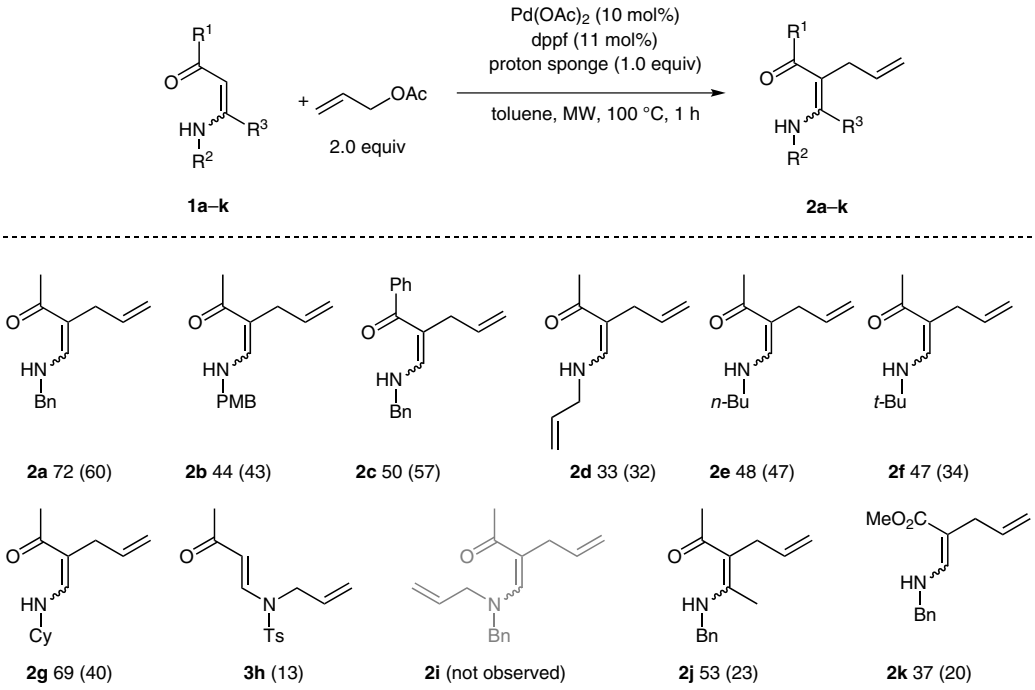
Table 3 Scope of the Allylation with Different Allylic Partners



Entry	LG	R^1	R^2	Yield (%)[a]
1	OAc	H	Me	**2l** 13 (14)[b]
2	$OP(O)(OEt)_2$	H	Me	–[c]
3	OAc	Me	H	**2m** 0
4	$OP(O)(OEt)_2$	Me	H	–[c]
5	OAc	Ph	H	**2n** 29
6	$OP(O)(OEt)_2$	Ph	H	**2n** 68 (42)[b]

[a] Spectroscopic (^{1}H NMR) yields using an internal standard (1,3,5-trimethoxybenzene).
[b] Isolated yield in parentheses.
[c] Degradation.

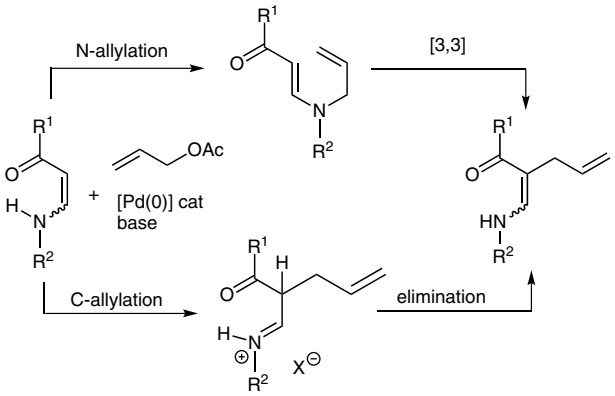
Next, we studied the reaction between β-enaminone **1a** and various allylic partners (Table 3). While but-3-en-2-yl acetate (Table 3, entry 1) only afforded the corresponding branched allylated enaminone **2l** with low yield, crotyl acetate gave no reaction (Table 3, entry 3). The corresponding phosphates led only to degradation (Table 3, entries 2 and 4). On the other hand, the use of cinnamyl acetate gave exclusively the linear product **2n** with 29% ^{1}H NMR yield without trace of the branched isomer (Table 3, entry



Scheme 3 Scope of the allylation with allyl acetate. NMR yields (%) given; isolated yields (%) given in parentheses.

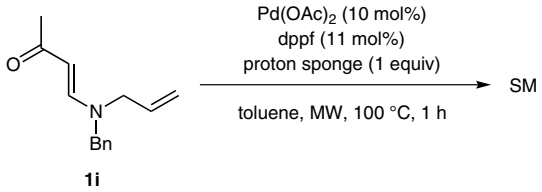
5). Nevertheless, an improved (68% ^{1}H MR, 42% isolated) yield was obtained when two equivalents of cinnamyl phosphate were used (Table 3, entry 6).

Finally, we wished to verify that this transformation takes place via a direct C-allylation as opposed to N-allylation and [3,3]-sigmatropic rearrangement (Scheme 4).



Scheme 4 Possible mechanistic paths toward the allylated product

To this purpose, tertiary enaminone **1i** was synthesized and submitted to the reaction conditions (in the absence of the allyl partner). After one hour under microwave heating at 100 °C, only unreacted starting material (SM) was recovered (Scheme 3 and Scheme 5). Consequently, we assume that a direct C-allylation mechanism is operating, leading to an iminium intermediate, which would then undergo elimination to regenerate the enamine function (Scheme 1, eq. 2; Scheme 2, right).[18]



Scheme 5 Control experiment

In summary, we have developed a palladium-catalyzed intermolecular C-allylation of β-enaminones under microwave irradiation, leading to the corresponding α-allylated substrate. The preservation of the nitrogen atom in this transformation is a new feature of high potential interest in relation to the synthesis of heterocyclic and biologically relevant targets. Extension of this methodology for the synthesis of nitrogen-containing frameworks is currently under way in our laboratory.

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Supporting Information for this article is available online at http://www.thieme-connect.com/products/ejournals/journal/10.1055/s-00000083.

References and Notes

(1) (a) Beller, M.; Bolm, C. *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals*, 2nd ed.; Vol. 1 and 2; Weinheim, Wiley-VCH **2004**. (b) Negishi, E. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Wiley-Interscience: New York, **2002**. (c) Tsuji, J. *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*; Wiley: New York, **2004**. (d) Diederich, F.; de Meijere, A. *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, **2004**, 2nd ed.

(2) For reviews, see: (a) Trost, B. M.; Vranken, D. L. V. *Chem. Rev.* **1996**, *96*, 395. (b) Trost, B. M. *Chem. Pharm. Bull.* **2002**, *50*, 1. (c) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921. (d) Lu, Z.; Ma, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 258.

(3) Poli, G.; Prestat, G.; Liron, F.; Kammerer-Pentier, C. In *Transition Metal Catalyzed Enantioselective Allylic Substitution in Organic Synthesis*; Kazmaier, U., Ed.; *Top. Organomet. Chem.* **2012**, *38*; 1.

(4) Tsuji, J.; Takahashi, H.; Morikawa, M. *Tetrahedron Lett.* **1965**, *6*, 4387.

(5) For examples of Pd-catalyzed enamine allylations, see: (a) Ibrahem, I.; Córdova, A. *Angew. Chem. Int. Ed.* **2006**, *45*, 1952. (b) Bihelovic, F.; Matovic, R.; Vulovic, B.; Saicic, R. N. *Org. Lett.* **2007**, *9*, 5063. (c) Liu, D.; Xie, F.; Zhang, W. *Tetrahedron Lett.* **2007**, *48*, 7591. (d) Mukherjee, S.; List, B. *J. Am. Chem. Soc.* **2007**, *129*, 11336. (e) Zhao, X.; Liu, D.; Xie, F.; Zhang, W. *Tetrahedron* **2009**, *65*, 512. (f) Usui, I.; Schmidt, S.; Breit, B. *Org. Lett.* **2009**, *11*, 1453. (g) Vulovic, B.; Bihelovic, F.; Matovic, R.; Saicic, R. N. *Tetrahedron* **2009**, *65*, 10485. (h) Zhao, X.; Liu, D.; Xie, F.; Liu, Y.; Zhang, W. *Org. Biomol. Chem.* **2011**, *9*, 1871. (i) Afewerki, S.; Ibrahem, I.; Rydfjord, J.; Breistein, P.; Córdova, A. *Chem. Eur. J.* **2012**, *18*, 2972. (j) Li, M.; Datta, S.; Barber, D. M.; Dixon, D. J. *Org. Lett.* **2012**, *14*, 6350. (k) Jiang, G.; List, B. *Angew. Chem. Int. Ed.* **2011**, *50*, 9471.

(6) For examples of Pd-catalyzed C-alkenylation of enamides with conservation of the nitrogen atom, see: (a) Gigant, N.; Gillaizeau, I. *Org. Lett.* **2012**, *14*, 3304. (b) Gigant, N.; Chausset-Boissarie, L.; Rey-Rodriguez, R.; Gillaizeau, I. *C. R. Chim.* **2013**, *16*, 358.

(7) For recent examples, see: (a) Kammerer, C.; Prestat, G.; Madec, D.; Poli, G. *Chem. Eur. J.* **2009**, *15*, 4224. (b) Vogel, S.; Bantreil, X.; Maitro, G.; Prestat, G.; Madec, D.; Poli, G. *Tetrahedron Lett.* **2010**, *51*, 1459. (c) Bantreil, X.; Prestat, G.; Moreno, A.; Madec, D.; Fristrup, P.; Norrby, P. O.; Pregosin, P. S.; Poli, G. *Chem. Eur. J.* **2011**, *17*, 2885. (d) Boutier, A.; Kammerer-Pentier, C.; Krause, N.; Prestat, G.; Poli, G. *Chem. Eur. J.* **2012**, *18*, 3840. (e) Giboulot, S.; Liron, F.; Prestat, G.; Wahl, B.; Sauthier, M.; Castanet, Y.; Mortreux, A.; Poli, G. *Chem. Commun.* **2012**, *48*, 5889. (f) Lorion, M. M.; Gasperini, D.; Oble, J.; Poli, L. *Org. Lett.* **2013**, *15*, 3050. (g) Rajabi, J.; Lorion, M. M.; Linh, Ly. V.; Liron, F.; Oble, J.; Prestat, G.; Poli, G. *Chem. Eur. J.* **2014**, *20*, 1539. (h) Mistico, L.; Ay, E.; Huynh, V.; Bourderioux, A.; Chaumeil, H.; Chemla, F.; Ferreira, F.; Oble, J.; Pérez-Luna, A.; Poli, G.; Prestat, G. *J. Organomet. Chem.* **2014**, *760*, 124. (i) Rigamonti, M.; Prestat, G.; Broggini, G.; Poli, G. *J. Organomet. Chem.* **2014**, *760*, 149. (j) Liron, F.; Oble, J.; Lorion, M. M.; Poli, G. *Eur. J. Org. Chem.* **2014**, in press; DOI: 10.1002/ejoc.201402049.

(8) During the redaction of this manuscript, a related study dealing with the Pd-catalyzed cyclization of N-tosyl-substituted β-enaminocarbonyl compounds with allylic bisacetates was reported, see: Yoshida, M.; Kinoshita, K.; Namba, K. *Org. Biomol. Chem.* **2014**, *12*, 2394; according to the authors, the corresponding N-benzylated substrates did not react under their reaction conditions.

(9) For reviews, see: (a) Elassar, A.-Z. A.; El-Khair, A. A. *Tetrahedron* **2003**, *59*, 8463. (b) Negri, G.; Kascheres, A. J. *J. Heterocycl. Chem.* **2004**, *41*, 461. (c) Stanovnik, B.; Steve, J. *Chem. Rev.* **2004**, 2433. (d) Ferraz, H. M. C.; Goncalo, E. R. S. *Quim. Nova* **2007**, *30*, 957. (e) Govindh, B.; Diwakar, B. S. Murthy Y. L. N. *Org. Commun.* **2012**, *5*, 105.

(10) For some selected Pd-catalyzed reactions, see: (a) Iida, H.; Yuasa, Y.; Kibayashi, C. *J. Org. Chem.* **1980**, *45*, 2938. (b) Kasahara, A.; Izumi, T.; Murakami, S.; Yanai, H.; Takatori, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 927. (c) Sakamoto, T.; Nagano, T.; Kondo, Y.; Yamanaka, H. *Synthesis* **1990**, 215. (d) Michael, J. P.; Chang, S.-F.; Wilson, C. *Tetrahedron Lett.* **1993**, *34*, 8365. (e) Koerber-Plé, K.; Massiot, G. *Synlett* **1994**, 759. (f) Chen, L.-C.; Yang, S.-C.; Wang, H.-M. *Synthesis* **1995**, 385. (g) Latham, E. J.; Stanfoth, S. P. *Chem. Commun.* **1996**, 2253. (h) Latham, E. J.; Stanfoth, S. P. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2059. (i) Blache, Y.; Sinibaldi-Troin, M.-E.; Voldoire, A.; Chavignon, O.; Gramain, J.-C.; Teulade, J.-C.; Chapat, J.-P. *J. Org. Chem.* **1997**, *62*, 8553. (j) Kirschbaum, S.; Waldmann, H. *J. Org. Chem.* **1998**, *63*, 4936. (k) Edmonson, S. D.; Mastracchio, A.; Parmee, E. R. *Org. Lett.* **2000**, *2*, 1109. (l) Yamazaki, K.; Kondo, Y. *J. Comb. Chem.* **2002**, *4*, 191. (m) Yamazaki, K.; Nakamura, Y.; Kondo, Y. *J. Org. Chem.* **2003**, *68*, 6011. (n) Sorensen, U. S.; Pombo-Villar, E. *Helv. Chim. Acta* **2004**, *87*, 82. (o) Dajka-Halász, B.; Monsieurs, K.; Eliás, O.; Károlyházy, L.; Tapolcsányi, P.; Maes, B. U. W.; Riedl, Z.; Hajós, G.; Dommisse, R. A.; Lemière, G. L. F.; Košmrlj, J.; Mátyus, P. *Tetrahedron* **2004**, *60*, 2283. (p) Gu, Z.-Y.; Zhu, T.-H.; Cao, J.-J.; Xu, X.-P.; Wang, S.-Y.; Ji, S.-J. *ACS Catal.* **2014**, *4*, 49. For some selected Cu-catalyzed reactions, see: (q) Yan, S.; Wu, H.; Wu, N.; Jiang, Y. *Synlett* **2007**, 2699. (r) Cacchi, S.; Fabrizi, G.; Filisti, E. *Org. Lett.* **2008**, *10*, 2629. (s) Bernini, R.; Fabrizi, G.; Cacchi, S. *Angew. Chem. Int. Ed.* **2009**, *48*, 8078. For Fe-catalyzed reactions, see: (t) Guan, Z.-H.; Ren, Z.-Y.; Liu, X.-Y.; Liang, Y.-M. *Chem. Commun.* **2010**, *46*, 2823. For Au-catalyzed reactions, see: (u) Arcadi, A.; Di Giuseppe, S.; Marinelli, F.; Rossi, E. *Tetrahedron: Asymmetry* **2001**, *12*, 2715. (v) Saito, A.; Konishi, T.; Hanzawa, Y. *Org. Lett.* **2010**, *12*, 372.

(11) Bromidge, S. M.; Entwistle, D. A.; Goldstein, J.; Orlek, B. S. *Synth. Commun.* **1993**, *23*, 487.

(12) In order to avoid the hydrolysis of the unreacted starting material and/or the product, the yields were determined by ^{1}H NMR spectroscopy of the crude mixture (obtained after rapid filtration on silica gel and evaporation) using 1,3,5-trimethoxybenzene as internal standard.

(13) In general, the allylated product **2a** was obtained with an average 1:1 *E*/*Z* ratio (determined by ^{1}H NMR spectroscopy of the crude mixture). This ratio is variable and can change during silica gel purification.

(14) For a recent review, see: Caddick, S.; Fitzmaurice, R. *Tetrahedron* **2009**, *65*, 3325.

(15) See Supporting Information.

(16) When the reaction was carried out without either the precatalyst/ligand system or the precatalyst, only unreacted enaminone **1a** was recovered with traces of the corresponding imino–enol tautomer **1a′** (see Supporting Information).

(17) **General Procedure**

To a suspension of $Pd(OAc)_2$ (13 mg, 0.057 mmol, 10 mol%), dppf (35 mg, 0.063 mmol, 11 mol%), and proton sponge (0.12 g, 0.57 mmol, 1 equiv) in THF (0.5 mL) in a Schlenk flask equipped with a septum, under argon atmosphere, was added allyl acetate (0.12 mL, 1.14 mmol, 2.0 equiv). After 5 min stirring, a solution of enaminone **1a** (100 mg, 0.57 mmol, 1 equiv) in THF (0.5 mL) was added, the flask was sealed, and the mixture was stirred during 1 h under microwave irradiation at 100 °C. The resulting crude was filtered on a plug of silica gel. The solvent was removed, and the mixture was purified by flash chromatography on silica gel (EtOAc–cyclohexane, 20:80) to afford 86 mg of the allylated enaminone **2a** as a mixture of *Z* and *E* isomers.

Analytical Data for Compound 2a

Yield 60%; yellow oil; *Z*/*E* ratio = 1.7:1 (analysis of the crude ^{1}H NMR spectrum showed a *Z*/*E* ratio of 1:1). IR (film): 3272, 3030, 2920, 1638 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.24 [br s, 1 H, $NH_{(Z)}$], 7.42–7.25 [m, 11 H, $=CHNH_{(E)}$ + $C\underline{H}_{Ar(Z+E)}$], 6.66 [d, J = 12.4 Hz, 1 H, $=CHNH_{(Z)}$], 5.94–5.71 [m, 2 H, $HC=CH_{2(Z+E)}$], 5.10–4.99 (m, 4 H, $HC=CH_{2(Z+E)}$], 4.43 (d, J = 5.9 Hz, 2 H, $CH_2Ph_{(E)}$], 4.39 (d, J = 6.1 Hz, 2 H, $CH_2Ph_{(Z)}$], 3.12 [dt, J = 6.0, 1.6 Hz, 2 H, $CH_2CH=CH_{2(E)}$], 2.94 [dt, J = 5.8, 1.6 Hz, 2 H, $CH_2CH=CH_{2(Z)}$], 2.22 (s, 3 H, $CH_3CO_{(E)}$], 2.13 (s, 3 H, $CH_3CO_{(Z)}$]. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.2, 194.2, 153.0, 149.5, 138.6, 138.5, 138.4, 136.0, 128.9, 128.8, 127.8, 127.6, 127.0, 126.9, 114.8, 114.6, 102.8, 52.5, 52.2, 35.6, 28.0, 27.6, 24.4. HRMS: m/z calcd for $C_{14}H_{17}NONa$ $[M + Na]^+$: 238.1208; found: 238.1204.

(18) Formation of the linear product, when using cinnamyl acetate, is a further proof of the direct C-allylation mechanism.

