

Review

The Beneficial Synergy of MW Irradiation and Ionic Liquids in Catalysis of Organic Reactions

Barbara Floris, Federica Sabuzi, Pierluca Galloni and Valeria Conte * 

Dipartimento di Scienze e Tecnologie Chimiche, Università degli Studi di Roma "Tor Vergata", via della Ricerca Scientifica snc, 00133 Rome, Italy; floris@uniroma2.it (B.F.); federica.sabuzi@uniroma2.it (F.S.); galloni@scienze.uniroma2.it (P.G.)

* Correspondence: valeria.conte@uniroma2.it; Tel.: +39-06-72594014

Received: 26 July 2017; Accepted: 23 August 2017; Published: 1 September 2017

Abstract: The quest for sustainable processes is becoming more and more important, with catalysis playing a major role in improving atom economy and reducing waste. Organic syntheses with less need of protecting/de-protecting steps are highly desirable. The combination of microwave irradiation, as energy source, with ionic liquids, as both solvents and catalysts, offered interesting solutions in recent years. The literature data of the last 15 years concerning selected reactions are presented, highlighting the importance of microwave (MW) technology coupled with ionic liquids.

Keywords: catalysis; microwave; ionic liquids; C–C bond formation; oxidation

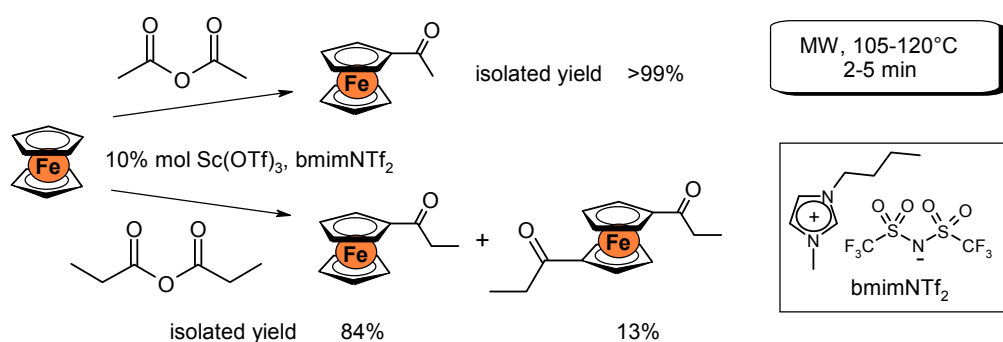
1. Introduction

Twenty years have elapsed since the publication of the seminal book by Anastas and Warner [1], where principles of Green Chemistry were formulated and presented in a systematic discussion. Since then, the idea of “eco-friendly” or “sustainable” ways to obtain and to transform chemicals has increasingly spread among the scientific community [2].

Catalysis is an important tool for the development of sustainable processes; among the other ones, alternative energy sources (as provided by microwave heating) and alternative solvents (for example, ionic liquids, ILs) are of major importance. Microwave irradiation rapidly gained importance and was widely applied as a “green” way to provide the necessary energy to reactions. In 2002, a book appeared [3] containing many examples of applications to organic synthesis, followed in 2006 by an increased second edition. In addition, ILs were the object of a book that became a two-volume set after few years [4]. Since then, reviews appeared discussing several aspects of both microwave (MW) and ILs topics, separately (see, for example [5–11]) and together (for selected examples, see [12–16]).

Nowadays, the use of ILs is quite diffuse, but a brief illustration of their characteristics may be useful for people not yet familiar with them. According to the generally accepted definition [4], Ionic Liquids are salts that are liquid at room temperature (or, at least, below 100 °C). They are non-volatile and non-flammable, which make them interesting substitutes for volatile organic solvents. Their properties depend on the nature of both cation and anion, thus giving access to a large number of compounds, often tailor-made, on the basis of reaction requirements. Moreover, depending on their miscibility or non-miscibility with water or organic solvents, they can be easily recycled, simply by distilling off (or filtering) the reaction product at the end of the reaction, washing with water, drying and reusing them. Generally, catalysts remain in the IL phase, so that addition of reagents allows a second reaction run. Thus, on the basis of their properties, ILs are considered “green solvents”. They are commercially available, with prices that became accessible with time, although purity is still a crucial item. Therefore, it is advisable to prepare them by known, simple, and reproducible procedures, rather than to buy commercial products [4].

One of us became involved in MW-assisted reactions in ILs since 2003, investigating oxidation of electrophilic alkenes by hydrogen peroxide in presence of a base [17]. ILs with 1-butyl-3-methylimidazolium cation and different counteranions were used. Generally, epoxides formed quantitatively within few minutes at room temperature. The sustainability of the reaction was granted by the safe and inexpensive oxidant, by the non-volatile solvents, and, moreover, by the extraction of the organic product, performed with supercritical carbon dioxide. Later, screening the oxidation of different substrates with H_2O_2 and $\text{V}^{\text{V}}\text{O}$ complexes in ILs, we found that MW irradiation had a beneficial effect in oxidation of organic sulfides [18], where a significant improvement in the rate of reaction and an increase in selectivity have been observed, when hydrophobic ILs were used in combination with MW activation. A completely different reaction we investigated was the C–C bond formation in ferrocene Friedel-Craft acylation [19]. Acylation of ferrocene with carboxylic anhydrides, catalyzed by $\text{Sc}(\text{OTf})_3$ in bmimNTf_2 occurred with high yields and excellent selectivity (Scheme 1). MW heating decreased reaction times from 50 to 60 min (conventional heating) to 1.5–4.5 min.



Scheme 1. Ferrocene Friedel-Craft acylation in bmimNTf_2 , under microwave (MW) irradiation.

After almost a decade, we are interested in examining the state of the art as to the combination of MW as the heating source and ionic liquids as solvents. Considering the literature of the last 15 years only, the number of publication is impressive, amounting to more than five hundred. About 20% of them use the combination ILs/MW to transform biomasses or biomolecules (see, for example, [20–24]), a few papers used MW irradiation to facilitate the IL synthesis (e.g., [25,26]), some recent paper used ILs for the MW-assisted formation of nanoparticles to be used successively (for example, [27–32]), and the large majority of reports deal with organic synthesis, with ILs acting as solvents and/or as catalysts. Many organic reactions have been performed combining ILs and MW irradiation: esterification of alcohols [33] and of carboxylic acids [34–36], formation of diphenylmethyl ethers from alcohols [37], Michael addition of sulfonamides [38,39], asymmetric organocatalysis [40] or thiol-ene “click” reaction [41], to cite only a few.

In this review, we will focus our attention on oxidation and C–C bond formation reactions, published between 2002 and the beginning of 2017 that benefited from the combined use of microwaves and ionic liquids. Moreover, carbon dioxide functionalization, a hot topic nowadays, will be considered.

Structures and abbreviations of ionic liquids reported in the review are collected in Figure 1.

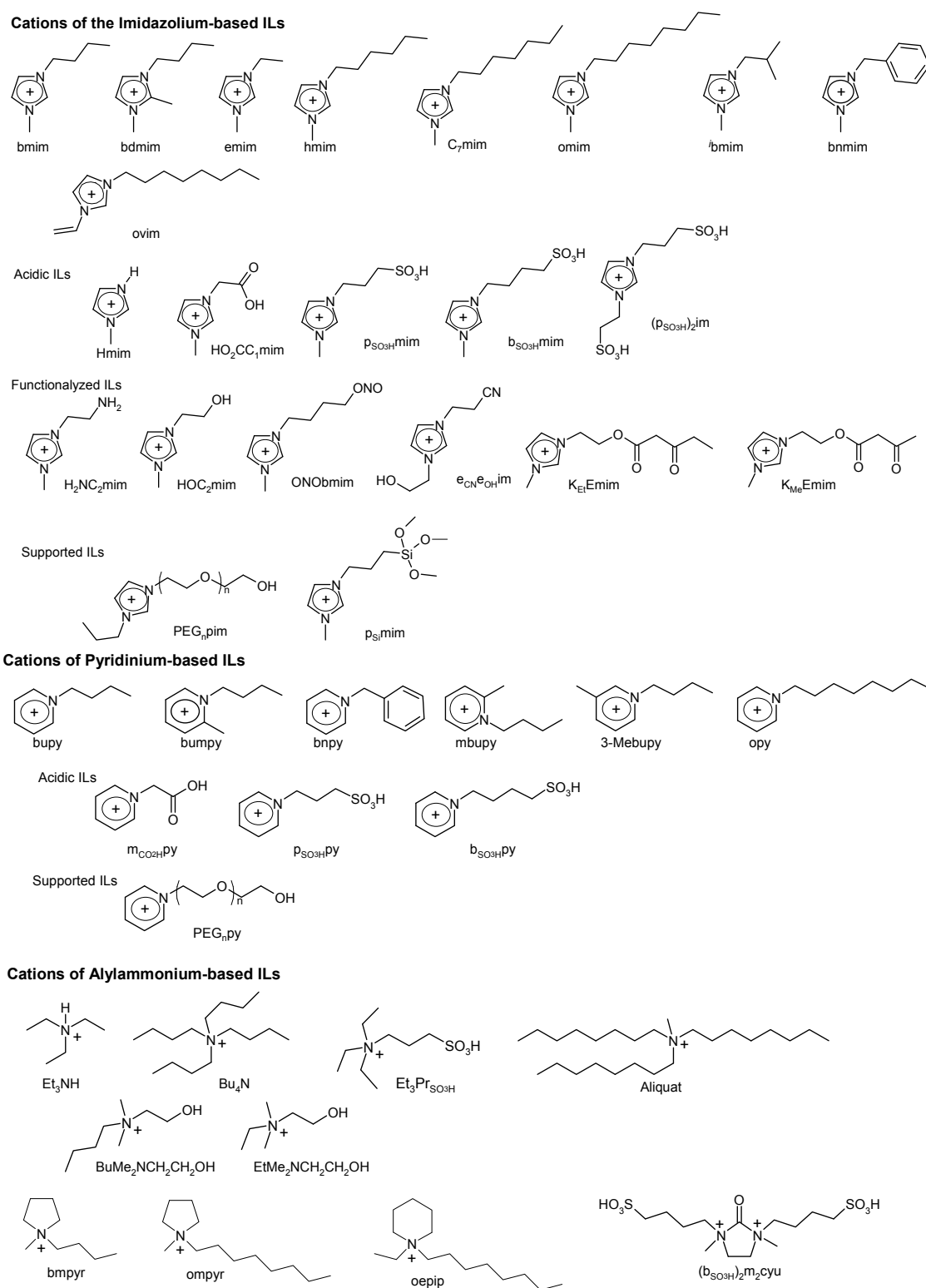


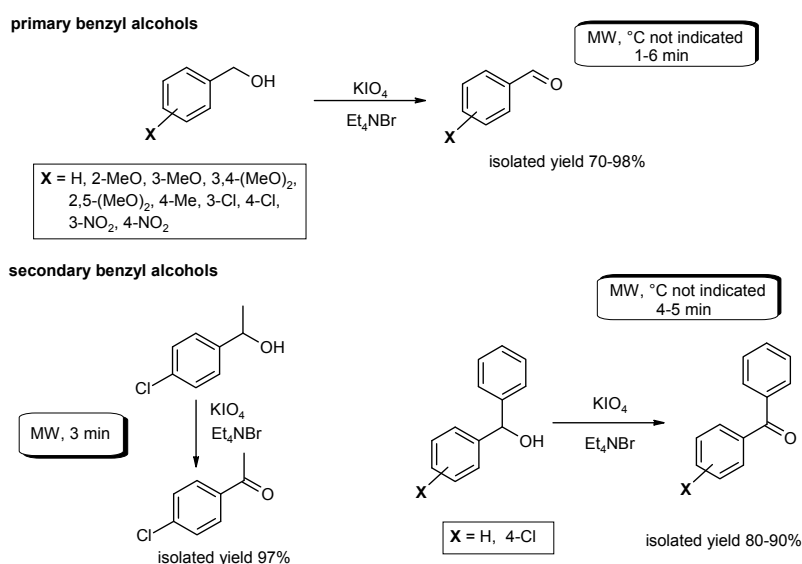
Figure 1. Structures and abbreviations of ionic liquids (ILs) encountered in the review.

2. Oxidation Reactions

Different functional groups have been oxidized in ILs with MW assistance. H_2O_2 is one of the “greenest” oxidant, considering that it reduces to water, but also other primary oxidants have been

used. Hydrogen peroxide needs an activator, either acid or metal-based. In the latter case, the choice of metal is important to ensure sustainability of the process.

Alcohols—Primary and secondary benzylic alcohols were oxidized to the corresponding carbonyl derivatives using KIO_4 as the primary oxidant, tetraethylammonium bromide (Et_4NBr) as ionic liquid, irradiated with MW without any other solvent [42], as illustrated in Scheme 2.

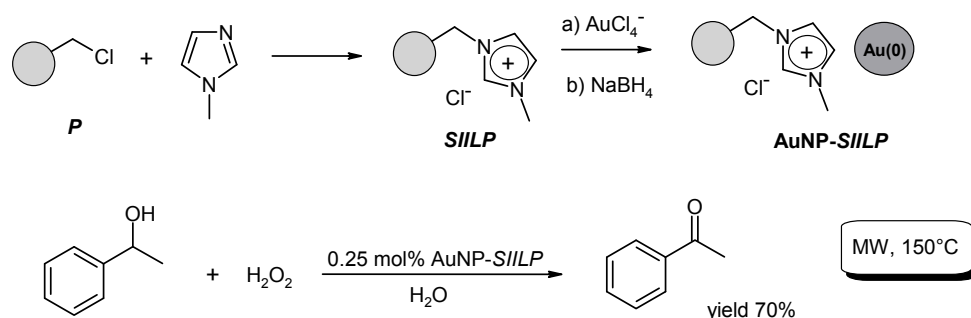


Scheme 2. Oxidation of primary and secondary benzylic alcohols, with KIO_4 , Et_4NBr , and MW heating [42].

The selectivity is excellent, because carboxylic acids were never detected and competition experiments showed high substrate selectivity. Even more important, blank experiments demonstrated that oxidation without Et_4NBr does not occur at all, while scarce oxidation products were observed after conventional heating, even with prolonged reaction times. Therefore, the combination IL/MW is necessary to make the reaction efficient (although, strictly speaking, Et_4NBr is not a real IL, since it should be liquid at ambient temperature or below $100\text{ }^\circ\text{C}$). The same reaction resulted much less efficient with other alkyl alcohols.

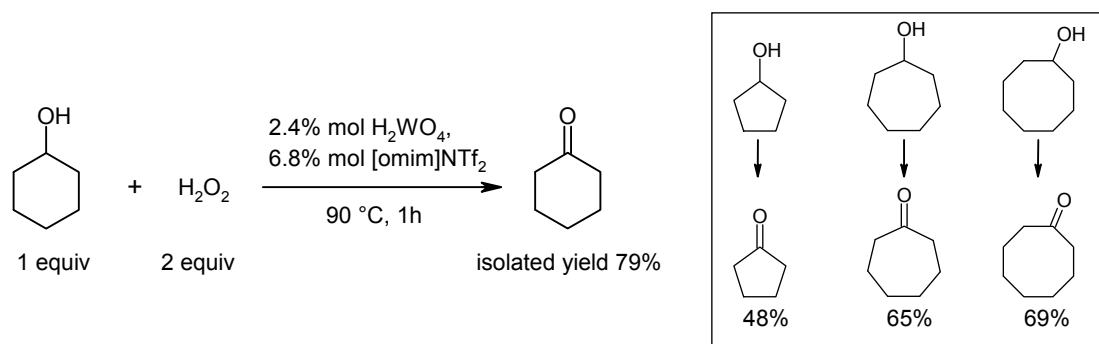
Immobilized IL on AuNP was an efficient catalyst in oxidation of benzyl alcohol by H_2O_2 in water [43]. The rationale of the method was to prepare polymeric materials based on poly(ionic liquids), to give the so-called “supported ionic liquid-like phases” (SILLPs). They combine the characteristics of ILs with those of polymers, in particular the ability to stabilize metal nanoparticles. Thus, stable AuNPs of different sizes were prepared, taking advantage of the ability of supported ILs to absorb inorganic or organic anions from a solution. AuNPCs–SILLPs were used to efficiently catalyze the oxidation of 1-phenylethanol in water, with H_2O_2 as the primary oxidant and MW irradiation as energy source. While with conventional heating the catalytic efficiency is higher with low-size AuNP [44], here the authors found that higher yields were obtained with the largest AuNPs. A polystyrene-divinylbenzene resin was used for a Merrifield-type linking of imidazolium cation with different anions (Scheme 3). The anion influenced the turnover frequency, with the best TOF (1383 h^{-1}) obtained when BF_4^- was the anion.

Interestingly, lignin-derived bio-oils, obtained by pyrolysis or MW heating, containing several benzyl alcohol functionalities, are reported to undergo aerobic oxidation [45] catalyzed by oxidovanadium or copper complexes in ILs. However, the paper is centered mainly on bio-oils and therefore it will not be discussed further.



Scheme 3. AuNPs-supported ionic liquid-like phases (SIILPs) as catalyst in 1-phenylethanol oxidation with H_2O_2 and MW heating [43].

Aliphatic alcohols are more difficult to oxidize than benzyl ones. An accurate screening on cyclohexanol oxidation showed that it can be selectively oxidized by H_2O_2 with different catalysts in the presence of ILs [46], Scheme 4. The screening examined different catalysts (H_2WO_4 resulted the best one), the influence of the amounts of oxidant, catalyst and ionic liquid, and the nature and role of ILs (considering both the cation and the anion). Imidazolium- ([omim]NTf₂), pyridinium- ([opy]NTf₂), and alkylammonium salts ([oepip]NTf₂, [ompyr]NTf₂, AliquatCl—also known as Aliquat336—and AliquatNTf₂) were used. Structures are reported in Figure 1. The authors concluded that ILs act as phase-transfer catalysts. Finally, MW irradiation was compared to conventional heating and resulted in reduced reaction times (from 90 min to 2.5 min, with Aliquat 336; with sonication, 7.5 min were necessary). Other cycloalkanols resulted less reactive than cyclohexanol. However, with all cycloalkanols, the corresponding cycloalkanones constituted more than 99% of the obtained products.

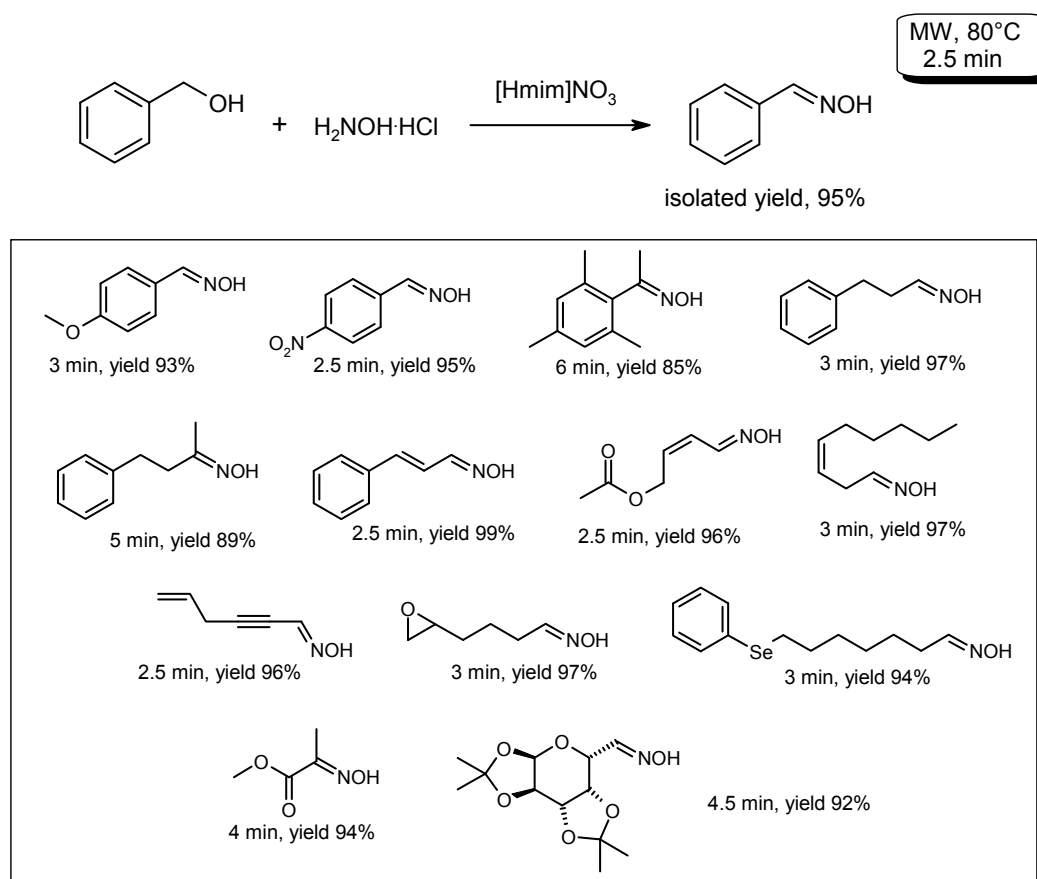


Scheme 4. Oxidation of cycloalkanols with H_2O_2 [46].

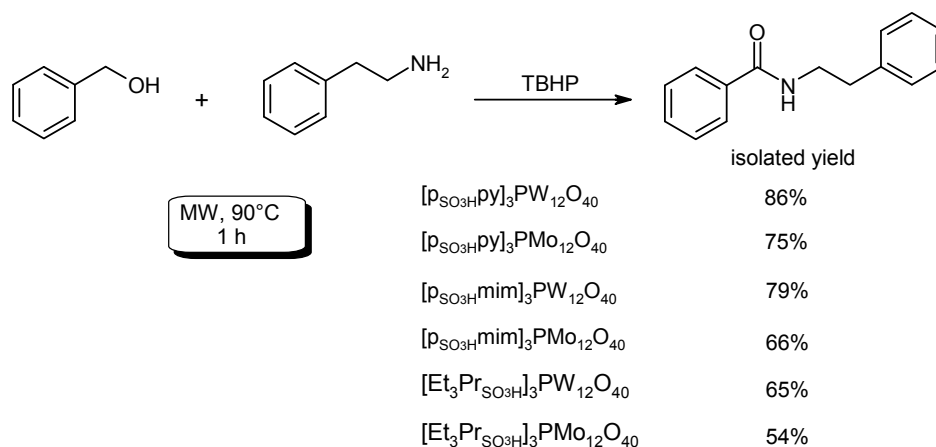
Alcohols were converted into oximes by reaction with hydroxylamine hydrochloride in ILs with MW irradiation [47]. Among the investigated ILs, 1-methylimidazolium nitrate, [Hmim]NO₃, gave the best results (Scheme 5).

The scope of the reaction is wide and, according to the authors, the protocol presents attractive features such as reduced reaction times, high yields and economic viability of the ionic liquid. Moreover, the IL could be reused at least three times, with limited activity reduction.

Oxidative amidation of alcohols was reported using *tert*-butylhydroperoxide (TBHP) as the oxidant, task-specific ILs, with cations bearing the $-\text{SO}_3\text{H}$ functionality and polyoxometalate anions, as catalysts, under MW-assisted and solvent-free conditions [48]. A wide range of alcohols and amines were used, the IL catalyst could be recycled six times, maintaining good activity, and when comparison with conventional heating was possible, MW conditions gave better yields in addition to reduced reaction times. One example is shown in Scheme 6.



Scheme 5. Synthesis of benzaldehyde oxime in [Hmim]NO₃ [47].



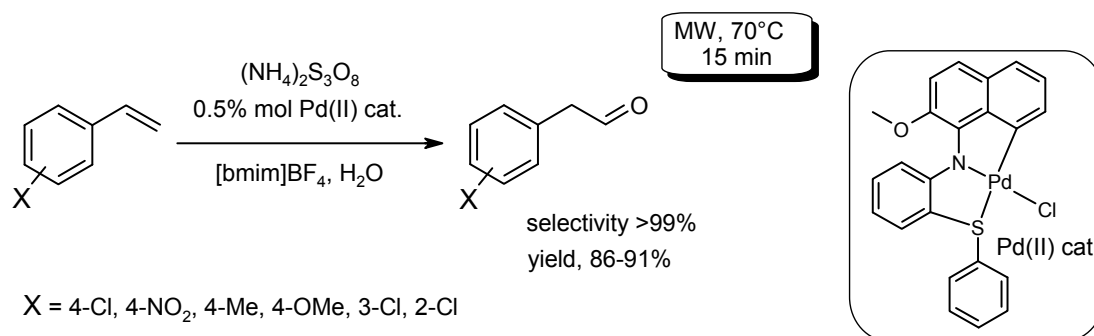
Scheme 6. Oxidative amidation of phenylmethanol with *tert*-butylhydroperoxide (TBHP) under MW irradiation, with task-specific IL catalysts [48].

The same research group applied the procedure to oxidative amidation of aldehydes with *N*-heteroarylamines [49]. The results are in line with those obtained with alcohols and the best catalyst was again 1-(3-sulfopropyl)pyridiniumphosphotungstate.

Alkenes—The alkene epoxidation was obtained with TBHP, using $\text{CpMo}(\text{CO})_3\text{CH}_3$ as the catalyst precursor, at 55 °C [50]. Interestingly, the study compared the reaction output in conventional solvents (1,2-dichloroethane, toluene, hexane) with that in biphasic liquid-liquid, using 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim]BF₄. Moreover, conventional oil-bath heating

was compared with MW irradiation. From the comprehensive screening, MW irradiation emerged as the most efficient heating, shortening reaction times without affecting selectivity, which was 100% epoxide from cyclooctene. Efficiency was enhanced by microwave absorbing solvents, such as bmimBF₄. Another Mo catalyst was tested for cyclooctene epoxidation, i.e., pyimMo(CO)₄ (where pyim is *N*-(propyl)-2-pyridylmethanimine) and the immobilized version of it, grafted on mesoporous silica MCM-41 [51]. However, in this example, MW heating was used only to prepare the catalyst, whereas [bmim]BF₄ was used in the subsequent cyclooctene epoxidation.

An interesting oxidation of terminal alkenes to aldehydes by ammonium persulfate was reported [52]; a palladacycle complex was the catalyst and [bmim]BF₄ the solvent (Scheme 7).

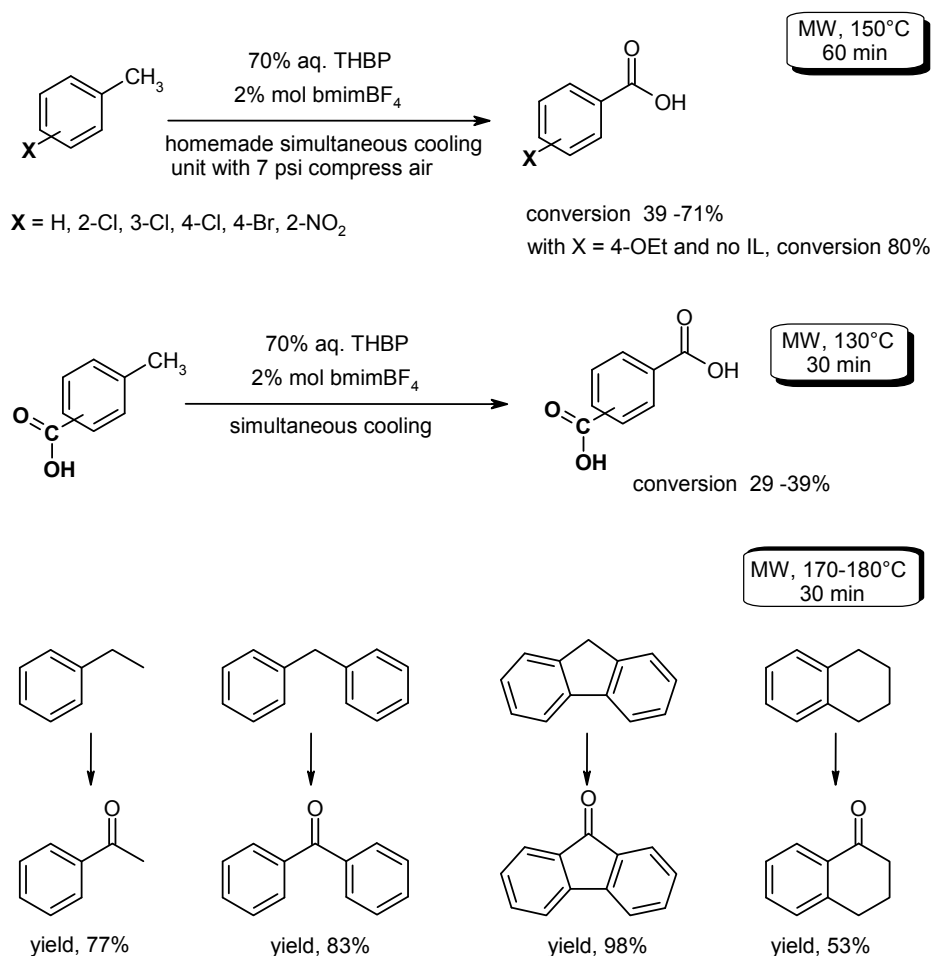


Scheme 7. Pd-catalyzed MW-assisted oxidation of styrenes to aldehydes in IL [52].

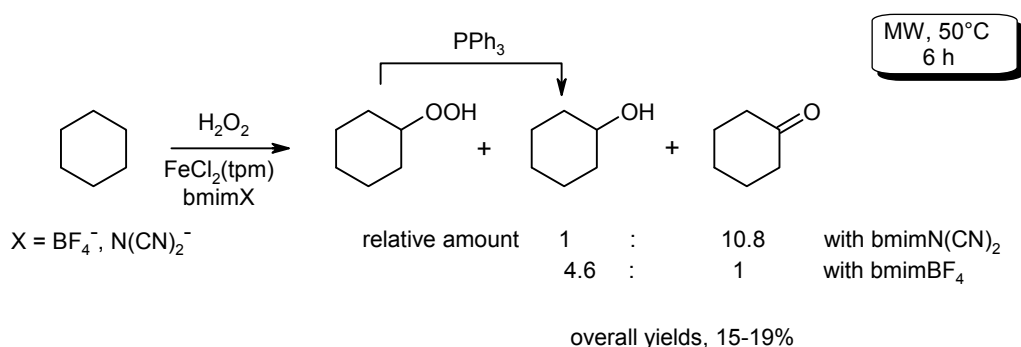
The reaction was highly selective in IL solvent, where only traces of ketone were observed, at variance with organic solvents, where phenylpropanone formed in amounts up to 25–40%. In the absence of Pd(II) catalyst no oxidation was observed. MW heating made the reaction to complete in 15 min at 70 °C with 89% yield, while conventional heating required 24 h, with yield decreasing to 73%.

Alkanes—Alkyl substituted aromatics were oxidized by aqueous TBHP in the presence of small amount of bmimBF₄, under microwave irradiation [53]. No other catalyst was necessary. Toluene and substituted methylbenzenes were transformed in the corresponding benzoic acids, while aromatic compounds with other alkyl groups were oxidized to ketones (Scheme 8). Without the IL, the reaction was much less efficient, requiring higher temperatures and prolonged reaction times, to give lower yields. No experiment was performed with conventional heating.

Finally, a recent report illustrated cyclohexane oxidation at 50 °C, under MW irradiation, by H₂O₂ and FeCl₂(tpm) catalyst [54] (tpm = hydrotris-(pyrazol-1-yl)methane). A variety of reaction conditions were investigated, varying the solvent, the reaction time, without or with additives (pyrazinecarboxylic acid, nitric acid, potassium carbonate). At the end of the reaction, before workup, triphenylphosphine was added to reduce the eventually formed cyclohexyl hydroperoxide to cyclohexanol. Although the best overall product yield (28% in 1 h) was obtained in MeCN with pyrazinecarboxylic acid as additive, the authors prefer the reaction in IL, because the relative ratio alcohol:ketone can be tuned changing the anion of IL (Scheme 9). Moreover, higher catalytic activities under additive-free conditions were achieved and the catalyst could be re-used in several catalytic cycles, especially in bmimBF₄ (13 runs), maintaining its activity and selectivity.

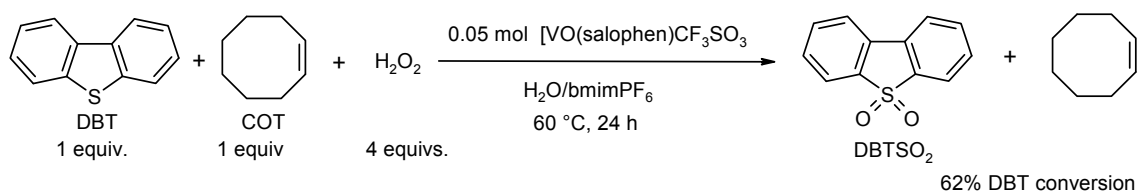


Scheme 8. Oxidation of methyl, dimethyl, and alkyl benzenes with aqueous TBHP and [bmim]BF₄ under MW heating [53].



Scheme 9. Cyclohexane oxidation by H₂O₂, catalyzed by FeCl₂(tpm), in ILs, under MW irradiation [54].

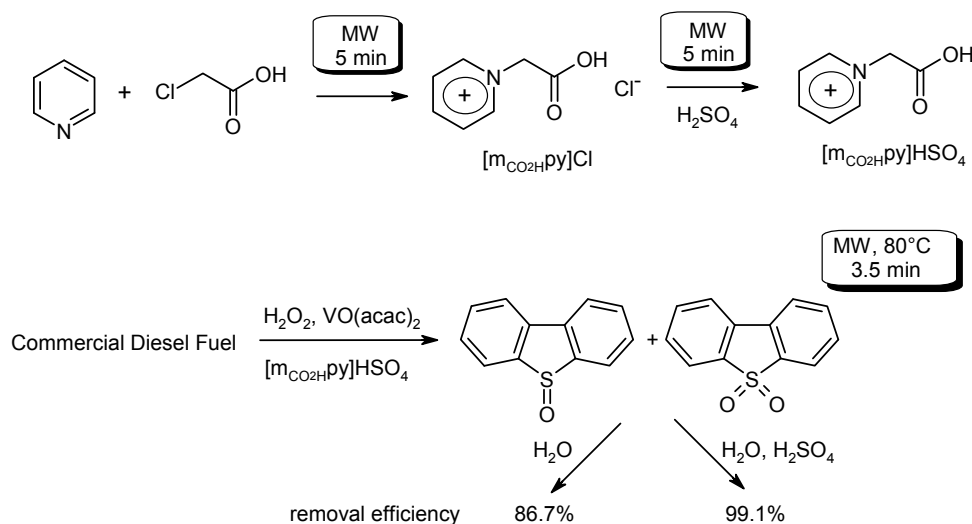
Sulfides—Oxidation of organic sulfides is a very easy reaction that generally does not require harsh conditions. However, this is not the case of thiophene and related sulfur-containing heteroaromatic compounds. Their difficult oxidation requires conditions under which also alkenes are oxidized. This makes the use of oxidative desulfurization of fuels (ODS) not practicable, since, for a valuable fuel, alkenes should remain unaltered. Thus, taking advantage of the chemoselectivity shown by oxido vanadium(V) salen and salophen complexes, able to catalyze sulfides oxidation with H₂O₂, but almost inert towards alkene oxidation, dibenzothiophene was oxidized to the corresponding sulfone, while cyclooctene, chosen as model of alkenes, remained unaffected [55,56] (Scheme 10).



Scheme 10. Selective oxidation of dibenzothiophene by H_2O_2 , in the presence of cyclooctene [55,56].

Reduced reaction times to minutes were obtained substituting external heating (oil bath) with MW irradiation [57]. A three-phase system was implemented for VO(V)-catalyzed desulfurization of a model fuel: an organic phase containing benzene, cyclooctene and dibenzothiophene, an aqueous phase containing H_2O_2 , and the IL phase with the catalyst. At the end of the reaction, dibenzothiophene sulfone was in IL, while unreacted cyclooctene was in the upper benzene phase.

A similar rationale led to the recently reported extractive catalytic oxidative desulfurization (ECODS) process of diesel fuel model [58] that used H_2O_2 as the primary oxidant, a task-specific IL ($[\text{mCO}_2\text{Hpy}]\text{HSO}_4$) as the extractant solvent, and $\text{VO}(\text{acac})_2$ as the catalyst. Microwave irradiation was used both for the IL synthesis and for the oxidation reaction (Scheme 11).



Scheme 11. MW-assisted extractive catalytic oxidative desulfurization by H_2O_2 in IL [58].

3. Carbon-Carbon Bond Formation

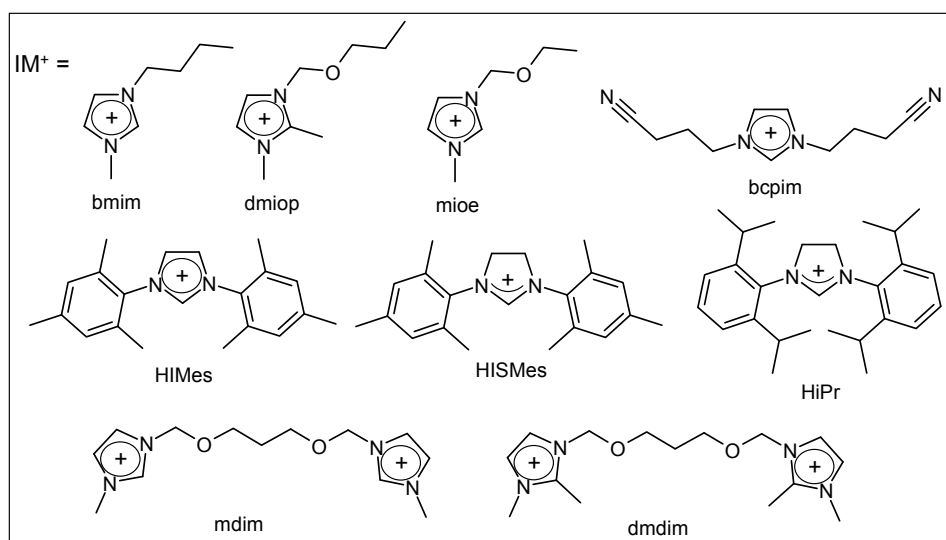
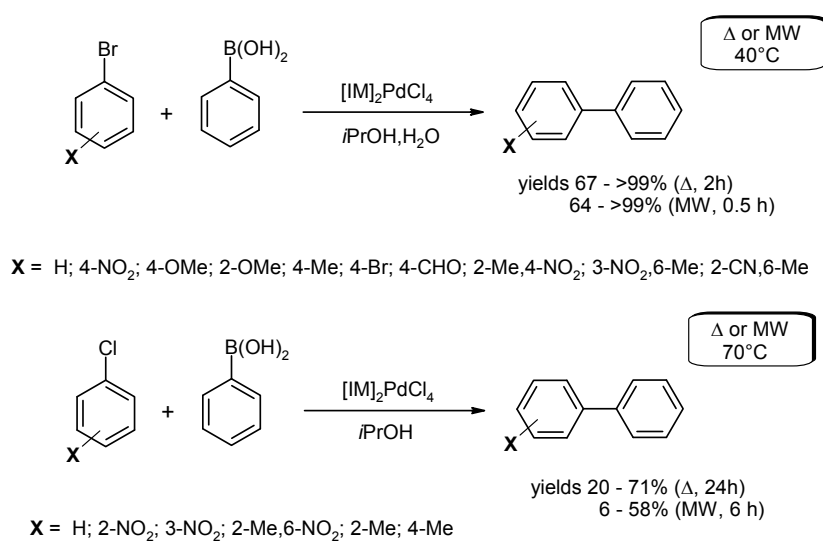
3.1. Transition Metal-Catalyzed C–CCoupling Reactions

Reactions catalyzed by transition metals (*in primis* palladium) that lead to C–C bond formation are of the utmost importance in organic synthesis and it is not surprising that the problem to make them more sustainable received attention, considering in particular the use of microwave activation [59]. Palladium-catalyzed alkoxy carbonylation reaction was recently reviewed considering, among improvements, the use of alternative solvents (ILs, scCO_2) and MW heating [60]. It is worth marking the asymmetric Pd(II)-catalysed oxycarbonylation of racemic pent-4-ene-1,3-diol by kinetic resolution in ILs using a chiral ligand for palladium. MW irradiation was used to shorten reaction time [61]. A selection of transition metal-catalyzed coupling reactions are considered in the following.

Suzuki-Miyaura reaction—Palladium-catalyzed C–C coupling reaction between aromatic halides and areneboronic acids has been considered one of the most versatile approaches among the cross-coupling reactions. Several modifications of the original protocol were aimed at improving

it not only from the scientific point of view, but also considering sustainability problems, that led to environmentally friendly Suzuki aryl-aryl coupling reaction, as reviewed in 2005 [62]. Good results were obtained in water [63], where aryl bromides reacted with benzeneboronic acid in a few minutes (1–5 min), with a benzimidazole-oxime Pd(II)-complex as catalyst and MW irradiation. The same system was used in the Heck reaction (*vide infra*) of aryl and heteroaryl bromides, such as 2-acetyl-5-bromobenzofuran [64].

In more recent examples, it was performed using as catalysts Pd complexes of imidazolium-type cations and 2-propanol/water as reaction medium [65]. It was shown that Pd(0) nanoparticles form in solution, but they act mainly as a source of catalytically active soluble palladium species. The reaction gave high yields under moderate heating (40–70 °C) with a variety of aromatic halides (Scheme 12). Conventional and MW heating were compared; the latter resulted in halved reaction times with analogous yields.

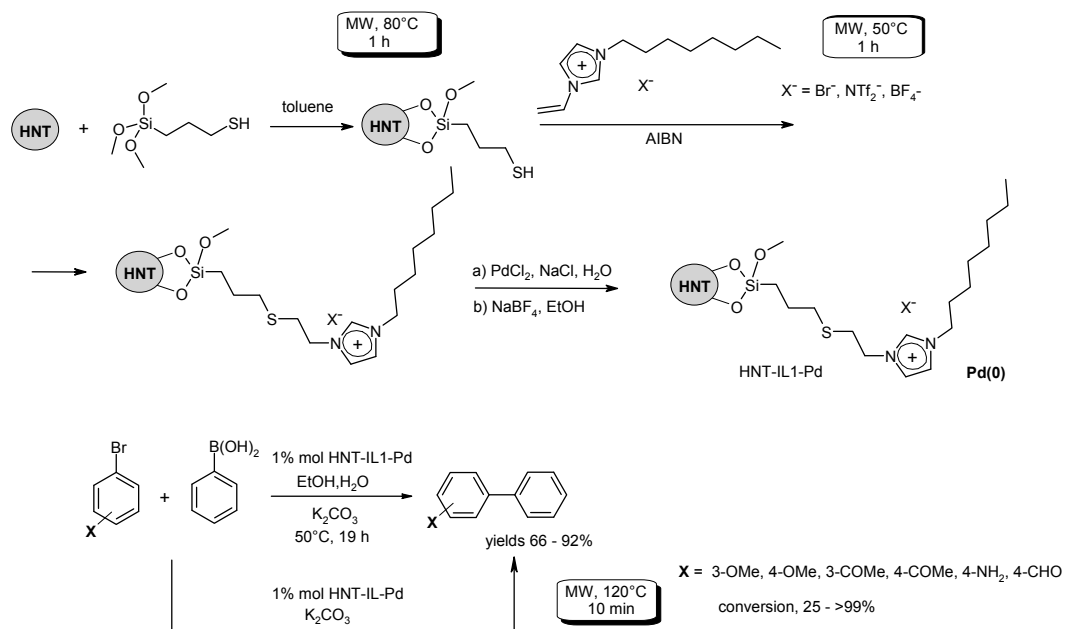


Scheme 12. Palladium-catalyzed Suzuki-Miyaura reaction catalyzed by Pd-IL complexes [65].

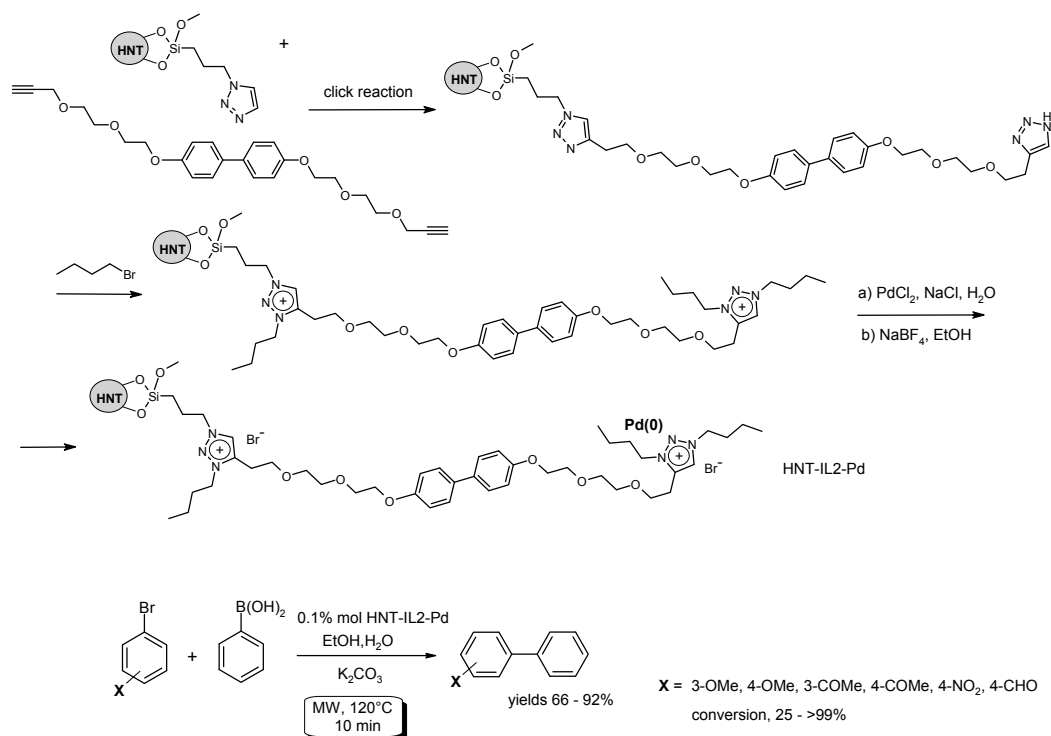
The use of nanoparticles has become increasingly diffused in catalysis, because NPs allow very easy recovery of the catalyst, thus rendering transformations eco-friendly.

The combination MW/ILs was used to prepare heterogeneous catalysts, efficient in Suzuki-Miyaura reaction performed under conventional heating [66]. Only in a second paper the

reaction was performed in water under MW irradiation [67]. Halloysite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, a naturally occurring aluminosilicate nanoclay with a tubular shape, was functionalized on the external surface by MW-assisted grafting of (3-sulfanylpropyl)trimethoxysilane, thus allowing anchoring of vinylimidazolium ionic liquids by a thiol-ene reaction. Two types of Halloysite nano tubules were prepared and used in coupling reaction, as shown in Schemes 13 and 14.



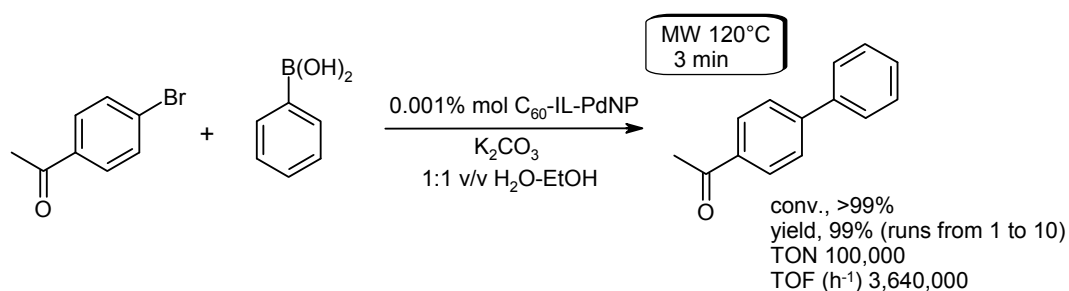
Scheme 13. Halloysite nano tubules (HNT) functionalized with ILs used to stabilize Pd nanoparticles, eco-friendly catalysts in MW-assisted Suzuki reaction [67]. First-generation HNT-IL-Pd catalyst [67].



Scheme 14. Halloysite nano tubules (HNT) functionalized with ILs used to stabilize Pd nanoparticles, eco-friendly catalysts in MW-assisted Suzuki reaction [67]. Second-generation HNT-IL-Pd catalyst [67].

The second generation HNT-IL2-Pd catalyst is definitely more troublesome to prepare than the first generation catalyst, but it has the advantage that could be used in five consecutive runs maintaining high efficiency, while HNT-IL1-Pd catalyst lost some efficiency in the second and third run (86% and 85% conversion from 95% in the first run) and became scarce after the fourth run (27% conversion).

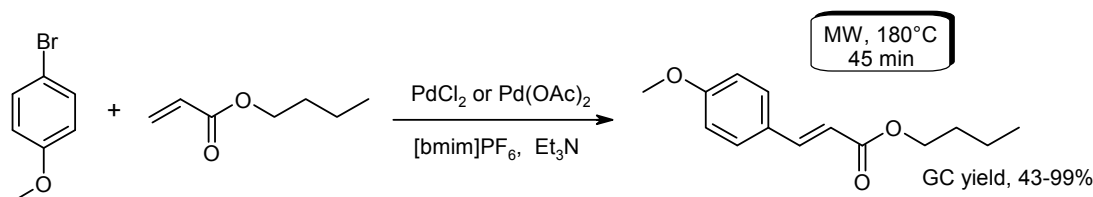
An original and very efficient catalyst was recently developed preparing a supported ionic liquid-like phase (SILLP) covalently linking a C₆₀-IL hybrid to silica-based solid supports [68,69] (Scheme 15). This SILLP is able to immobilize and stabilize palladium nanoparticles in a system that was dubbed by the authors as “a sort of matryoshka” system. The silica catalysts are highly recyclable with no leaching above the limit of detection (0.5 ppm).



Scheme 15. Example of the MW-irradiated Suzuki reaction catalyzed by PdNPs in C₆₀-IL hybrid supported on mesoporous silica [68,69].

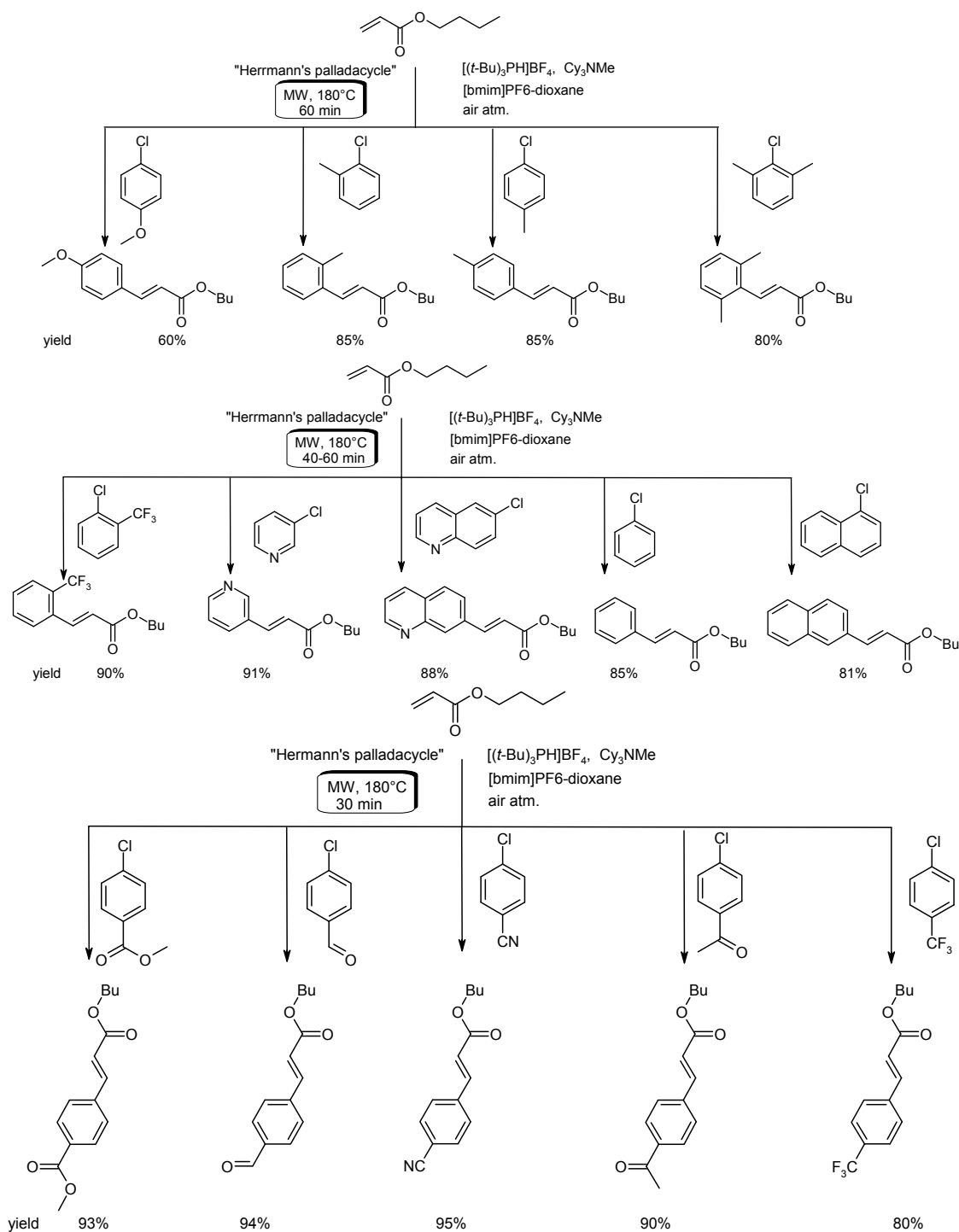
Heck reaction—Palladium-catalyzed vinylation of aryl halides or triflates has been investigated in a variety of non-conventional systems, from supercritical fluids to ionic liquids, from fluorous media to aqueous solvents, and with a variety of energy sources (microwave, ultrasound, high pressure), as a consequence of its synthetic value [70]. Interestingly, with the aid of microwaves, highly regioselective internal Heck arylation of hydroxyalkyl vinyl ethers by aryl halides could be performed in the “green” solvent water [71].

Considering ILs and MW together, in 2002 it was reported that 4-bromomethoxybenzene reacted quite easily with butyl propenoate when treated with palladium catalysts in IL and with MW heating (Scheme 16), even without addition of phosphine ligands [72], in more eco-friendly conditions than the usual ones.



Scheme 16. Palladium-catalyzed Heck reaction of aryl bromides in [bmim]PF₆ with MW heating [72].

The same research group succeeded in alkenylating the generally sluggish aryl chlorides, that reacted in the air, in a mixture of 1,4-dioxane-IL, with MW heating [73]. The reaction worked well not only with the most reactive electron-poor aryl chlorides, but also with electron-rich substrates, simply varying reaction times. [bmim]PF₆ was used with 10 mol % tri(*t*-butyl) phosphonium tetrafluoroborate, (*t*-Bu)₃PH]BF₄, with the so called “Herrmann’s palladacycle”, *trans*-di(μ -acetato)bis[*o*-(*di*-*o*-tolylphosphino)benzyl]-dipalladium(II) as catalyst. Reaction times varied from 30 min for the reactive halides to 60 min for the electron rich ones (Scheme 17).

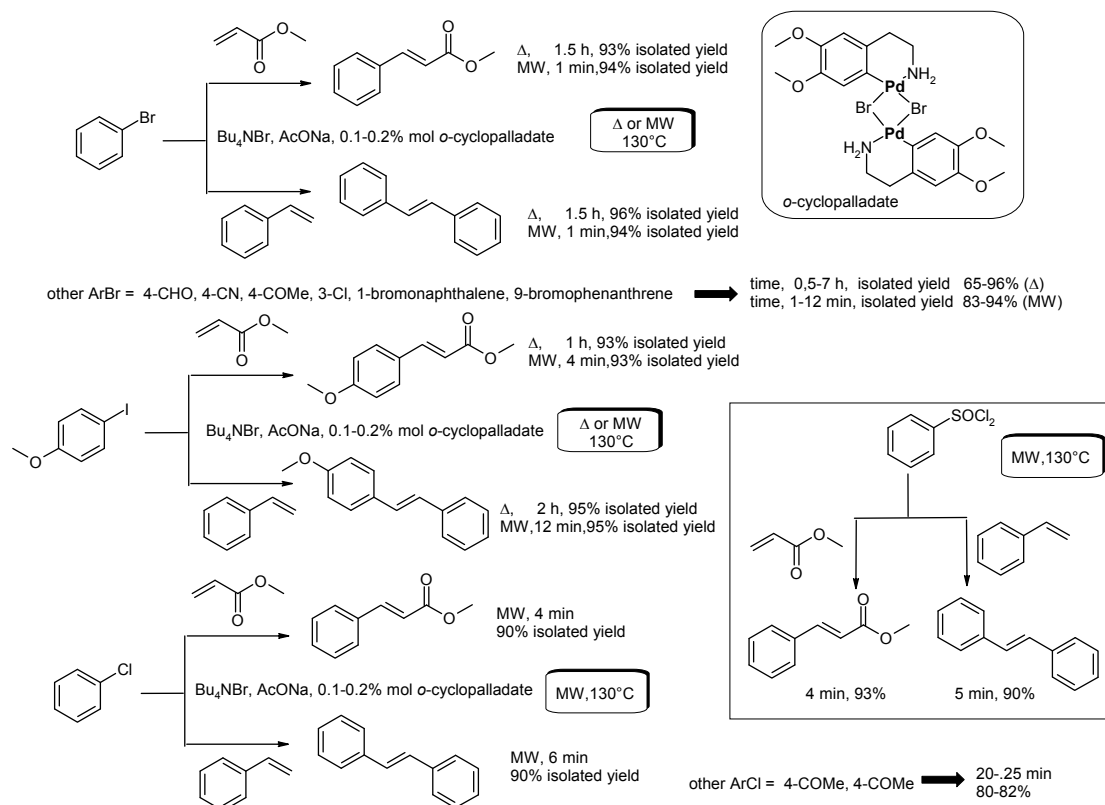


Scheme 17. Palladium-catalyzed Heck reaction of aryl chlorides in [bmim]PF₆-dioxane with MW heating [73].

Butyl propenoate was used as vinylating agent of aryl iodides in a Heck reaction in [omim]BF₄ with a simple Pd/C catalyst (3 mol %), that could be recycled up to five times with scarce loss of activity [74]. MW irradiation made reaction times very short (0.5 min), but yields were not always satisfactory; moreover, aryl halides were inert in these conditions.

Instead, Heck alkenylation was successfully achieved on aryl iodides, bromides and chlorides, using an *ortho*-palladated complex in non-aqueous ionic liquid, such as Bu₄NBr, Bu₄NCl, and

[bmim]Br [75]. Other conditions being equal, Bu_4NBr gave the best conversion of halides and therefore was the solvent of choice for the reaction screening. Conventional heating and MW heating were compared, with the latter favoring the reaction in terms of reduced reaction times, thanks to microwave-absorbing nature of Bu_4NBr . Selected results are presented in Scheme 18.

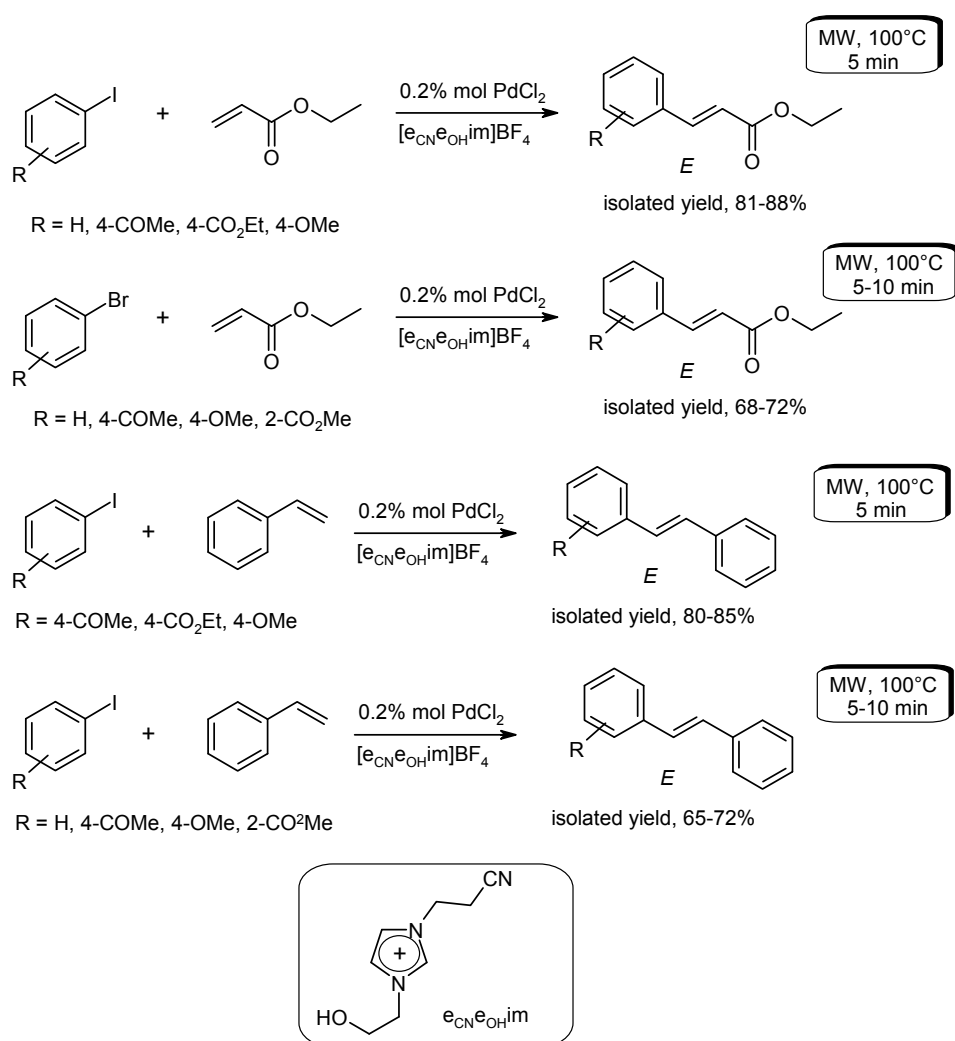


Scheme 18. Palladium-catalyzed Heck reaction of aryl halides in Bu_4NBr [75].

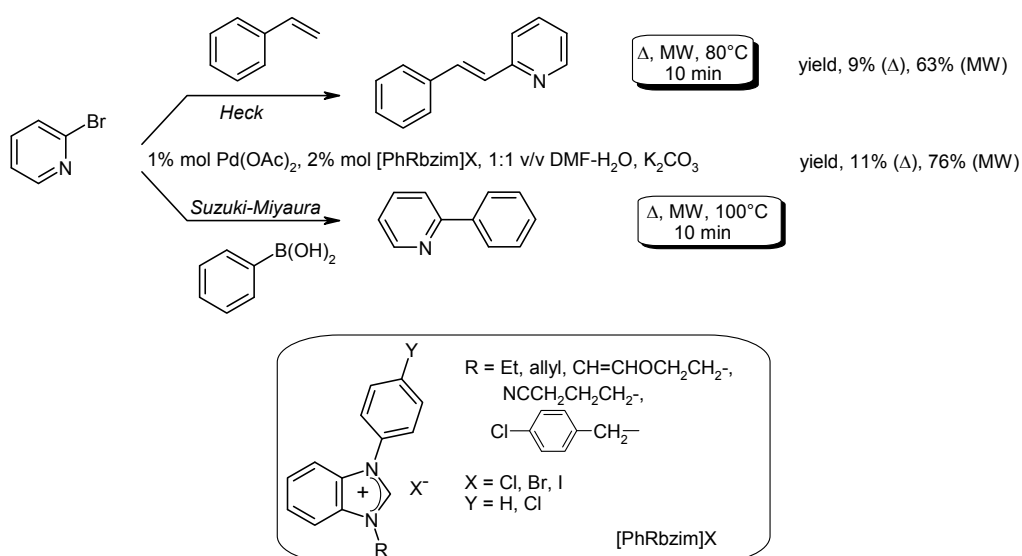
Regioselectivity was discussed in detail in a study that examined the Heck reaction in DMSO/[bmim]BF₄, with MW as heating source [76]. It was observed that regioselectivity was higher in IL solvent and that MW heating reduced the reaction time from hours to minutes. As the catalyst, Pd₂(dba)₃ was used together with a sugar-derived phosphine ligand (methyl 4,6-*O*-benzylidene-3-deoxy-3-(diphenylphosphino)- α -D-altropyranoside).

MW-assisted Heck reaction was performed using the IL 1-(2-cyanoethyl)-3-(2-hydroxyethyl)-1*H*-imidazol-3-ium tetrafluoroborate as solvent, ligand and base, i.e., an efficient, air stable and phosphine free catalytic system (PdCl₂ was the precursor of the actual catalyst) [77]. A variety of substrates, with different electronic and steric effects, were treated under these conditions. Significant results are collected in Scheme 19.

A different approach was used by other researchers, that focused on new *N*-phenylbenzimidazolium salts as ILs, while commercial Pd(OAc)₂ was the catalyst [78]. Actually, the salts are not liquid and were used in 2 mol % amounts, in solvents as DMF-H₂O or EtOH-H₂O. The system was used both in Heck and in Suzuki-Miyaura reactions on halopyridines. MW heating was determinant to obtain good results: there are examples of reactions not occurring at all under conventional heating that became practicable with MW irradiation. Reaction conditions are reported in Scheme 20.

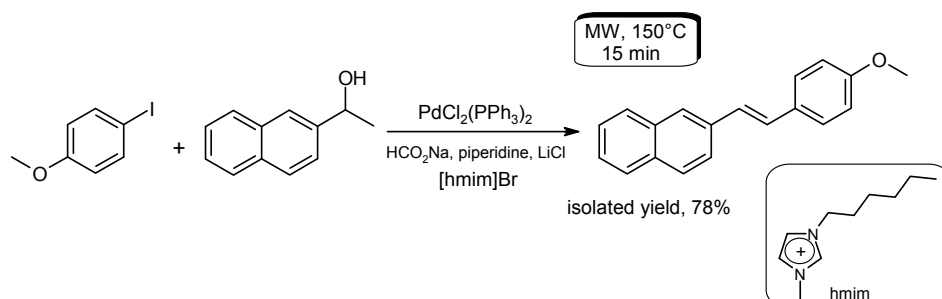


Scheme 19. MW-assisted, phosphine and base free Heck reaction in task-specific IL [77].



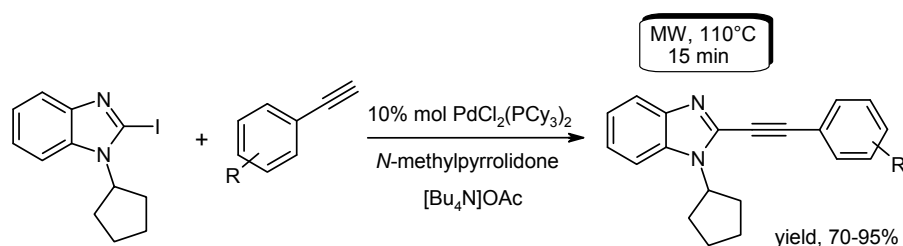
Scheme 20. Example of MW-assisted Pd-catalyzed Heck and Suzuki-Miyaura reactions of 2-bromopyrimidine [78].

An unusual Heck-type alkenylation was obtained directly from aryl alcohols instead of alkenes, in a one-pot reaction that was assisted by ILs and MW [79]. This procedure avoided prone to polymerization alkene reagents, did not require inert atmosphere, and could be applied to a wide range of substrates (Scheme 21).



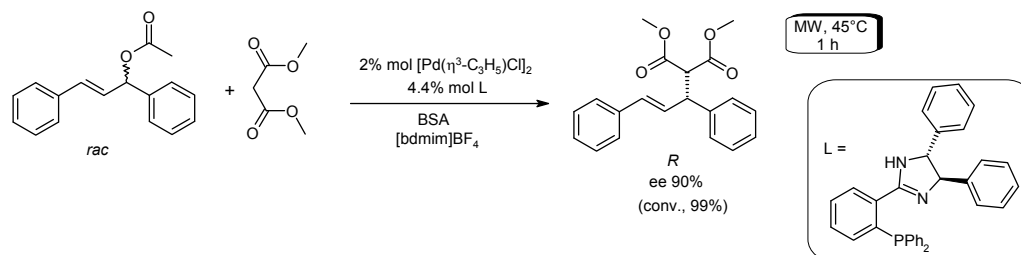
Scheme 21. IL- and MW-assisted Heck-type alkenylation of aryl alcohols [79].

Sonogashira reaction—The Pd-catalyzed coupling reaction of aryl chlorides and terminal alkynes was accomplished in 10 min using MW heating [80] and worked well also intramolecularly, leading to one-pot synthesis of indoles [81]. However, the procedures were far from being sustainable, since it was necessary to use phosphines, organic solvents, copper compounds, and a base. Instead, the Sonogashira reaction was made more eco-friendly when tetrabutylammonium acetate was introduced as an activator [82] in a copper-free system, with complete substrate disappearance within 15 min (Scheme 22).



Scheme 22. MW-irradiated Pd-catalyzed, amine and copper-free Sonogashira reaction with ammonium salt activator [82].

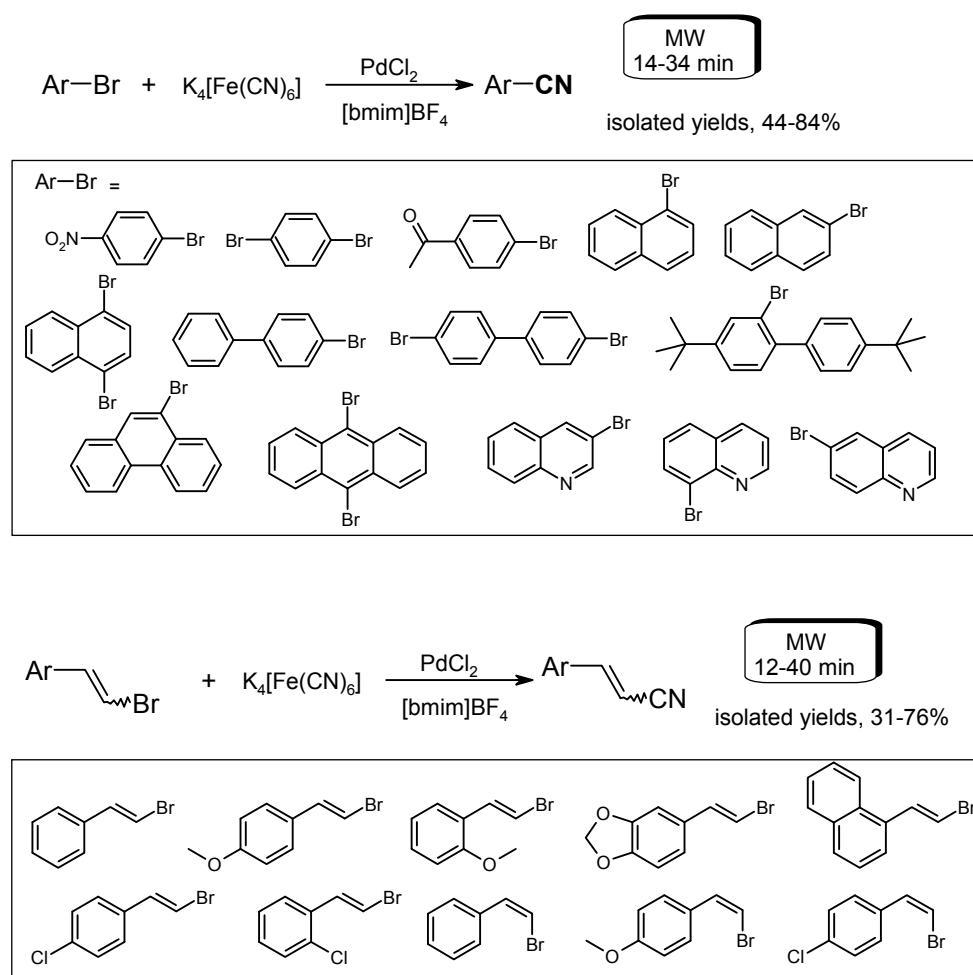
Allylic alkylation—Efficient allylic alkylation was performed in tailor-made ILs, with Pd catalysts having phosphine-imidazoline ligands and MW heating [83]. The accurate investigation considered different catalysts, different ILs, MW irradiation, recycling, and enantioselectivity. The best results are shown in Scheme 23. The actual catalyst is formed in situ, by the $[Pd(\eta^3\text{-allyl})Cl]_2$ precursor and a phosphine-imidazoline ligand in IL (preferably, $[bdmim]BF_4$). The reaction also occurred at room temperature, but heating increased enantioselectivity.



Scheme 23. Pd-catalyzed MW-assisted asymmetric allylic alkylation in IL [83].

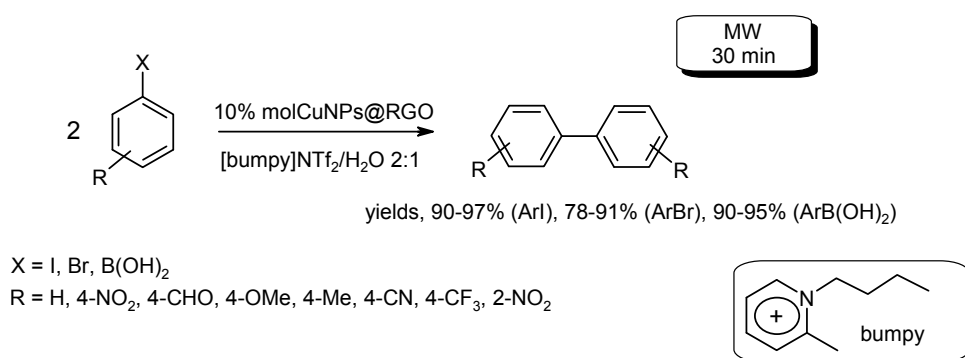
Cyanation of aryl and vinyl halides—Although with a less wide scope, this reaction is important to prepare aryl and arylvinyl nitriles, useful synthones in organic synthesis. Moreover, cyanide sources are notorious toxic compounds, thus rendering advisable any new eco-friendly procedure.

The non-toxic potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$, was used as cyanide source in a palladium-catalyzed reaction of several aryl and arylvinyl bromides, in ionic liquid under microwave irradiation [84] (Scheme 24). These conditions had the advantage not only to reduce the reaction time, but also to make product separation and catalyst recycle easier.



Scheme 24. Pd-catalyzed MW-assisted cyanation of aryl and arylvinyl bromides in [bmim]BF₄ [84].

Ullmann reaction—A “green” catalyst was prepared treating graphene oxide (GO) with $CuSO_4$ and then reducing with ascorbic acid. The resulting Cu nanoparticles on reduced graphene oxide (RGO), Cu NPs@RGO, were used to catalyze the Ullmann homocoupling reaction (Scheme 25) [85]. MW irradiation was used with different solvents, ILs included. Optimized conditions were aryl iodides (or areneboronic acids) as the substrates, 10 mol % CuNPs@RGO catalyst, 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide and H_2O (2:1 ratio) as solvent, and 30 min MW irradiation. Aryl bromides were less reactive, but still interesting yields were obtained (78–91%).

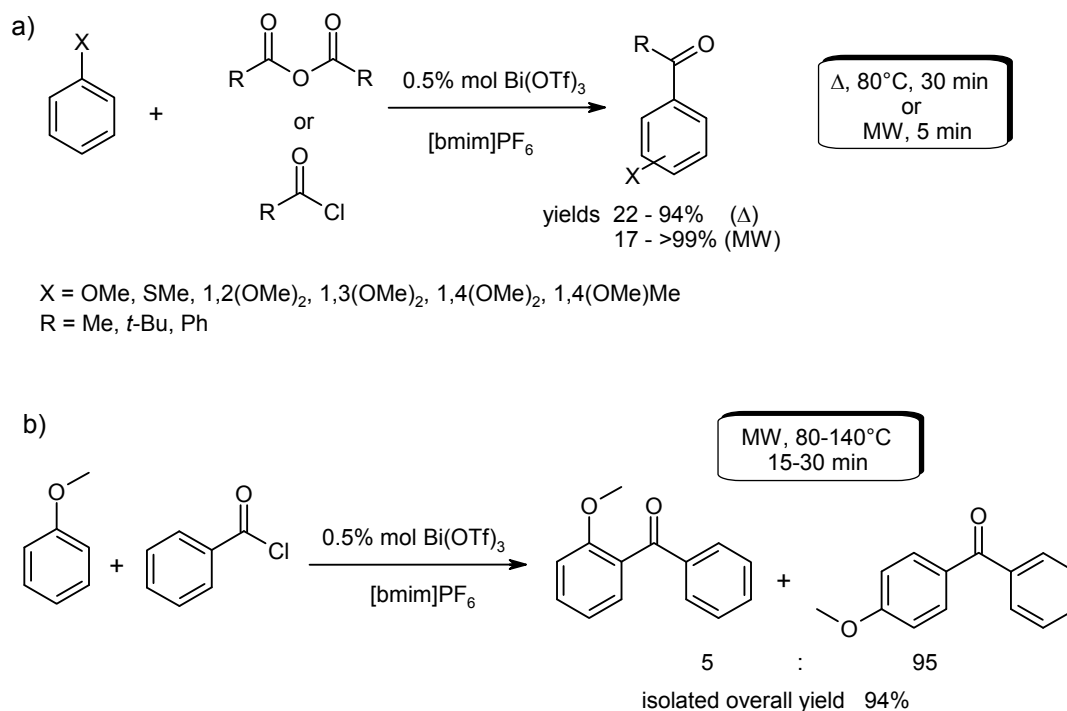


Scheme 25. MW-promoted Ullmann reaction catalyzed by Cu nanoparticles on reduced graphene oxide, in IL/H₂O [85].

3.2. Friedel-Crafts Aromatic Substitutions

Acylation Reactions—It is well known that Friedel-Crafts acylation is a powerful method to prepare aromatic ketones, but is far from being a “green” procedure, because it requires chlorinated solvents and a more than stoichiometric amount of the “catalyst” AlCl₃. Therefore, attempts have been made to achieve a sustainable electrophilic acylation. Following the finding of metal triflates that, still maintaining strong Lewis acid character, are water resistant [86], some of them were used as catalysts in IL solvents.

The acylation of ferrocene, already discussed in introduction [19], showed that Sc(OTf)₃, Y(OTf)₃, and Yb(OTf)₃, could be used in 10 mol % amount in bmimNTf₂ and was improved by MW heating. Later, Bi(OTf)₃ was used to efficiently acylate methoxybenzene with different carboxylic anhydrides or chlorides in bmimPF₆ [87] (Scheme 26a). MW irradiation efficiently accelerated the acylation with yields generally increased.

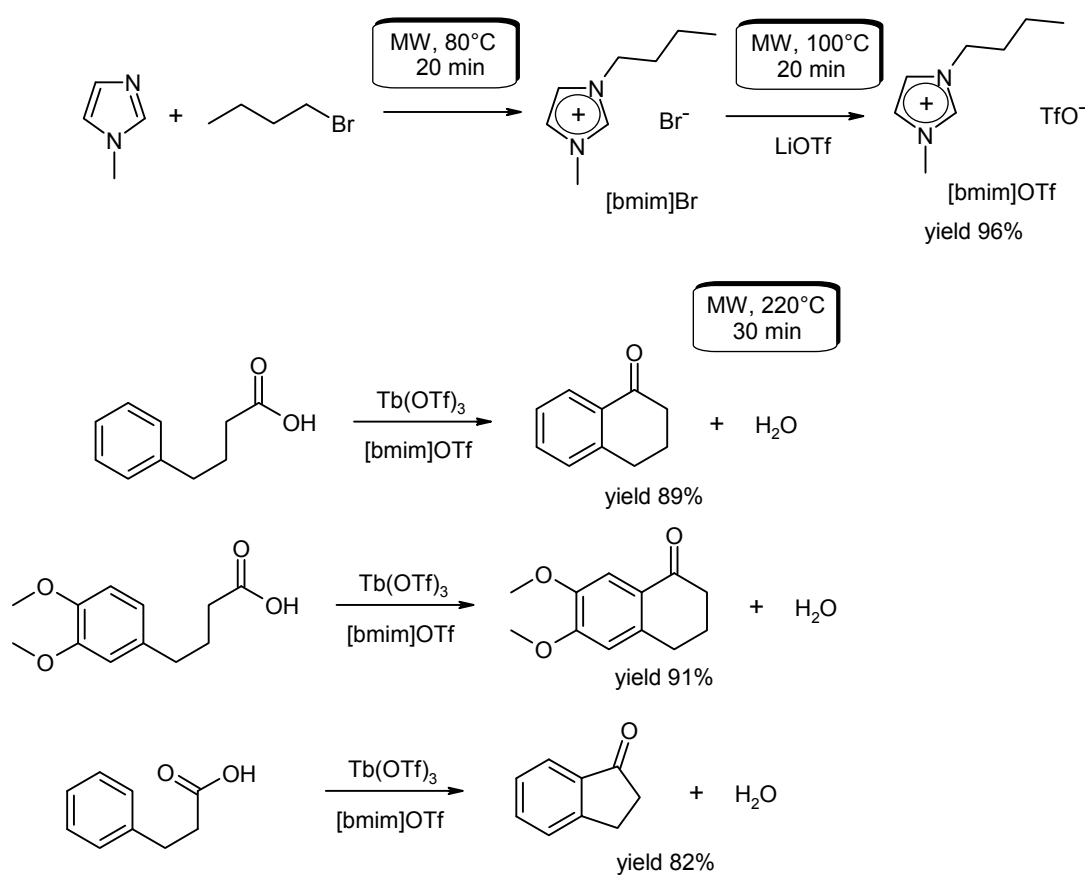


Scheme 26. MW-assisted Friedel-Craft acylation of aromatic compounds in [bmim]PF₆. (a) acylation of aromatic ethers by acyl anhydrides or chlorides [87], (b) benzoylation of methoxybenzene [88].

The attention was then focused on MW-assisted benzoylation of aromatic compounds that was explored with a variety of substrates, evidencing the product distribution and the high yields [88] (Scheme 26b).

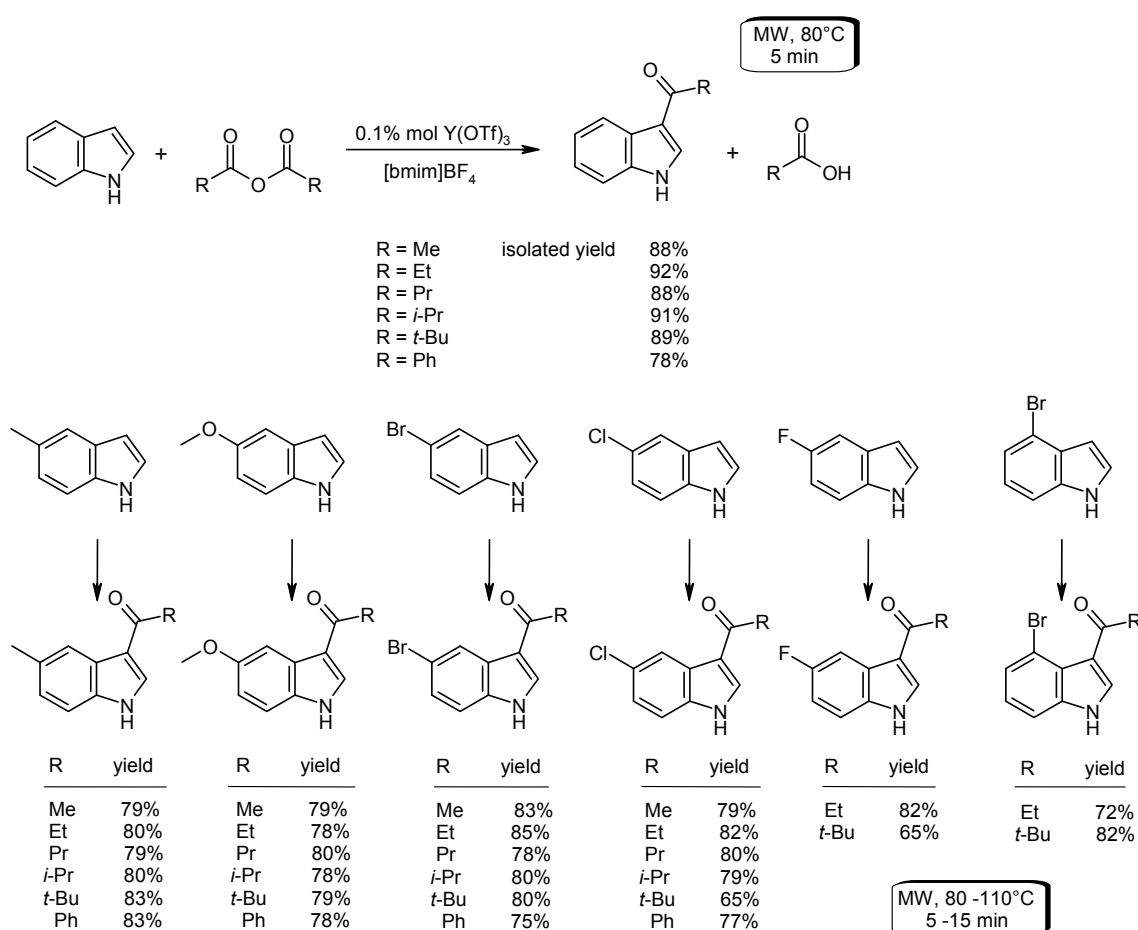
A screening of catalytic efficiency of various metal triflates was performed investigating acetylation of 1,3,5-trimethylbenzene with acetic anhydride [89]. Among the 14 metal triflates examined, $\text{In}(\text{OTf})_3$ gave the best results, being superior also to the above discussed $\text{Bi}(\text{OTf})_3$ catalyst. 1-isobutyl-3-methylimidazolium dihydrogen phosphate, $[\text{i}^{\text{b}}\text{mim}]\text{H}_2\text{PO}_4$ was the solvent of choice and the reaction was applied to a wide range of aromatic compounds. The combination carboxylic anhydride/ $[\text{i}^{\text{b}}\text{mim}]\text{H}_2\text{PO}_4/\text{In}(\text{OTf})_3/\text{MW}$ gave good performances and the catalyst could be easily recycled.

Considering the pharmaceutical importance of tetralone derivatives, such as donepezil hydrochloride, a “green” intramolecular Friedel-Craft acylation was carried out with $\text{Tb}(\text{OTf})_3$ catalyst, in ILs (bmim or bupy triflates), under MW irradiation, directly from carboxylic acid [90] (Scheme 27). $\text{Tb}(\text{OTf})_3$ emerged as the catalyst of choice after a screening of 19 metal triflates; moreover, it could be recovered and re-used three times, with only slight decrease in product isolated yield.



Scheme 27. Intramolecular Friedel-Craft acylation to tetralones catalyzed by $\text{Tb}(\text{OTf})_3$ in $[\text{bmim}]\text{OTf}$, under MW irradiation [90].

Another metal triflate, $\text{Y}(\text{OTf})_3$, was the best catalyst for regioselective 3-acylation of indoles [91]. MW irradiation and IL solvent ($[\text{bmim}]\text{BF}_4$) contributed to obtain high yields in few minutes (Scheme 28). Moreover, to further improve sustainability of the reaction, it was not necessary to protect the heterocyclic NH, thus eliminating the protection-deprotection steps, in agreement with the eighth principle of Green Chemistry [1].



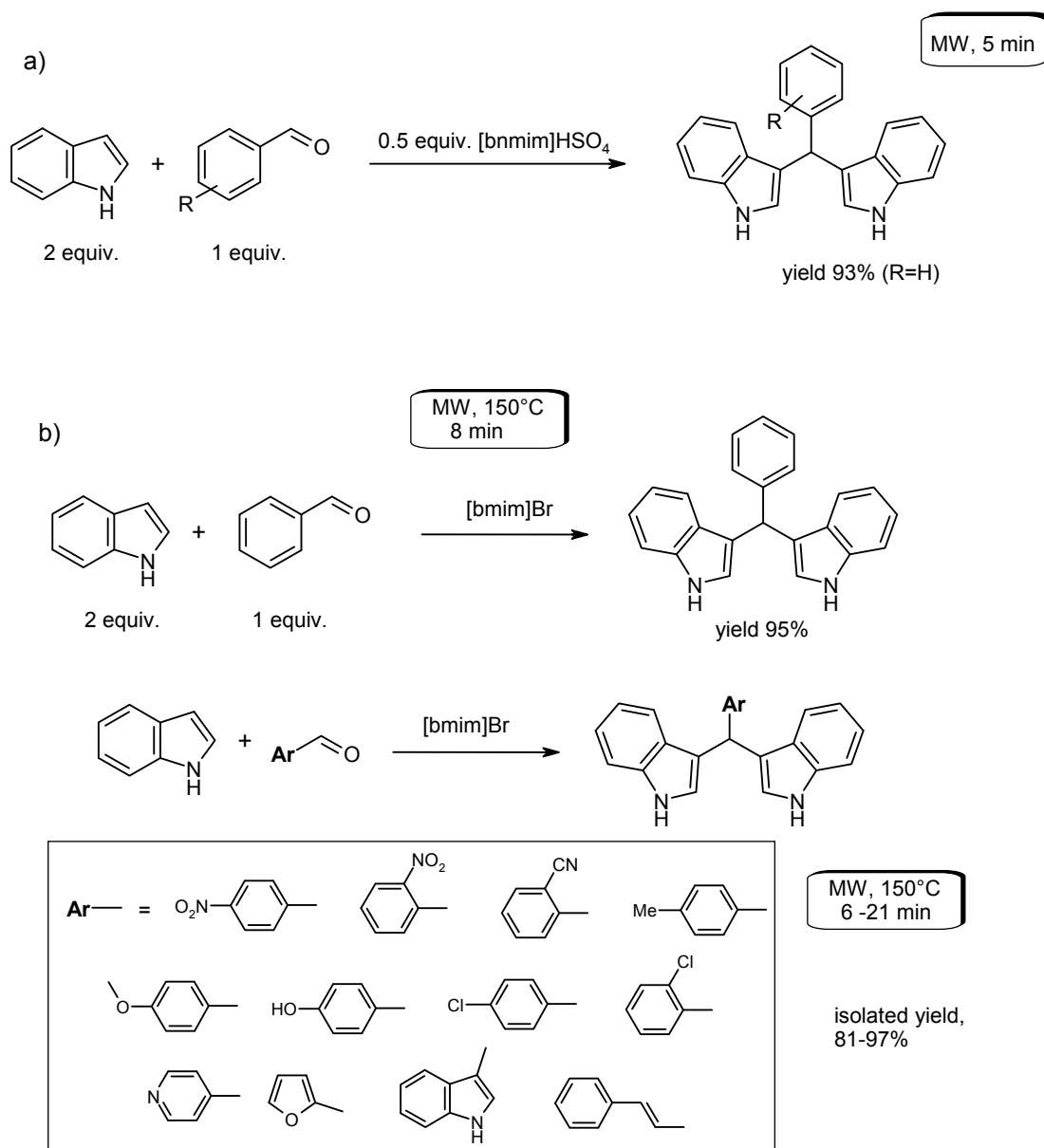
Scheme 28. MW-assisted Y(OTf)₃ catalyzed indole acylation in [bmim]BF₄ [91].

The recovery of yttrium triflate in [bmim]BF₄ was simple: after product extraction, the ionic liquid containing metal triflate was dried under vacuum and reused. Differently substituted indoles were also acylated in good yields and only few percents of *N*-acylindoles were occasionally observed.

Aromatic Substitutions by electrophilic aldehydes. The condensation of indoles with benzenecarbaldehyde was reported to be catalyzed by 1-benzyl-3-methyl imidazolium hydrogen sulphate, [bnmim]HSO₄, and improved by MW irradiation, in terms of higher yields and reduced reaction time [92] (Scheme 29a).

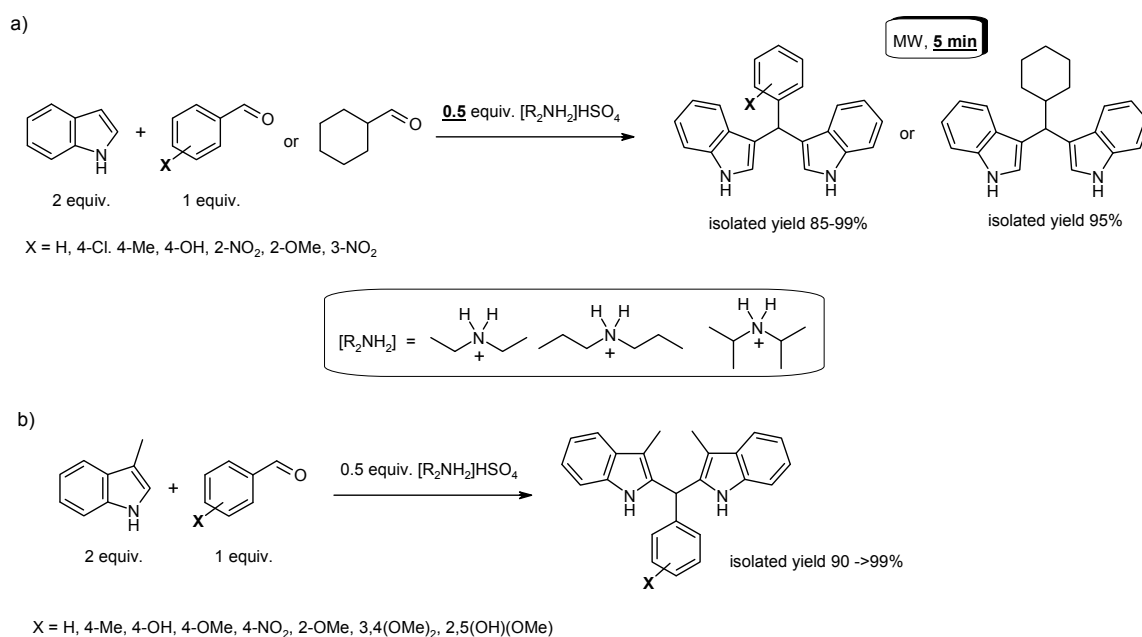
IL acted as an acid catalyst and MW heating shortened reaction times. A variety of aromatic aldehydes were used, with yields in the range 81–95% and reaction times varying from 5 to 19 min and the catalyst could be used in four consecutive runs, with negligible loss of activity.

Also [bmim]Br was found to catalyze reaction of aldehydes with indoles, probably behaving as both acid and base catalyst [93] (Scheme 29b). A wide range of aldehydes was reacted and, once again, the combination IL/MW was decisive in increasing yield and reducing reaction times, with the bonus of easy recovery and recycling.



Scheme 29. Formation of bis-indolylmethanes by MW-assisted electrophilic substitution catalyzed by [bnmim]HSO₄ (a) [92] and [bmim]Br (b) [93].

Later, the synthesis of aryl(bis-3,3'-indolyl)methanes was obtained in good yields with a variety of aldehydes, ammonium-based ionic liquids and microwave heating [94]. Mild reaction conditions were accompanied, according to the authors, by simple product recovery and recycle of ammonium salts. When the indole 3-position was occupied by a methyl group, the reaction worked as well and aryl or alkyl(2,2'-bis-3-methylindolyl)methanes were prepared (Scheme 30).

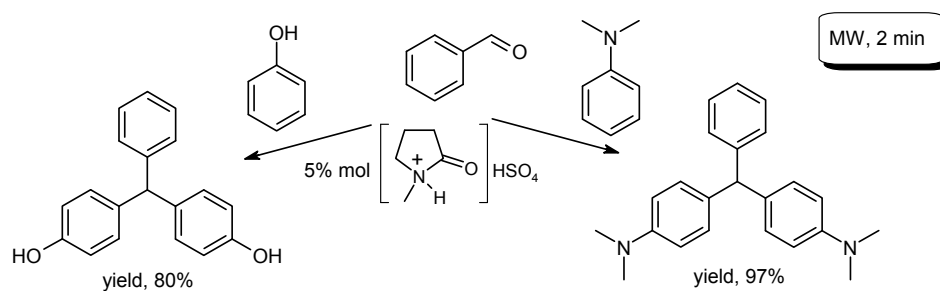


Scheme 30. MW-assisted dialkylammonium hydrogen sulfate-catalyzed reaction of aldehydes with indole (a) and 3-methylindole (b) [94].

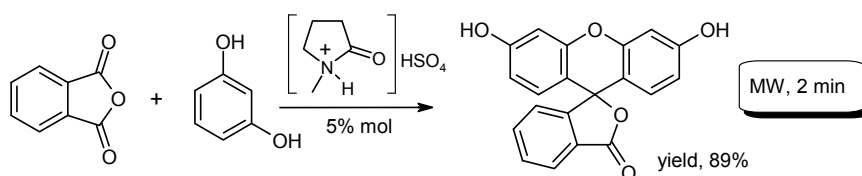
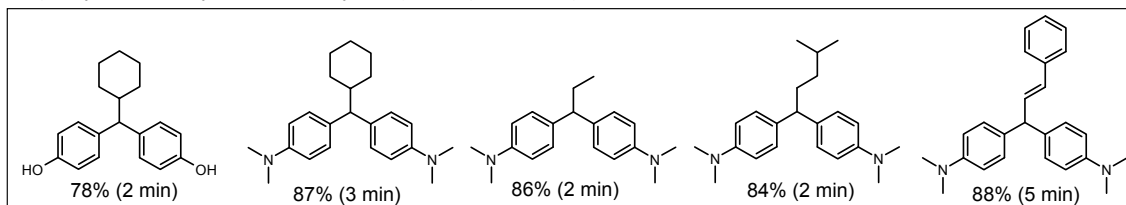
A related reaction, that probably goes through electrophilic aromatic substitution, formed triphenylmethane and phthalein with catalysis by Brønsted acid ionic liquids and heating by MW [95] (Scheme 31).

MW heating was more efficient than conventional one, reducing reaction time from hours to few minutes. The work up was easy, reaction rates were fast, reaction conditions were mild, yields were good, and ILs could be reused: the combination IL/MW gave facile access to families of compounds important in dyes chemistry and biologically active [95].

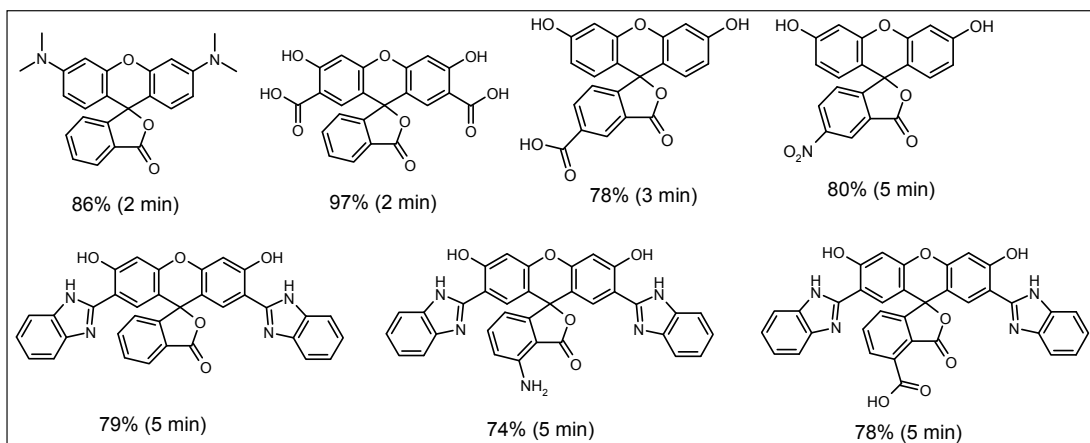
Alkylation Reactions—Friedel-Craft alkylation is scarcely used in organic synthesis, because generally it is affected by polysubstituted by-products, since the more alkyl groups are introduced, the more reactive is the aromatic compound. Nevertheless, an interesting report appeared in 2013, where indium(III) triflate catalyzed alkylation of benzenes by alcohols in IL solvents with MW irradiation [96]. Noticeably, only monoalkylated benzenes were obtained (Scheme 32) with benzyl, tertiary, and secondary (but not primary) alcohols as alkylating agents, thus suggesting the possible intermediacy of carbocations. A phosponium-based IL, trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl)imide, [tthdp]NTf₂, and the imidazolium-based [emim]NTf₂ were examined as solvents, with the latter giving the best results; energy-efficient heating was provided by MWs.



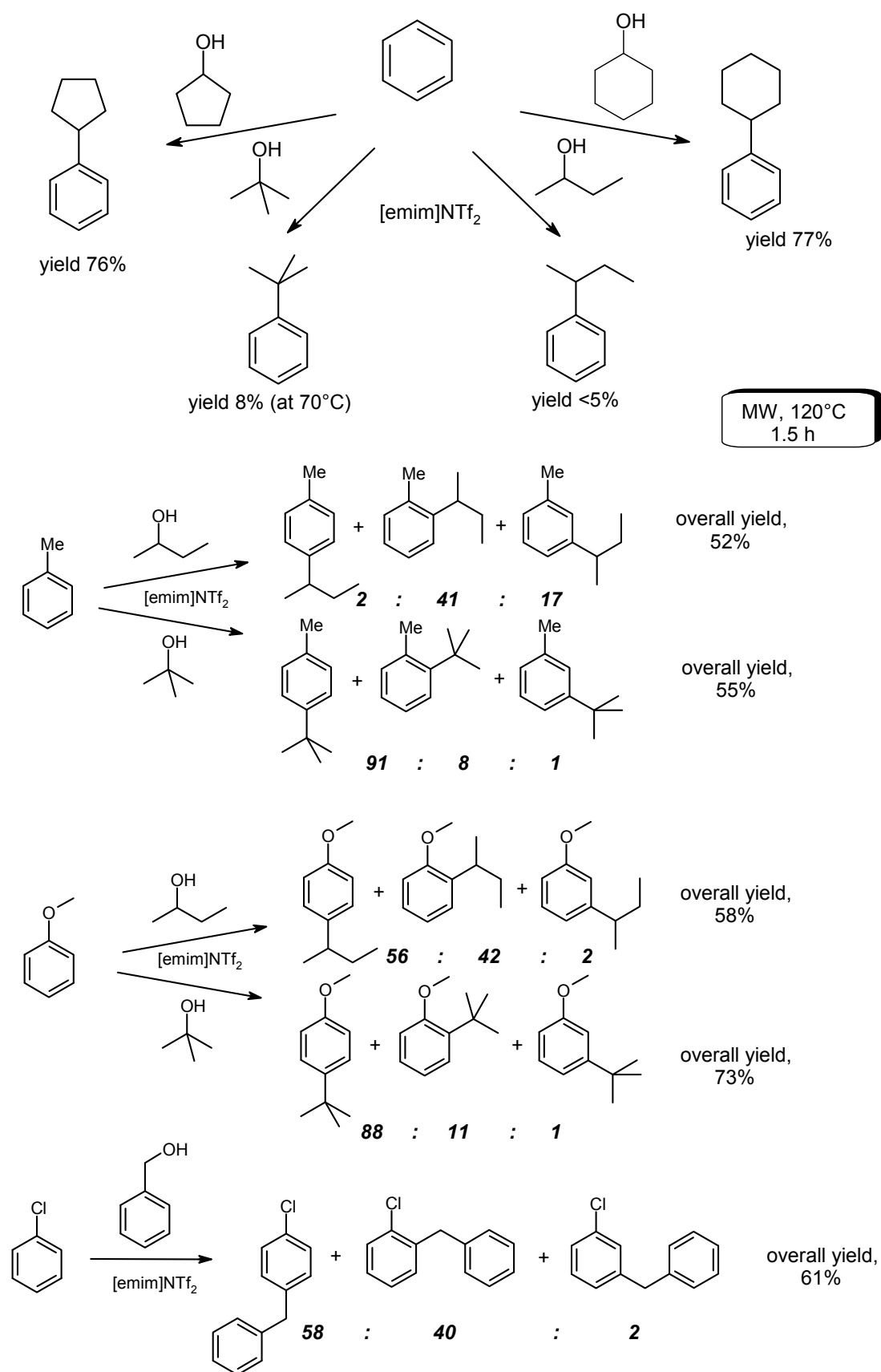
triphenylmethanes synthesized with yields (time in parenthesis)



phthaleins synthesized with yields (time in parenthesis)



Scheme 31. MW-activated acid IL-catalyzed synthesis of triphenylmethanes and phthaleins [95].

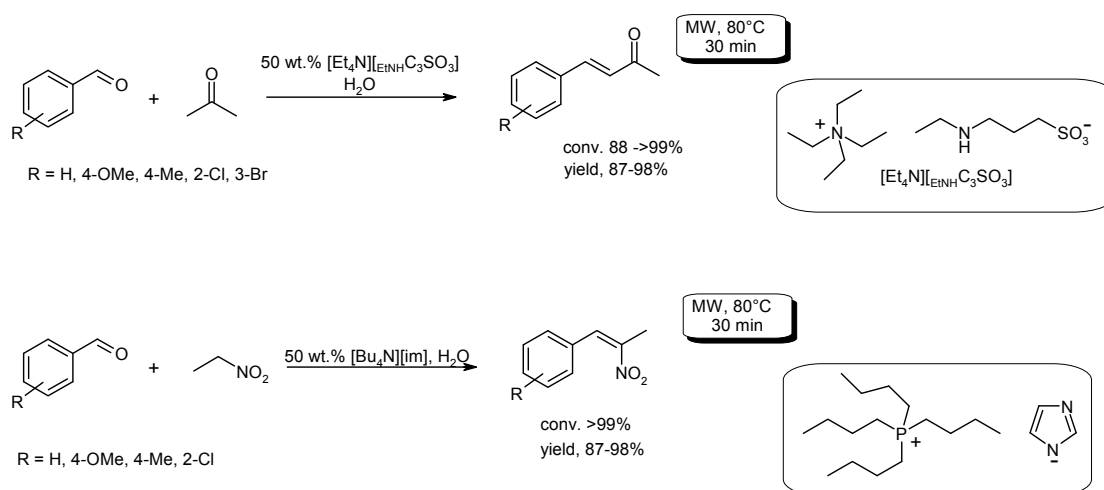


Scheme 32. MW-assisted $\text{In}(\text{OTf})_3$ catalyzed aromatic alkylation of benzenes with alcohols in $[\text{emim}]\text{NTf}_2$ [96].

3.3. C–C Bond Formation with C-Nucleophilic Reagents

Aldol-type reactions—It is well known that the aldol reaction is one of the most powerful tool for the construction of C–C bonds and it is considered relatively environmentally benign, being also highly atom-economic. However, due to the need of strong bases or acids, the “green” aspect can be improved, as discussed in a 2004 review [97]. Catalysis, biocatalysis, and alternative solvents, among which task-specific ionic liquids (TSILs) [98–100], have been the object of following research. Even a MW-assisted aldol reaction was carried on in absence of solvents [101].

The possibility to use together an alternative power source as MW and alternative solvents as ILs was explored in the aldol condensation reactions of aryl aldehydes with acetone [102]. Tetralkylammonium and tetrabutylphosphonium salts were prepared and used, with encouraging results (Scheme 33). The functionalized ILs acted as both solvents and the reaction did not require any strong acid or base to catalyze the aldol condensation. Aldehydes with electron-withdrawing substituents were—as expected—more reactive than the electron-rich ones. The system was effective also in the nitro-aldol condensation (Henry reaction). MW heating was confirmed to provide rate-enhancement with respect to conventional heating.

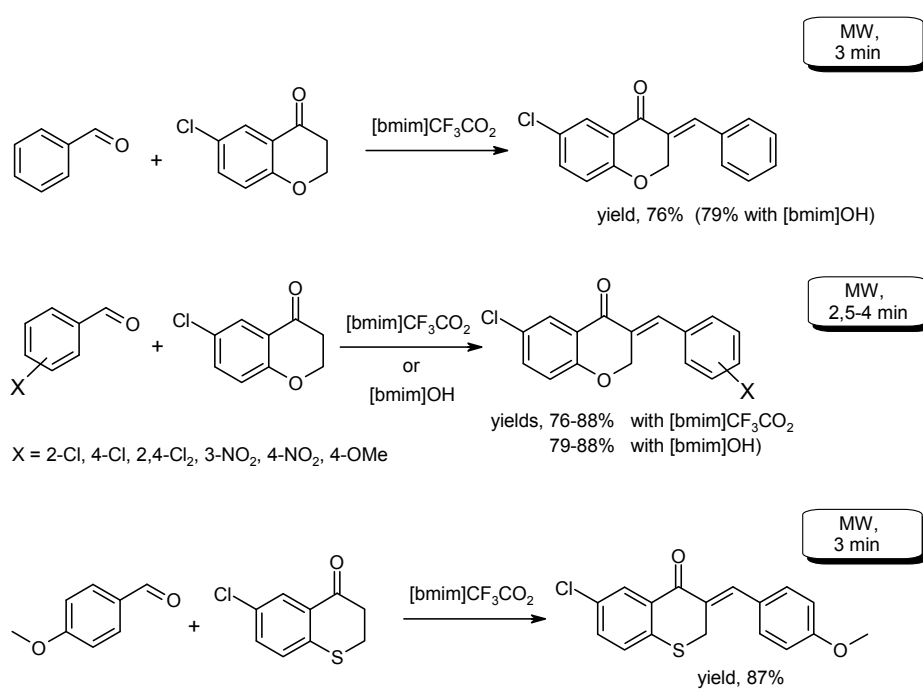


Scheme 33. MW-assisted aldol (top) and nitro-aldol (bottom) reactions with ILs catalytic systems [102].

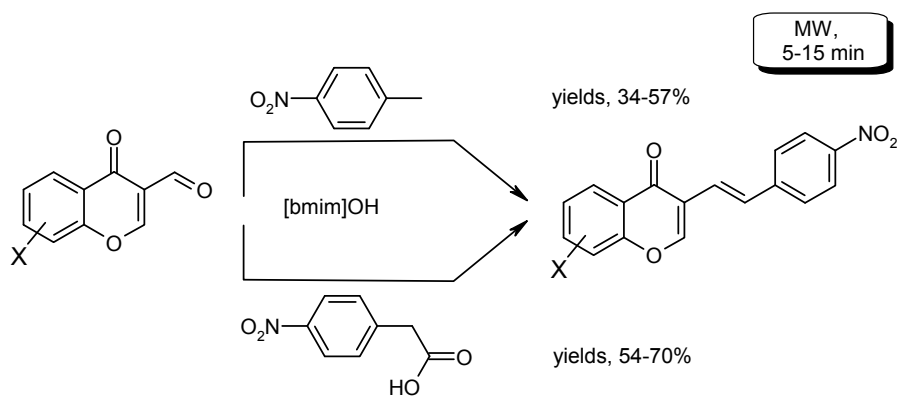
The condensation of aryl aldehydes with nucleophilic enolates was exploited to prepare bioactive heterocyclic compounds, such as chromanone and thiochromanone derivatives, in a MW-irradiated process, catalyzed by ILs with a basic anion [103] (Scheme 34).

The basic [bmim]OH IL catalyzed the synthesis of 3-styrylchromones from 3-formylchromones and a carbanion precursor, under MW irradiation [104] (Scheme 35). The authors pointed at the advantages of the method (easy work-up, short reaction times, satisfactory yields, reusable catalyst) and at the cytotoxicity of products.

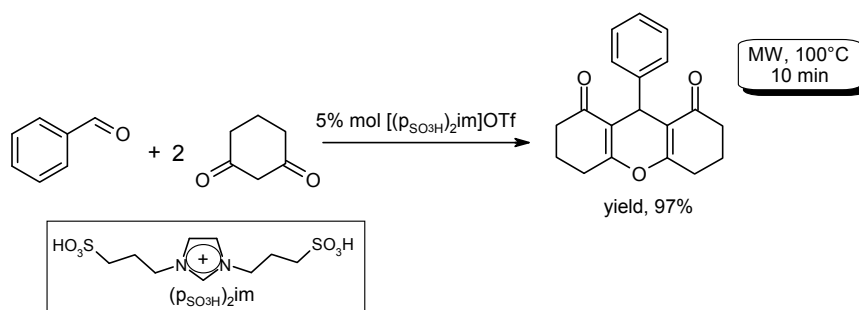
The condensation of aryl aldehydes was achieved also with Brønsted acid ILs, giving xantenedione derivatives [105] (Scheme 36), in a process made fast by MW irradiation. In such reaction, products were simply isolated by filtration and the catalyst reused without treatment, although a dramatic drop in yield was reported from the second run (from 97% to 9%). However, a direct comparison of yields is difficult, because also the reaction time changed (from 10 to 1 min).



Scheme 34. MW-irradiated condensation of aryl aldehydes with chromanones and thiochromanones, catalyzed by ILs [103].



Scheme 35. MW-irradiated [bmim]OH-catalyzed formation of 3-styrylchromones [104].

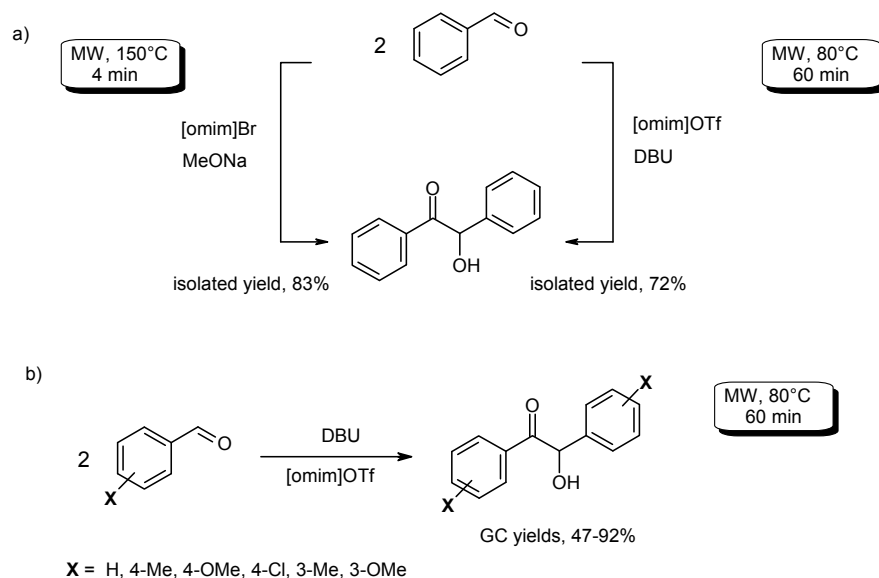


Scheme 36. MW-assisted, Brønsted acid IL-catalyzed condensation of benzencarbaldehyde with 1,3-cyclohexanedione [105].

The reaction was extended to substituted aldehydes and diketones, with yields in the range 90–97%.

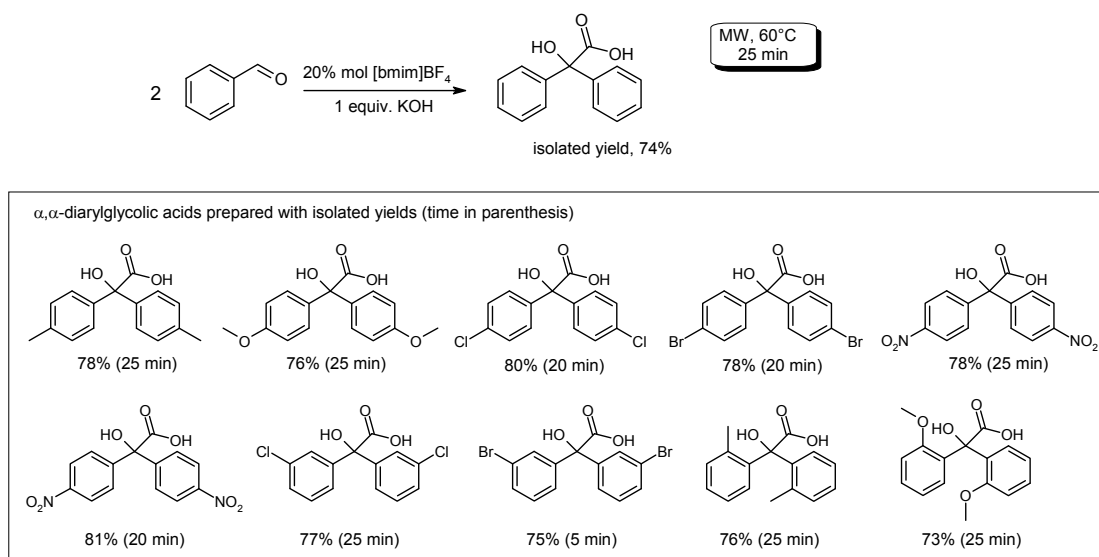
Benzoin condensation—Benzene carbaldehyde underwent benzoin condensation in 1-octyl-3-methyl imidazolium bromide that acted also as catalyst under MW [106] (Scheme 37a) as well as ultrasound [107] irradiation.

Similar results were obtained by another research group that used MW irradiation also in the ILs preparation [108] (Scheme 37b).



Scheme 37. MW- and base-promoted benzoin condensation with 1-octyl-3-methyl imidazolium bromide (a) [106] and triflate (b) [108].

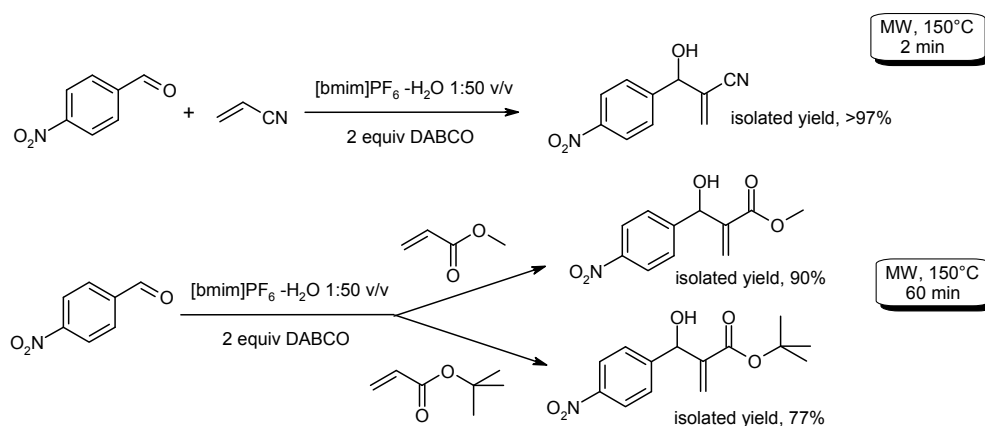
A further development was the preparation of diarylglycolic acids in [bmim]BF₄ and KOH, with MW heating [109]. Likely, KOH should deprotonate the imidazolium salt, forming the actual catalyst. This one-pot procedure resulted easy and efficient and was applied to substituted aromatic aldehydes, with results summarized in Scheme 38.



Scheme 38. MW-heated synthesis of diarylglycolic acids in [bmim]BF₄ [109].

Morita-Baylis-Hillman reaction—DABCO-catalyzed C–C bond formation between an alkene bearing an electron-withdrawing substituent and an electrophilic carbon could be performed in water

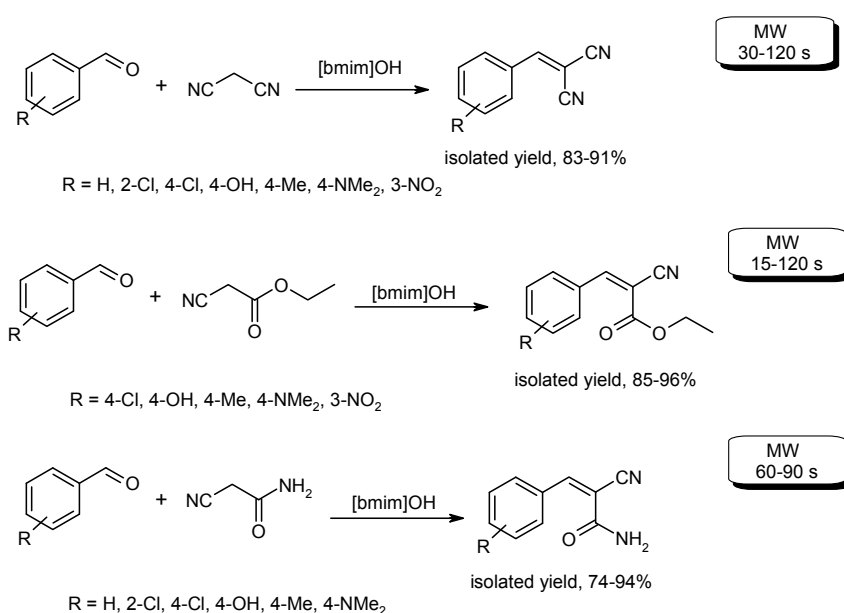
containing IL, only if MW heating was provided [110]. Under conventional heating, no reaction occurred in 3 h, while with MW irradiation the product formed almost quantitatively (isolated yield, >97%) within 3–7 min, that arrived at 20–40 s, if the reaction is carried on under 40 *psi* pressure. Nucleophilic α,β -unsaturated esters are less reactive, but the reaction still gives satisfactory yields, even with the sterically crowded *t*-butyl ester (Scheme 39).



Scheme 39. The MW-promoted DABCO catalyzed Morita-Baylis-Hillman reaction in water-[bmim]PF₆ [110].

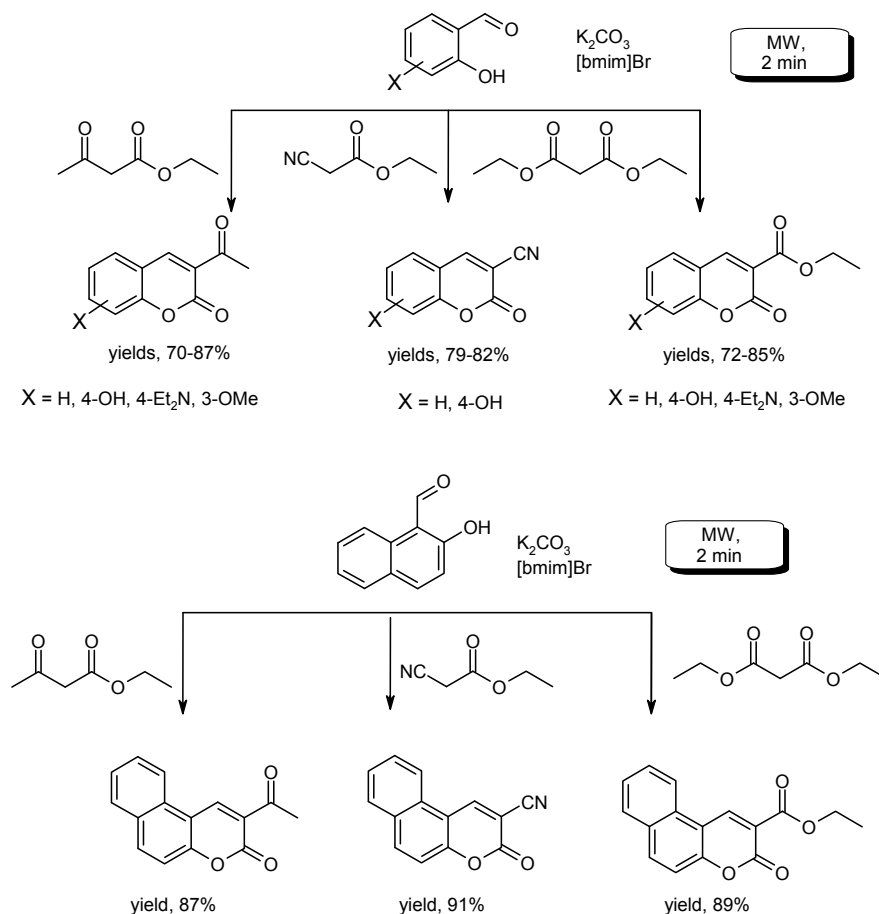
The reaction was tested with good results also varying the aldehyde.

Knoevenagel reaction—In order to solve the scarce sustainability of catalysts used in Knoevenagel reaction, that is the C–C bond formation between aldehydes and active methylene compounds, a range of homogeneous and heterogeneous catalysts have been applied with varying results. Among them, the functionalized ionic liquid [bmim]OH was chosen to catalyze the reaction, because it can provide the necessary basic environment, beside the ionic one [111]. The section was performed in absence of other solvents, under grinding, conventional heating, and microwave irradiation conditions. The first method required longer reaction time than the other two and yields are comparable in all cases. Selected examples are shown in Scheme 40.



Scheme 40. MW-promoted IL-catalyzed Knoevenagel reaction [111].

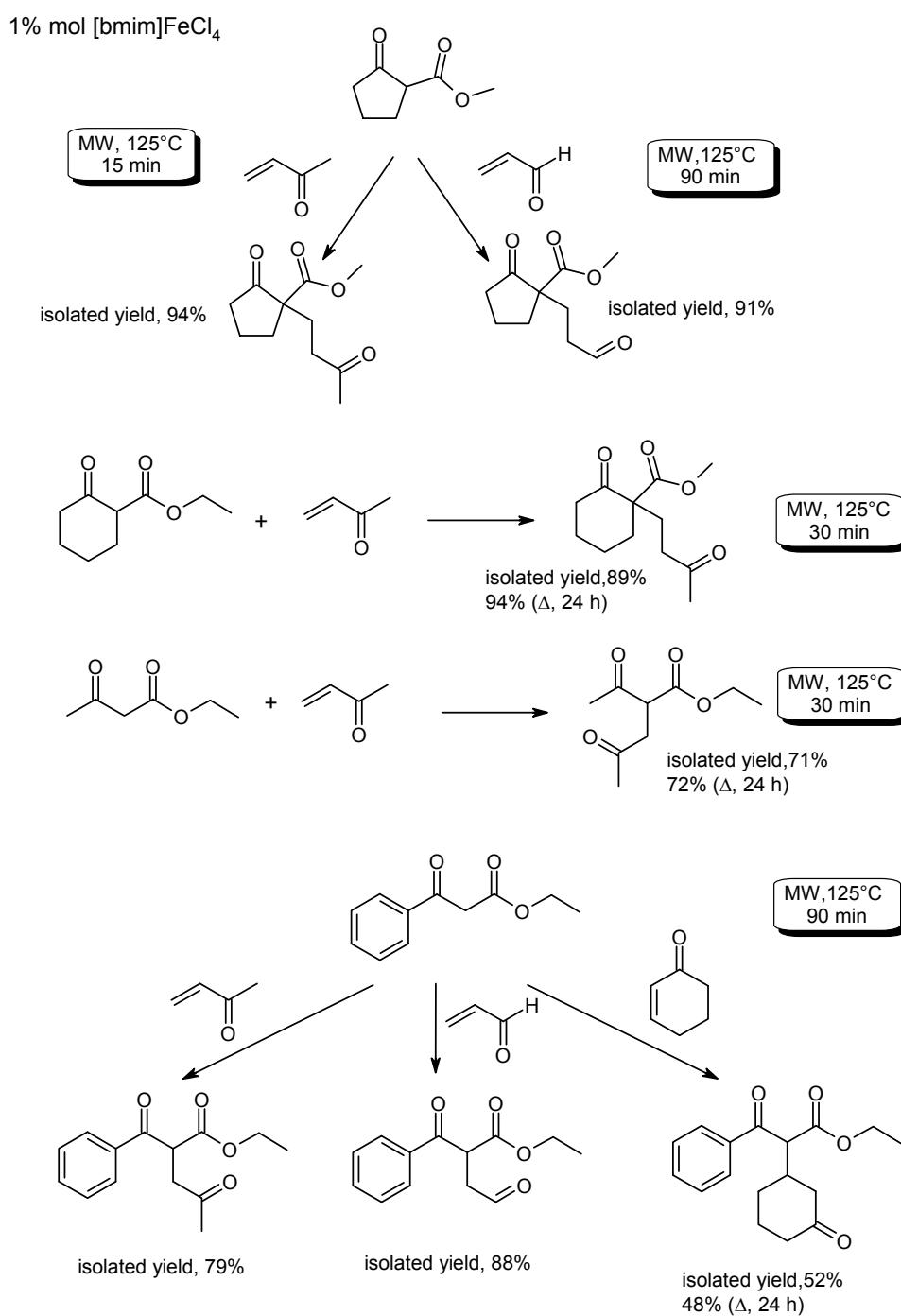
An application of MW-assisted Knoevenagel reaction to the synthesis of heterocyclic compounds was also reported [112]. Coumarin derivatives were prepared in high yields, in the determinant presence of imidazolium-based IL that rendered fast an otherwise sluggish reaction (Scheme 41).



Scheme 41. MW-assisted Knoevenagel synthesis of coumarins in IL [112].

Michael reaction—This well-known and versatile conjugated addition could not escape the attention of research aimed at applying modern eco-friendly procedures. Solvent-free metal-catalyzed Michael addition of β -ketoesters to enones was accomplished in tailor made IL, 1-butyl-3-methylimidazolium tetrachloroferrate, with MW irradiation [113]. The IL acted as iron catalyst and the system could be reused, after removal of products by distillation. The synthesis of [bmim]FeCl₄ was straightforward, simply mixing commercial solid [bmim]Cl with FeCl₃·6H₂O and removing the resulting upper aqueous phase (Scheme 42).

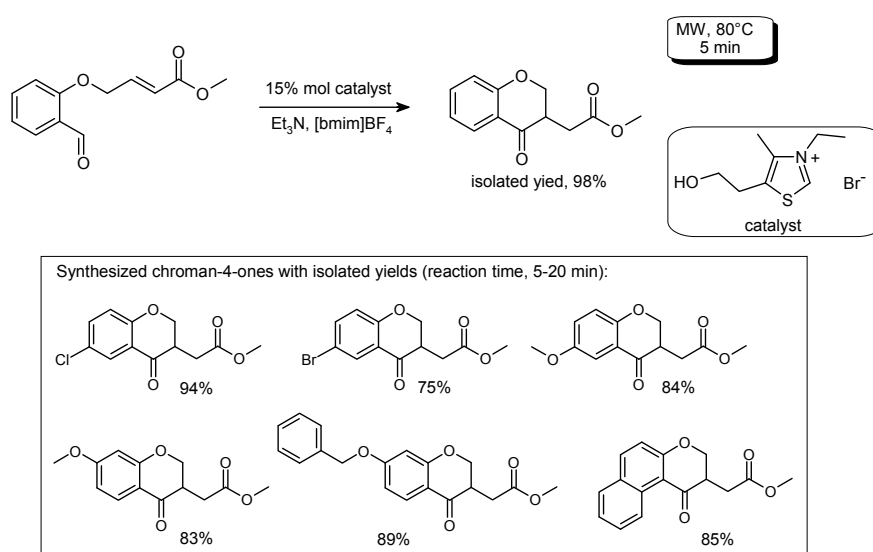
Although not pertinent here (because a bond different from C–C is also formed), *aza*-Michael reaction has to be mentioned, because the pharmaceutically important family of *N*-alkyl sulfonamides could be prepared in ILs under MW heating, with green and reusable catalysts MgO [38] and ZnO [39]. Moreover, the addition of imidazole to cyclohex-2-en-1-one, followed by lipase-catalyzed kinetic resolution, led to optically active ILs [114].



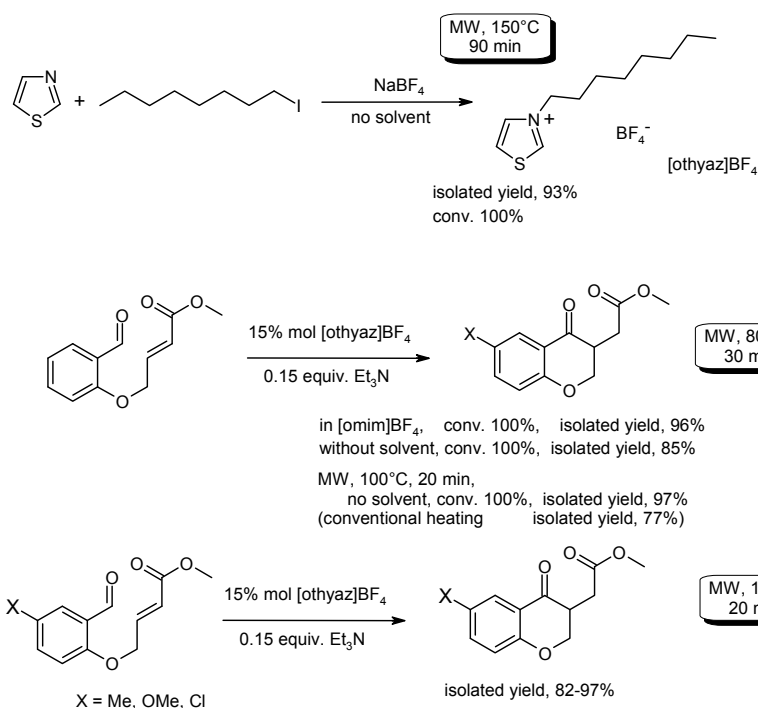
Scheme 42. MW-heated iron-catalyzed Michael addition in [bmim]FeCl₄ IL [113].

Stetter reaction—1,4-Bifunctional compounds, key intermediates in organic synthesis, can be obtained by this reaction, that was investigated in the intramolecular version using IL solvents and microwave irradiation, since ILs only were not much efficient [115]. Among the tested ILs, [bmim]BF₄ allowed best results; 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide was used as the catalyst, with best performances observed when it was 15 mol %. A number of aldehydes were reacted, producing a library of substituted chroman-4-ones (Scheme 43).

Intramolecular Stetter reaction was performed under MW irradiation, either solventless or in ILs, with thiazolium-based ionic liquids that, in turn, were prepared by a one-pot, solvent-free, MW-assisted reaction (Scheme 44) [116].



Scheme 43. MW assisted intramolecular Stetter reaction in $[\text{bmim}]\text{BF}_4$ [115].

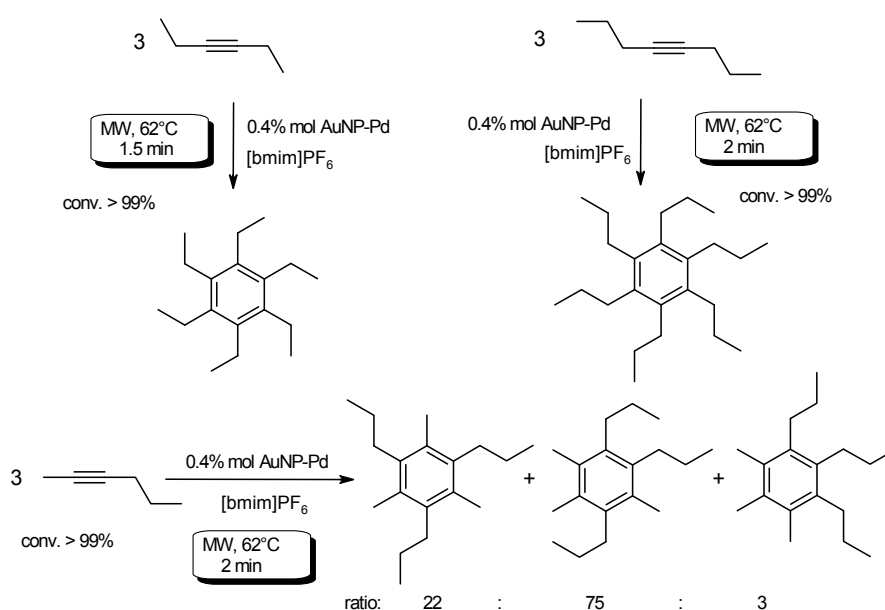


Scheme 44. MW-assisted thiazolium salts-catalyzed intramolecular Stetter reaction [116].

Blank experiments demonstrated that thiazolium salts are real catalysts, since no reaction occurs without them; the base was necessary as well, while the IL solvent was of help, but the results were satisfactory also under no-solvent conditions.

3.4. Cyclization Reactions to Carbocycles with C–C Bond Formation

Cyclotrimerization of alkynes to benzenes was brilliantly achieved using Pd catalyst supported on Au nanoparticles stabilized with thiolates [117]. With a loading of 4 mol % Au-bound Pd(II) catalyst, most of tested alkynes reacted completely in 1 h. The method became appealing when MW heating was used in IL solvent. Under such conditions, 1–5 min were sufficient to obtain quantitative alkyne conversion and good selectivity (Scheme 45).



Scheme 45. MW-promoted AuNP-Pd catalyzed cyclotrimerization of alkynes in IL [117].

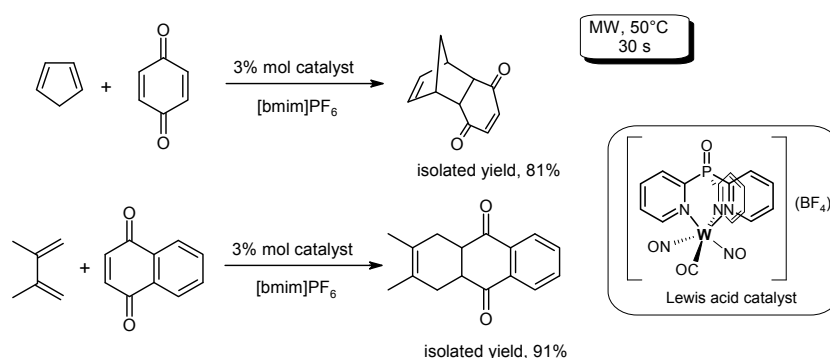
Diels-Alder reaction—ILs were used as solvents also in this reaction and with time new ILs were synthesized on purpose. For example, a number of ammonium salts were prepared from 2-dimethylaminoethanol and used as the medium of the uncatalyzed and catalyzed Diels-Alder reaction [118]. Cyclopentadiene was chosen as the probe diene and was reacted with a number of dienophiles, with and without Lewis acids (triflates of Y, Sc, Yb, Al, Cu, Zn, Mg, Li).

One of the first studies aimed at investigating ILs combined with microwave heating was applied to Diels-Alder reaction [119]. Actually, the authors were interested in heating non polar solvents above their boiling point in sealed vessels adding a small amount of an ionic liquid, thus rendering the medium more polar and thereby usable for microwave-assisted chemistry. They also checked eventual contamination by IL decomposition after MW irradiation and found almost none, even after prolonged times (30 min at 300 °C). As the probe reaction, they tested the [4+2] cycloaddition between 2,3-dimethylbutadiene and methyl acrylate, that takes 18–24 h in boiling toluene or xylene to occur. Adding a small amount of 1-isopropyl-2-methylimidazolium hexafluorophosphate, [ipmim]PF₆, to toluene and irradiating with MW, 80% Diels-Alder adduct formed in 5 min. Noticeably, MW irradiation of toluene without IL required 5 h to give 73% adduct.

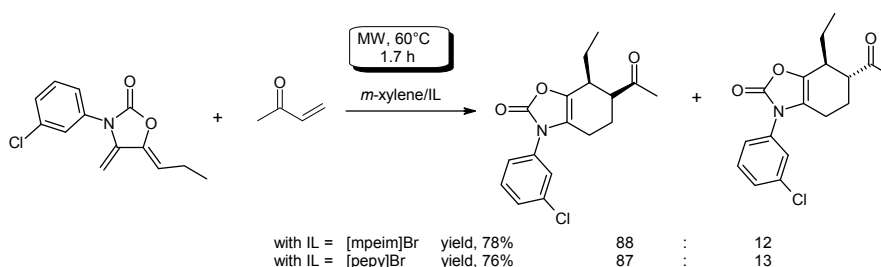
Successively, other studies combined MW heating and ILs in Diels-Alder reaction, often in conjunction with Lewis acid catalysts.

A tungsten Lewis acid catalyst was prepared and used in Diels-Alder cycloaddition of a variety of dienes and dienophiles [120]. Water or [bmim]PF₆ were the solvents and MW irradiation accelerated the reaction in both solvents, decreasing them from hours to seconds. However, the selectivity reaction and the catalyst recycling were more favorable in the IL than in H₂O. Selected examples are shown in Scheme 46. The procedure was tested with several combinations of dienes and dienophiles, all with good yields (71–96%) and reaction times from 25 to 60 s.

Unusual dienes derived from oxazolidinone underwent Diels-Alder cycloaddition under different conditions, among which MW heating and IL solvents [121] (Scheme 47). In this case there is not a clear advantage in using the combination MW/IL with respect to the other conditions, shorter reaction time notwithstanding. In fact, yields and selectivity were much better in dichloromethane at −78 °C.



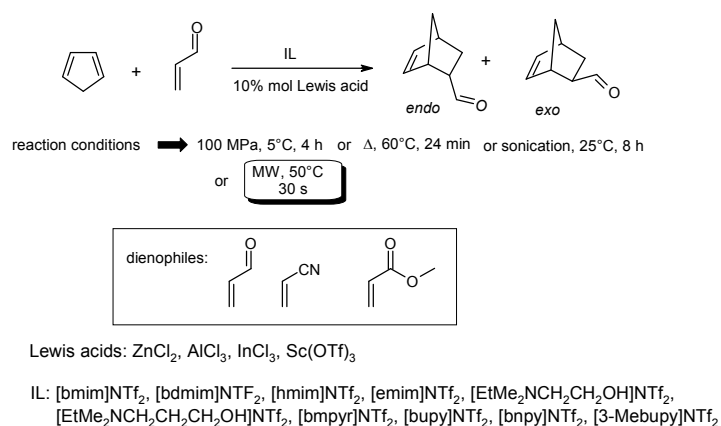
Scheme 46. Selected examples of W-catalyzed MW-assisted Diels-Alder reaction in [bmim]PF₆ IL [120].



Scheme 47. Example of Diels-Alder cycloaddition of 2-oxazolidinone dienes, MW-heated and ILs-catalyzed [121].

Other procedures used heterogeneous catalysts, such as montmorillonite (a mineral of hydrated aluminum silicate that is neutralized by exchangeable cations and interacts with organic molecules via electrostatic interaction, among alia), embedded in bmim-type ILs (changing the anion did not make any substantial difference) [122]; this protocol gave better yields than the reaction in ILs without montmorillonite and was accelerated by MW irradiation.

A screening of different Lewis acids, different ILs, and different activation modes (high pressure, ultrasound, and MW heating) was performed on Diels-Alder reaction of cyclopentadiene with some dienophiles [123] (Scheme 48).



Scheme 48. Summary of Lewis acids-catalyzed Diels-Alder reaction in ILs, under different activation modes [123].

From the huge amount of collected data, the authors concluded that: (i) the relatively high concentration of Lewis acid catalysts improved selectivity and the yields; (ii) high pressure

accelerated the catalysed reaction, with only minor improvements in the selectivity; (iii) microwave irradiation accelerated the reaction considerably; (iv) ultrasound irradiation led to increased yields and selectivities.

A noticeable synergistic effect of the combination of microwave irradiation and protic ILs was evidenced in the Diels-Alder reactions between methylbutadiene and heterocycles as dienophiles [124]. The study was accompanied by DFT calculations, aimed at elucidating the role of IL. It was suggested that the protic IL protonates the pyrrole nitro group, thus favoring an asynchronous transition state.

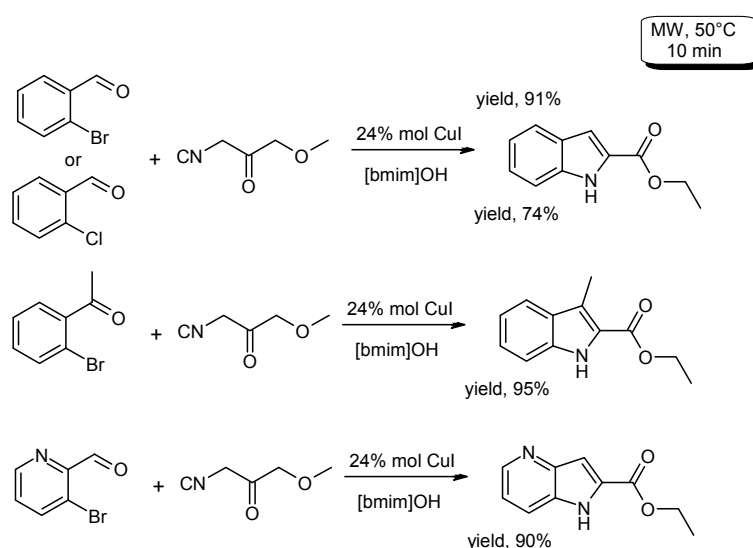
Further examples of MW-activated Diels-Alder reaction in ILs were provided by the study in imidazolium-base tetrachloroaluminates [125,126]. Lithium bis(trifluoromethylsulfonamide) was used as Lewis acid, but resulted not much determinant in the output of the reaction. Instead, once again, MW irradiation accelerated the reaction, bringing it to completion in few minutes from hours (6–12) of conventional heating.

3.5. Cyclization Reactions to Heterocycles with C–C Bond Formation

The importance of heteroaromatic compounds, especially in pharmaceutical chemistry, is well known. Thus, it is not surprising that the synthesis of key rings has been explored in terms of sustainability, as well illustrated in 2014 reviews discussing alternative reaction methods for the synthesis of quinoline [127] and benzothiazole [128] derivatives, including syntheses promoted by microwave or ultrasound, recyclable and reusable catalysts, non-volatile solvents as ILs, or solvent-free conditions.

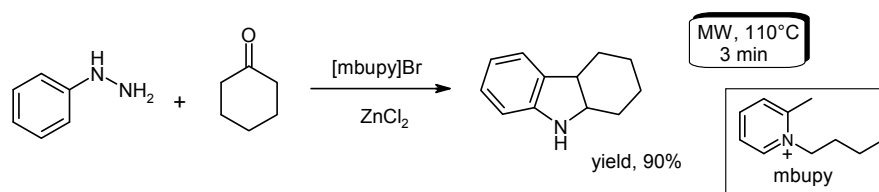
Other heteroaromatic compounds were prepared taking advantage of the MW-IL synergistic efficiency. The synthesis of benzofuran derivatives was promoted by [meim]Br and basic alumina [129]. Salicylaldehyde cyclocondensed with α -chloro ketones and esters. MW irradiation was compared to conventional heating and resulted more efficient as to reaction time, but almost the same yields were obtained with the two methods.

Twenty-five aromatic and heteroaromatic haloaldehydes and haloketones were cyclocondensed with ethyl isocyanoacetate to give 2-ethoxycarbonylindoles in a reaction catalyzed by CuI and [bmim]OH, under MW irradiation [130] (Scheme 49).



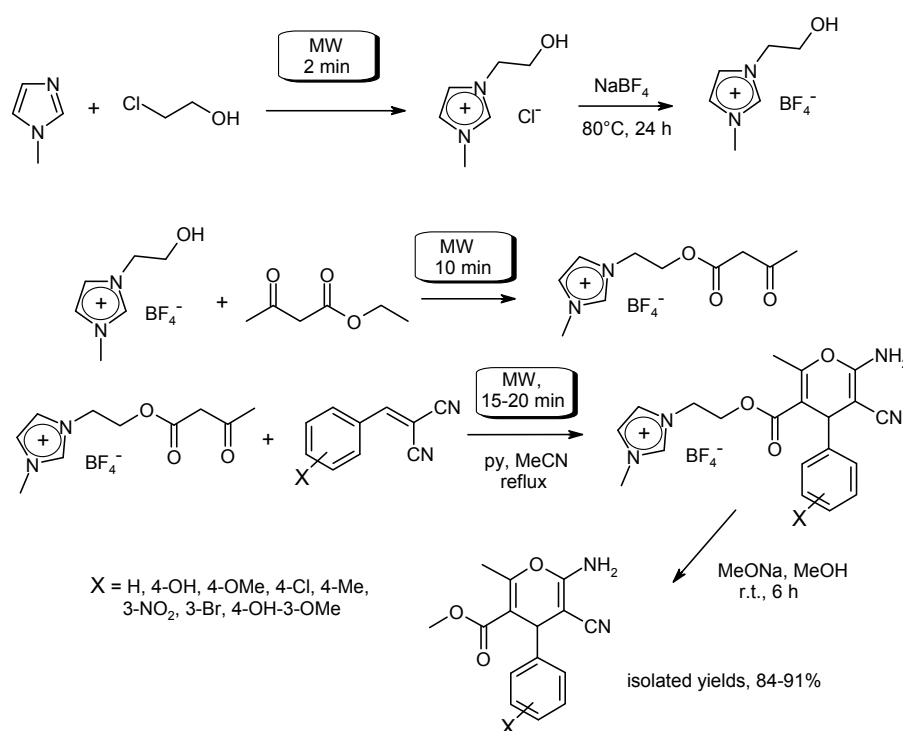
Scheme 49. Examples of MW-assisted cyclocondensation reaction to indole derivatives in IL [130].

Tetrahydrocarbazole was prepared in a Fischer-type cyclocondensation catalyzed by pyridinium-based ILs and MW irradiated [131]. Different temperatures and different pyridinium ILs—with and without Lewis acid ($ZnCl_2$)—were tested; optimized conditions are shown in Scheme 50.



Scheme 50. MW-assisted and ILs-catalyzed Fischer synthesis of tetrahydrocarbazole [131].

An original approach to substituted pyranes was the functionalization of ionic liquid, in order to obtain a soluble support for one reactant and the successive cyclization, followed by detachment of the formed pyrane [132] (Scheme 51).



Scheme 51. MW-irradiated synthesis of pyranes using functional ILs as soluble support [132].

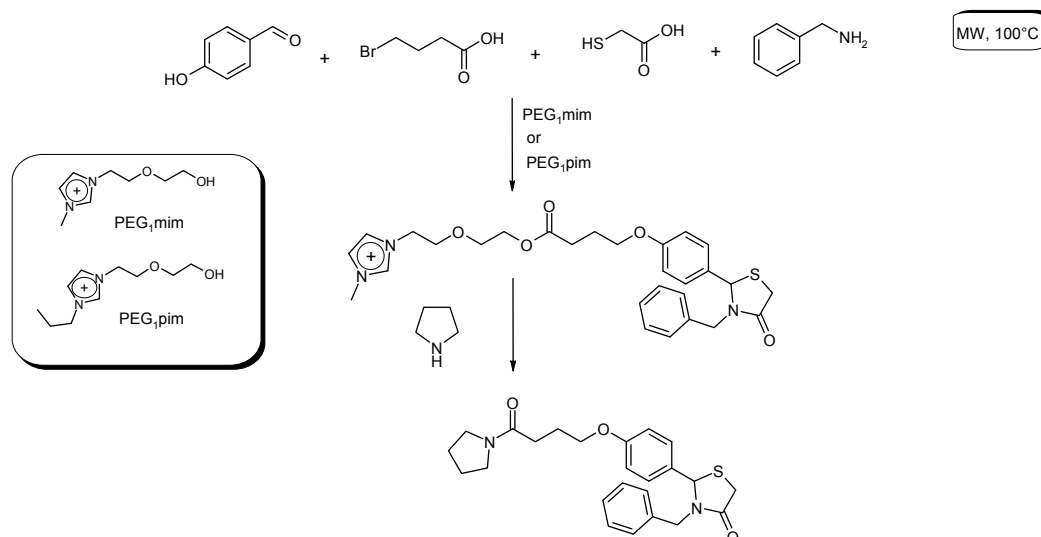
3.6. Multi-Component Reactions (MCRs) with C–C Bond Formation

Among the examples of carbon-carbon bond forming reactions, the protocols of multi-components reactions were revised, looking for eco-friendly conditions. For example, the Mannich reaction, i.e., the formation of β -amino carbonyl compounds from a non-enolizable aldehyde with an enolizable carbonyl compound and an amine (either primary or secondary), was thoroughly examined, also in view of the opportunity to be involved in tandem or cascade processes, with consequent high atom economy, as discussed in recent reviews [133–135].

The features that make MCRs appealing are the possibility of one-pot formation of two bonds and, even more interesting, is the easy access of libraries of compounds, simply changing substituents in any of the component. Ionic liquids and MW technique found application in the MCRs, at first separately [135–137], but quite soon the two were used together.

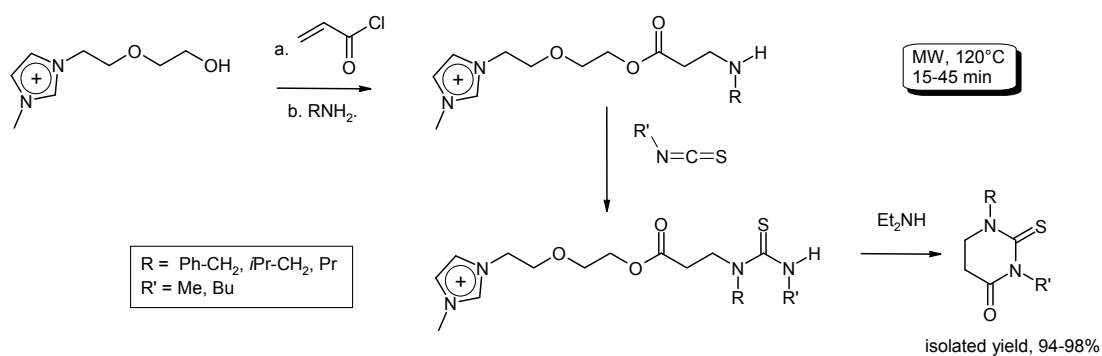
A strategy to use task-specific ionic liquids was developed and applied to the one-pot three-component synthesis of heterocyclic compounds, together with MW irradiation [138]. Imidazolium-based ILs were linked to poly(ethyleneglycol) (PEG), giving matrices to be used for the so called Ionic Liquid Phase Organic Synthesis (IoLiPOS). This method offers the advantage of

solid-state synthesis, since side products can be easily removed by simple washing IL-PEG system. Moreover, the combination of IL-PEG/microwave decreases the viscosity of the reaction medium with consequent rate enhancement. Thiazolidinone formation was achieved in 1–2 h in good yields by microwave irradiation with IL-phase bound arylidene imine derivatives (Scheme 52). Primary or secondary amines performed easy cleavage of the ILP-bound thiazolidinones.



Scheme 52. Example of thiazolidinone formation via Ionic Liquid Phase Organic Synthesis [138].

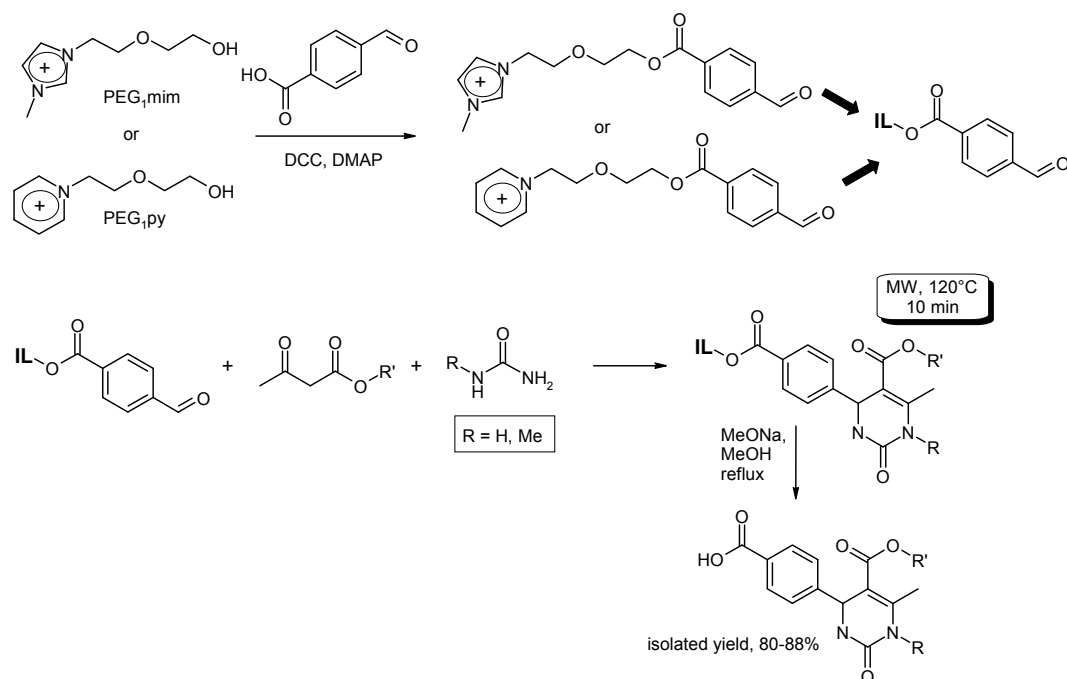
By the same procedure, 2-thioxotetrahydropyrimidin-4-(1*H*)-ones were prepared in good yields in 15 min [139] (Scheme 53). In the latter case, however, MWs were used only in the transesterification reaction to link the IL and the β -ketoester.



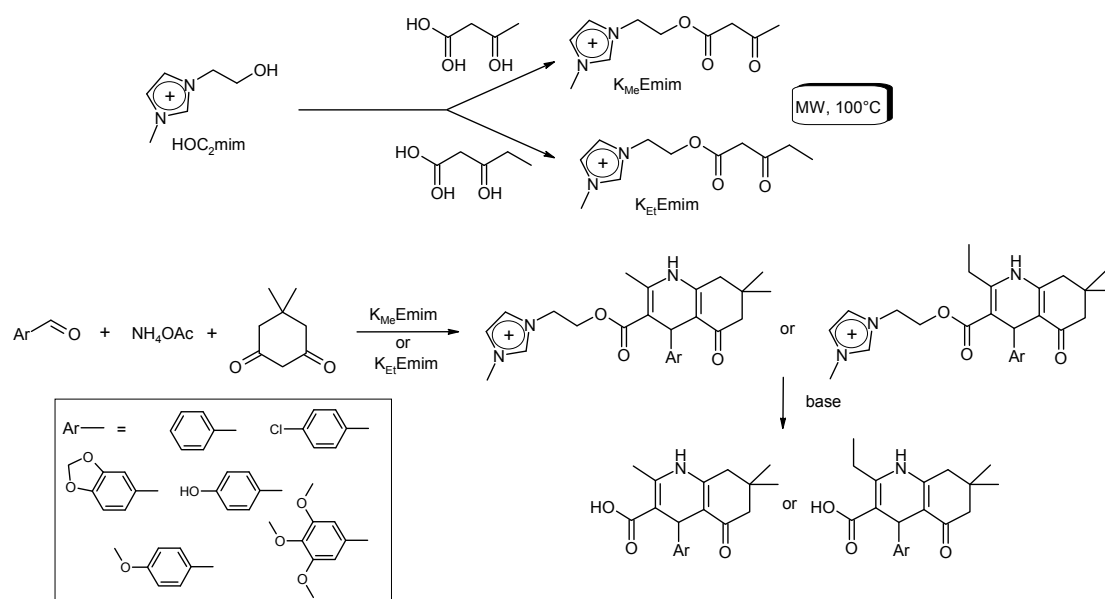
Scheme 53. Synthesis of 2-thioxotetrahydropyrimidin-4-(1*H*)-ones via Ionic Liquid Phase Organic Synthesis [139].

The same research group applied the same strategy for the synthesis of dihydropyrimidinones [140] (Scheme 54).

Polyhydroquinolines were prepared by a three-component reaction using ionic liquid-phase bound β -oxo esters that were synthesized by a solventless transesterification without catalyst, under microwave irradiation [141] (Scheme 55). MW heating was not used in the multi-component synthesis.

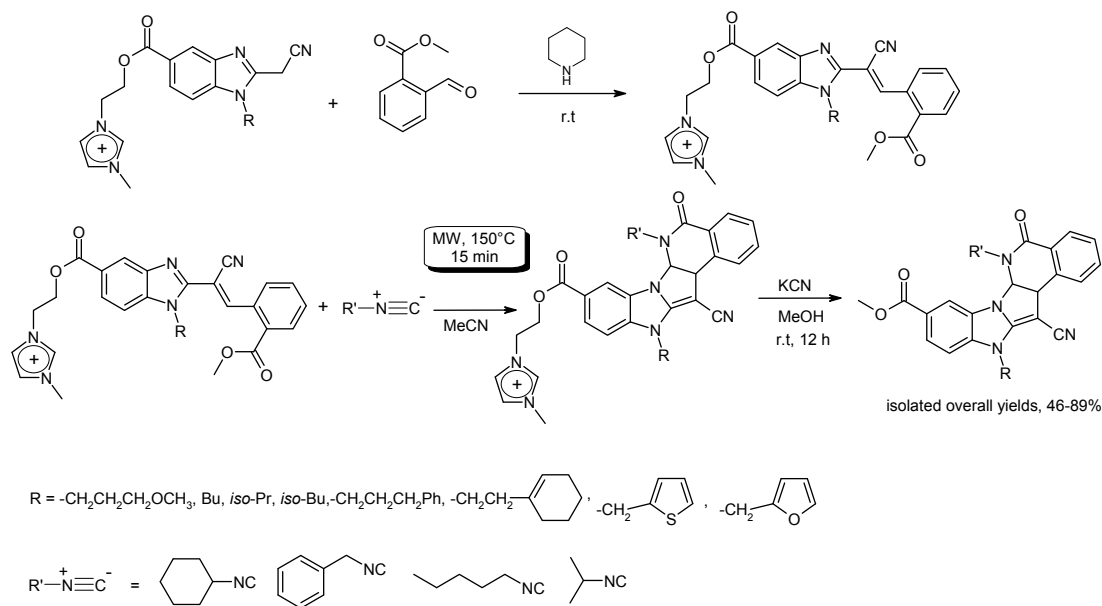


Scheme 54. Synthesis of dihydropyrimidinones via MW-assisted Ionic Liquid Phase Organic Synthesis [140].



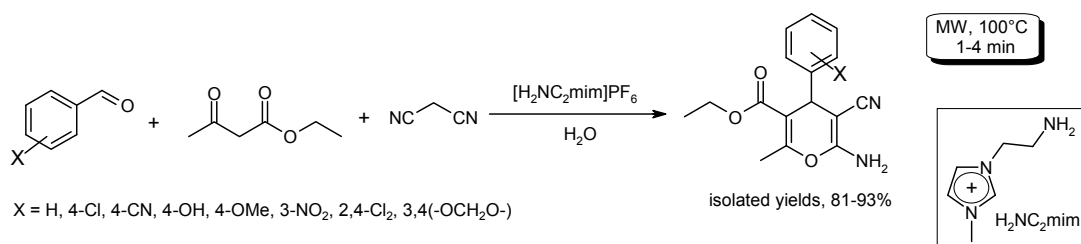
Scheme 55. Example of polyhydroquinoline formation via Ionic Liquid Phase Organic Synthesis [141].

A complex system of condensed heterocycles was developed by two steps, three-components cascade reactions performed with ionic liquid supported 2-cyanomethylbenzimidazoles, coupled with 2-formylbenzoate and isocyanides under microwave irradiation [142]. All the combinations of *N*-substituted benzimidazoles and different isocyanides gave the desired polycyclic isoquinolines, with good overall isolated yields, after detachment from IL (Scheme 56).



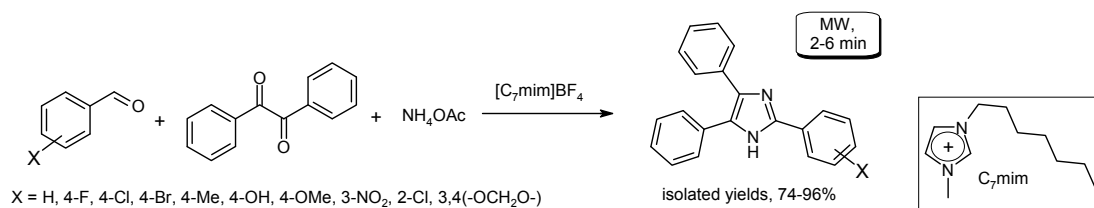
Scheme 56. Three-components cascade synthesis of benzimidazo[1',2':1,5]pyrrolo[2,3-c]isoquinolines with 2-cyanomethylbenzimidazoles supported on IL and MW irradiation [142].

A functional ionic liquid, 1-(2-aminoethyl)-3-methylimidazolium hexafluorophosphate, catalyzed the synthesis of pyrans with MW heating [143] (Scheme 57). Water was the co-solvent and the aqueous IL was reused, after filtering off the insoluble reaction product, in six more runs, retaining its efficiency.



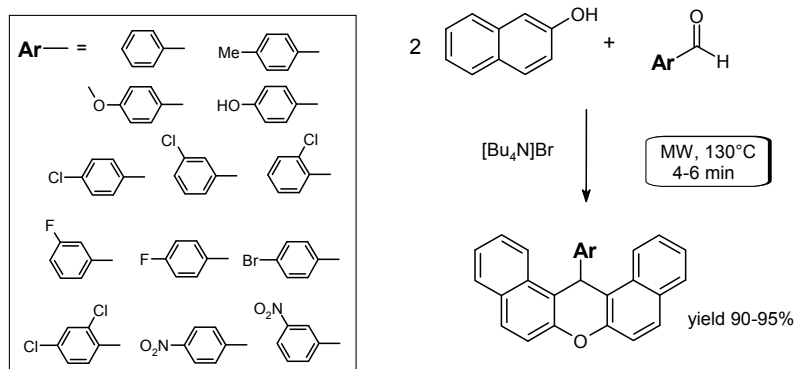
Scheme 57. MW-assisted, functional IL-catalyzed multi component synthesis of pyrans [143].

Imidazolium salts with different alkyl chains were used as catalysts in a MW-irradiated MCR leading to tri-substituted imidazoles [144]. The most efficient catalyst was 1-heptyl-3-methylimidazolium tetrafluoroborate that was also easy to recover and recycle. Different aryl aldehydes reacted within few minutes with excellent yields, as shown in Scheme 58. With conventional heating, in the same IL, the reaction took more than 2 h to complete; however, it is not clear whether IL is really a catalyst, because no blank experiment was reported.



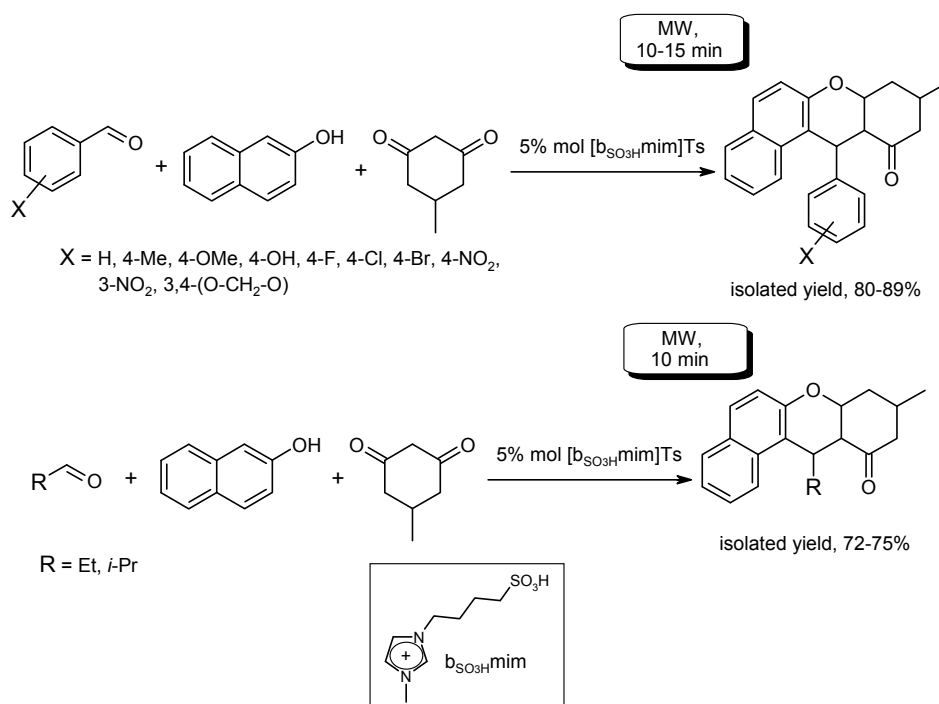
Scheme 58. Tri-substituted imidazoles via MW-heated, IL-catalyzed MCR [144].

Molten tetrabutylammonium bromide, Bu_4NBr , resulted an efficient and recyclable catalyst for the MCR of β -naphthol and aromatic aldehydes that produced dibenzoxanthenes [145] (Scheme 59). Compared to other catalysts (Brønsted or Lewis acids), Bu_4NBr was one of the most efficient, giving the same yield than those reported for *p*-toluenesulfonic or sulfamic acids (90–94%). On the other hand, other conditions being the same, reaction times dropped from 60–90 min with conventional heating to 4–6 min with MW irradiation.



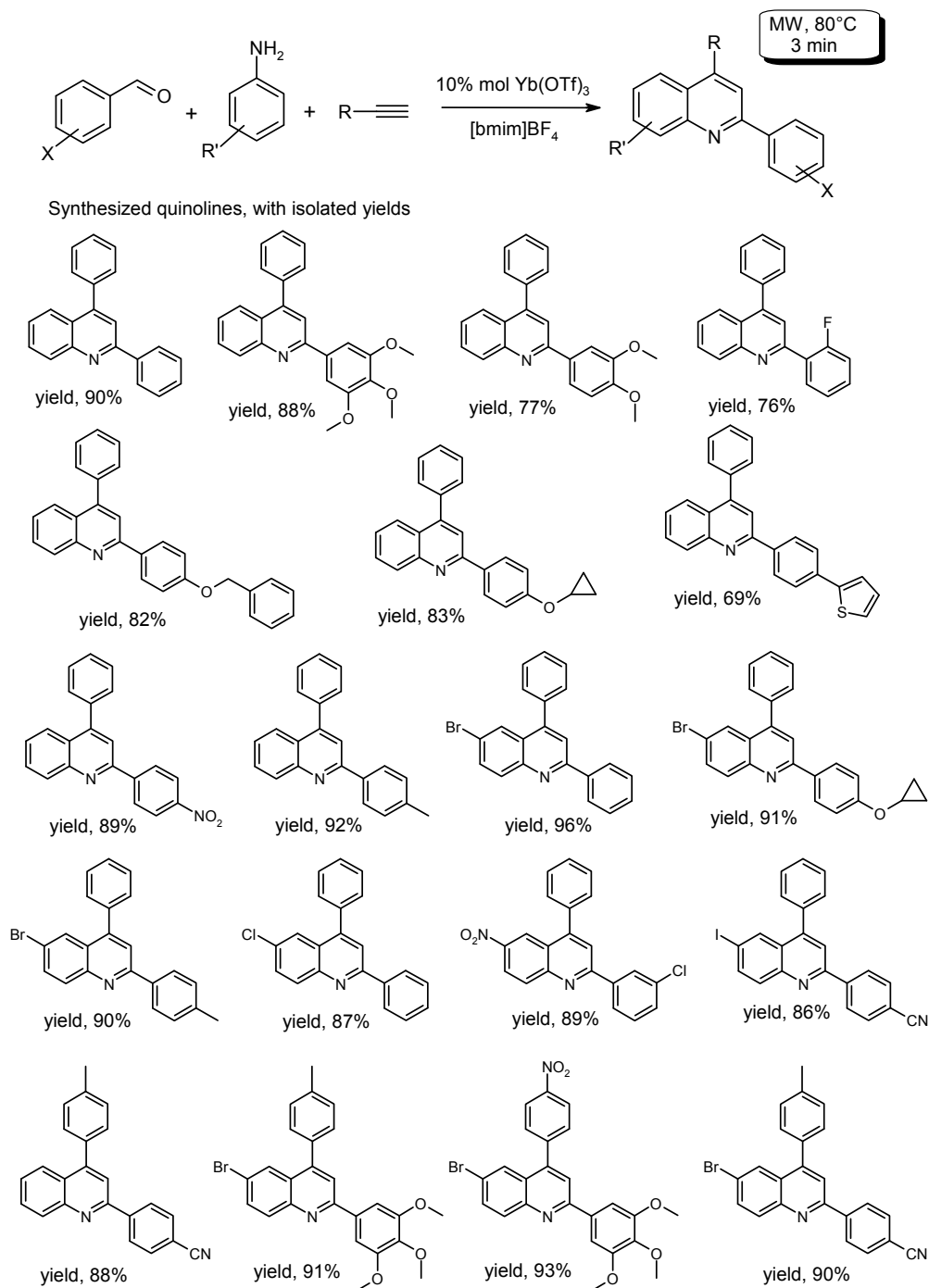
Scheme 59. MW-assisted and Bu_4NBr -catalyzed multicomponent synthesis of xanthenes [145].

Xanthenones were synthesized in a solvent-free one-pot MCR catalyzed by task-specific IL and assisted by MW [146] (Scheme 60). 2-Naphthol, aryl and alkyl aldehydes, and cyclic 1,3-dicarbonyl compounds condensed in the presence of a Brønsted acid IL. Optimization of the reaction conditions showed that 5 mol % functional IL was the best catalyst load and the reaction scope was investigated with different substrates. The reaction worked well with all the types of aldehydes, aromatic, aliphatic and even acid-sensitive ones, but 2-naphthol was the only possible phenolic reagent, while neither 1-naphthol nor phenol reacted at all.



Scheme 60. MW-irradiated, acidic IL-catalyzed one-pot synthesis of xanthenones [146].

Substituted quinolines could be prepared in IL solvent by a MCR with a Lewis acid catalyst, with MW heating [147]. Different ILs and different metal triflates were used to optimize the reaction conditions that were successively used for the reaction with different substrates. The results are summarized in Scheme 61.



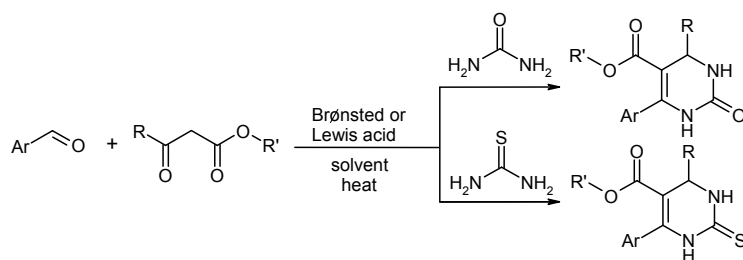
Scheme 61. Multi-Component Reaction (MCR) to quinolines in IL and $\text{Yb}(\text{OTf})_3$ under MW heating [147].

In other cases, the three-component reaction worked better in VOCs than in ILs. For example the best conditions to prepare 3-amino-substituted imidazo[1,2-*a*]pyridines from 2-aminopyridines,

aldehydes and isocyanides were montmorillonite as the catalyst and toluene as the solvent, under MW conditions. On the other hand, in bmim ILs, lower yields and decomposition were observed [148].

Biginelli reaction—As reported in the 2014 chapter on carbonyl compounds as electrophilic reagents in multicomponent reactions [149], the so called Biginelli reaction is one of the most investigated one, with more than 1000 papers and almost 100 reviews at the time [150]. Since 2014, more than 300 other publications appeared, 17 of which are reviews. The interest is mainly due to the importance of multicomponent reactions for drug synthesis.

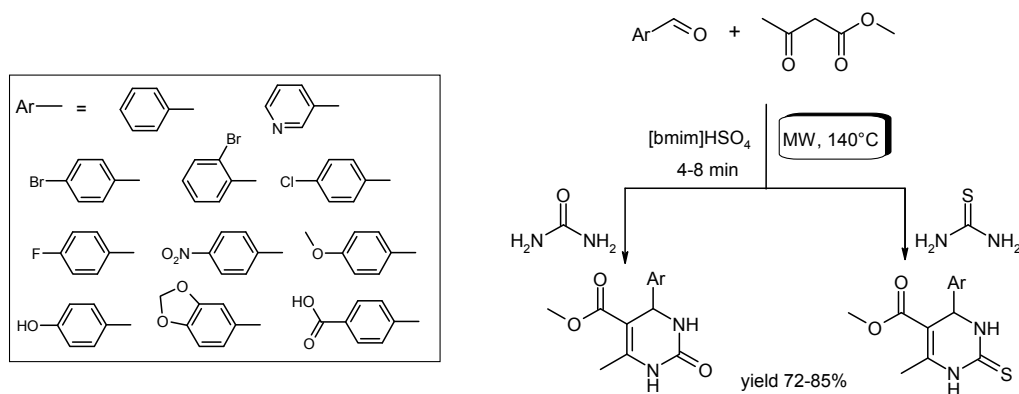
Classical conditions involve heating in an organic solvent, in the presence of acid catalyst, of an aromatic aldehyde with a 1,3-dicarbonyl compound and urea or thiourea, as in Scheme 62, although the role of the catalyst has been questioned [151].



Scheme 62. Classical three-component Biginelli reaction.

A sustainable breakthrough was the Biginelli reaction catalyzed by ionic liquids in solvent-free conditions [152], while MWs were introduced later. We want to discuss here examples of the reaction that took advantage of the combined use of MW heating and ILs. The interested reader can find the other details in [150] and references therein.

The ad hoc prepared [bmim]HSO₄ IL in 10 mol % catalyzed a solvent-free Biginelli condensation to dihydropyrimidinones and dihydropyrimidinethiones, with high yields obtained after few minutes, under MW irradiation at 140 °C (Scheme 63) [153]. The procedure resulted in an improvement of reaction output as well as of sustainability.

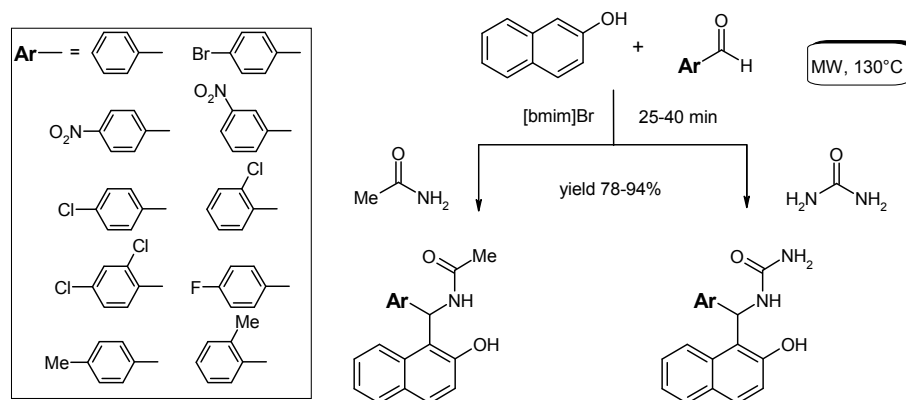


Scheme 63. MW-assisted, acidic IL-catalyzed Biginelli synthesis of dihydropyrimidinones and thiones [153].

The heterocyclic products are of potential medical interest, the procedure is sustainable, yields are from moderate to high (75–90% using MW, 67–80% using sonication), and MW irradiation was definitely superior in reducing reaction times (5–10 min, vs. 40–55 min with ultrasounds). However, it must also be considered that the reactions with sonication were performed at 50 °C, a temperature lower than that of MW irradiation. [bSO₃HPy]HSO₄[−] resulted the most efficient catalyst and could

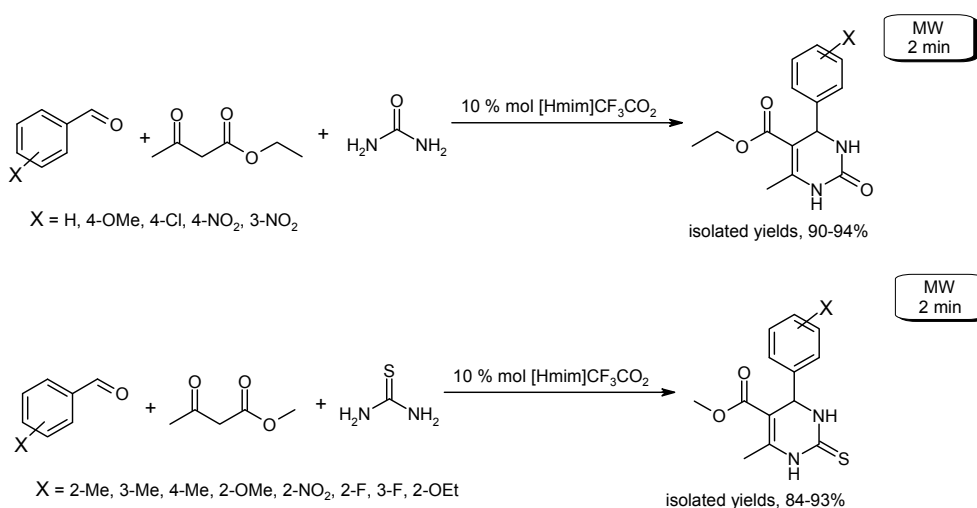
be recycled at least four times with no significant loss of activity. The reaction performed with conventional heating at 70 °C without solvents also gave high yields in 15 min [154].

Later, the multi-component condensation of β -naphthol with aromatic aldehydes and acetamide or urea was performed in [bmim]Br with MW irradiation [155] (Scheme 64). When a comparison is possible, yields are better than those previously described and reaction times are among the shortest reported. Moreover, the IL could be reused other three times, with negligible difference in results. Thus the procedure can be considered a sustainable alternative for the family of 1-amidoalkyl-2-naphthols, precursors of biologically active 1,3-oxazines.



Scheme 64. “Three-component synthesis” of 1-amidoalkyl-2-naphthols, in IL and MW irradiation [155].

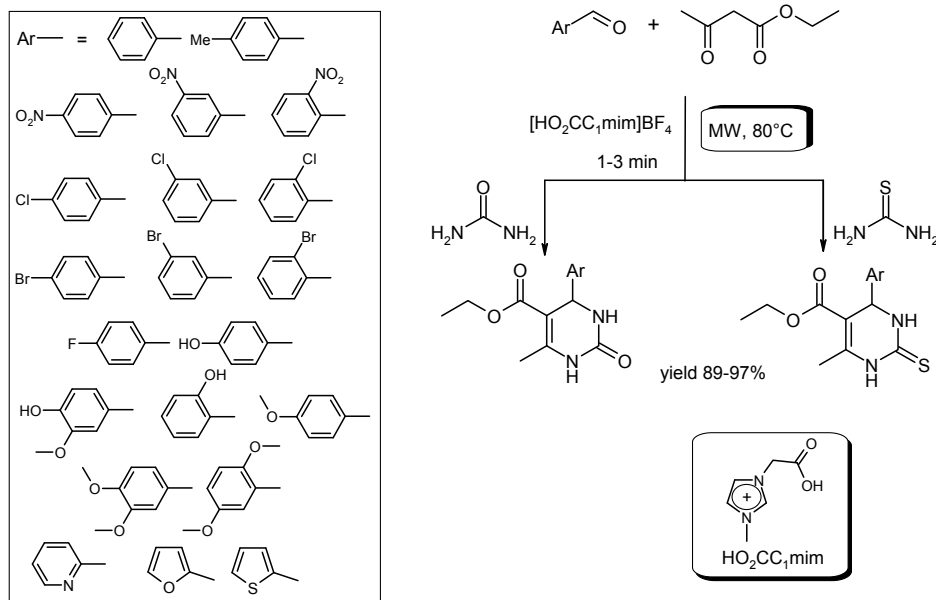
A model Biginelli reaction (benzenecarbaldehyde, ethyl 3-oxobutanoate and urea) was performed testing different ILs as catalyst [156]. [Hmim]CF₃CO₂ performed better than [Hmim]HSO₄ and much better than non Brønsted acid ILs ([bmim]PF₆ and [bmim]BF₄). Under MW irradiation the reaction was complete in 2 min (99% yield), an improvement with respect to conventional heating that required 2 h at 100 °C. Thirty dihydropyrimidin-2(1H)-ones or thiones were obtained in high yields (Scheme 65).



Scheme 65. Examples of MW-heated and IL-catalyzed formation of dihydropyrimidin-2(1H)-ones and thiones [156].

An example where the synergy between IL catalyst and MW energy source is evident, is the formation of 3,4-dihydropyrimidin-2-(1H)-ones (Scheme 66) [157]. Using the same IL (1-carboxymethyl-3-methylimidazolium tetrafluoroborate), yields are better and reaction times sensibly

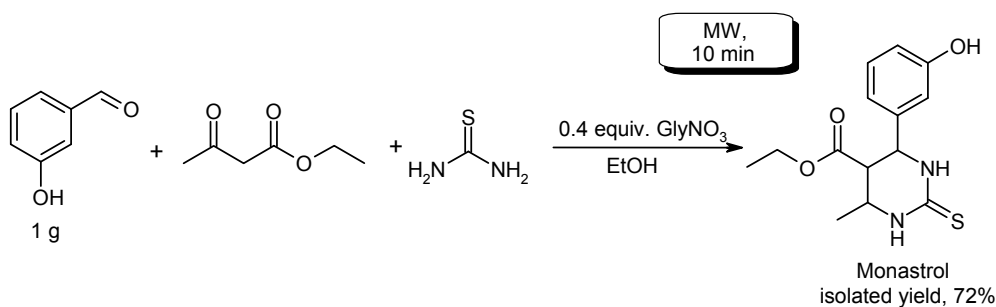
lower with MW irradiation than with conventional heating. The IL—probably acting as a Brønsted acid catalyst—could be easily recovered and reused for six consecutive runs, showing almost no loss of activity.



Scheme 66. Synthesis of 3,4-dihydropyrimidin-2-(1H)-ones via microwave promoted Biginelli reaction [157].

A modification of bmim side chain introduced the nitrite group. The prepared [ONObmim]Cl was used to catalyze the formation of dihydropyrimidin-2(H)-ones and thiones, with MW heating at 80 °C. Within 3–4 min, products formed in 87–91% isolated yield. [ONObmim]Cl could be recycled and reused with the same performance for at least five runs [158].

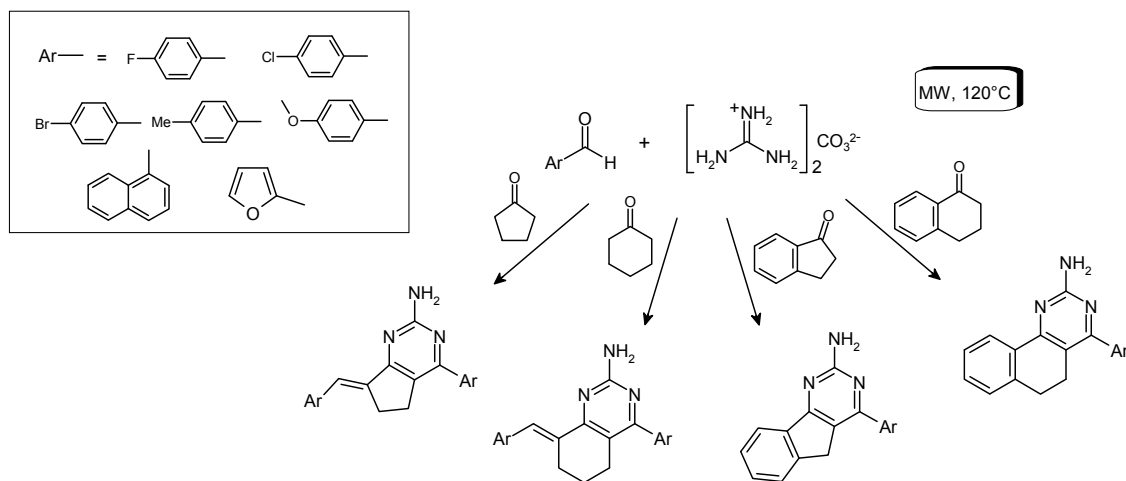
An amino acid ionic liquid, glycine nitrate, was used as catalyst for the multicomponent synthesis of 3,4-dihydropyrimidin-2(1H)-ones and thiones with MW heating [159]. An ample range of substituents on aryl aldehydes confirmed the generality of the reaction. MW irradiation ensured fast reactions (10 min with urea, 20 min with thiourea). Comparing their results to those of previously reported protocols, the authors state that their catalyst is biodegradable and recyclable and could be reused for more than ten cycles without significant loss of activity. Moreover, gram scale synthesis was performed, forming the biologically active Monastrol, a mitotic kinesin Eg5 inhibitor (Scheme 67).



Scheme 67. Gram scale preparation of Monastrol via Biginelli reaction catalyzed by glycine nitrate (GlyNO₃) IL and promoted by MW irradiation [159].

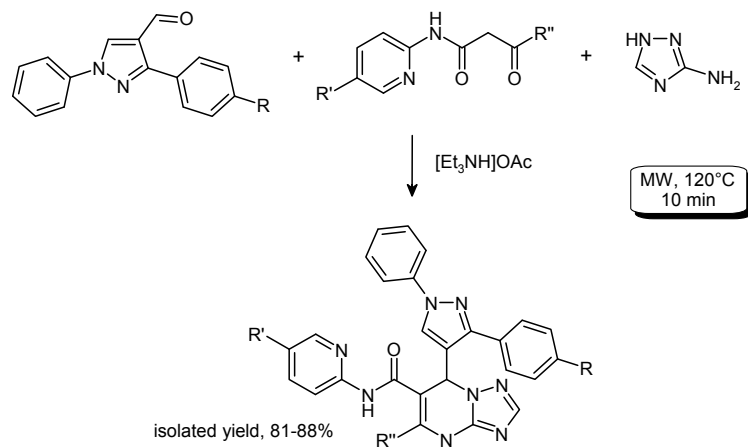
Another IL, $[\text{bSO}_3\text{Hpy}]_3\text{PW}_{12}\text{O}_{40}^{3-}$, was used more recently as catalyst, under MW irradiation (120°C), yielding in 5–10 min several polysubstituted dihydropyrimidinones and thiones [160]. However, the polyanion seems not to be really important, while the acidic functionality of the cation plays a major role in catalyzing the reaction.

The “three-component synthesis” of amino-substituted 1,3-diaza heteroaromatic derivatives was investigated using a variety of ILs, i.e., [bmim] with different counterions (Cl^- , Br^- , AcO^- , BF_4^- , HSO_4^-), $[\text{bSO}_3\text{Hmim}]$ with HSO_4^- or TfO^- anions, $[\text{bSO}_3\text{Hpy}]\text{HSO}_4$, and $[\text{bSO}_3\text{Hm}_2\text{cyu}](\text{HSO}_4)_2$ (Figure 1), that acted as catalysts with MW irradiation and as both catalysts and solvents when an ultrasound irradiation was used [161] (Scheme 68).



Scheme 68. “Three-component synthesis” of amino-substituted 1,3-diaza heteroaromatic compounds, with IL catalysts and MW irradiation [161].

The versatility of the MW assisted and IL-catalyzed Biginelli reaction prompted the extension of the method to the synthesis of other pharmaceutically relevant heterocyclic compounds. Thus, potentially non-classical malarial antifolates made of pyrazole-linked triazolo-pyrimidine hybrids were prepared by Biginelli-type reaction, using the inexpensive triethylammonium acetate as IL catalyst and MW heating [162]. A library of 30 compounds was prepared, simply changing substituents in the heteroaromatic aldehyde and in the β -dicarbonyl compound (Scheme 69). The IL could be reused at least five times, with some loss in yield only after the third run. MW heating lowered reaction times to 2–3 min from 2.5 to 3.5 h with conventional heating.



Scheme 69. MW assisted and IL-catalyzed Biginelli reaction pyrazole derivatives [162].

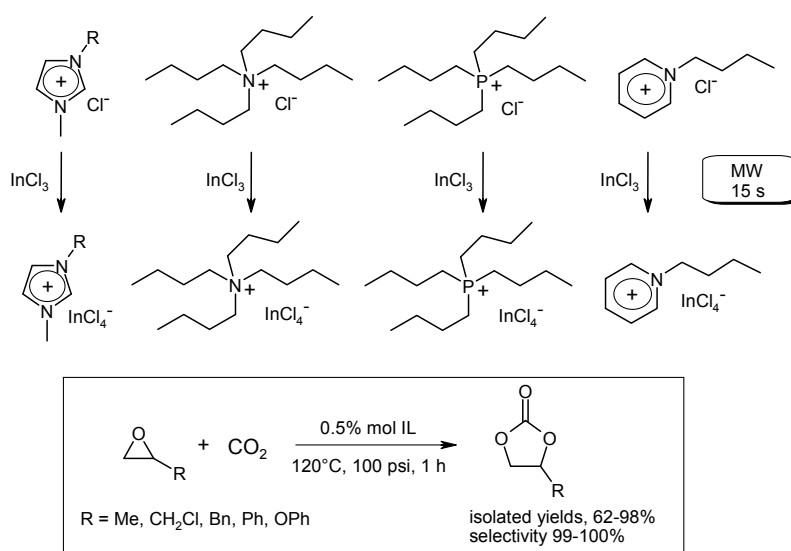
Solid-supported IL was prepared from 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium hydrogen sulfate, $[p_{55}\text{mim}]\text{HSO}_4$, and Fe_3O_4 nanoparticles. The magnetic nanoparticles were used in MW-assisted solvent-free Biginelli reaction [163]. According to the authors, this is an eco-friendly method that represents an improvement in terms of reduced reaction times, high turnover frequency, high yields of products, absence of solvent and recyclability.

4. Carbon Dioxide Transformation

The environmental impact of carbon dioxide excessive emission is well known and worldwide research is currently aimed at addressing and possibly solving the problem [164]. Although catalytic technologies were developed by chemical industry to transform carbon dioxide into valuable building blocks, not to speak of polycarbonates or polycarbamates, much more should be done and achieved by targeted research.

Carbon dioxide is thermodynamically stable and kinetically inert, so that activation by catalysts is necessary and the MW/IL combination might play a major role. In the field of carbon dioxide activation, one of the processes most investigated is the formation of organic carbonates, in view of their increasing importance as sustainable and environmentally-friendly alkylating agents [165].

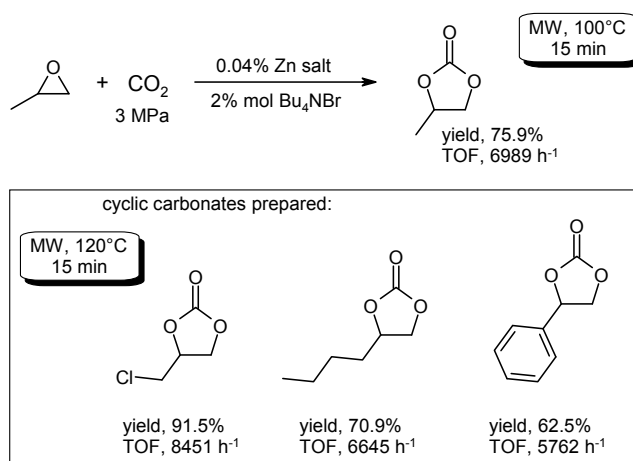
ILs with tetrahaloindate as the anion were used to catalyze the transformation of oxacyclopropanes into cyclic carbonates, but MW irradiation was used only to synthesize them [166] (Scheme 70).



Scheme 70. MW-assisted synthesis of tetrachloroindate ILs and their use in CO_2 reaction with oxacyclopropanes [166].

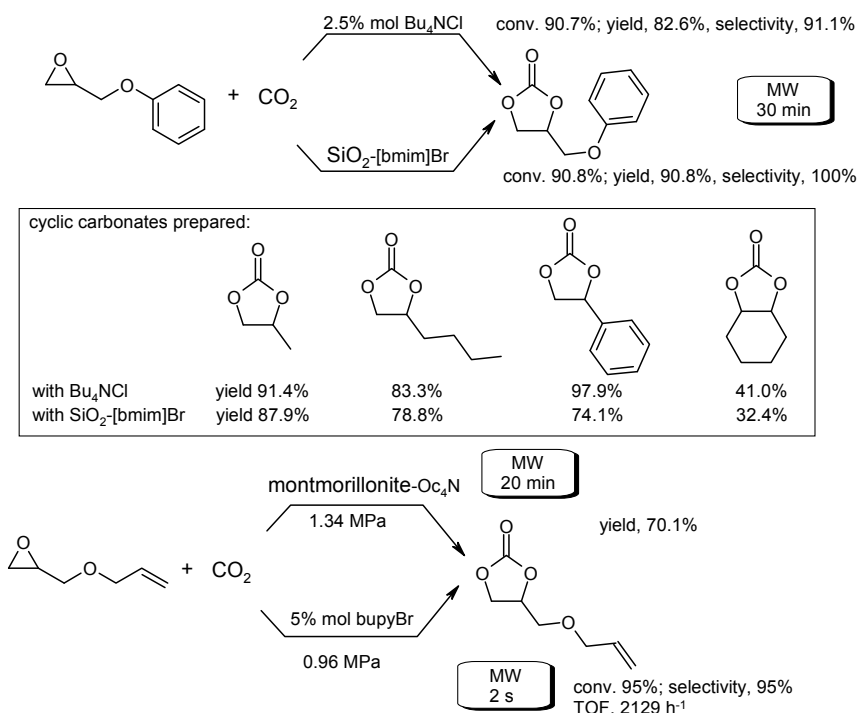
A mechanistic reaction scheme was proposed, where the superior performance of imidazolium tetrachloroindate was attributed to hydrogen bonding formation between Cl of the anion and the H in position 2 of imidazolium cation that increases the Lewis acidity of In(III).

Only years later MW irradiation was used together ILs to form cyclic carbonates from CO_2 and epoxides. The solvent-free coupling reaction of CO_2 with methyloxacyclopropane to produce cyclic carbonate under microwave irradiation was performed in the presence of catalytic amounts of Zn(II) salts and ILs [167], with different combinations of the two. An 11.2–278% TOF increment was observed (depending on the different combination of zinc salt and ionic liquid) with MW heating with respect to oil bath. With the five different ILs tested, the activity order observed is $\text{Bu}_4\text{NBr} > [\text{Hmim}]\text{Br} > [\text{bmim}]\text{Br} > [\text{emim}]\text{Br} > \text{Bu}_4\text{I}$. Under the optimized conditions, other oxacyclopropanes were reacted, with good results (Scheme 71).



Scheme 71. MW-heated formation of cyclic carbonates with Zn(II) salts and Bu_4NBr catalysts [167].

A large number of papers dealing with formation of cyclic carbonates is due to the group of Dae-Won Park. They used MW activation without ILs [168–170], or ionic liquids without microwave activation [171–176], as well as the combination of the two that will be discussed here. ILs with different cations (ammonium, imidazolium) and different anions (chloride, bromide, iodide) were tested as catalysts in MW-assisted reaction of 2-(phenoxymethyl)oxacyclopropane with CO_2 [177]. The study indicated an inverse dependence of reactivity on the ion dimension, with chloride and emim giving the best combination. [bmim]Cl and [bmim]Br were chosen to be grafted on SiO_2 , in order to investigate the heterogeneous catalysis. The reaction slowed (from 5 to 30 min with the same IL) but selectivity improved and the catalyst was easily recovered and reused. Finally, different epoxides were reacted, confirming the applicability of the procedure. Significant results are in Scheme 72.



Scheme 72. MW-assisted CO_2 reaction with oxacyclopropanes catalyzed by homogeneous and heterogeneous ILs [177–180].

The effects of variations in the morphology of silica support was investigated and published separately [178]. The same research group tested a different solid support, montmorillonite clay [179]. Tetraoctylammonium chloride was immobilized on K^+ -montmorillonite by ion exchange and was suggested to act both as an activator of the reaction mixture and as a catalyst. The substrate was 2-(allyloxymethyl)oxacyclopropane, that was converted in the corresponding cyclic carbonate without solvent in good yield. The catalyst was reused three times, with yields decreasing slowly from 70.1% in the first run to 66.7% in the fourth one. The same epoxide was subjected to carbon dioxide reaction in a solvent-free treatment with pyridinium-based ILs, under WM heating [180]. Considering conversion, selectivity (vs. polymerization) and TOF, the best catalyst was bupyBr, but what makes the system especially appealing is the reaction time, 20 s, instead of 20–30 min of previous protocols (Scheme 72).

Finally, metal-organic framework (MOF) ligands carboxyl spacers were used to synthesize cyclic carbonates from oxacyclopropane and CO_2 [181]. The carboxyl functional molecular ribbon catalyst (containing bipyridyl, benzenedicarboxylic acid, and Cu or Zn cations) was synthesized with the help of MW irradiation and the formation of the cyclic carbonate benefited of IL co-catalyst, but the MW/IL has not yet tested with this MOF.

Much less investigated was the CO_2 transformation into non-cyclic carbonates. Carbon dioxide was reacted with methanol to yield dimethyl carbonate with K_2CO_3/CH_3I catalyst, with MW heating, in a process that required lower temperature and shorter reaction time when performed in [bmim]Cl [182]. According to the authors, the IL not only accelerates the reaction because it facilitates MW heating, but also, on the basis of density functional theory calculations, it interacts with CO_2 , activating it.

5. Outlook

The picture that emerges from survey of the recent literature points at an increasing importance of microwaves as energy source, especially with modern instruments, with infrared temperature control and possibility to regulate pressure, very far from pioneering “domestic” oven of early papers. In addition, the use of ionic liquids evolved over several years, from solvents with peculiar properties to recyclable ones, to catalysts, homogeneous or supported on liquid phase heterogeneous or supported on solid phase. After testing a huge number of cation/anion combinations and after the idea of task-specific ILs, the trend now seems to be to use small amounts of robust ILs, in solvent-free reactions, under MW heating. This makes work-up particularly easy, with less waste and little need for other solvents for product extraction.

The large majority of papers were interested only in the reactions outcome, with wide screening of reaction conditions, experiments performed with systematic change of type and amount of catalyst and eventual additive, temperature, heating modes, accurate choice of IL and even synthesis of task-specific IL, investigation of substituent effects and of reproducibility, recycling of the IL/catalyst system. Unfortunately, scarce, if any, attention was paid to the role played by ILs in combination with MW irradiation. The only paper reporting an investigation aimed at investigating the combination IL/MW was interested in studying their effect on organic solvents, that could be heated in sealed vials, well above their boiling point [119], thus being usable in MW promoted reactions. Therefore, it is difficult to understand the real role of ILs in MW heated reactions. Generally, they may increase the MW heating efficiency rendering the reaction medium more polar. This resulted mainly in increased yields, lower temperatures and reduced reaction times. However, in some reactions they seemed to act as real catalysts.

It always dangerous to foresee the future, but our feeling is that, with melioration of MW instruments technology, the range of reactions performed preferably by MW irradiation with the aid of ILs will increase and, eventually, MW heating will substitute, at least at lab level, oil bath heating, in the same way that this substituted the free flame Bunsen burner.

Finally, it must be stressed that, although beyond the scope of the present review, there are other fields where a development may be found in the near future for the MW/IL combination, such as, for

example, the shape memory polymer composites (SMPC), combining the advantages of microwaves and polyIL [183] or microwave therapy [184,185].

Acknowledgments: University of Rome Tor Vergata “Ricerca Scientifica d’Ateneo 2015-SMART project” is acknowledged for financial support.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

Ac	acetyl, CH ₃ CO
acac	anion of 2,4-pentanedione(acetylacetone)
Cp	cyclopentadienyl anion
dba	dibenzylideneacetone
DABCO	1,4-diazabicyclo[2.2.2]octane
DMSO	dimethylsulfoxide
ECODS	extractive catalytic oxidative desulfurization
GO	graphene oxide
IL	ionic liquid
MCR	multi-component reaction
NP	nanoparticle
NTf ₂	bis(trifluorometanesulfonyl) amide
PEG	poly(ethyleneglycol)
ODS	oxidative desulfurization
py	pyridine
SILLP	supported ionic liquid-like phases
TBHP	<i>tert</i> -butylhydroperoxide
TfO ⁻	triflate CF ₃ SO ₃ ⁻ (IUPAC trifluoromethanesulfonate)
TOF	turnover frequency
tpm	hydrotris-(pyrazol-1-yl)methane
Ts	tosylate (<i>p</i> -toluenesulfonate)
VOC	volatile organic compound

References

1. Anastas, P.T.; Warner, J.C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, UK, 1998.
2. Varma, R.S. Journey on greener pathways: From the use of alternate energy inputs and benign reaction media to sustainable applications of nano-catalysts in synthesis and environmental remediation. *Green Chem.* **2014**, *16*, 2027–2041. [[CrossRef](#)]
3. Loupy, A. (Ed.) *Microwaves in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2002.
4. Wasserscheid, P.; Welton, T. (Eds.) *Ionic Liquids in Synthesis*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2008.
5. Kappe, C.O. Controlled microwave heating in modern organic synthesis. *Angew. Chem. Int. Ed.* **2004**, *43*, 6250–6284. [[CrossRef](#)] [[PubMed](#)]
6. Olivier-Bourbigou, H.; Magna, L.; Morvan, D. Ionic liquids and catalysis: Recent progress from knowledge to applications. *Appl. Catal. A Gen.* **2010**, *373*, 1–56. [[CrossRef](#)]
7. Strauss, C.R. A strategic, green approach to organic chemistry with microwave assistance and predictive yield optimization as core, enabling technologies. *Aust. J. Chem.* **2009**, *62*, 3–15. [[CrossRef](#)]
8. Pârvulescu, V.I.; Hardacre, C. Catalysis in ionic liquids. *Chem. Rev.* **2007**, *107*, 2615–2665. [[CrossRef](#)] [[PubMed](#)]
9. Liu, S.; Xiao, J. Toward green catalytic synthesis—Transition metal-catalyzed reactions in non-conventional media. *J. Mol. Catal. A Chem.* **2007**, *270*, 1–43. [[CrossRef](#)]
10. Keglevich, G.; Grun, A.; Balint, E.; Kiss, N.Z.; Kovacs, R.; Molnar, I.G.; Blastik, Z.; Toth, R.V.; Fehervari, A.; Csontos, I. Green chemical tools in organophosphorus chemistry—Organophosphorus tools in green chemistry. *Phosphorus Sulfur Silicon Relat. Elem.* **2011**, *186*, 613–620. [[CrossRef](#)]
11. Varma, R.S. “Greener” chemical syntheses using mechanochemical mixing or microwave and ultrasound irradiation. *Green Chem. Lett. Rev.* **2007**, *1*, 37–45. [[CrossRef](#)]

12. Kumar, V.; Nigam, K.D.P. Process intensification in green synthesis. *Green Proc. Synth.* **2012**, *1*, 79–107. [[CrossRef](#)]
13. Toma, Š.; Šebesta, R.; Mečiarova, M. Organocatalytic reactions under unusual conditions. *Curr. Org. Chem.* **2011**, *15*, 2257–2281. [[CrossRef](#)]
14. Martínez-Palou, R. Microwave-assisted synthesis using ionic liquids. *Mol. Divers.* **2010**, *14*, 3–25. [[CrossRef](#)] [[PubMed](#)]
15. Leadbeater, N.E.; Torenius, H.M.; Tye, H. Microwave-promoted organic synthesis using ionic liquids: A mini review. *Comb. Chem. High Throughput Screen.* **2004**, *7*, 511–528. [[CrossRef](#)]
16. Ogawa, C.; Kobayashi, S. Catalytic asymmetric synthesis in nonconventional media/conditions. In *Catalytic Asymmetric Synthesis*, 3rd ed.; Ojima, I., Ed.; John Wiley & Sons: Hoboken, NJ, USA, 2010; pp. 1–35.
17. Bortolini, O.; Campestrini, S.; Conte, V.; Fantin, G.; Fogagnolo, M.; Maietti, S. Sustainable epoxidation of electron-poor olefins with hydrogen peroxide in ionic liquids and recovery of the products with supercritical CO₂. *Eur. J. Org. Chem.* **2003**, *2003*, 4804–4809. [[CrossRef](#)]
18. Conte, V.; Fabbianesi, F.; Floris, B.; Galloni, P.; Sordi, D.; Arends, I.W.C.E.; Bonchio, M.; Rehder, D.; Bogdal, D. Vanadium-catalyzed, microwave-assisted oxidations with H₂O₂ in ionic liquids. *Pure Appl. Chem.* **2009**, *81*, 1265–1277. [[CrossRef](#)]
19. Berardi, S.; Conte, V.; Fiorani, G.; Floris, B.; Galloni, P. Improvement of ferrocene acylation. Conventional vs. microwave heating for scandium-catalyzed reaction in alkylmethylimidazolium-based ionic liquids. *J. Organomet. Chem.* **2008**, *693*, 3015–3020. [[CrossRef](#)]
20. Zhang, C.; Cheng, Z.; Fu, Z.; Liu, Y.; Yi, X.; Zheng, A.; Kirk, S.R.; Yin, D. Effective transformation of cellulose to 5-hydroxymethylfurfural catalyzed by fluorine anion-containing ionic liquid modified biochar sulfonic acids in water. *Cellulose* **2017**, *24*, 95–106. [[CrossRef](#)]
21. Goswami, S.R.; Dumont, M.-J.; Raghavan, V. Starch to value added biochemicals. *Starch* **2016**, *68*, 274–286. [[CrossRef](#)]
22. Xu, J.-K.; Chen, J.-H.; Sun, R.-C. Hydrothermal microwave valorization of eucalyptus using acidic ionic liquid as catalyst toward a green biorefinery scenario. *Bioresour. Technol.* **2015**, *193*, 119–127. [[CrossRef](#)] [[PubMed](#)]
23. Wang, J.; Zhou, M.; Yuan, Y.; Zhang, Q.; Fang, X.; Zang, S. Hydrolysis of cellulose catalyzed by quaternary ammonium perchlorates in 1-allyl-3-methylimidazolium chloride. *Bioresour. Technol.* **2015**, *197*, 42–47. [[CrossRef](#)] [[PubMed](#)]
24. Ren, H.; Zhan, Y.; Fang, X.; Yu, D. Enhanced catalytic activity and thermal stability of 2,4-dichlorophenol hydroxylase by using microwave irradiation and imidazolium ionic liquid for 2,4-dichlorophenol removal. *RSC Adv.* **2014**, *4*, 62631–62638. [[CrossRef](#)]
25. Qian, E.W.; Tominaga, H.; Chen, T.L.; Isoe, R. Synthesis of functional ionic liquids and their application for the direct saccharification of cellulose. *J. Chem. Eng. Jpn.* **2016**, *49*, 466–474. [[CrossRef](#)]
26. Truong, T.-K.-T.; Vo-Thanh, G. Synthesis of functionalized chiral ammonium, imidazolium, and pyridinium-based ionic liquids derived from (–)-ephedrine using solvent-free microwave activation. Applications for the asymmetric Michael addition. *Tetrahedron* **2010**, *66*, 5277–5282. [[CrossRef](#)]
27. Jadhav, A.H.; Lim, A.C.; Thorat, G.M.; Jadhav, H.S.; Seo, J.G. Green solvents ionic liquids: Structural directing pioneers for microwave assisted synthesis of controlled MgO nanostructures. *RSC Adv.* **2016**, *6*, 31675–31684. [[CrossRef](#)]
28. Vollmer, C.; Redel, E.; Abu-Shandi, K.; Thomann, R.; Manyar, H.; Hardacre, C.; Janiak, C. Microwave irradiation for the facile synthesis of transition-metal nanoparticles (NPs) in ionic liquids (ILs) from metal-carbonyl precursors and Ru-, Rh-, and Ir-NP/IL dispersions as biphasic liquid-liquid hydrogenation nanocatalysts for cyclohexene. *Chem. Eur. J.* **2010**, *16*, 3849–3858. [[CrossRef](#)] [[PubMed](#)]
29. Polshettiwar, V.; Nadagouda, M.N.; Varma, R.S. Microwave-assisted chemistry. A rapid and sustainable route to synthesis of organics and nanomaterials. *Aust. J. Chem.* **2009**, *62*, 16–26. [[CrossRef](#)]
30. Lang, X.; Shi, M.; Chu, Y.; Liu, W.; Chen, Z.; Ma, C. Microwave-assisted synthesis of Pt-WC/TiO₂ in ionic liquid and its application for methanol oxidation. *J. Solid State Electrochem.* **2013**, *17*, 2401–2408. [[CrossRef](#)]
31. Safavi, A.; Momeni, S.; Tohidi, M. Silver-Palladium nanoalloys modified carbon ionic liquid electrode with enhanced electrocatalytic activity towards formaldehyde oxidation. *Electroanalysis* **2012**, *24*, 1981–1988. [[CrossRef](#)]

32. Hu, H.; Yang, H.; Huang, P.; Cui, D.; Peng, Y.; Zhang, J.; Lu, F.; Liand, J.; Shi, D. Unique role of ionic liquid in microwave-assisted synthesis of monodisperse magnetite nanoparticles. *Chem. Commun.* **2010**, *46*, 3866–3868. [[CrossRef](#)] [[PubMed](#)]
33. Gaudino, E.C.; Cravotto, G.; Garella, D.; Tagliapietra, S.; Bonrath, W. Esterification of terpene alcohols catalyzed by acidic Brønsted ionic liquids. *Org. Prep. Proced. Int.* **2012**, *44*, 175–179. [[CrossRef](#)]
34. Du, H.; Zhang, X.; Kuang, Y.; Tan, Z.; Song, L.; Han, X. Catalytic activity and process variables optimization during microwave synthesis of methyl caprylate over various multi-SO₃H functionalized ionic liquids. *J. Taiwan Inst. Chem. Eng.* **2015**, *49*, 51–57. [[CrossRef](#)]
35. Xiong, X.; Yi, C.; Han, Q.; Shi, L.; Li, S. I₂/ionic liquid as a highly efficient catalyst for per-O-acetylation of sugar under microwave irradiation. *Chin. J. Catal.* **2015**, *36*, 237–243. [[CrossRef](#)]
36. Arfan, A.; Bazureau, J.P. Efficient combination of recyclable task specific ionic liquid and microwave dielectric heating for the synthesis of lipophilic esters. *Org. Process Res. Dev.* **2005**, *9*, 745–748. [[CrossRef](#)]
37. Altimari, J.M.; Delaney, J.P.; Servinis, L.; Squire, J.S.; Thornton, M.T.; Khosa, S.K.; Long, B.M.; Johnstone, M.D.; Fleming, C.L.; Pfeffer, F.M.; et al. Rapid formation of diphenylmethyl ethers and thioethers using microwave irradiation and protic ionic liquids. *Tetrahedron Lett.* **2012**, *53*, 2035–2039. [[CrossRef](#)]
38. Zare, A.; Hasaninejad, A.; Khalafi-Nezhad, A.; Moosavi Zare, A.R.; Parhami, A. Organic reactions in ionic liquids: MgO as efficient and reusable catalyst for the Michael addition of sulfonamides to α,β -unsaturated esters under microwave irradiation. *Arch. Org. Chem.* **2007**, *2007*, 105–115.
39. Zare, A.; Hasaninejad, A.; Moosavi Zare, A.R.; Parhami, A.; Sharghi, H.; Khalafi-Nezhad, A. Zinc oxide as a new, highly efficient, green, and reusable catalyst for microwave-assisted Michael addition of sulfonamides to α,β -unsaturated esters in ionic liquids. *Can. J. Chem.* **2007**, *85*, 438–444. [[CrossRef](#)]
40. Hernández, J.G.; Juaristi, E. Recent efforts directed to the development of more sustainable asymmetric organocatalysis. *Chem. Commun.* **2012**, *48*, 5396–5409. [[CrossRef](#)] [[PubMed](#)]
41. Kumar, R.; Saima; Sharda, A.; Andhare, N.H.; Richa; Sinha, A.K. Thiol–Ene “Click” Reaction Triggered by Neutral Ionic Liquid: The “Ambiphilic” Character of [hmim]Br in the Regioselective Nucleophilic Hydrothiolation. *Angew. Chem. Int. Ed.* **2015**, *54*, 828–832. [[CrossRef](#)] [[PubMed](#)]
42. Hajipour, A.R.; Rafiee, F.; Ruoho, A.E. Oxidation of benzylic alcohols to their corresponding carbonyl compounds using KIO₄ in ionic liquid by microwave irradiation. *Synth. Commun.* **2006**, *36*, 2563–2568. [[CrossRef](#)]
43. Restrepo, J.; Lozano, P.; Burguete, M.I.; Garcia-Verdugo, E.; Luis, S.V. Gold nanoparticles immobilized onto supported ionic liquid-like phases for microwave phenylethanol oxidation in water. *Catal. Today* **2015**, *255*, 97–101. [[CrossRef](#)]
44. Haider, P.; Kimmerle, B.; Krumeich, F.; Kleist, W.; Grunwaldt, J.-D.; Baiker, A. Gold-catalyzed aerobic oxidation of benzyl alcohol: Effect of gold particle size on activity and selectivity in different solvents. *Catal. Lett.* **2008**, *125*, 169–176. [[CrossRef](#)]
45. Díaz-Urrutia, C.; Hurisso, B.B.; Gauthier, P.M.P.; Sedai, B.; Singer, R.D.; Baker, R. Catalytic aerobic oxidation of lignin-derived bio-oils using oxovanadium and copper complex catalysts and ionic liquids. *J. Mol. Catal. A Chem.* **2016**, *423*, 414–422. [[CrossRef](#)]
46. Chatel, G.; Monnier, C.; Kardos, N.; Voiron, C.; Andrioletti, B.; Draye, M. Green, selective and swift oxidation of cyclic alcohols to corresponding ketones. *Appl. Catal. A Gen.* **2014**, *478*, 157–164. [[CrossRef](#)]
47. Mirjafari, A.; Mobarrez, N.; O’Brien, R.A.; Davis, J.H., Jr.; Noei, J. Microwave-promoted one-pot conversion of alcohols to oximes using 1-methylimidazolium nitrate, [Hmim][NO₃], as a green promoter and medium. *Comptes Rendus Chim.* **2011**, *14*, 1065–1070. [[CrossRef](#)]
48. Fu, R.; Yang, Y.; Feng, W.; Ge, Q.; Feng, Y.; Zeng, X.; Chai, W.; Yi, J.; Yuan, R. An efficient, eco-friendly and sustainable tandem oxidative amidation of alcohols with amines catalyzed by heteropolyanion-based ionic liquids via a bifunctional catalysis process. *Tetrahedron* **2016**, *72*, 8319–8326. [[CrossRef](#)]
49. Fu, R.; Yang, Y.; Jin, W.; Gu, H.; Zeng, X.; Chai, W.; Ma, Y.; Wang, Q.; Yi, J.; Yuan, R. Microwave-assisted heteropolyanion-based ionic liquid promoted sustainable protocol to N-heteroaryl amides via N-directing dual catalyzed oxidative amidation of aldehydes. *RSC Adv.* **2016**, *6*, 107699–107707. [[CrossRef](#)]
50. Abrantes, M.; Neves, P.; Antunes, M.M.; Gago, S.; Almeida Paz, F.A.; Rodrigues, A.E.; Pillinger, M.; Goncalves, I.S.; Silva, C.M.; Valente, A.A. Microwave-assisted molybdenum-catalyzed epoxidation of olefins. *J. Mol. Catal. A Chem.* **2010**, *320*, 19–26. [[CrossRef](#)]

51. Gomes, A.C.; Bruno, S.M.; Gago, S.; Lopes, R.P.; Machado, D.A.; Carminatti, A.P.; Valente, A.A.; Pillinger, M.; Goncalves, I.S. Epoxidation of cyclooctene using soluble or MCM-41-supported molybdenum tetracarbonyl-pyridylimine complexes as catalyst precursors. *J. Organomet. Chem.* **2011**, *696*, 3543–3550. [[CrossRef](#)]
52. Sarma, K.; Devi, N.; Sutradhar, D.; Sarma, B.; Chandra, A.K.; Barman, P. Synthesis of a novel six membered CNS palladacycle; TD-DFT study and catalytic activity towards microwave-assisted selective oxidation of terminal olefin to aldehyde. *J. Organomet. Chem.* **2016**, *822*, 20–28. [[CrossRef](#)]
53. He, H.; Pei, B.-J.; Lee, A.W.M. Metal free oxidation of alkyl substituted aromatics with aqueous *tert*-butyl hydroperoxide under microwave irradiation. *Green Chem.* **2009**, *11*, 1857–1861. [[CrossRef](#)]
54. Ribeiro, A.P.C.; Martins, L.M.D.R.S.; Kuznetsov, M.L.; Pombeiro, A.J.L. Tuning cyclohexane oxidation: Combination of microwave irradiation and ionic liquid with the C-scorpionate [FeCl₂(Tpm)] catalyst. *Organometallics* **2017**, *36*, 192–198. [[CrossRef](#)]
55. Coletti, A. From Catalysis to Electron Transfer Processes: Sustainability as Guideline. Ph.D. Thesis, Università di Roma Tor Vergata, Rome, Italy, 2012.
56. Floris, B.; Sabuzi, F.; Coletti, A.; Conte, V. Sustainable vanadium-catalyzed oxidation of organic substrates with H₂O₂. *Catal. Today* **2017**, *285*, 49–56. [[CrossRef](#)]
57. Conte, V.; Galloni, P.; Centazzo, M.; Coletti, A. Process for Desulphurisation of Fuels. Patent PCT WO2015 162162 A1, 29 October 2015.
58. Mesdour, S.; Lekbir, C.; Doumandji, L.; Hamada, B. Microwave-assisted extractive catalytic-oxidative desulfurization of diesel fuel via a VO(acac)₂/ionic liquid system with H₂O₂ and H₂SO₄ as oxidizing agents. *J. Sulfur Chem.* **2017**. [[CrossRef](#)]
59. Mehta, V.P.; Van der Eycken, E.V. Microwave-assisted C–C bond forming cross-coupling reactions: An overview. *Chem. Soc. Rev.* **2011**, *40*, 4925–4936. [[CrossRef](#)] [[PubMed](#)]
60. Kalck, P.; Urrutigoity, M. Recent improvements in the alkoxyacylation reaction catalyzed by transition metal complexes. *Inorg. Chim. Acta* **2015**, *431*, 110–121. [[CrossRef](#)]
61. Doháňošová, J.; Lásíková, A.; Toffano, M.; Gracza, T.; Vo-Thanh, G. Kinetic resolution of pent-4-ene-1,3-diol by Pd(II)-catalysed oxycarbonylation in ionic liquids. *New J. Chem.* **2012**, *36*, 1744–1750. [[CrossRef](#)]
62. Bai, L.; Wang, J.-X. Environmentally friendly Suzuki aryl-aryl cross-coupling reaction. *Curr. Org. Chem.* **2005**, *9*, 535–553. [[CrossRef](#)]
63. Dawood, K.M.; El-Deftar, M.M. Microwave-assisted C–C cross-coupling reactions of aryl and heteroaryl halides in water. *Arch. Org. Chem.* **2010**, *2010*, 319–330.
64. Shaaban, M.R.; Darweesh, A.F.; Dawood, K.M. Mizoroki-Heck cross-couplings of 2-acetyl-5-bromobenzofuran and aryl halides under microwave irradiation. *Arch. Org. Chem.* **2010**, *2010*, 208–225.
65. Silarska, E.; Trzeciak, A.M.; Pernak, J.; Skrzypczak, A. [IL]₂[PdCl₄] complexes (IL = imidazolium cation) as efficient catalysts for Suzuki-Miyaura cross-coupling of aryl bromides and aryl chlorides. *Appl. Catal. A Gen.* **2013**, *466*, 216–223. [[CrossRef](#)]
66. Massaro, M.; Riela, S.; Cavallaro, G.; Gruttadauria, M.; Milioto, S.; Noto, R.; Lazzara, G. Eco-friendly functionalization of natural halloysite clay nanotube with ionic liquids by microwave irradiation for Suzuki coupling reaction. *J. Organomet. Chem.* **2014**, *749*, 410–415. [[CrossRef](#)]
67. Massaro, M.; Riela, S.; Cavallaro, G.; Colletti, C.G.; Milioto, S.; Noto, R.; Parisi, F.; Lazzara, G. Palladium supported on halloysite-triazolium salts as catalyst for ligand free Suzuki cross-coupling in water under microwave irradiation. *J. Mol. Catal. A Chem.* **2015**, *408*, 12–19. [[CrossRef](#)]
68. Campisciano, V.; La Parola, V.; Liotta, L.F.; Giacalone, F.; Gruttadauria, M. Fullerene-Ionic liquid conjugates: A new class of hybrid materials with unprecedented properties. *Chem. Eur. J.* **2015**, *21*, 3327–3334. [[CrossRef](#)] [[PubMed](#)]
69. Giacalone, F.; Campisciano, V.; Calabrese, C.; La Parola, V.; Liotta, L.F.; Aprile, C.; Gruttadauria, M. Supported C₆₀-IL-PdNPs as extremely active nanocatalysts for C–C cross-coupling reactions. *J. Mater. Chem. A* **2016**, *4*, 17193–17206. [[CrossRef](#)]
70. Alonso, F.; Beletskaya, I.P.; Yus, M. Non-conventional methodologies for transition-metal catalyzed carbon-carbon coupling: A critical overview. Part 1: The Heck reaction. *Tetrahedron* **2005**, *61*, 11771–11835. [[CrossRef](#)]
71. Arvela, R.K.; Pasquini, S.; Larhed, M. Highly regioselective internal Heck arylation of hydroxyalkyl vinyl ethers by aryl halides in water. *J. Org. Chem.* **2007**, *72*, 6390–6396. [[CrossRef](#)] [[PubMed](#)]

72. Vallin, K.S.A.; Emilsson, P.; Larhed, M.; Hallberg, A. High-speed Heck reactions in ionic liquid with controlled microwave heating. *J. Org. Chem.* **2002**, *67*, 6243–6246. [[CrossRef](#)] [[PubMed](#)]
73. Datta, G.K.; Vallin, K.S.A.; Larhed, M. A rapid microwave protocol for Heck vinylation of aryl chlorides under air. *Mol. Divers.* **2003**, *7*, 107–114. [[CrossRef](#)] [[PubMed](#)]
74. Xie, X.; Lu, J.; Chen, B.; Han, J.; She, X.; Pan, X. Pd/C-catalyzed Heck reaction in ionic liquid accelerated by microwave heating. *Tetrahedron Lett.* **2004**, *45*, 809–811. [[CrossRef](#)]
75. Hajipour, A.R.; Rafiee, F. Accelerated Heck reaction using ortho-palladated complex in a nonaqueous ionic liquid with controlled microwave heating. *Appl. Organomet. Chem.* **2011**, *25*, 542–551. [[CrossRef](#)]
76. Zhou, Z.; Xie, Y.; Du, Z.; Hu, Q.; Xue, J.; Shi, J. Highly regioselective Heck-Mizoroki reaction catalyzed by Pd/phosphine ligand in DMSO/[bmim][BF₄] under microwave irradiation. *Arch. Org. Chem.* **2012**, *2012*, 164–172.
77. Dighe, M.G.; Degani, M.S. Microwave-assisted ligand-free, base-free Heck reactions in a task-specific imidazolium ionic liquid. *Arch. Org. Chem.* **2011**, *2011*, 189–197.
78. Yilmaz, U.; Kucukbay, H.; Deniz, S.; Sireci, N. Synthesis, characterization and microwave-promoted catalytic activity of novel *N*-phenylbenzimidazolium salts in Heck-Mizoroki and Suzuki-Miyaura cross-coupling reactions under mild conditions. *Molecules* **2013**, *18*, 2501–2517. [[CrossRef](#)] [[PubMed](#)]
79. Kumar, R.; Shard, A.; Bharti, R.; Thopate, Y.; Kumar Sinha, A. Palladium-catalyzed dehydrative Heck olefination of secondary aryl alcohols in ionic liquids: Towards a waste-free strategy for tandem synthesis of stilbenoids. *Angew. Chem. Int. Ed.* **2012**, *51*, 2636–2639. [[CrossRef](#)] [[PubMed](#)]
80. Huang, H.; Liu, H.; Jiang, H.; Chen, K. Rapid and efficient Pd-catalyzed Sonogashira coupling of aryl chlorides. *J. Org. Chem.* **2008**, *73*, 6037–6040. [[CrossRef](#)] [[PubMed](#)]
81. Chen, Y.; Markina, N.A.; Larock, R.C. An efficient, microwave-assisted, one-pot synthesis of indoles under Sonogashira conditions. *Tetrahedron* **2009**, *65*, 8908–8915. [[CrossRef](#)] [[PubMed](#)]
82. Sajith, A.M.; Muralidharan, A. Exploration of copper and amine-free Sonogashira cross coupling reactions of 2-halo-3-alkyl imidazo[4,5-*b*]pyridines using tetrabutyl ammonium acetate as an activator under microwave enhanced conditions. *Tetrahedron Lett.* **2012**, *53*, 5206–5210. [[CrossRef](#)]
83. De la Fuente, V.; Fleury-Bregeot, N.; Castillon, S.; Claver, C. Recycling of allylic alkylation Pd catalysts containing phosphine-imidazoline ligands in ionic liquids. *Green Chem.* **2012**, *14*, 2715–2718. [[CrossRef](#)]
84. Li, L.-H.; Pan, Z.-L.; Duan, X.-H.; Liang, Y.-M. An environmentally benign procedure for the synthesis of aryl and arylvinyl nitriles assisted by microwave in ionic liquid. *Synlett* **2006**, *13*, 2094–2098. [[CrossRef](#)]
85. Zhao, H.; Mao, G.; Han, H.; Song, J.; Liu, Y.; Chu, W.; Sun, Z. An effective and environment-friendly system for Cu NPs@RGO-catalyzed C–C homocoupling of aryl halides or arylboronic acids in ionic liquids under microwave irradiation. *RSC Adv.* **2016**, *6*, 41108–41113. [[CrossRef](#)]
86. Kobayashi, S.; Sugiura, M.; Kitagawa, H. Rare-Earth metal triflates in organic synthesis. *Chem. Rev.* **2002**, *102*, 2227–2302. [[CrossRef](#)] [[PubMed](#)]
87. Tran, P.H.; Duus, F.; Le, T.N. Friedel-Crafts acylation using bismuth triflate in [BMI][PF₆]. *Tetrahedron Lett.* **2012**, *53*, 222–224. [[CrossRef](#)]
88. Tran, P.H.; BichLe Do, N.; NgocLe, T. Improvement of the Friedel-Crafts benzoylation by using bismuth trifluoromethanesulfonate in 1-butyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid under microwave irradiation. *Tetrahedron Lett.* **2014**, *55*, 205–208. [[CrossRef](#)]
89. Tran, P.H.; Hansen, P.E.; Hoang, H.M.; Nguyen Chau, D.-K.N.; Le, T.N. Indium triflate in 1-isobutyl-3-methylimidazolium dihydrogen phosphate: An efficient and green catalytic system for Friedel-Crafts acylation. *Tetrahedron Lett.* **2015**, *56*, 2187–2192. [[CrossRef](#)]
90. Tran, P.H.; Huynh, V.H.; Hansen, P.E.; Nguyen Chau, D.-K.N.; Le, T.N. An efficient and green synthesis of 1-indanone and 1-tetralone via intramolecular Friedel-Craft acylation reaction. *Asian J. Org. Chem.* **2015**, *4*, 482–486. [[CrossRef](#)]
91. Tran, P.H.; Tran, H.N.; Hansen, P.E.; Do, M.H.N.; Le, T.N. A simple, effective, green method for the regioselective 3-acylation of unprotected indoles. *Molecules* **2015**, *20*, 19605–19619. [[CrossRef](#)] [[PubMed](#)]
92. Sadaphal, S.A.; Shelke, K.F.; Sonar, S.S.; Shingare, M.S. Ionic liquid promoted synthesis of bis(indolyl)methanes. *Cent. Eur. J. Chem.* **2008**, *6*, 622–626. [[CrossRef](#)]
93. Zare, A.; Parhami, A.; Moosavi Zare, A.R.; Hasaninejad, A.; Khalafi-Nezhad, A.; Beyzavi, M.H. A catalyst-free protocol for the green and efficient condensation of indoles with aldehydes in ionic liquids. *Can. J. Chem.* **2009**, *87*, 416–421. [[CrossRef](#)]

94. Das, P.J.; Das, J. Synthesis of aryl/alkyl(2,2'-bis-3-methylindolyl)methanes and aryl(3,3'-bisindolyl)methanes promoted by secondary amine based ionic liquids and microwave irradiation. *Tetrahedron Lett.* **2012**, *53*, 4718–4720. [[CrossRef](#)]
95. Chaudhari, A.S.; Parab, Y.S.; Patil, V.; Sekar, N.; Shukla, S.R. Intrinsic catalytic activity of Bronsted acid ionic liquids for the synthesis of triphenylmethane and phthalein under microwave irradiation. *RSC Adv.* **2012**, *2*, 12112–12117. [[CrossRef](#)]
96. Mack, R.; Askins, G.; Lowry, J.; Hurley, N.; Reeves, P.C. Indium(III) triflate—A catalyst for greener aromatic alkylation reactions. *Can. J. Chem.* **2013**, *91*, 1262–1265. [[CrossRef](#)]
97. Mestres, R. A green look at the aldol reaction. *Green Chem.* **2004**, *6*, 583–603. [[CrossRef](#)]
98. Zhu, A.; Jiang, T.; Wang, D.; Han, B.; Liu, L.; Huang, J.; Zhang, J.; Sun, D. Direct aldol reactions catalyzed by 1,1,3,3-tetramethylguanidine lactate without solvent. *Green Chem.* **2005**, *7*, 514–517. [[CrossRef](#)]
99. Zhu, A.; Jiang, T.; Han, B.; Huang, J.; Zhang, J.; Ma, X. Study on guanidine-based task-specific ionic liquids as catalysts for direct aldol reactions without solvent. *New J. Chem.* **2006**, *30*, 736–740. [[CrossRef](#)]
100. Hu, S.; Jiang, T.; Zhang, Z.; Zhu, A.; Han, B.; Song, J.; Xie, Y.; Li, W. Functional ionic liquid from biorenewable materials: Synthesis and application as a catalyst in direct aldol reactions. *Tetrahedron Lett.* **2007**, *48*, 5613–5617. [[CrossRef](#)]
101. Limnios, D.; Kokotos, C.G. Microwave-assisted organocatalytic cross-aldol condensation of aldehydes. *RSC Adv.* **2013**, *3*, 4496–4499. [[CrossRef](#)]
102. Wang, C.; Liu, J.; Leng, W.; Gao, Y. Rapid and efficient functionalized ionic liquid-catalyzed aldol condensation reactions associated with microwave irradiation. *Int. J. Mol. Sci.* **2014**, *15*, 1284–1299. [[CrossRef](#)] [[PubMed](#)]
103. Li, H.-Y.; Li, S.-N.; Wang, Q.; Wang, S.-X.; Zhu, B.-C. Imidazolium ionic liquids as catalyst for synthesis of (*E*)-3-arylidene(thio)chroman-4-ones under microwave irradiation. *J. Chem. Res.* **2012**, *36*, 635–637. [[CrossRef](#)]
104. Shelke, K.F.; Sapkal, S.B.; Shitole, N.V.; Shingate, B.B.; Shingare, M.S. Microwave-assisted synthesis of 3-styrylchromones in alkaline ionic liquid. *Bull. Korean Chem. Soc.* **2009**, *30*, 2883–2886. [[CrossRef](#)]
105. Li, B.L.; Liang, H.D.; Zhong, A.G.; Xu, D.Q. The novel SO₃H-functionalized ionic liquids promoted synthesis of xanthenedione derivatives in Aqueous media under microwave irradiation. *Adv. Mater. Res.* **2012**, *391–392*, 1354–1357. [[CrossRef](#)]
106. Estager, J.; Leveque, J.-M.; Turgis, R.; Draye, M. Solventless and swift benzoin condensation catalyzed by 1-alkyl-3-methylimidazolium ionic liquids under microwave irradiation. *J. Mol. Catal. A Chem.* **2006**, *256*, 261–264. [[CrossRef](#)]
107. Estager, J.; Leveque, J.-M.; Turgis, R.; Draye, M. Neat benzoin condensation in recyclable room-temperature ionic liquids under ultrasonic activation. *Tetrahedron Lett.* **2007**, *48*, 755–759. [[CrossRef](#)]
108. Aupoix, A.; Pegot, B.; Vo-Thanh, G. Synthesis of imidazolium and pyridinium-based ionic liquids and application of 1-alkyl-3-methylimidazolium salts as pre-catalysts for the benzoin condensation using solvent-free and microwave activation. *Tetrahedron* **2010**, *66*, 1352–1356. [[CrossRef](#)]
109. Singh, N.; Singh, S.K.; Khanna, R.S.; Singh, K.N. Ionic liquid/potassium hydroxide catalyzed solvent-free, one-pot synthesis of diarylglycolic acids from aromatic aldehydes under microwave. *Tetrahedron Lett.* **2011**, *52*, 2419–2422. [[CrossRef](#)]
110. De Souza, R.O.M.A.; de Souza, A.L.F.; Fernandez, T.L.; Silva, A.C.; Pereira, V.L.P.; Esteves, P.M.; Vasconcellos, M.L.A.A.; Antunes, O.A.C. Morita-Baylis-Hillman reaction in water/ionic liquids under microwave irradiation. *Lett. Org. Chem.* **2008**, *5*, 379–382. [[CrossRef](#)]
111. Wang, D.-Y.; Xi, G.-H.; Ma, J.-J.; Wang, C.; Zhang, X.-C.; Wang, Q.-Q. Condensation reactions of aromatic aldehydes with active methylene compounds catalyzed by alkaline ionic liquid. *Synth. Commun.* **2011**, *41*, 3060–3065. [[CrossRef](#)]
112. Valizadeh, H.; Shockravi, A.; Gholipur, H. Microwave assisted synthesis of coumarins via potassium carbonate catalyzed Knoevenagel condensation in 1-*n*-butyl-3-methylimidazolium bromide ionic liquid. *J. Heterocycl. Chem.* **2007**, *44*, 867–870. [[CrossRef](#)]
113. Vasiloiu, M.; Gaertner, P.; Bica, K. Iron-catalyzed Michael addition. Chloroferrate ionic liquids as efficient catalysts under microwave conditions. *Sci. China Chem.* **2012**, *55*, 1614–1619. [[CrossRef](#)]

114. Paul, C.E.; Gotor-Fernandez, V.; Lavandera, I.; Montejo-Bernardo, J.; Garcia-Granda, S.; Gotor, V. Chemoenzymatic preparation of optically active 3-(1H-imidazol-1-yl)cyclohexanol-based ionic liquids: Application in organocatalysis and toxicity studies. *RSC Adv.* **2012**, *2*, 6455–6463. [[CrossRef](#)]
115. Zhou, Z.-Z.; Ji, F.-Q.; Cao, M.; Yang, G.-F. An efficient intramolecular Stetter reaction in room temperature ionic liquids promoted by microwave irradiation. *Adv. Synth. Catal.* **2006**, *348*, 1826–1830. [[CrossRef](#)]
116. Aupoix, A.; Vo-Thanh, G. Solvent-free synthesis of alkylthiazolium-based ionic liquids and their use as catalysts in the intramolecular Stetter reaction. *Synlett* **2009**, *12*, 1915–1920.
117. Lin, Y.-Y.; Tsai, S.-C.; Yu, S.J. Highly efficient and recyclable Au nanoparticle-supported Palladium(II) interphase catalysts and microwave-assisted alkyne cyclotrimerization reactions in ionic liquids. *J. Org. Chem.* **2008**, *73*, 4920–4928. [[CrossRef](#)] [[PubMed](#)]
118. Janus, E.; Syguda, A.; Materna, K. Ionic liquids—Deanol derivatives as the Diels-Alder reaction solvents. *Cent. Eur. J. Chem.* **2010**, *8*, 1140–1146. [[CrossRef](#)]
119. Leadbeater, N.E.; Torenus, H.M. A study of the ionic liquid mediated microwave heating of organic solvents. *J. Org. Chem.* **2002**, *67*, 3145–3148. [[CrossRef](#)] [[PubMed](#)]
120. Chen, I.-H.; Young, J.-N.; Yu, S.J. Recyclable organotungsten Lewis acid and microwave-assisted Diels-Alder reactions in water and in ionic liquids. *Tetrahedron* **2004**, *60*, 11903–11909. [[CrossRef](#)]
121. Fuentes, A.; Martinez-Palou, R.; Jimenez-Vazquez, H.A.; Delgado, F.; Reyes, A.; Tamariz, J. Diels-Alder reactions of 2-oxazolidinone dienes in polar solvents using catalysis or non-conventional energy sources. *Monatsh. Chem.* **2005**, *136*, 177–192. [[CrossRef](#)]
122. López, I.; Silvero, G.; Arevalo, M.J.; Babiano, R.; Palacios, J.C.; Bravo, J.L. Enhanced Diels-Alder reactions: On the role of mineral catalysts and microwave irradiation in ionic liquids as recyclable media. *Tetrahedron* **2007**, *63*, 2901–2906. [[CrossRef](#)]
123. Vidiš, A.; Kusters, E.; Sedelmeier, G.; Dyson, P.J. Effect of Lewis acids on the Diels-Alder reaction in ionic liquids with different activation modes. *J. Phys. Org. Chem.* **2008**, *21*, 264–270. [[CrossRef](#)]
124. Mancini, P.M.E.; Ormachea, C.M.; Della Rosa, C.D.; Kneeteman, M.N.; Suarez, A.G.; Domingo, L.R. Ionic liquids and microwave irradiation as synergistic combination for polar Diels-Alder reactions using properly substituted heterocycles as dienophiles. A DFT study related. *Tetrahedron Lett.* **2012**, *53*, 6508–6511. [[CrossRef](#)]
125. Rajendran, A.; Kumar, G.V. Sustainable Diels-Alder syntheses in imidazolium ionic liquids. *Synth. Commun.* **2016**, *46*, 483–496.
126. Rajendran, A.; Kumar, G.V. Ultra-rapid green microwave Diels-Alder reactions using ionic liquid. *Curr. Microw. Chem.* **2016**, *3*, 55–59. [[CrossRef](#)]
127. Prajapati, S.M.; Patel, K.D.; Vekariya, R.H.; Panchal, S.N.; Patel, H.D. Recent advances in the synthesis of quinolines: A review. *RSC Adv.* **2014**, *4*, 24463–24476. [[CrossRef](#)]
128. Prajapati, N.P.; Vekariya, R.H.; Borad, M.A.; Patel, H.D. Recent advances in the synthesis of 2-substituted benzothiazoles: A review. *RSC Adv.* **2014**, *4*, 60176–60208. [[CrossRef](#)]
129. Sapkal, S.B.; Shelke, K.F.; Shingate, B.B.; Shingare, M.S. An efficient synthesis of benzofuran derivatives under conventional/non-conventional method. *Chin. Chem. Lett.* **2010**, *21*, 1439–1442. [[CrossRef](#)]
130. Gu, L.; Li, X. Microwave-assisted synthesis of indole-2-carboxylic acid esters in ionic liquid. *J. Braz. Chem. Soc.* **2011**, *22*, 2036–2039. [[CrossRef](#)]
131. Eduque, R.M., Jr.; Creencia, E.C. Microwave-assisted Fischer Indole synthesis of 1,2,3,4-tetrahydrocarbazole using pyridinium-based ionic liquids. *Procedia Chem.* **2015**, *16*, 413–419. [[CrossRef](#)]
132. Yi, F.; Peng, Y.; Song, G. Microwave-assisted liquid-phase synthesis of methyl 6-amino-5-cyano-4-aryl-2-methyl-4H-pyran-3-carboxylate using functional ionic liquid as soluble support. *Tetrahedron Lett.* **2005**, *46*, 3931–3933. [[CrossRef](#)]
133. Mamaghani, M.; Nia, R.H. Recent developments in the MCRs synthesis of pyridopyrimidines and spiro-pyridopyrimidines. *J. Heterocycl. Chem.* **2017**, *54*, 1700–1722. [[CrossRef](#)]
134. Sreevalli, W.; Ramachandran, G.; Madhuri, W.; Sathiyarayanan, K.I. Green trends in Mannich reaction. *Mini-Rev. Org. Chem.* **2014**, *11*, 97–115. [[CrossRef](#)]
135. Syamala, M. A decade of advances in three-component reactions. A review. *Org. Prep. Proced. Int.* **2005**, *37*, 103–171. [[CrossRef](#)]
136. Patil, V.; Padalkar, V.; Chaudhari, A. Intrinsic catalytic activity of an acidic ionic liquid as a solvent for quinazoline synthesis. *Catal. Sci. Technol.* **2012**, *2*, 1681–1684. [[CrossRef](#)]

137. Mert-Balci, F.; Imrich, H.-G.; Conrad, J.; Beifuss, U. Influence of guanidinium salts and other ionic liquids on the three-component aza-Diels-Alder reaction. *Helv. Chim. Acta* **2013**, *96*, 1681–1692. [[CrossRef](#)]
138. Fraga-Dubreuil, J.; Bazureau, J.P. Efficient combination of task-specific ionic liquid and microwave dielectric heating applied to one-pot three component synthesis of a small library of 4-thiazolidinones. *Tetrahedron* **2003**, *59*, 6121–6130. [[CrossRef](#)]
139. Hakkou, H.; Vanden Eynde, J.J.; Hamelin, J.; Bazureau, J.P. Ionic liquid phase organic synthesis (IoLiPOS) methodology applied to the three component preparation of 2-thioxotetrahydropyrimidin-4-(1H)-ones under microwave dielectric heating. *Tetrahedron* **2004**, *60*, 3745–3753. [[CrossRef](#)]
140. Legeay, J.-C.; Vanden Eynde, J.J.; Bazureau, J.P. Ionic liquid phase technology supported the three component synthesis of Hantzsch 1,4-dihydropyridines and Biginelli 3,4-dihydropyrimidin-2(1H)-ones under microwave dielectric heating. *Tetrahedron* **2005**, *61*, 12386–12397. [[CrossRef](#)]
141. Legeay, J.C.; Goujon, J.Y.; Vanden Eynde, J.J.; Toupet, L.; Bazureau, J.P. Liquid-phase synthesis of polyhydroquinoline using task-specific ionic liquid technology. *J. Comb. Chem.* **2006**, *8*, 829–833. [[CrossRef](#)] [[PubMed](#)]
142. Narhe, B.D.; Tsai, M.-H.; Sun, C.-M. Rapid two-Step synthesis of benzimidazo[1',2':1,5]pyrrolo [2,3-c]isoquinolines by a three-component coupling reaction. *ACS Comb. Sci.* **2014**, *16*, 421–427. [[CrossRef](#)] [[PubMed](#)]
143. Peng, Y.; Song, G. Amino-functionalized ionic liquid as catalytically active solvent for microwave-assisted synthesis of 4H-pyrans. *Catal. Commun.* **2007**, *8*, 111–114. [[CrossRef](#)]
144. Xia, M.; Lu, Y. A novel, neutral ionic liquid-catalyzed, solvent-free synthesis of 2,4,5-trisubstituted imidazoles under microwave irradiation. *J. Mol. Catal. A Chem.* **2007**, *265*, 205–208. [[CrossRef](#)]
145. Kantevari, S.; Chary, M.V.; Rudra Das, A.P.; Vuppapalapati, S.V.N.; Lingaiah, N. Catalysis by an ionic liquid: Highly efficient solvent-free synthesis of aryl-14H-dibenzo[a,j]xanthenes by molten tetrabutylammonium bromide under conventional and microwave heating. *Catal. Commun.* **2008**, *9*, 1575–1578.
146. Kundu, D.; Majee, A.; Hajra, A. Task-specific ionic liquid-catalyzed efficient microwave-assisted synthesis of 12-alkyl or aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-ones under solvent-free conditions. *Green Chem. Lett. Rev.* **2011**, *4*, 205–209. [[CrossRef](#)]
147. Kumar, A.; Rao, V.K. Microwave-assisted and Yb(OTf)₃-promoted one-pot multicomponent synthesis of substituted quinolines in ionic liquid. *Synlett* **2011**, *2011*, 2157–2162. [[CrossRef](#)]
148. Mert-Balci, F.; Conrad, J.; Beifuss, U. Microwave-assisted three-component reaction in conventional solvents and ionic liquids for the synthesis of amino-substituted imidazo[1,2-a]pyridines. *Arch. Org. Chem.* **2012**, *2012*, 243–256.
149. Chebanov, V.A.; Gorobets, N.Y.; Sedash, Y.V. Reactions involving a carbonyl compound as electrophilic component. Third component 1,3-dicarbonyl compound (with ureas: Biginelli reaction). In *Science of Synthesis, Multicomponent Reactions*; Mueller, T.J.J., Ed.; Thieme: Stuttgart, Germany, 2014; Volume 1, pp. 29–66.
150. Suresh; Sandhu, J.S. Past, present and future of the Biginelli reaction: A critical perspective. *Arch. Org. Chem.* **2011**, *2012*, 66–133.
151. Kolosov, M.A.; Orlov, V.D.; Beloborodov, D.A.; Dotsenko, V.V. A chemical placebo: NaCl as an effective, cheapest, non-acidic and greener catalyst for Biginelli-type 3,4-dihydropyrimidin-2(1H)-ones (-thiones) synthesis. *Mol. Divers.* **2009**, *13*, 5–25. [[CrossRef](#)] [[PubMed](#)]
152. Peng, J.; Deng, Y. Ionic liquids catalyzed Biginelli reaction under solvent-free conditions. *Tetrahedron Lett.* **2001**, *42*, 5917–5919. [[CrossRef](#)]
153. Arfan, A.; Paquin, L.; Bazureau, J.P. Acidic task-specific ionic liquid as catalyst of microwave-assisted solvent-free Biginelli reaction. *Russ. J. Org. Chem.* **2007**, *43*, 1058–1064. [[CrossRef](#)]
154. Rong, L.; Han, H.; Wang, H.; Jiang, H.; Tu, S.; Shi, D. An efficient and facile synthesis of pyrimidine and quinazoline derivatives via one-pot three-component reaction under solvent-free conditions. *J. Heterocycl. Chem.* **2009**, *46*, 152–157. [[CrossRef](#)]
155. Zare, A.; Hasaninejad, A.; Salimi Beni, A.; Moosavi-Zare, A.R.; Merajoddin, M.; Kamali, E.; Akbari-Seddigh, M.; Parsaee, Z. Ionic liquid 1-butyl-3-methylimidazolium bromide ([Bmim]Br) as a green and neutral reaction media for the catalyst-free synthesis of 1-amidoalkyl-2-naphthols. *Sci. Iran.* **2011**, *18*, 433–438. [[CrossRef](#)]
156. Srivastava, V. An improved protocol for Biginelli reaction. *Green Sustain. Chem.* **2013**, *3*, 38–40. [[CrossRef](#)]

157. Dadhania, A.N.; Patel, V.K.; Raval, D.K. A facile approach for the synthesis of 3,4-dihydropyrimidin-2-(1H)-ones using a microwave promoted Biginelli protocol in ionic liquid. *J. Chem. Sci.* **2012**, *124*, 921–926. [[CrossRef](#)]
158. Mirzai, M.; Valizadeh, H. Microwave-promoted synthesis of 3,4-dihydropyrimidin-2(1H)-(thio)ones using IL-ONO as recyclable base catalyst under solvent-free conditions. *Synth. Commun.* **2012**, *42*, 1268–1277. [[CrossRef](#)]
159. Sharma, N.; Sharma, U.K.; Kumar, R.; Richa; Sinha, A.K. Green and recyclable glycine nitrate (GlyNO₃) ionic liquid triggered multicomponent Biginelli reaction for the efficient synthesis of dihydropyrimidinones. *RSC Adv.* **2012**, *2*, 10648–10651. [[CrossRef](#)]
160. Fu, R.; Yang, Y.; Lai, W.; Ma, Y.; Chen, Z.; Zhou, J.; Chai, W.; Wang, Q.; Yuan, R. Efficient and green microwave-assisted multicomponent Biginelli reaction for the synthesis of dihydropyrimidinones catalyzed by heteropolyanion-based ionic liquids under solvent-free conditions. *Synth. Commun.* **2015**, *45*, 467–477. [[CrossRef](#)]
161. Zakeri, M.; Nasef, M.M.; Abouzari-Lotf, E. Eco-safe and expeditious approaches for synthesis of quinazoline and pyrimidine-2-amine derivatives using ionic liquids aided with ultrasound or microwave irradiation. *J. Mol. Liquids* **2014**, *199*, 267–274. [[CrossRef](#)]
162. Bhatt, J.D.; Chudasama, C.J.; Patel, K.D. Microwave assisted synthesis of pyrimidines in ionic liquid and their potency as non-classical malarial antiparasitics. *Arch. Pharm. Chem. Life Sci.* **2016**, *349*, 791–800. [[CrossRef](#)] [[PubMed](#)]
163. Zarnegar, Z.; Safari, J. Magnetic nanoparticles supported imidazolium-based ionic liquids as nanocatalyst in microwave-mediated solvent-free Biginelli reaction. *J. Nanoparticle Res.* **2014**, *16*, 2509. [[CrossRef](#)]
164. Martens, J.A.; Bogaerts, A.; De Kimpe, N.; Jacobs, P.A.; Marin, G.B.; Rabaey, K.; Saeys, M.; Verhelst, S. The chemical route to a carbon dioxide neutral world. *ChemSusChem* **2017**, *10*, 1039–1055. [[CrossRef](#)] [[PubMed](#)]
165. Kreye, O.; Over, L.C.; Nitsche, T.; Lange, R.Z.; Meier, M.A.R. Organic carbonates: Sustainable and environmentally-friendly ethylation, allylation, and benzylation reagents. *Tetrahedron* **2015**, *71*, 293–300. [[CrossRef](#)]
166. Kim, Y.J.; Varma, R.S. Tetrahaloindate(III)-based ionic liquids in the coupling reaction of carbon dioxide and epoxides to generate cyclic carbonates: H-bonding and mechanistic studies. *J. Org. Chem.* **2005**, *70*, 7882–7891. [[CrossRef](#)] [[PubMed](#)]
167. Ono, F.; Qiao, K.; Tomida, D.; Yokoyama, C. Rapid synthesis of cyclic carbonates from CO₂ and epoxides under microwave irradiation with controlled temperature and pressure. *J. Mol. Catal. A Chem.* **2007**, *263*, 223–226. [[CrossRef](#)]
168. Tharun, J.; Kim, D.W.; Roshan, R.; Hwang, Y.; Park, D.-W. Microwave assisted preparation of quaternized chitosan catalyst for the cycloaddition of CO₂ and epoxides. *Catal. Commun.* **2013**, *31*, 62–65. [[CrossRef](#)]
169. Dharman, M.M.; Yu, J.-I.; Ahn, J.-Y.; Park, D.-W. Selective production of cyclic carbonate over polycarbonate using a double metal cyanide-quaternary ammonium salt catalyst system. *Green Chem.* **2009**, *11*, 1754–1757. [[CrossRef](#)]
170. Tharun, J.; Mathai, G.; Kathalikkattil, A.C.; Roshan, R.; Kwak, J.-Y.; Park, D.-W. Microwave-assisted synthesis of cyclic carbonates by formic acid/KI catalytic system. *Green Chem.* **2013**, *15*, 1673–1677. [[CrossRef](#)]
171. Ju, H.-Y.; Dharman, M.M.; Kim, K.-H.; Park, S.-W.; Park, D.-W. Catalytic performance of quaternary ammonium salts in the reaction of butyl glycidyl ether and carbon dioxide. *J. Ind. Eng. Chem.* **2008**, *14*, 157–160. [[CrossRef](#)]
172. Udayakumar, S.; Lee, M.-K.; Shim, H.-L.; Park, S.-W.; Park, D.-W. Imidazolium derivatives functionalized MCM-41 for catalytic conversion of carbon dioxide to cyclic carbonate. *Catal. Commun.* **2009**, *10*, 659–664. [[CrossRef](#)]
173. Udayakumar, S.; Lee, M.-K.; Shim, H.-L.; Park, D.-W. Functionalization of organic ions on hybrid MCM-41 for cycloaddition reaction: The effective conversion of carbon dioxide. *Appl. Catal. A Gen.* **2009**, *365*, 88–95. [[CrossRef](#)]
174. Kathalikkattil, A.C.; Tharun, J.; Roshan, R.; Soek, H.-G.; Park, D.-W. Efficient route for oxazolidinone synthesis using heterogeneous biopolymer catalysts from unactivated alkyl aziridine and CO₂ under mild conditions. *Appl. Catal. A Gen.* **2012**, *447–448*, 107–114. [[CrossRef](#)]
175. Roshan, K.R.; Mathai, G.; Kim, J.; Tharun, J.; Park, G.-A.; Park, D.-W. A biopolymer mediated efficient synthesis of cyclic carbonates from epoxides and carbon dioxide. *Green Chem.* **2012**, *14*, 2933–2940. [[CrossRef](#)]

176. Kim, Y.-J.; Park, D.-W. Functionalized IRMOF-3: An efficient heterogeneous catalyst for the cycloaddition of allyl glycidyl ether and CO₂. *J. Nanosci. Nanotechnol.* **2013**, *13*, 2307–2312. [[CrossRef](#)] [[PubMed](#)]
177. Dharman, M.M.; Choi, H.-J.; Park, S.-W.; Park, D.-W. Microwave assisted synthesis of cyclic carbonate using homogeneous and heterogeneous ionic liquid catalysts. *Top. Catal.* **2010**, *53*, 462–469. [[CrossRef](#)]
178. Dharman, M.M.; Choi, H.-J.; Kim, D.-W.; Park, D.-W. Synthesis of cyclic carbonate through microwave irradiation using silica-supported ionic liquids: Effect of variation in the silica support. *Catal. Today* **2011**, *164*, 544–547. [[CrossRef](#)]
179. Kim, D.-W.; Kim, D.-K.; Kim, M.-I.; Park, D.-W. Microwave assisted synthesis of allyl glycidyl carbonate by using ionic liquid immobilized onto montmorillonite clay. *Catal. Today* **2012**, *185*, 217–223. [[CrossRef](#)]
180. Tharun, J.; Kathalikkattil, A.C.; Roshan, R.; Kang, D.-H.; Woo, H.-C.; Park, D.-W. Microwave-assisted, rapid cycloaddition of allyl glycidyl ether and CO₂ by employing pyridinium-based ionic liquid catalysts. *Catal. Commun.* **2014**, *54*, 31–34. [[CrossRef](#)]
181. Kathalikkattil, A.C.; Kim, D.-W.; Tharun, J.; Soek, H.-G.; Roshan, R.; Park, D.-W. Aqueous-microwave synthesized carboxyl functional molecular ribbon coordination framework catalyst for the synthesis of cyclic carbonates from epoxides and CO₂. *Green Chem.* **2014**, *16*, 1607–1616. [[CrossRef](#)]
182. Du, J.; Shi, J.; Li, Z.; Liu, Z.; Fan, X.; Tao, C. Ionic liquid mediated CO₂ activation for DMC synthesis. *J. Nat. Gas Chem.* **2012**, *21*, 476–479. [[CrossRef](#)]
183. Du, H.; Liu, X.; Yu, Y.; Xu, Y.; Wang, Y.; Liang, Z. Microwave-induced poly(ionic liquid)/poly(vinyl alcohol) shape memory composites. *Macromol. Chem. Phys.* **2016**, *217*, 2626–2634. [[CrossRef](#)]
184. Long, D.; Liu, T.; Tan, L.; Shi, H.; Liang, P.; Tang, S.; Wu, Q.; Yu, J.; Dou, J.; Meng, X. Multisynnergistic platform for tumor therapy by mild microwave irradiation-activated chemotherapy and enhanced ablation. *ACS Nano* **2016**, *10*, 9516–9528. [[CrossRef](#)] [[PubMed](#)]
185. Tang, S.; Du, Q.; Liu, T.; Tan, L.; Niu, M.; Gao, L.; Huang, Z.; Fu, C.; Ma, T.; Meng, X.; et al. In vivo magnetic resonance imaging and microwave thermotherapy of cancer using novel chitosan microcapsules. *Nanoscale Res. Lett.* **2016**, *11*, 334. [[CrossRef](#)] [[PubMed](#)]



© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).