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Advancing Sustainability: Reusable Indium Catalysts for Green Organic Transformations

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ABSTRACT

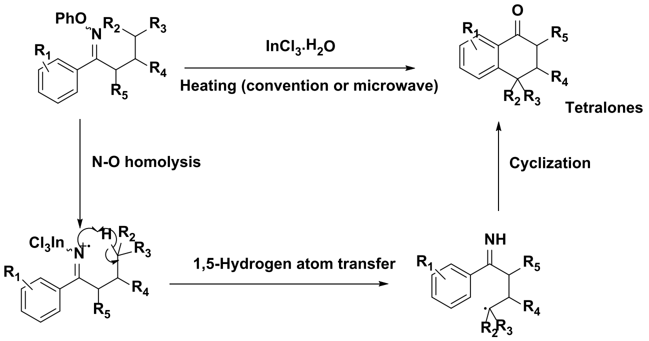
Sustainable chemistry aims to minimise environmental impact by designing efficient, eco-friendly processes, with catalysis playing a crucial role. Reusable catalysts enhance sustainability by allowing recovery, regeneration, and repeated use, which reduces resource depletion and operational costs. This chapter explores different methods for attaching homogeneous indium salts, e.g., ionic bonding with an ionic liquid, complexation with functionalised polymers like polyaniline, and integration into metal-organic frameworks (MOFs). Additionally, it provides a detailed discussion on the application of indium-based reusable catalysts in various organic transformations, along with their recovery and recyclability.

Keywords: *A3-Coupling; Aza-Michael Reaction; Indium Catalysis; Ionic Liquid; Metal-Organic Framework; Polyaniline; Strecker Reaction*

Introduction

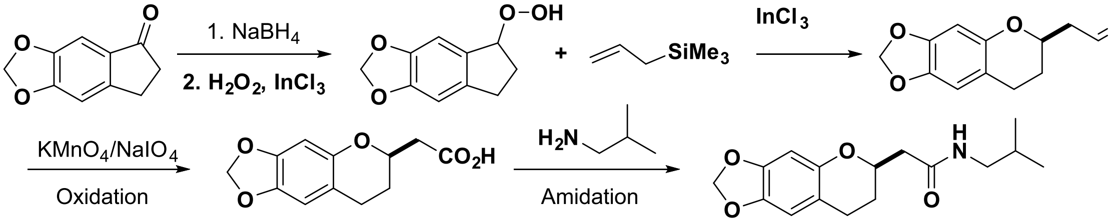
Catalytic reactions by indium salts are of immense importance in synthesising organic molecules of importance (Datta, 2021; Singh & Raghuvanshi, 2012). A Vast range of organic transformations is reported using homogeneous Indium catalysts as indium chloride is equally compatible with water and organic solvents. Moreover, Indium salts are stable in the presence of oxygen and nitrogen-containing nucleophiles (Cintas, 1995).

Recently, Jones *et al*. (2025) reported the synthesis of diversified tetralones, which is an important class of organic compounds via $InCl_3$-catalysed N-O homolysis-1,5- hydrogen atom transfer-cyclisation from O-phenyloximes (Scheme 1).



Scheme 1: Synthesis of Tetralones

In 2023, Bosnidou *et al*. reported “Tandem InCl3-Promoted Hydroperoxide Rearrangements and Nucleophilic Additions” as a strategy to synthesise different benzoxacycles such as erythrococcamide B (Scheme 2).



Erythrococcamide B

Scheme 2: Synthesis of Erythrococcamide B

Recent developments of indium chloride-catalysed synthesis of heterocycles are well depicted in the recent ACS Omega review by Mahato et al. (2020). Figure 1 summarises the wide application of $InCl_3$ in the synthesis of heterocycles.

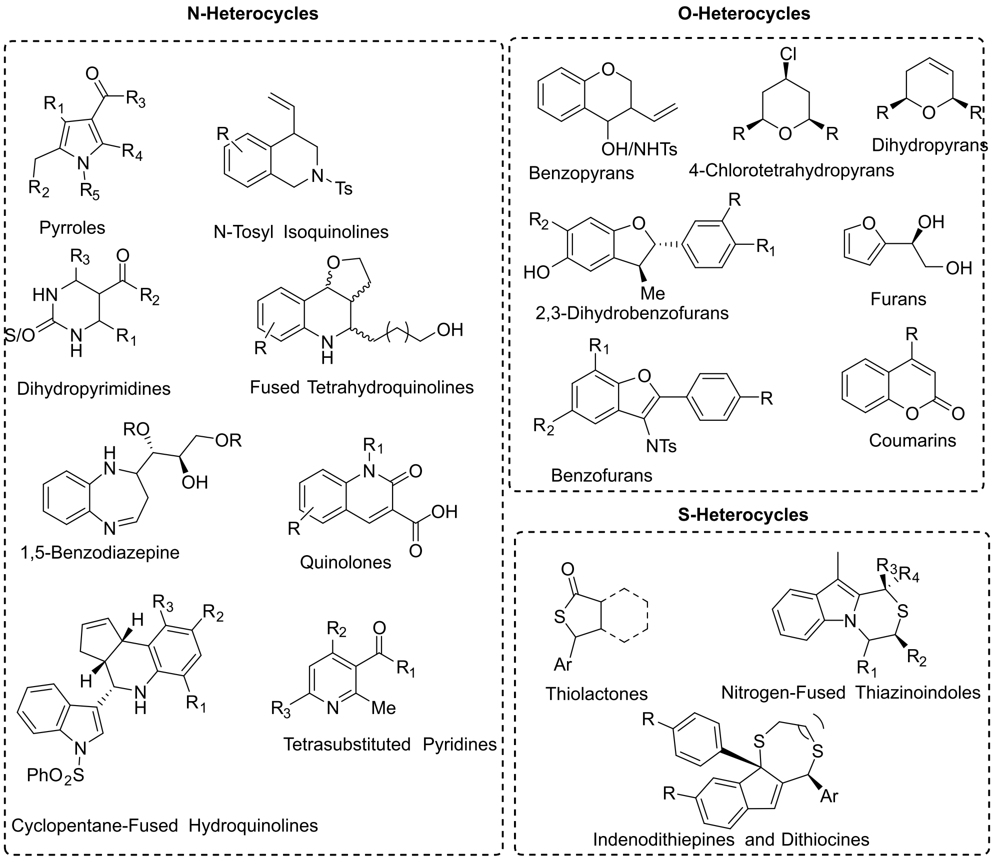


Figure 1: Selected Application of Indium Catalysis in the Synthesis of Heterocycles

As discussed, $InCl_3$ is a versatile catalyst and has found widespread application and acceptance among the organic synthetic community (Table 1).

Table 1: Representative Examples of the Homogeneous Indium Catalysis

Sl. No	Reaction Type	Reference
1	Aaz-Diels alder reaction	1. Sridharan *et al*., 2007 2. Li, Zhang & Li, 2003.
2	Aza-Michael reaction	Selvi & Velmathi, 2018
3	Strecker reaction	Shen, Ji & Loh, 2008
4	Mannich reaction	Loh & Wei, 1998
5	Sakurai reaction	Pinet, Figadère & Ferrié, 2020
6	Meyer-Schuster rearrangement of propargylic alcohols	Francos *et al*., 2015
7	Glycosylation	Yang *et al*., 2025
8	Thiolysis of α,β-Epoxycarboxylic Acids	Fringuelli *et al*., 2005
9	Cyclotrimerization of Alkynes	Xu *et al*., 2011
10	Selective Reduction of the *α,β*-Carbon−Carbon Double Bond in Highly Activated α,β,γ,δ-Unsaturated Alkenes	Ranu & Samanta, 2003

For sustainability and green chemistry, reusable catalysts are preferable to their homogeneous counterparts due to their obvious advantages, such as reduced waste and lower cost.

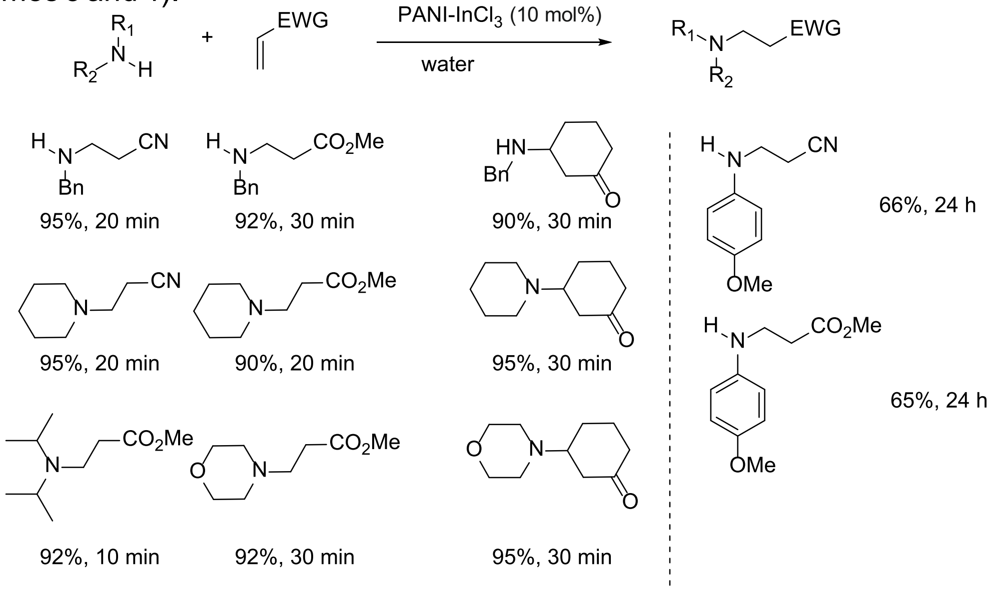
Reusable Indium Catalysis

Immobilized Indium Catalyst on Polyaniline Support and Used in Aza-Michael and Aza-Diels-Alder Reaction

Aza-Michael and aza-Diels-Alder reactions are efficient tools for organic chemists to synthesise complex molecules. In his two important reviews on the aza-Michale reaction, Rulev (2011, 2023) aptly captured the development and use of the aza-Michael reaction. Aza-Diels alder reaction is an equally important method for accessing biologically important molecules (Cao, Green & Xu, 2017).

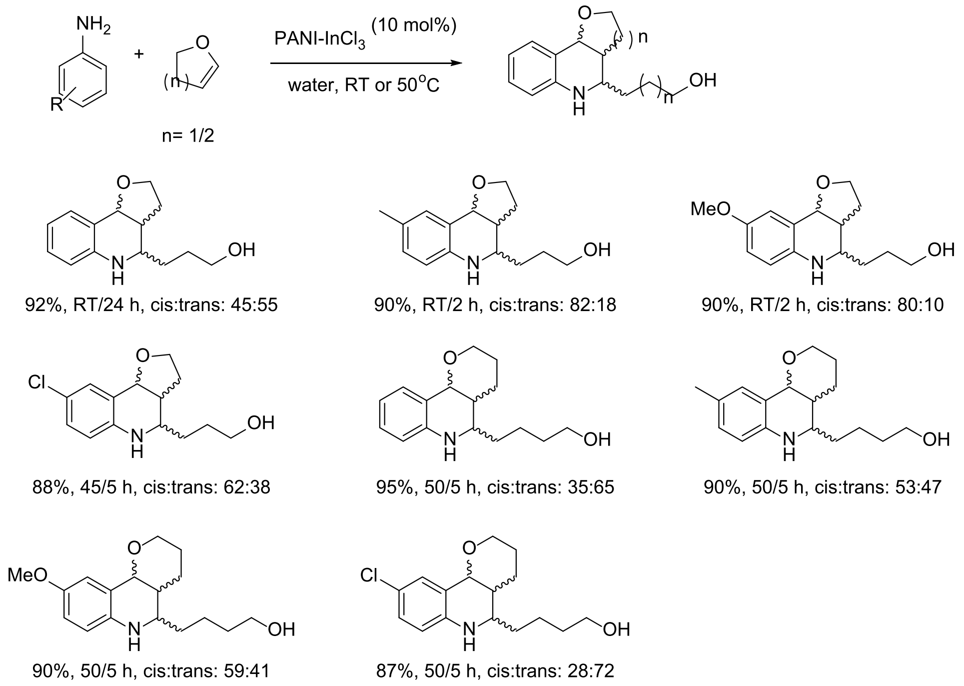
The immobilisation of metal salts onto a functionalised polymer is a well-established strategy to prepare new heterogeneous catalysts. Kantam *et al*. (2007) used an indium chloride solution in acetonitrile and polyaniline base to prepare a polyaniline-supported indium catalyst (PANI-In). It has been extensively characterised by FTIR, XPS, scanning electron microscopy–energy dispersive X-ray spectroscopy, and inductively coupled plasma atomic emission spectroscopy. FTIR showed a new peak at 1136 cm^{-1}, indicating the complexation of indium with polyaniline. X-ray photoelectron spectroscopy clearly showed the presence of Indium and Chlorine as revealed by a peak In 3d5/2 at 445.17 eV and Cl 2p at 198.58 eV. Scanning electron microscopy (SEM) analysis showed a very low deformation of the polymeric structure of the polyaniline backbone. Energy dispersive X-ray and inductively coupled plasma-atomic emission spectroscopy were used to analyse the indium content, which was ~0.67 mmol/g.

The as-synthesised PANI-In catalyst was explored in two different organic transformations: the Aza-Michael reaction and the aza-Diels-Alder reaction in water (Schemes 3 and 4).



Scheme 3: Aza-Michael Reaction Catalyzed by PANI-In

Aza-Michael reaction of aliphatic amines was quicker in comparison with aromatic amines, and mono-selectivity was very high wherever applicable.



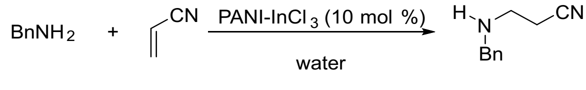
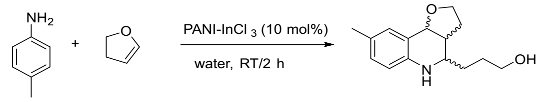
Scheme 4: Aza-Diels-Alder Reaction Catalyzed by PANI-In

The Aza-Diels-Alder reaction of substituted anilines with dihydrofuran or dihydropyran efficiently yielded tetrahydroquinolines in high yield.

Reusability

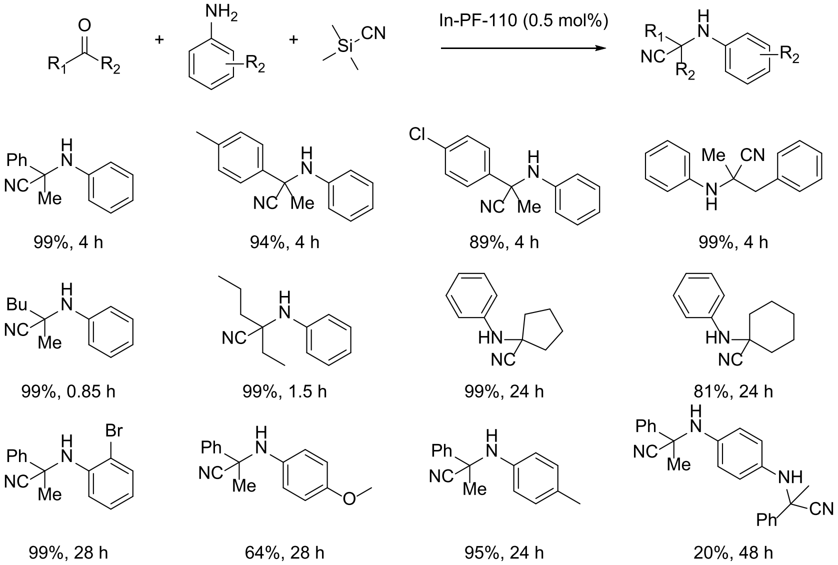
PANI-In was recovered by filtration and reused multiple times with minimal loss activity in both the aza-Michael and aza-Diels-Alder reactions (Table 2).

Table 2: Recyclability of PANI-In Catalysts

Aza-Michael		**Aza-Diels-Alder**	
			
Cycle	Yield (%)	Cycle	Yield (%)
1	95	1	90
6	92	6	87

Indium-Based Metal-Organic Framework (MOF) Catalysts for Organic Transformations

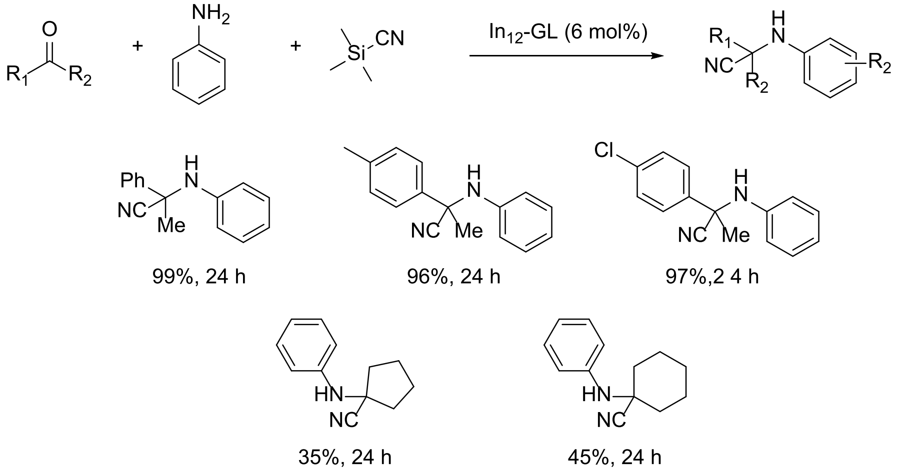
Recently, MOFs are getting considerable attention for their unique properties and catalytic activities. Reinares-Fisac *et al*. (2016) synthesised indium-based MOF and showed its excellent catalytic activity in the Strecker reaction of ketones. Strecker synthesis provides easy access to α-aminonitriles, which are important intermediates for the synthesis of many organic compounds, mainly amino acid derivatives. The catalyst was prepared from $In(NO_3)_3$ and 1,3,5-tris(4-carboxyphenyl) benzene, and it was denoted as InPF-110 (indium polymeric framework). It was well characterised by XRD and TPD for Brunauer−Emmett−Teller surface area. It is mesoporous in nature. The catalyst was employed in the Strecker reaction of ketones (Scheme 5).



Scheme 5: Strecker Reaction Using InPF-110

α-Aminonitriles were afforded in good yield. The catalyst was filtered off and recycled 10 times in the reaction of acetophenone, aniline, and trimethylsilyl cyanide. Very consistent yield was obtained even after the 10th cycle (1st : 98%, 2nd : 98%; 3rd: 97%, 4th : 98%; 5th : 99%, 6th : 99%, 7th: 99%, 8th : 95%, 9th : 94%, 10th : 91%).

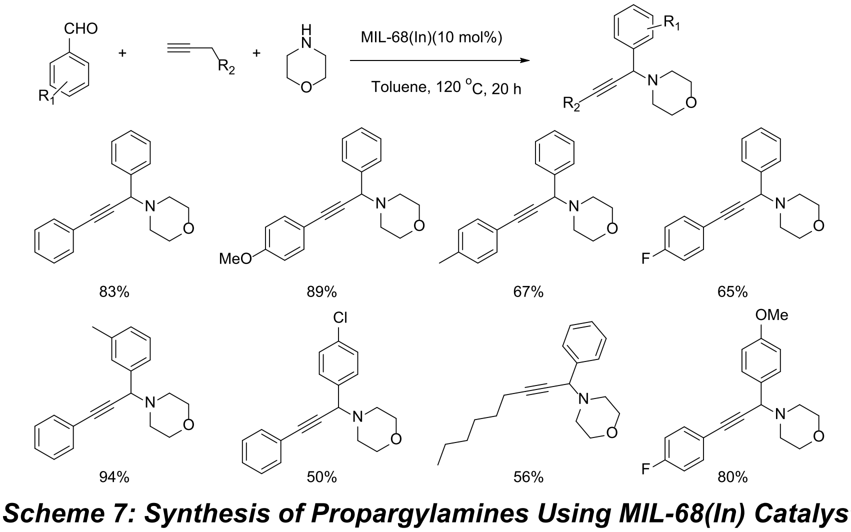
Liang *et al*. (2020) prepared another indium-based MOF In12-GL, and used the catalyst for the Stecker synthesis. Details are captured in Scheme 6.



Scheme 6: Strecker Reaction Using In12-GL Catalyst

In12-GL exhibited minimal reduction in activity even after five cycles in the Strecker reaction involving aniline, acetophenone, and TMS-CN.

Lam *et al*. (2016) investigated another indium-based MOF, MIL-68(In), for its application in propargylamine synthesis. Propargylamines are a significant class of building blocks. MIL-68(In) facilitated the coupling of aldehydes, alkynes, and amines to produce propargylamines (Scheme 7).

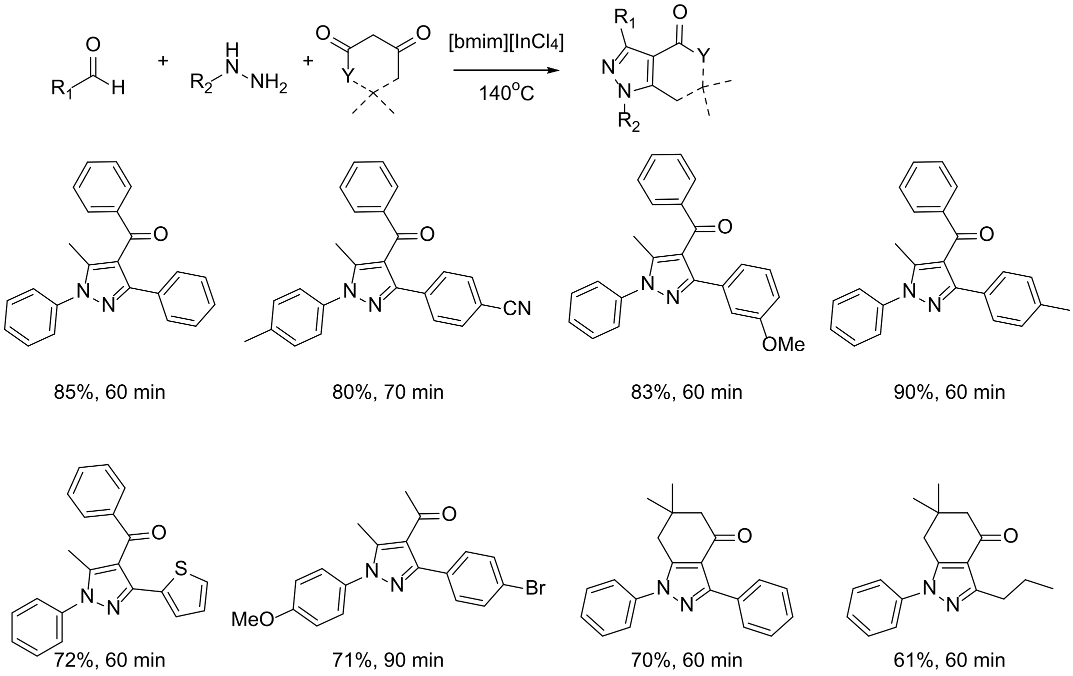


Scheme 7: Synthesis of Propargylamines Using MIL-68(In) Catalyst

MIL-68(In) catalyst was recovered by filtration and reused for seven cycles in the coupling of phenylacetylene, benzaldehyde, and morpholine with similar catalytic efficiency.

Ionic Liquid-Anchored Indium Catalysts

Ionic liquid gained considerable attention for its efficient recovery and solubility for many catalytic systems. Safaei *et al*. (2013) reported a tetrachloroindate-based ionic liquid catalysed efficient and regioselective formation of pyrazoles.



Scheme 8: Synthesis of Substituted Pyrazoles Using [bmim]$[InCl_4]$ Catalyst

Details are presented in Scheme 8. The authors demonstrated that a room-temperature ionic liquid containing an indium catalyst provided superior regioselectivity compared to the homogeneous $InCl_3$ catalyst (100:0 vs. 80:20). Furthermore, the catalyst was efficiently recovered by adding water to the reaction mixture, precipitating the product, and subsequently removing water under reduced pressure. Notably, the catalyst retained its activity over three cycles without any loss.

Conclusion

This review highlights the significance of indium catalysis in organic synthesis and its progression toward sustainability through the development of easily recoverable and recyclable indium catalysts. It discusses three distinct classes of heterogeneous indium catalysis, categorised based on their efficiency and recyclability. This insight is expected to serve as a valuable guide for future advancements in the field of indium catalysis.

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