Tetrahedron 65 (2009) 8769–8780

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Tetrahedron report number 888

Recent advances in the Pd-catalyzed chemical transformations of Baylis–Hillman adducts

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ARTICLE INFO

Article history:
Received 30 June 2009
Available online 16 July 2009

Keywords:
Baylis–Hillman adducts
Palladium catalyst
Heterocycles
π-Allylpalladium
Cross-coupling
Decarboxylative protonation

Contents

1. Introduction

The Baylis–Hillman reaction, which involves the coupling of activated vinylic systems with electrophiles under the catalytic influence of a tertiary amine, gives rise to adducts (Baylis–Hillman adducts) with a new stereocenter and has proven to be a very useful carbon–carbon bond-forming method in the synthesis of highly functionalized molecules.[1]

In 1963, Rauhut and Currier disclosed a patent describing a phosphine-catalyzed dimerization of activated alkenes.[2] This reaction involved a reversible phosphine conjugate addition to the

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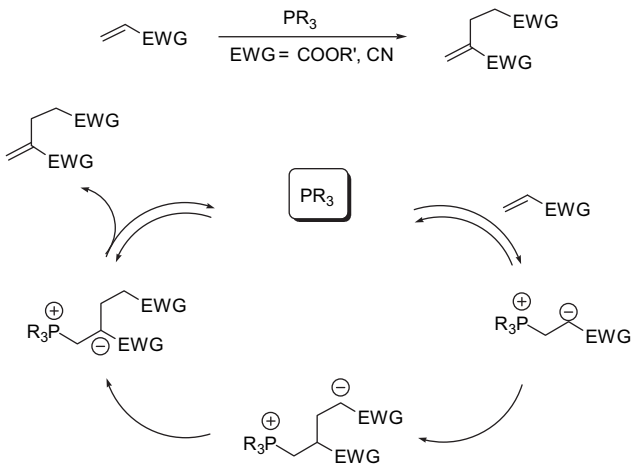
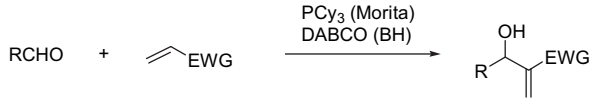
0040-4020/$ – see front matter
doi:10.1016/j.tet.2009.07.034

activated alkene, followed by a Michael reaction of the enolate with the second activated alkene. A prototropic shift followed by an elimination process forms the dimer and releases the phosphine.



The zwitterionic phosphonium Michael adducts can be trapped with other electrophiles such as aldehydes. The Rauhut–Currier dimerization of activated alkenes provided a clue to the advent of the finding of Morita.[3] The Morita–Baylis–Hillman reaction is an atom-economical coupling of an activated alkene and an aldehyde in the presence of a nucleophilic catalyst. The reaction was first discovered and reported by Morita and co-workers in 1968[3] and by Baylis and Hillman in 1972.[4] The nucleophilic catalyst employed by Morita was tricyclohexylphosphine, while Baylis and Hillman used tertiary amines such as DABCO. Activated alkenes include acrylic esters, acrylonitrile, vinyl ketones, phenyl vinyl sulfone, phenyl vinyl sulfonate, vinyl phosphonate, and acrolein.[1]



In 1983, Hoffmann and Rabe suggested the first arrow-pushing mechanism for the Baylis–Hillman reaction.[5] Later, Hill and Issacs reported a mechanism, which was accepted as the most probable mechanism for a long time.[6] Very recently, however, McQuade and co-workers suggested a new mechanism based on the reaction rate data collected in aprotic solvents.[7] They found that the rate-determining step is second order in aldehyde and first order in DABCO and acrylate. On the basis of these data, they have proposed a new mechanism involving a hemiacetal intermediate.

The Baylis–Hillman adducts have proved to be very useful multifunctional synthons for the preparation of many important cyclic and acyclic compounds.[1] There were, however, no outstanding investigations during almost two decades since the early 1970s after the initial finding of the Baylis–Hillman reaction. In the mid-1990s, the Basavaiah and Kim groups independently started extensive investigations with these useful Baylis–Hillman adducts. Later, many research groups reported further information and useful improvements in the Baylis–Hillman chemistry.[1] The number of published papers involving the Baylis–Hillman reaction has increased dramatically recently.

Palladium-catalyzed chemical transformations of modified Baylis–Hillman adducts started very recently, but have already provided many interesting results. We therefore believe that a compilation of such Pd-mediated chemical transformations of Baylis–Hillman adducts would be highly meaningful and timely.

This mini-review deals with almost all Pd-mediated syntheses involving the use of Baylis–Hillman adducts. The contents are subdivided into six sections, namely reactions involving the π-allylpalladium intermediate, synthesis of heterocyclic compounds, synthesis of carbocyclic compounds, synthesis of β-branched B–H adducts, Pd-catalyzed decarboxylative protonation and allylation, and some selected examples on the use of other transition-metal catalysts.

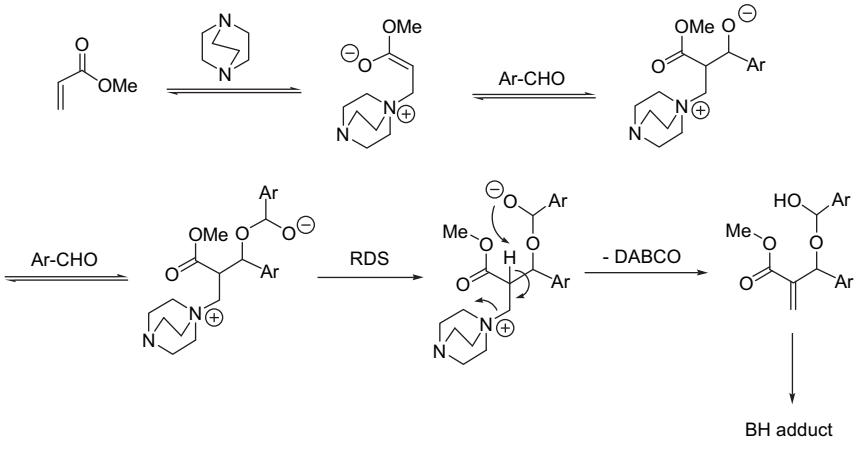
2. Use of π-allylpalladium intermediates

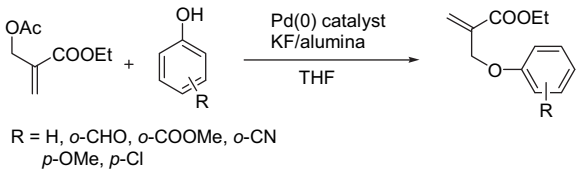
Palladium-catalyzed allylic substitution has been used in a wide variety of synthetically useful reactions involving the introduction of various oxygen and nitrogen nucleophiles. In addition, palladium-catalyzed cross-coupling reactions to form carbon–carbon bonds have been applied extensively in Baylis–Hillman chemistry. This section is divided into five subjects including the introduction of oxygen nucleophiles, introduction of nitrogen nucleophiles, cross-coupling reactions, synthesis of metal-containing Baylis–Hillman adducts, and miscellaneous reactions.

2.1. Introduction of *O*-nucleophiles

Introduction of phenols to the primary position of Baylis–Hillman acetates has been examined in the presence of a Pd(0) catalyst and/or KF/alumina.[8] In some cases, the use of one of these two reagents was sufficient to promote the OAc/OAr exchange, but, in general, faster reactions and higher yields were obtained when both reagents were used together.

Trost and co-workers used the carbonate of a Baylis–Hillman adduct for their synthesis of the key backbone of furaquinocins.[9] They introduced 2-iodoresorcinol at the secondary position of the





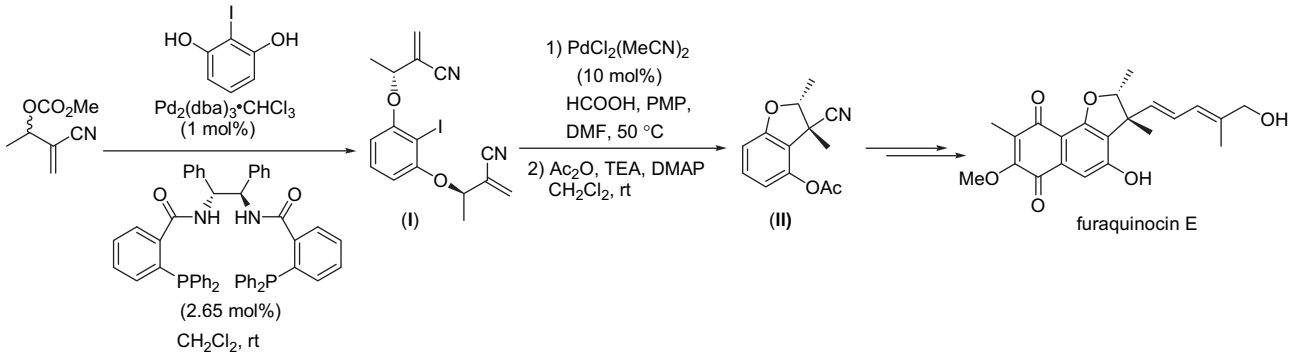
Baylis–Hillman adduct first via the π-allylpalladium intermediate and then used a Pd-mediated reductive Heck reaction strategy. A Pd-catalyzed dynamic kinetic asymmetric transformation (DYKAT) on the carbonate, derived from the Baylis–Hillman adduct, using the chiral ligand shown in Scheme 1 led to the product (**I**) in good yield with high diastereoselectivity.

Introduction of hydroxylamine derivatives as the aminoxy equivalents of nucleophiles in palladium-catalyzed additions to Baylis–Hillman acetate adducts has been reported by Reddy and co-workers.[12] The reaction afforded substituted allyloxy amines in good yields and selectivity.

Lee and co-workers have reported a Pd-catalyzed isomerization of Baylis–Hillman acetates under the catalytic influence of $Pd(OAc)_2$ into thermodynamically more stable trisubstituted alkenes.[13]

2.2. Introduction of *N*-nucleophiles

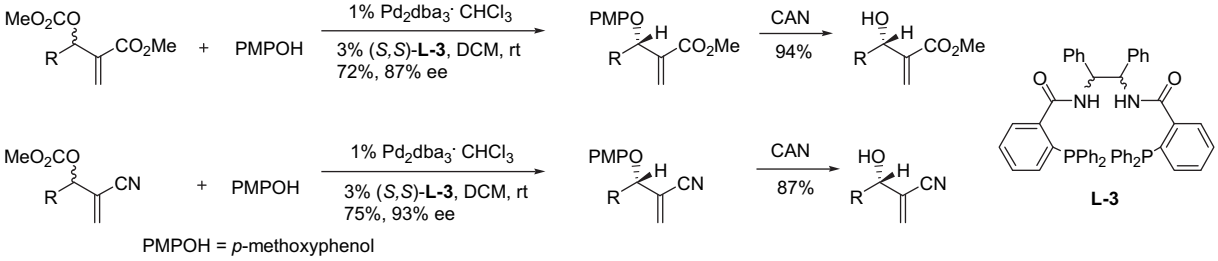
Iqbal and co-workers have reported an efficient Pd-mediated introduction of amines to Baylis–Hillman adducts via the π-allyl-



Scheme 1.

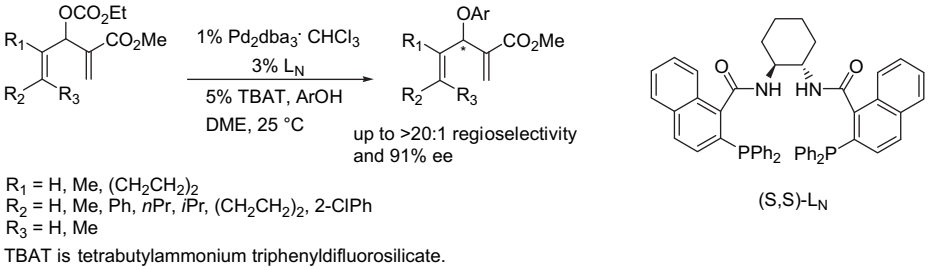
Trost and co-workers have also demonstrated a concise and highly selective deracemization of achiral Baylis–Hillman adducts using aliphatic alcohol nucleophiles.[10] They applied this novel protocol to the total synthesis of the gastrulation inhibitor, (+)-hippospongic acid A.

palladium intermediate in a regioselective manner.[14] The regioselectivity of the reaction can be controlled by temperature and the reaction medium, as shown in Table 1, to afford α-dehydro-β-amino esters. They applied this methodology to the synthesis of α-dehydro-β-amino acid-derived cyclic peptides as constrained β-turn mimics.

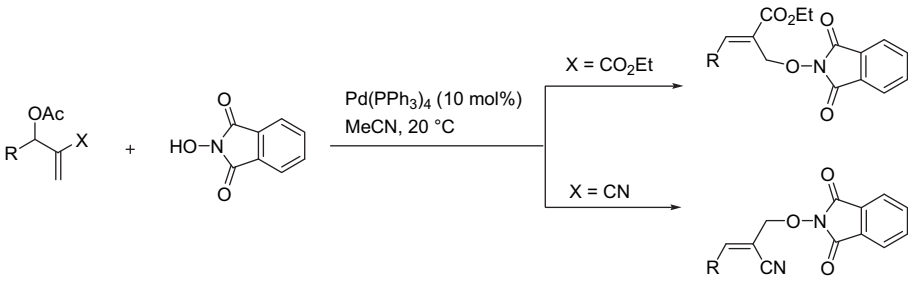


A Baylis–Hillman diene adduct has been successfully employed in a palladium-catalyzed asymmetric allylic alkylation reaction with a variety of phenols in good regio- and enantioselectivity.[11] In this paper, Trost and Brennan used bis-allylic carbonates derived from Baylis–Hillman adducts and a chiral phosphine ligand shown in Scheme 2.

Similar Pd-catalyzed asymmetric allylic aminations of Baylis–Hillman adduct-type carbonates have been reported by Hamada and co-workers involving the use of chiral diaminophosphine oxides, DIAPHOXs.[15] The corresponding chiral aza-Baylis–Hillman adducts were obtained in excellent yield with up to 99% ee, and this method could be applied to the synthesis of chiral cyclic β-amino acids.



Scheme 2.



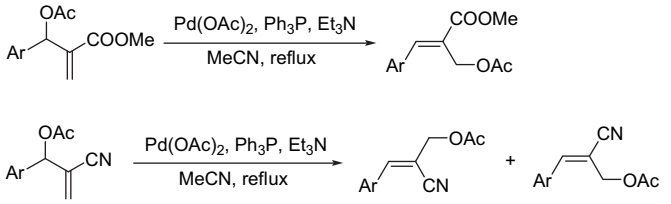
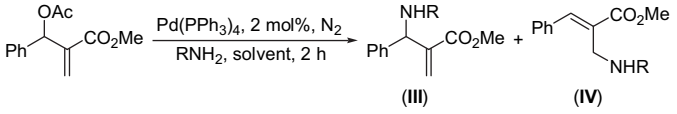


Table 1
Amination of Baylis–Hillman adducts



Entry	Amine (R)	THF, rt (conditions A)		MeCN, reflux (conditions B)	
		Ratio (**III**/**IV**)	Yield (%)	Ratio (**III**/**IV**)	Yield (%)
1	C_6H_5	3:1	65	1:8	68
2	*p*-$MeOC_6H_5$	6:1	59	1:10	61
3	*p*-MeC_6H_5	5:1	61	1:7	57
4	*p*-ClC_6H_5	3:1	56	1:10	60

Pd-catalyzed arylation, allylation, and vinylation of Baylis–Hillman adducts by cross-coupling reactions with organostannanes.[17b]

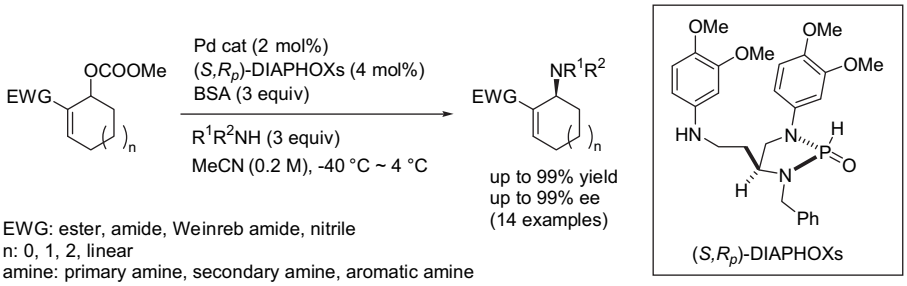
Stereoselective synthesis of trisubstituted alkenes has been carried out by Ranu and co-workers by the reaction of Baylis–Hillman acetates and triorganoindiums.[18] The addition of several trialkyl or triarylindium reagents to the acetates of Baylis–Hillman adducts proceeds readily under the catalysis of copper and palladium derivatives. The reactions of trialkylindiums are catalyzed efficiently by CuI, whereas the additions of triarylindiums produce better results with $Pd(PPh_3)_4$.

Yamamoto and co-workers have reported the synthesis of alkylidenesuccinates via the Pd-catalyzed carbonylation of Baylis–Hillman adducts.[19] The stereoselectivity for the *E* and *Z* isomers of the carbonylation products was found to differ remarkably, depending upon the three types of substrates, EWG=COOEt, SO_3Ph, and $CONMe_2$.

Shi and co-workers reported a Pd-mediated introduction of malonate at the modified Baylis–Hillman adduct.[20] In their work, malonate was introduced both at the allyl and vinyl positions. The same starting material has also been used for the Suzuki-type cross-coupling reaction with phenylboronic acid to form the diarylated product both at the allyl and vinyl positions.

2.4. Metal-attached Baylis–Hillman adducts

Kabalka and co-workers have reported the synthesis of allylboronates from Baylis–Hillman acetates and bis(pinacolato)di-



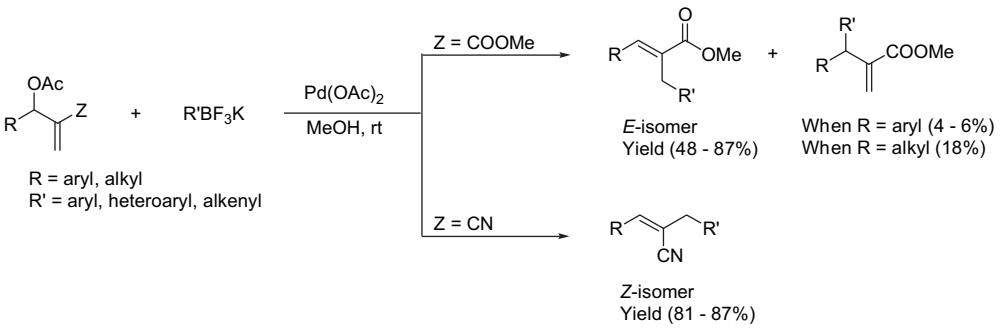
EWG: ester, amide, Weinreb amide, nitrile
n: 0, 1, 2, linear
amine: primary amine, secondary amine, aromatic amine

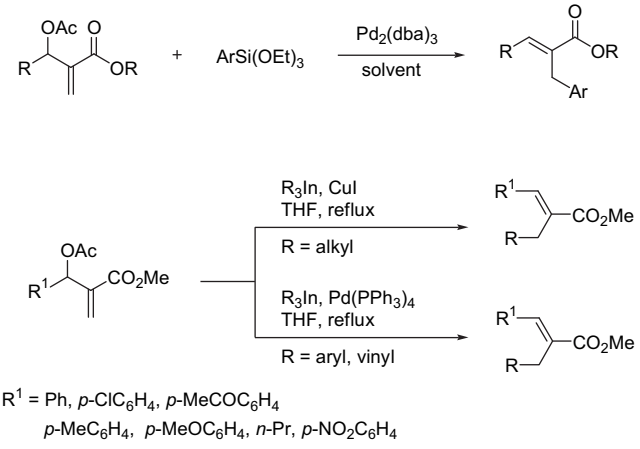
2.3. Cross-coupling reactions

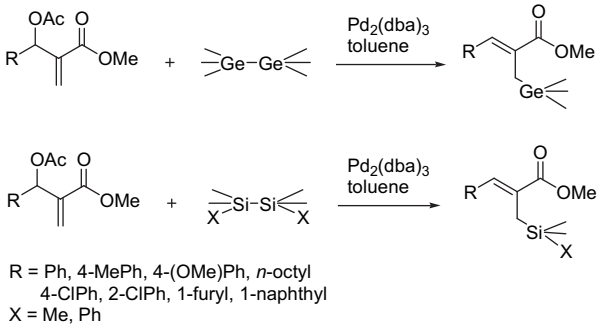
Kabalka and co-workers have developed a Pd-catalyzed cross-coupling reaction of potassium organotrifluoroborates and Baylis–Hillman acetate adducts.[16] The protocol was applicable to aryl, heteroaryl, and alkenyltrifluoroborate salts. The reaction of vinylborates was stereospecific. No additional base or ligand was required, and the reaction took place at room temperature in a straightforward fashion.

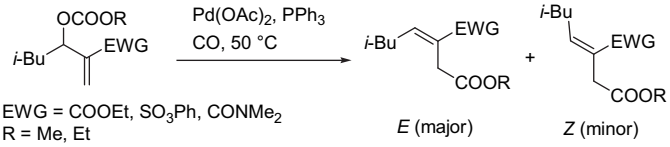
Kabalka's group has also reported an efficient Pd-catalyzed cross-coupling of Baylis–Hillman acetate adducts and organosilanes to produce aryl-substituted rearranged Baylis–Hillman adducts.[17a] Very recently, Kim and co-workers also reported boron by Pd-mediated cross-coupling.[21] These allylboronate derivatives were converted into the more stable allyltrifluoroborate salts by treatment with aqueous KHF_2. Both the allylboronate and allyltrifluoroborate derivatives react with aldehydes to afford functionalized homoallylic alcohols stereoselectively.

Kabalka's group also synthesized allylgermane and allylsilane derivatives by the Pd-mediated cross-coupling reaction between the acetates of Baylis–Hillman adducts and bimetallic reagents (Si–Si, Ge–Ge).[22] They prepared these compounds regioselectively and stereoselectively under phosphine-free conditions. Very recently, we have also reported Pd-catalyzed synthesis of cinnamyltin compounds.[17b]

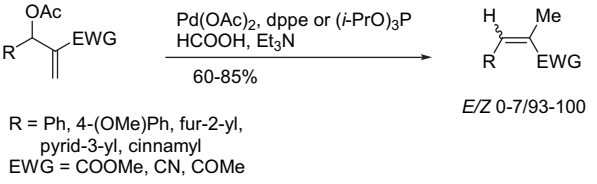


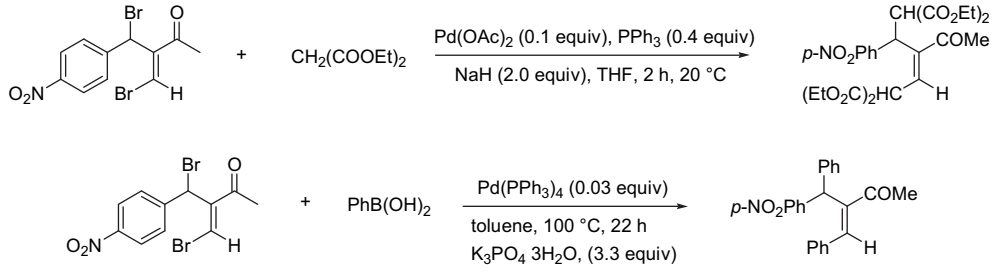


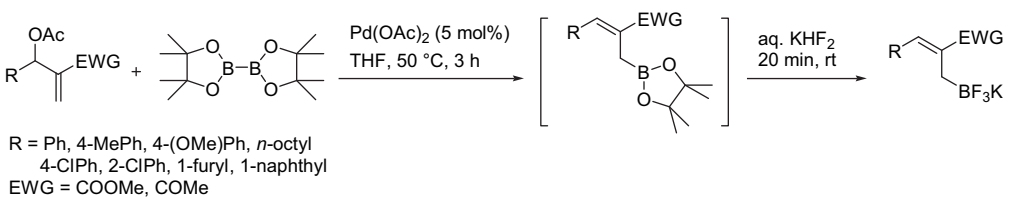




$Pd(OAc)_2/Et_3N/HCOOH$ conditions.[23] Irrespective of the EWG of the Baylis–Hillman acetate, the product was obtained in a *Z*-selective manner.





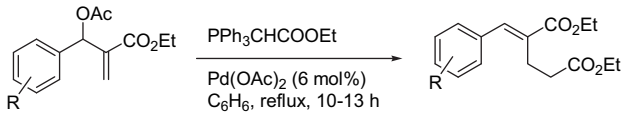


2.5. Miscellaneous

Vankar and co-workers reported the synthesis of trisubstituted alkenes from the Baylis–Hillman acetates under the influence of

A simple and efficient stereoselective synthesis of *Z*- and *E*-isomers of trisubstituted alkenes has been developed by treating the Baylis–Hillman acetates with $Pd(OAc)_2$ and the stabilized ylide, (ethoxycarbonylmethylene)triphenylphosphorane.[24a] The syntheses

of these 5-arylpent-4-enoate compounds have also been reported by Kim and co-workers without the use of a palladium catalyst.[24b] The synthesis was carried out by the preparation of a phosphonium salt from the reaction of the Baylis–Hillman acetate and the ylide, and hydrolysis with aqueous KCN.



R = H, Me, OMe, NO_2, Br

3. Synthesis of heterocyclic compounds

Pd-catalyzed chemical transformations of the Baylis–Hillman adducts have obtained great achievements in the area of heterocyclic compound synthesis. This section is categorized into three parts comprising nitrogen-containing heterocyclic compounds, oxygen-containing heterocyclic compounds, and miscellaneous examples.

3.1. Nitrogen-containing heterocyclic compounds

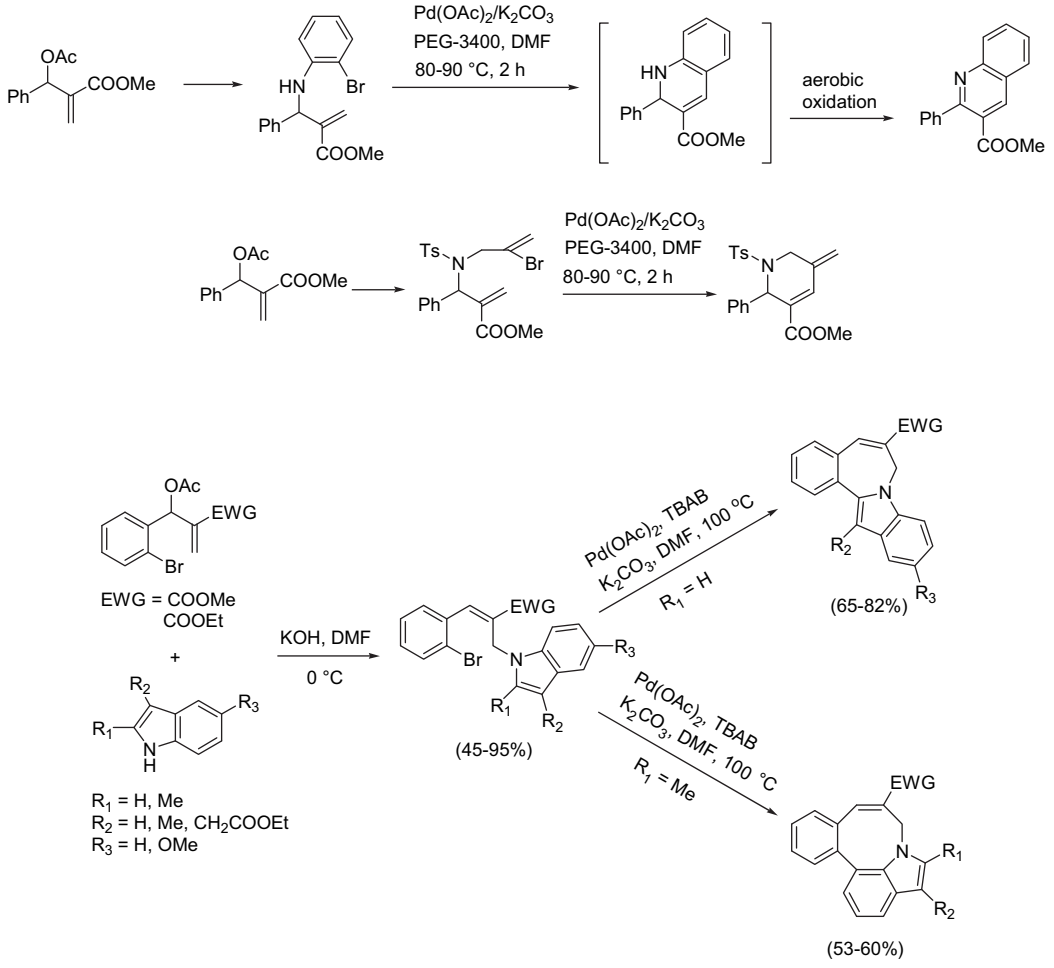
Various 2-arylquinolines and tetrahydroquinolines were synthesized from the Baylis–Hillman adducts by the Pd-catalyzed Heck-type reaction by Kim and co-workers.[25] 2-Arylquinolines were prepared from the Baylis–Hillman adduct modified with 2-bromoaniline via the Pd-mediated cyclization and concomitant aerobic oxidation mechanism. Under the same reaction conditions, the vinyl bromide derivatives produced methylene tetrahydropyridines.

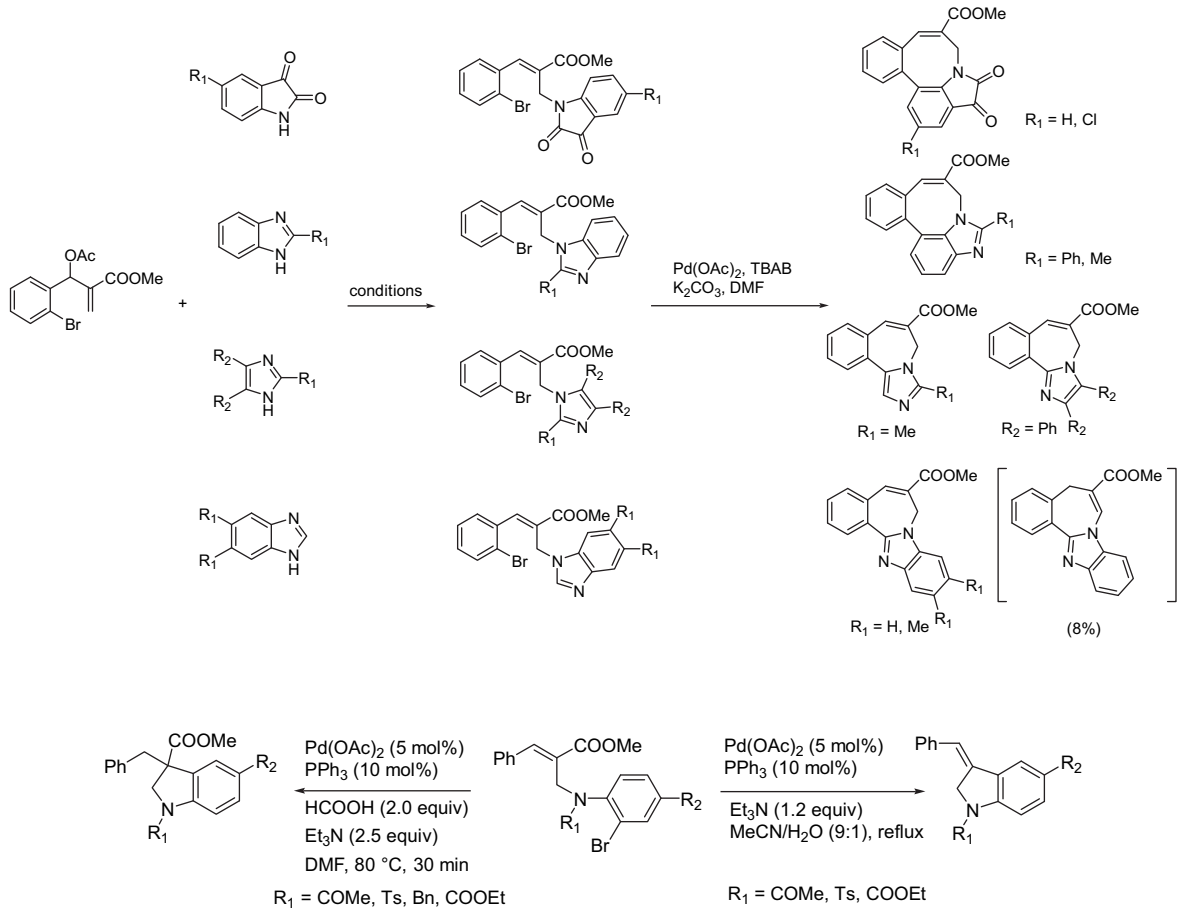
Kim and co-workers reported a novel Pd-catalyzed synthesis of 7*H*-benzo[3,4]azepino[1,2-*a*]indole-6-carboxylic acid derivatives from indole-containing Baylis–Hillman adducts.[26] Depending upon the substitution pattern of the indole moiety, seven- and eight-membered ring compounds were formed selectively. For the indole derivatives with R_1=H, the reactions produced seven-membered benzoazepino[1,2-*a*]indole derivatives in good yields (65–82%). A 2-methyl group in the indole (R_1=Me), however, rendered the formation of a seven-membered ring impossible, and aryl–aryl bond formation occurred to form the eight-membered ring compounds in moderate yields (53–60%).

In continuation of this work, Kim et al. examined the synthesis of various poly-fused heterocyclic compounds from the Baylis–Hillman adducts modified with imidazole, benzimidazole, and isatins.[27] These heterocycles were introduced at the primary position of the Baylis–Hillman adduct and subjected to Pd-mediated Heck-type reaction conditions to produce tri- and tetra-fused heterocyclic systems. The products were obtained in reasonable yields (36–71%) in a short time.

Modified Baylis–Hillman adducts having a 2-bromoaniline moiety at the primary position underwent Pd-mediated reductive Heck-type cyclization to produce dihydroindole derivatives.[28] The same starting materials can also be used for the synthesis of indole derivatives under slightly different conditions via the concomitant δ-carbon elimination and decarboxylation process.

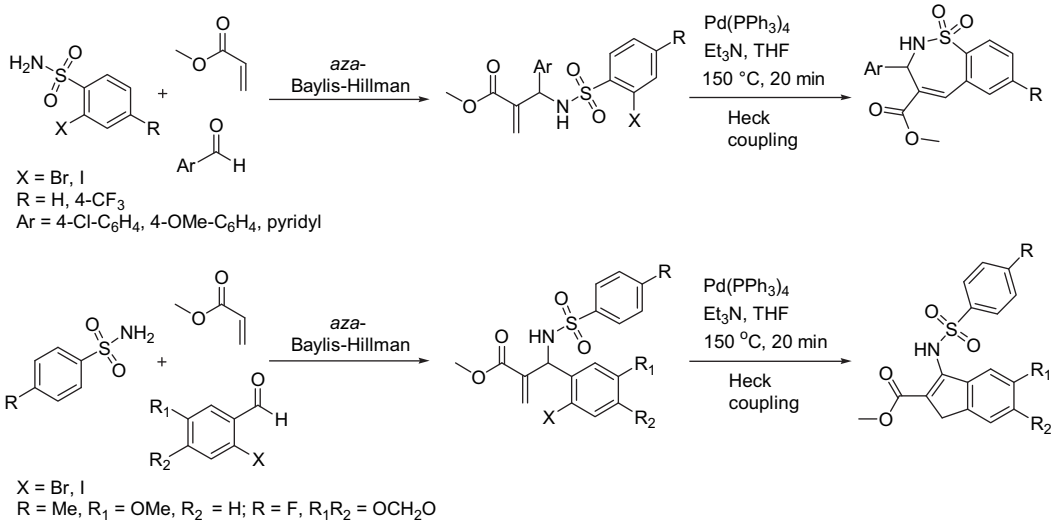
Vasudevan and co-workers have reported the synthesis of seven-membered heterocyclic compounds by using a Pd-mediated





intramolecular Heck coupling reaction of aza-Baylis–Hillman adducts having a 2-halosulfonamide moiety.[29] They also reported the synthesis of indene derivatives by using a similar protocol from the aza-Baylis–Hillman adducts derived from 2-halobenzaldehydes.

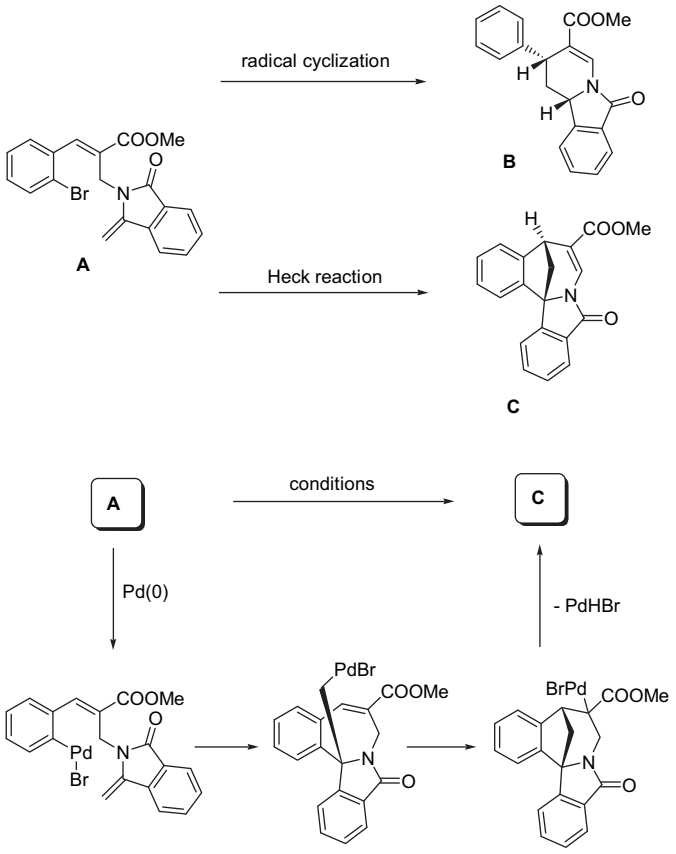
in Scheme 3. Previously, these workers also reported the synthesis of the tetrahydropyrido[2,1-*a*]isoindole derivative **B** under typical radical cyclization conditions (*n*-Bu_3SnH/AIBN) from the same starting materials.[31]



The Pd-catalyzed synthesis of a novel pentacyclic benzoazepino[2,1-*a*]isoindole **C** from the enamide of the Baylis–Hillman adduct **A** was reported by Kim and co-workers.[30] These compounds were formed via a double carbopalladation mechanism, as shown

3.2. Oxygen-containing heterocyclic compounds

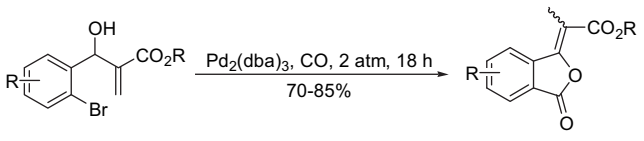
Novel 1-phenyl-1,6a-dihydro-6-oxacyclopropa[*a*]indene-1a-carboxylic acid derivatives, cyclopropane-fused dihydrobenzofurans,



Scheme 3.

were prepared starting from the Baylis–Hillman adducts modified with 2-bromophenol via the palladium-mediated domino carbopalladation involving activation of a C(sp^3)–H bond.[32] Two diastereoisomers were formed together with small amounts of the 3-benzylidene dihydrobenzofuran, which was formed via a δ-carbon elimination mechanism.[28,32]

An efficient approach for the stereoselective synthesis of 3-alkenyl phthalides was developed by Coelho and co-workers[33] involving Pd-catalyzed carbonylative cyclization of Baylis–Hillman adducts. These compounds were also synthesized directly by Kim and co-workers[34] from the Baylis–Hillman reaction between activated alkenes and 2-carboxybenzaldehyde catalyzed by 2.0 equiv of DABCO.



Very recently, Tong and co-workers reported the $Pd(OAc)_2$-catalyzed cyclization–oxidation of 1,6-enynes, which were derived from the Baylis–Hillman adducts, in the presence of $PhI(OAc)_2$, to afford multi-substituted bicyclo[3.1.0]hexanes.[35] The mechanism involved *anti*-acetoxypalladation of the Pd(II)-coordinated alkyne to afford a vinylpalladium(II) intermediate, *endo* cyclization and oxidation to a Pd(IV) intermediate with $PhI(OAc)_2$, an S_N2-type attack by the enol acetate, and final hydrolysis.

Lamaty and co-workers have developed a simple and an efficient method for the synthesis of a wide range of functionalized 3,3-disubstituted-2,3-dihydrobenzofurans via Pd-catalyzed tandem cyclization/Suzuki cross-coupling.[36]

3.3. Miscellaneous

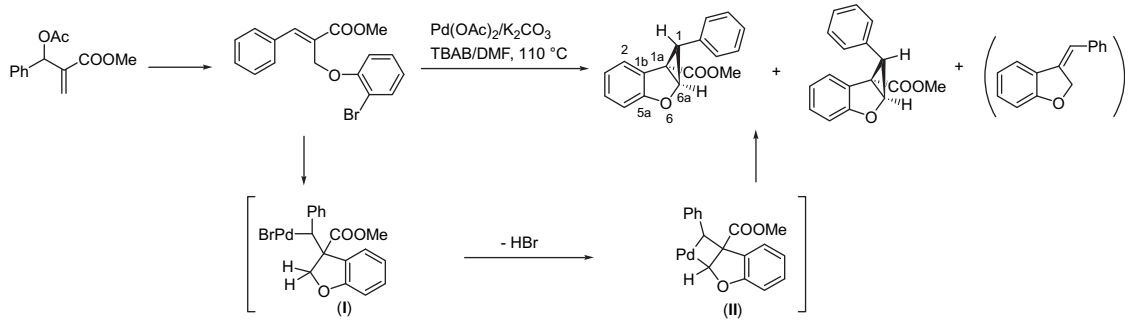
Regioselective functionalization of the *ortho*-position at the aryl moiety of poly-substituted pyridines by using $Pd(OAc)_2$/Oxone in PEG-3400 was reported by Kim and co-workers.[37] The starting materials, poly-substituted pyridines, were also prepared by the same group from the Baylis–Hillman adducts via a [3+2+1] annulation protocol.[38] Oxidative insertion of Pd(0) into the weak *O–O* bond of Oxone was proposed as a plausible mechanism.

4. Synthesis of carbocyclic compounds

Although various types of carbocyclic compounds could be efficiently produced from the Baylis–Hillman adducts by using the Pd-catalyzed chemical transformations, this potential has not been realized until recently. Lee and co-workers reported the synthesis of indanones via an intramolecular Heck reaction of Baylis–Hillman adducts of 2-iodobenzaldehyde.[39]

2-Carbonyl-1-indanols were synthesized in moderate-to-good yields by the reaction of *ortho*-halogenated aryl aldehydes with Baylis–Hillman adducts via a one-pot, palladium-catalyzed tandem Heck–aldol reaction.[40]

Krische and co-workers demonstrated the feasibility of nucleophilic catalysis as a means of enolate generation in metal-catalyzed cross-coupling, as evidenced by the development of a catalytic enone cycloaddition methodology.[41] The transformation

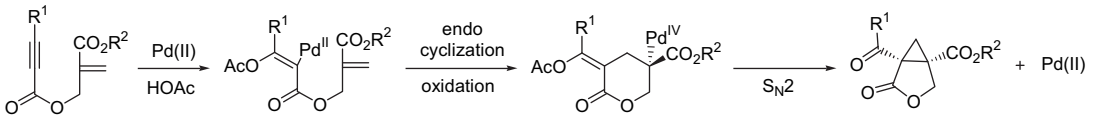


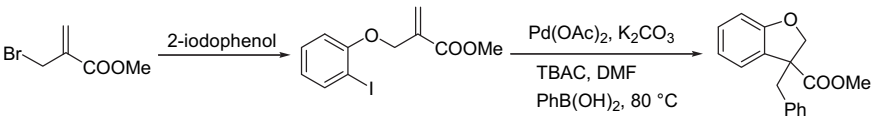
was carried out through the use of a two-component catalyst system that unites the nucleophilic features of the Baylis–Hillman reaction with the electrophilic features of the Trost–Tsuji reaction.

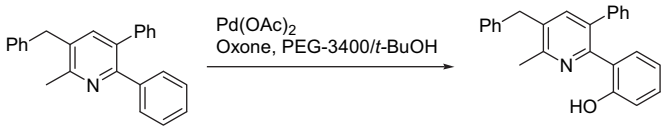
Various naphthalenes and spiro dihydronaphthalenes were prepared by a Pd-catalyzed, one-pot reaction involving consecutive allylation and arylation reactions from Baylis–Hillman acetates and activated methylene compounds.[42]

5. Synthesis of β-branched B–H adducts

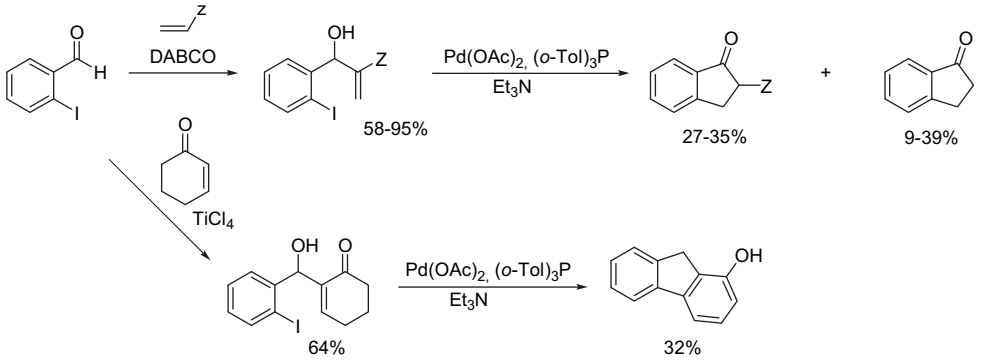
The synthesis of β-branched Baylis–Hillman adducts has remained unsolved, although a few approaches have been reported.

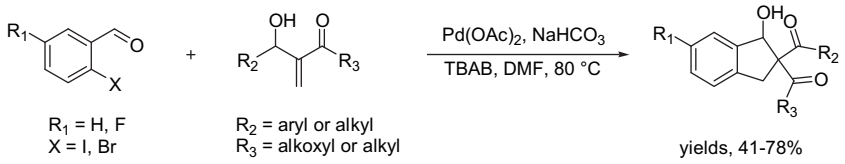


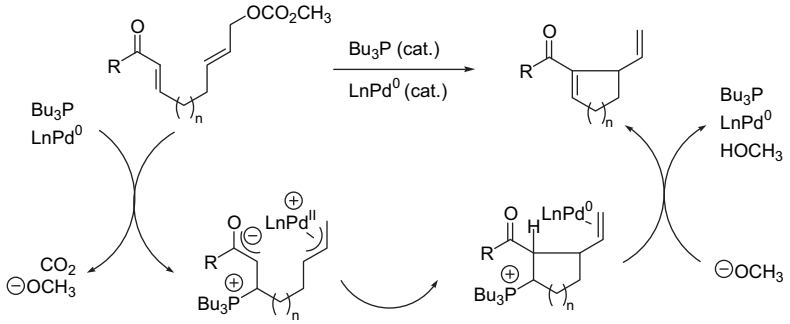


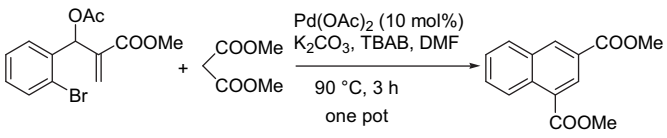


In this context, synthetic efforts have been focused on β-aryl Baylis–Hillman adducts via Pd-mediated Heck-type approaches. Unfortunately, the benzyl-substituted β-keto ester was the major product, although this compound is another product, which could be formed via the Heck reaction mechanism.[43]

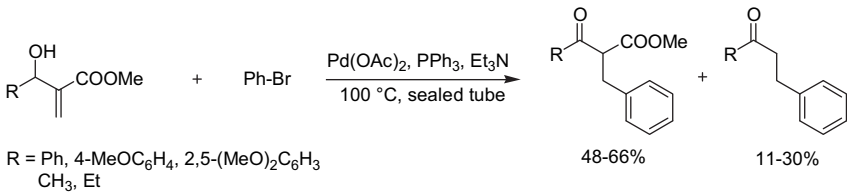


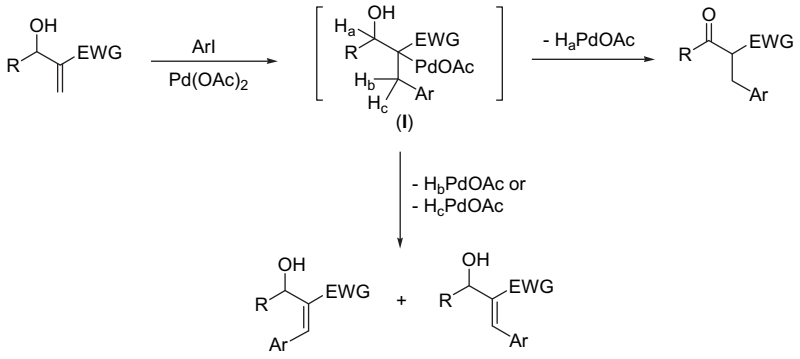




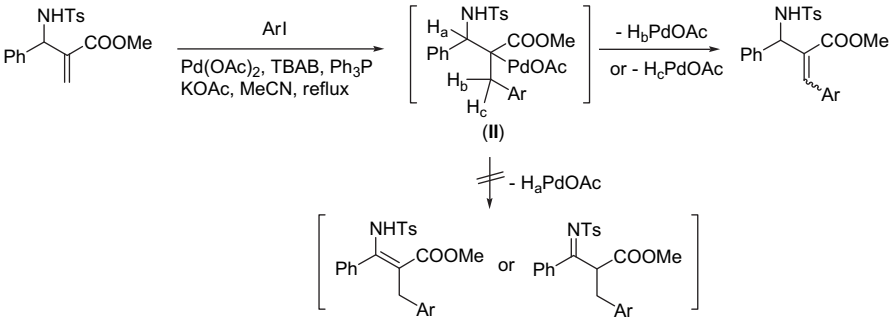


Very recently, the successful synthesis of β-aryl-substituted Baylis–Hillman adducts has been reported by Kim and co-workers by an intermolecular Heck reaction between the Baylis–Hillman adducts and aryl iodides under the conditions of $Pd(OAc)_2$/*n*-Bu_4NBr/KOAc in MeCN in good-to-moderate yields.[44a]





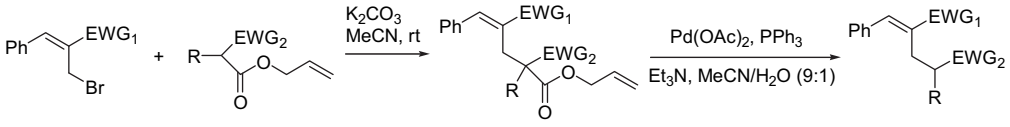
In addition, they also applied their conditions to *N*-tosyl aza-Baylis–Hillman adducts and obtained the corresponding β-aryl-substituted derivatives in moderate yields as an *E/Z* mixture.[44b]



6. Pd-catalyzed decarboxylative protonation and allylation

Recently, Kim and co-workers reported the synthesis of 1,5-dicarbonyl and related compounds from the Baylis–Hillman adducts via the Pd-catalyzed decarboxylative protonation protocol.[45a] The required starting materials were synthesized by an S_N2 reaction between the cinnamyl bromide and active methylene compounds having an allyl ester moiety. These compounds were transformed into the products under Pd-mediated decarboxylative protonation conditions in aqueous MeCN. Later, these workers showed that the 1,5-dicarbonyl compounds could also be prepared via decarboxylative protonation catalyzed by K_2PtCl_4 or a Grubbs' catalyst.[45b]

Kim and co-workers reported an efficient method for the synthesis of 2,5-dihydrofurans and 2,5-dihydropyrroles from suitably modified Baylis–Hillman adducts via a ruthenium-catalyzed RCM (ring-closing metathesis) reaction.[46] Adolfsson and Balan also reported the synthesis of 2,5-dihydropyrroles independently by using the same RCM protocol.[47]

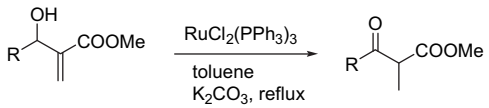


7. Use of other transition-metal catalysts

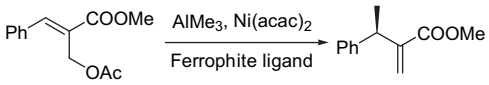
Chemical transformations of Baylis–Hillman adducts catalyzed by palladium metal have achieved significant advances recently. On the contrary, the use of other transition-metal catalysts has been relatively unexplored until now.

The $RuCl_2(PPh_3)_3$-catalyzed isomerization of the Baylis–Hillman adducts, methyl 3-aryl-3-hydroxy-2-methylenepropanoates, to methyl 3-aryl-2-methyl-3-oxopropanoates has been reported by Basavaiah and Muthukumaran.[48]

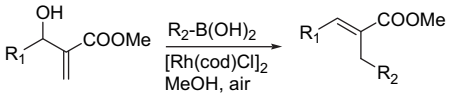
Nickel-catalyzed methylation of primary Baylis–Hillman acetates via a π-allylnickel intermediate has been reported.[49] The enantioselectivities realized are significant (49–94% ee) and partial



control of the regiochemistry of the addition can be attained through the ligand (up to α/γ=0.16).



Genet and co-workers have reported an efficient synthesis of trisubstituted alkenes from the reaction of the Baylis–Hillman adducts and arylboronic acids[50a] or potassium trifluoro(organo)borates[50b] in the presence of a rhodium catalyst. Later, Kantam and co-workers used a rhodium fluorapatite catalyst for the synthesis of the same compounds under very similar conditions.[51]



We have included only a limited number of papers involving the use of other transition-metal catalysts, although there have been published many interesting results using metal catalysts.[52] The use of other metal catalysts is, however, somewhat limited, compared to the use of palladium catalysts in the chemical transformations of Baylis–Hillman adducts.

8. Conclusions

As this mini-review illustrates, chemical transformations of the Baylis–Hillman adducts can provide a variety of important substances. Many kinds of orthodox reactions like Friedel–Crafts reactions, substitution reactions (S_N2 and S_N2'), conjugate additions, S_NAr reactions, radical cyclizations, and condensation reactions have been used successfully during the last two decades.[1] Palladium-catalyzed chemical transformation is, however, in its infancy. Based on the high potential of palladium chemistry, Pd-catalyzed chemical transformations of the Baylis–Hillman adducts are likely to provide some very interesting substances in the future.

Acknowledgements

J. N. Kim wishes to thank his previous and present members, Dr. H. J. Lee, Dr. K. Y. Lee, Dr. S. Gowrisankar, J. S. Son, K. S. Jung, M. R. Seong, H. N. Song, H. S. Kim, T. Y. Kim, Y. M. Chung, J. H. Gong, Y. J. Im, J. M. Kim, C. G. Lee, J. E. Na, M. J. Lee, S. C. Kim, D. Y. Park, S. J. Kim, H. S. Lee, S. H. Kim, J. M. Kim, H. S. Kim, K. H. Kim, S. H. Kim, and E. S. Kim.

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Jae Nyoung Kim was born in 1960 in Seoul, Korea. He received his B.S. degree from Seoul National University in 1984, his M.S. in 1986 and Ph.D in 1992 from Korea Advanced Institute of Science and Technology. After spending 10 years as a senior research scientist at Korea Research Institute of Chemical Technology (1984–1994), he joined Chonnam National University as an assistant professor of organic chemistry in 1995. Currently, he is a full professor of organic chemistry at the same university. He received *Tetrahedron* Most Cited Paper 2003–2006 Award with *Tetrahedron* **2003**, *59*, 385–390, *Tetrahedron* Most Cited Paper 2005–2008 Award with *Tetrahedron* **2005**, *61*, 1493–1499, *Tetrahedron Letters* Most Cited Paper 2003–2006 Award with *Tetrahedron Lett*. **2003**, *44*, 6737–6740, and *Tetrahedron Letters* Most Cited Paper 2005–2008 Award with *Tetrahedron Lett*. **2005**, *46*, 4859–4863. He is a recipient of the Award for the Advancement of Science (2000) from Korean Chemical Society. He is a recipient of the Award for Excellent Research Paper (2006) from Korean Chemical Society. He is a recipient of the Great Yong-Bong Academic Award (2006) from Chonnam National University. His current research interests are mainly focused on the chemical transformations of Baylis–Hillman adducts by using metal catalysts.

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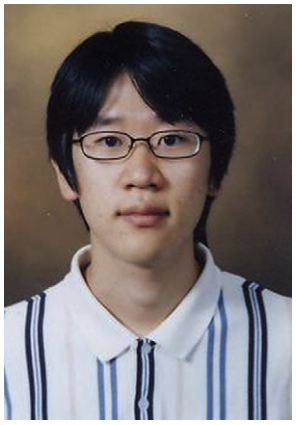

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