

# New Applications of Indium Catalysts in Organic Synthesis

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**Abstract:** Indium(III) salts have received considerable attention as Lewis acids in recent years. Their stability to co-ordinating atoms present in organic substrates makes them excellent catalysts in substoichiometric quantities. Stability in water allows aqueous recycling and often the use of water as a reaction solvent. This review will focus on describing new developments in the application of indium catalysts in synthetic organic chemistry. Transformations that will be covered include aromatic functionalisation, cycloaddition reactions, conjugate additions and multi-component coupling reactions.

**Keywords:** Indium, Lewis acid, Catalysis, Friedel-Crafts, Cycloadditions.

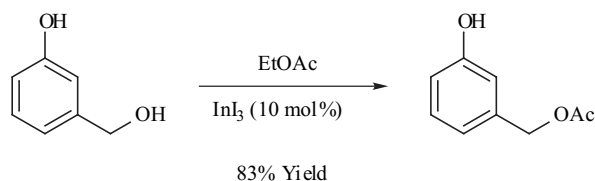


It is known that organoindium compounds are less reactive than alkyllithiums and Grignard reagents. However, indium metal can react with an organic substrate to generate an organoindium species *in situ*, thus avoiding the use of sensitive, toxic or expensive organometallics. Therefore, allylation, cyclopropanation and Reformatsky reactions can be affected using indium metal and the corresponding allyl halides, methylene dibromides and  $\alpha$ -haloesters [1 (a)-(d)]. Whilst indium is not unique in its ability to carry out such reactions (it is comparable with tin and zinc), its exceptional stability to water and air allows such reactions to be carried out under aqueous conditions. The associated practical advantages of water as a solvent has led to an explosion of interest in indium mediated processes. Recently, indium(III) complexes have received a great deal of interest as Lewis acid catalysts [2]. Although comparatively weak when compared to their aluminium and boron counterparts, indium(III) salts are stable to water and are reusable. This review highlights recent developments and opportunities in the application of indium salts to *catalytic* organic synthesis.

Transesterification of esters to the corresponding analogues with higher alcohol moieties is well documented, however the reverse transformations are not. Ranu and co-workers have resolved this using indium iodide. The reaction provides a simple and effective method for transesterification and is superior to reported aluminium and titanium reagents [3]. Transesterification to a *tert*-butyl ester, which is often problematic in acid-catalysed reactions, has been realised using this method.

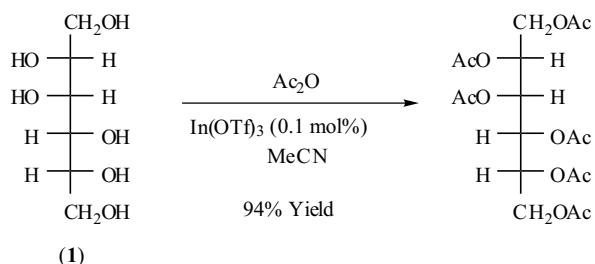
In an extension of this methodology, the same group carried out indium iodide-catalysed heteroatom acylation using ethyl acetate in a transesterification process [4]. Using 10 mol%  $\text{InI}_3$  (prepared *in situ* from indium metal and iodine) in an excess of refluxing ethyl acetate catalyses the acylation of amines and primary alcohols in the presence of secondary and phenolic alcohols as shown in Scheme 1. The same system has been employed in the conversion of MOM-

and tetrahydropyran-protected alcohols to the corresponding acetates in one step [5,6]. The reaction being chemoselective for primary alcohols; secondary and phenolic ethers were simply deprotected to the parent alcohols.



**Scheme 1.**

Mineno has demonstrated that indium(III) triflate is an efficient catalyst for the tetrahydropyranylation of alcohols. In addition, indium(III) triflate catalyses the deprotection of such products to the parent alcohol or their conversion to the corresponding acetates [7]. The Frost group have reported the use of indium(III) triflate in the acylation of alcohols and amines with acetic anhydride under very mild conditions [8]. The acylation of heteroatoms in excellent yield at room temperature may be achieved with catalyst loadings as low as 0.1 mol%, as illustrated in Scheme 2 for D-mannitol (1). The same group note that catalytic indium(III) triflate in combination with stoichiometric lithium perchlorate promotes the acylation of alcohols with isopropenyl acetate, generating acetone as the predominant side-product [9].

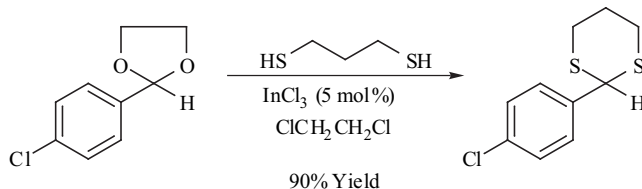


**Scheme 2.**

The conversion of aldehydes to *gem*-diacetates in high to quantitative yields using catalytic indium(III) chloride was reported by Yadav and co-workers [10]. A range of aryl and alkyl aldehydes were readily converted to the corresponding diacetates at room temperature, although ketones did not

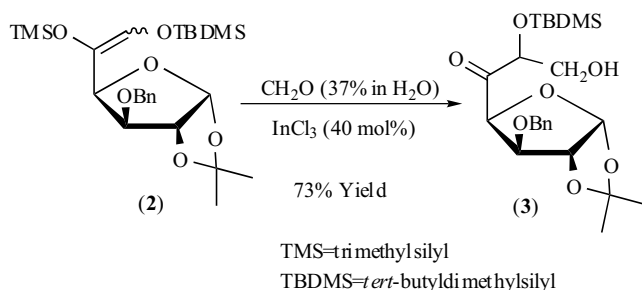
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react. Indium(III) halides are also effective in the related thioacetalisation reactions [11,12]. Ranu and co-workers have shown that indium(III) chloride catalyses the transthoacetalisation of *O,O*-acetals in excellent yields under mild conditions [13]. Cyclic and acyclic *O,O*-acetals undergo efficient transthoacetalisation reactions as delineated in Scheme 3.



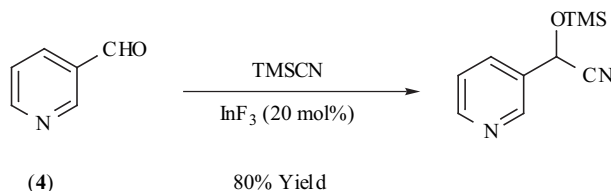
Scheme 3.

Indium trichloride is an efficient catalyst in Mukaiyama aldol reactions of aldehydes with silyl enol ethers in water at room temperature [14,15]. In an improvement to the reported methodology, Kobayashi and co-workers proved that the addition of small amounts of surfactant was beneficial to the overall efficiency of the reaction [16]. Loh and co-workers have reported the chain elongation of the glucose-derived silyl enol ether (**2**) with commercially available aqueous formaldehyde solution to afford (**3**), as described in Scheme 4 [17].



Scheme 4.

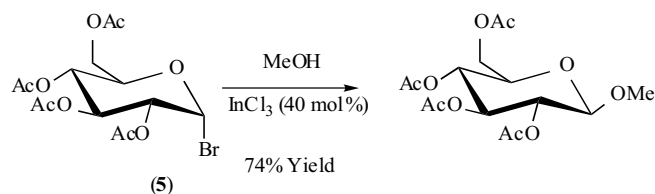
Aldol reactions involving glyoxylate or glyoxylic acid have, in most cases, proved inefficient despite harsh reaction conditions [18]. Loh and co-workers reported that indium(III) chloride promotes the reaction of ketones with glyoxylic acid and methyl glyoxylate under sonication, furnishing the biologically and synthetically important  $\alpha$ -hydroxy acids and esters in excellent yields [19]. Indium(III) fluoride is reported to catalyse the addition of trimethylsilyl cyanide (TMSCN) to aldehydes including (**4**) in aqueous media as shown in Scheme 5 [20]. The products of these reactions are versatile synthetic intermediates, allowing access to  $\alpha$ -hydroxy aldehydes,  $\alpha$ -hydroxy ketones,  $\alpha$ -amino acids and  $\beta$ -hydroxy amines.



Scheme 5.

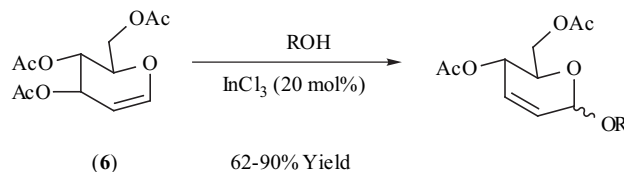
It has also been established that indium(III) salts are effective catalysts for the cyanation of ketones, a more demanding process than the cyanation of aldehydes or

imines [21]. Upon testing a range of Lewis acids, indium(III) bromide was found to be the most effective catalyst. The formation of oligosaccharides through the glycosidation reaction of glycosyl bromides is usually promoted by toxic heavy metals such as HgO/HgBr<sub>2</sub> or Ag<sub>2</sub>CO<sub>3</sub>/AgClO<sub>4</sub>. Chowdary and co-workers have detailed the efficient use of indium(III) chloride in coupling glycosyl bromides with alcohols [22]. In all cases glycosides and disaccharides were obtained with pronounced  $\beta$ -selectivity in good overall yield. The reaction of glycosyl bromide (**5**) with methanol in the presence of 40 mol% indium(III) chloride is shown in Scheme 6.

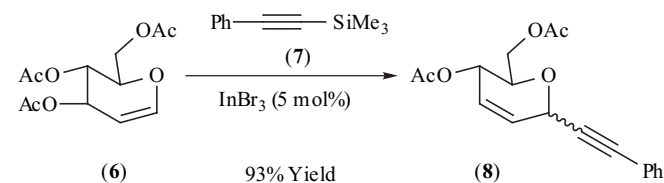


Scheme 6.

Indium(III) chloride is also an effective catalyst for the synthesis of alkyl and aryl 2,3-unsaturated glycopyranosides *via* the Ferrier rearrangement [23]. The general process is illustrated in Scheme 7, tri-*o*-acetyl-D-glucal (**6**) reacts with a range of alcohols in high yield. Where a monosaccharide is used, the disaccharide is formed in good overall yield. Indium(III) chloride has been shown to have superior catalytic activity than a number of Lewis acids including BF<sub>3</sub>, SnCl<sub>4</sub>, LiBF<sub>4</sub> and LiClO<sub>4</sub>.



Scheme 7.



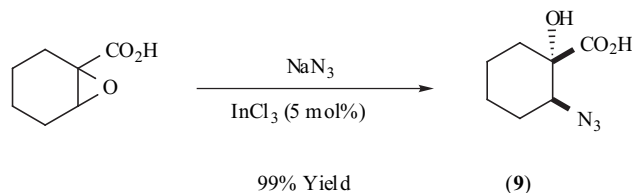
Scheme 8.

In a related process, Yadav and Reddy have shown that glucals react smoothly with silyl nucleophiles in the presence of indium(III) bromide to form *C*-glycosides [24]. This methodology has also been applied to the reaction of glycols with alkynylsilanes to afford the corresponding alkynyl sugars in excellent yields [25]. Scheme 8 illustrates the reaction of (**6**) with phenyl (trimethylsilyl)acetylene (**7**) that results in the formation of the corresponding alkynyl *C*-glycoside (**8**) in 93% yield. The  $\alpha$ -anomer was obtained as the predominant product.

The same group have also shown that glycols react with heterocycles in the presence of catalytic indium(III) chloride to provide C<sub>3</sub> substituted glycols [26].

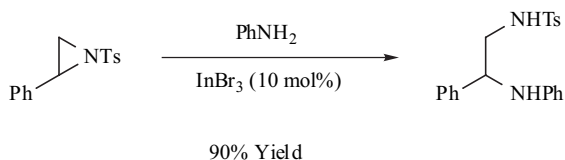
The ring opening of  $\alpha$ - $\beta$ -epoxy carboxylic acids by halide ions yields carboxyhalohydrins, important synthetic intermediates, precursors of such compounds as  $\alpha$ -hydroxy-

$\beta$ -amino- and  $\alpha$ -amino- $\beta$ -hydroxycarboxylic acids. Pizzo and co-workers have reported the indium(III) halide catalysed bromolysis and iodolysis of  $\alpha$ - $\beta$ -epoxy carboxylic acids in water with a high degree of regio- and stereoselectivities [27]. Similarly, indium(III) chloride is demonstrated to be an efficient catalyst for the azidolysis of  $\alpha$ - $\beta$ -epoxy carboxylic acids with sodium azide [28]. This is illustrated in Scheme 9, the catalytic formation of  $\beta$ -azido- $\alpha$ -hydroxy carboxylic acid (**9**) in an aqueous solution at pH 4.0 proceeds with excellent yield and high diastereo- and regioselectivity (>99%). The reaction is sluggish when run in the absence of catalyst, in organic solvents or at neutral pH. A range of mono- and disubstituted  $\alpha$ - $\beta$ -epoxy carboxylic acids undergo azidolysis under these conditions.

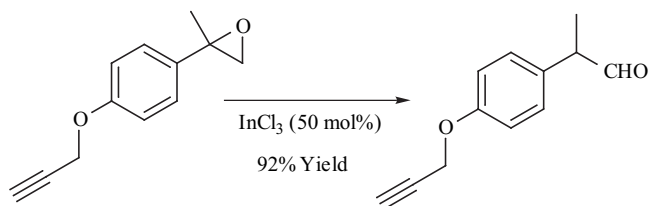


Scheme 9.

Yadav and co-workers reported the indium(III) triflate catalysed ring opening of aziridines with carboxylic acids to give  $\beta$ -aminoesters in high yield [29]. The reactions proceed smoothly at room temperature in the presence of 5 mol% catalyst. Aryl-*N*-tosyl aziridines underwent attack at the benzylic position, whilst alkyl-*N*-tosyl aziridines underwent terminal cleavage. Likewise, *N*-tosyl aziridines are opened regioselectively with trimethylsilyl azide in the presence of indium(III) chloride to afford the corresponding azido amines in high yield [30].

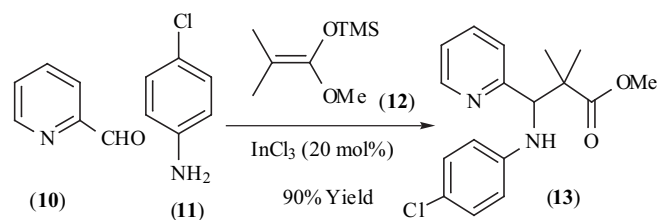


Scheme 10.



Scheme 11.

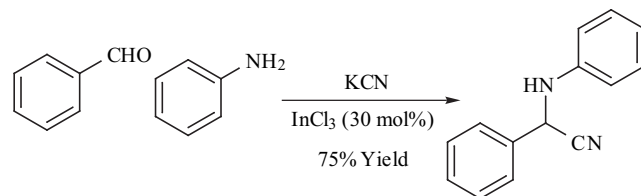
The same group has also detailed the indium(III) bromide catalysed aminolysis of activated aziridines with anilines under mild conditions [31]. Vicinal amines are formed in high yield (78-92%) at ambient temperature as illustrated in Scheme 10. The Ranu group have reported a simple and efficient procedure for the rearrangement of substituted epoxides catalysed by indium(III) chloride [32]. Aryl substituted epoxides isomerise with complete regioselectivity to form a single carbonyl compound (Scheme 11). With close to thirty examples this methodology enables an efficient synthesis of benzylic aldehydes or ketones.



Scheme 12.

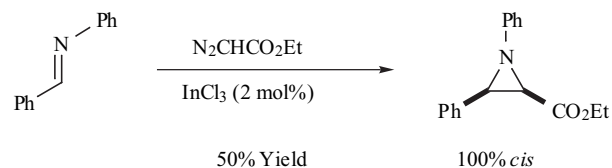
The Mannich reaction is a classic method for preparing  $\beta$ -amino acids, esters, ketones and aldehydes. To circumvent the problems associated with synthesis and purification of imines, an elegant one-pot Mannich-type reaction has been developed employing indium(III) chloride as catalyst [33]. The reaction between aldehyde (**10**), amine (**11**) and silyl enol ether (**12**) is catalysed by 20 mol % indium(III) chloride in water and affords the  $\beta$ -aminoester (**13**) in high yield (Scheme 12). The use of glyoxylic acid monohydrate yields  $\alpha$ -amino acids, although yields ranged from low to moderate [34].

A similar strategy has been used by Ranu and co-workers in a one-pot synthesis of  $\alpha$ -amino phosphonates from the 3-component condensation of carbonyl compounds, amines and diethylphosphite [35].  $\alpha$ -Amino nitriles are of considerable interest, particularly in the synthesis of  $\alpha$ -amino acids. In a useful modification to the Strecker reaction shown in Scheme 13, Ranu and co-workers have demonstrated that indium(III) chloride catalyses the one-pot three-component coupling of a carbonyl compound, amine and potassium cyanide [36]. Aromatic, aliphatic and heterocyclic aldehydes react smoothly at room temperature.



Scheme 13.

Russowsky and co-workers have reported that indium(III) chloride catalyses the addition of carbon nucleophiles to aromatic aldimines and cyclic *N*-acyliminium ions [37]. The synthesis of  $\alpha$ -amino- $\gamma$ -lactones can be achieved by an indium(III) chloride mediated three-component reaction of alkenes, glyoxylates and amines [38]. The indium catalysed reaction of ethyl diazoacetate with aldimines affords aziridine carboxylates under mild conditions and low catalyst loading (Scheme 14) [39]. The best results were limited to aldimines derived from electron deficient aromatic aldehydes.



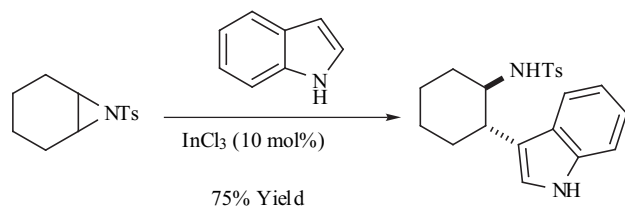
Scheme 14.

The Bayliss-Hillman reaction is commonly used for the coupling of Michael acceptors with aldehydes to give  $\beta$ -hydroxy- $\alpha$ -methylene esters/ketones/nitriles. The use of

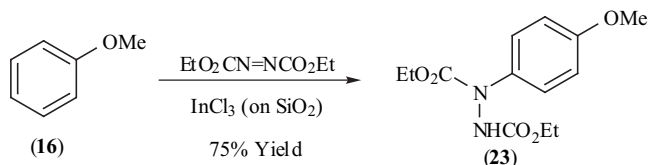




The catalyst ( $\text{InCl}_3\text{-SiO}_2$ ) was prepared by adding silica gel to a solution of  $\text{InCl}_3$  in acetonitrile followed by evaporation of the solvent.

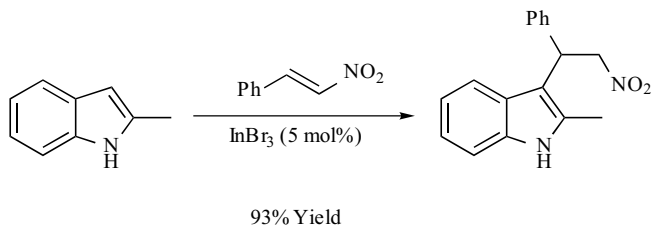


Scheme 20.

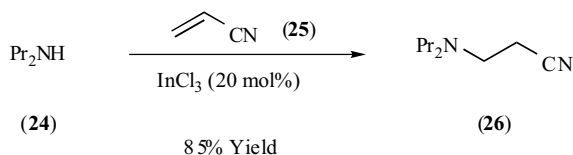


Scheme 21.

Heterocycles such as pyrrole and indole are of great interest because of the great number of their derivatives occur in Nature and possess a variety of biological activities. The derivatisation of such heterocycles remains difficult due to their acid sensitivity. Yadav and co-workers have reported that indium(III) chloride is an excellent catalyst for the addition of pyrroles and indoles to electron-deficient olefins [49,50]. It has been similarly noted that indium(III) bromide promotes the addition of indoles to nitroalkenes in aqueous media [51]. The protocol was effective for the addition of several electron-rich indoles and even indoles bearing electron-withdrawing groups. Consecutive reactions were carried out using catalyst recycled from the aqueous layer with no significant loss of activity (Scheme 22).



Scheme 22.

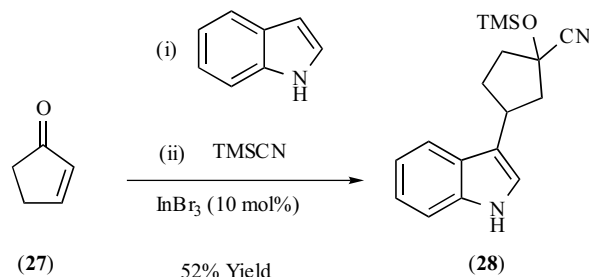


Scheme 23.

Indium(III) chloride has been reported to promote the Michael reaction between amines and  $\alpha,\beta$ -ethylenic compounds in water and under mild conditions [52]. As indicated in Scheme 23, the reaction of dipropylamine (**24**) with acrylonitrile (**25**) proceeds in high yield to give product (**26**). The catalyst can be recovered from the aqueous phase and reused without loss of activity. Under solvent-free conditions, indium(III) chloride also catalyses the Michael reaction of silyl enol ethers with enones and alkenoates [53].

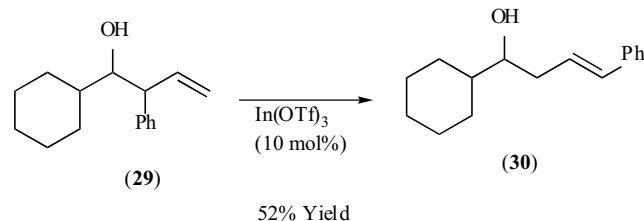
Cozzi and co-workers have harnessed the remarkable tolerance of indium salts toward co-ordinating functional

groups in a sequential one-pot 1,4- then 1,2-nucleophilic addition to enones [54]. The group demonstrated that indium(III) bromide catalyses the 1,4 conjugate addition of indoles and thiols to  $\alpha,\beta$ -unsaturated ketones under mild conditions. In addition, subsequent 1,2 addition of trimethylsilylcyanide (TMSCN) to the  $\beta$ -substituted ketones can be carried out in one pot. Thus, cyclopentenone (**27**) undergoes 1,4 addition of indole and subsequent 1,2 addition of TMSCN, to give product (**28**) (Scheme 24).



Scheme 24.

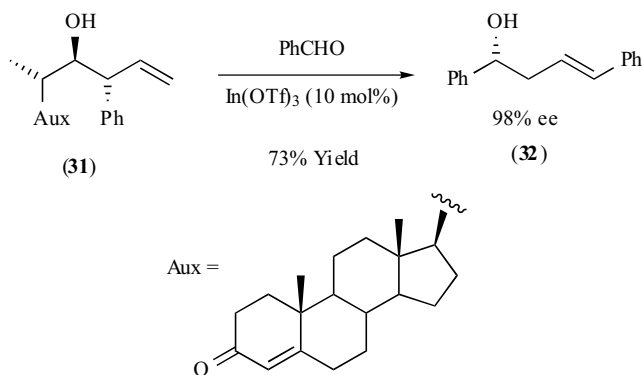
The allylation of carbonyl compounds and the carbonyl-ene reaction offer ready access to synthetically useful homoallylic alcohols. However, both these reactions produce predominantly  $\gamma$ -adducts. Loh and co-workers have reported the indium(III) triflate catalysed conversion of branched homoallylic alcohols to the thermodynamically preferred linear regioisomers [55]. Under the reaction conditions, branched homoallylic alcohol (**29**) is converted to the linear product (**30**) in good yield (Scheme 25). A correlation between the relative stereochemistry of the substrate and the geometry of the double bond in the product was observed, with *syn* substrates leading to *Z* products and *anti* substrates leading to *E* products.



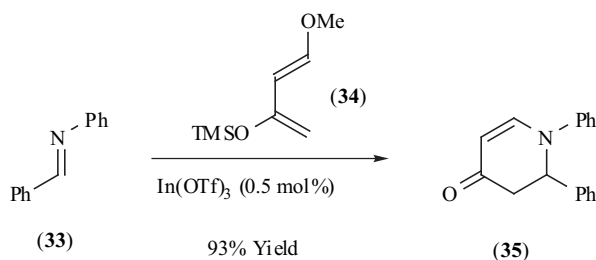
Scheme 25.

The Loh group reported a homoallylic sterol/indium(III) Lewis acid reagent system for the enantioselective and  $\alpha$ -regioselective allylation of aldehydes [56]. Allyl transfer from  $\gamma$ -adduct homoallylic sterol (**31**) to benzaldehyde furnishes the  $\alpha$  adduct (**32**) in good yield, excellent ee and *E*-configuration of the double bond (Scheme 26).

The Diels-Alder reaction is known to show increased reactivity rates in water, especially when catalysed by a Lewis acid. Loh and co-workers showed that indium(III) chloride catalyses the Diels-Alder reaction between dienes and dienophiles under aqueous conditions [57]. The Frost group has demonstrated the use of indium(III) triflate as a catalyst for hetero Diels-Alder reactions [58]. In the presence of just 0.5 mol% of catalyst the imino Diels-Alder reaction of imine (**33**) and diene (**34**) provides the product (**35**) in excellent yield (Scheme 27). A three component coupling of aldehyde, amine and diene was also reported.

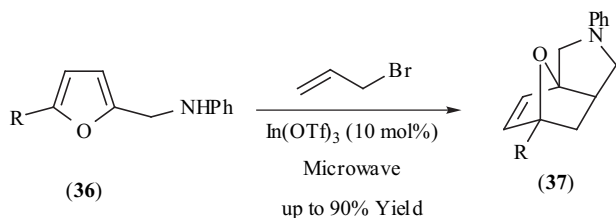


Scheme 26.



Scheme 27.

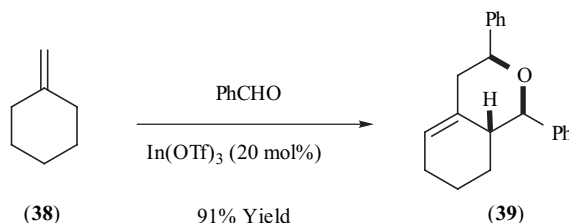
Perumal and co-workers have utilised indium(III) chloride in the hetero Diels–Alder reactions of hetero dienes derived from aromatic amines. The reaction of Schiff's bases with cyclopentadiene, cyclohexen-2-one and cyclohepten-2-one results in rapid synthesis of cyclopentaquinolines, azabicyclooctanones and azabicyclononanones respectively [59]. Indium(III) triflate catalyses the intramolecular Diels–Alder reaction of furans in aqueous media under microwave irradiation [60]. In a one-pot procedure, allyl bromide reacts with (2-furfuryl)anilines (36) affording the intramolecular Diels–Alder products (37) in good to excellent yield, in very short reaction times (Scheme 28). Under thermal conditions, yields of 40–45% are obtained. Such products allow access to indole derivatives through cleavage of the epoxy bridge and aromatization.



Scheme 28.

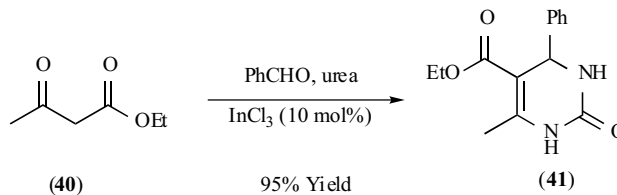
Li and Zhang have reported the indium(III) chloride catalysed aza-Diels–Alder reaction as part of a domino reaction of aromatic amines with cyclic enol ethers [61]. Yadav and co-workers showed that indium(III) chloride catalyses the aza-Diels–Alder reaction efficiently in organic solvents [62]. An array of multi-substituted tetrahydrofurans and tetrahydropyrans can be prepared through the indium catalysed ene-type cyclisations [63–65]. In one example, the efficient formation of tetrahydropyran rings through the self-tandem carbonyl–ene, intramolecular (2,5) oxonium–ene cyclisation of aldehydes and methylene cyclohexane is demonstrated. Methylene cyclohexane (38) and benzaldehyde

react initially to afford a homoallylic alcohol, subsequent 2,5 oxonium–ene cyclisation involving a further molecule of aldehyde provides the tetrahydropyran (39) in very good yield and excellent diastereoselectivities, favouring the 2,3 *anti*, 2,6 *syn* isomers (Scheme 29).



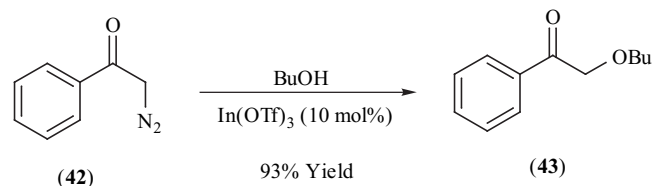
Scheme 29.

Ranu and co-workers reported that indium trichloride is an excellent catalyst for the Biginelli reaction [66]. Both  $\beta$ -keto esters and  $\beta$ -diketones are reported to participate in this reaction. Aromatic, aliphatic and heterocyclic aldehydes undergo cyclisation and both urea and thiourea react readily. On reaction of ethyl acetoacetate (40), benzaldehyde and urea at reflux in THF in the presence of  $\text{InCl}_3$  (10 mol%), dihydropyrimidinone (41) is formed in excellent yield (Scheme 30). Other researchers note that indium(III) bromide is also an effective catalyst for the Biginelli reaction [67].

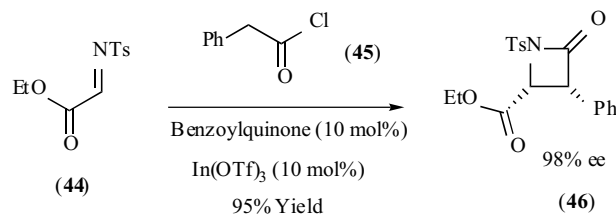


Scheme 30.

Muthusamy and co-workers have reported the indium(III) triflate catalysed OH insertion reaction of  $\alpha$ -diazo ketones [68]. In the presence of 10 mol% of catalyst, a range of alcohols and thiols decomposed a variety of aromatic and aliphatic diazo compounds affording the respective  $\alpha$ -alkoxy ketones under mild conditions. Thus, Scheme 31 shows that diazoacetophenone (42) in butanol reacts to give alkoxy ketone (43) in excellent yield.



Scheme 31.



Scheme 32.

The Lectka group has published a catalytic, asymmetric synthesis of  $\beta$ -lactams using a bifunctional catalyst system

consisting of a chiral nucleophile (benzoylquinone) and indium(III) triflate [69]. For the reaction of *N*-tosyl imine (**44**) with ketene precursor, phenylacetyl chloride (**45**) the  $\beta$ -lactam (**46**) was obtained in excellent yield and high enantioselectivity (Scheme 32).

## REFERENCES

- [1] (a) Cintas, P. *Synlett*, **1995**, 1087. (b) Li, C. -J.; Chan, T.-H. *Tetrahedron*, **1999**, *55*, 11149; (c) Ranu, B. C. *Eur. J. Org. Chem.*, **2000**, 2347; (d) Li, C.-J. *Tetrahedron*, **1996**, *52*, 5643.
- [2] Frost, C.G.; Chauhan, K. K. *J. Chem. Soc. Perkin Trans. 1*, **2000**, 3015.
- [3] Ranu, B. C.; Dutta, P.; Sakar, A. *J. Org. Chem.*, **1998**, *63*, 6027.
- [4] Ranu, B. C.; Dutta, P.; Sakar, A. *J. Chem. Soc., Perkin Trans. 1*, **2000**, 2223.
- [5] Ranu, B. C.; Hajra, A. *J. Chem. Soc. Perkin Trans. 1*, **2001**, 355.
- [6] Ranu, B. C.; Hajra, A. *J. Chem. Soc. Perkin Trans. 1*, **2001**, 2262.
- [7] Mineno, T. *Tetrahedron Lett.*, **2002**, *43*, 7975.
- [8] Frost, C.G.; Chauhan, K. K.; Love, I.; Waite, D. *Synlett*, **1999**, 1743.
- [9] Chapman, C. J.; Frost, C. G.; Hartley, J. P.; Whittle, A. J. *Tetrahedron Lett.*, **2001**, *42*, 773.
- [10] Yadav, J. S.; Reddy, B. V. S.; Srinivas, C. *Synthetic Comm.*, **2002**, *32*, 2169.
- [11] Ceschi, M. A.; Felix, L. A.; Peppe, C. *Tetrahedron Lett.*, **2000**, *41*, 9695.
- [12] Muthusamy, S.; Babu, S. A.; Gunanathan, C. *Tetrahedron Lett.*, **2001**, *42*, 359.
- [13] Ranu, B. C.; Das, A.; Samanta, S. *Synlett*, **2002**, 727.
- [14] Mukaiyama, T.; Ohno, T.; Han, J. S.; Kobayashi, S. *Chem. Lett.*, **1991**, 949.
- [15] Loh, T. P.; Pei, J.; Cao, G.-Q. *Chem. Commun.*, **1996**, 1819.
- [16] Kobayashi, S.; Busujima, T.; Nagayama, S. *Tetrahedron Lett.*, **1998**, *39*, 1579.
- [17] Loh, T. P.; Cao, G.-Q.; Vittal, J. J.; Wong, M.-W. *Chem. Commun.*, **1998**, 861.
- [18] Bianchi, M.; Butti, A.; Christidis, Y.; Perronnet, J.; Barzaghi, F.; Cesana, F.; Necioni, A. *Eur. J. Med. Chem.*, **1988**, *23*, 45.
- [19] Loh, T. P.; Feng, L.-C.; Wei, L.-L. *Tetrahedron*, **2001**, *57*, 4231.
- [20] Loh, T. P.; Xu, K.-C.; Sook Chiang Ho, D.; Sim, K.-Y. *Synlett*, **1998**, 369.
- [21] Bandini, M.; Cozzi, P. G.; Melchiorre, P.; Umani-Ronchi, A. *Tetrahedron Lett.*, **2001**, *42*, 3041.
- [22] Mukherjee, D.; Ray, P. K.; Chowdhury, U. S. *Tetrahedron Lett.*, **2001**, *42*, 7701.
- [23] Babu, B. S.; Balasubramanian, K. K. *Tetrahedron Lett.*, **2000**, *41*, 1271.
- [24] Yadav, J. S.; Reddy, B. V. S. *Synthesis*, **2002**, 511.
- [25] Yadav, J. S.; Reddy, B. V. S.; Krishnam Raju, A.; Venkateswara Rao, C. *Tetrahedron Lett.*, **2002**, *43*, 5437.
- [26] Yadav, J. S.; Reddy, B. V. S.; Raman, J. V.; Niranjan, N.; Kiran Kumar, S.; Kunwar, A. C. *Tetrahedron Lett.*, **2002**, *43*, 2095.
- [27] Amantini, D.; Fringuelli, F.; Pizzo, F.; Vaccaro, L. *J. Org. Chem.*, **2001**, *66*, 4463.
- [28] Fringuelli, F.; Pizzo, F.; Vaccaro, L. *J. Org. Chem.*, **2001**, *66*, 3554.
- [29] Yadav, J. S.; Reddy, B. V. S.; Sadashiv, K.; Harikishan, K. *Tetrahedron Lett.*, **2002**, *43*, 2099.
- [30] Yadav, J. S.; Reddy, B. V. S.; Mahesh Kumar, G.; Murthy, Ch. V. S. R. *Synthetic Comm.*, **2002**, *32*, 1797.
- [31] Yadav, J. S.; Reddy, B. V. S.; Vishweshwar Rao, K.; Saritha Raj, K.; Prasad, A.R. *Synthesis*, **2002**, 1061.
- [32] Ranu, B.C.; Jana, U. *J. Org. Chem.*, **1998**, *63*, 8212.
- [33] Loh, T. P.; Wei, L. L. *Tetrahedron Lett.*, **1998**, *39*, 323.
- [34] Loh, T. P.; Liung, S. B. K. W.; Tan, K.-L.; Wei, L. L. *Tetrahedron*, **2000**, *56*, 3227.
- [35] Ranu, B.C.; Hajra, A.; Jana, U. *Org. Lett.*, **1999**, *1*, 1141.
- [36] Ranu, B.C.; Dey, S. S.; Hajra, A. *Tetrahedron*, **2002**, *58*, 2529.
- [37] Russowsky, D.; Petersen, R. Z.; Godoi, M. N.; Pilli, R. A. *Tetrahedron Lett.*, **2000**, *41*, 9939.
- [38] Li, C.-J.; Huang, T. *Tetrahedron Lett.*, **2000**, *41*, 9747.
- [39] Sengupta, S.; Mondal, S. *Tetrahedron Lett.*, **2000**, *41*, 6245.
- [40] Aggarwal, V. K.; Martin Castro, A. M.; Mereu, A.; Adams, H. *Tetrahedron Lett.*, **2002**, *43*, 1577.
- [41] Nagarajan, R.; Perumal, P. T. *Tetrahedron*, **2002**, *58*, 1229.
- [42] Ranu, B. C.; Hartley, J. P.; Whittle, A. J. *Synlett*, **2001**, 6, 830.
- [43] Frost, C. G.; Hartley, J. P.; Griffin, D. *Tetrahedron Lett.*, **2002**, *43*, 4789.
- [44] Frost, C. G.; Hartley, J. P.; Griffin, D. *Synlett*, **2002**, *11*, 1928.
- [45] Yadav, J. S.; Reddy, B. V. S.; Srinivasa Rao, R.; Veerendhar, G.; Nagaiah, K. *Tetrahedron Lett.*, **2001**, *42*, 8067.
- [46] Yadav, J. S.; Reddy, B. V. S.; Abraham, S.; Sabitha, G. *Tetrahedron Lett.*, **2002**, *43*, 1565.
- [47] Yadav, J. S.; Reddy, B. V. S.; Parimala, G. *Synlett*, **2002**, *7*, 1143.
- [48] Yadav, J. S.; Reddy, B. V. S.; Mahesh Kumar, G.; Madan, C. *Synlett*, **2001**, *11*, 1781.
- [49] Yadav, J. S.; Reddy, B. V. S.; Abraham, S.; Sabitha, G. *Tetrahedron Lett.*, **2001**, *42*, 8063.
- [50] Yadav, J. S.; Reddy, B. V. S.; Abraham, S.; Sabitha, G. *Synthesis*, **2001**, *14*, 2165.
- [51] Bandini, M.; Melchiorre, P.; Melloni, A.; Umani-Ronchi, A. *Synthesis*, **2002**, *8*, 1110.
- [52] Loh, T. P.; Wei, L. L. *Synlett*, **1998**, 975.
- [53] Loh, T. P.; Wei, L. L. *Tetrahedron*, **1998**, *54*, 7615.
- [54] Bandini, M.; Cozzi, P. G.; Giacomini, M.; Melchiorre, P.; Selva, S.; Umani-Ronchi, A. *J. Org. Chem.*, **2002**, *67*, 3700.
- [55] Loh, T. P.; Tan, K.-T.; Hu, Q.-Y. *Angew. Chem. Int. Ed.*, **2001**, *15*, 2921.
- [56] Loh, T. P.; Tan, K.-T.; Hu, Q.-Y.; Chok, Y.-K. *Tetrahedron Lett.*, **2001**, *42*, 9277.
- [57] Loh, T. P.; Pei, J.; Lin, M. *Chem. Commun.*, **1996**, 2315.
- [58] Ali, T.; Chauhan, K. K.; Frost, C. G. *Tetrahedron Lett.*, **1999**, *40*, 5621.
- [59] Babu, G.; Perumal, T. *Tetrahedron*, **1998**, *54*, 1627.
- [60] Babu, G.; Perumal, T. *Tetrahedron Lett.*, **1998**, *39*, 3225.
- [61] Zhang, J.; Li, C.-J. *J. Org. Chem.*, **2002**, *67*, 3969.
- [62] Yadav, J. S.; Reddy, B. V. S.; Srinivasa Rao, R.; Kirin Kumar, S.; Kunwar, A. C. *Tetrahedron*, **2002**, *58*, 7891.
- [63] Loh, T. P.; Hu, Q.-Y.; Ma, L.-T. *J. Am. Chem. Soc.*, **2001**, *123*, 2450.
- [64] Loh, T. P.; Tan, K.-T.; Hu, Q.-Y.; Cheng, H.-S. *Org. Lett.*, **2001**, *17*, 2669.
- [65] T. P. Loh, L.-F. Feng and J.-Y. Yang; *Synthesis*, **2002**, *7*, 937-940.
- [66] Ranu, B. C.; Hajra, A.; Jana, U. *J. Org. Chem.*, **2000**, *65*, 6270.
- [67] Fu, N.-Y.; Yuan, Y.-F.; Cao, Z.; Wang, S.-W.; Wang, J.-T.; Peppe, C. *Tetrahedron*, **2002**, *58*, 4801.
- [68] Muthusamy, S.; Babu, S. S.; Gunanathan, C. *Tetrahedron Lett.*, **2002**, *43*, 3133.
- [69] France, S.; Wack, H.; Hafez, A. M.; Taggi, A. E.; Witsil, D. R.; Lectka, T. *Org. Lett.*, **2002**, *9*, 1603.