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Green innovations in C–H bond functionalisation: exploring homogeneous recyclable catalytic systems

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C–H bond functionalisation is a pivotal approach in contemporary fabrication of organic compounds, and enables straightforward transformation of inert C–H bonds exempt from needing pre-functionalisation. Homogeneous recyclable catalytic systems upsurge sustainability by empowering catalyst recovery and reuse. This review combines the advantages of both these protocols by exploring a range of recyclable catalytic systems for functionalisation of C–H bonds, concentrating on green and sustainable approaches. We delve into the utilisation of various media and catalytic systems, including polyethylene glycols (PEG), ionic liquids (ILs), deep eutectic solvents (DESs), micellar systems, biphasic systems and systems allowing simple filtration or extraction to enhance catalytic efficiency and recyclability. The discussion encompasses a variety of metal-based catalysts, including rhodium (Rh), ruthenium (Ru), palladium (Pd), copper (Cu) and cobalt (Co), as well as catalyst-free approaches. The recyclability potential of most of these catalytic systems has also been explored. The atom economy and environmental advantages of employing these recyclable systems are highlighted in this review by giving an extensive overview of these innovative methods. Also, this seeks to motivate further exploration in the realm of functionalisation of C–H bonds and foster the progress of sustainable and environmentally conscious synthetic methods.

Green foundation

1. This review discusses advances in green chemistry through homogeneous recyclable catalytic systems for C–H bond functionalisation, including the use of sustainable media. It highlights efficient recovery and reuse of metal catalysts as well as metal-free methods promoting sustainable organic synthesis.
2. The study addresses a critical aspect of modern organic synthesis, C–H bond functionalisation, while emphasising on green and sustainable methodologies. By highlighting homogeneous recyclable catalytic systems that combine the benefits of both homogeneous and heterogeneous catalysis, this review aligns with green chemistry principles by incorporating environmentally friendly media, recyclability, waste minimisation, and atom economy, advancing the field.
3. Although notable homogeneous recyclable catalytic systems for C–H functionalisation have been developed, further work is needed to improve efficiency, scalability, substrate versatility, and the scope for other transition metals. Optimisation for industrial applications, cost-effectiveness, and reduced energy consumption with enhanced catalyst reuse remains a key focus.

1. Introduction

While functional group interconversion is a renowned and vital technique in organic synthesis, its conventional applications often lead to significant waste generation. This is because achieving the anticipated functional group through interconversion frequently requires multiple sequential reactions, starting from a previously functionalised molecule. Subsequently, the fine chemical and pharmaceutical sectors are encountering substantial environmental pressure, driving them to seek ways to minimize or eliminate waste, as well as avoid hazardous and cumbersome methodologies. Thus,

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modern-day chemistry has focused noteworthy effort on developing ideal synthetic tactics that are efficient, economical, and environmentally friendly for the development of complex molecules.

In this regard, C–H activation represents a groundbreaking tactic in the development of organic compounds, allowing straightforward transformation of inactive C–H bonds that do not require pre-functionalisation of substrates (Fig. 1).[1–9] Unlike traditional approaches, activation of C–H bonds avoids preliminary functionalisation (for instance, halogenation or borylation) of the target molecules that reduces the number of steps. Ideally, multiple step synthesis could thus be modified into single-step synthesis allowing a straightforward approach to projected frameworks, thus decreasing the quantity of undesirable refuse of multistep transformations. This stands out as a greener and more sustainable tactic in chemical synthesis owing to its inherent alignment with the principles of green chemistry.[8] This method significantly improves atom economy and step economy, diminishing the need for pre-functionalised starting materials and their associated waste streams.[2,4,8] This decrease in synthetic steps and the avoidance of stoichiometric byproducts directly address the principle of waste prevention.[2,8] The current development of catalytic systems based on Earth-abundant metals and the investigation of milder reaction conditions, along with the use of greener solvents, actively endorse the principles of catalysis, energy efficiency design, safer solvents and accident prevention. Practically, the evolution of C–H activation methodologies towards more selective, efficient, and environmentally benign procedures represents a commitment to the core tenets of green chemistry, paving the way for more sustainable chemical transformations.

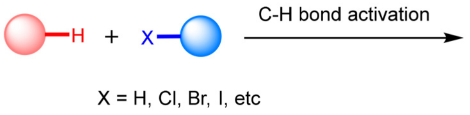

Fig. 1 Schematic representation of C–H activation reactions.

Transition metal catalysis plays a vital role by enabling precise regioselectivity and reactivity.[10–20] This practice has become pivotal for assembling complex molecules in pharmaceuticals, agrochemicals, and advanced materials.[21–28] Homogeneous catalytic systems are employed in the majority of these reactions.

Homogeneous catalytic systems offer numerous compensations, with meticulous regulation of reaction parameters, resulting in higher selectivity and yield. They facilitate molecular-level tunability, and often operate under milder conditions. Moreover, they allow better interaction with substrates, attaining transformations not possible with heterogeneous systems.[29–32] On account of its remarkable activity and selectivity, homogeneous catalytic systems have several industrial applications and can be significantly more efficient than their corresponding heterogeneous counterparts.[33] Conversely, heterogeneous catalysis shows reduced reactivity and selectivity, mainly due to the restricted accessibility of active sites. These confines are associated with steric hindrances imposed by support matrices and mass transport constraints, as active sites are often deeply embedded within these structures, impeding reactant access.[34]

Although homogeneous catalysis outperforms in reactivity and selectivity, it often faces limitations in catalyst recovery and recycling. In order to get over this, researchers have developed heterogeneous catalytic systems, providing efficient and reusable replacements for chemical transformations including C–H bond functionalisation.[35–37] Nonetheless, a significant impediment in the employment of heterogeneous catalytic setups is the potential catalyst percolation into the reaction medium, which consequently limits its applicability. Furthermore, homogeneous catalysts exhibit additional advantages, including markedly elevated turnover number and turnover frequency.

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Sanjay Singh, born in Ramban, Jammu and Kashmir, India, earned his Master's degree from the University of Jammu and completed his Ph.D. at the Indian Institute of Technology Delhi, India, under the guidance of Prof. Ravi P. Singh. In 2024, he embarked on his independent academic career at Pandit Deendayal Energy University (PDEU), Gandhinagar, Gujarat, India. Currently, Dr Singh is a Postdoctoral Research Associate at the Institute for Basic Science (IBS), KAIST, South Korea, in Prof. Sungwoo Hong's group, where he is focusing on sustainable asymmetric catalysis using 3d transition metals.

The recyclability constraint in homogeneous catalysis considerably impedes its large-scale application, making it pivotal to enhance the reuse of these catalytic systems. Enhanced recyclability can lower costs and minimize waste, thus encouraging the sustainable production of fine chemicals. Consequently, alternatives that not only enhance catalyst recycling but also maintain its competitiveness with traditional homogeneous and heterogeneous methods are urgently required. Extensive study is underway to advance strategies that integrate the beneficial properties of both catalyst types. The prime aim is to formulate a catalyst that exhibits a high degree of reactivity, complete product selectivity, stability under specific reaction conditions, and the capacity for recyclability. Accomplishing these properties in catalyst designing and fruitfully applying them at both the laboratory and industrial levels will significantly cut the total reaction system expenditure.

To address the demanding challenge of sustainable catalysis, the emergence of homogeneous recyclable catalytic systems has gathered noteworthy attention as a promising and innovative solution.[38–46] Homogeneous recyclable catalytic systems represent a substantial development in sustainable catalysis by combining the high activity and selectivity frequently associated with homogeneous catalysts with the ease of separation and reuse conventionally characteristic of heterogeneous catalysts. These systems characteristically involve a catalyst that exists in the same phase as the reactants, enabling close contact and efficient transformations. However, contrasting traditional homogeneous catalysts that are frequently challenging to separate from the reaction mixture, recyclable versions are precisely designed with characteristics that allow for their recovery and subsequent use in multiple catalytic cycles. This recyclability not only diminishes the amount of catalyst needed over time, thus lowering costs and minimising waste generation, but also addresses environmental concerns. By enabling catalyst reuse, these systems contribute to greener and more sustainable chemical procedures, in line with the principles of atom economy, waste reduction, *etc.* in modern chemical synthesis.

Researchers have made substantial advancements in strengthening the recyclability of these systems through various strategies, including the use of polyethylene glycol (PEG),[47–53] ionic liquids (ILs),[54–59] micellar catalysis,[60,61] deep eutectic solvents (DESs),[62–66] nanofiltration,[67,68] biphasic systems,[69–71] supported catalysts,[72] supercritical carbon dioxide[73,74] *etc.* all while retaining catalytic activity. By enabling easy separation and reuse, these systems endorse waste minimisation, atom economy, and the employment of environmentally benign solvents, eventually contributing to a more sustainable tactic for chemical processes while reducing waste and cost.

Such homogeneous, recyclable catalytic systems are similarly employed in facilitating C–H functionalisation reactions. This review article provides a summary of current advancements in homogeneous recyclable catalytic systems for C–H bond activations, concentrating on sustainable methodologies and innovative strategies. By highlighting diverse tactics that employ deep eutectic solvents (DESs), ionic liquids, polyethylene glycol (PEG), micellar, biphasic and simple filtration or extraction systems, we aim to illustrate the advancement made toward greener and more efficient synthetic methodologies. By incorporating green chemistry principles, the objective of this review article is to present a cohesive understanding of the breakthroughs in recyclable catalytic systems and their role in promoting environmentally accountable synthetic strategies. The ultimate objective is to recognize trends and investigating the recycling efficiency of various catalytic frameworks for the activation and functionalisation of C–H bonds.

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2. Homogeneous recyclable polyethylene glycol (PEG) media

Among the best recyclable and superior catalytic methodologies for C–H bond functionalisation reaction is the employment of polyethylene glycols (PEGs), which have the potential to substitute conventional solvents in organic chemistry. Due to the peculiar attributes like reduced vapour pressure, cost-effectiveness, thermal stability, and biodegradability, stability under basic and acidic conditions, ready retrieval and less harmful nature, they function as an appropriate solvent for environmentally sympathetic and benign organic transformations.[75–77] Additionally, possessing specific features, PEGs were utilised for immobilizing the catalyst,[78] stabilisation of nanoparticles,[79] ligand and stabilisation[80] and as phase transfer catalysts.[81]

Considering the pre-eminence demonstrated by PEG, an environmentally friendly solvent system, it has been prolifically used as medium in favour of the metal-facilitated cross-coupling reactions in particular Heck reaction,[82] Suzuki reaction,[83,84] the homocoupling and cross-coupling of aryl halides,[85] carbonylative Suzuki coupling,[86] carbonylative Sonogashira coupling,[76] hydrosilylation of terminal alkynes,[87] click reaction of fluorescent organic probes,[88] and one-pot synthesis of chromenes[89] with solvents and precious metals being easily reusable. A concise overview of the innovative aspects and illustrative examples of recycling methods using PEG media for C–H activation reactions that take account of toxicity, cost-effectiveness, technical utility, and sustainable chemistry has been described here.

2.1 C–H functionalisation using ruthenium catalysts in polyethylene glycol

In the year 2015, Cai and co-workers described that the catalytic system [{$RuCl_2$(*p*-cymene)}$_2$], when used within a PEG-400/water combination, competently enables the cross-dehydrogenative C–H alkenylation of benzoic acids **1** with alkenes **2**.[90] The stated protocol established the oxidative alkenylation of benzoic acids using butyl or ethyl acrylates, as well as with acrylonitriles. This system offers an incredibly efficient and ecologically sound method to encourage this transformation, illustrating its potential for deployment in green chemistry applications. A mixture of PEG-400 and H_2O proved more effective than using PEG-400 alone as a solvent. The reaction conducted solely in PEG-400 yielded the desired product at only 61%. In contrast, employing a PEG-400/H_2O (3 : 2) mixture resulted in a significantly improved yield of 95% and reduced the reaction time by half. Furthermore, with an initial Ru catalyst loading of 2 mol%, no additional catalyst was required during the recycling process. A range of derivatives of phthalides can be generated in yields that are good to outstanding during the mild reaction that uses $Cu(OAc)_2 \cdot H_2O$ playing the role of an oxidant while the reaction proceeds at a temperature of 80 °C (Scheme 1).

In an extensive examination of catalyst reusability, 2-methylbenzoic acid and butyl acrylate were employed to evaluate oxa-Michael addition and oxidative alkenylation as a tandem reaction under the influence of [{$RuCl_2$(*p*-cymene)}$_2$] (2.0 mol%) and $Cu(OAc)_2 \cdot H_2O$ (2 eq.) in a PEG-400/H_2O mixture (3 : 2, 5 g) at 80 °C. Having high yields (ranging from 93% to 96%) across every cycle, the catalytic system demonstrated remarkable stability over the course of six successive reaction runs (Fig. 2). Equivalent activity and yields were constantly demonstrated over multiple runs in the reaction between 2,4-dimethylbenzoic acid and acrylonitrile under the same conditions. Ultimately, there was no discernible decrease in catalytic activity during recycling and reusing the catalysts for both of the reactions.

Zhu and co-workers reported a similar protocol as depicted in Scheme 1 utilising a rhodium catalyst where catalyst recycling was not a priority.[91] Their method involved the use of Rh as a catalyst and employed a higher catalyst loading com-

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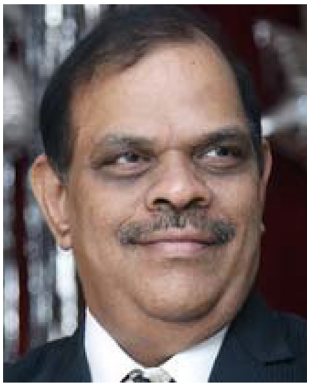

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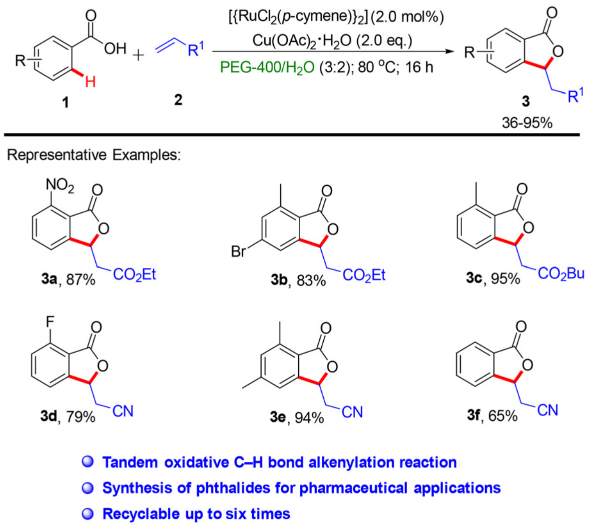
Bhalchandra M. Bhanage obtained his doctorate from Pune University in 1996. He is a Professor of Industrial and Engineering Chemistry at the Institute of Chemical Technology, Mumbai, India. His research interest includes developing novel catalytic systems for carbonylation, CO_2 fixation for valuable chemicals, asymmetric hydrogenation of ketones, hydroformylation, various coupling reactions, amination reactions, C–H activation etc. He is also working on nanomaterials, enzymatic catalysis and the use of non-conventional techniques like ultra-sound and microwaves for various reactions.



Scheme 1 Alkenylation of benzoic acids by the ruthenium catalyst in PEG-400/water medium.

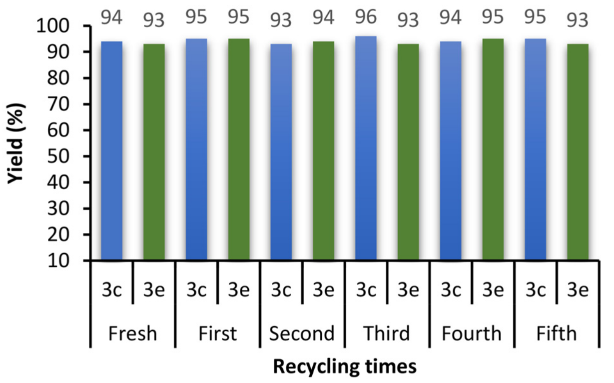
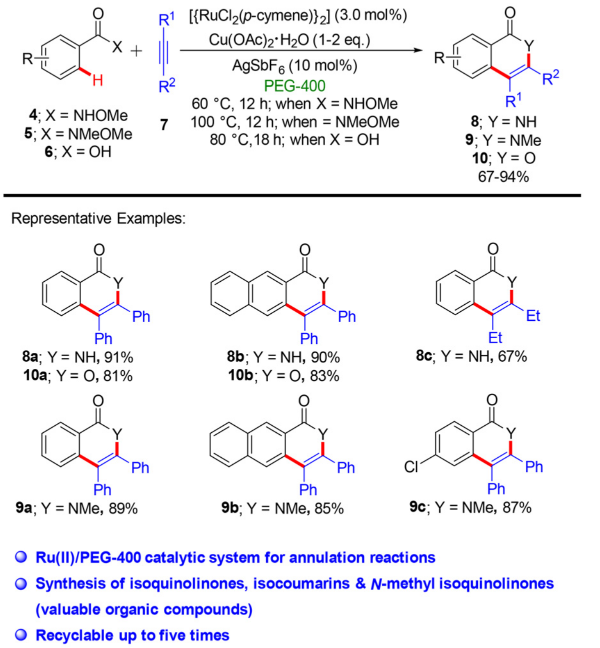
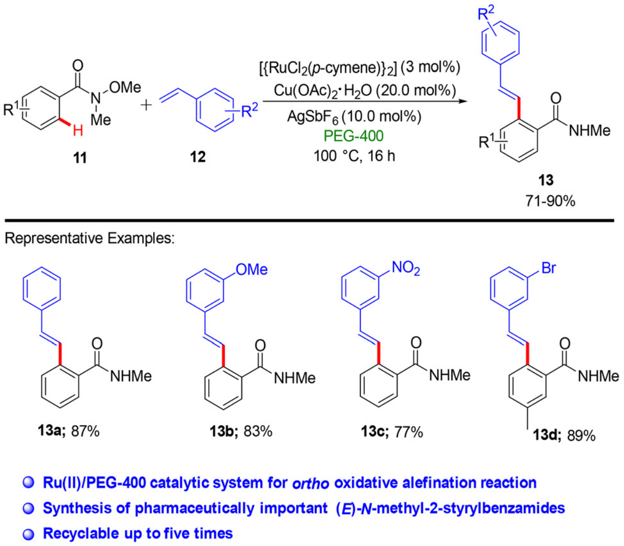


Fig. 2 Recycling study of the [{RuCl$_2$(*p*-cymene)}$_2$]/Cu(OAc)$_2$·H$_2$O/PEG-400/H$_2$O catalytic system designed for the alkenylation reactions.



Scheme 2 Annulation reactions of amides and acids with alkynes catalysed by ruthenium.



Scheme 3 Ru-catalysed olefinations of Weinreb amides.

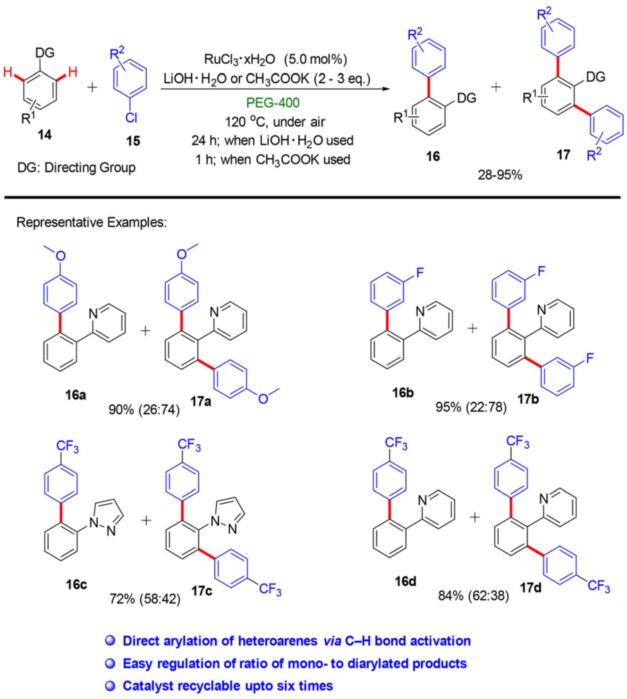
pared to the protocol outlined in Scheme 1. Furthermore, the reported yields were also comparable. An advantage associated with this scheme is the use of water as a green and sustainable solvent.

Later in the subsequent year, Yedage and colleagues defined an effective and sustainable method for annulation and olefination through C–H bond activation employing Ru(II) in PEG-400 as a reusable and green catalytic system.[92] They reported oxidation-driven annulations of *N*-methoxybenzamides **4** and benzoic acids **6** with alkynes catalysed by ruthenium to synthesize isoquinolinones **8** and isocoumarins **10**, respectively (Scheme 2). Additionally, they conducted annulation reactions of *N*-methoxy-*N*-methylbenzamides **5** catalysed by ruthenium in order to synthesize *N*-methyl isoquinolinones **9** (Scheme 2). Oxidative olefination of Weinreb amides **11** catalysed by ruthenium was also carried out (Scheme 3). The recyclable solvent system based on PEG-400 proved to be more effective than other tested PEG solvents (PEG-200, PEG-600, PEG-2000, and PEG-6000). Interestingly, the addition of water to PEG-400 did not enhance its performance, and a 3 mol% initial Ru catalyst loading eliminated the need for further additions during recycling. This protocol enables the regioselective and stereoselective formation of fresh C–C, C–O, and C–N bonds through a one-step cleavage of C–H, N–H, O–H and N–O bonds. The established technique reveals key sustainable features, including moderate reaction conditions, high atom economy, and the ability to reuse the expensive ruthenium-based homogeneous catalyst. Significantly, the method is scalable to the gram level with a simple extraction process, making it appropriate for large-scale synthesis.

The reusability of Ru(II) in the PEG-400 catalyst setup was systematically inspected for annulation and *ortho*-olefination reactions of amides with alkynes and styrenes. During the reaction, a notable colour change from brown to blue directed completion, and phase separation enabled simple catalyst and product recovery. The catalytic system, after being cooled and treated with diethyl ether, was reused for subsequent reaction cycles, representing consistent catalytic activity until the fourth cycle with minimal decrease in yield. For instance, the yields of **8a**, **10a**, **9a**, and **13a** remained above 86% after four cycles (Fig. 3).

Guimond and co-workers described a related protocol with Scheme 2 employing a rhodium catalyst,[93] but catalyst recovery was not a focus of their work. While their method used rhodium, it required a lower catalyst loading than the procedure detailed in Scheme 2. However, the reported product yields of both the methodologies were broadly similar.

In 2017, Li and co-workers introduced a straightforward and recyclable catalytic framework for activating C–H bonds to directly arylate heteroarenes **14** with aryl chlorides **15**, employing $RuCl_3{\cdot}xH_2O$ as a cost-effective catalyst and PEG-400 as a sustainable solvent (Scheme 4).[94] Initial solvent screening revealed the unsuitability of toluene and water for the generation of the target products. While ethylene glycol afforded a moderate yield of 57%, methanol proved ineffective for direct arylation, likely due to its low boiling point limiting the achievable reaction temperature. Polyethylene glycol (PEG) demonstrated superior performance as a solvent compared to ethylene glycol and offered the additional advantage of recyclability over other tested solvents. Furthermore, the potentially weak interaction between PEG and the ruthenium species might enhance reactivity, drawing a parallel to the coordination effects observed with crown ethers and ruthenium catalysts. The system required no additional ligands or additives showing outstanding compatibility of functional groups, and the ratio of mono- to diarylated products could be effortlessly controlled by regulating reaction parameters. Additionally, the transformation progressed efficiently under ambient air conditions, and the reaction could be scaled up to gram quantities with a minimal loading of the catalyst (0.3 mol%).



Scheme 4 *ortho* arylation of heteroarenes catalysed by ruthenium.

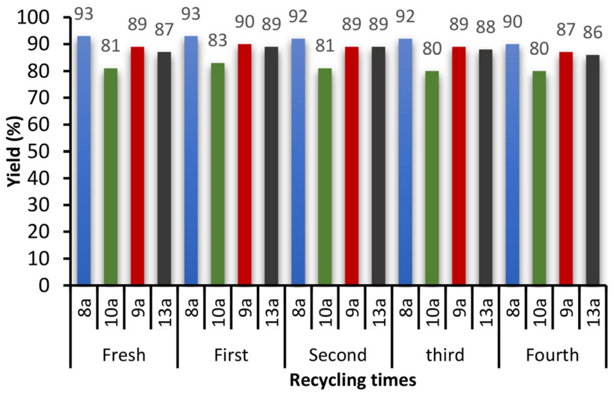


Fig. 3 Recyclability of Ru catalyst for the annulations and olefination reactions.

The recycling potential of the catalytic system was examined by performing a sequence of recycling experiments. For each cycle, the reaction was executed by stirring a combination of 2-phenylpyridine, 1-chloro-3-fluorobenzenes, and $LiOH{\cdot}H_2O$ in PEG-400 containing 5 mol% $RuCl_3{\cdot}xH_2O$ at 120 °C under air for 24 hours. Subsequent to completion, diethyl ether (50 mL) was used to extract the reacting mass when it reached ambient temperature. The recovered PEG solution, comprising the catalyst, was directly reused by adding fresh reactants under similar conditions. Even after six consecutive cycles, the system preserved a high yield of 85%; however a gradual decline in selectivity was detected (Fig. 4).

During the same time, Cai and colleagues again established the competence of a ruthenium-based catalytic system, $[Ru_2Cl_3(p\text{-cymene})_2][PF_6]$, during the oxidation-induced annulation of alkynes **19** with *N*-2-pyrimidyl-substituted anilines **18** to produce indoles **20** (Scheme 5).[95] The reaction occurs effectively in a PEG-400 and water mixture at 100 °C, employing Cu $(OAc)_2{\cdot}H_2O$ as an oxidising agent. The PEG-400/H_2O solvent system demonstrated superior performance compared to other tested systems for these reactions, exhibiting higher product yields and faster reaction times. While using pure PEG-400 as the solvent resulted in a 53% yield of the target product, employing a 3 : 2 mixture of PEG-400 and H_2O significantly improved the outcome, yielding 93%. For catalyst recycling, the reaction was initially performed with 3 mol% of Ru catalyst, and subsequent reaction runs were conducted by simply adding fresh substrates without replenishing the catalyst.

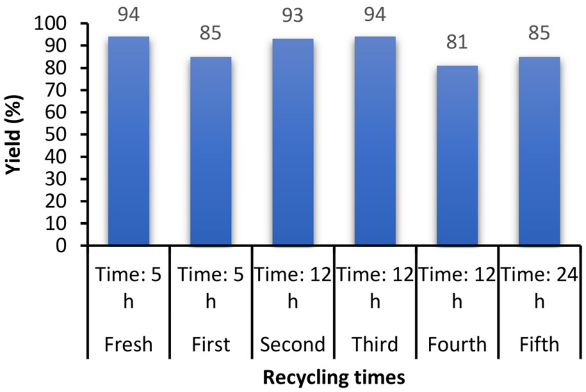
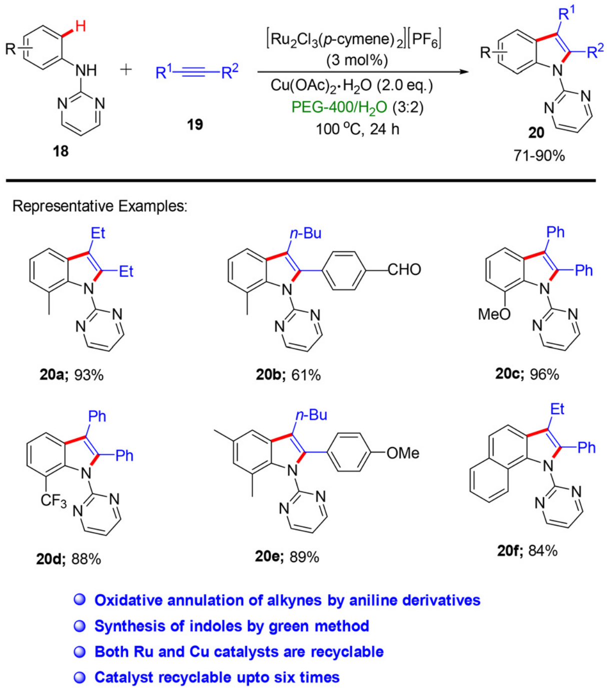


Fig. 4 Recycling study of the Ru catalyst for direct arylation reaction.

To test the robustness of this recyclable system, the annulation of 2-methoxy-*N*-(2-pyrimidyl)aniline using an internal alkyne (diphenylacetylene) was employed as a prototypical reaction. Product isolation is conveniently attained by extraction with petroleum ether, further contributing to the practicality of the method. Under these conditions, the catalytic system showed outstanding reusability, with both the $[Ru_2(p\text{-cymene})_2Cl_3][PF_6]$ catalyst and $Cu(OAc)_2$ oxidising agent being recycled and re-utilised as long as six times without any considerable decline in the performance of the catalyst. Steady yields were obtained over six successive runs (96%, 94%, 96%, 95%, 95%, and 94%, respectively) with minimal variation in reaction time (Fig. 5). This result highlights the stability and efficacy of the catalytic system.



Scheme 5 Preparation of indoles by annulation reaction catalysed by ruthenium.

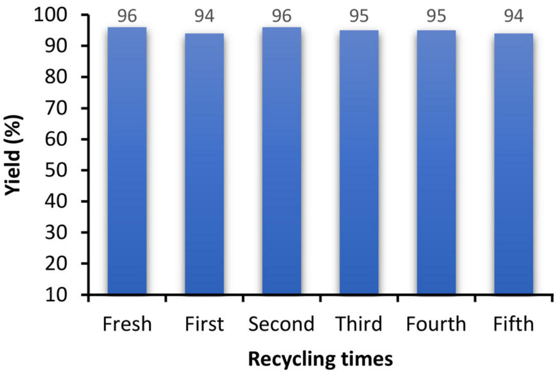
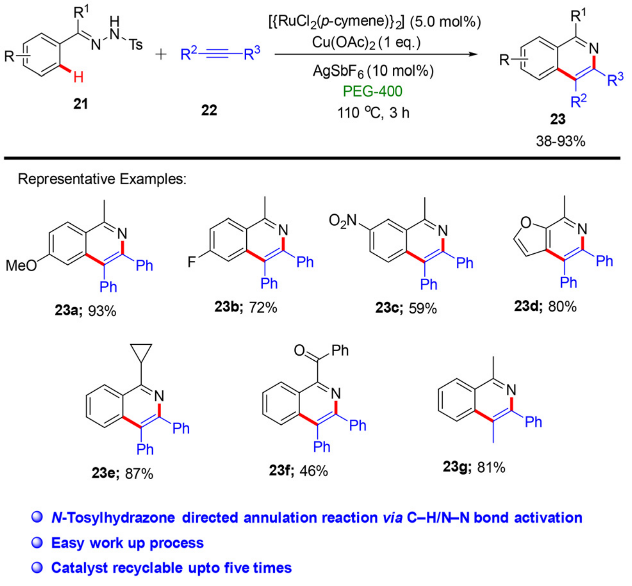


Fig. 5 Recycling study of the Ru-catalysed annulation of 2-methoxy-*N*-(2-pyrimidyl)aniline using an internal alkyne.

Later, a study by the Bhanage group offers an environmentally friendly and sustainable approach in order to generate isoquinoline derivatives **23** employing a homogeneous reusable Ru(II)/PEG-400 catalytic system (Scheme 6).[96] This method employs *N*-tosylhydrazone **21**, a seldom utilised directing group, to enable annulation reactions using alkynes **22** through C–H/N–N activation. Initially, 1,2-DCE proved to be an efficient solvent for the proposed protocol giving 76% product yield. However, this solvent could not be applied for recyclability, so in order to achieve recyclability, evaluation of various polyethylene glycols (PEG-200, PEG-600, PEG-2000, and PEG-6000) revealed that only the lower molecular weight PEGs, specifically PEG-200 and PEG-600, were effective in driving the reaction to completion. The reaction proceeded smoothly in biodegradable PEG-400, affording the desired product in a gratifying 74% yield with additional merits of recyclability and greener media.



Scheme 6 Ruthenium-catalysed annulation reactions between *N*-tosylhydrazones and internal alkynes.

The main strengths of these procedures encompass a quick reaction period, an easy extraction procedure, extensive variety of substrates and exceptional yields of products, as well as readily accessible substrates. The usage of biodegradable solvents and the scalability of the system to gram levels additionally improve its sustainability and competence.

The potential for the reuse of the Ru(II) in PEG-400 system was thoroughly verified performing the cyclisation reaction of 4-methyl-*N*′-(1-phenylethylidene)benzenesulfonylhydrazide using diphenylacetylene under standard conditions. With an initial Ru catalyst loading of 5 mol%, subsequent recycling of the catalyst proceeded without the need for any further additions. After the reaction completion, the reaction composition was retrieved using diethyl ether, while the leftover PEG-catalyst layer was reutilised for successive cycles. The catalyst was able to preserve consistent yields (86%, 86%, 85%, and 83%) over four successive cycles with minimal reduction in yield owing to product loss during the work-up (Fig. 6).

Extending their work, the same research group reported a green and atom-efficient protocol for synthesising isoquinolines **26** and isoquinolinones **28** using a reusable ruthenium catalyst in polyethylene glycol (PEG) solvent, aided by microwave energy.[97] Using the proposed catalytic system, ketazines **24** first underwent an annulation reaction with internal alkynes **25** (Scheme 7). Then, a novel approach was employed, utilising dibenzoylhydrazine **27** for the first time as a directing group in the annulation reaction with internal alkynes **25** (Scheme 8). Under comparable reaction conditions, a range of reaction media, such as PEG-200, PEG-600, and ethylene glycol, were evaluated. However, PEG-400 showed superior efficacy. Specifically, employing PEG-400 as the solvent yielded the target product with an 89% yield. In contrast, the utilisation of alternative solvents led to considerably diminished yields or a complete absence of the desired compound. The approach is environmentally gentle, necessitating no external oxidant or silver/antimony salts, and offers high atom economy with an easy extraction procedure. The reaction completes quickly due to microwave assistance, dropping the overall reaction time. It also establishes broad substrate compatibility, gram-scale synthesis potential, and steadily high product yields.

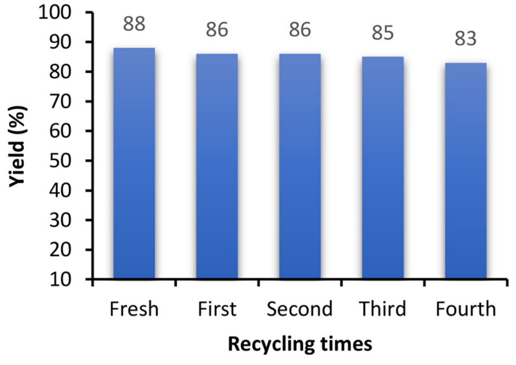
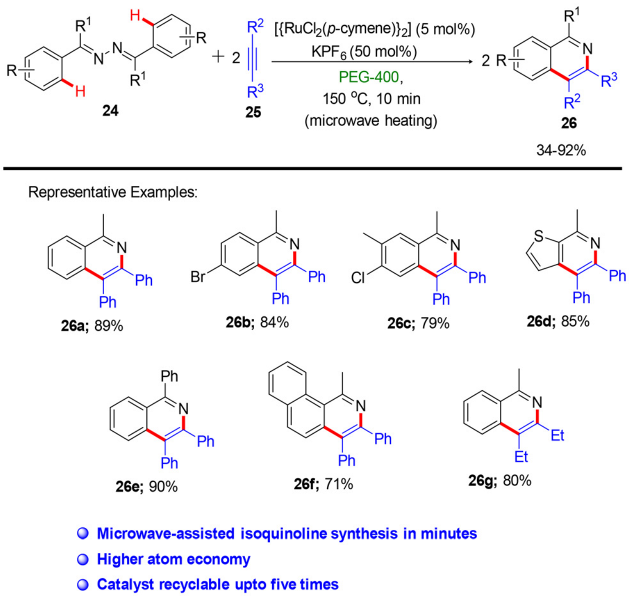
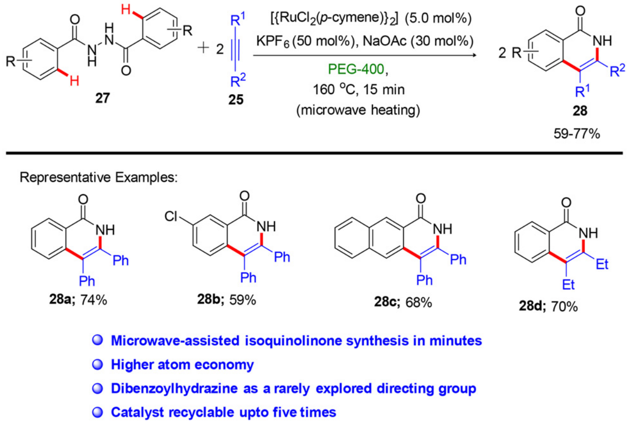


Fig. 6 Recycling study of the Ru catalyst for annulation reaction of 4-methyl-*N*′-(1-phenylethylidene)benzenesulfonylhydrazide.



Scheme 7 Ru-catalysed rapid annulation reaction of ketazines with internal alkynes.



Scheme 8 Ru-catalysed rapid annulation reaction of dibenzoylhydrazine using internal alkynes.

The reusability of the Ru catalyst in PEG-400 media was inspected by performing repetitive annulation reactions of 1,2-bis(1-phenylethylidene)hydrazine and *N*,*N*′-dibenzoylhydrazine using an internal alkyne, diphenylacetylene, under optimised conditions. The Ru catalyst, initially loaded at 5 mol%, was successfully recycled in subsequent reactions without requiring an additional catalyst. Upon finishing every cycle, the reaction composition was separated with diethyl ether, and then the remaining catalytic medium, containing $RuCl_2(p\text{-cymene})_2$ in PEG-400, was reused after heating to remove remaining ether. The yields across five runs remained high, exhibiting minimal variation: for ketazine, the product (**26a**) yields ranged from 89% to 83%, and for dibenzoylhydrazine (product **28a**), from 74% to 70% (Fig. 7).

Han *et al.* reported a related protocol with Scheme 7 utilising a rhodium catalyst,[98] where, catalyst recovery was not a focus of their study. While their method employed rhodium, it achieved comparable yields to that in Scheme 7 with a lower catalyst loading (2 mol%) and was operated under milder conditions at 25 °C.

Inspired from the earlier studies reported on C–H activation reactions utilising $[RuCl_2(p\text{-cymene})]_2$ as a homogeneous reusable catalyst in PEG-400, the Jadhav group proposed a sustainable and effective protocol for the preparation of 1-phenyl isoquinolines **31** (Scheme 9).[99] This catalytic system is accompanied by $Cu(OAc)_2$ acting as an oxidising agent and $AgSbF_6$ as an additive. The reaction works through C–H and N–N functionalisation between 1-(diphenylmethylene)hydrazine **29** and aryl-substituted acetylenes **30**. Several reaction media were evaluated, including ethanol (EtOH), toluene, and dichloromethane (DCM). Compared to these, PEG-400 not only provided comparable or higher product yields but also offered the key advantage of being a biodegradable and "green" solvent, making it a more environmentally sustainable choice for the reaction medium. This method delivers numerous advantages, including an easy extraction process, the use of an eco-friendly solvent, high atom economy, and a reusable catalytic system. With the catalyst loading of 10 mol%, the approach reveals broad substrate scope, yielding a variety of 1-phenyl isoquinoline derivatives **31** with outstanding efficiency and high yields.

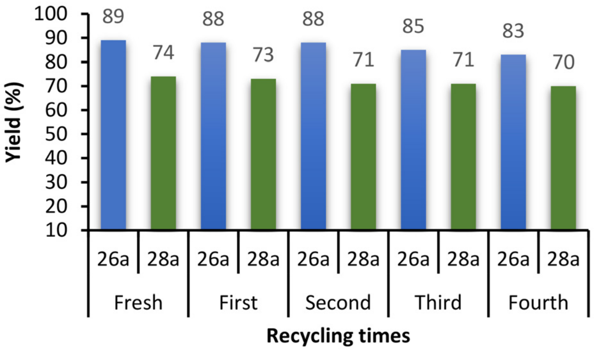
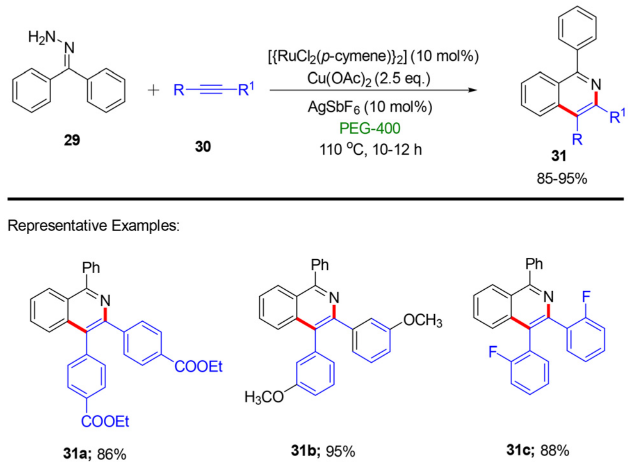


Fig. 7 Recycling analysis of annulation reactions of 1,2-bis(1-phenylethylidene)hydrazine and *N*,*N*′-dibenzoylhydrazine.

Recently, Li *et al.* have established a remarkably effective and reusable catalytic system implementing $[\{RuCl_2(p\text{-cymene})\}_2]$ in a PEG-400/water mixture for the annulation reaction of *N*-methoxybenzamides **32** using alkynes **33** to give isoquinolones **34** (Scheme 10).[100] This system functions under mild conditions (60 °C) with $MesCO_2K$ as a co-catalytic additive and does not necessitate an external oxidant, making it a green and sustainable method.

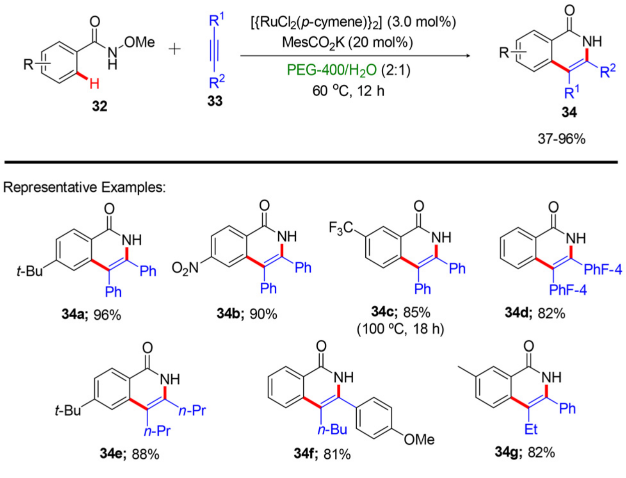
In the optimisation study, the homogeneous catalytic system PEG-400/H_2O showed superiority over other systems for the proposed reaction, as it gave better product yields compared to using PEGs alone. The enhanced effectiveness of the PEG-400/H_2O mixture is due to the role of H_2O in facilitating the dissolution of the additive ($MesCO_2K$) and the subsequent formation of the active catalytic species. Furthermore, this mixed solvent system also outperformed water alone, providing higher yields. However, this system has a limitation in recyclability. To enhance recyclability, employing a PEG-400/H_2O mixture emerged as the optimal choice for the protocol. This protocol yields a range of isoquinolone derivatives with good to outstanding efficacy.

The reusability of this catalytic methodology was confirmed using the reaction of 4-*tert*-butyl-*N*-methoxybenzamide and



- Hydrazine directed C–H activation for annulations reaction
- Higher atom economy
- Simple extraction procedures

Scheme 9 Ru-catalysed annulation of hydrazines using alkynes in order to develop isoquinolines.



- Annulation reaction of *N*- Methoxybenzamides*via* C–H bond activation reaction
- External oxidant free
- Catalyst recyclable upto six times

Scheme 10 Ru-catalysed cyclisation reaction of *N*-methoxybenzamides using internal alkynes.

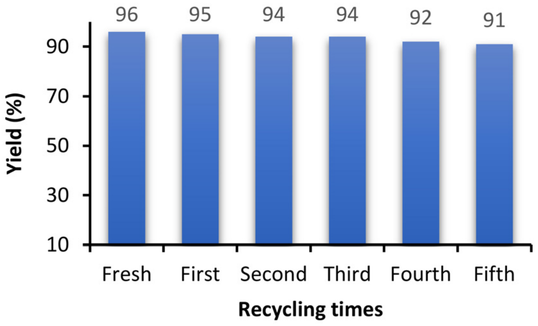


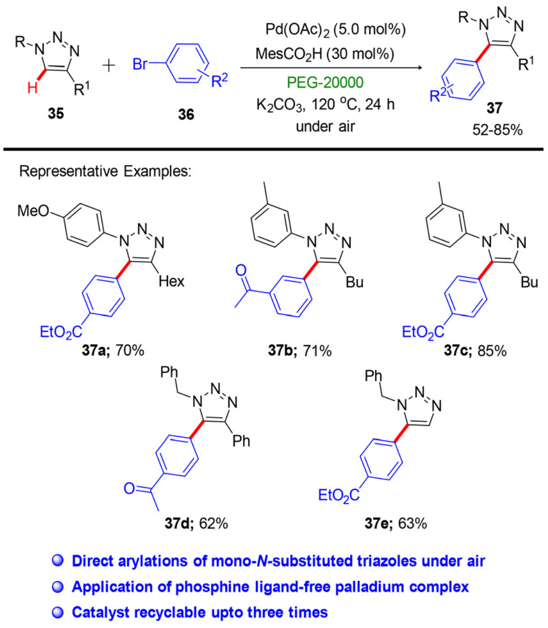
Fig. 8 Recycling study of the $[RuCl_2(p\text{-cymene})]_2$/PEG-400/$H_2O$ catalytic framework for annulation reaction of 4-*tert*-butyl-*N*-methoxybenzamide.

diphenylacetylene, where the $[RuCl_2(p\text{-cymene})]_2$ catalyst with an initial catalyst loading of 3 mol%, under the similar conditions, was reused for six cycles without requiring an additional catalyst (Fig. 8). After each cycle, the reaction mixture was isolated using diethyl ether, and inductively coupled plasma (ICP) analysis suggested minimal ruthenium percolation, characterised by a level of 2.7 ppm in the product.

2.2 C–H functionalisation reactions in PEG catalysed by palladium

Palladium was correspondingly studied for the homogeneous recyclable C–H functionalisation reactions using PEG media. On the other hand, 1,2,3-triazole-based directing groups (DGs) have emerged as a superior substitute to the widely employed 8-aminoquinoline DG.[101–103] This is primarily due to their modular synthesis and the mild conditions required for their removal. Furthermore, their tuneable electronic properties and structural flexibility have enabled unprecedented reactivities in C–H activation protocols. In contrast to other directing groups, the triazole moiety is highly desirable due to its multifunctionality. Remarkably, it serves as a bio isostere of amide bonds in medicinal and biological applications, making it valuable in drug discovery and biomolecular research.

These triazoles underwent arylation reactions *via* Pd-catalysed C–H activation in PEG media, providing an efficient and recyclable approach for the synthesis of arylated triazoles under green and sustainable conditions. The Ackermann group in 2009 proposed an innovative method for Pd-catalysed straightforward arylation reactions of various triazoles bearing directing groups **35** in polyethylene glycol (PEG), contributing to substantial development of user-friendly catalytic systems (Scheme 11).[104] This method applied a recyclable palladium(0) complex without the need for phosphine ligands, simplifying the method and making it more sustainable. The palladium-catalysed functionalisations of C–H bonds were conducted under atmospheric air conditions, evading the necessity of an inert atmosphere. The utilisation of carboxylic acid $MesCO_2H$ as a co-catalyst further improved the reaction's efficiency.



Scheme 11 Pd-catalysed direct arylation reactions of arenes.

Various solvent systems were evaluated for this reaction and PEG-20000 showed superior performance as a solvent compared to other systems. While organic solvents like NMP, DMA, and 1,4-dioxane resulted in low conversions, and lower molecular weight PEGs (PEG-400 and PEG-2000) produced products in lower yields, the use of PEG-20000, particularly in combination with the additive $MesCO_2H$, significantly improved catalytic efficacy, leading to a higher product yield of 74%. Furthermore, the non-toxic and non-volatile nature of PEG-20000 contributes to a greener process and facilitates the recycling of the catalyst, a feature not typically associated with organic solvents, thus contributing to a more sustainable process.

A crucial discovery from the research was the reusability of the Pd(0) catalyst using PEG-20000 as the reaction solvent. To examine the recyclability of the initially loaded 5 mol% Pd catalyst, the arylation reaction was realised in order to synthesize product **37c** and the researchers could reuse the catalytic system for the further cycles (Fig. 9). Even though the catalytic activity reduced to some extent upon recycling, this characterised the pioneering case of a reusable transition metal-based catalyst employed to achieve straightforward arylations *via* C–H bond activation.

Ackermann and co-workers, later in 2019, advanced a sustainable methodology for C–H arylation of 1,2,3-triazoles through dehydrogenation using a reusable palladium catalyst in polyethylene glycol (PEG).[105] This oxidative palladium-catalysis approach facilitated the formation of functionalised 1,2,3-triazoles with wide compatibility with functional groups and a broad range of substrates.

Various triazole-fused chromenes (Scheme 12), isoindoline-fused triazoles (Scheme 13), phenanthrene-fused triazoles and bio-active triazole compounds (Scheme 12) were synthesised using the proposed protocol. The application of PEG as an environmentally benign solvent highlighted the environmental

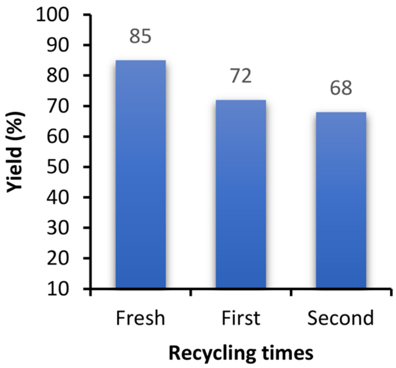
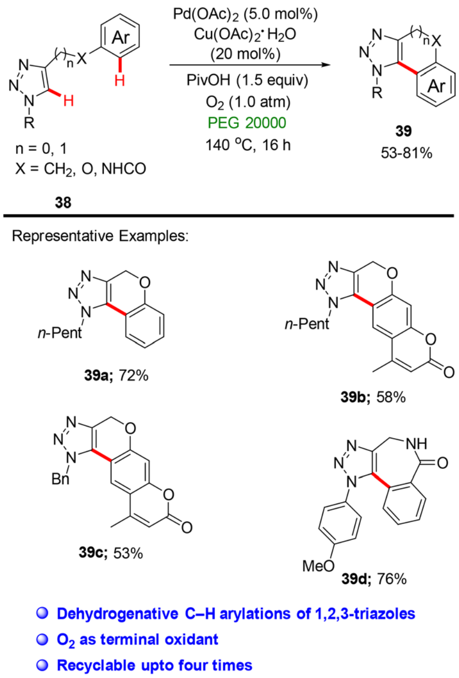
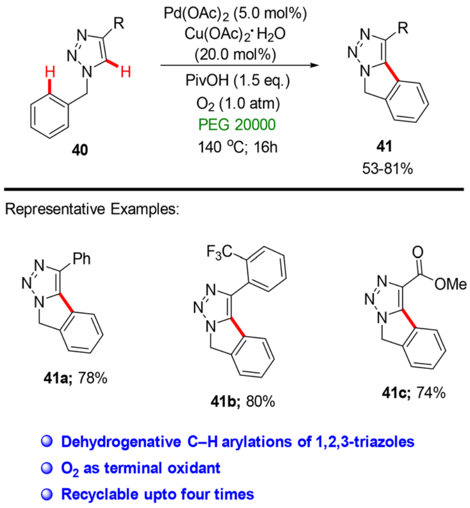


Fig. 9 Recycling study of the Pd catalyst for direct arylation reactions of arenes.



Scheme 12 Pd catalysed synthesis of triazole-fused chromenes and bio-active triazole compounds.



Scheme 13 Pd-catalysed synthesis of isoindoline-fused triazoles.

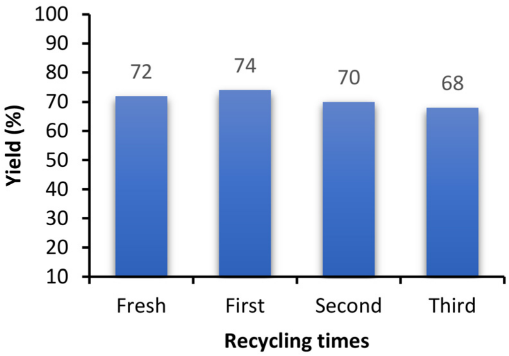


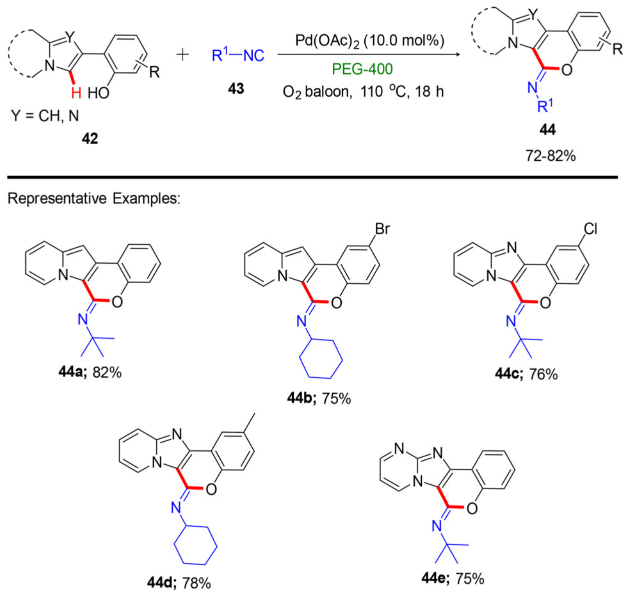
Fig. 10 Recycling study of the Pd@PEG catalyst for arylation reaction.

advantages and also confirmed the competence to reuse both the Pd catalyst and the reaction medium.

Recycling studies of the catalyst were carried out for the synthesis of product **39a** which demonstrated that the optimal reaction conditions led to a minor but acceptable decline in catalytic efficacy over consecutive runs (Fig. 10). The catalyst, combined with catalytic amounts of copper acetate and pivalic acid, was reused in at least four successive reactions. To ascertain the catalyst's stability and recovery during the recycling process, the palladium loading within the catalytic system was rigorously analysed. Following the reaction, the solid-phase material (PEG/Pd) was isolated *via* precipitation, and the palladium content was quantified using ICP-AES. This analysis revealed that the palladium loading remained essentially unchanged throughout the consecutive runs, confirming the catalyst's durability and minimal loss under the reaction conditions.

Besides the methodologies involving C–H arylations of triazoles, in 2018, Kumar and colleagues recognised an effective procedure for producing indolizine/imidazoline-fused heterocycles **44** *via* Pd catalysed activation of C(sp^2)–H accompanied by isocyanide **43** incorporation, employing PEG-400 as reusable reaction medium (Scheme 14).[106] The authors specifically examined water also as a solvent and found it to be ineffective. This ligand, base, and metal oxidant-free method utilises oxygen as an external oxidant, making the process environmentally friendly.

The recyclability of PEG-400 was examined through reactions of 2-(indolizin-2-yl)phenol with *tert*-butyl isocyanide. Following initial experimentation, the reaction mixture underwent ether extraction, and the isolated PEG was subjected to a subsequent cycle of C–H activation and isocyanide insertion. This second run involved charging the PEG with the same substrate and introducing additional Pd(OAc)$_2$. The findings indicated that PEG-400 remained effective through three cycles of



- C–H activation without the use of ligands, bases, or metal oxidants
- Potential uses include the development of highly fluorescent probes and organic light-emitting diodes (OLEDs).
- Solvent recyclable upto three times

Scheme 14 Palladium catalysed preparation of indolizine/imidazoline-fused heterocyclic compounds.

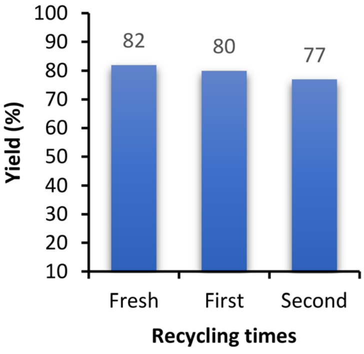
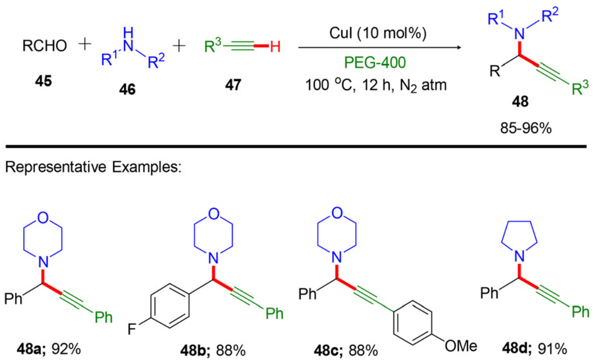


Fig. 11 Recyclability of PEG-400 for reaction between 2-(indolizin-2-yl)phenol and *tert*-butyl isocyanide.

reuse for the synthesis of **44a** with minimal loss in catalytic activity (82%, 80%, and 77%) (Fig. 11).

2.3 C–H functionalisation in PEG catalysed by copper

Copper was likewise testified for the functionalisation of C–H bond reactions in PEG media. Zhang and research team in 2010 described a competent and practical way for generating propargylamines **48** *via* a three component A3 coupling of aldehydes **45**, amines **46**, and alkynes **47** (Scheme 15).[107] The reaction employs 10 mol% copper(I) iodide (CuI) as a sole catalyst in a polyethylene glycol (PEG) medium, enabling C–H activation. Various solvents were screened for the reaction, including water, THF, CH_3CN, and an ionic liquid, $[Bmim]PF_6$, and PEG was found to be the most effective solvent. The product was generated with a 92% yield in PEG, whereas other solvents resulted in much lower yields. For example, the reaction in H_2O resulted in only a 27% yield. Additionally, PEG-400 offers greener and recyclability advantages contrasting with the hazardous nature and other limitations associated with many traditional organic solvents. This method, noteworthy for its simplicity and the sustainable use of PEG as the reaction medium, demonstrates versatility across an extensive array of substrates, yielding propargylamines **48** in moderate to outstanding yields.



- Cu catalyzed A3 coupling reaction of aldehyde, amine and alkyne *via* C–H activation
- Three component one-pot synthesis of propargylamines
- Catalyst recyclable upto five times

Scheme 15 Synthesis of propargylamines by copper-catalysed A3 coupling reaction.

Additionally, the catalytic system, including CuI and PEG, was effectively retrieved and reused repeatedly avoiding a substantial loss in catalytic efficiency, preserving high productivity across multiple cycles. For instance, the reaction between benzaldehyde, morpholine, and phenylacetylene to produce **48a** confirmed that the leftover PEG with CuI has the potential to be reutilised until five repeated cycles with consistent results (Fig. 12). Remarkably, no additional copper salt was required in subsequent cycles, further contributing to the reaction's sustainability.

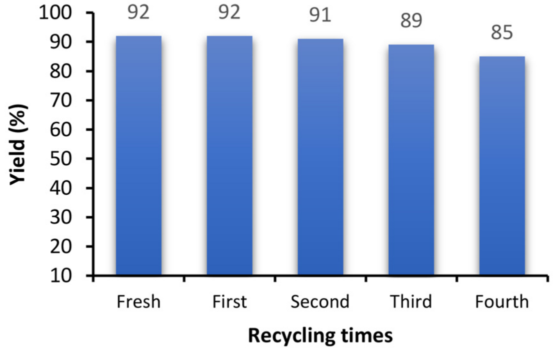
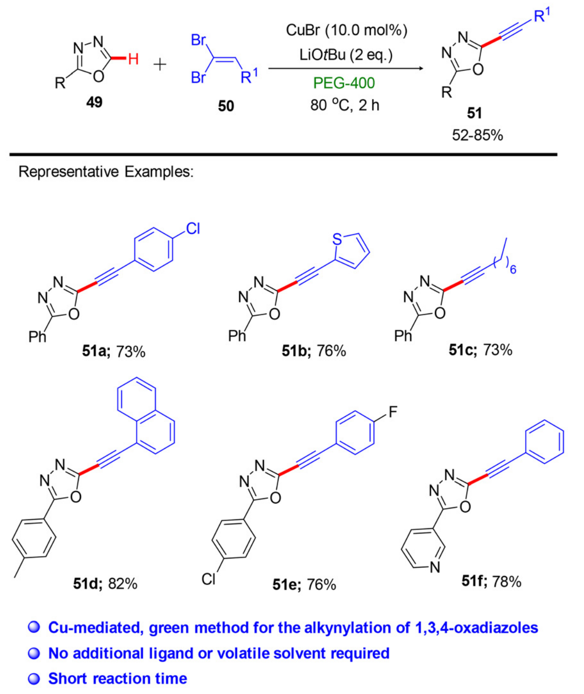
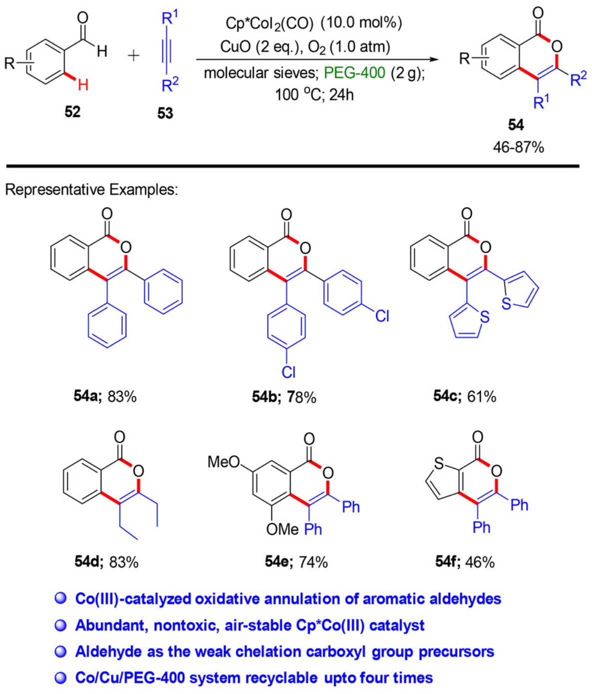


Fig. 12 Reuse of the copper catalyst in PEG to synthesize propargylamines.



Scheme 16 Cu-mediated alkenylation of 1,3,4-oxadiazoles using 1,1-dibromo-1-alkenes.



Scheme 17 Cobalt catalysed annulation of aldehydes for the production of isocoumarins.

Later, the Das research group established an efficient and green approach to achieve direct alkynylation of the C–H bonds of 1,3,4-oxadiazoles **49** using 1,1-dibromo-1-alkenes **50**, catalysed by 10 mol% CuBr and LiO*t*Bu in PEG-400 at 80 °C (Scheme 16).[108] The reaction exhibited high product conversion within 2 hours, with no requirement of additional ligands. When dichloromethane (CH_2Cl_2) and acetonitrile (CH_3CN) were employed as solvents instead of PEG-400, no reaction was observed. Also, PEG-400 acts as a non-toxic, reusable medium, eliminating the necessity for hazardous organic solvents, which highlights its eco-friendly nature. The process is a valuable green synthetic approach that eliminates the use of expensive palladium-based catalysts and works under mild conditions with straightforward procedures. It also offers high efficiency, rapid product formation, and significant sustainability advantages.

2.4 C–H functionalisations in PEG by cobalt catalysis

PEG mediated C–H functionalisation reactions were extended to cobalt catalysis also. The Tao research group employed PEG-400 as a sustainable and reusable solvent, accompanied by the Co(III) and Cu-based catalysts for the annulation reaction of aromatic aldehydes **52** with internal alkynes **53** in order to achieve the production of isocoumarins **54** (Scheme 17).[109] Compared to conventional solvents like toluene and DMF, PEG-400 demonstrated superior effectiveness in the tested application. Furthermore, the Co/Cu/PEG-400 system offers significant advantages of recyclability and reusability, which present notable economic and environmental benefits. The method functions through oxidation, weak chelation-assisted C–H functionalisation, and annulation cascades, representing outstanding functional group tolerance and considerable atom efficiency. This recyclable approach not only confirms high yields and selectivity but also decreases waste and resource consumption.

Recyclability was verified in the annulation of benzaldehyde with diphenylacetylene in order to synthesize isocoumarin **54a** utilising the $Cp^*Co(CO)I_2/CuO$/PEG-400 catalytic framework comprising 10 mol% Co catalyst. Over three cycles, the protocol preserved a steady conversion rate without the need to add a fresh catalyst or solvent, only demanding replenishment of oxygen (Fig. 13). Though a minor decrease in yield occurred due to slight cobalt catalyst losses, the system remained efficient, delivering good yields in each cycle.

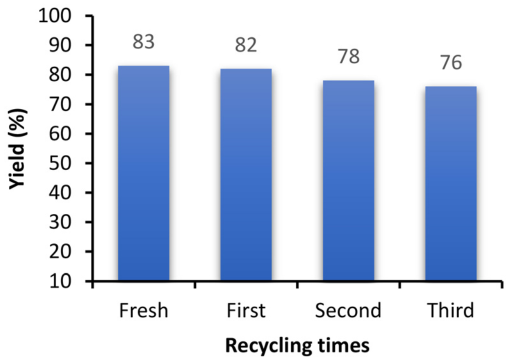
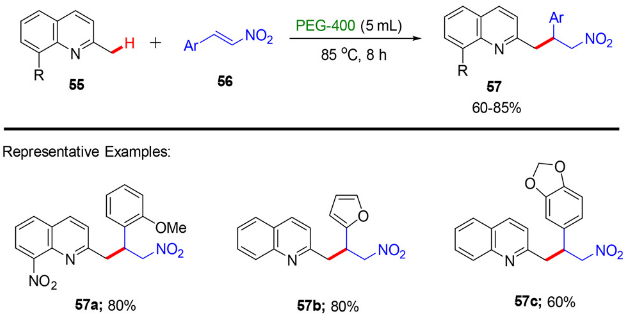


Fig. 13 Recycling study of Co-catalysed production of isocoumarin by annulation of benzaldehyde with diphenylacetylene.



- Metal-free C–H activation of methyl quinolines
- PEG-400 mediated approach for the synthesis of alkyl aza-arenes
- Reusable reaction medium that eliminates the requirement for additives or acid catalysts.

Scheme 18 Preparation of alkyl aza-arenes in PEG-400 medium.

2.5 Metal catalyst free C–H functionalisations in PEG

PEG-400 was used as the reaction medium under metal-free conditions by Yeramanchi and colleagues for an effective and green approach for the C–H activation of methyl quinolines.[110] This method enables the addition of methyl quinolines **55** to various β-nitro styrenes **56** under mild conditions (Scheme 18). PEG-400 is a sustainable solvent that is affordable, recyclable, and compliant with green chemistry guidelines. Water was also used as a test medium for the reaction. However, the limited solubility of nitro styrene in water at higher temperatures led to the generation of unwanted byproducts. Significantly, the reaction takes place without the need for any metal catalysts, additives, or acid catalysts, making it a metal-free protocol. It is a valuable achievement that the generation of corresponding alkyl aza-arenes **57** with high yields is made feasible by the gentle reaction parameters and practical ease of execution.

3. Homogeneous recyclable ionic liquid (IL) media

Ever since ionic liquids (ILs) were discovered, they have been simply described as liquids composed entirely of cations and anions.[111] They have progressively established as a leading edge in the fields of chemical and materials sciences. This is principally because of exceptional key characteristics, such as excellent chemical and thermal stability, strong solvation capabilities, less volatility and vapor pressure, as well as high polarity and conductivity, *etc.*[112] These features make ionic liquids a suitable substitute to traditional organic solvents, mainly in the context of eco-conscious and green chemical methods. This resulted in an array of potential industrial or commercial practices for ILs.[113–115]

A primary advantage of ionic liquids in catalysis is their ability for reusability.[116–119] As homogeneous recyclable catalytic systems, ionic liquids can be conveniently isolated from the reaction composition, for the retrieval and reuse of the catalyst, thus lessening waste and enhancing the overall efficacy of the method. Besides, the capability to modify the physical and chemical characteristics of ionic liquids through careful cation and anion selection allows for the creation of customised catalytic systems for specific reactions.[120–124]

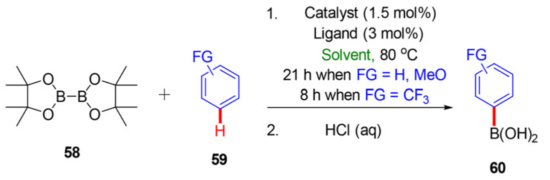
In the past few years, C–H activation reactions have also been fruitfully described using recyclable ionic liquid catalytic systems. In this section, we focus on the application of homogeneous recyclable ionic liquid systems in C–H activations. For clearness along with inclusive understanding, we have further categorised the discussion into two subsections: (1) C–H bond functionalisation catalysed by transition metals in ionic liquids and (2) ionic liquid catalysed C–H functionalisations.

3.1 C–H bond functionalisation catalysed by transition metals in ionic liquids

Transition metals are extensively used as catalysts to perform homogeneous recyclable C–H activation reactions in ionic liquids. In 2007, Yinghuai and colleagues established a catalytic system using a iridium(I) salicylaldiminato-cyclooctadiene complex Ir(–*o*-O–C_6H_4–CH=N–CH_2Ph)(cod) for the arylborylation of arenes **59** with bis(pinacolato)diboron **58** *via* C–H activation, in the presence of tetra-2-pyridinylpyrazine (TPy) and an ionic liquid (tributyltetradecylphosphonium dodecylbenzenesulfonate (TBPD)) (Scheme 19).[125] This catalytic system accomplished up to 91% isolated yield and confirmed excellent recyclability compared to other systems. In contrast, other systems, such as those involving N-heterocyclic carbene complexes of Ir(I), are found to be not reusable, which increases the cost of such synthetic schemes.

1.5 mol% catalyst was loaded in the starting of the reaction. After each borylation reaction, the solvent was eliminated, and boroxine products were obtained by distillation at reduced pressure. The residual catalyst mixture was reutilised for at least three additional runs without losing activity. Hydrolysis of the distillate yielded the final products, permitting efficient catalyst recovery and reuse.

Ruthenium was also explored as a catalyst for ionic liquid mediated C–H activation reactions. Biletzki and colleagues highlighted a noteworthy development in the catalytic develop-



Catalyst: Ir(–*o*-O–C_6H_4–CH=N–CH_2Ph)(COD) FG = H, MeO, CF_3
Ligand: Tetra-2-pyridinylpyrazine (TPy)
Solvent: Benzene, DCM and ionic liquid (tributyltetradecylphosphonium dodecylbenzenesulfonate (TBPD))

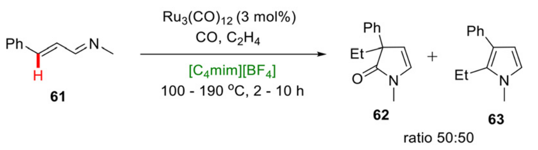
- Arylborylation reaction by Ir-based catalyst through C–H activation
- Recyclable catalytic system

Scheme 19 Borylation of arenes catalysed by iridium(I) salicylaldiminato-cyclooctadiene complexes.

ment of chiral 2,3-dihydropyrrolones **62** and 2,3-disubstituted pyrroles **63** through the combination of α,β-unsaturated imines **61**, carbon monoxide, and ethylene in the presence of 3 mol% $Ru_3(CO)_{12}$ as a precatalyst.[126] This reaction was performed across a variety of ionic liquids, demonstrating improved efficiency compared to that of conventional organic solvents. In particular, optimisation in the ionic liquid $[C_4mim][BTA]$ revealed that moderate conditions, with respect to reaction time and gas pressures, yielded better results giving both the products in a 50 : 50 ratio in the first catalytic cycle (Scheme 20).

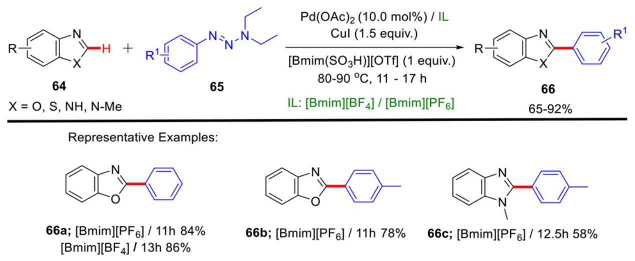
The ruthenium species remained active in the ionic liquid phase, allowing reuse after product extraction without a considerable decrease in catalytic performance or selectivity, particularly in $[C_4mim][BF_4]$. However, after 1–3 cycles, the activity began to decline, likely due to the development of ruthenium nanoparticles, as verified by dynamic light scattering study. The gradual transition from homogeneous to heterogeneous catalysis reduced efficiency over time, highlighting the role of nanoparticle formation in deactivating the catalyst.

The study was expanded to a palladium catalyst also. Sutar and co-workers, in the year 2020, established a green protocol for C–H functionalisation of azole-based substrates **64**, particularly benzoxazole, benzothiazole, and benzimidazole employing 1-aryltriazenes **65** as arylating agents (Scheme 21).[127] The protocol utilises a catalytic system comprising 10 mol% $Pd(OAc)_2$ and CuI in hydrophilic $[Bmim][BF_4]$ or hydrophobic $[Bmim][PF_6]$ ionic liquid (IL) media, accompanied by $[BMIM(SO_3H)][OTf]$ as a booster. This approach facilitates the efficient C2-arylation of azoles, providing 2-aryl-substituted azoles **66** in satisfactory to high yields while exhibiting tolerance to an array of functional groups. Furthermore, the study's objectives of green chemistry are supported by the ionic liquid's recyclable and reusable nature, which provides a sustainable substitute for conventional arylation strategies.



- Multicomponent reaction of α,β-unsaturated imines, carbon monoxide, and ethylene
- Synthesis of chiral 2,3-dihydropyrrolones and 2,3-disubstituted pyrroles
- Both the products in 50:50 yield ratio
- Recyclable catalytic system in some cases

Scheme 20 Ru-catalysed preparation of 2,3-dihydropyrrolones and 2,3-disubstituted pyrroles from α,β-unsaturated imines.



- Electrophilic C2-arylation of azoles
- Base/ligand free and open-air Pd/Cu catalyzed protocol
- IL recyclable upto five times

Scheme 21 Pd-catalysed arylation of azoles with 3,3-diethyl-1-(phenyl)-triaz-1-ene.

To assess the reusability, a C2-cross coupling between 3,3-diethyl-1-phenyltriaz-1-ene and benzoxazole was performed under optimal conditions using fresh, reused, and recycled ILs. The results, presented in Fig. 14, showed negligible yield loss with reused ILs and a slight decrease in yield for recycled ILs, confirming the reusability of the ionic solvents.

A relevant protocol shown in Scheme 21, reported by Zhang's group, also employed a Pd catalyst, albeit without prioritising catalyst recycling.[128] This method required similar loadings of Pd and Cu salts but utilised DMF as the solvent and necessitated higher reaction temperatures compared to the IL-based system in Scheme 21.

In Scheme 22, Xu and Kong have used manganese as a catalyst for amidation reactions of C–H bonds in ionic liquids. They presented a novel tactic for the amidation of aromatic oximes **67** through activation of C–H bonds, employing simply accessible sulfonyl azides **68** as reagents for amidation.[129] The transformation is enabled using a base-metal catalyst, $MnBr(CO)_5$/[Hmim]OTf with 5 mol% cat. loading, which not only achieves outstanding chemical yields but also shows remarkable regioselectivity and compatibility with functional groups. The catalytic system offers advantages like recyclability compared to other screened systems. This recyclability makes it more practical for large-scale C–H amidation reactions. Ionic liquid: [Hmim]OTf enhances catalytic reactions compared to traditional organic solvents. This is because the weakly coordinating counter anion in the ionic liquid likely interacts with

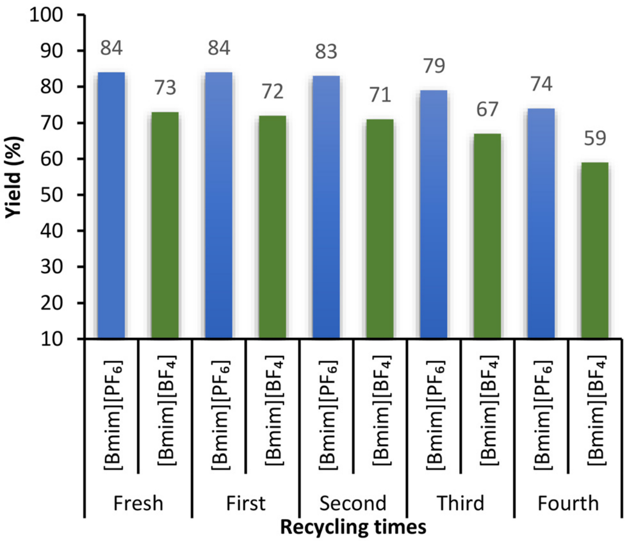
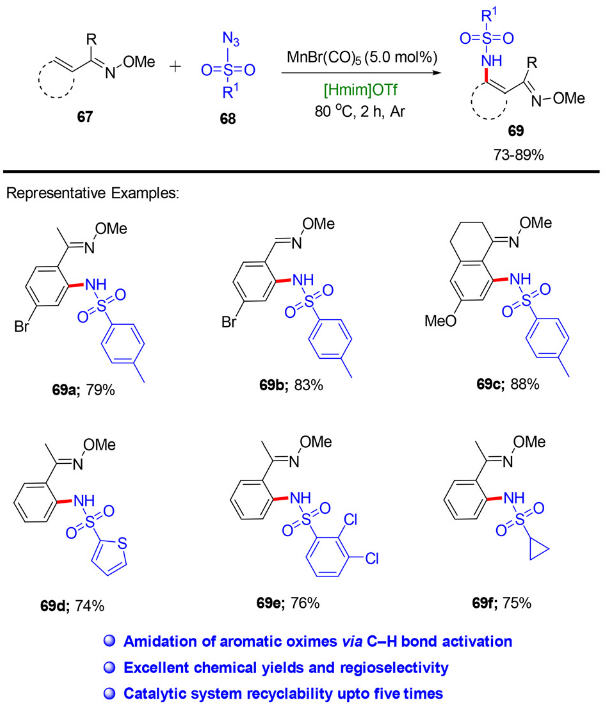


Fig. 14 Recycling study for Pd-catalysed C2-cross coupling between 3,3-diethyl-1-phenyltriaz-1-ene and benzoxazole.



Scheme 22 Mn-catalysed amidation of aromatic ketones.

the bromide in $MnBr(CO)_5$, forming a more reactive Mn-catalyst.

The reutilisation of the $MnBr(CO)_5$/[Hmim]OTf framework was systematically studied, revealing its capacity for recycling through a simple phase separation process. Upon accomplishment of the reaction, the catalyst has the potential to be recovered by extracting the reaction composition with solvents like diethyl ether, allowing for efficient isolation of the organic products from the ionic liquid medium containing most of the manganese catalyst. Impressively, the system maintained its catalytic activity across five successive runs, though a decline in performance was observed after this point (Fig. 15), attributed to increased emulsion formation and phase separation difficulties.

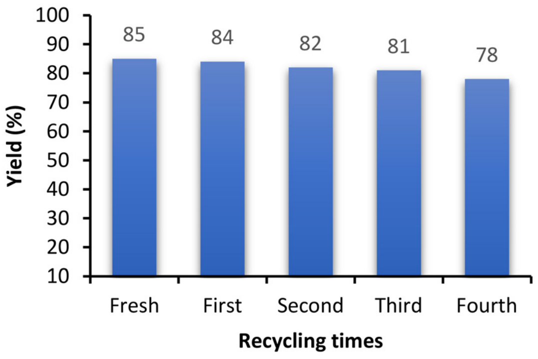
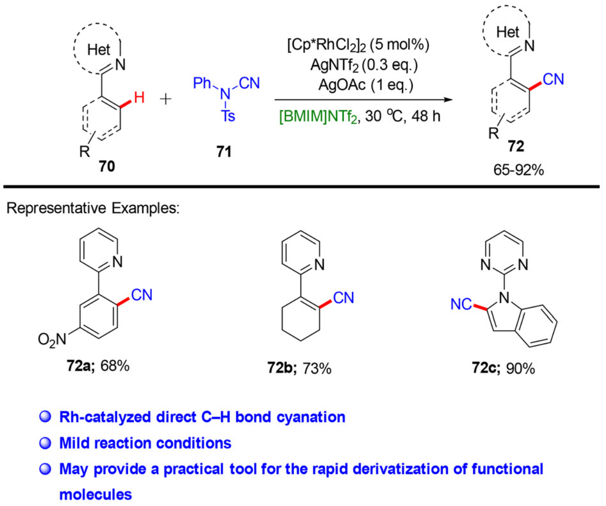


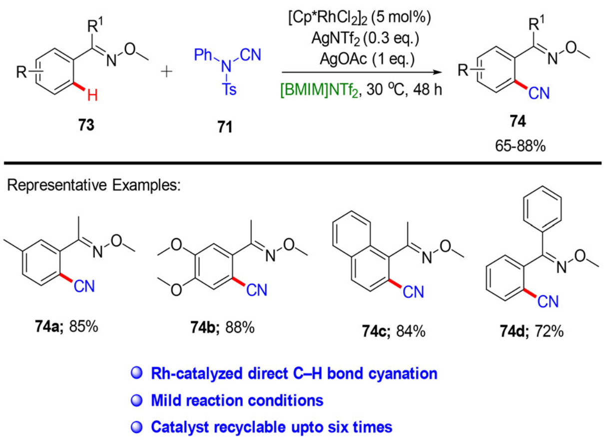
Fig. 15 Recycling of the Mn-catalytic system for amidation of aromatic ketones.

Several studies on Rh catalysed functionalisation reactions of C–H bonds in ionic liquids exist in published reports. In an innovative study reported in year 2018, Lv and colleagues presented an innovative Cp*Rh(III)/ionic liquid (IL)-based system (with 5 mol% cat. loading) to achieve the straightforward cyanation of C–H bonds, representing the first fruitful development of this method.[130] They prepared aryl nitriles by reacting *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide **71** with 2-phenylpyridines **70** (Scheme 23) and oxime ethers **73** (Scheme 24) in separate reactions. This method is distinguished for its gentle reaction parameters, excellent competence, and recyclability, allowing the generation of aryl nitriles from an extensive array of substrates. The system showed compatibility with numerous directing groups and also tolerated a variety of functional groups, showcasing its versatility in synthetic applications.

The reaction's practicality was also established through a 10-fold scale-up, attaining a remarkable yield of the anticipated molecule **74a**, even when cutting down the loading of



Scheme 23 Rh-catalysed cyanation reaction of 2-phenylpyridines.



Scheme 24 Rh-catalysed cyanation of aryl ketone oxime ethers.

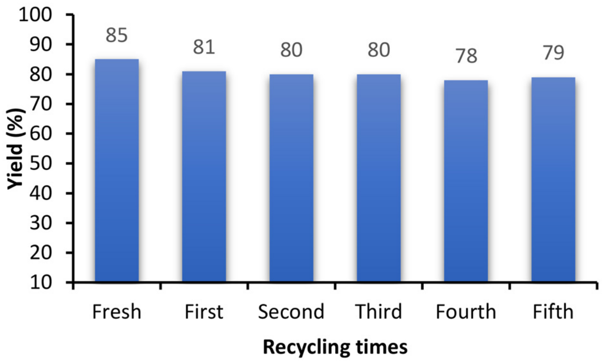
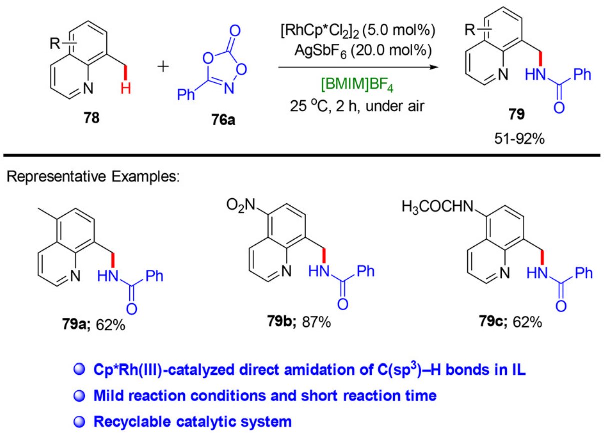


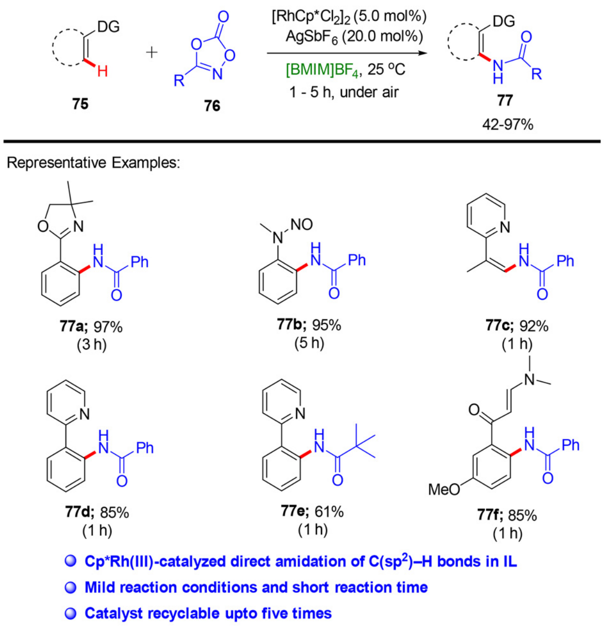
Fig. 16 Reusability of the catalyst and solvent for cyanation reaction of aryl ketone oxime ether.



Scheme 26 C(sp^3)–H amidation of 8-methylquinolines by the rhodium catalyst.

catalyst to 2.5 mmol%. The study also highlighted the recyclability of the catalyst and the ionic liquid as the reaction medium. After six cycles of reuse without reloading the Rh catalyst, only a minor decline in product yield was observed, emphasising the effectiveness of the IL as a recyclable solvent (Fig. 16).

Concurrently that year, Ma *et al.* recognised an innovative protocol for Cp*Rh(III) catalysed direct amidation of C–H bonds using ionic liquids, showcasing a highly efficient and environmentally benign technique.[131] Various directing group comprising substrates, including synthetically valuable N-containing heterocycles, amides, ketoximes, and *N*-oxides, were precisely amidated using dioxazolones **76** as shown in Scheme 25. This approach allows the selective amidation of dual C(sp^2)–H bonds in (hetero)arenes along with alkenes. Furthermore, the protocol's applicability has been widened to 8-methylquinolines **78** also (Scheme 26), functionalising unactivated C(sp^3)–H bonds, achieving outstanding yields accompanied by significant tolerance for various functional groups. The application of the Cp*Rh(III)/[BMIM]BF$_4$ system further enhances the process by excluding the use of harmful organic solvents and allowing for catalyst reuse, promoting sustainability in chemical synthesis.



Scheme 25 Rh catalysed C(sp^2)–H amidation of substrates containing directing groups.

The study examined the reusability of the Cp*Rh(III)/[BMIM]BF$_4$ system across multiple catalytic cycles specifically in the synthesis of product **77d** (Fig. 17). Starting with 5 mol% of catalyst and after completing the reaction, the catalyst and solvent were separated, and the recovered system was employed in subsequent reactions with different substrates without significant loss in activity. Remarkably, the system maintained its efficiency for at least five cycles, enabling fruitful amidation of diverse substrates, including various N-comprising heterocycles.

The Liu research group, in the subsequent year, has established a robust catalytic protocol for the formation of 1,2-benzothiazines through Rh(III) catalysed activation of C–H bonds and cyclisation of NH-sulfoximines.[132] This innovative approach employs a mixture of Cp*Rh(III), AgSbF$_6$, and the

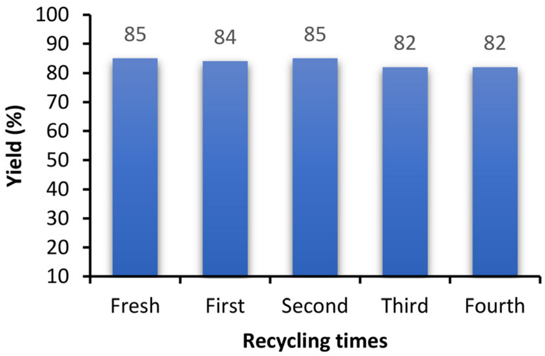
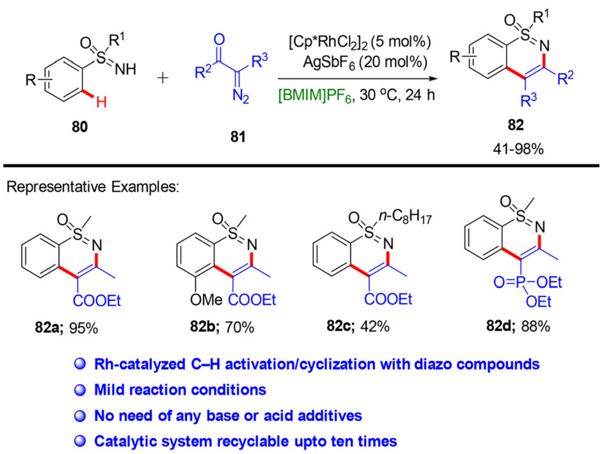


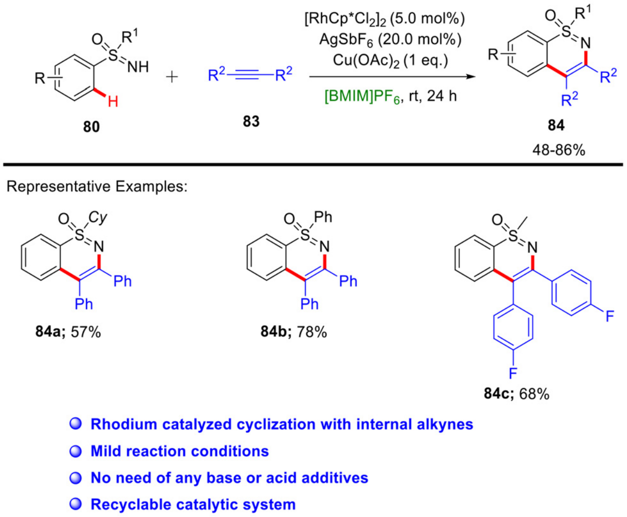
Fig. 17 Reusability of the rhodium catalyst in the C–H amidation reaction involving phenylpyridine and dioxazolone.

ionic liquid [BMIM][PF_6], enabling a mild reaction environment that eliminates the need for additional base or acid additives. Various ionic liquids and a deep eutectic solvent were tested in this methodology. The results indicated that using [BMIM][PF_6] as the medium yielded the best results. Other ionic liquids did not improve the yield and the deep eutectic solvent, ChCl–EG (1 : 1.5), did not produce the desired product. The protocol shows scope for an extensive range of substrates, encompassing a variety of NH-sulfoximines and coupling partners, and consistently achieves excellent product yields. Diverse coupling partners include diazo compounds **81** (Scheme 27), internal alkynes **83** (Scheme 28), and sulfoxonium ylides **85** (Scheme 29).

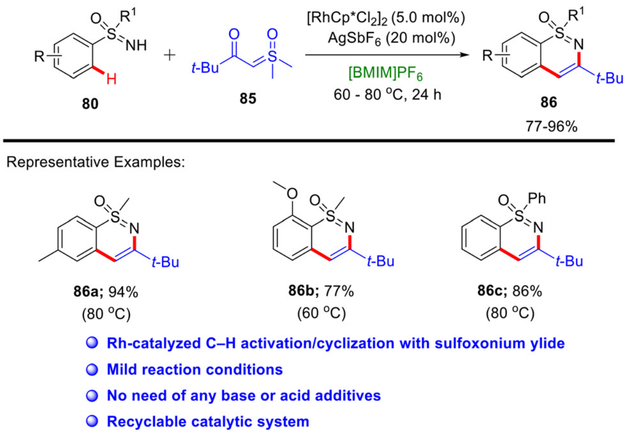
To examine the stability and recyclability of this catalytic system, the investigators conducted extensive experimentations with the reaction involving NH-sulfoximine and diazo compound, proving that the [Cp*Rh(III)]/$AgSbF_6$/[BMIM][PF_6] system containing 5 mol% Rh catalyst could be effectively reused a minimum of ten times, consistently providing the desired product **82a** with over 84% yield in the first ten cycles (Fig. 18). The product separation is simple, relying on ether extraction after the completion of reaction. Other experiments involving sulfoximines and diphenylacetylenes confirmed that the system retains its catalytic efficiency, even with the introduction of the oxidant $Cu(OAc)_2$, attaining moderate to good yields over eight cycles.



Scheme 27 Rh-catalysed cyclisation between NH-sulfoximines and diazo compounds.



Scheme 28 Rh-catalysed cyclisation of NH-sulfoximines with internal alkynes.



Scheme 29 Rh-catalysed cyclisation reaction between NH-sulfoximines and sulfoxonium ylide.

In recent times, Rui and colleagues have proposed a novel rhodium(III)-catalysed protocol in order to generate C–S and C–Se bonds utilising acetanilide **87** and diaryl disulfides **88** or diaryl diselenides **90** in an ionic liquid (IL) medium.[133] This reaction occurs *via* activation of C–H bonds, producing the corresponding C–H thiolation (Scheme 30) and C–H selenation products (Scheme 31), respectively. This method is notable for its efficiency and sustainability, as it abolishes the need for additional silver salts as additives. The reactions in non-ionic liquids did not proceed, indicating that ionic liquids were crucial not only as solvents but also as additives to facilitate the reaction. The catalytic system demonstrates excellent com-

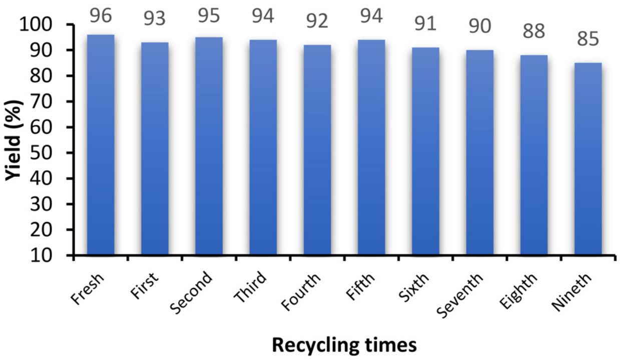
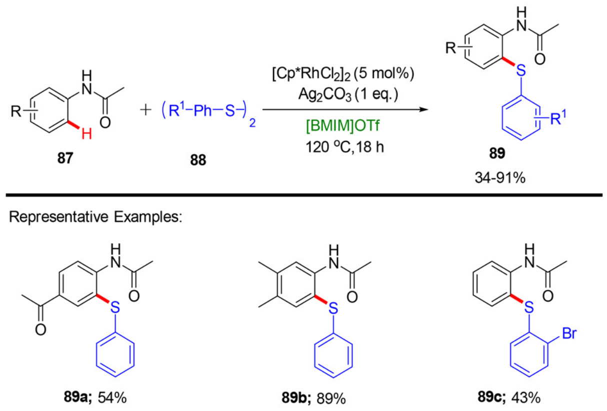
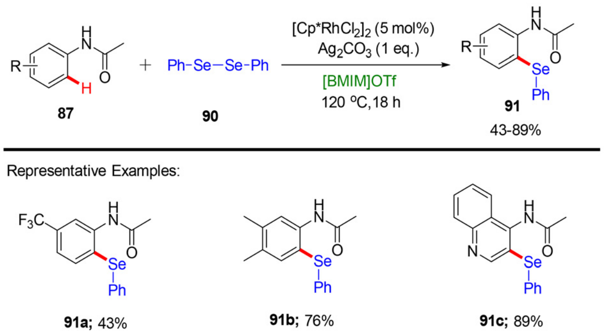


Fig. 18 Reuse of the [Cp*Rh(III)]/$AgSbF_6$/[BMIM][PF_6] catalytic system for the production of product **82a**.



- Rh(III)-catalyzed and IL-mediated C–S bond formation
- Easily removable directing group
- Thiolation products can be developed into biologically active phenothiazine scaffolds
- [BMIM]OTf as a recyclable medium

Scheme 30 Rh-catalysed, ionic liquid mediated thiolation of the C–H bonds of *N*-phenylacetamides.



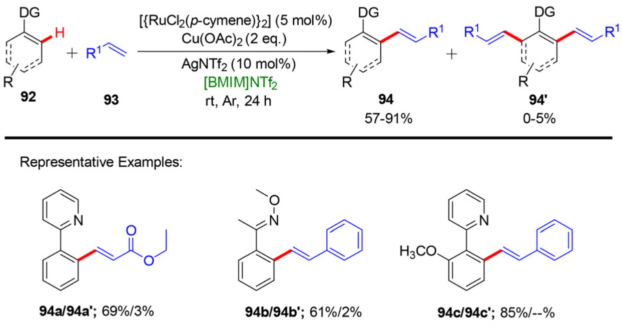
- Rh(III)-catalyzed and IL-mediated C–Se bond formation
- Easily removable directing group
- [BMIM]OTf as a recyclable medium

Scheme 31 Rh-catalysed, ionic liquid-mediated selenation of the C–H bonds of *N*-phenylacetamides.

patibility with various functional groups and facilitates the straightforward removal of the directing group.

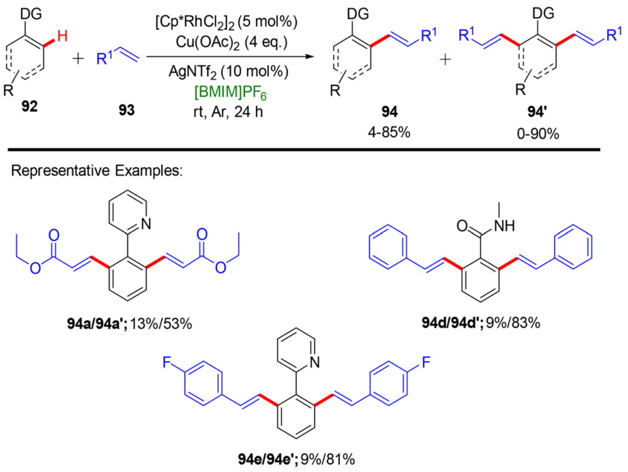
The investigation also underscores the sustainable application of the ionic liquid and the rhodium catalyst. After the initial reaction with 5 mol% catalyst loading, the product can be retrieved using an organic solvent, allowing the reuse of the IL for subsequent reactions without the necessity for an additional Rh(III) catalyst. Remarkably, the system demonstrated stability across five cycles, with only a gradual reduction in product yield, indicating an effective recycling strategy that preserves precious metal resources.

Du and Yao testified ruthenium and rhodium both for the monitored mono- and diolefination of arenes in ionic liquids. The catalytic systems, precisely [BMIM]NTf_2 and [BMIM]PF_6, empowered controlled mono- and di-olefination of arenes **92** at ambient temperature by means of activation of C–H bonds.[134] This pioneering strategy eliminates the need for heating equipment, representing a substantial energy-saving route for industrial production. Their catalyst screening revealed that 5 mol% $[RuCl_2(p\text{-cymene})]_2$ principally produced mono-olefinated products **94** (Scheme 32), while 5 mol% $[RhCp^*Cl_2]_2$ exclusively produced di-olefinated products **94′** (Scheme 33). The optimised catalytic system provides advantages like recyclability compared to other screened systems, including traditional organic solvents like toluene, CH_2Cl_2, *t*-AmOH, HFIP, and DMF, which could not produce the desired reaction products. The utilisation of these green, recyclable ionic liquids not only ensured the absence of volatile and toxic organic solvents but also made the reaction process safer, as it



- Catalyst controlled mono-olefination
- Probable effect of IL in olefination selectivity
- Energy-saving route without need of heating equipment
- No need of pressure-tight equipments
- Recyclable reaction media

Scheme 32 Ru-catalysed single and double olefination of arenes in ionic liquids.



- Catalyst controlled di-olefination
- Probable effect of IL in olefination selectivity
- Energy-saving route without need of heating equipment
- No need of pressure-tight equipments
- Recyclable reaction media

Scheme 33 Rh-catalysed single and double olefination of arenes in ionic liquids.

required no pressure-tight apparatus. The protocol showcased an extensive substrate scope, achieving excellent yields and selectivity, yet in gram-scale applications.

For examining the reusability of the catalysts, they employed 2-phenylpyridine and styrene in a prototype reaction. Subsequent to the extraction of the product using diethyl ether, the catalytic systems were recycled for at least six cycles, indicating consistent high yields with only a minor decline in competence.

3.2 Ionic liquid catalysed C–H functionalisations

Ionic liquids (ILs) have also emerged as catalysts in favour of C–H activations. In Scheme 34, the Wang lab established a novel approach that encourages the C(sp^3)–H bond functionalisation of alkyl azaarenes **96**, enabling effective nucleophilic addition reaction to aldehydes **95**.[135] In particular, [Hmim][H_2PO_4] acid ionic liquids are employed in an H_2O/dioxane solvent system. Under mild reaction conditions, this approach yields alkyl-substituted aza-arene derivatives **97** in good to excellent yields, showing its significant versatility. Utilising acidic ionic liquids enhances reaction efficiency and creates novel possibilities in order to synthesize bioactive molecules, especially derivatives of quinoline and pyridine, which are highly desirable in medicinal chemistry. The reusability of ionic liquids was examined in the production of alkyl-substituted azaarene **97e**. The capability of the acidic ionic liquids to be recycled up to six-times with no substantial reduction in their catalytic activity is a significant attribute of this method (Fig. 19). After the reaction concludes, dioxane is eliminated under vacuum, and the residue is extracted using ether before being removed. This process leaves the aqueous phase containing the acidic ionic liquids behind.

Later, in order to develop benzyl esters despite the need for metals, Liu and colleagues outlined a heterocyclic ionic liquid-catalysed straightforward oxidative esterification of the benzylic Csp^3–H bond in hydrocarbons **99** with carboxylic acids **98** (Scheme 35).[136] They provided a novel protocol, utilising 20 mol% 1-butylpyridinium iodide ([BPy]I) as an efficient and recyclable catalyst. Various benzyl ester derivatives **100** could be prepared using the mentioned approach with yields ranging from good to excellent.

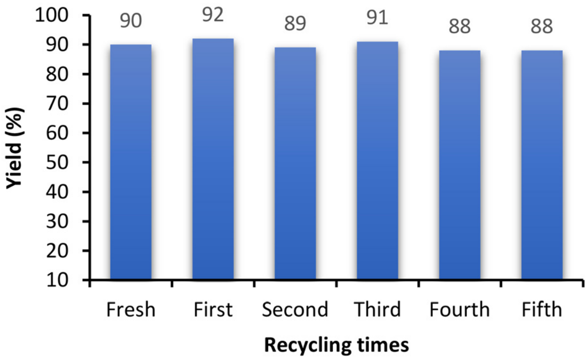
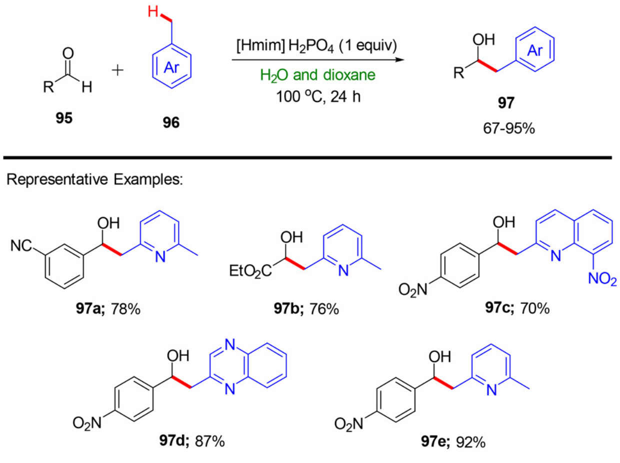


Fig. 19 Recycling study of ionic liquid promoted addition reaction of *p*-nitrobenzaldehyde to 2,6-lutidine.

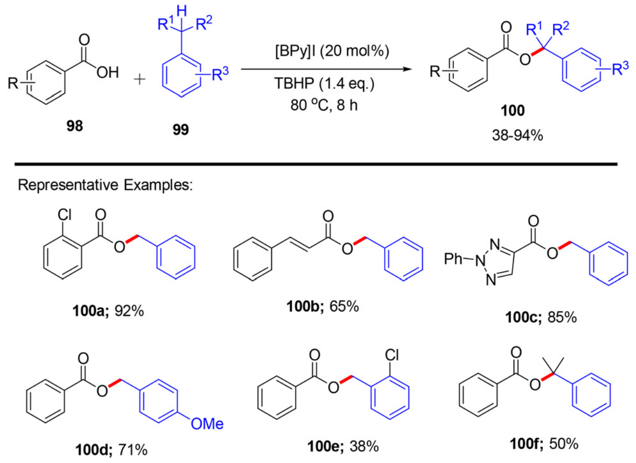
The recyclability of the ionic liquid catalyst [BPy]I was testified by the reaction of 2-chlorobenzoic acid and methylbenzene under standard reaction conditions which afforded the product **100a**. A minimum of four reaction cycles could be accomplished with this catalyst without a considerable decrease in its activity (Fig. 20). They demonstrated that catalyst retrieval is convenient from the aqueous phase by adding ethyl acetate and water on the completion of the reaction, using 2-chlorobenzoic acid and methylbenzene as representative substrates.

Feng *et al.* reported a pertinent protocol (as in Scheme 35) utilising Bu_4NI;[137] however, this method did not focus on re-



- Acid IL enhanced functionalization of C(sp3)–H bonds
- An effective method for synthesizing alkyl-substituted azaarene derivatives
- Attractive method for the generation of biologically active pyridine and quinoline derivatives IL recyclable upto six times

Scheme 34 Ionic liquid enabled C(sp^3)–H bond functionalisation of alkyl azaarenes for reaction with aldehyde.



- Direct oxidation of the Csp^3–H bond to form an ester
- IL catalyzed/metal-free protocol
- IL recyclable upto five times

Scheme 35 [BPy]I catalysed esterification of benzoic acids.

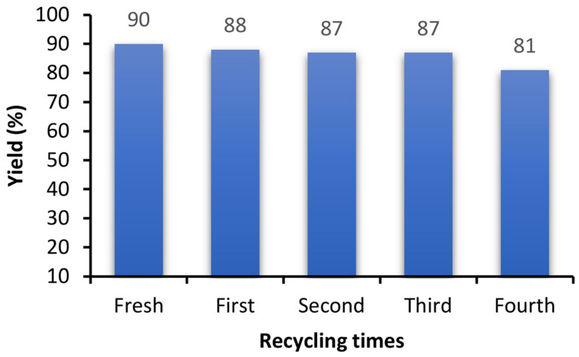
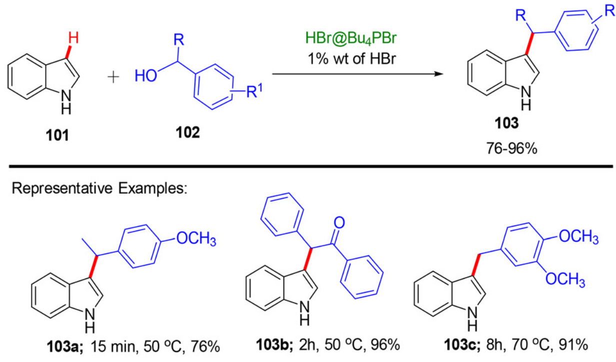


Fig. 20 The recyclability of the ionic liquid in the reaction of 2-chlorobenzoic acid and methylbenzene.

cycling the reaction medium. Notably, the protocols by Feng *et al.* and Liu *et al.* operate at the same reaction temperature and employ identical catalyst loadings, achieving efficient generation of the desired ester products.

The following year, Cirujano and co-workers underscored the significance of catalytic systems competent in being recovered and reused though sustaining the exceptional efficiency and selectivity typical of homogeneous catalysts.[138] They demonstrated that enhancing the flexibility of the catalytic environment, such as transitioning from rigid microporous structures to adaptable ionic liquids, increases the catalytic site turnover count. They evaluated the HBr@Bu_4PBr ionic liquid system for the green alkylation of indoles **101** with alcohols **102** under gentle, solventless parameters. C3 monoalkylated indole **103** has been generated by this system efficiently (Scheme 36). The HBr@Bu_4PBr system demonstrates good catalytic performance and maintains its activity in recycling. Indole derivatives can be easily separated through hydrocarbon solvent extraction in this quasi-homogeneous system, which merges the efficiency of homogeneous catalysts with the recyclability characteristic of heterogeneous ones. This allows for reuse in subsequent reaction cycles. The reusability provides a significant advantage compared to traditional homogeneous catalysts, which often suffer from difficult product recovery, deactivation, and moderate selectivity. Notably, the authors claim that HBr@Bu_4PBr is the lone recyclable framework described to date to attain high yields of the large indole derivative **103**, with consistent performance across five cycles without any noticeable decline in efficiency.

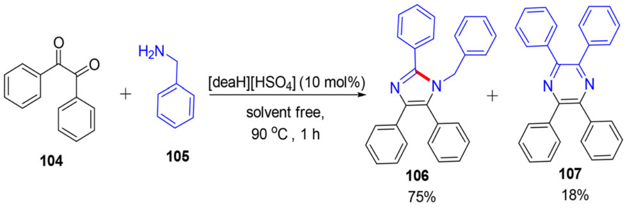


- Green alkylation of indoles with alcohols
- Mild and solvent-free condition
- HBr@Bu_4PBr as *quasi*-homogeneous catalyst
- Alternative reusable catalysts and reaction media to (porous) solid catalysts

Scheme 36 HBr@Bu_4PBr ILs for the alkylation reaction of indoles.

Afterwards, in Scheme 37, Valiyev and co-workers examine the utilisation of Brønsted acidic ionic liquids (ILs) as catalysts in order to prepare tetrasubstituted imidazoles (PRO1, **106**) and pyrazines (PRO2, **107**) from 1,2-diketones **104** and aliphatic amines **105** without the use of metals or solvents.[139] Among various screened ILs, the most effective were [deaH][HSO_4] and [taH_4][I_4], with [deaH][HSO_4] getting a 75% yield of PRO1 and 18% yield of PRO2 at 90 °C in an hour. The IL catalyst's robustness has been shown by catalyst recycling tests (Fig. 21), where PRO1 yields remained steady over three reuses. Surprisingly, PRO2 yields varied very little over the course of eight reuses, indicating that during brief reaction times, its formation is less dependent on the catalyst.

In recent work, Chu *et al.* designed an electrochemical approach that uses aryl tetrafluoroborate diazonium salts **109** in an ionic liquid [EMIM]BF_4 (1-ethyl-3-methylimidazolium



- Brønsted acidic IL catalyzed benzylic C(sp^3)–H bond activation
- Metal and solvent free synthesis of tetrasubstituted imidazoles and tetrasubstituted pyrazines
- Short reaction time
- IL recyclable upto eight times

Scheme 37 [deaH][HSO_4] catalysed preparation of tetrasubstituted imidazoles and pyrazines.

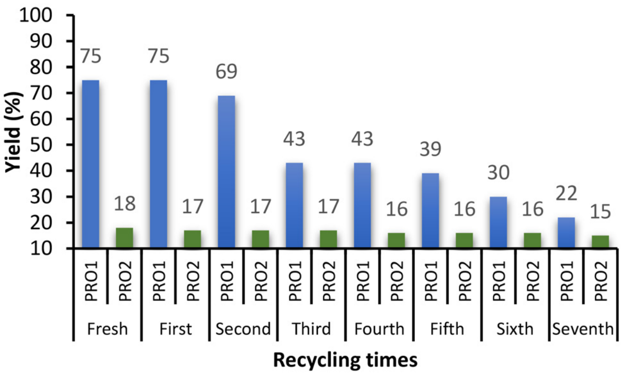
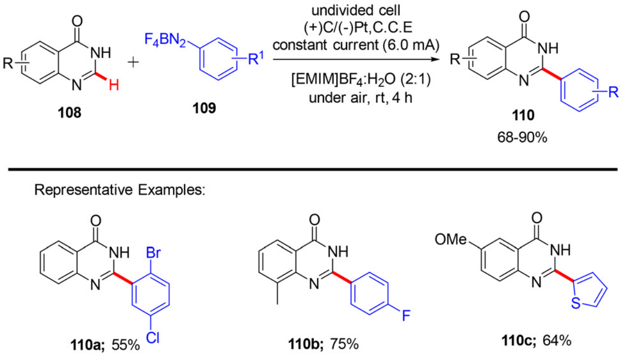


Fig. 21 Recycling test of the IL [deaH][HSO_4] for the synthesis of tetrasubstituted imidazoles and pyrazines.



- Electrochemical arylation of C–H bonds in quinazolinone
- Mild and green synthesis of 2-arylquinazolinones
- Application for the synthesis of a key intermediate of an IKK *β*-inhibitor CU160 and a quinazolinone alkaloid 2-(1H-indol-3-yl)quinazolin-4(3H)-one
- IL recyclable upto seven times

Scheme 38 Arylation reaction of quinazolinones in [EMIM]BF_4.

tetrafluoroborate) (2 : 1) as the electrolyte to directly arylate quinazolinones **108**.[140] Moderate to good yields of 2-arylquinazolinones **110** were effectively produced using this green, catalyst-free process (Scheme 38). Using [EMIM]BF_4 (2 : 1) as the electrolyte, a number of reaction cycles were executed to investigate the reusability of the ionic liquid medium. The mixture was extracted following each reaction, and the ionic liquid was preserved for use in later cycles. Over the course of four cycles, the system remained effective with the accumulation of impurities leading to only a slight yellowing of the ionic liquid. The electrochemical process in ionic liquids avoids the addition of a supporting electrolyte due to their inherent conductivity. This non-volatile system not only replaces the traditional organic solvent/supporting electrolyte system but also simplifies the product separation process, making it an ideal medium for electrochemistry.

4. Deep eutectic solvents (DESs) as homogeneous recyclable catalysts

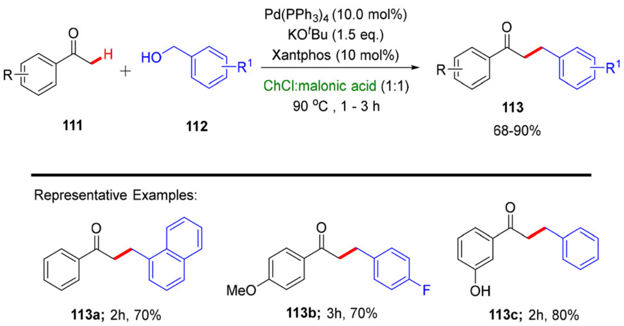
A deep eutectic solvent (DES) is a eutectic mixture of two or more constituents that forms a stable, low-melting liquid through hydrogen bonding interactions. DESs have captured growing attention in the past few years as promising solvents for catalysis reactions owing to their outstanding characteristics like excellent solubility, a broad viscosity range, low toxicity, and simple recoverability.[141] DESs have further showed distinguished catalytic activity, particularly as an eco-friendly substitute to traditional solvents and catalysts in abundant chemical transformations.[142–147] The efficiency of these eutectic blends as solvents or catalysts in organic synthesis and catalytic processes has been proved, emphasising their reusability.[148,149] They have also shown several advantages over conventional solvents and catalysts, such as simple synthesis from inexpensive and renewable raw materials, low toxicity, and biodegradability (especially regarding natural deep eutectic solvents), along with easy recycling and reuse in multiple reaction cycles, making them a sustainable and environmentally friendly alternative.[150]

Recent years have seen the successful demonstration of C–H activation reactions with recyclable deep eutectic solvent (DES) catalytic devices. The implementation of homogeneous recyclable DES systems in C–H activation methods is emphasised in this section. We have separated the discussion into two subsections for the sake of simplicity and complete interpretation: (1) DES mediated C–H functionalisations catalysed by transition metals and (2) C–H functionalisation catalysed by deep eutectic solvents.

4.1 DES mediated C–H functionalisations catalysed by transition metals

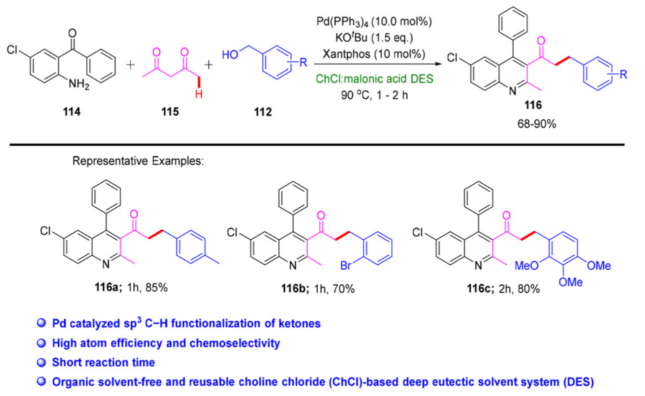
Various transition metals played a significant role as catalytic agents in DES-mediated modifications of C–H bonds. Teja and Khan in 2019 applied an environmentally friendly alternative for volatile organic solvents for sp^3-C–H functionalisation: a choline chloride-based deep eutectic solvent (DES) system.[151] In Scheme 39, they demonstrated how to functionalise acetophenones **111** with benzyl alcohols **112** *via* sp^3-C–H bonding, developing the corresponding α,β-saturated ketones **113**. 10 mol% palladium-tetrakis(triphenylphosphine) [$Pd(PPh_3)_4$] was utilised as the catalyst and Xantphos as a ligand to successfully accomplish the process, which involved a sequential dehydrogenation–aldol condensation process and the hydrogen transfer mechanism. Interesting findings were also obtained when the team examined a stepwise Friedländer reaction of 2-aminobenzophenone **114**, followed by the palladium-catalysed α-alkylation of quinolinyl methyl ketone using benzyl alcohols **112**, performed with a deep eutectic solvent (DES) system based on ChCl (Scheme 40).

A hydrogen bond donor and an acceptor—choline chloride in this instance—combine to form DESs, which are well-known for their biodegradability and low toxicity. Palladium-



- Pd catalyzed sp^3 C–H functionalization of methyl ketones
- High atom efficiency and chemoselectivity
- Short reaction time
- Organic solvent-free and reusable choline chloride (ChCl)-based deep eutectic solvent system (DES)

Scheme 39 Pd-catalysed α-alkylation of acetophenones.



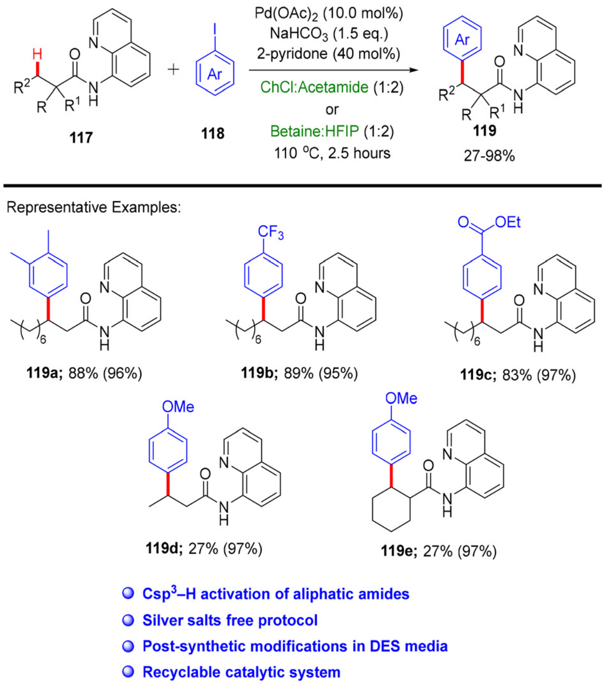
Scheme 40 Cascade Friedländer reaction: 4-α-alkylation of N-heterocyclic ketones.

catalysed dehydrogenation–aldol condensation was effectively mediated by the DES, which improved the process's atom efficiency and chemoselectivity.

This DES system's reusability is one of its main benefits; several reaction cycles were conducted without significant reduction in catalytic efficiency. Following the reaction, the DES could be recovered using a simple aqueous workup, in which the products were precipitated by diluting the reaction composition with water. After that, the filtrate was removed by evaporation to recover the remaining DES-catalyst composition, subsequently utilised for additional reactions. Through the use of dichloromethane or ether to extract it from the aqueous phase, the DES itself was recycled, and FT-IR analysis was employed to confirm its functional integrity.

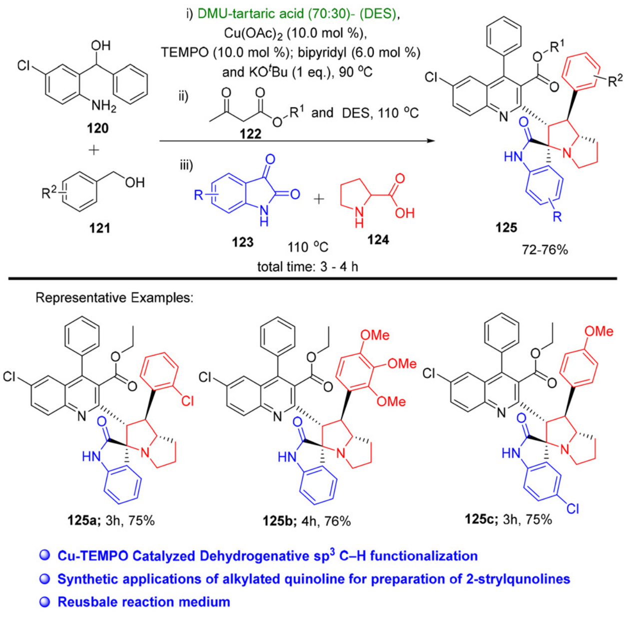
In deep eutectic solvents (DESs), palladium acetate (10 mol%) acts as the central catalyst in Marset's catalytic framework for the Csp^3–H activation of aliphatic amides.[152] In the DES [ChCl : acetamide (1 : 2) or betaine : HFIP (1 : 2)] under an air atmosphere, they reported an arylation reaction integrating aryl halides **118** and amides derived from 8-aminoquinoline **117** (Scheme 41). In contrast to traditional organic solvents, the optimised catalytic system using deep eutectic solvents (DESs) provides improved yields, safer solvent options, and enhanced reactivity. The reaction conditions are more cost-effective and sustainable because of this novel system's elimination of the need for Ag salts, which are frequently employed in similar transformations. The catalyst can be reused, further emphasising the environmental and economic advantages of this approach, because of the DESs, which also maximise reaction yields.

Upon the reaction's completion, the system is brought to a lower temperature, and then two immiscible phases are generated by the addition of 2-MeTHF, a green solvent. The palladium catalyst and the DES stay in the reaction vessel, while the organic phase containing the product is isolated. For two more cycles, the reaction can be restarted with new starting materials without the need for extra palladium or ligand.



Scheme 41 Palladium catalysed arylation of aliphatic amides.

A robust approach to generate spiro[indoline-3,3′-pyrrolizin] was described by Pavithra *et al.* in the year 2020. The dehydrogenative Friedländer annulation catalysed by Cu(OAc)$_2$/TEMPO, followed by sp^3 C–H functionalisation and regioselective 1,3-dipolar cycloaddition, yielded the compound spiro[indoline-3,3′-pyrrolizin]-2′-yl)-4-phenylquinoline-3-carboxylate **125** (Scheme 42).[153] 2-Amino-5-chlorobenzhydrol **120**, benzyl alcohols **121**, and methyl or ethyl acetoacetate **122** are the starting materials employed in this reaction.



Scheme 42 Cu-TEMPO catalysed generation of spiro[indoline-3,3′-pyrrolizin]-2′-yl)-4-phenylquinoline-3-carboxylate.

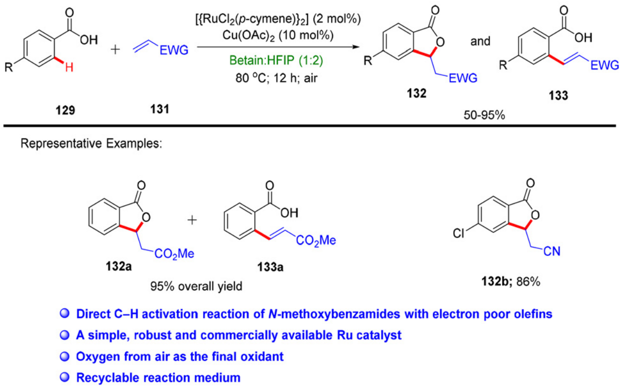
At first, the dehydrogenative Friedländer annulation is performed in a deep eutectic solvent using $Cu(OAc)_2$/TEMPO with 10 mol% Cu catalyst, bipy, KO*t*Bu, and ethyl or methyl acetoacetate **122**. The resulting 2-styrylquinolines, generated *in situ*, then undergo 1,3-dipolar cycloaddition under the influence of isatin **123** and L-proline **124**, yielding the final product, spiro[indoline-3,3′-pyrrolizin]-2′-yl)-4-phenylquinoline-3-carboxylate **125**.

The application of 1,3-dimethyl urea-tartaric acid offers multiple benefits, including minimal toxicity, affordability, biodegradability, and reusability. The stability of the DES was shown by its infrared (IR) spectra before and after the reaction, which additionally verified the preservation of hydrogen bonding and catalytic activity. There were no significant modifications in the key stretching and bending vibrations.

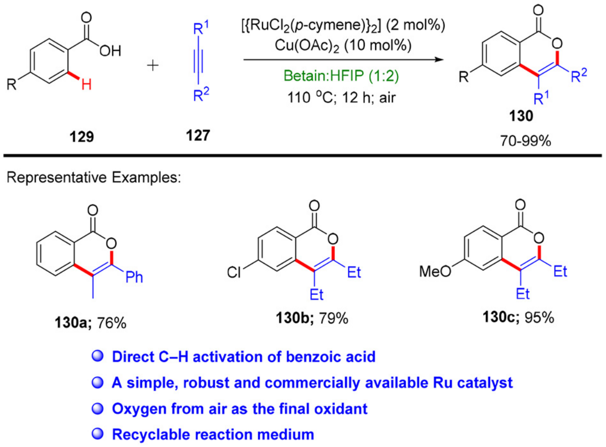
In order to facilitate greener Ru-catalysed C–H functionalisation transformations, González-Gallardo and coworkers recently proposed deep eutectic solvents (DESs).[154] Using sodium acetate as an additive and a DES consisting of ethylene glycol and choline chloride (in a 1 : 2 ratio), the group carried out a model Ru-catalysed C–H functionalisation reaction of *N*-methoxybenzamides **126** in the presence of internal alkynes **127**. Derivatives of isoquinolones **128** were generated as an outcome of this protocol (Scheme 43). Acyclic and cyclic products were generated when they investigated the reactivity of *N*-methoxybenzamides with electron-deficient olefins under the same conditions.

Furthermore, the DES system was replaced with betaine : HFIP (with a ratio of 1 : 2) to test another C–H functionalisation reaction. C–H activation of *N*-phenoxyacetamide with diphenylacetylene was performed to give the corresponding disubstituted benzofuran with 70% product yield.

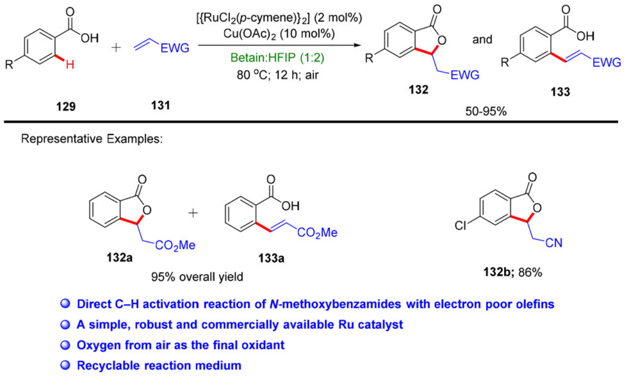
Using copper(II) acetate as an additive, the team then turned its focus to the C–H activation of benzoic acid **129** to react with internal alkynes **127**, which generated isocoumarin derivatives **130** in high to outstanding yields with high efficiency (Scheme 44). They additionally examined how benzoic acid **129** reacted with different electron-deficient olefins **131**, resulting in both cyclic and acyclic products (Scheme 45). It is worth mentioning that, depending on the substrate used, methyl acrylate reactions can yield both acyclic and cyclic products.



Scheme 43 Ruthenium catalysed C–H annulation of *N*-methoxybenzamides.



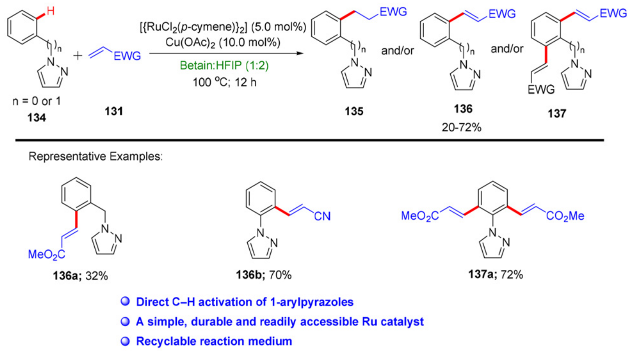
Scheme 44 Ru-catalysed C–H annulation of benzoic acids with internal alkynes.



Scheme 45 Ru-catalysed C–H activation reaction of benzoic acids with electron poor olefins.

Shang and co-workers also described a related protocol (as in Scheme 44) using a similar Ru catalyst.[155] While this method, unlike the one in Scheme 44, did not address reaction medium recycling, it offered the advantages of milder temperatures and the use of water as a sustainable solvent, with air as the sole oxidant. It is worth noting, however, that this protocol required a higher catalyst loading compared to that in Scheme 44.

Following that, investigations have been carried out with an array of electron-deficient olefins **131** and 2-thiophenecarboxylic acid, which successfully produced cyclic products. In Scheme 46, the group explored the reactivity of aryl pyrazole derivatives **134** with electron-deficient olefins **131** in a further extension of their research. Both saturated **135** and unsaturated compounds **136** were produced by this reaction. It is interesting to point out that minor amounts of monoalkenylated target molecules were seen along with the double addition products **137** when alkyl acrylate derivatives were employed.



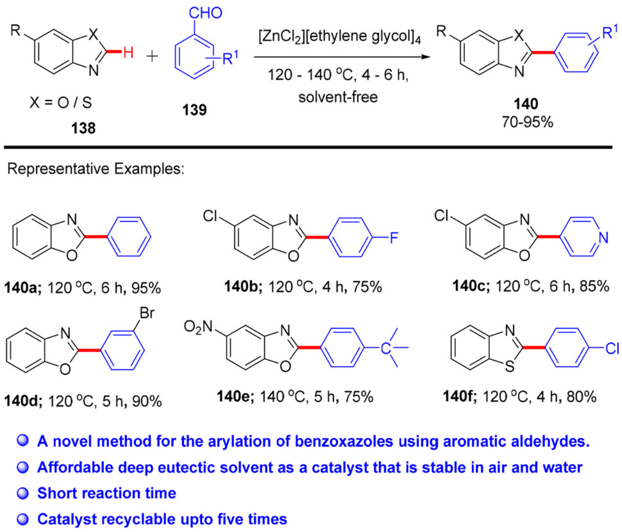
Scheme 46 Ru-catalysed C–H activation of 1-arylpyrazole derivatives with electron poor olefins.

Their straightforward approach efficiently produces fascinating heterocyclic compounds by activating a broad array of aromatic reactants. On employing a commercially available ruthenium catalyst, the method works well with both internal and external oxidants, including atmospheric oxygen, and achieves similar or better results compared to previous techniques. The advantages of DESs are emphasised during the investigation, particularly their efficiency and recyclability. Recycling the DES is made feasible by the extraction of the organic products from each reaction using a solvent derived from biomass. Even though yields begin to drop after the fifth cycle, the method can support gram-scale reactions that require fewer purification steps, which minimises wasteful solvent use.

4.2 C–H functionalisation catalysed by deep eutectic solvents

Beside the transition metal catalysed functionalisation of C–H bonds in DES media, deep eutectic solvents (DESs) can also act as catalysts themselves. Following this, in 2018, Tran and Hang established an innovative competent protocol to achieve the arylation of benzoxazoles **138** and benzothiazoles with aromatic aldehydes **139**.[156] DES catalysts, such as [$ZnCl_2$][ethylene glycol]$_4$, demonstrate superior catalytic activity, yielding higher product yields (95%) compared to metal catalysts like $ZrCl_4$ (70%), $ZnCl_2$ (20%), $FeCl_3$ (75%), and $HfCl_4$ (73%). This highlights DESs' effectiveness in promoting the reaction, making them a compelling alternative to conventional metal catalysts. Within a brief time frame, the reaction generated the anticipated arylated benzoxazoles **140** (Scheme 47) and benzothiazoles in high yields while operating smoothly across a variety of substrates. The technique is cost-effective and safe for the environment owing to the easily recoverable and reusable nature of the deep eutectic solvent, which consists of zinc chloride and ethylene glycol. This work demonstrates that DES-mediated arylation, which uses only catalytic amounts of DES for the reaction under solvent-free conditions, offers an appealing alternative to expensive palladium catalysts.

A model reaction, involving arylation of benzoxazole with benzaldehyde to generate arylated benzoxazoles **140a**, was employed to test the DES's recyclability, with the catalyst being used five times in sequence (Fig. 22). Utilising diethyl ether, the final product was separated from each reaction, and the DES was separated, vacuum-dried, and re-used with little to no decrease in activity. Just a minor quantity of zinc leaching (0.08 ppm) was noticed during the work-up process by inductively coupled plasma mass spectrometry (ICP-MS), while IR spectroscopy confirmed that there was no apparent structural degradation of the DES after recycling. Though there was a small drop in catalytic activity following several recycling cycles, this study highlights the effectiveness, durability, and sustainability of the DES, establishing it as a sustainable replacement for the C2-arylation of benzoxazoles and benzothiazoles.



Scheme 47 Arylation reaction of benzoxazoles catalysed by a deep eutectic solvent.

Through a three-component reaction featuring 1*H*-pyrazol-5-amine **141**, isatin **142**, and an enolisable C–H activated compound **143**, Zhang and colleagues later established a sustainable protocol in order to synthesize pyrazolo[3,4-*b*]quinoline spirooxindoles **144** by a one pot approach (Scheme 48).[157] The

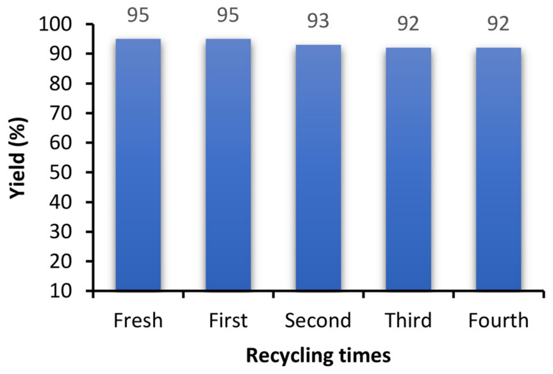
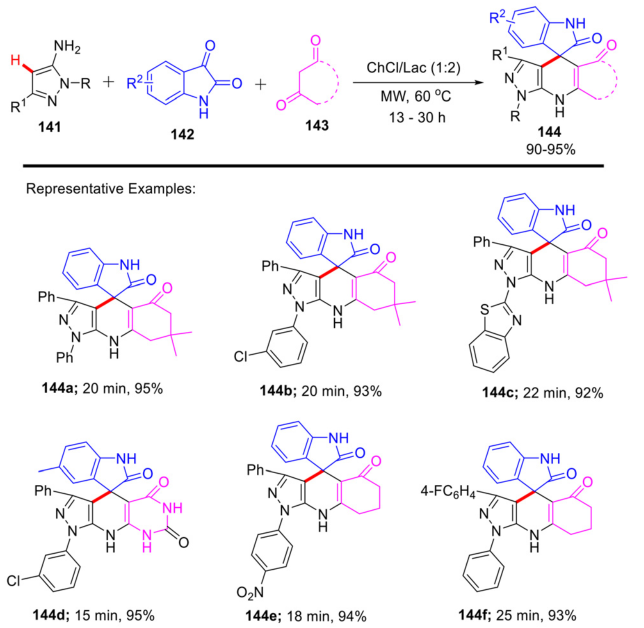


Fig. 22 Recycling of the [$ZnCl_2$][ethylene glycol]$_4$ catalyst for the arylation reaction.



- **Three component reaction**
- **One-pot synthesis of pyrazolo[3,4-b]quinoline spirooxindoles**
- **Short reaction time**
- **Catalyst and media recyclable upto eight times**

Scheme 48 Preparation of pyrazolo[3,4-*b*]quinoline spirooxindoles in a ChCl/Lac deep eutectic solvent.

optimised catalytic system using a natural deep eutectic solvent (NADES) offers advantages over organic solvents by providing higher product yields, facilitating a cleaner and more cost-effective reaction, simplifying the procedure, and allowing for reusability. The reaction becomes easier by microwave irradiation in a natural deep eutectic solvent (NADES) comprising choline chloride and lactic acid, which is biodegradable, recyclable, and reusable. The technique is distinctive in that it does not require chromatography and is straightforward, scalable, high-yielding, and clean. Excellent yields were maintained when the model reaction was tested on a 100 mmol scale to establish the reaction's robustness and scalability.

The assessment of the NADES's recyclability was examined in the synthesis of product **144a** which demonstrated that, regardless of eight recycling cycles, the system retained a 78% yield of the desired compound (Fig. 23). The reason for this insignificant yield drop is believed to be a small amount of solvent lost during the work-up process.

In 2021, Nguyen *et al.* have shown that the catalytic system [CholineCl][$ZnCl_2$]$_3$ is successfully recyclable when applying 2-naphthol **145**, benzaldehyde **146**, and benzamide **147** in the multi-component preparation of 1-amidoalkyl naphthols **148** (Scheme 49).[158] The applied DES system showed higher efficiency (94% yield) than metal catalysts like $ZnCl_2$ (61%), $FeCl_2$ (65%), and $AlCl_3$ (74%) for the proposed protocol. This process is a sustainable substitute for traditional methods since it works at low temperatures, has short reaction times, and does not need volatile or hazardous organic solvents. The DES affects product selectivity in addition to enabling the reaction with high yields. With the addition of aldehydes **149**, dimedone **150**, ethyl acetoacetate **151**, and ammonium acetate, the proposed catalytic system has been further expanded for the generation of polyhydroquinolines **152** (Scheme 50). The catalyst [CholineCl][$ZnCl_2$]$_3$ has outstanding recyclability; it could be reused thrice without going through substantial performance loss while retaining high catalytic activity. After every reaction cycle, the catalyst's structure remained largely unchanged, as determined by FT-IR analysis. The FT-IR spectra of the fresh and recovered catalysts indicated nearly identical results, suggesting that the deep eutectic solvent (DES) had been effectively recovered and employed again in later runs. This minimal structural degradation highlights the stability and durability of the [CholineCl][$ZnCl_2$]$_3$ system in multicomponent reactions.

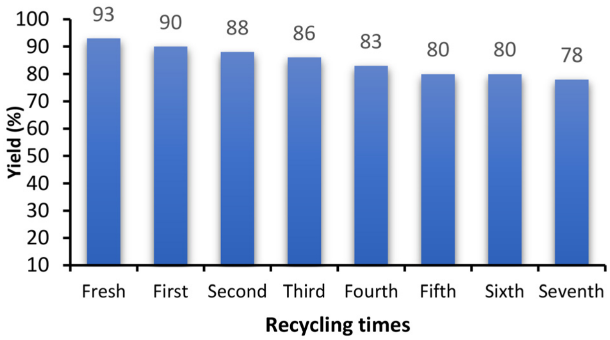
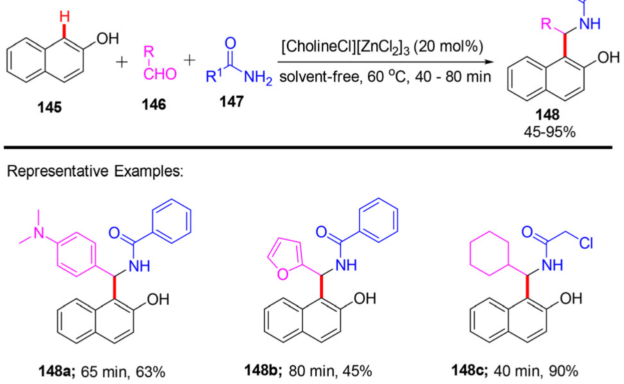
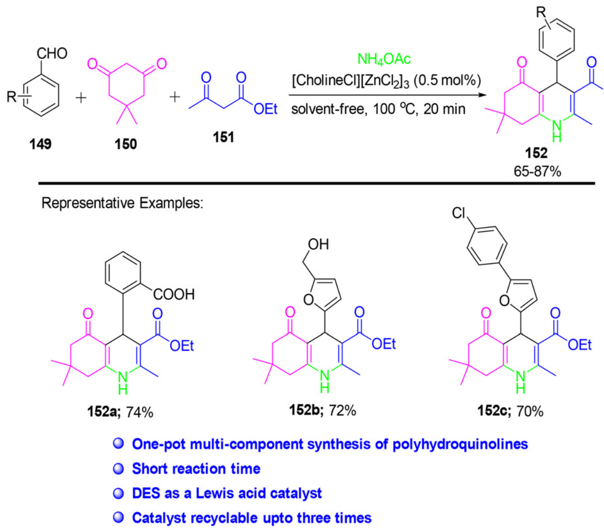


Fig. 23 Recyclability of the NADES catalytic system in the synthesis of pyrazolo[3,4-*b*]quinoline spirooxindole (**144a**).



- **One-pot three-component synthesis of 1-amidoalkyl naphthols**
- **Low temperature and short reaction time method**
- **DES as a Lewis acid catalyst**
- **Catalyst recyclable upto three times**

Scheme 49 [CholineCl][$ZnCl_2$]$_3$ catalysed synthesis of 1-amidoalkyl naphthol.



Scheme 50 [CholineCl][ZnCl$_2$]$_3$-catalysed synthesis of polyhydroquinolines.

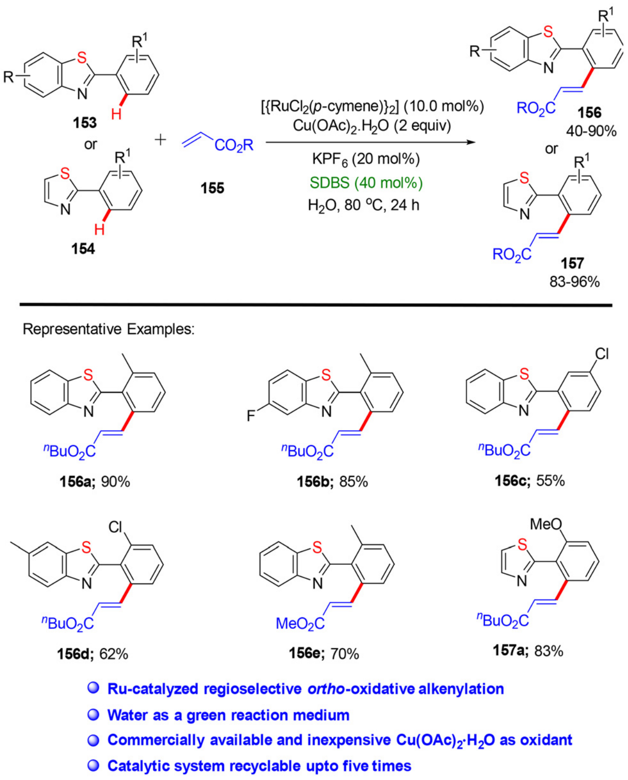
5. Homogeneous recyclable micellar catalysts

Micellar catalysts are self-assembled structures produced by surfactants, and can serve as a homogeneous, recyclable, and efficient catalytic system. These catalysts show exclusive characters, such as the capability to solubilise both polar and nonpolar reactants, and the ability to be readily recovered and reused, making them a desirable choice for a variety of chemical transformations. Recent research has emphasised on the potentiality of micellar catalysts in a wide variety of uses, including organic synthesis, biocatalysis, and environmental remediation.[159–161]

A primary benefit of micellar catalysts is its competence to be readily retrieved and reutilised, which can substantially contribute to the environmental friendliness of chemical processes.[162,163] Micellar catalysts, identical to heterogeneous catalysts, can be easily recovered using straightforward tactics, like centrifugation or extraction, and then reintroduced into the reaction system, making them a financially and environmentally sound choice.

The development of micellar catalysts as an effective replacement for traditional homogeneous and heterogeneous catalysts has risen in significance as the demand for efficient and sustainable chemical processes keeps rising. Micellar catalysts can also be effectively employed for C–H functionalisation reactions.[164,165] This section emphasizes the implementation of protocols involving homogeneous recyclable micellar catalytic systems for the functionalisation of C–H bonds.

In accordance with Scheme 51, Ping *et al.* developed a benign and competent Ru(II)-catalysed *ortho*-oxidative alkenylation of 2-arylbenzo[*d*]thiazoles **153**, which comprises the activation of two C–H bonds.[166] The catalytic system uses 10 mol% ruthenium complex in conjunction with an aqueous solution of the anionic surfactant sodium dodecylbenzenesulfonate (SDBS). Among other screened phase transfer catalysts, SDBS (sodium dodecylbenzenesulfonate) was found to be the most effective, yielding the desired product with the highest yield. This ecologically benign setup utilises aqueous solvent and activated olefins **155** as coupling partners. Remarkably, this transformation progresses under mild conditions (80 °C) and requires a catalytic quantity of the inexpensive oxidant Cu(OAc)$_2$·H$_2$O. The application of SDBS improves the effectiveness and selectiveness of the alkenylation, facilitating the reaction on a gram scale with high regioselectivity toward *ortho*-C–H bond activation. Moreover, the system is applicable to a broad array of substrates, comprising both 2-arylbenzo[*d*]thiazoles **153** and 2-arylthiazoles **154**, and generates alkenylated products with high yields.



Scheme 51 Ruthenium catalysed alkenylation of 2-arylbenzo[*d*]thiazoles and 2-arylthiazoles.

The reusability of this Ru-catalyst was also studied, indicating robust performance over three successive cycles with negligible decline in performance. Specifically, the alkenylation of 2-(*o*-tolyl)benzo[*d*]thiazole using *n*-butyl acrylate was carried out under ambient conditions to synthesize product **156a** in order to assess the recyclability (Fig. 24). The results established the efficiency and sustainability of the Ru/SDBS system, which retained its catalytic activity throughout the trials.

Miura and his team also reported a related approach (as illustrated in Scheme 51) for synthesising compounds **156** using a similar ruthenium catalyst.[167] Although this alternative method, unlike the previously mentioned protocol in

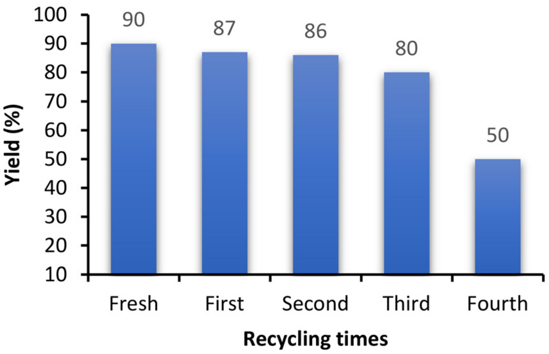
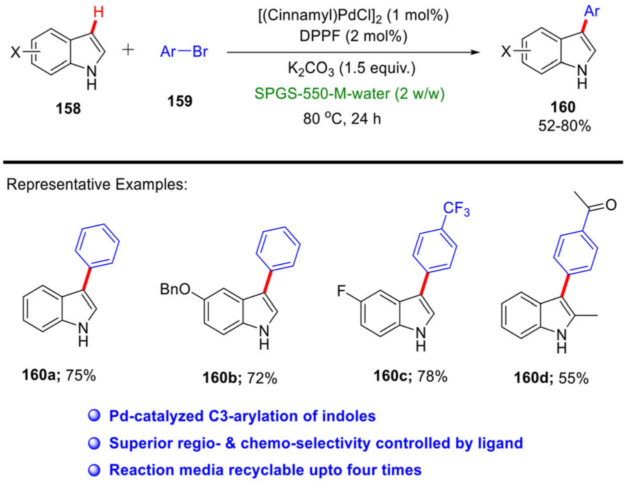


Fig. 24 Recycling study of the ruthenium catalyst in the alkenylation of 2-(*o*-tolyl)benzo[*d*]thiazole.

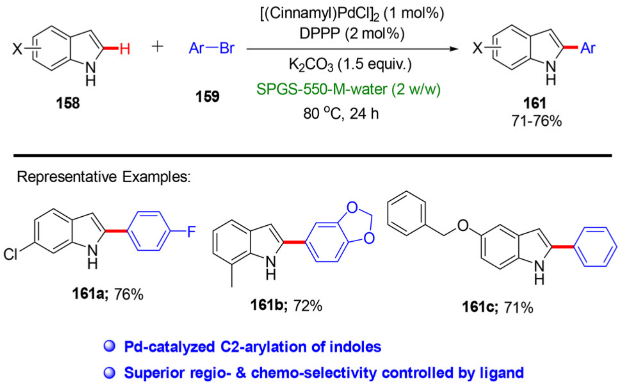
Scheme 50, did not incorporate reaction medium recycling, it boasted a shorter reaction time. However, achieving this outcome necessitated higher temperatures and the inclusion of a silver salt.

The Kumar research group in the year 2019 employed a micellar catalysis strategy to establish a sustainable and selective arylation of C–H bonds in indoles **158**.[168] They performed this by employing a palladium catalyst known as [(Cinnamyl)PdCl]$_2$ (1 mol%) and the third-generation designer surfactant SPGS-550-M. Fundamental principles of green chemistry are achieved by this catalytic system, facilitating the selective arylation of indoles at either the C-2 or C-3 position under mild conditions. In order to direct the site-selectivity and promote arylation at C-3 (Scheme 52) and C-2 (Scheme 53), correspondingly, the selection of phosphine ligands—specifically, DPPF and DPPP—was critical. Using water as the solvent, the reaction demonstrates high chemo- and regio-selectivity and can tolerate an extensive range of functional groups.

The reusability of the catalyst has been accessed in the synthesis of **160a**. Yields would not be impacted by repeated applications of the surfactant-containing aqueous micellar solution (Fig. 25). Each reaction cycle enabled easy separation of the SPGS-550-M-containing aqueous layer from organic residues, allowing it to be reused in later batches without suffering a significant decrease in conversion efficiency.



Scheme 52 Pd based catalyst for C3-selective arylation of indoles using aryl bromides.



Scheme 53 Pd based catalyst for C3-selective arylation of indoles using aryl bromides.

In the same year, with the support of micellar catalysis, the Ackermann group established a chemoselective C–H arylation approach applying a single-component ruthenium catalyst.[169] Through weak chelation assistance, this innovative strategy achieved a broad range of C–H arylated ferrocenes **164** with a high compatibility for an array of functional groups. The homogeneous catalysis in aqueous media was facilitated by the properties of [Ru(*p*-cymene)(O$_2$CAd)$_2$] and [Ru(OAc)$_2$(PPh$_3$)$_2$] in the ruthenium(II)-catalysed C–H arylation system. By utilising micellar systems, this technique was able to exhibit outstanding sustainability and maintain high reactivity and selectivity, even with sensitive functional groups. The wide-ranging C–H arylation enabled by ruthenium failed to be exclusive to mono-substituted ferrocenes. In fact, it emerged that ferrocenes could also be employed as effective substrates to develop the arylated products **164** (Scheme 54). Furthermore, in the scope of the Ru-catalysed C–H activation protocol, it was found that differently substituted arenes **165**

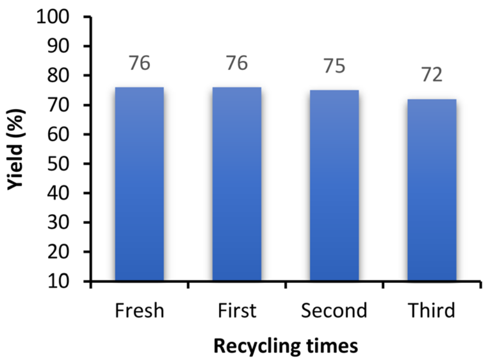
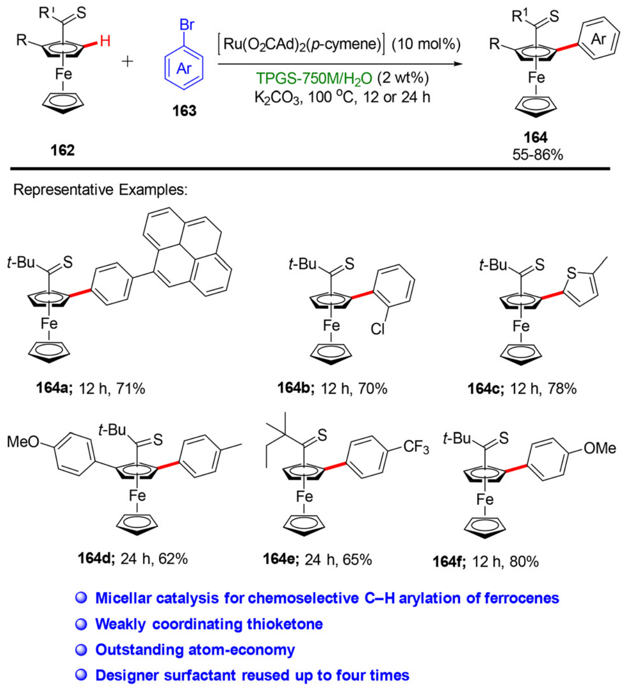
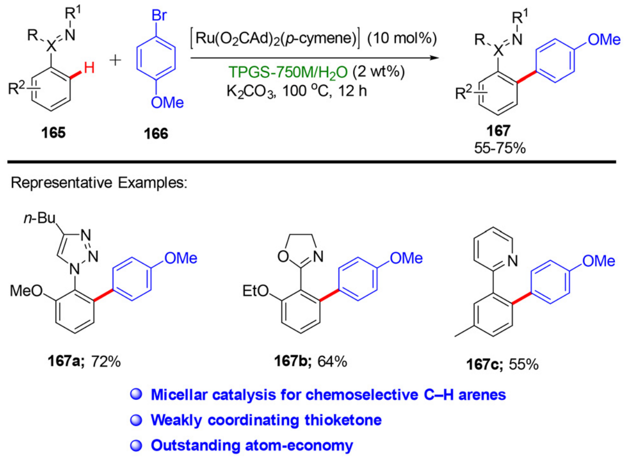


Fig. 25 Recycling study of Pd catalysed C3-selective arylation of indoles to synthesize **160a**.



Scheme 54 Micellar C–H arylations of ferrocenes using aryl bromides.



Scheme 55 Micellar C–H arylations of arenes using aryl bromides.

were also arylated (Scheme 55). The used micellar system enables C–H arylations with high chemoselectivity and broad functional group tolerance, demonstrates high catalytic performance and water stability, allows for catalyst recycling, and provides a more sustainable process with a low *E* factor.

A recycling study of the surfactant has been performed in the synthesis of **164f** and the fact that it could be recycled up to four times without going through an apparent reduction in catalytic efficiency highlights the method's practical and environmental advantages (Fig. 26). After the reaction ended, ethyl acetate was introduced, and the solution was gently agitated over five minutes. A centrifuge was then utilised to separate the organic layer, and the solvent was concentrated while the pressure was decreased. The anticipated product was obtained through column chromatography purification. Without the need for an extra surfactant, the aqueous layer that was left over after separation was kept for additional recycling research.

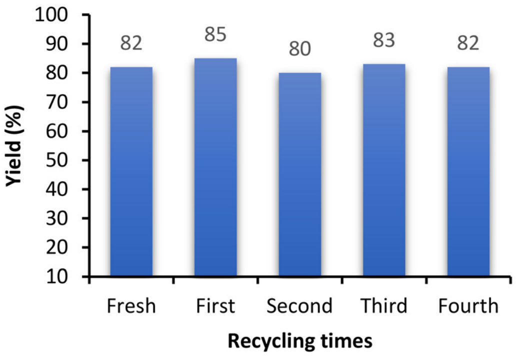


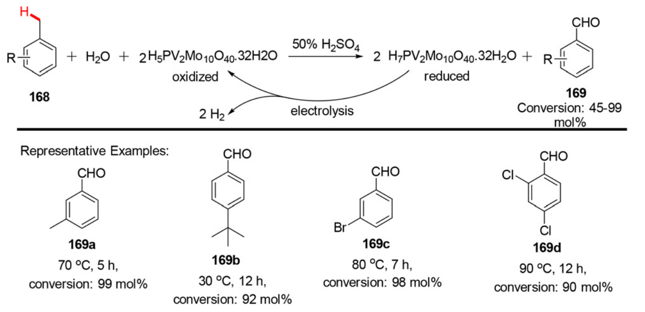
Fig. 26 Recycling study of the surfactant in the synthesis of **164f**.

6. Biphasic systems for homogeneous recyclable catalysis

A biphasic catalytic system is a specialised catalytic system in which the catalyst is either dissolved or immobilised in one of the two immiscible phases, typically an organic phase and an aqueous phase. This system improves the efficiency of catalytic methods by enabling easier catalyst retrieval from the reaction mixture.[170,171] The investigation of biphasic catalytic systems has gathered extensive emphasis in recent years, mainly owing to their capability to improve the efficiency and sustainability of chemical processes.[172–179] The increasing need for green chemistry solutions that address both ecological and financial concerns has encouraged the development of recyclable biphasic systems.[180–192]

Recently, the employment of these systems to C–H activation reactions has shown substantial potential. With the combination of biphasic systems with C–H activation protocols it was intended to take advantage of the distinguished reactivity and efficiency of homogeneous catalysis accompanied by the practical benefits of heterogeneous systems, such as recyclability and ease of separation. This review section will focus on the advancement of homogeneous recyclable biphasic catalytic systems for C–H activation transformations, highlighting the recyclability of the proposed systems.

By utilising a polyoxometalate catalyst, namely $H_5PV_2Mo_{10}O_{40}$, to oxygenate methylarenes **168**, Neumann's research team, during the year 2015, created a highly effective technique for synthesising benzaldehyde derivatives **169** (Scheme 56).[193] Since it prevents the excessive waste produced by traditional techniques and avoids over-oxidation to benzoic acids, this reaction is highly interesting. It also has a 100% atom economy. Utilising an aqueous sulphuric acid solvent in



- Polyoxometalate mediated electron transfer-oxygen transfer reaction
- 100% theoretical atom economy
- No 'over oxidation' to benzoic acids
- Recyclable catalytic system

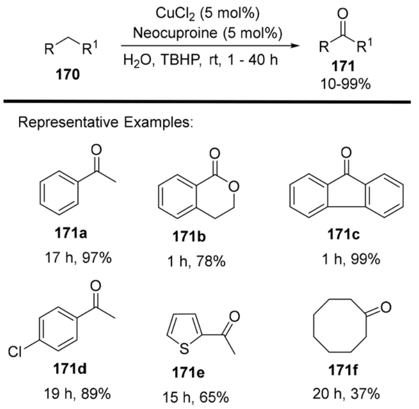
Scheme 56 Polyoxometalate catalysed oxygenation of methylarenes to benzaldehydes.

a biphasic mode, the system makes it easier to recover and recycle the catalyst while also facilitating the catalytic reaction. Aiming to promote the selective conversion of methylarenes **168** into benzaldehyde derivatives **169**, the polyoxometalate is protonated by the acid solvent. This allows for subsequent proton and electron transfers. This method releases H_2 during electrolysis and permits additional reaction cycles. It additionally yields over 95% and allows multiple catalytic cycles with almost no waste.

Using substrates such as toluene and its derivatives, the polyoxometalate catalyst's recyclability was thoroughly evaluated in multiple cycles, showing its stability and efficiency over five oxygenation–electrolysis cycles. The biphasic aqueous sulphuric acid medium enabled the catalyst's easy reoxidation and recovery without requiring removal, leading to high conversion rates and product selectivity with only minor variations of ±3% between cycles.

Later in 2016, a promising catalytic system to achieve C–H bond functionalisation of arylalkane **170** and substrates with an array of methylene groups was contributed by Hossain and Shyu's work.[194] As shown in Scheme 57, the method transforms the substrates into the corresponding ketones **171**. *tert*-Butyl hydroperoxide (TBHP), an environmentally harmless solvent, is used as the oxidant in water to catalyze the reaction, which is mediated by 5 mol% copper salts. The reaction conditions have been rendered easier by not using phase-transfer catalysts or bases, and the process is conducted at room temperature. Its ability to tolerate an array of functionalised arylalkanes and activate C–H bonds outside of the usual benzylic methylene positions is one of its primary advantages. The ease with which products can be separated, without requiring chromatographic workup, enhances its applicability in synthetic applications.

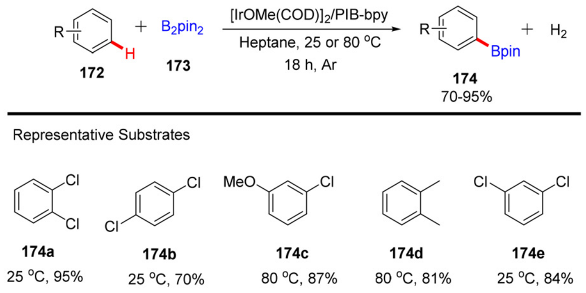
The catalyst's ability to be recycled over multiple reaction cycles attested its sustainability. After every reaction, the product was transferred to the organic layer using ethyl acetate, retaining the copper catalyst in the aqueous phase. The catalyst remained stable and active since there was no apparent percolation of the neocuproine ligand inside the organic medium. The system is highly recyclable as it can be used until seven times without compromising catalytic efficacy. In addition, it proved that the catalytic process is scalable, showing consistent performance in reactions at the gram scale, underscoring its potential for use in industrial settings.



- Copper-catalyzed activation of C–H bonds in arylalkanes in a biphasic system.
- Water as an environmentally friendly solvent
- Mild reaction conditions
- Catalyst recyclable up to seven times

Scheme 57 Biphasic copper-catalysed oxidation of arylalkanes into ketones.

In the subsequent year, Mamlouk *et al.* showed how to successfully use PIB oligomers functionalised with bipyridine (bpy) ligands and iridium complexes derived from Ir(I) precursors as recyclable catalysts to achieve the borylation of arenes **172** with bis(pinacolato)diboron **173** (Scheme 58).[195] This oligomer-supported catalyst generated a variety of arylboronates **174** under mild operating conditions that were identical to those from its non-recyclable counterparts. The system's creative design and efficient biphasic separation made it feasible to recover the catalyst with very little iridium leaching in the first cycle and almost none in the second and third. The catalyst demonstrated outstanding stability for up to eight cycles,



- Ir-catalyzed C–H borylation reaction of arenes
- Pure products by simple extraction
- Mild reaction conditions
- Catalyst recyclable up to eight times

Scheme 58 Ir-catalysed borylation of aromatic compounds.

allowing high yields of arylboronate products **174** without requiring further purification.

A simple extraction technique was employed to carry out the recycling process, by making use of the PIB-bound iridium complex's differing solubilities in nonpolar solvents like heptane, while the arylboronate products were extracted into acetonitrile. The method guaranteed full catalyst recovery for future applications and high product purity (>97%). Approximately 90% of the 1,2-dichlorobenzene and 84% of the 1,3-dichlorobenzene borylation yields were retained in subsequent catalytic runs, proving the robustness and generality of the recycling process.

7. Homogeneous recyclable C–H functionalisation reactions by simple filtration or extraction

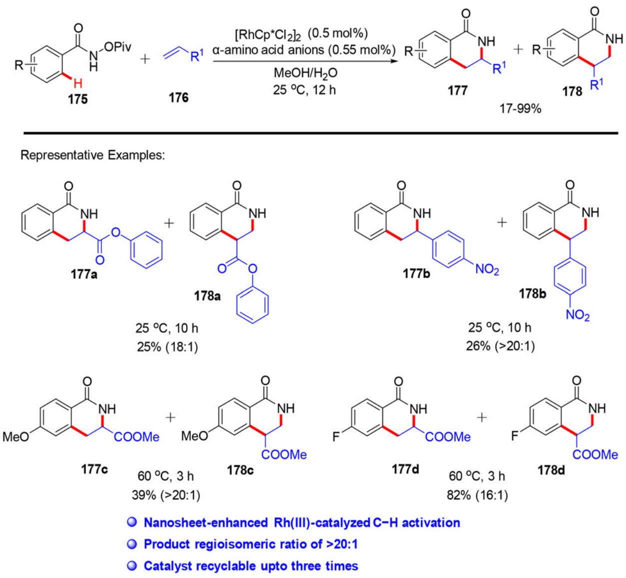
Homogeneous recyclable catalytic systems offer the rewards of high activity and selectivity, while enabling efficient recovery and reuse. Attempts to erase the boundary between homo- and heterogeneous catalysis towards enhanced catalytic activity, selectivity, and cost-effectiveness are dominant.[196,197] Beside the approaches discussed in previous sections of this review article, some tactics are reported in the literature which combine the merits of both homogeneous and heterogeneous catalysis through simple filtration[198–201] or extraction[202] techniques. The progress in such practices bridges the boundary between homogeneous and heterogeneous catalysis.

This section highlights such homogeneous recyclable catalytic systems for C–H functionalisation reactions, where catalysts are dissolved in media and used for unambiguous separation and reuse on completion of the reaction.

7.1 Rh-catalysed C–H functionalisation reactions

Rhodium is again at the centre when considering homogeneous recyclable C–H functionalisations by these strategies. Employing ligand-attached nanosheets of layered double hydroxides (LDHs), the He research group in 2014 established a pioneering rhodium catalysed C–H bond activation system that significantly improves catalytic efficiency and regioselectivity.[203] In their system shown in Scheme 59, the nanosheets offer an ideal foundational environment for facilitating the combination of alkenes **176** and *N*-(pivaloyloxy) benzamide **175** in high yields (>99%) and remarkable regioisomeric ratios (>20 : 1). The LDH nanosheets specifically substitute α-amino acid (AA) ligands, ensuring precise regioselectivity and a highly effective system for selective C–H activations.

The regioisomeric ratio remained constant, but the rhodium(III) catalyst having delaminated Mg/Al-Ala-LDHs showed limited recyclability (Fig. 27), with yields descending from >99% to 63% in the 2nd cycle and 19% in the 3rd cycle. Yields were boosted to 86% in the fourth cycle and 74% in the fifth by adding new Mg/Al-CO_3-LDHs. Decreased reusability was not caused by rhodium leaching, as proven by the minimal amount (<3.2%); rather, hydroxyl groups on the LDH layers were probably consumed. The reintroduction of LDHs led to partial regeneration.



Scheme 59 Nanosheet enhanced Rh-catalysed combination of alkenes and *N*-(pivaloyloxy)benzamides.

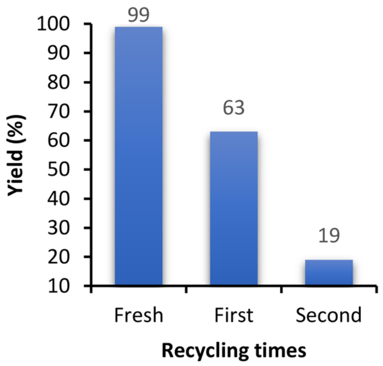


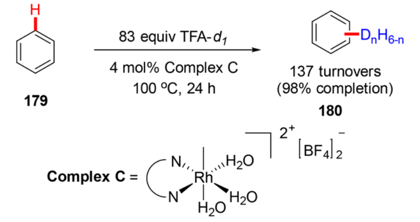
Fig. 27 Recycling study of the nanosheet enhanced rhodium catalytic system for coupling reactions.

Guimond and his team also explored a similar strategy, depicted in Scheme 59, to synthesize compounds **177** and **178** using the same rhodium catalyst.[204] While this alternative method shared identical catalyst loading and temperature, and comparable reaction times with the previously described protocol in Scheme 59, it lacked the reaction medium recycling capability. Thus, the earlier protocol outlined in Scheme 59 offered an additional advantage of catalyst recycling.

In the successive year, Jones and co-workers synthesised and characterised four novel water- and air-stable organometallic Rh(III) complexes, namely: *trans*-Rh^{III}(α-diimine)(CO)MeI_2 (complex **A**), [Rh^{III}(α-diimine)$(H_2O)_3$(C(O)Me)]$[BF_4]_2$ (complex **B**), [Rh^{III}(α-diimine) $(H_2O)_3$Me]$[BF_4]_2$ (complex **C**), and Rh^{III}(α-diimine)(H_2O)(C(O)Me)(OC(O)CF_3)$_2$ (complex **D**), where α-diimine refers to 1,4-bis(Ar)-2,3-dimethyl-1,4-diaza-1,3-butadiene and Ar = 3,5-dimethylphenyl. With 4 mol% of the complex, complex **C** showed significant catalytic activity in order to achieve the H/D exchange among benzene **179** and TFA-d1, attaining 98% conversion with 91% deuterium incorporation in 24 hours (Scheme 60).[205] Complex **C** retained its catalytic activity, according to recycling experiments (Fig. 28), but its efficiency reduced with each cycle owing to the generation of breakdown products and low water solubility, which prevented complete recovery. Water was additionally found to slow down the rate of reaction, suggesting that aquo ligand fragmentation is necessary to maintain catalytic activity.

Using rhodium catalysis, Meng *et al.* recently established a highly competent and sustainable C–H activation followed by [4 + 2] annulation of aryl amides **181** with propargyl alcohols **182** in order to prepare isoquinolones **183** (Scheme 61).[206] Screening a range of transition-metal catalysts, including $MnBr(CO)_5$, $Pd(OAc)_2$, $Cp^*Co(CO)I_2$, $[Ru(p\text{-cyeme})Cl_2]_2$, and $[Cp^*RhCl_2]_2$, in the presence of NaOAc at room temperature revealed that only $[Cp^*RhCl_2]_2$ efficiently catalysed the reaction. The desired product was also obtained through simple filtration in various solvents, including ethyl acetate, methanol, DCE, MeCN, THF, and DCM. Given the environmental friendliness and efficiency of ethanol in this reaction, it was selected as the preferred solvent. The reaction exhibited unique characteristics, such as outstanding regioselectivity and the utilisation of ethanol as a green solvent that reacts both with water and air. Surprisingly, the reaction proceeds under mild conditions, could be scaled up to gram levels, and has a lower rhodium catalyst loading (0.5 mol%). The study indicates that propargyl alcohol moieties, the hydroxy group, and the pivaloyl fragment in the substrates are crucial for controlling chemoselectivity. This process makes simple product purification feasible, and also does not depend on a metal oxidant.

The recycling study of the catalytic framework was performed in the preparation of product **183a** (Fig. 29). When the reaction was completed, Na_2CO_3 granules were removed using



- Electrophilic activation of the C–H bond in benzene
- Air and water stable, organometallic rhodium(III) complex
- Catalyst recyclable upto four times

Scheme 60 Catalytic activity of complex **C** containing Rh towards the H/D exchange among benzene and TFA-d1.

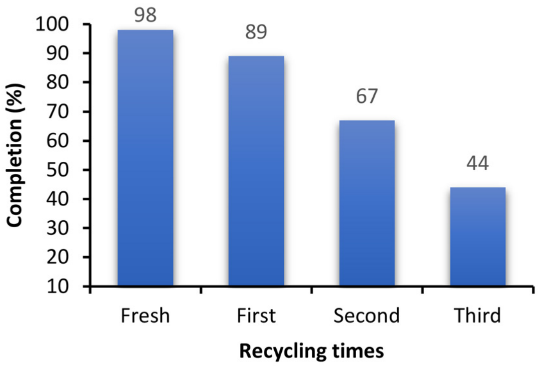
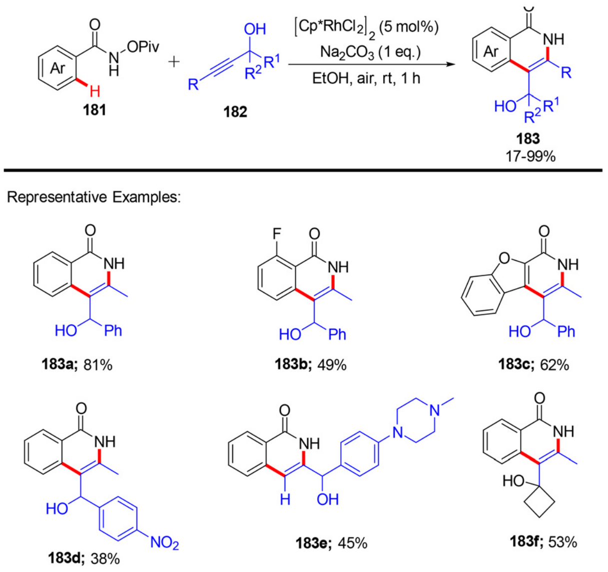


Fig. 28 Recyclability of complex **C** for the H/D exchange reaction.



- Rh-catalyzed [4+2] annulation *via* C–H activation
- Ethanol as the environmentally benign solvent
- High regioselectivity
- Catalyst compatible with air and water
- Mild reaction conditions
- Catalytic system recyclable upto eleven times

Scheme 61 Rh-catalysed annulation reaction of aryl amides.

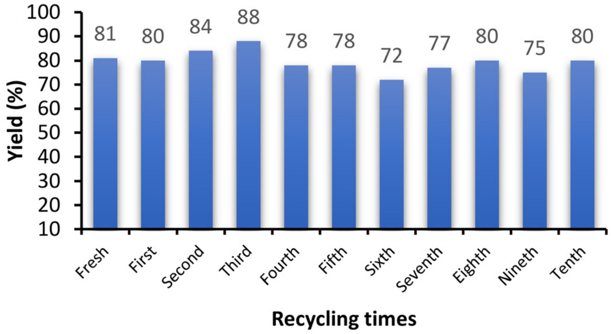
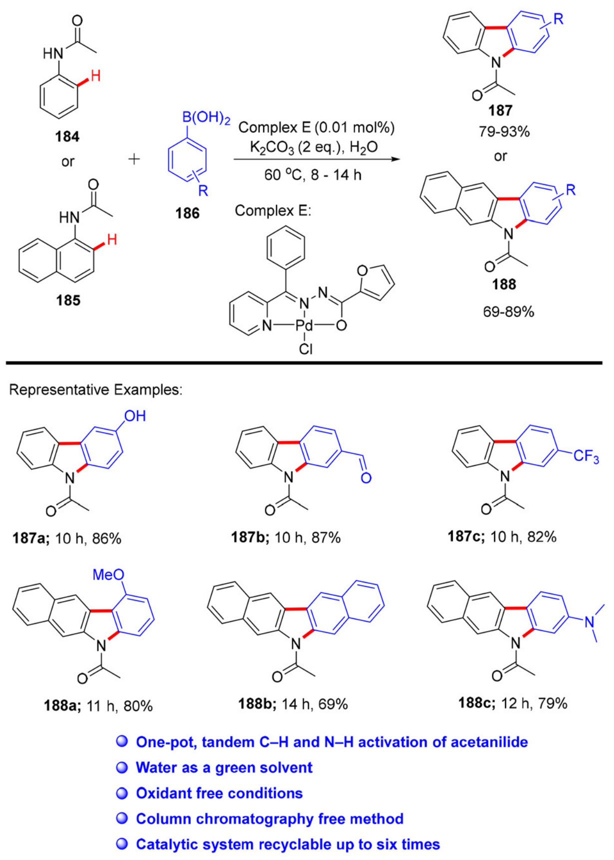


Fig. 29 Recycling study of the rhodium catalytic system in isoquinolone synthesis.

a Pasteur pipette, and the product readily solidified, which could enable easy separation employing filtration. The precipitate was rinsed with ethanol and dried *in vacuo*. Throughout ten cycles, the filtrate, which was concentrated and reused without an extra rhodium catalyst, was consistent. Without having a substantial depletion of activity, the catalytic system showed outstanding recyclability. Isoquinolone synthesis remained ecologically sound and cost-effective over a three-day period.

7.2 C–H functionalisation reactions catalysed by palladium

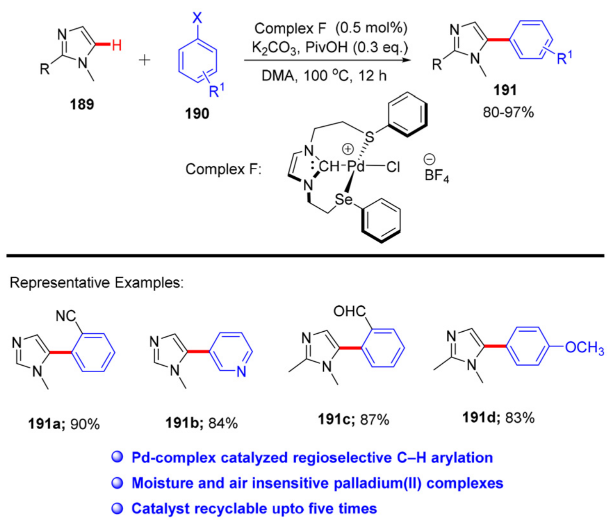
These strategies worked efficiently for Pd catalysts also. For an efficient single pot tandem C–H and N–H activation of acetanilides (**184** or **185**) with aryl boronic acids **186**, Nallasamy and colleagues developed a novel catalytic system that employs a water-soluble NNO pincer type Pd(II) complex, [Pd(L)Cl], wherein L = nicotinic acid (phenyl-pyridin-2-ylmethylene)-hydrazide or furan-2-carboxylic acid (phenyl-pyridin-2-yl-methylene)-hydrazide (Scheme 62).[207] This reaction utilises an exceptionally low catalyst loading of only 0.01 mol% and takes place in neat water under aerobic conditions. The approach not only exhibits good yields of functionalised carbazoles (**187** or **188**) with compatibility with an extensive range of substrates, but it additionally makes the synthesis of these compounds simpler. The catalyst's novel design enhances its solubility and efficiency in aqueous media by using either furan-2-carboxylic acid or nicotinic acid as a ligand.



Scheme 62 C–H/N–H activation of acetanilides catalysed by a Pd(II) pincer type complex to form functionalised carbazoles.

The recycling study of the catalyst was performed in a reaction of acetanilide and phenylboronic acid. On termination of the reaction, the solid product underwent filtration, and the resulting filtrate was diluted with ethyl acetate to separate the catalyst and inorganic salt as a by-product. After being dried, the recycled catalyst was used in further cycles with similar reaction parameters. The remarkable recyclability of the catalytic system, which maintains activity over six successive runs, is an important aspect of this work. Melting point data, TLC analysis results, and ^{1}H NMR spectroscopy results all confirm the stability of the recovered catalyst, despite a progressive decline in efficiency with each cycle. This feature emphasises the methodology's practicality by facilitating the generation of biologically relevant carbazoles in a simple and environmentally friendly way without requiring tedious column chromatography for product isolation.

Building on the exploration of palladium-catalysed reactions in aqueous media, Bhatt and colleagues later fruitfully developed three novel, air- and moisture-insensitive palladium (II) complexes, two of which contained an S,C$_{NHC}$ half-pincer ligand, while the third featured the first Se,C$_{NHC}$,S-type pincer ligand.[208] These complexes showed outstanding thermal stability and resistance to moisture and air, rendering them predominantly suitable for the regioselective C–H bond arylation of imidazoles under gentle reaction parameters. Remarkably, the complex [Pd(L3-HBr)Cl]BF$_4$ (complex **F**), characterised by S, C$_{NHC}$,Se coordination, exhibited excellent catalytic activity, enabling the C-5 arylation of imidazoles **189** with aryl bromides **190** in the vicinity of K$_2$CO$_3$ and pivalic acid (Scheme 63). It attained yields up to 97% within 12 hours, using only 0.5 mol% of catalyst. The methodology was established to be highly versatile, with remarkable functional group



Scheme 63 Pd-complex catalyst for the regioselective arylation of C–H bonds in imidazoles.

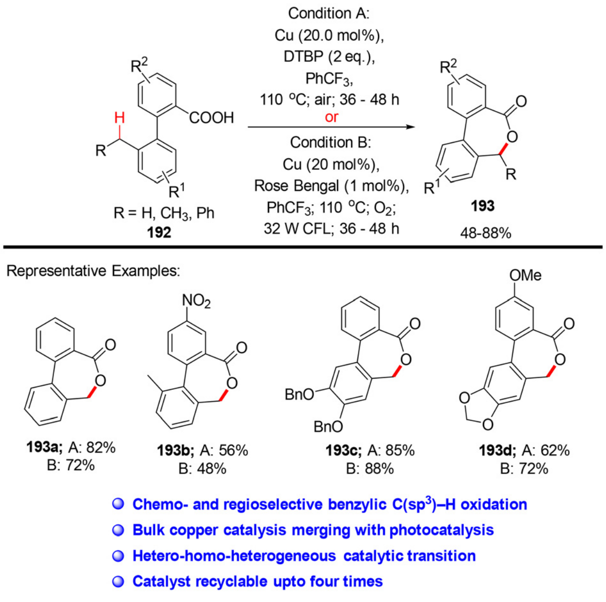
compatibility across an extensive variety of substrates, confirming broad applicability and high efficiency.

The reusability of complex **F** was examined in the arylation of 1-methyl-1*H*-imidazole with 1-bromo-4-nitrobenzene. Following the accomplishment of maximum conversion in the initial reaction cycle, fresh aliquots of initial reactants, K_2CO_3, and pivalic acid were incorporated into the reaction vessel for succeeding cycles. Complex **F** exhibited admirable recyclability over the following five reaction cycles, revealing only an insignificant reduction in catalytic competence thereafter.

7.3 Copper catalysed C–H functionalisation reactions

A simple filtration or extraction strategy was used for the copper catalyst by Nandi *et al.* in Scheme 64. They reported a low-cost chemoselective benzylic sp^3 C–H activation catalysed by copper powder in order to synthesize seven-membered dibenzo[*c*,*e*]oxepin-5(7*H*)-ones **193** directly.[209] With the utilisation of di-*tert*-butyl peroxide (DTBP) and an affordable metallic copper catalyst, the reaction proceeds with no difficulty. Surprisingly during the reaction, the copper powder forms a highly reactive, substrate-influenced soluble catalyst that inhibits the formation of six-membered lactones by activating the sp^2 C–H bond and attaining a distinct chemoselective benzylic sp^3 C–H oxidation. In addition, they invented a green metallic copper/Rose bengal dual catalytic system coupled with molecular oxygen that substitutes DTBP due to the risks associated with it.

The heterogeneous catalyst is subsequently precipitated out and collected for application in the following processes *via* straightforward filtration, leveraging the merits of both homogeneous and heterogeneous catalysts. By repeating the procedure with a copper catalyst and di-*tert*-butyl peroxide (DTBP) in four separate runs without adding more copper catalyst, the yields of the anticipated product **193a** were 82%, 75%, 66%, and 48%, respectively (Fig. 30). Likewise, the catalysts with Rose bengal were also recycled and reused in the Cu/O_2 system (condition B).



Scheme 64 Cu-catalysed chemo- and regioselective benzylic $C(sp^3)$–H oxidation of biaryl substrates bearing methyl and carboxylic acid.

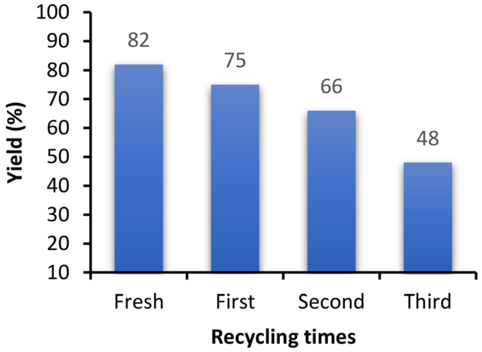


Fig. 30 Recyclability of the copper catalyst in benzylic $C(sp^3)$–H oxidation reactions.

8. Homogeneous recyclable catalytic systems for C–H activation conforming to green chemistry

Homogeneous catalytic systems for C–H activation are most traditionally used in the organic synthesis that leads to diverse organic transformations by dropping the energy of activation.[210] Moreover, this homogeneous catalytic system offered high product selectivity under relatively mild reaction conditions. Conversely, the major challenge related to homogeneous catalytic systems for C–H activation is the single use of catalyst and product separation difficulties from the reaction system. These issues tend to lead to a huge amount of waste generation through steps of catalyst fabrication and downstreaming of product separation. Thus, single use of the catalyst in a homogeneous system has a negative impact on the environment and process economics. Compared to this, the products and catalysts are finely separated in a heterogeneous catalytic system for C–H activation reactions,[35–37] whereas, selectivity, mass transfer and use of higher reaction temperature for catalyst activation are major issues in heterogeneous catalytic systems. Though direct C–H functionalisation reactions stand out as a greener and more sustainable tactic in synthetic organic chemistry[211] and the use of catalysis is one of the major principles of green chemistry,[212] from the green chemistry and sustainability point of view, there are still silent concerns about the selection of ideal catalytic systems for C–H activation. In this context, catalytic systems that offer the advantages of both homogeneous and heterogeneous catalysis are highly desirable. Homogeneous recyclable catalytic systems for C–H activation exemplify this approach. Over the last few decades, attention has been paid to following green chemistry principles to improve overall sustainability of C–H activation reactions which typically involve a clean environment, energy optimisation, safer chemical synthesis, and product design.[211,213] The principles of green chemistry are upheld by utilising homogeneous recyclable catalytic systems for C–H functionalisation reactions.

8.1 Prevention of waste

Direct functionalisation of C–H bonds reduces the need for pre-functionalisation steps; on the other hand, in recyclable homogeneous catalysis for C–H activation, the prevention of waste can be attributed to recycling of the catalytic system and catalysts. Recycling of the catalytic system for the same consecutive reaction reduces waste generation and the subsequent *E*-factor. Furthermore, the used catalyst allows retrieval of valued metals like Pt, Rh, Ru, Pd, Co, *etc*. Such recovered metals can be used to produce new catalysts that helps in minimizing the environmental effect allied with disposal of industrial metal catalysts.

8.2 Atom economy

C–H activation leads to a higher proportion of reactant atoms ending up in the desired product. With this approach, there is no necessity to use pre-functionalised starting materials, which would result in wasteful atom loss. Selectivity is the major concern in these reactions that can be well accomplished by homogeneous recyclable catalytic systems. It is a crucial parameter in maximising the atom economy that ensures minimisation of waste and byproduct formation.

8.3 Safer solvents and auxiliaries

A homogeneous recyclable catalytic protocol for C–H activation uses safer greener solvent media involving the PEG, IL, DES and micellar systems that possess greener physicochemical properties. Furthermore, PEG, IL, DES and micellar systems offer easy catalyst solubilisation and recovery from reaction media for next reuse by a simple work-up process. Recycling and reuse of greener solvents from homogeneous reaction systems reduce waste generation to advocate limited use of solvents for reactions.

8.4 Catalysis

The major principle of green chemistry to use catalysts/catalysis is well followed by recyclable homogeneous catalytic systems during C–H activation that typically involves a catalytic quantity of catalyst (avoids stochiometric use) to perform transformation. It is noteworthy to mention that, most of the blank/control reactions (without a catalytic system) do not offer C–H activation/functionalisation products, indicating the unique role of catalysis in sustainable synthesis.

8.5 Design for energy efficiency

The use of a catalyst from a homogeneous recyclable system in the C–H activation reactions reduces the requirement of activation energy that ultimately minimizes the possibility of harsh reaction conditions.

8.6 Reduce derivatives

Conventional functionalisation of inert C–H bonds involves multiple pre-functionalisation steps that causes an increase in waste generation, stoichiometric use of reagents, and protection and deprotection reactions, whereas, a modern approach involving the use of minimum steps for the direct C–H functionalisation can be well executed by homogeneous recyclable catalytic systems.

However, no system follows 100% of the 12 principles of green chemistry, and certain green chemistry principles are still challenging to address and "can be" addressed in near future to make the homogeneous recyclable catalytic system a complete "green and sustainable system for C–H activation and functionalisation".

Table 1 provides a concise overview of various catalytic systems employed for C–H bond functionalisation reactions, with an emphasis on their recyclability and key features. Several catalytic systems, including polyethylene glycols (PEG), ionic liquids (ILs), deep eutectic solvents (DES), micellar systems, biphasic systems, and systems allowing simple filtration or extraction, have verified efficiency in supporting a range of metal catalysts such as Ru, Rh, Pd, Cu, Co, Ir, and Mn.

Each catalytic system presents exclusive merits. For instance, PEG-based systems show negligible vapor pressure, cost-effectiveness, thermal stability, and biodegradability, making them environmentally benign substitutes. Ionic liquids are characterised by their chemical and thermal stability, strong solvation capabilities, low volatility, and high polarity and conductivity, offering a versatile medium for numerous reactions. Deep eutectic solvents exhibit excellent solubility, a broad viscosity range, low toxicity, and simple recoverability, in line with green chemistry principles. Micellar systems can solubilise both polar and non-polar reactants and are easily recoverable and reusable. Biphasic systems enable simple separation and recycling, with potential for continuous operation, enhancing process efficacy. Lastly, systems allowing simple filtration or extraction minimize work-up requirements, simplify separation and recycling, and reduce metal contamination, contributing to cleaner product development.

The number of recycles attained diverges across the systems, ranging from 3 to 11, demonstrating the potential for prolonged use and reduced waste generation. While this highlights the key features and recyclability of these catalytic systems, a more in-depth analysis of their catalytic activity, substrate scope, reaction kinetics, and long-term stability would provide a more comprehensive understanding of their applicability and limitations in different C–H bond functionalisation reactions.

Recyclability and product selectivity are the major advantages of the homogeneous recyclable catalytic systems for C–H functionalisation reactions. However, loss of catalytic activity/rate is a possible penalty attributed to catalyst deactivation during the reaction or isolation process. Basically, the catalyst reduces the activity due to chemical, mechanical, physical and thermal deactivation. Apart from this, metal leaching is a notable cause for the decrease of catalytic activity which involves escaping of the metal from the complex system. Above all, penalties are very common in the use of the recyclable cata-

Table 1 Overview of homogeneous recyclable catalytic systems applied for C–H bond functionalisation reactions

Entry	Catalytic system type	Metal catalyst(s)	Recyclable system/medium	Number of recycles	Key features
1	Polyethylene glycol (PEG)	Ru, Pd, Cu, Co	PEG-400, PEG-400/H_2O, PEG-20000	3–6	Negligible vapor pressure, inexpensive, thermally stable, biodegradable
2	Ionic liquids (ILs)	Ir, Ru, Pd, Mn, Rh	TBPD, [C_4MIM][BF_4], [BMIM][BF_4], [BMIM][PF_6], [HMIM]Otf, [BMIM]NTf_2, [BMIM]Otf, [Hmim][H_2PO_4], [BPy]I, HBr@Bu_4PBr, [deaH][HSO_4], [EMIM]BF_4:H_2O	3–10	Chemically and thermally stable, strong solvation capabilities, less volatility and vapor pressure, high polarity and conductivity
3	Deep eutectic solvents (DESs)	Pd, Cu, Ru	ChCl : malonic acid, ChCl : acetamide, betaine : HFIP, DMU : tataric acid, ChCl : ethylene glycol, betaine : HFIP, [$ZnCl_2$][ethylene glycol]$_4$, ChCl/Lac, [CholineCl][$ZnCl_2$]$_3$	3–8	Excellent solubility, broad viscosity range, low toxicity, simple recoverability
4	Micellar systems	Ru, Pd	SDBS, SPGS-550-M-water, TPGS-750M/H_2O	4–5	Capability to solubilise both polar and non-polar reactants, ability to be readily recovered and reused
5	Biphasic systems	Cu, Ir	Aqueous biphasic medium, heptane : acetonitrile	5–8	Simple separation and recycling, potential for continuous operation
6	Systems allowing simple filtration or extraction	Rh, Pd, Cu	Extraction or filtration of products	3–11	Minimal work-up requirements, simple separation and recycling, potential for continuous operation, reduction of metal contamination

lytic system for C–H activation which may result in the decrease of the catalytic activity, selectivity, conversion efficiency and yield of the reaction. Nevertheless, it is important to mention that, catalyst deactivation is more simply prohibited by controlling reaction conditions and temperature. The mild reaction conditions are more favorable for retaining the catalytic activity for the next recycle which is a characteristic feature of recyclable homogeneous catalytic systems for C–H activation compared to heterogenous systems.

Sometimes, to retain the maximum catalytic activity various regeneration and rejuvenation strategies are applied which are beyond the scope of the present review. Another strategy to maintain optimal reaction performance in the recycling process is to compensate the loss of catalyst loading during recyclability by adding a fresh catalyst which in turn increases the process economics. However, a question arises about the quantity of fresh catalyst to be added for the next cycle which is to be determined. Hence, two parameters, namely, the turnover number (TON) and turnover frequency (TOF) are crucial to assess the recyclability of the catalytic system. TON mentions the catalyst's life-time and sturdiness before losing its activity while TOF mentions the efficiency and activeness of the reusable catalyst. Higher values of the TON and TOF are desirable for the subsequent recycling of the catalyst.

9. Challenges and viewpoints

Chemical catalysis and biological catalysis in the form of heterogeneous and homogeneous catalysis are widely reported in the 21st century for various sustainable applications such as production of fuel (bio-methanol, bio-ethanol, bio-butanol, and higher saturated/unsaturated hydrocarbons like diesel/wax), biomass valorisation (obtaining valuable chemicals from waste), C–H activation (for the synthesis of fine, bulk and pharmaceutical intermediates, for CO_2 fixation *etc.*).[35,214–219] In the context of historical development of green chemistry and process economics, heterogeneous catalysis was successfully applied to a large extent at the lab-scale processes.[220,221] Although heterogeneous catalysis has challenges of requirement of activation energy gaps and deficit of molecular level mechanistic knowledge, the ratio of applications of homogeneous to heterogeneous catalysis in industrial synthesis is about 40 : 60.[222] Homogeneous catalysis is still facing several challenges considering catalyst stability, large-scale applicability and profitability at the industrial level.

Considering the green aspects, although biomass-derived solvents for transition metal catalysed sustainable C–H activation offer a promising direction,[223] more challenges and opportunities remain, particularly in the development of homogeneous recyclable catalytic systems for C–H activation. Looking at the goal of green chemistry and sustainability to synthesize the fine chemicals at the industrial scale, the first major contribution towards green chemistry is attributed to "generation of NO waste" which is closely associated with the factor "selectivity" (one product–NO waste). This selectivity factor is very genuine during the C–H activation reactions attributed to homogeneous reactions, since a number of C–H bonds are available at the organic reacting substrate. Furthermore, another most important factor towards green chemistry is recyclability that ultimately makes the process industrially feasible which is the real challenge for the development of homogeneous recyclable C–H activation systems. Hence, catalyst designing needs special attention in developing catalytic systems for sustainable homogeneous recyclable C–H activation reactions which involve catalyst designing with (i) appropriate selectivity, (ii) catalytic reaction rate (iii) recyclability and (iv) stability to the reaction environment and conditions.[222,224,225]

More commonly, homogeneous catalysts decompose at higher temperature, whereas C–H activation is carried out at elevated temperature and hence a temperature sensitive catalyst may decompose during the reactions which cannot be isolated/recycled. Under such conditions, attention should be paid during catalyst designing so that the catalyst is stable towards higher temperature and can be easily recycled without modification after higher temperature exposure to C–H activation reaction. Heterogenisation of a homogeneous catalyst with appropriate use of a solid recyclable support is a new strategy that can be used to obtain a recyclable homogeneous catalytic system.[226–228] The support material for anchoring of the catalyst plays a crucial role in the development of the catalyst.[41,196,229] Designing of the heterogenised supported homogeneous catalyst is a tedious concept but can be helpful for achieving the goal of green chemistry and sustainability. Furthermore, the anchoring support should be free from the active C–H groups, completely inert to reaction media and easily isolatable from the reaction media. The linkages of the active catalyst and support should be strong enough to avoid the leaching of catalysts.

Apart from this, the catalyst must be sufficiently stable to inhibitory substances formed during the reaction. Separation strategies are essential to consider, since those of a homogeneous catalyst may result in the physical disintegration of the catalyst and hamper further catalyst reusability. Many times, such separation strategies completely decay the catalyst which involves vacuum distillation, evaporation and other sophisticated downstream treatments. It is advisable that, a minimum number of downstream processing steps (such as extraction, precipitation, crystallisation, separation, and distillation) should be performed to retain the catalyst reusability and economic viability. Since isolation of the homogeneous catalyst is the key to obtain further recyclable systems, the use of biphasic media or a phase enhancing solvent system or a co-solvent to precipitate the catalyst/separate products is another approach. Furthermore, the use of a neutral inert solvent is essential to recover the catalyst from the reaction phase, because reactive or nucleo-/electro-philic solvents during subsequent processing steps may cause catalyst leaching and disintegration or catalyst derivatisation or deactivation through blocking of active catalytic sites. Hence, the catalyst designing can be modified for scale-up after knowing or optimising the requisite reaction conditions at the lab scale. Such a kind of strategy of knowing reaction specifications and then fabrications of the catalyst may have a great impact on the development of a recyclable homogeneous catalyst.

The barrier between homogeneous and heterogeneous catalysis for C–H activation can be crossed by the use of several novel strategies involving the use of polyethylene glycol, biphasic media, fluorous solvent/ionic liquid/supercritical fluids, insoluble supports, micellular media, soluble–precipitating supports, nanoparticles as a support/catalyst, magnetically separable nano-particles and nano-filtration which can be applied to successfully obtain recyclable homogeneous C–H activation catalytic systems. Various ideas of catalyst designing and C–H activation reaction from the academics can be tested at the lab scale wherein the catalyst can be further modified as per the reaction requisite for the successful implementation of process scale up and industrial applications. The union of the academia and industry and collaborations can be helpful in crossing over hurdles to obtain a stable, robust, efficient and green homogeneous reusable catalytic C–H activation system.

10. Conclusion

The search for effective and sustainable synthetic methodologies has resulted in notable progress within the realm of C–H bond functionalisation in recent years. The use of homogeneous recyclable catalytic systems has emerged as an promising strategy to tackle the challenges related to traditional synthetic methods. This review has demonstrated the development and the potential of various media, including PEG, ILs, DESs, and micellar systems, to improve the catalytic performance and recyclability of metal-based and metal-free catalysts. By enabling facile catalyst recovery and reuse, these systems offer substantial environmental and economic advantages. Additionally, biphasic catalytic systems have showcased outstanding efficiency in simplifying catalyst separation and purification processes. The application of simple filtration or extraction techniques allows for effective catalyst recovery and reuse, thus minimising waste generation and reducing the overall cost of the reaction. These systems are in line with green chemistry principles, encouraging efficient, scalable, and eco-friendly synthesis of complex organic molecules.

While substantial development has been made, further research is advantageous for the progress of further robust, selective, and efficient catalytic systems. Discovering novel catalyst designs, optimising reaction conditions, and expanding the scope of functionalisation reactions are crucial areas of future research. By continuing to revolutionize in this field, we can reveal the complete potential of C–H bond functionalisation and contribute to the progress of sustainable and environmentally friendly synthetic approaches.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

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