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Conceptual Influence of the Baylis-Hillman Reaction on Recent Trends in Organic Synthesis

Deevi Basavaiah* and Bharat Chandra Sahu

Abstract: This mini review describes our endeavors for the last 28 years in understanding and developing the Baylis-Hillman reaction as an useful and powerful tool in synthetic chemistry. We have also mentioned briefly how we initiated the research program in this area.

Keywords: Activated alkenes · Atom economy · Baylis-Hillman reaction · Organocatalysis · Proximal functional molecules

Deevi Basavaiah was born in 1950 in Valiveru (a village near Tenali), India. He obtained his BSc degree from Andhra University (India) in 1970 and a MSc (Organic Chemistry) degree from the Banaras Hindu University (BHU) (India) in 1972. He received the BHU Gold Medal for obtaining First Rank in the M.Sc examinations. Afterwards he obtained his PhD degree from BHU in the year 1979, working under the supervision of Professor Gurbakhsh Singh. Subsequently he worked as a post-doctoral fellow in the research group of Professor Herbert C. Brown at Purdue University (August 1980 to November 1983), USA. After returning to India, he worked as Scientist C for a few months (January to June 1984) at the National Chemical Laboratory, Pune. Afterwards he joined the School of Chemistry, University of Hyderabad, Hyderabad in June 1984 where he is currently a Professor. He has been teaching organic chemistry to MSc students for the past 28 years at the University of Hyderabad. Since 1984, he has been working on various aspects of the Baylis-Hillman reaction with the main objective of developing this reaction into a useful and powerful tool in synthetic chemistry. He has, in fact, made, fundamental, original and outstanding contributions in this direction.

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1. Introduction

During the last century, particularly after the famous discovery of the Diels-Alder reaction, organic synthesis has indeed undergone high levels of changes, not only in terms of the development of new concepts and reactions but also in introducing novel reagents leading to the evolution of new trends in the domain of organic chemistry in general and in the area of organic synthesis in particular.[1a,b] The present day trends with ever-increasing demands in organic synthesis emphasize the need for the continuous generation of strategies based on the concepts of i) atom-economy,[2a] ii) organocatalysis,[2b] iii) performing the reactions at carbon(s) containing less activated hydrogen(s),[2c] iv) easy construction of C–C bonds leading to the production of molecules having several (different) functional groups in proximity facilitating further introduction of carbon framework,[2d] v) opportunities to perform asymmetric synthesis,[2e] vi) provision to develop intramolecular and its asymmetric versions[2f] and vii) one-pot reaction[2g] (pictorially presented in Fig 1). It is gratifying to note that all the above-mentioned seven unique features are reasonably and meticulously well embodied in the Baylis-Hillman reaction (also known as the Morita-Baylis-Hillman reaction) (Scheme 1).[3]

We have been working for the past twenty eight years towards understanding the Baylis-Hillman reaction, its applications, scope, and influence on modern trends in synthetic chemistry. This brief review will present mainly our contributions (our vision, experience, and endeavors) for the development of the Baylis-Hillman reaction while giving credit to the important contributions from other workers. We also thought it will be useful and appropriate to start from the point from where we originated the idea of working on this reaction and then highlight our efforts in developing this reaction into a powerful and useful synthetic tool for construction of carbon framework.

2. Where and How We Started

Permit me (DB) to start the story from the very beginning. During the time (1970–1972) of my post-graduation (M.Sc.) at Banaras Hindu University (BHU) I was impressed by the concepts and high magnitude of applications of the Diels-Alder reaction in organic synthesis. This single reaction had, indeed, exhibited a great impact on my thinking about organic chemistry in general and synthetic chemistry in particular. We had the opportunity of having excellent teachers during that time; Professor Gurbakhsh Singh (who did his Ph.D. at Harvard with Professor R. B. Woodward) taught the basic principles of organic synthesis in a highly inspiring way. From his teaching it became quite

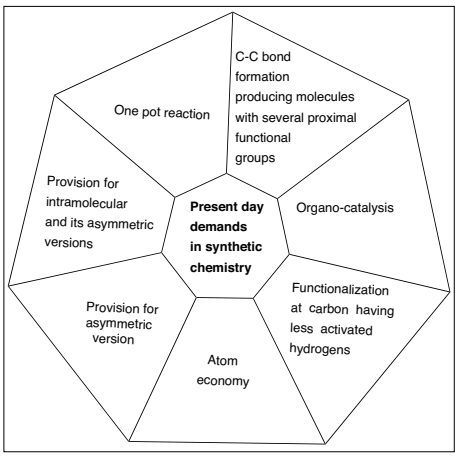
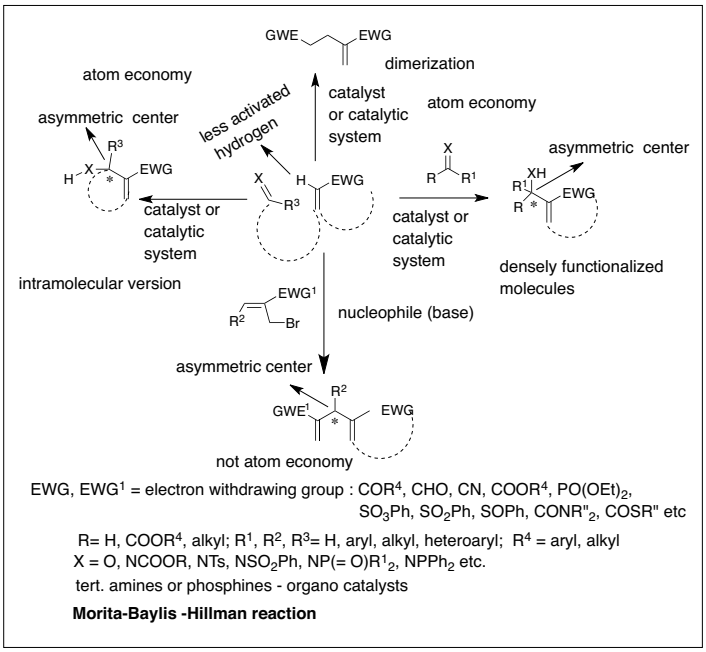


Fig. 1. Organic synthesis: The present day demands.



Scheme 1.

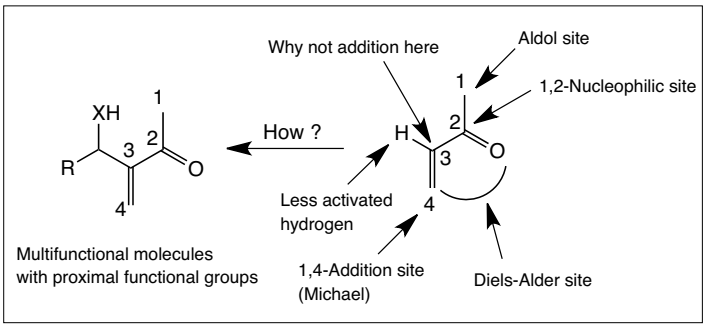
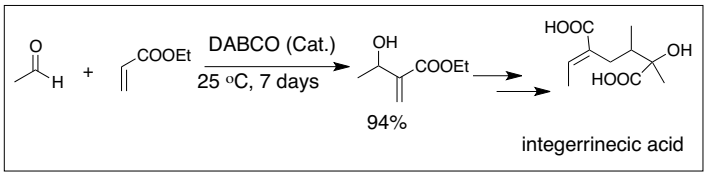
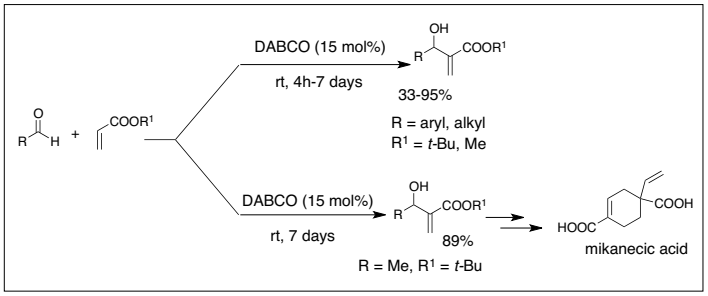


Fig. 2. Versatile synthetic applications of MVK.



Scheme 2.



Scheme 3.

evident that there was a need to discover many more new reactions like the Diels-Alder reaction and also to develop new synthetic strategies. It was also very clear to us from his thought-provoking lectures that discovering and developing new useful organic reaction(s) will not only be extremely difficult but also will be the most challenging research endeavors that need several years of hard work and dedicated efforts. I was also attracted by the high reactivity and versatility [(aldol reaction[4a] at C(1); 1,2-addition[4b] at C(2); Michael reaction[4c] at C(4); and as diene for Diels-Alder reaction[4d]] of methyl vinyl ketone (MVK) (Fig. 2). At that time I used to think why the addition reaction cannot be done at C(3) of MVK as shown in Scheme 1. I asked Professor Gurbakhsh Singh one day the same question after his lecture. He appreciated my question and told that this aspect had not been studied till then in the literature and it would, in fact, be a challenging and useful endeavor. It was indeed a very interesting answer to me.

Inspired by his excellent teaching lectures I joined the research group of Professor Gurbakhsh Singh for the Ph.D. program at BHU. I had also the opportunity of having excellent senior colleagues. On the advice of some of them I developed the habit of looking into the patents in Chemical Abstracts in order to generate new ideas in research work. It was during that time I came across an inspiring patent by Baylis and Hillman (which I noted in my research note book) in 1972.[5] This patent describes an amine-catalyzed coupling reaction between the α-position of acrylates / acrylonitrile/ methyl vinyl ketone/ acrylamide with aldehydes providing multifunctional molecules. In fact, this patent had a tremendous impact on my research career. I became interested in this patent from that time onwards and started keeping track of any research work in the literature on the basis of this patent. I obtained my Ph.D. degree for thesis work entitled *'Total synthesis of cladosporin a new antifungal metabolite'* in 1979. Subsequently, I worked in the research group of Professor Herbert C. Brown at Purdue University for three years, that is, during 1980–1983 as a postdoctoral fellow.

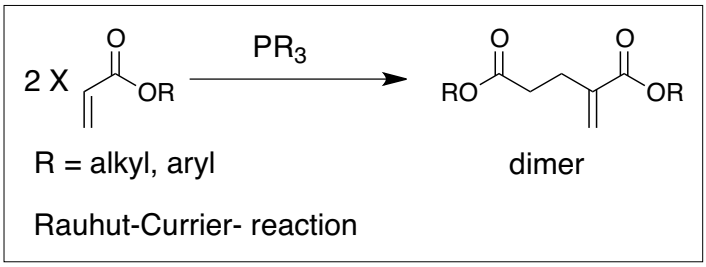
It was interesting to note that there was no literature report on this patent for almost a decade (during 1972–1981). During my postdoctoral tenure at Purdue University I saw the first paper on the application of patents of Baylis-Hillman[5] in 1982 by Drewes and Emslie from South Africa. They performed the reaction between ethyl acrylate and acetaldehyde in the presence of DABCO as a catalyst to provide the corresponding adduct which was subsequently converted into integerrinecic acid (Scheme 2).[6]

In the next year (1983), there were two interesting publications by Hoffmann and Rabe (from Germany) describing the coupling of methyl and *tert.* butyl acrylates with aldehydes.[7a] The adduct thus obtained *via* the reaction of acetaldehyde with *tert.* butyl acrylate was used efficiently for synthesis of mikanecic acid as shown in Scheme 3.[7b]

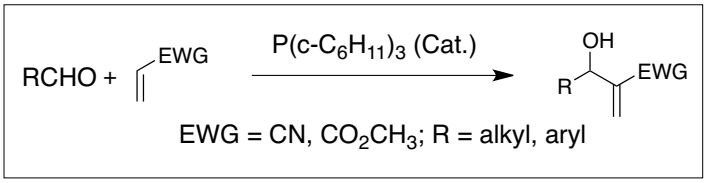
3. Our Vision and Contributions

When I joined the University of Hyderabad in June 1984, there was no further information available in the literature on the application of this patent. We envisioned at that time that this reaction would not only have a great potential in the synthetic and mechanistic domain but also offer challenging opportunities to create new directions in organic chemistry in the years to come. With this objective in mind, we looked into the literature carefully. We noticed that Rauhut and Currier reported in 1963 an interesting trialkylphosphine-catalyzed dimerization of alkyl acrylates to produce dialkyl 2-methyleneglutarate derivatives (Scheme 4).[8a]

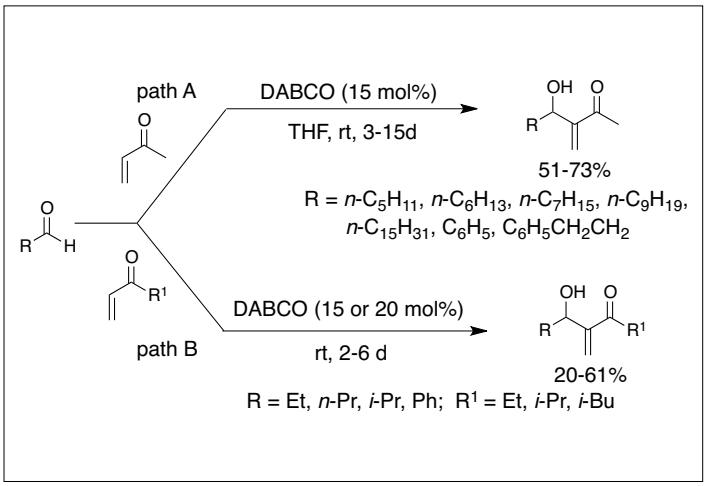
In 1968 Morita and coworkers described a coupling reaction of aldehydes with acrylates or acrylonitrile using tricyclohexylphosphine as a catalyst to provide 2-methylene-3-hydroxyalkanoates (or alkanenitriles) (Scheme 5).[8b,c]



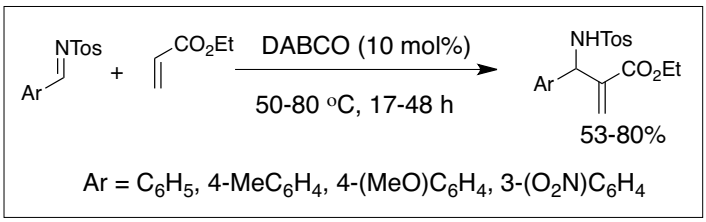
Scheme 4.



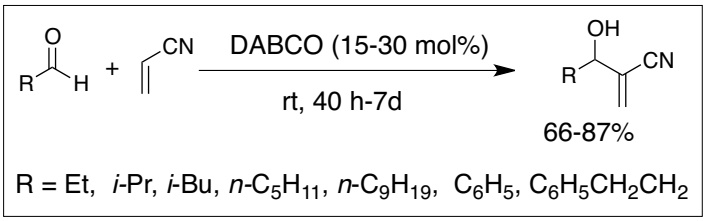
Scheme 5.



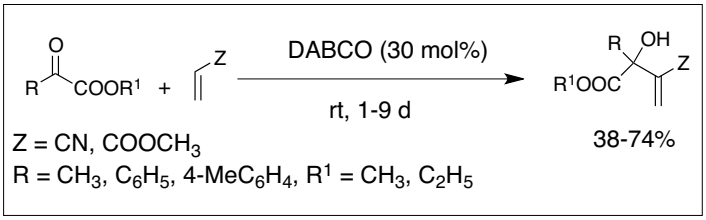
Scheme 6.



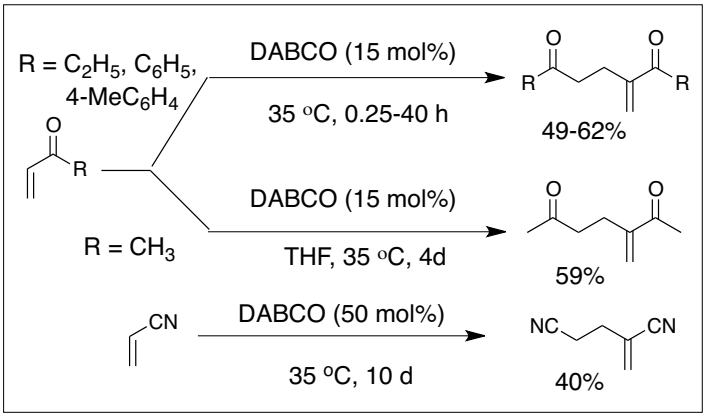
Scheme 7.



Scheme 8.



Scheme 9.



Scheme 10.

With the above-mentioned information we initiated a major long-term research program in 1984 towards understanding and expanding the potential and scope of this reaction. In fact we have been working for the past 28 years and contributed significantly to the growth of this reaction. We first examined the applicability of methyl vinyl ketone (MVK) as a substrate for coupling with aldehydes under the catalytic influence of DABCO. We were pleased to see that this coupling worked well and the desired adducts were obtained in reasonably good yields (Scheme 6: Path A).[9] Encouraged by these results we extended this methodology to other activated alkenes (Scheme 6: Path B).[10]

While we were working in this direction an interesting paper appeared in 1984 by Perlmutter and Teo on the application of aldimine derivatives as electrophiles for coupling with acrylates to produce allyl amine derivatives (Scheme 7).[11]

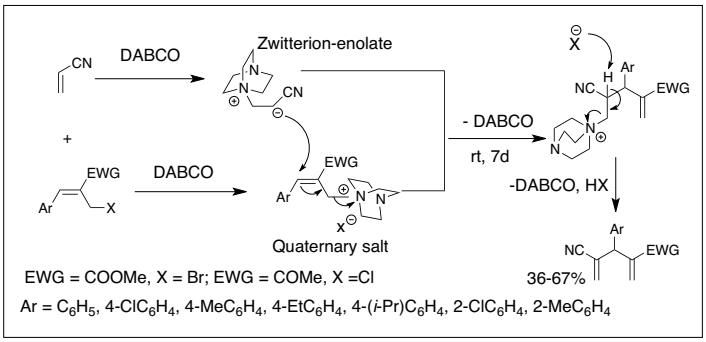
We have next successfully used acrylonitrile as an activated alkene for coupling with aldehydes in the presence of DABCO as a catalyst to provide 2-(hydroxyalkyl) acrylonitriles in good yields (Scheme 8).[12] About the same time (before our publication) Amri and co-workers reported a facile coupling of acrylonitrile as activated alkene with aldehydes in the presence of DABCO.[13]

We noticed that α-keto esters couple comfortably with methyl acrylate as well as with acrylonitrile as activated alkenes to produce the corresponding densely functionalized *tertiary* allyl alcohols (Scheme 9).[14]

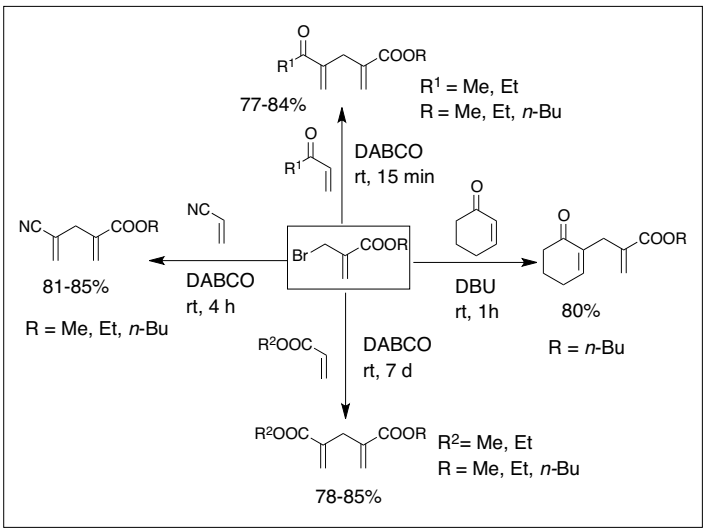
We subsequently observed a remarkable dimerization of alkyl vinyl ketones, in the presence of DABCO as a catalyst, in a Michael type-fashion producing 2-methylidene-1,5-diketones (Scheme 10).[15] Under similar conditions MVK dimerizes to yield 3-methylideneheptane-2,6-dione while acrylonitrile provides 2,4-dicyanobut-1-ene (Scheme 10).[15]

We have for the first time utilized the Baylis-Hillman bromides as electrophiles for the reaction with activated alkenes in the presence of DABCO thus providing simple and convenient protocols for the synthesis of functionalized 1,4-pentadiene derivatives (Schemes 11 and 12).[16,17]

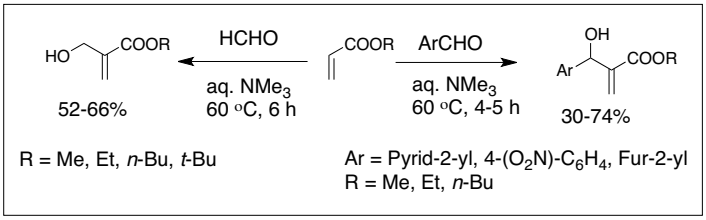
Our research group has also successfully employed trimethyl amine (tertiary amine containing the minimum number of carbons) as a promoter for the BH reaction. Thus trimethyl amine mediates the coupling of aldehydes with acrylates in aqueous media to provide the desired adducts (Scheme 13).[18] Under similar conditions cyclohex-2-enone dimerizes to produce the corresponding Michael-type



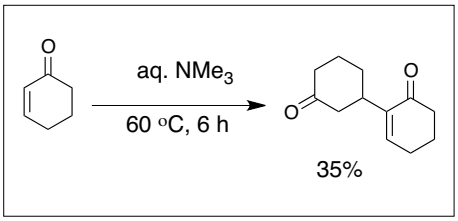
Scheme 11.



Scheme 12.



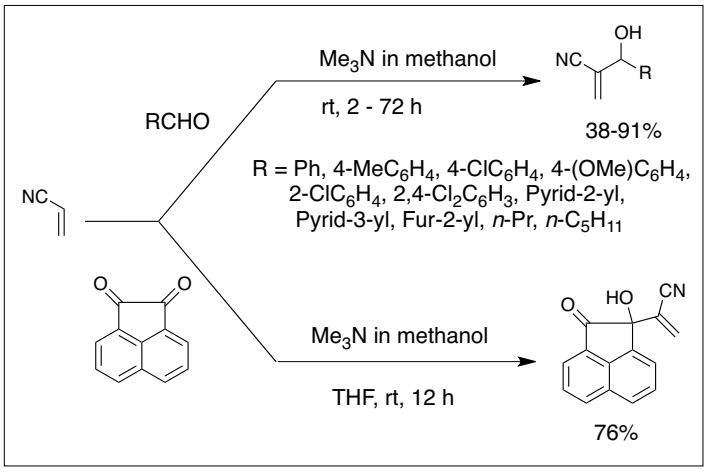
Scheme 13.



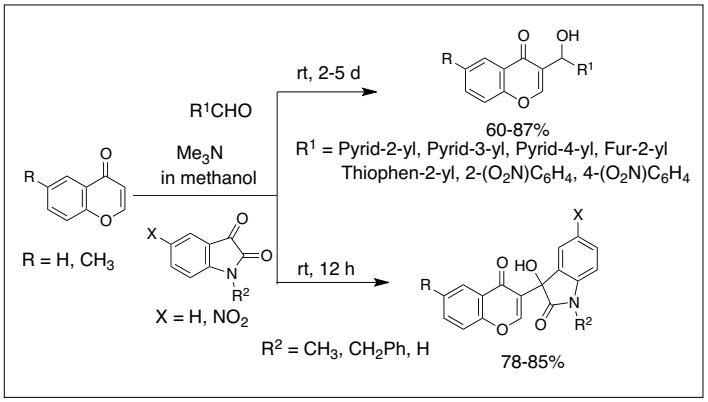
Scheme 14.

dimer (Scheme 14).[18] Similarly acrylonitrile reacts with aldehydes (and also with 1,2-diones) under the influence of trimethyl amine in methanolic medium to furnish the required allyl alcohols (Scheme 15).[19]

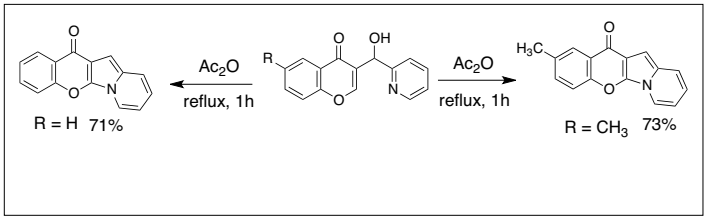
We have also comfortably utilized 1-benzopyran-4(4H)-ones as activated alkenes for coupling with various reactive electrophiles using aqueous trimethylamine as a promoter. Two such Baylis-Hillman adducts derived from pyridine-2-carboxaldehyde were conveniently transformed into fused indolizine-benzopyrans in high yields (Schemes 16 and 17).[20]



Scheme 15.



Scheme 16.



Scheme 17.

3. Chalcogeno-Baylis-Hillman Reaction

Kataoka and co-workers reported an elegant coupling of activated alkenes with electrophiles under the catalytic influence of chalcogenides in the presence of $TiCl_4$ to produce the corresponding adducts in high yields (one representative example is presented in Scheme 19).[21a–c]

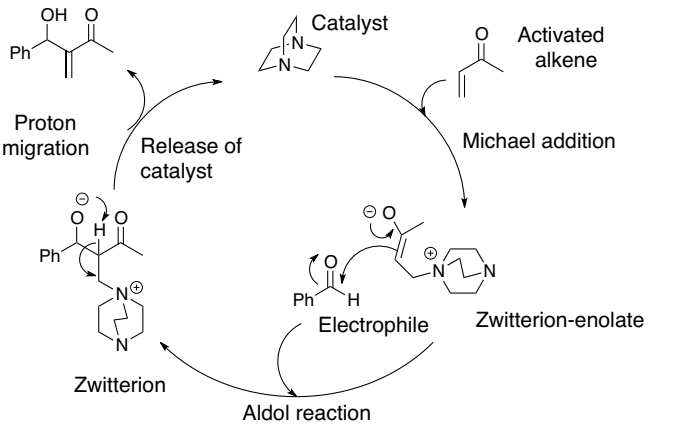
This report has prompted us to examine the reaction between α-keto esters and alkyl vinyl ketone under the influence of Me_2S as a catalyst in the presence of $TiCl_4$. The resulting adducts were obtained in good yields (Scheme 20).[22]

3.1 *Generally Accepted Mechanism*

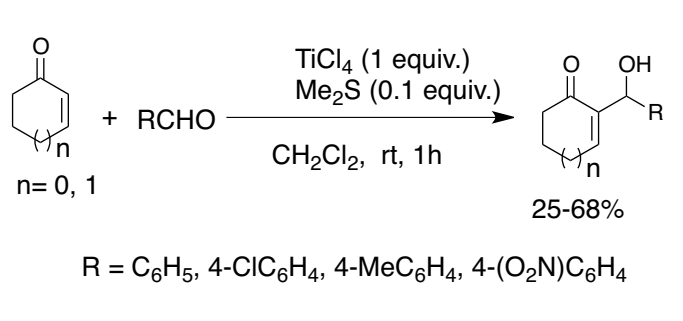
The generally accepted mechanism involves the Michael addition of catalyst to activated alkene generating the zwitterionic enolate which then adds on to the electrophile in aldol fashion to provide multi-functional molecules after release of the catalyst. A model case is presented in Scheme 18 taking the reaction between MVK and benzaldehyde using DABCO as a catalyst.[3]

5. $TiCl_4$-mediated Baylis-Hillman Reactions

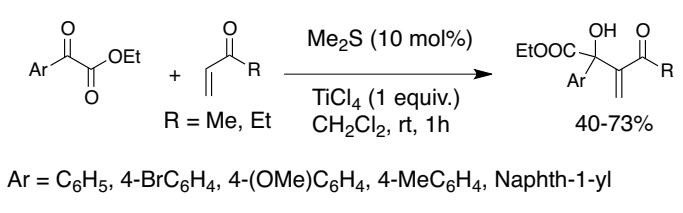
Two interesting publications appeared from the research group of Li in 2000 demonstrating the application of $TiCl_4$ for Baylis-Hillman coupling between alkyl vinyl ketones and aldehydes (Scheme 21).[23a,b]



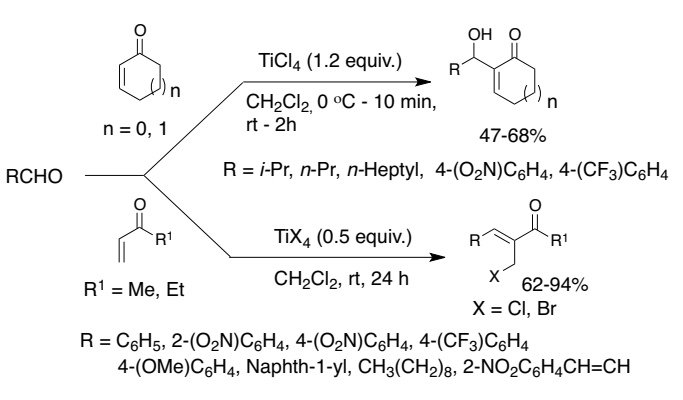
Scheme 18.



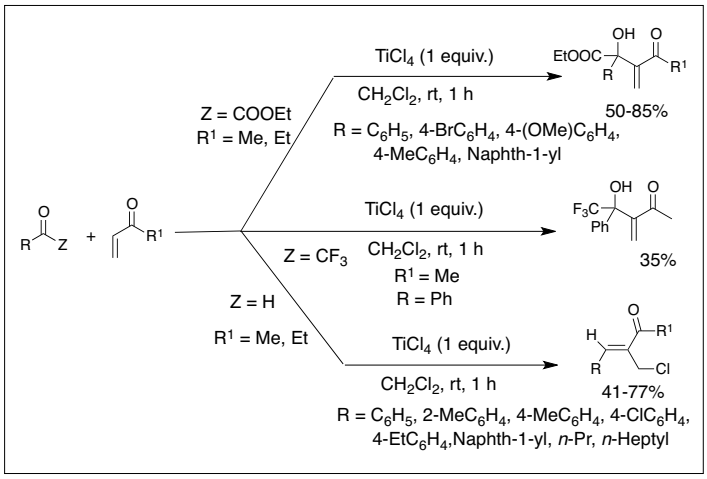
Scheme 19.



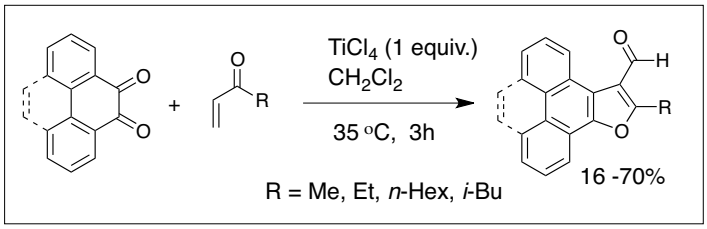
Scheme 20.



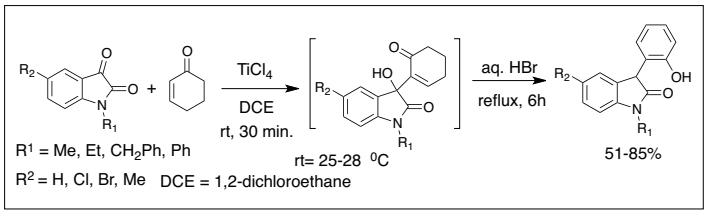
Scheme 21.



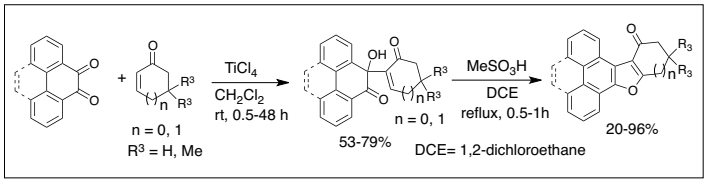
Scheme 22.



Scheme 23.



Scheme 24.

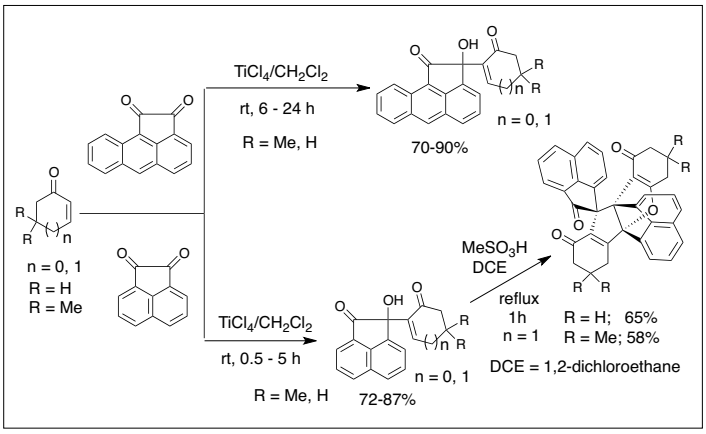


Scheme 25.

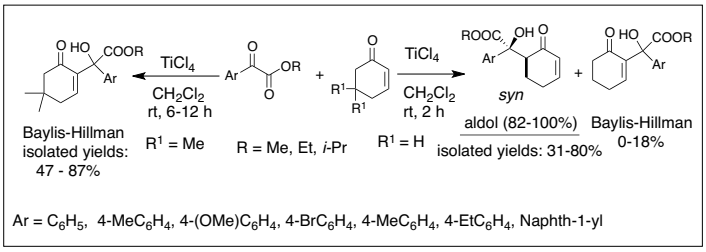
We performed the reaction between α-keto esters and alkyl vinyl ketones under the influence of $TiCl_4$ and were pleased to see the formation of desired BH adducts in high yields. Under these conditions trifluoromethyl phenyl ketone also couples with MVK to provide the corresponding adduct in 35% yield. We also noticed that the reaction between aldehydes and alkyl vinyl ketones in the presence of $TiCl_4$ produced (*Z*)-allyl chlorides (Scheme 22).[24]

Interestingly we noticed the formation of 2-alkylfuran-3-carboxaldehydes when we performed the reaction between aromatic 1,2-diones with alkyl vinyl ketones under the influence of $TiCl_4$ at room temperature (35 °C) (Scheme 23).[25]

We also have developed a facile strategy for the synthesis of 3-(2-hydroxyphenyl)indolin-2-ones *via* Baylis-Hillman coupling between cyclohex-2-enone and isatins followed by the treatment of the *in situ* formed adducts with aq. HBr according to the reaction sequence as shown in Scheme 24. A similar $TiCl_4$-induced BH reaction between 1,2-aromatic diones with cycloalk-2-enones followed by the treatment of the resulting adducts with methanesulfonic acid provided fused fu-



Scheme 26.



Scheme 27.

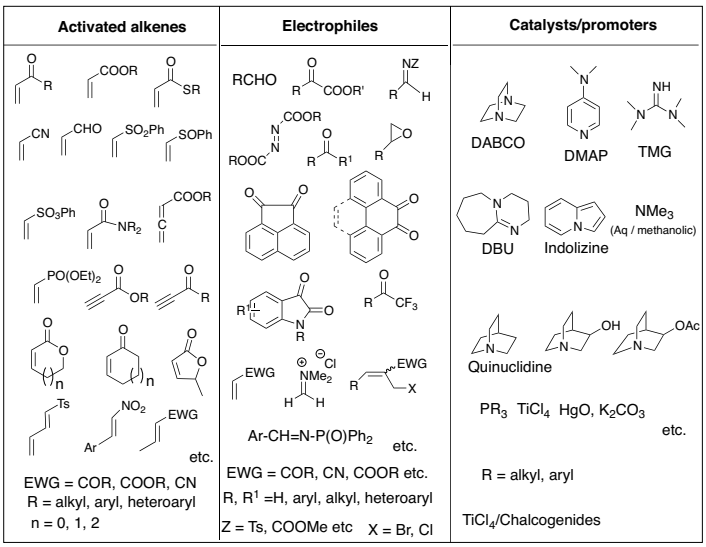
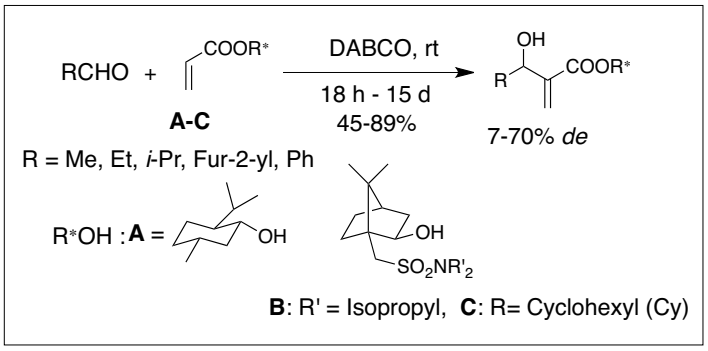
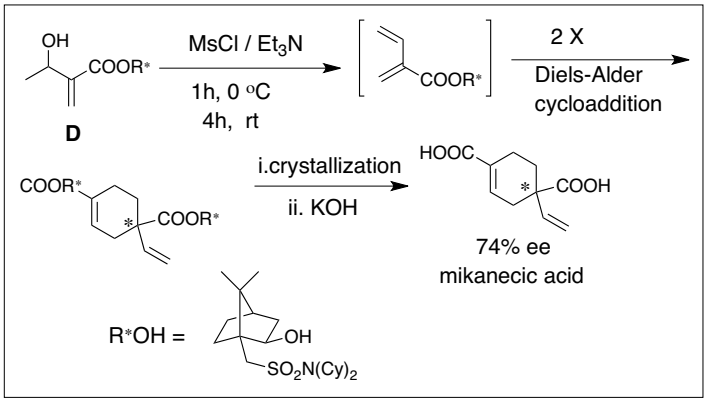


Fig. 3. Essential components known in the literature.[3]



Scheme 28.



Scheme 29.

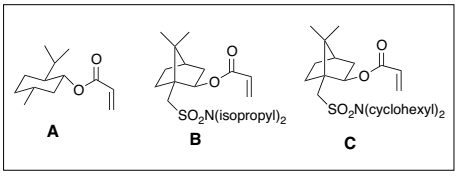


Fig. 4.

ran derivatives (Scheme 25).[26] Titanium tetrachloride also mediates the coupling of [9,10]-phenanthrenedione (and 1,2-aceanthrenequinone) with cycloalk-2-enone derivatives to produce the corresponding allyl alcohols (Scheme 26). Two such alcohols obtained from [9,10]-phenanthrenedione were transformed into fused-spiro compounds (Scheme 26).[26]

We have also demonstrated the influence of steric factors in directing the Baylis-Hillman and aldol reactions in the $TiCl_4$-mediated treatment of cyclohex-2-enone derivatives with α-keto esters. Thus sterically demanding 4,4-dimethylcyclohex-2-enone provides the Baylis-Hillman adducts exclusively while the simple cyclohex-2-enone (with no steric hindrance) furnished aldol (*anti*) products in major amounts along with minor amounts of BH adducts (Scheme 27).[27]

During the last two decades the BH reaction has grown from rare patent level to high synthetic utility levels. Thus several activated alkenes, electrophiles and catalysts have been successfully employed in various Baylis-Hillman reactions. Many research groups have been working in this area and made significant contributions to the growth of this reaction with respect to all three essential components. A list of some important activated alkenes, electrophiles and catalysts/promoters is presented in Fig. 3.

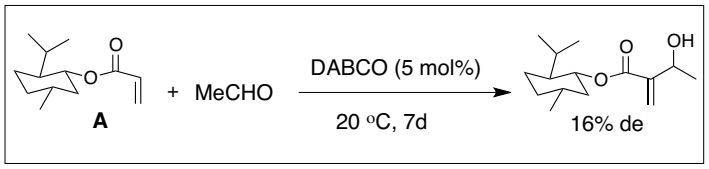
6. Towards an Asymmetric Baylis-Hillman Reaction

6.1 *Chiral Acrylates as Activated Alkenes*

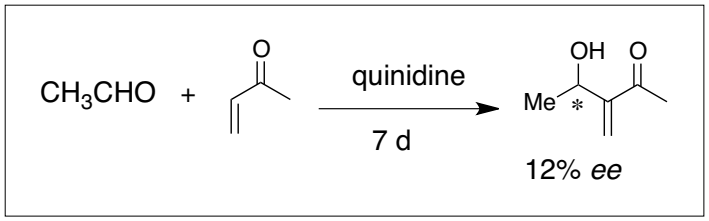
In 1990 we examined the application of chiral acrylates (A–C) (Fig. 4) as activated alkenes in the Baylis-Hillman reaction with aldehydes under the catalytic influence of DABCO to provide the resulting adducts up to 70% diastereoselectivity (Scheme 28).[28a] The BH adduct (D) obtained *via* the reaction between chiral acrylate (C) and acetaldehyde was conveniently transformed into mikanecic acid with high enantiomeric purities (Scheme 29).[28b]

It should be mentioned here that in 1986 Brown and co-workers, in the course of homogeneous hydrogenation studies, reported the coupling of (L)-menthyl acrylate with acetaldehyde to provide the corresponding adduct in 16% diastereoselectivity (Scheme 30).[29]

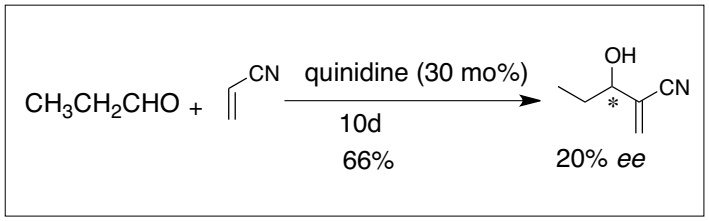
Drewes[3m] and we[31,30] independently examined possible application of cinchona alkaloids as catalysts to perform



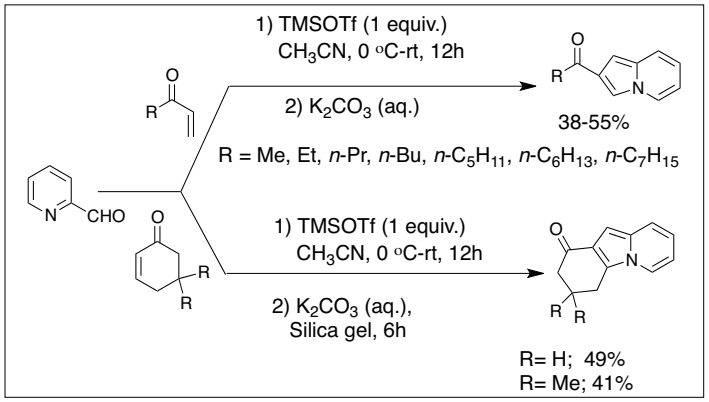
Scheme 30.



Scheme 31.



Scheme 32.



Scheme 33.

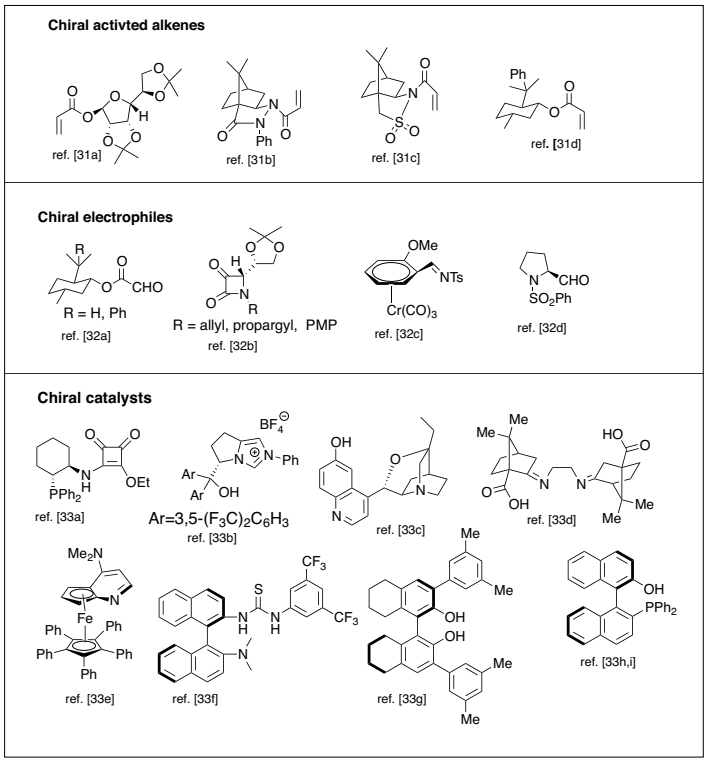


Fig. 5. Essential components for asymmetric BH reaction.[3d]

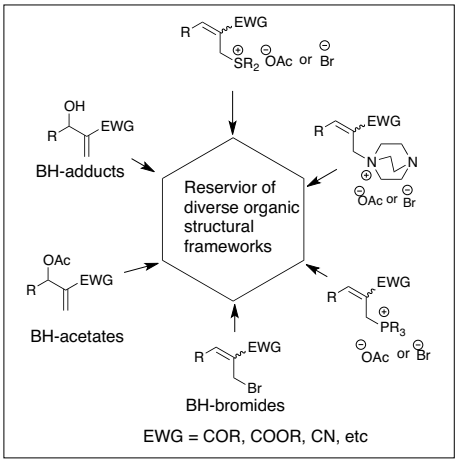


Fig. 6. Strategies for synthetic applications of BH adducts and derivatives.

an asymmetric BH reaction. Coupling of MVK with acetaldehyde in the presence of quinidine as a catalyst provided the resulting adduct in 12% *ee* (Scheme 31).[3m] Quinidine-catalyzed reaction between acrylonitrile and propionaldehyde gave the corresponding adduct in 20% enantiomeric purity (Scheme 32).[31,30] Although the enantioselectivities are low, these reactions certainly indicate that there is every possibility to design better catalysts that can offer higher enantioselectivities.

During the past 25 years investigations in asymmetric BH reactions has grown considerably in terms of all the three essential components, that is, chiral activated alkenes,[31] electrophiles,[32] catalysts (or additives).[33] Some recent and interesting examples of these chiral components are listed in Fig. 5.

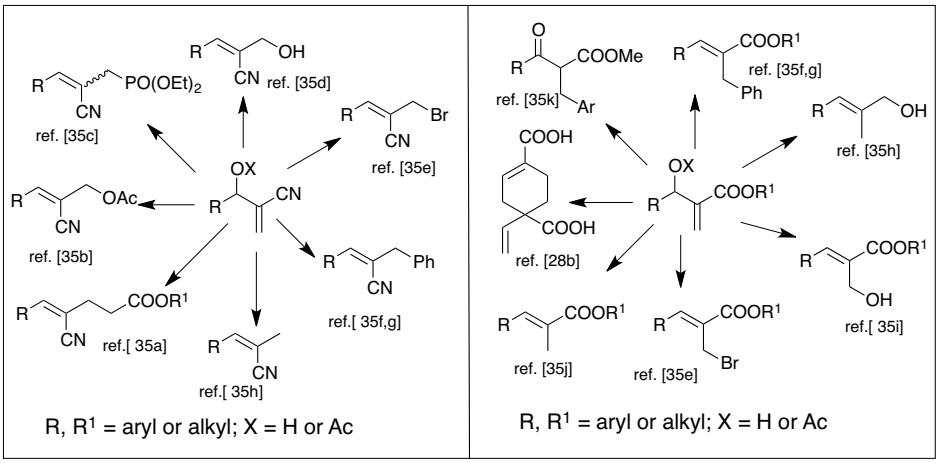


Fig. 7. Organic transformations using the BH adducts and their derivatives.

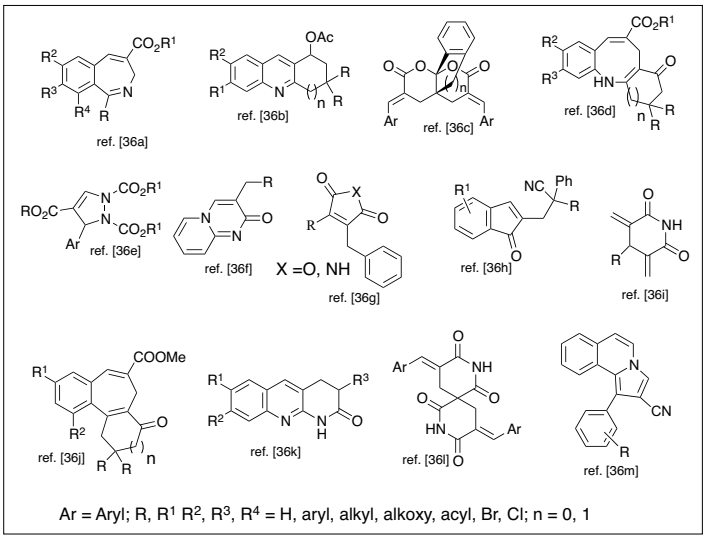


Fig. 8. Selected carbocyclic and heterocyclic frameworks synthesized using the BH-adducts.

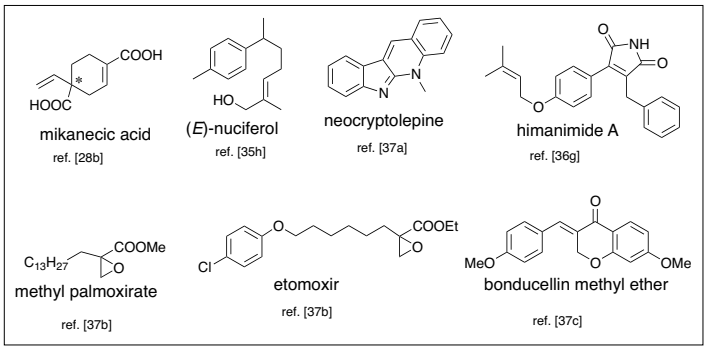


Fig. 9. Selected natural products synthesized using the BH-adducts.

7. Electrophile-induced BH Reaction

We have demonstrated the application of pyridine-2-carboxaldehyde as a source of two components, that is, electrophile (aldehyde group) and catalyst (pyridine ring nitrogen) species, for coupling with activated alkenes under the influence of TMSOTf, thus providing a facile strategy for obtaining indolozine frameworks (Scheme 33).[34] This methodology opens up the possibilities of developing several more similar two-component (by designing substrates containing electrophile and catalyst species) BH reactions and also paves the way for achieving single component BH reactions after appropriately designing the substrates (containing all the three species, that is, activated alkene, electrophile and catalyst).[34]

8. Baylis-Hillman Adducts, Acetates and Bromides in Organic Synthesis

Organic synthesis and its growth mostly depend not only on the availability of functional groups but also on the strategies of how to utilize them in highly efficient way in building up the carbon framework. It is believed that substrates containing several chemospecific functional groups in proximity offer more interesting and unique reactivity profiles which will be useful for constructing any carbon structural frameworks of synthetic/medicinal importance.[3b,d] The BH reaction provides such interesting molecules containing a minimum of three chemospecific functional groups in close proximity (α,α to each other).[3b] We envisioned that these densely functional molecules would offer diverse opportunities for various transformations and also for building different classes of carbon skeletons. We also envisaged that the BH acetates, bromides and their derivatives would constitute an unending source of synthons for obtaining carbocyclic/heterocyclic compounds of medicinal relevance (Fig. 6).

Accordingly we have systematically employed these adducts as valuable substrates in various organic transformation methodologies (Fig. 7–9).[35–37] Our research group also successfully used Baylis-Hillman adducts for developing convenient protocols for syntheses of several molecules[36] of biological importance including representative natural products, such as neocryptolepine,[37a] himanimide A,[36g] etomoxir,[37b] methyl palmoxirate,[37b] bonducellin,[37c] (*E*)-nuciferol,[35h] (+)mikanecic acid[28b] *etc*.

9. Conclusions and Future Perspectives

We have presented in this mini-review our contributions to the development of the Baylis-Hillman reaction with respect to all three essential components, that is, activated alkenes, electrophiles and catalysts. We have also briefly discussed our efforts towards applications of the BH-adducts and derivatives in organic synthesis. Many research groups in the world work in this area and have contributed significantly to the growth of this reaction. These research groups have successfully employed the BH-adducts in various facets of organic synthesis thus demonstrating the ever increasing expansion of this reaction. It is not possible for us to cite all these references since this is a mini review mostly highlighting our work. However, wherever necessary, important and essential references (giving credit to the other workers) have been cited.

We are sure that this area will continue to grow further in all directions. More emphasis will be made on the development of new aspects such as two component (with substrates containing electrophile and catalyst species) and single component (with substrates containing all the three species, that is, activated alkene, electrophile and catalyst) and multi-Baylis-Hillman reactions, in the coming years.

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