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REVIEW

Harnessing DABCO ionic salts for synthesis of heterocycles via multi-component reactions

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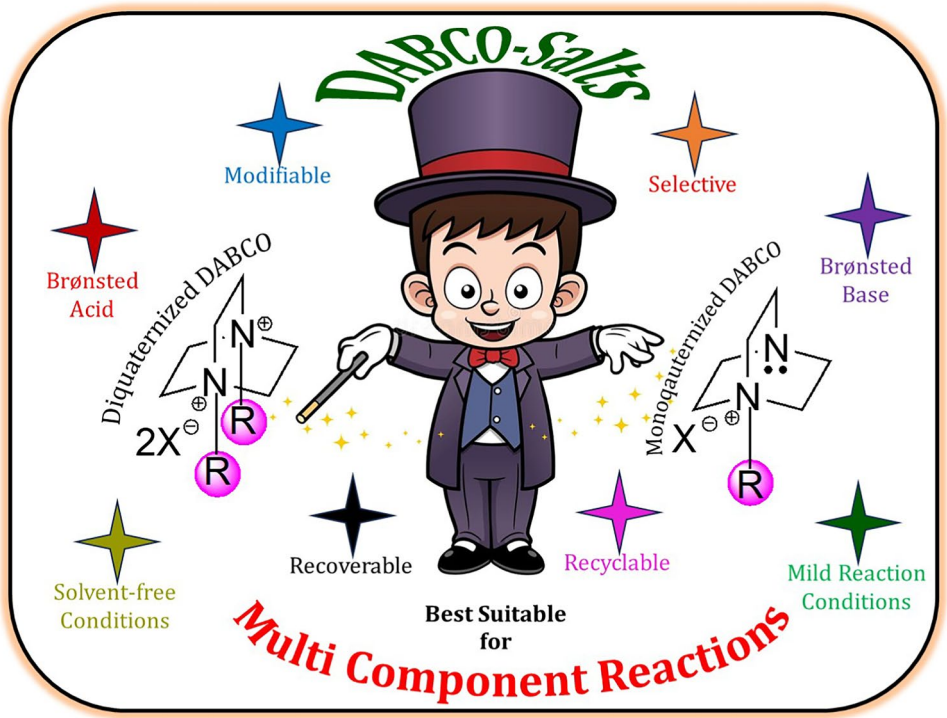
Abstract

The review article discusses the advancements in synthesis and applications of acidic, basic, and neutral 1,4-diazabicyclo[2.2.2]octane (DABCO) ionic salts in multi-component reactions. Compared to imidazolium-based ionic salts, the number of DABCO-based ionic salts is significantly lower. Recently, there has been increasing focus on these salts due to their selective salt formation capabilities. A significant challenge lies in the limited availability of physical data regarding DABCO-based ionic salts; hence, most of them are not ionic liquids. While many of these salts could be reused several times with only a minimal reduction in their catalytic effectiveness, there is a significant limitation in the availability of DABCO-based salts.

Graphical abstract



Keywords 1,4-Diazabicyclo[2.2.2]octane · Ionic salts · Multi-component reactions · Recyclability

Extended author information available on the last page of the article

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Abbreviations

CH_3CN	Acetonitrile
CMC	Critical micelle concentration
DABCO	1,4-Diazabicyclo[2.2.2]octane
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCM	Dichloromethane
DDIL	Dicationic DABCO ionic liquids
DEILs	Deep eutectic ionic liquids
DESs	Deep eutectic solvents
DHQs	2,3-Dihydroquinazolin-4(*1H*)-ones
DMAD	Dimethylacetylenedicarboxylate
EtOH	Ethanol
HBD	Hydrogen bond donor
HILs	Hydroxy ionic liquids
HTILs	High-temperature ionic liquids
ILs	Ionic liquids
MCRs	Multi-component reactions
MDIS	Monocationic DABCO ionic salts
$NaBF_4$	Sodium tetrafluoroborate
NaOAc	Sodium acetate
PDIL	Polycationic DABCO ionic liquids
PEG	Polyethylene glycol
PILs	Polymeric ionic liquids
QASs	Quaternary ammonium salts
RT	Room temperature
RTILs	Room temperature ionic liquids
TDIS	Tetracationic DABCO ionic salts
THF	Tetrahydrofuran
TSILs	Task-specific ionic liquids
US	Ultrasound

Introduction

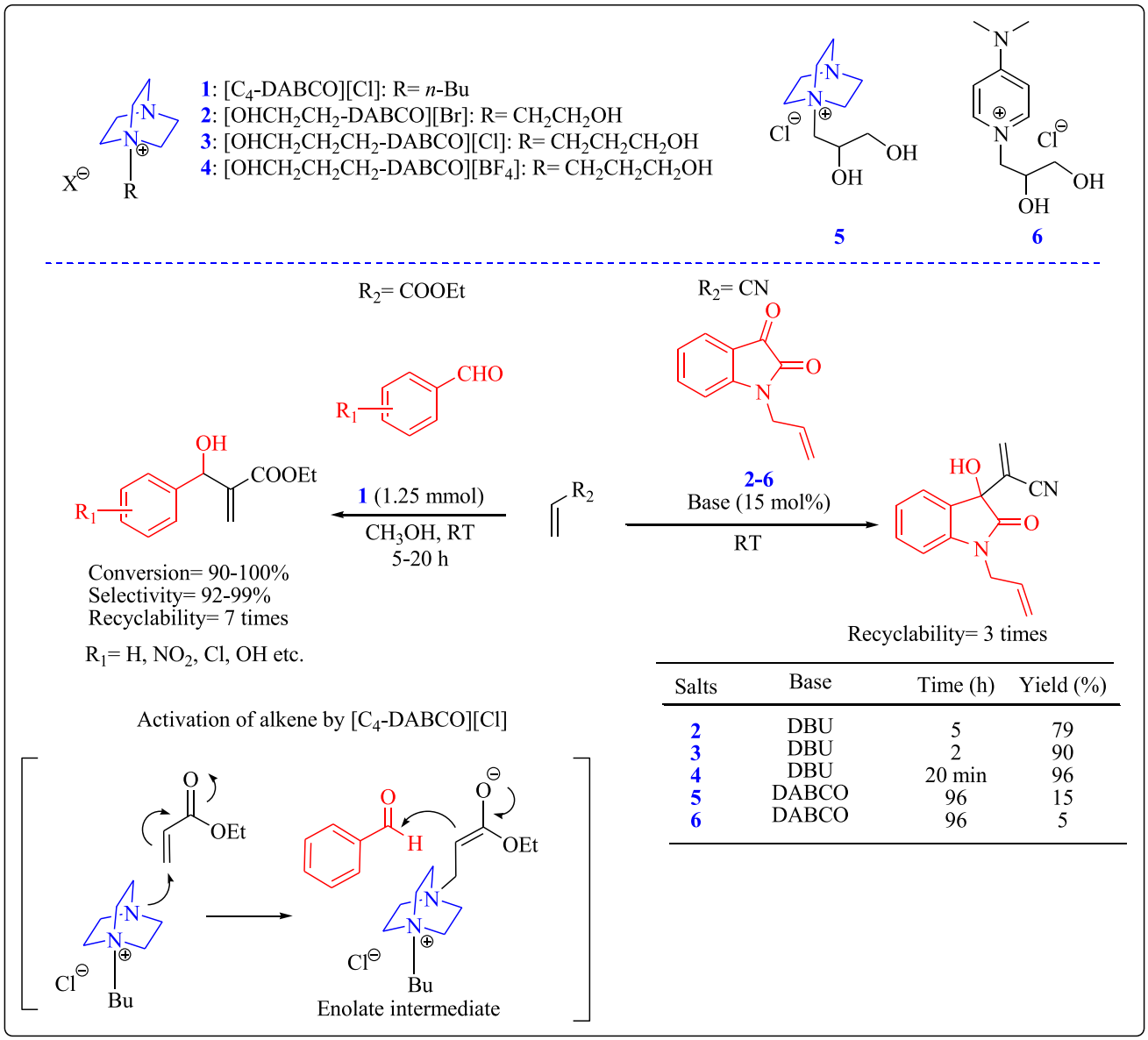
The unique properties of ionic liquids (ILs), such as structural tunability, good solubility, chemical and thermal stability, favorable biocompatibility, and simplicity of preparation (Rooney et al. 2009; Wang et al. 2014; Eyckens & Henderson 2019), have led to its a wide range of applications in the pharmaceutical and biomedical fields (Egorova et al. 2017; Zhuo et al. 2024). ILs can be classified based on structural features, functional properties, and their applications (Lei et al. 2017) as follows

1. Based on the type of cations: These ILs involve imidazolium (Pandolfi et al. 2022), pyridinium (Stepnowski et al. 2006), pyrrolidinium (McGrath & Rohan 2020), quaternary ammonium (Shaoo et al. 2019), phosphonium (Alper et al. 2018), and sulfonium (Yue et al. 2019) cations.
2. Based on the type of anions: These ILs involve halides, PF_6, BF_4, sulfonates, carboxylates, dicyanamide and tricyanomethanide, and bis(trifluoromethyl sulfonyl)imide (NTf_2) anions.
3. Based on the functionality: These are protic ionic liquids (PILs) (Greaves and Drummond 2008), aprotic ionic liquids (AILs) (Koutsoukos et. al. 2022), and basic ionic liquids (Hajipour and Rafiee 2009).
4. Task-specific ionic liquids (TSILs): These are designed with specific functional groups for particular chemical tasks (Neto et al. 2022).
5. Polymeric ionic liquids (PILs): These ILs contain ionic polymers that exhibit properties similar to ILs, effectively combining the advantages of both materials (Mecerreyes et al. 2011).
6. Based on physical state and phase: These are room-temperature ionic liquids (RTILs) (Javed et al. 2018) and high-temperature ionic liquids (HTILs) (El Abedin and Endres 2007).
7. Deep eutectic solvents (DESs): Mixtures of ionic and non-ionic components that exhibit ionic liquid properties (Płotka-Wasylka et al. 2020).

Each class of ILs is tailored for specific applications based on their unique properties, making them highly versatile in various fields of chemistry. Among these ILs 1,4-diazabicyclo[2.2.2]octane (DABCO)-based ILs have generated significant attention in different fields (D'Andrea et al. 2019; Goreshnik et al. 2023; Turguła et al. 2020a, 2020b) due to their unique and advantageous properties. Most importantly, DABCO-based ILs offer several advantages in organic transformations (Bugaenko et al. 2020; Jarrahi et al. 2022) due to their unique properties such as:

- The ionic character of DABCO ILs boosts their reactivity and selectivity, enhancing catalytic performance in organic reactions.
- They display strong nucleophilicity and basicity and act as both solvents and catalysts to streamline reactions
- DABCO ILs are thermally stable, non-volatile, and relatively less toxic, making them safer than volatile organic solvents for lab use.
- Their properties can be customized by modifying anions and cations to optimize solubility and polarity.
- They dissolve various compounds and can facilitate biphasic systems, simplifying product separation.
- Additionally, these ILs can be recycled several times, offering sustainability and cost-effectiveness.

These advantages make DABCO ILs a valuable addition to the field of green chemistry, offering more sustainable and efficient alternatives for organic synthesis. A significant challenge is the limited availability of physical data on DABCO-based ionic salts (IS). Therefore, many of these



Salts	Base	Time (h)	Yield (%)
2	DBU	5	79
3	DBU	2	90
4	DBU	20 min	96
5	DABCO	96	15
6	DABCO	96	5

Scheme 1 DABCO ionic salts-catalyzed Baylis–Hillman reactions

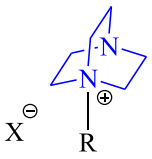
substances are not genuine ionic liquids (ILs) but ionic salts. The review article discusses the advancements in synthesizing and applying acidic, basic, and neutral DABCO-based ionic salts, especially in multi-component reactions (MCRs).

Applications of monocationic DABCO ionic salts (MDIS) in multi-component reactions

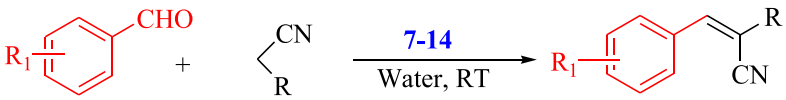
Various monoquaternized DABCO salts were developed for different organic transformations. Generally, they act as powerful Brønsted bases and catalyze different base-catalyzed MCRs.

Considering the importance of the Baylis–Hillman reaction in the synthesis of various bioactive compounds (Basavaiah et al. 2003; Maneesha et al. 2024), a chloride salt of DABCO ([C_4-DABCO][Cl]) (**1**) was synthesized by Cai et al (2007) and used in the Baylis–Hillman reaction (Scheme 1). The white-colored solid ionic salt can be easily prepared by treating DABCO with 1-chlorobutane in refluxing CH_3CN. By reacting aromatic and aliphatic aldehydes with ethyl acrylate, the corresponding Baylis–Hillman adducts were obtained in good to excellent yields (90–100% conversion) and high selectivity (92–99%) in methanol at room temperature (RT). The catalyst could be reused five times with consistent activity (conversion: 100%) and a slight decrease in selectivity. In this reaction, the free nitrogen of DABCO

Scheme 2 DABCO salt-catalyzed Knoevenagel condensation



7: [C_2-DABCO][Br]: R= Et
8: [C_2-DABCO][BF_4]: R= Et
9: [C_4-DABCO][Br]: R= *n*-Bu
10: [C_4-DABCO][BF_4]: R= *n*-Bu
11: [C_8-DABCO][Br]: R= *n*-Oct
12: [Bn-DABCO][Br]: R= Bn
13: [$OHCH_2CH_2$-DABCO][Br]: R= CH_2CH_2OH
14: [$NH_2CH_2CH_2CH_2$-DABCO][Br]: R= $CH_2CH_2CH_2NH_2$



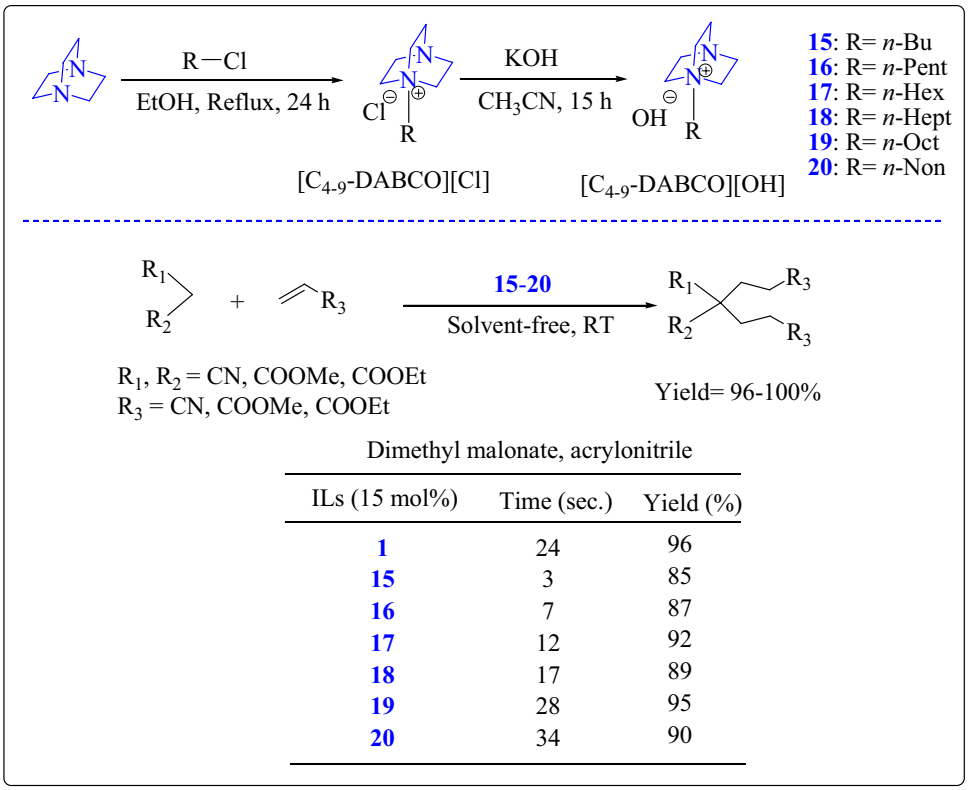
R= CN, COOEt

Salts	Solvent	Time (min)	Yield (%)
	R= CN		
7 (15 mol%)	[BMIM][BF_4]	4	98
8 (15 mol%)	[BMIM][BF_4]	<1	100
9 (15 mol%)	[BMIM][BF_4]	7	99
10 (15 mol%)	[BMIM][BF_4]	<1	100
11 (15 mol%)	[BMIM][BF_4]	13	99
12 (15 mol%)	[BMIM][BF_4]	10	98
10 (15 mol%)	Water	<1	100
	R= COOEt		
7 (12 mmol)	Water, US	3 h	90
10 (12 mmol)	Water, US	3 h	91
12 (12 mmol)	Water, US	3 h	98
13 (12 mmol)	Water, US	29	92
14 (10 mmol)	Water, US	25	98
14 (14 mmol)	Water, US	15	99

increases the nucleophilicity of the activated alkene, forming an enolate intermediate. The resulting intermediate becomes more nucleophilic than the starting alkene, enabling it to attack the aldehyde or ketone effectively.

It was found that the hydroxy-based ILs acts as an excellent protic solvent for various applications. In connection with this DABCO-based hydroxy ionic liquids (HIL) (**2–5**) and pyridine-based salt **6** was used in the synthesis of biologically active compounds from isatin, ninhydrin, 1,2-acenaphthylenequinone, and benzil via Baylis–Hillman reaction in presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (15 mol%) (Khalafi-Nezhad et al. 2012). The salts were obtained in excellent yields and are solid at RT (Thomas et al. 2009). Salts **1**, **2**, **5,** and **6** are solids, while **3** and **4** are viscous liquids at RT. It was observed that **2–5** act as a protic solvent. In DBU, IL **4** showed higher activity as compared to other ILs for the reaction of N-allyl isatin and acrylonitrile at RT and could be reused at least three times.

Knoevenagel condensation is one of the most important reaction used to synthesize different bioactive compounds (Johari et al. 2024; Appaturi et al. 2021; Nayl et al. 2022; Meng et al. 2018). In this regard, Wang and coworkers (Xu et al. 2010a, b) reported a convenient and rapid Knoevenagel



Scheme 3 [C_4-C_9-DABCO][OH] ILs for the Michael addition of active methylene compounds

Dimethyl malonate, acrylonitrile

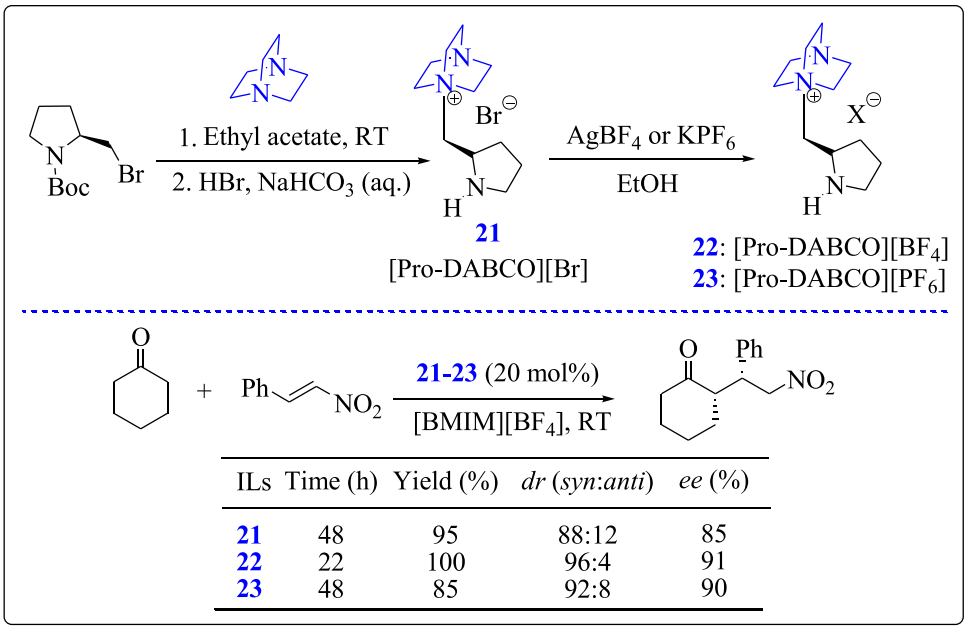
ILs (15 mol%)	Time (sec.)	Yield (%)
1	24	96
15	3	85
16	7	87
17	12	92
18	17	89
19	28	95
20	34	90

condensation of various aromatic/aliphatic/heterocyclic/*α,β*-unsaturated aldehydes and ketones with malononitrile/ethyl cyanoacetate using catalytic amount (15 mol%) of series of DABCO-based ionic salts (Scheme 2). The ionic salts **7–13** were prepared by monoquaternizing DABCO with corresponding alkyl halides. These salts on anion exchange with $AgBF_4$ gave BF_4 salts (Marra et al 2008; Lall et al. 2002). This method affords the corresponding substituted electrophilic alkenes with excellent yields (90–100%) at RT in water. Though all the salts worked well in water, the use of [C_4-DABCO][BF_4] (**10**) makes the procedure more convenient and showed the seventh time recyclability with declined yield from 100 to 92%. The Knoevenagel reactions of malononitrile with aromatic aldehydes are faster than the ethyl cyanoacetate as malononitrile is more active than ethyl cyanoacetate and readily reacts with aromatic aldehydes. Here the quaternization of DABCO salt enhances the solubility of reagents in water, whereas the free tertiary N of DABCO salt activates the malononitrile by abstracting acidic hydrogen to form its anion enabling it to attack the aldehyde/ketone effectively.

In a recent study, Zhao et al. (2024) investigated the Knoevenagel condensation catalyzed by [$NH_2CH_2CH_2CH_2$-DABCO][Br] salt (**14**) under ultrasound (360 w, 40 Hz) at 35 °C. The gray-colored ionic solid **14** (mp = 180.5 °C) was prepared by reacting DABCO with 3-bromopropylamine in ethyl acetate at reflux. They found that aromatic aldehydes with electron-donating and electron-withdrawing groups yielded the desired products with 79–99% yield. Additionally, the catalyst could be reused at least six times without any loss in its catalytic activity.

Keithellakpam and Laitonjam (2014) developed a series of DABCO-based hydroxide ILs [C_4-C_9-DABCO][OH] (**15–20**), for the Michael addition of active methylene compounds to *α,β*-unsaturated carboxylic esters, and nitriles at RT (Scheme 3). The viscous ILs were obtained by treating the corresponding DABCO chloride salt with KOH in dry acetonitrile at RT (Yang et al. 2010). The optimization of the reaction conditions with dimethyl malonate and acrylonitrile showed that IL **15** (5 mol%) was highly efficient under solvent-free conditions at RT. Thus **15** acts as an efficient catalyst for the Michael addition of a wide range of active methylene compounds with *α*, *β*-unsaturated carboxylic esters, and nitriles, providing excellent yields in short durations. The method is simple, and the yields are high. The IL **15** can be recycled six times with decreased yield from 100 to 92%. In addition, the IL **10** acted as an efficient catalyst for the Henry reaction of various carbonyl compounds with

Scheme 4 Chiral pyrrolidine-DABCO-type ILs for asymmetric Michael addition



ILs	Time (h)	Yield (%)	*dr* (*syn*:*anti*)	*ee* (%)
21	48	95	88:12	85
22	22	100	96:4	91
23	48	85	92:8	90

nitro-alkanes affording very high yields (Keithellakpam et al. 2014).

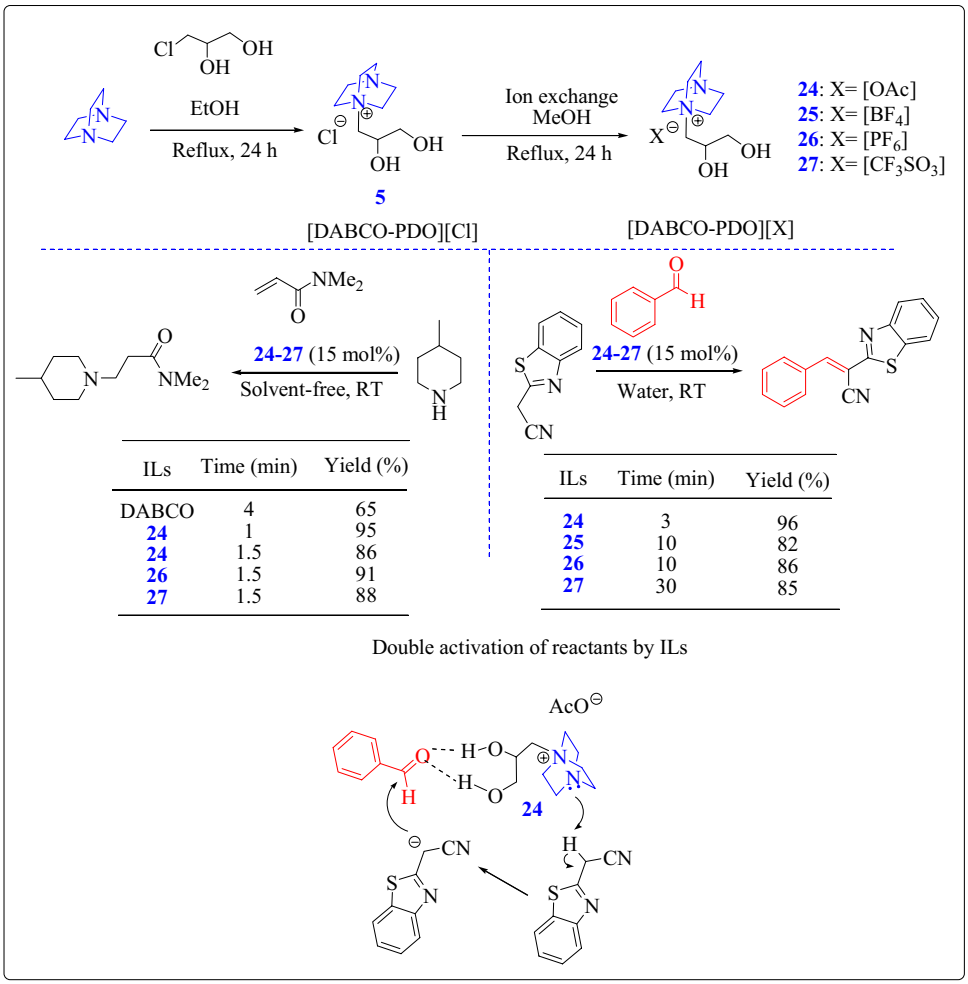
Xu et al. (2010a, b) described the synthesis of a series of chiral pyrrolidine-DABCO-type ILs [Pro-DABCO][X] (**21–23**) using *N*-Boc-(*L*)-prolinol from the 'chiral pool' strategy (Scheme 4). All these ILs are pale yellow-colored liquids. These ILs were used as chiral catalysts (20 mol%), that exhibited high efficiency in asymmetric Michael addition reactions of ketones and aldehydes to nitro-olefins. The ILs achieved excellent yields (up to 100%), diastereoselectivities (up to *syn*/*anti* = 96:4), and enantioselectivities (up to 91%) in [BMIM][BF_4] at RT. The IL **22** demonstrated six times reusability with good stereoselectivity (*ee* > 90%; *syn*/*anti* > 93:7), but with a slight decrease in activity.

Ying and coworkers (2014a, 2014b, Hou et al. 2015) described basic DABCO-based RTILs (**24–27**) containing hydroxy groups known as [DABCO-PDO][X] that are used in various organic transformations. The IL is prepared in two steps, where DABCO and 3-chloro-1,2-propanediol are reacted in refluxing ethanol to produce [DABCO-PDO][Cl] (**5**). Subsequently, the resulting ionic salt **5** is treated with ion exchange reagents such as KOAc, $NaBF_4$, KPF_6, or KSO_3CF_3 in refluxing methanol to obtain the desired ILs **24–27** (Scheme 5). They successfully used all the ILs for the solvent-free aza-Michael addition of *α,β*-unsaturated amides. The IL showed good to excellent results in a short time at RT and could be reused up to eight times while maintaining consistent catalytic activity. Additionally, a plausible mechanism was proposed through FT-IR and computational studies. It was suggested that the lone pair of electrons of the N atom of the IL could deprotonate the hydrogen atom of amines, thereby enhancing the nucleophilicity of amines. Furthermore, the hydroxyl groups of the IL and the carbonyl group of α, β-unsaturated amides could form hydrogen-bonding interactions, making *α, β*-unsaturated amides more susceptible to attack by amines.

The ILs **24–27** (15 mol%) effectively catalyzed the Knoevenagel condensation of different aromatic and heteroaromatic aldehydes to produce *α*-heteroaromatic/polyaromatic substituted methylene compounds in water at RT (Ying, et al. 2014a, b). The yield of the desired products was good to excellent. According to an optimization study, the IL-containing acetate anion (**24**) exhibited superior catalytic activity. In this reaction, the lone pair of electrons on the free N atom of the IL abstracts the hydrogen atom of the active methylene compound, leading to the formation of the corresponding active carbanion. According to NMR studies, the -OH groups of the IL increase the electrophilicity of the aldehyde's carbonyl group. This dual catalytic effect results in excellent yields of the desired products in a short reaction time. Furthermore, the IL **24** can be reused up to seven times without significant loss of catalytic activity. They also applied this protocol in a reaction involving benzaldehyde and 4-methyl-3-oxo-*N*-phenylpentanamide, an important step in the synthesis of atorvastatin.

Similar dihydroxy ILs [DABCO-DOL][X] (**28–31**) were prepared from DABCO and 2-chloro-1,3-propandiol

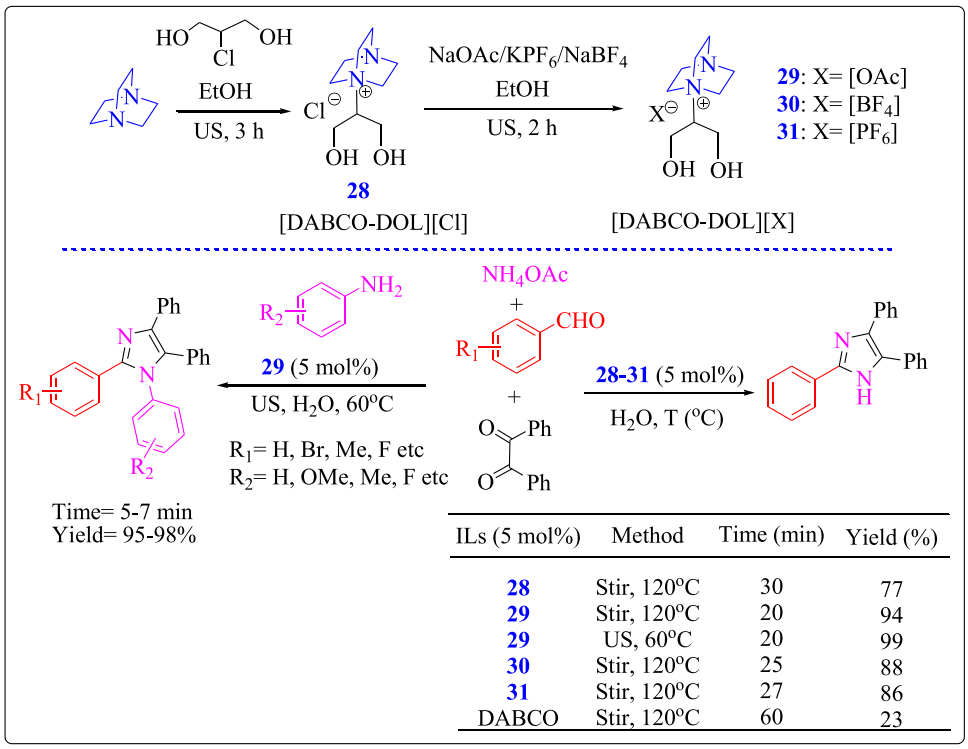
Scheme 5 [DABCO-PDO][X] ILs-catalyzed aza-Michael addition and Knoevenagel condensation



ILs	Time (min)	Yield (%)
DABCO	4	65
24	1	95
24	1.5	86
26	1.5	91
27	1.5	88

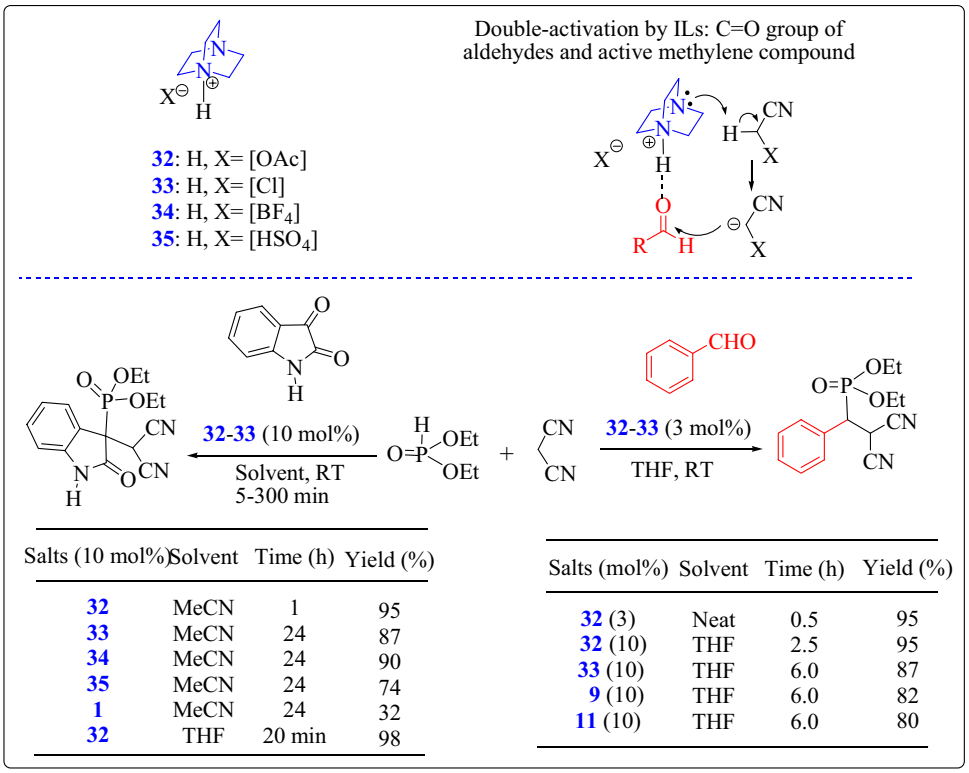
ILs	Time (min)	Yield (%)
24	3	96
25	10	82
26	10	86
27	30	85

Scheme 6 [DABCO-DOL][X] ILs-catalyzed synthesis of functionalized annulated imidazoles



ILs (5 mol%)	Method	Time (min)	Yield (%)
28	Stir, 120°C	30	77
29	Stir, 120°C	20	94
29	US, 60°C	20	99
30	Stir, 120°C	25	88
31	Stir, 120°C	27	86
DABCO	Stir, 120°C	60	23

Scheme 7 [H-DABCO][X] salts-catalyzed tandem Knoevenagel–Phospha-Michael reaction



Salts (10 mol%)	Solvent	Time (h)	Yield (%)
32	MeCN	1	95
33	MeCN	24	87
34	MeCN	24	90
35	MeCN	24	74
1	MeCN	24	32
32	THF	20 min	98

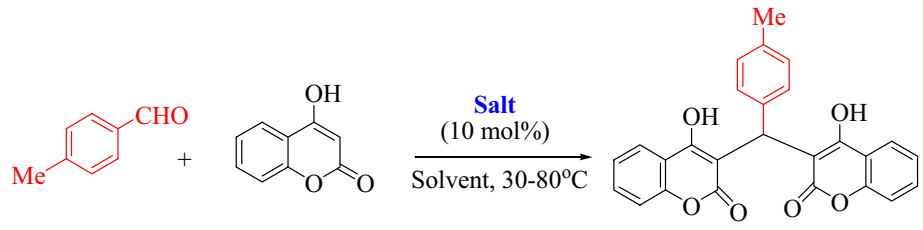
Salts (mol%)	Solvent	Time (h)	Yield (%)
32 (3)	Neat	0.5	95
32 (10)	THF	2.5	95
33 (10)	THF	6.0	87
9 (10)	THF	6.0	82
11 (10)	THF	6.0	80

followed by anion exchange with different salts (Ahmed Arafa et al. 2018). The acetate anion containing IL **29** (5 mol%) efficiently delivered functionalized annulated imidazoles under the sonochemical condition, via one-pot three-component reactions of benzil, various aryl aldehydes, and NH_4OAc in water at 60 °C with excellent yields (Scheme 6). They also explored the applicability of the **29** (5 mol%) for constructing the tri-substituted imidazoles via a one-pot, four-component reaction comprising benzil, aldehydes, substituted anilines, and NH_4OAc. The IL **29** showed at least seven times recyclability with negligible activity loss.

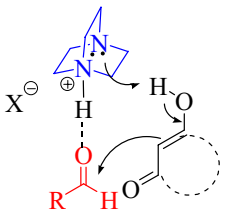
In continuation of their previous work on DABCO-based quaternary ammonium salts (QASs) for Michael addition and Knoevenagel condensation, Yu and coworkers reported a series of organic transformations using [H-DABCO][X] salts (**32–35**) under various reaction conditions. It was observed that the QAS [(H-DABCO][AcO] (**32**) showed excellent activity as compared to other salts. Initially, they used **32** and **33** salts to synthesize *β*-phosphonomalonates through a tandem Knoevenagel–Phospha-Michael reaction (Yu et al. 2015a, 2015b, 2015c) (Scheme 7). They found that compared to salts **9** and **11**, QAS **32** (3 mol%) was particularly effective in catalyzing the reaction between 4-methylbenzaldehyde, malononitrile, and diethyl phosphite in THF at RT. However, the **32** showed excellent activity in the one-pot synthesis of *α*-aminophosphonates by the reaction of aldehydes or ketones with amines and diethyl or triethyl phosphite in methanol at RT. In addition, the method is also extended for one-pot synthesis of 2-oxindol-3-ylphosphonates via tandem Knoevenagel–Phospha-Michael reactions (Song et al. 2017) of isatin/acenaphthenequinone, malononitrile, and diethyl phosphite (Scheme 7). The salt **32** (7 mol%) delivered the desired products with good to excellent yields at RT. The salt facilitates the double activation of the carbonyl group of aldehydes and malononitrile. The QAS **32** could be easily recovered and reused at least six to seven times for both reactions with consistent activity.

In a subsequent study, the same group used these salts for the synthesis of various bisphenols through a domino Knoevenagel–Michael reaction in aqueous media (Scheme 8) (Yang et al. 2016). It was observed that **32** (10 mol%) was highly efficient and reacted a wide range of aldehydes with enol compounds, such as 4-hydroxycoumarin, 2,4-dihydro-3H-pyrazol-3-one, cyclohexane-1,3-dione, Meldrum's acid, and 2-hydroxy-1,4-naphthoquinone (lawsone) in water at 80 °C. The salt **32** can be recycled five times without any loss in activity. These salts promote a typical domino reaction through double-activation, wherein the carbonyl group

Scheme 8 [DABCO-H][AcO]-catalyzed domino Knoevenagel–Michael reaction

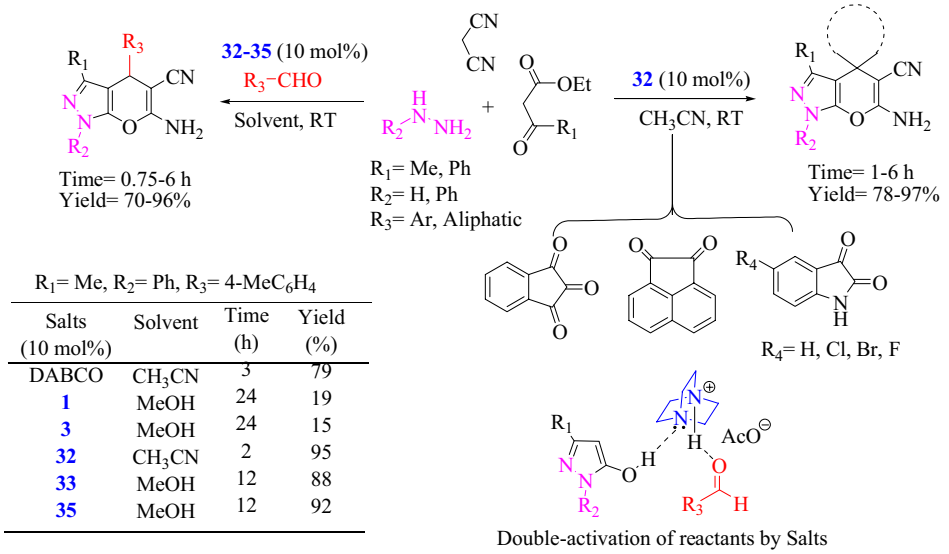


Double-activation of reactants by salt



Salt (10 mol%)	Solvent	T (°C)	Time (h)	Yield (%)
1	EtOH	30	4	88
3	EtOH	30	4	83
5	EtOH	30	4	71
9	EtOH	30	3	94
32	EtOH	30	4	95
33	EtOH	30	4	90
34	EtOH	30	4	85
32	Water	30	4	96
32	Water	80	0.25	96

Scheme 9 [DABCO-H][AcO] salt-catalyzed synthesis of pyrano[2,3-c]pyrazoles

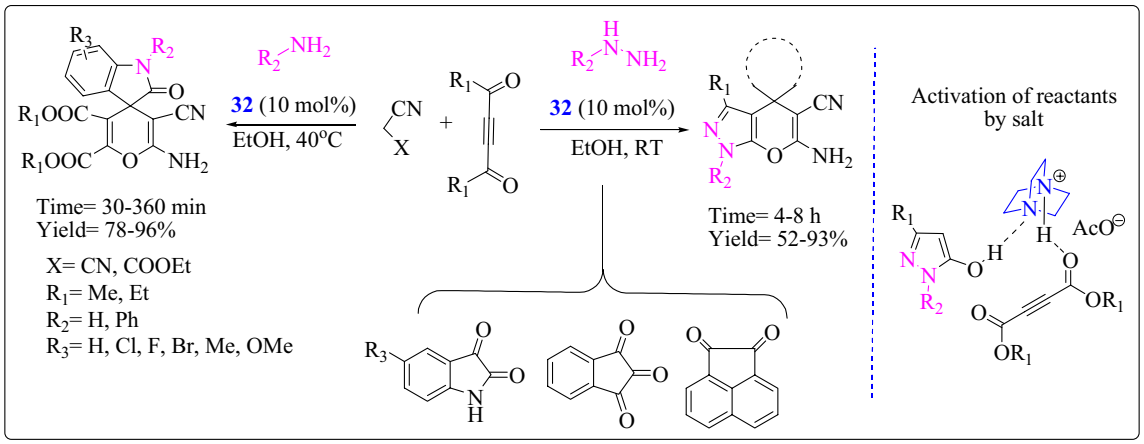


R1= Me, R2= Ph, R3= 4-MeC6H4

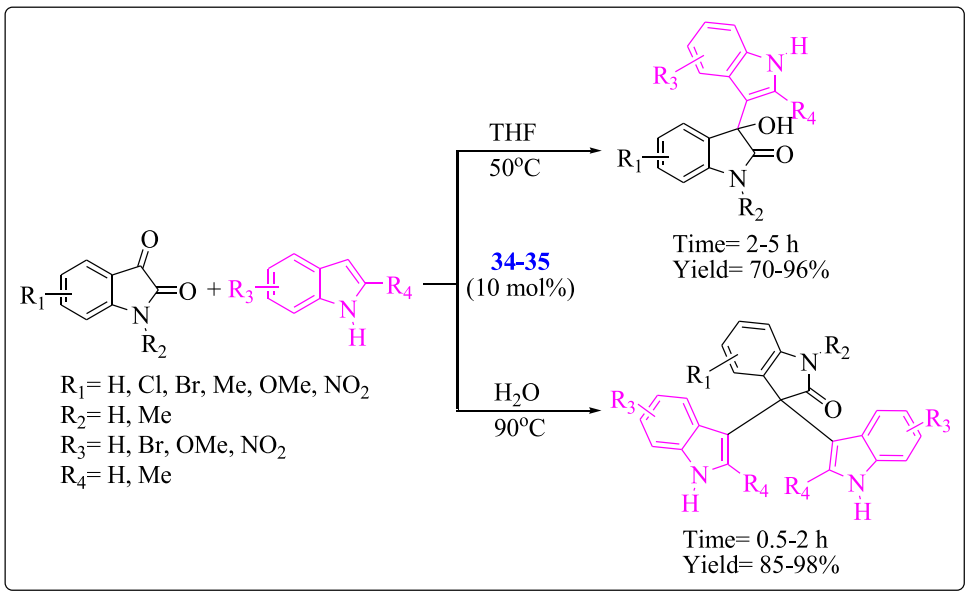
Salts (10 mol%)	Solvent	Time (h)	Yield (%)
DABCO	CH_3CN	3	79
1	MeOH	24	19
3	MeOH	24	15
32	CH_3CN	2	95
33	MeOH	12	88
35	MeOH	12	92

of aldehydes is activated by acidic hydrogen and enols by free nitrogen base to form a Knoevenagel adduct.

The same salt (**32**) (10 mol%) also served as an efficient catalyst for the synthesis of functionalized pyrano[2,3-c] pyrazoles through four-component reactions involving benzaldehydes, acetoacetates, phenylhydrazines, and malononitrile (Scheme 9) (Liu et al. 2017). It demonstrated excellent activity in acetonitrile at RT. Under the optimized conditions, the salts **32** showed superior activity in the four-component reaction of ethyl acetoacetate, phenylhydrazine, 4-methylbenzaldehyde, and malononitrile. The reaction starts with the formation of pyrazolone in which the tertiary nitrogen of salt abstracts hydrogen from pyrazolone. Meanwhile, the acidic hydrogen of the catalyst activates



Scheme 10 [DABCO-H][AcO] salt-catalyzed synthesis of spiro derivatives by 'single reactant replacement' method

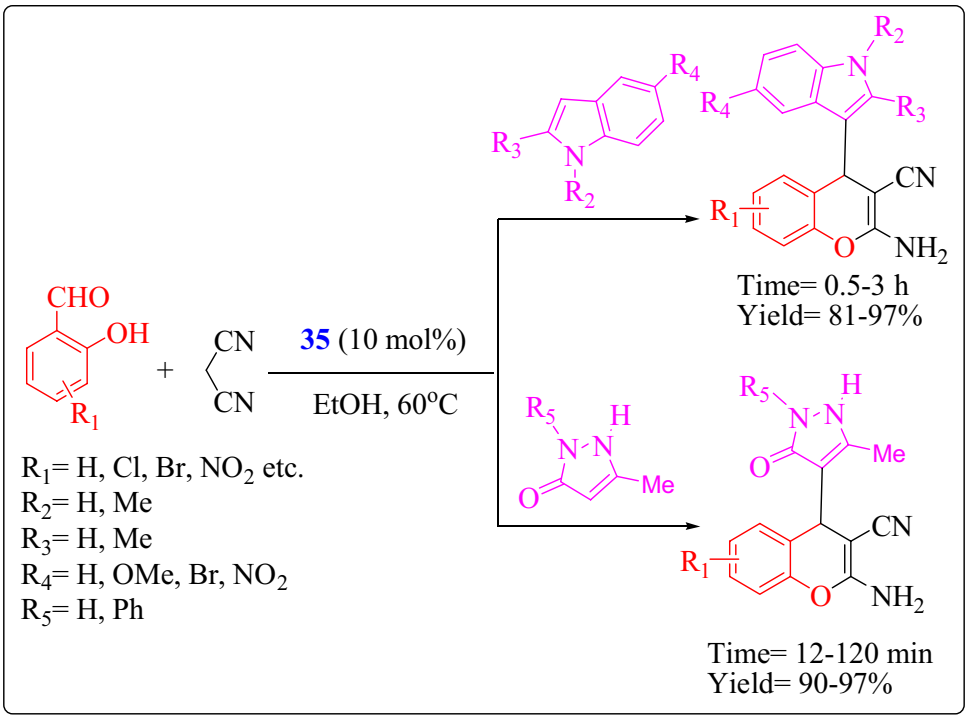


Scheme 11 [DABCO-H] salts of $[BF_4]$- and $[HSO_4]$-catalyzed synthesis of oxindoles via Friedel–Crafts reactions

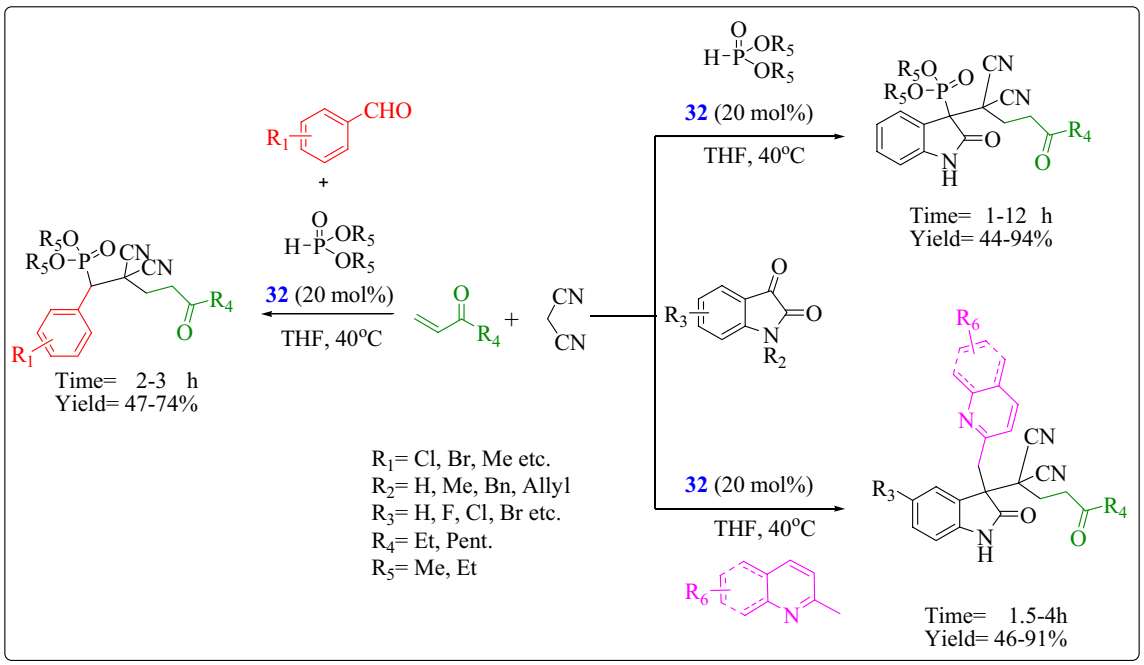
the carbonyl group and facilitates Knoevenagel condensation. The salt **32** can be recycled at least seven times with a decreased yield from 95 to 87%.

They also disclosed that the salt **32** acts as a highly efficient catalyst for the synthesis of spiropyrano[2,3-c] pyrazoles and spiro 1,4-dihydropyridines via the one-pot, four-component reactions by using the"single reactant replacement"method (Scheme 10) (Liu et al. 2018). The reaction of hydrazines, isatins, active methylenes, and dialkyl acetylenedicarboxylates afforded the desired spiro pyrano[2,3-c]pyrazoles in 78–96% yields. The aromatic amines delivered spiro 1,4-dihydropyridines in 52–93% yields. The salt **32** could be recycled at least five times. The catalyst activates dialkyl acetylenedicarboxylate, while free nitrogen of salt abstracts hydrogen from pyrazolone.

In a study conducted by Tong et al. (2017a, 2017b), a synthesis of 3-indolyl-3-hydroxy oxindoles and 3, 3-diindolyl oxindoles was carried out using **34–35** salts via Friedel–Crafts reactions (Scheme 11). The selectivity of the reaction is influenced by the type of solvent used. When THF was used as the solvent, the reaction resulted in the formation of a monoindolylation product of 3-indolyl-3-hydroxy oxindoles in 70–96% yields. On the other hand, when water was used as the solvent, only 3, 3-diindolyl oxindoles were obtained as the sole products in 85–98% yields at 90 °C. The salt could be reused at least five times to synthesize 3,3-diindolyl oxindole in good yields.



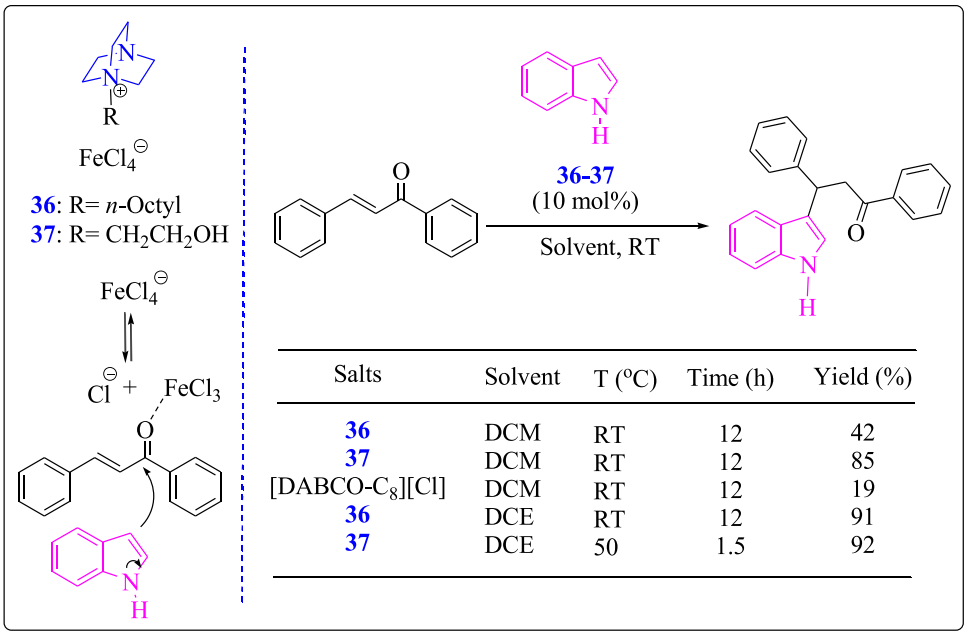
Scheme 12 [DABCO-H][HSO_4] salt-catalyzed synthesis of chromenes via a tandem Knoevenagel–Pinner cyclization–Michael reaction



Scheme 13 [DABCO-H][AcO] salt for a four-component reaction to create acyclic nitrile-substituted all-carbon quaternary centers

The salt **35** was also applied to Friedel–Crafts alkylation in the synthesis of different bis(naphthol)methane and bis(indolyl)methane derivatives (Tong et al. 2016). The salt **35** (10 mol%) delivered the desired products under solvent-free conditions with good to excellent yields in short times at 90 °C and can be recycled at least six times with decreased yield from 97 to 90%. In continuation with this, an efficient method for the construction of

Scheme 14 [DABCO-C_8][$FeCl_4$] salt-catalyzed direct Friedel–Crafts–Michael-type C_3 alkylations



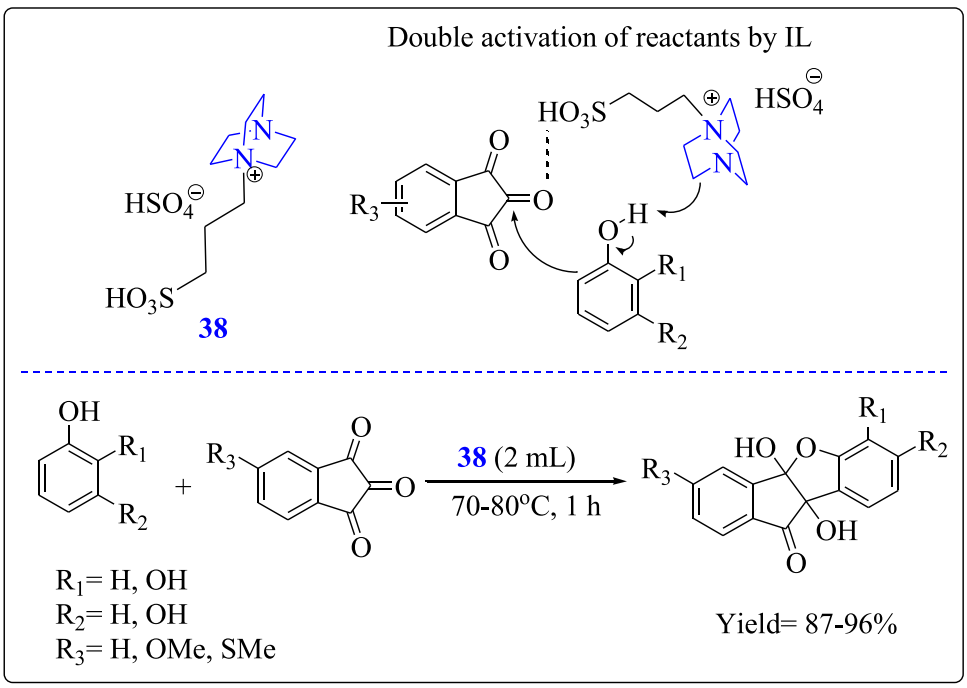
Salts	Solvent	T (°C)	Time (h)	Yield (%)
36	DCM	RT	12	42
37	DCM	RT	12	85
[DABCO-C_8][Cl]	DCM	RT	12	19
36	DCE	RT	12	91
37	DCE	50	1.5	92

2-amino-4-(indol-3-yl)−4*H*-chromenes and 2-amino-4-(pyrazol-4-yl)−4*H*-chromenes via a tandem Knoevenagel–Pinner cyclization–Michael reaction has been developed using **35** (Scheme 12) (Li et al. 2018). The desired products were obtained in 81–97% yields in EtOH at 60 °C within short reaction times and can be reused at least seven times without significant loss in activity.

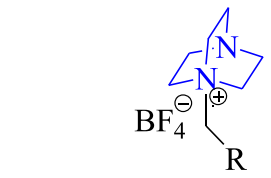
Hu et al. (2022) recently utilized salt **32** in a four-component reaction to create acyclic nitrile-substituted all-carbon quaternary centers (Scheme 13). The **32** (20 mol%) effectively facilitated the reaction with a variety of substrates such as isatins, aromatic aldehydes, malononitrile, phosphites, and enones in THF at 40 °C. Many of the resulting compounds exhibited significant antifungal activity against specific fungi *Magnaporthe oryzae* and *Sclerotinia sclerotiorum*.

A magnetically separable and recyclable ionic salts, [C_8-DABCO][$FeCl_4$] (**36**) and [DABCO-CH_2CH_2OH][$FeCl_4$] (**37**) was reported for direct Friedel–Crafts–Michael–type C_3 alkylation of indoles with

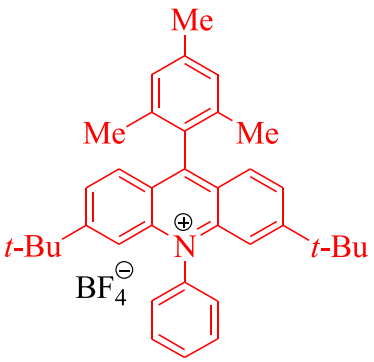
Scheme 15 Synthesis of indeno-benzofurans using acidic [DABCO-$C_3H_6SO_3H$][HSO_4] ionic salt



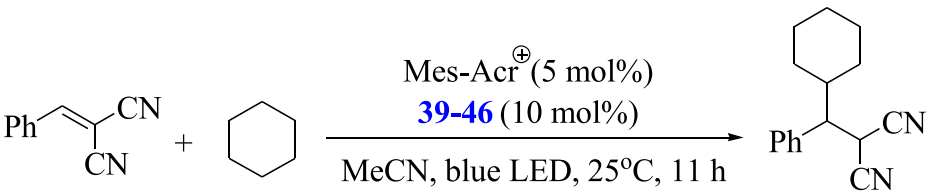
Scheme 16 Hydrogen atom transfer (HAT) catalysts containing cationic DABCO salts



39: R= Cl
40: R= C_6H_5
41: R= 4-$OMeC_6H_4$
42: R= 3,5-$OMe_2C_6H_3$
43: R= 4-$CF_3C_6H_4$
44: R= 3,5-$(CF_3)_2C_6H_3$
45: R= 4-PhC_6H_4
46: R= 1-Naphthyl



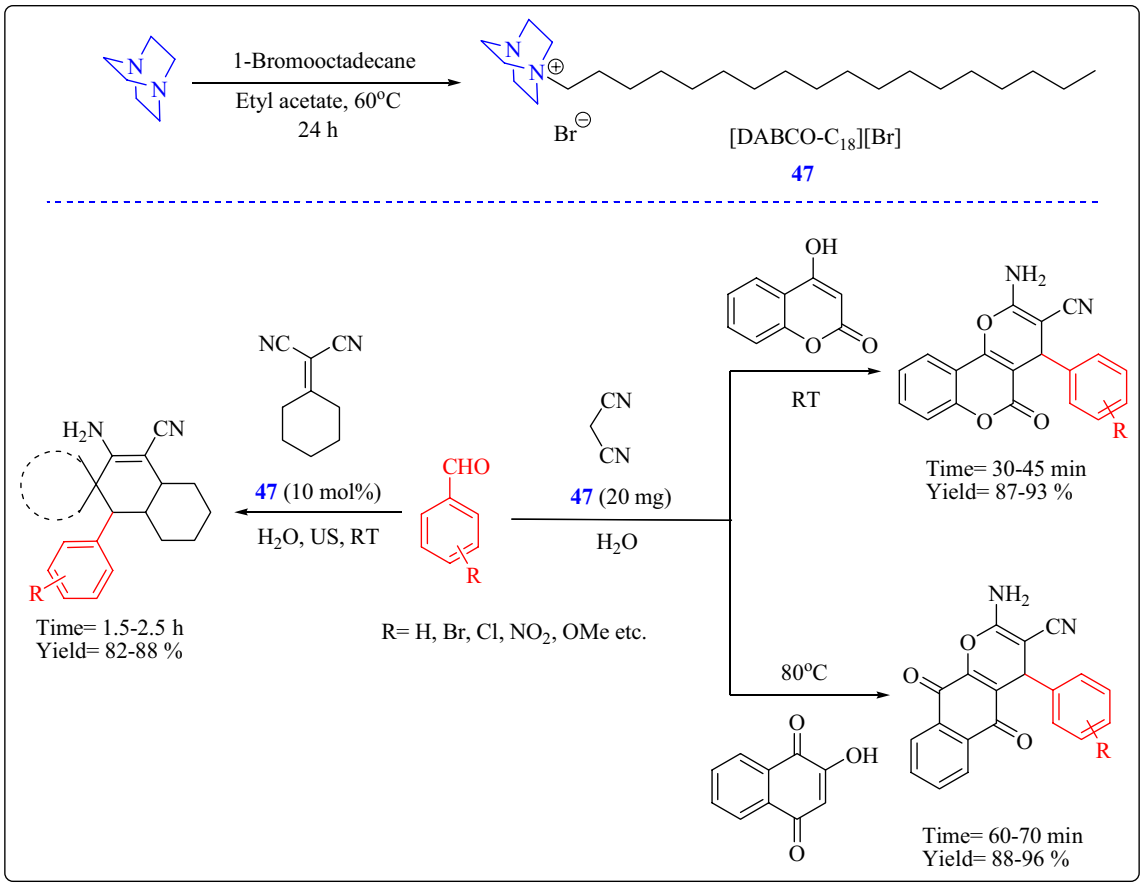
Mes-Acr$^{\ominus}$



Salts	Conversion (%)	Yield (%)
39	17	14
40	42	34
41	99	93
42	9	9
43	43	35
44	24	24
45	99	89
46	99	95

electron-deficient olefins such as chalcones, enones, and nitro-olefins (Su and Xu 2017). The magnetic salts were prepared by mixing corresponding Cl salts with $FeCl_3$ in methanol at RT. The salts were characterized by Raman spectroscopy. The salt **37** (10 mol%) was more efficient than **36** for the reaction of indole and chalcone (Scheme 14). Thus, salt **37** produced the corresponding 3-alkyl indole derivatives in good to excellent yields within short periods and can be recycled four times with minimal loss of activity. Additionally, the Lewis acid $FeCl_3$, a product of the reversible reaction of $[FeCl_4]^-$, activates the carbonyl group of enone through the coordination of the carbonyl oxygen to the Fe(III) center.

A simple and effective method for the synthesis of indeno-benzofurans by reacting polyphenols and ninhydrins is explored by using a DABCO-based acidic ionic salt [DABCO-$C_3H_6SO_3H$][HSO_4] (**38**) (Scheme 15) (Saqa et al. 2022). Salt **38** was synthesized according to the Menshutkin reaction (Sola et al 1991) from DABCO and 1,3-propane sultone in toluene at 75 °C followed by the addition of H_2SO_4 in DCM. The white salt having mp 148–151 °C was confirmed by using ^{1}H NMR, ^{13}C NMR,

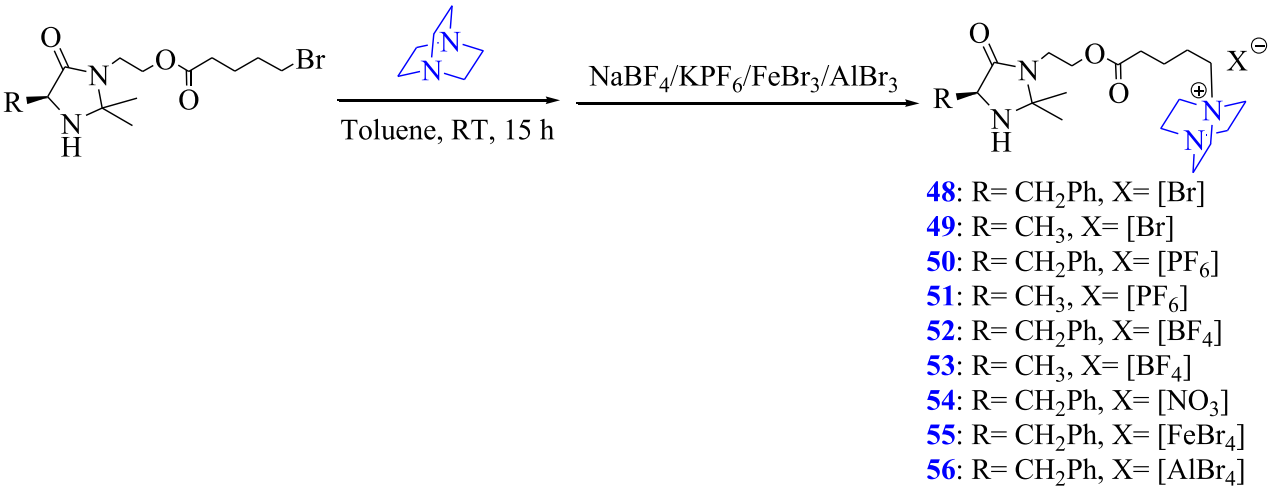


Scheme 17 [DABCO-C_{18}][Br] ionic salt-catalyzed synthesis of spiro carbocycles, dihydropyrano [3,2-c]chromenes and 4-hydroxycoumarins

and mass spectroscopy. These derivatives were also investigated for antioxidant and antidiabetic activities. Though these compounds were synthesized without catalysts, the yields of the products were very low; however, with **38**, the yields are excellent in short reaction times. Here salt **38** activates the carbonyl group of ninhydrin and free nitrogen of DABCO or HSO_3^- facilitating the nucleophilic attack of phenol on carbonyl carbon.

A new type of hydrogen atom transfer (HAT) catalysts (**39–46**) containing cationic DABCO has been developed by Matsumoto et al. (2022). The ability of photoinduced HAT catalysis was demonstrated using an acridinium-based organic photo redox catalyst in the selective C–H alkylation of inactivated hydrocarbons to produce complex molecules (Scheme 16). The substituents adjacent to a nitrogen atom in the HAT catalyst further improved the selectivity in degassed MeCN under light irradiation (blue LED, 448 nm) at 25 °C. Ionic salt **46** showed excellent activity as compared to other salts. Mechanistic studies suggested that the N-substituent of the catalyst plays a crucial role by assisting in the generation of a dicationic aminium radical as an active species for the HAT process.

Recently, our group synthesized a [DABCO-C_{18}][Br] salt (**47**) which is a monoquaternized octadecyl-1,4-diazabicyclo[2.2.2]octane bromide (Scheme 17). It has good surfactant properties as its critical micelle concentration (CMC) is ~ 1.0 mM (Buettner et al. 2022). We also studied the catalytic efficiency of **47**, a tertiary base surfactant, for the synthesis of spiro carbocycles in water under ultrasonic conditions (Lohar et al. 2019) and dihydropyrano [3,2-c] chromenes via one-pot three-component reactions involving aromatic aldehydes, malononitrile, and 4-hydroxycoumarin in water at RT (Rajmane et al. 2023). The method was also extended for synthesizing 2-aminobenzochromenes via one-pot three-component reactions of aromatic aldehydes, malononitrile, and lawsone in water at 80 °C. All the products were obtained with good to excellent yields in 30–60 min. In addition, the aqueous solution with **47** was reused up to four times with a minor reduction in product output. The protocol is fast, energy-efficient, and can be used on a large

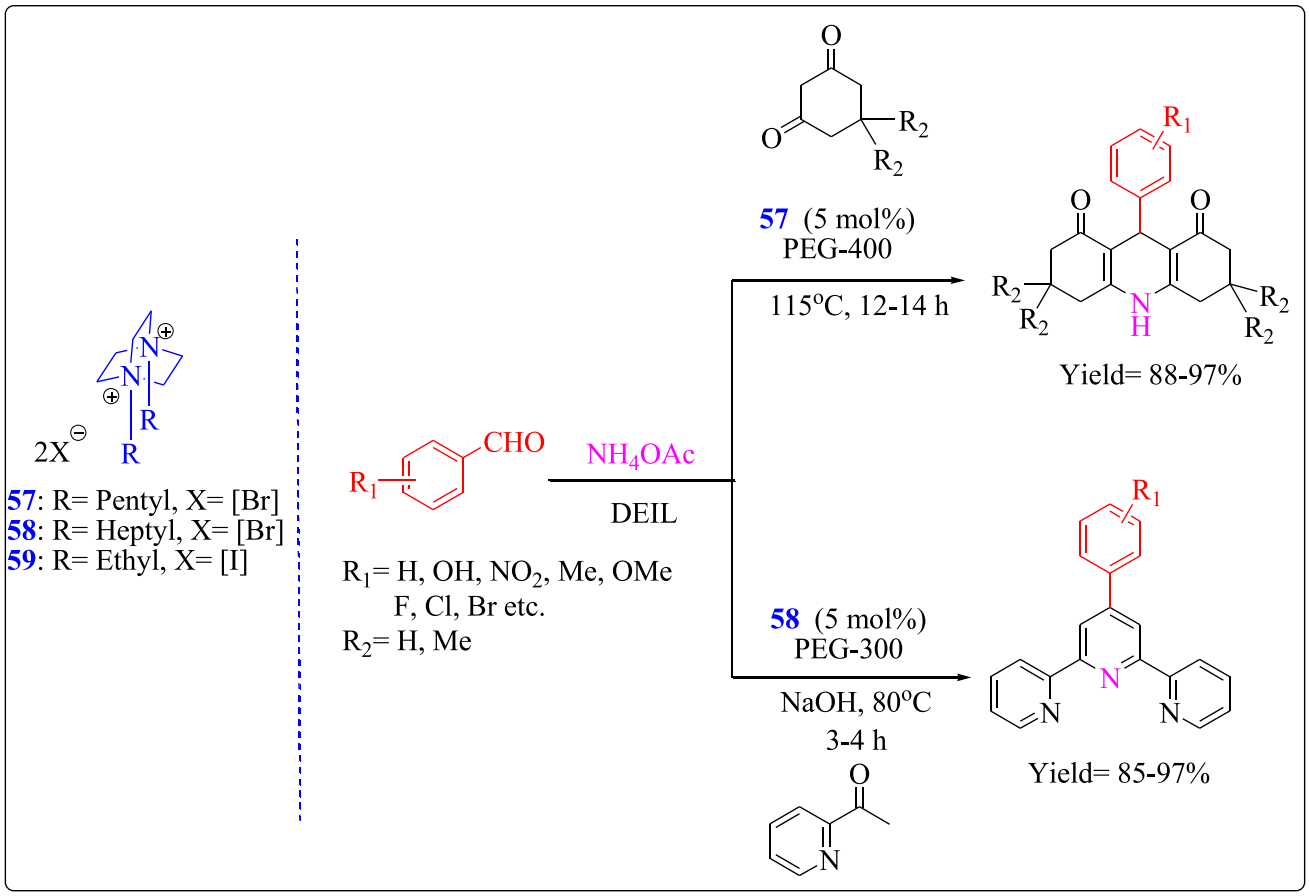


ILs (5 mol%)	Conv. (%)	*exo/endo*	*ee* (%) *endo*
48	78	1/1.1	82
49	16	1/1.1	36
50	94	1/1.2	86
51	24	1/1.0	37
52	80	1/1.2	81
53	36	1/1.2	37
54	91	1/1.1	85
55	78	1/0.9	15
56	55	1/1.2	36

Scheme 18 DABCO-based chiral ILs for asymmetric Diels–Alder reaction

scale for synthetic purposes. Additionally, it boasts impressive environmentally friendly credentials.

Recently, DABCO-based chiral ILs modified with MacMillan catalyst (**48–56**) were reported for asymmetric Diels–Alder reaction (Scheme 18) (Alam et al. 2022). The catalysts were synthesized by a reaction of bromo esters obtained from (*L*)-phenylalanine, (*L*)-alanine, and DABCO in toluene at RT, followed by anion exchange with different anions with good yields. The ILs were evaluated in asymmetric Diels–Alder reaction of cyclopentadiene with *α,β*-unsaturated aldehydes or 4-phenyl-3-buten-2-one. The ILs modified with MacMillan catalyst having a DABCO cation and hexafluorophosphate anion (**50**) (5 mol%) act as an excellent organocatalyst for the Diels–Alder reaction of crotonaldehyde and cyclopentadiene in the presence of CF_3COOH (5 mol%), in CH_3CN:H_2O (95:5) mixture at 25 °C in 2 h. The CF_3COOH acts as a Brønsted acidic cocatalyst as it increases the reactivity and stereoselectivity by stabilizing the conformation of iminium ions formed by the reaction of IL and crotonaldehyde. The free tertiary N atom of DABCO can be quaternized by CF_3COOH, which increases catalyst activity with an increased reaction rate. The scope and limitations of the catalysis were also studied using cyclopentadiene and *α,β*-unsaturated aldehydes, and the Diels–Alder products were obtained in 18–92% yields with 68–93% *ee*. The catalyst was recycled and reused for up to six cycles with a slight drop in *ee* (87–79%) and product yield (98–63%).



Scheme 19 DABCO-PEG DEIL for synthesis of diverse heterocycles

Applications of dicationic DABCO ionic salts (DDIS) in multi-component reactions

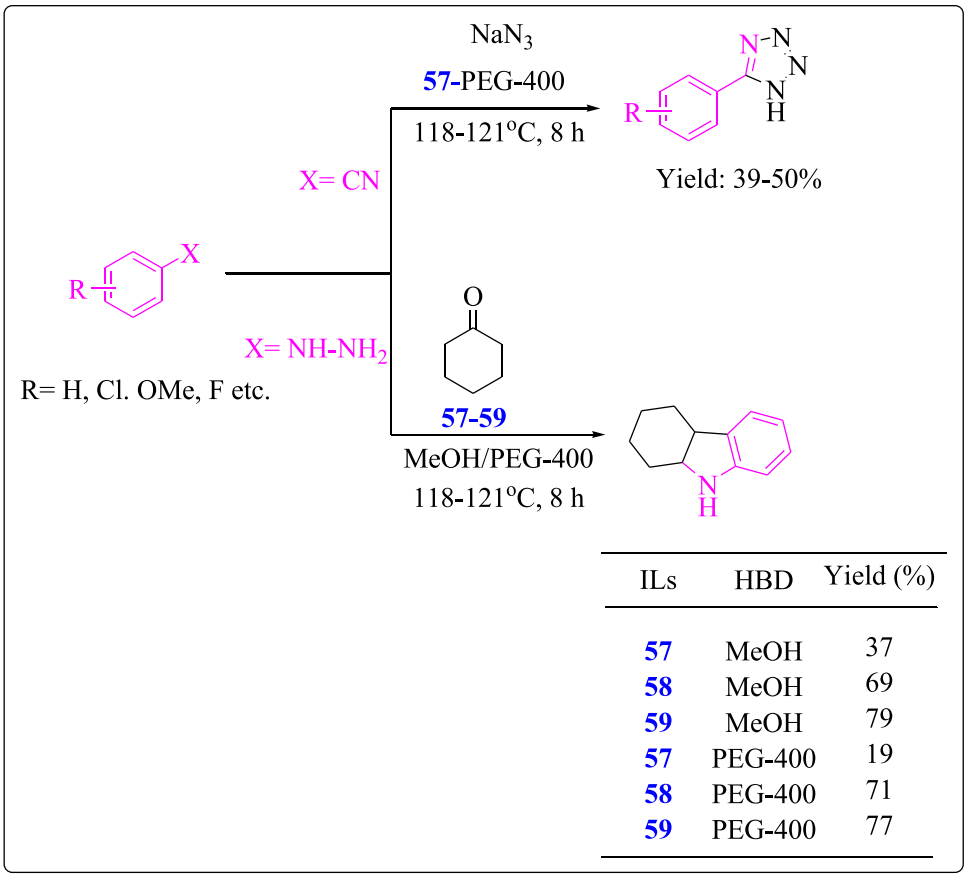
Various diquaternized DABCO salts were developed for different organic transformations. Typically, these salts act as powerful Brønsted acids and catalyze different acid-catalyzed multi-component reactions.

Faisal and coworkers developed deep eutectic ionic liquids (DEILs) systems of methanol or polyethylene glycol (PEG) based on DABCO-derived quaternary ammonium salts for various organic synthesis. They synthesized DABCO–PEG-400 DEIL by heating DABCO-IL (**57**) with PEG-400 or MeOH as a hydrogen bond donor (HBD) (Faisal et al. 2018). This DEIL showed good activity in synthesizing acridine analogous via a three-component reaction of aromatic aldehydes, dimedone, and NH_4OAc at 115–116 °C (Scheme 19).

Similarly, the DEIL containing **58** and PEG-300 showed excellent activity in the synthesis of terpyridines through Kröhnke reaction at 80 °C (Faisal et al. 2019) (Scheme 19). The formation of deep eutectic solvent was confirmed by freezing point depression, and composition through phase diagram. The results show that various terpyridines can be obtained in reasonable yields (85–97%) by the one-pot reaction of 2-, 3- or 4-acetylpyridine with a variety of aromatic aldehydes in the presence of DEIL as a reaction medium, NaOH as a base and NH_4OAc as a cyclizing agent. Importantly, these DEILs can be reused several times without appreciable loss of catalytic activity.

In connection with this, recently Ezaz and coworkers (2024) used a **57**-PEG-400 catalytic system for the synthesis of flavanone derivatives in the presence of K_2CO_3 at 115–125 °C. The **57**-PEG-400 delivered the target flavanone such as 2-(4-isobutylphenyl)chroman-4-one with high yields. In addition, they carried out in silico studies of synthesized compounds with proteins ribonucleotide reductase and tyrosinase and exhibit good binding

Scheme 20 DABCO-PEG-400 DEIL for the synthesis of diverse heterocycles



ILs	HBD	Yield (%)
57	MeOH	37
58	MeOH	69
59	MeOH	79
57	PEG-400	19
58	PEG-400	71
59	PEG-400	77

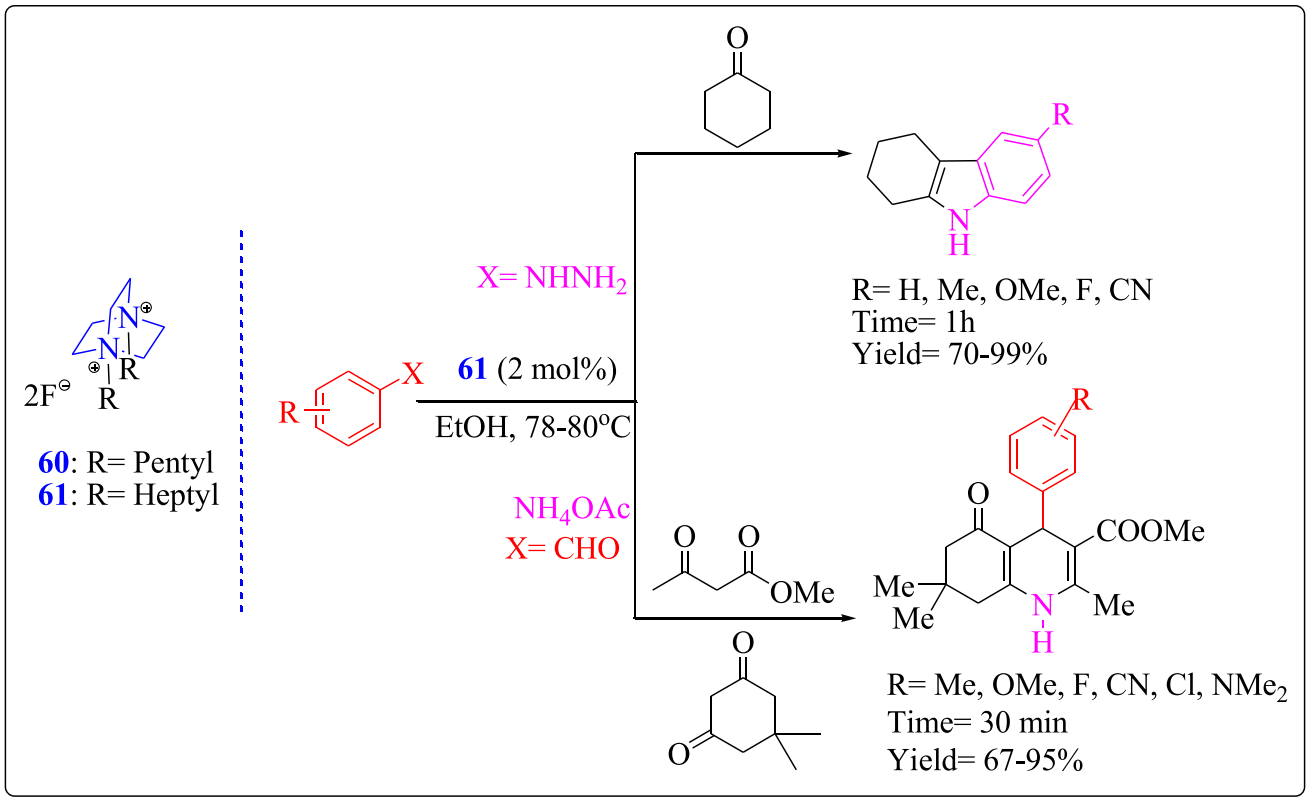
energies. The ILs activate aldehyde/ketone that undergoes the Claisen–Schmidt condensation reaction followed by intramolecular Michael addition.

The **57–59** DEIL were also successfully employed to synthesize various indoles by Fischer indole synthesis and 1*H*-tetrazoles by click chemistry (Scheme 20) (Ali Ghumro et al. 2017). Though comparable yields were observed in alcohols and PEGs, the use of PEG in DES is a much safer, non-volatile, and environmentally friendly reaction medium than alcohols. However, the **57**-PEG-400 showed moderate activity in the synthesis of 1*H*-tetrazoles.

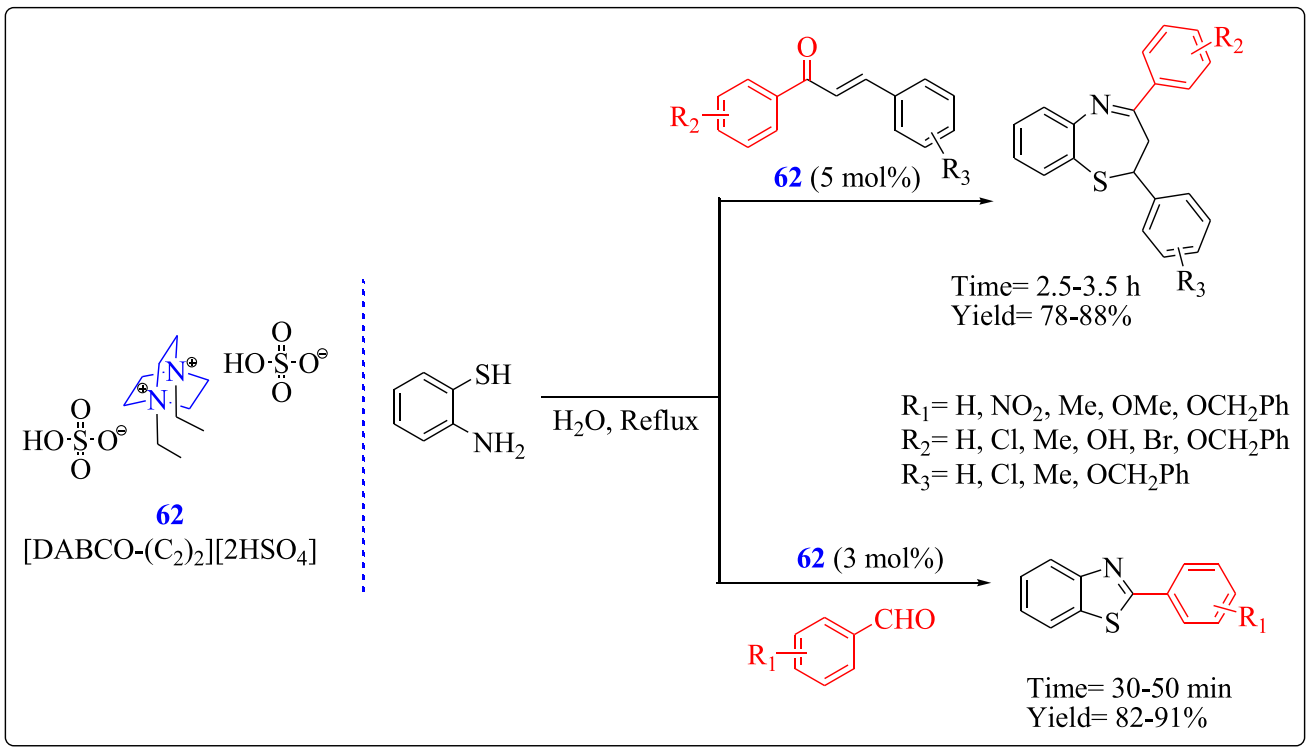
Ishtiaq and coworkers synthesized [$C_{5\text{-}7}$-DABCO-$C_{5\text{-}7}$][2F] ionic salts (**60–61**) (Scheme 21) (Ishtiaq et al. 2022). The preparation of salts involves the first quaternization of DABCO with *n*-pentyl or *n*-heptyl bromide followed by ion exchange of Br by F using AgF. Quantum mechanical calculations were performed to find the optimized geometry configuration of ILs. Their stability was evaluated via binding energy calculation obtained from the MP2 method. Salt **61** was better than salt **60** in terms of yield for the Fischer indolization reaction utilizing cyclohexanone in EtOH at 78–80 °C. The salt **61** showed good to excellent efficiency in the synthesis of various indoles and 1,4-dihydropyridines.

Recently, Pinate and Makone (2022) synthesized [DABCO-$(C_2)_2$][2HSO_4] DDIL (**62**) synthesized from bromoethane and DABCO in DCM followed a reaction with H_2SO_4 (70%) in diethyl ether at 0 °C. Salt **62** was successfully utilized for the synthesis of 2,3-dihydro-1,5-benzothiazepine and 2-phenylbenzothiazole derivatives in water at reflux with good to excellent yields (Scheme 22). Moreover, the IL displays five times recyclability without a considerable loss in activity.

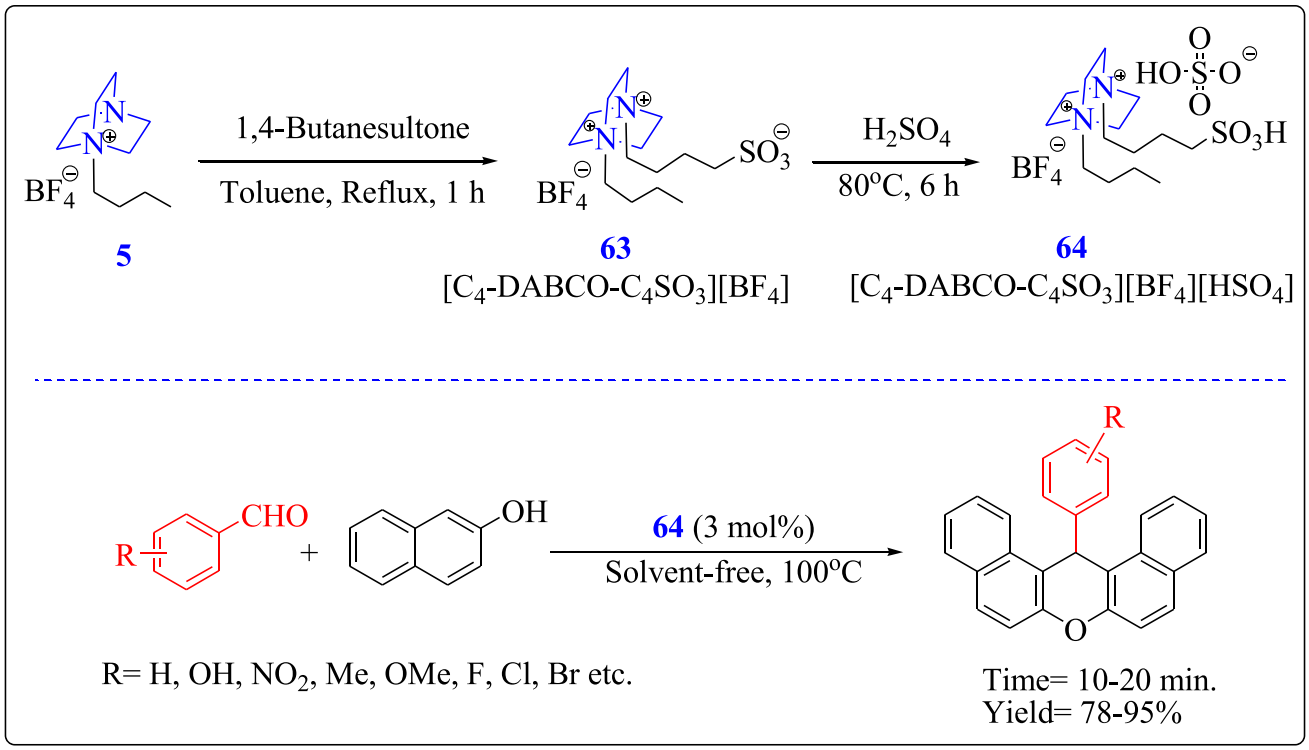
A Brønsted acidic RTIL was efficiently synthesized from [C_4-DABCO][BF_4] (**5**) and 1,4-butane sultone in toluene under reflux to form the zwitterion, [C_4-DABCO-C_4SO_3][BF_4] (**63**). This zwitterion was then treated with a stoichiometric amount of concentrated H_2SO_4 (98%) at 80 °C, resulting in the formation of viscous clear [C_4-DABCO-C_4SO_3H][BF_4][HSO_4] (**64**) IL (Zare-Bidaki et al. 2012). The IL **64** efficiently catalyzed the synthesis of 14-aryl-14*H*-dibenzo[a,j]xanthenes at 100 °C under solvent-free conditions with good to excellent yields (Scheme 23). Furthermore, the



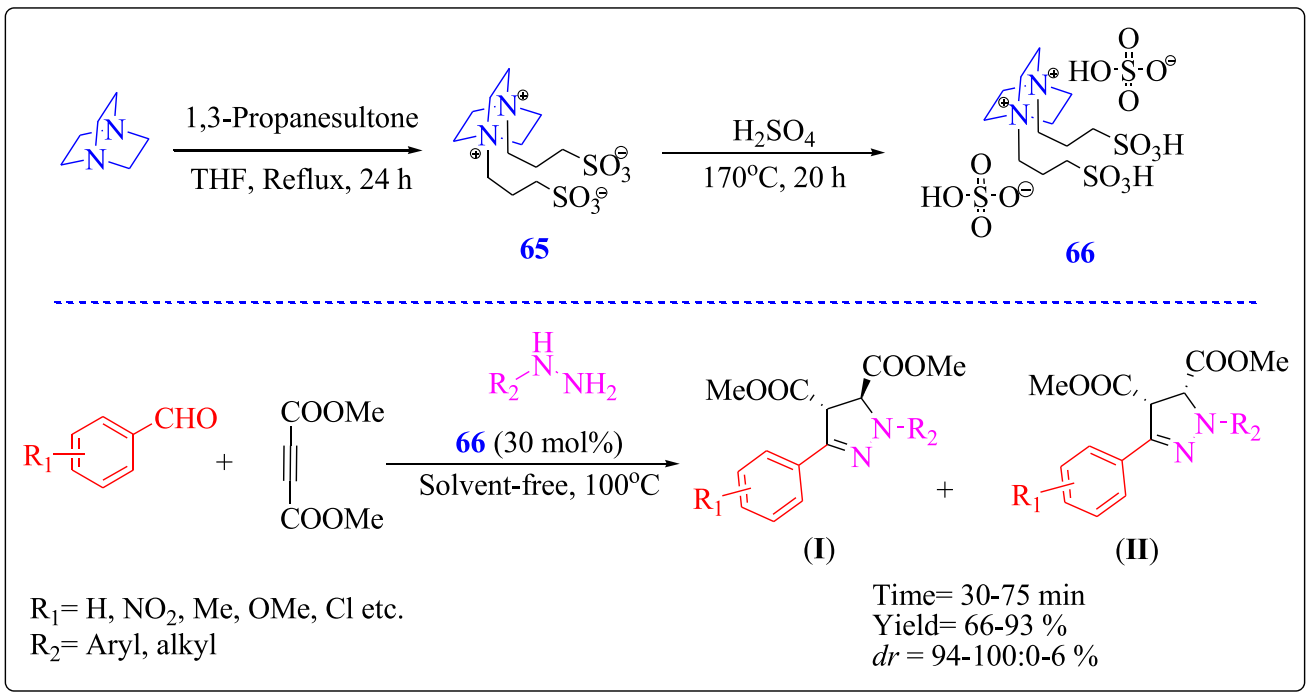
Scheme 21 [R-DABCO-R][2F] ILs-catalyzed synthesis of 1,4-dihydropyridines



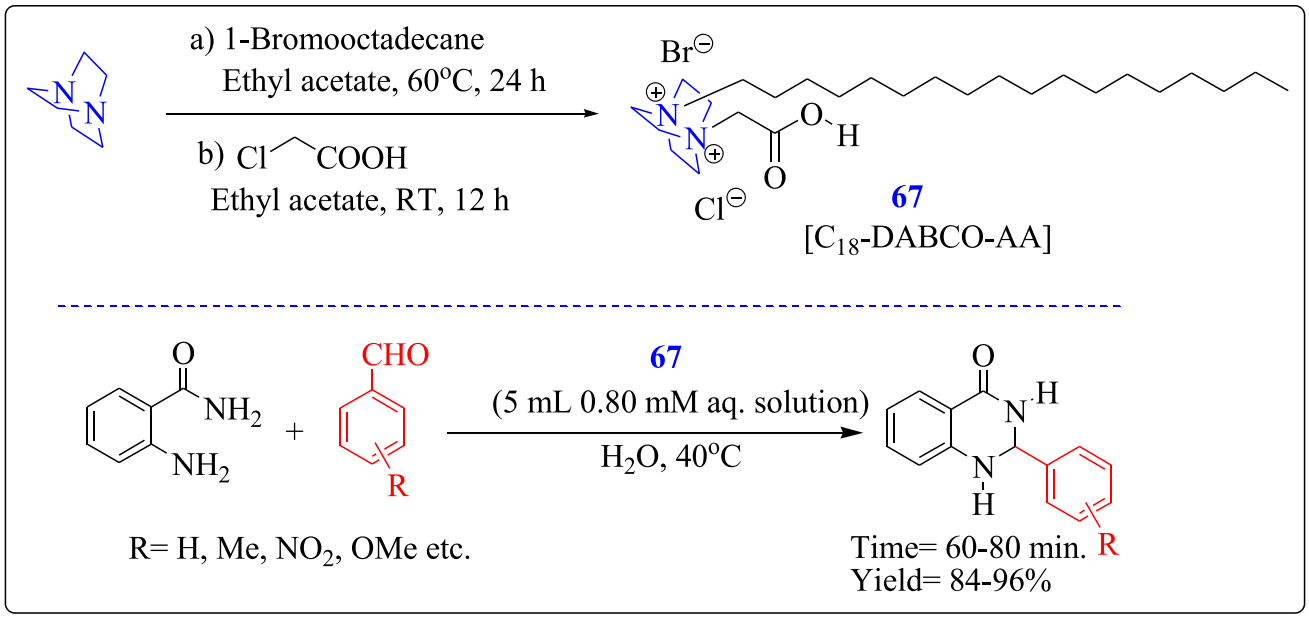
Scheme 22 [DABCO-$(C_2)_2$][$2HSO_4$] DDIL for the synthesis of benzothiazepine and benzothiazoles



Scheme 23 $[C_4\text{-DABCO-}C_4SO_3][BF_4]$ IL-catalyzed synthesis of xanthenes



Scheme 24 Diastereoselective synthesis of pyrazolines using a DABCO Brønsted acidic IL



Scheme 25 [C_{18}-DABCO-AA] salt-catalyzed synthesis of 2,3-dihydroquinazolin–4(1*H*)-ones

catalyst can be recovered and reused three times with only slightly reduced catalytic activity.

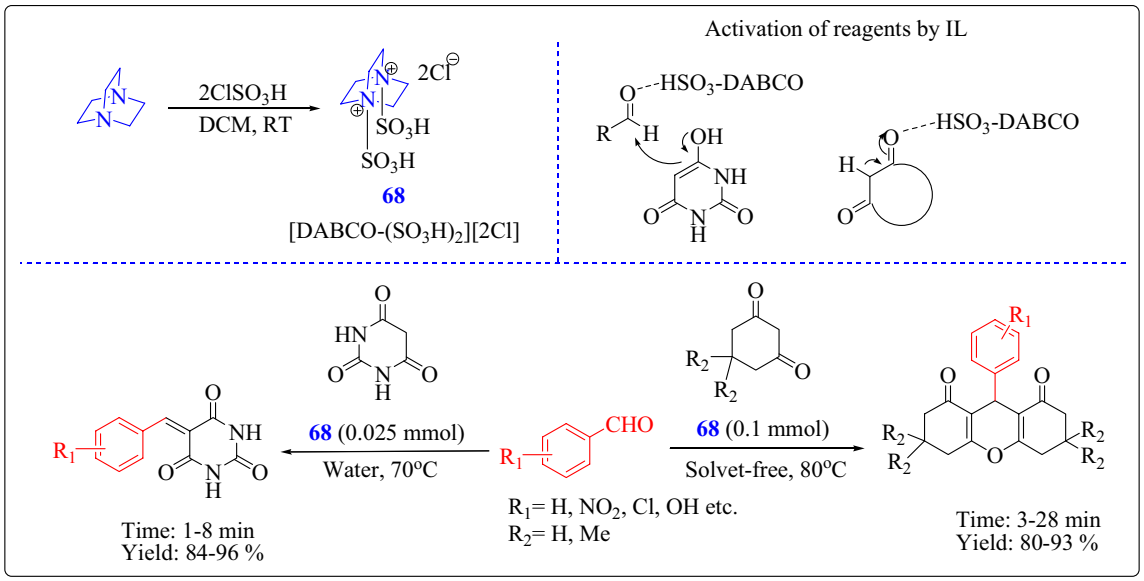
Similarly, Safaei et al. (2012) reported the diastereoselective synthesis of pyrazolines via a three-component reaction of aldehydes, hydrazines, and dimethyl acetylenedicarboxylate (DMAD) using a Brønsted acidic IL (**66**) as a reusable catalyst under solvent-free conditions (Scheme 24). The **66** was prepared by reacting DABCO with 1,3-propane sultone in THF to produce a white solid zwitterion (**65**) followed by treatment with sulfuric acid. The desired pyrazolines were obtained in high yields with excellent diastereomeric excess.

Recently, we have successfully synthesized a new acidic salt [C_{18}-DABCO-AA] (**67**), which contains octadecyl and acetic acid substituents on the DABCO unit, with an excellent yield (Rajmane et al 2024). The synthesized salt was analyzed using FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopic techniques. Its thermal behavior was analyzed by using the TGA–DTA technique. The synthesized salt has excellent surfactant properties having a critical micelle concentration (CMC) of 0.80 mM as determined by the conductivity method and UV–vis absorption measurement. Salt also showed strong acidic properties with a *p*Ka of 3.3. It was the best catalyst for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones (DHQs) in water at a CMC concentration (0.80 mM) of **64** at 40 °C (Scheme 25). Additionally, the aqueous solution containing **64** was reused up to five times with a minor decrease in product yield.

Shirini and coworkers developed the acidic ionic salt called 1,4-disulfo-1,4-diazabicyclo[2.2.2]octane-1,4-diium dichloride [DABCO-$(SO_3H)_2$][2Cl] (**68**) (Shirini et al. 2015). The white salt (mp = 75 °C) of **68** was synthesized by treatment of DABCO with chlorosulfonic acid in dry DCM at RT (Scheme 26). This IL acts as a mild and efficient catalyst for the synthesis of 1,8-dioxo-octahydro-xanthene under solvent-free conditions at 70 °C as well as the synthesis of 5-arylmethylene-pyrimidine-2,4,6-triones in water at 70 °C. The IL showed at least six times reusability in the synthesis of 5-arylmethylene-pyrimidine-2,4,6-trione and four times reusability in the synthesis of 1,8-dioxo-octahydro-xanthene derivative of 4-chlorobenzaldehyde.

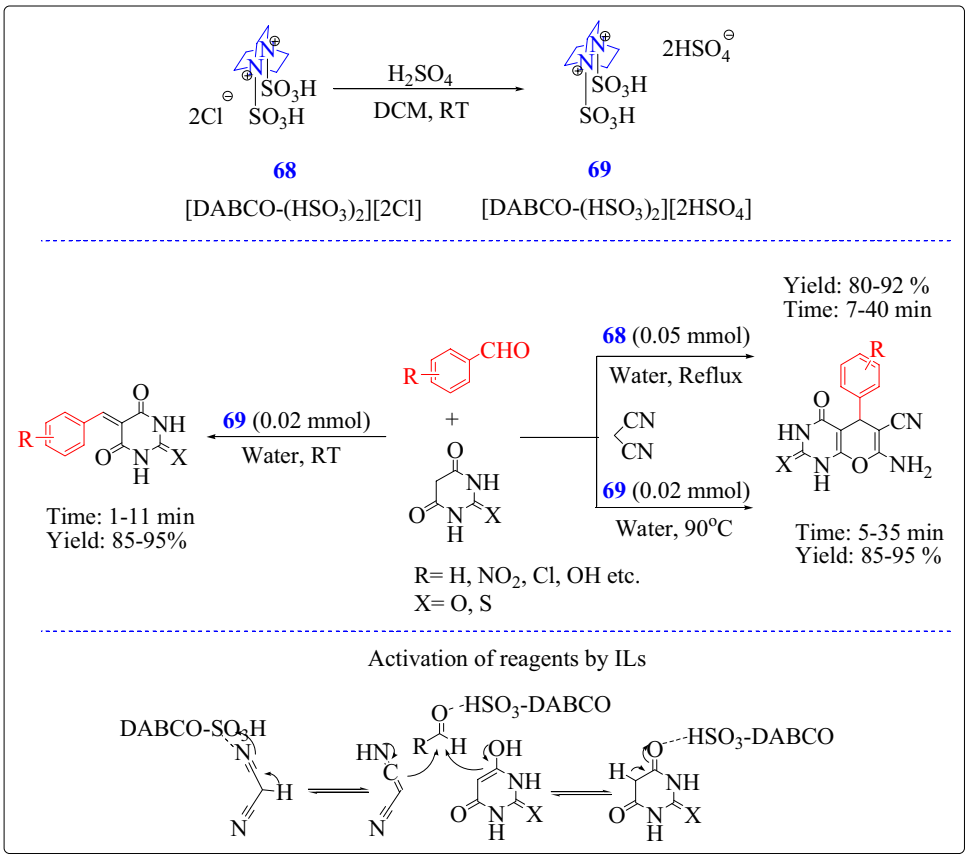
As an extension, a new and straightforward method for synthesizing 5-arylamine barbituric and thiobarbituric acids via Knoevenagel condensation using 1,4-disulfo-1,4-diazabicyclo[2.2.2]octane-1,4-diium dihydrogen sulfate ([DABCO-$(SO_3H)_2$][2HSO_4] (**69**) was reported by same group (Scheme 27) (Seyyedi et al. 2016). The white salt (mp = 70 °C) was synthesized by treating [DABCO-$(SO_3H)_2$][2Cl] (**68**) with sulfuric acid in DCM. The same IL was also used in the preparation of pyrano[2,3-d]-pyrimidinediones via a three-component reaction involving aldehydes, barbituric/thiobarbituric acid, and malononitrile in water at RT. The IL used in both reactions can be recycled multiple times. In this reaction, the acidic part of IL activates the malononitrile/barbituric acid by protonating the N/C = O groups, enabling it to attack the activated aldehyde effectively.

In continuation with this, they also reported a simple and convenient method for the synthesis of [1,2,4]triazolo/benzimidazolo quinazolinone and [1,2,4]triazolo[1,5-*a*] pyrimidine derivatives using **68** and **69** under solvent-free conditions at 100 °C (Scheme 28) (Seyyedi et al. 2017). The ILs delivered a variety of [1,2,4]triazolo/benzimidazolo



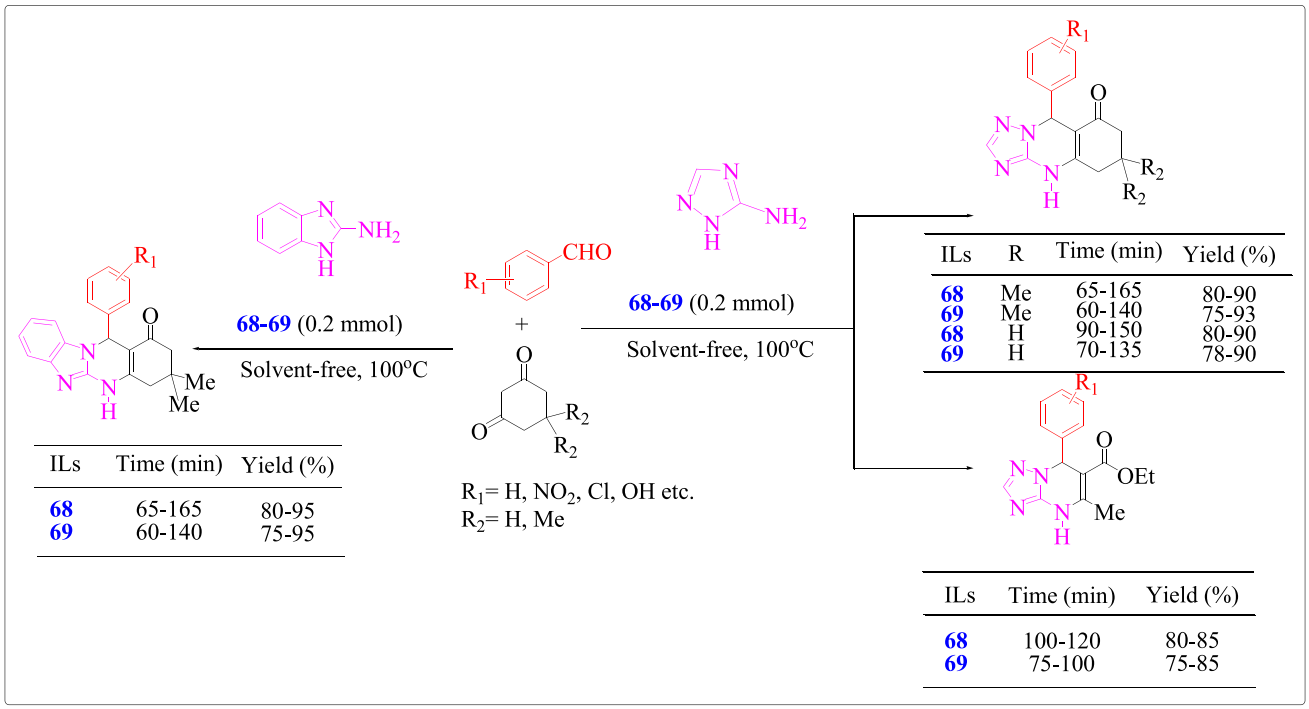
Scheme 26 [DABCO-$(SO_3H)_2$][2Cl] IL for the synthesis of 5-arylmethylene-pyrimidine-2,4,6-triones and 1,8-dioxo-octahydro-xanthenes

Scheme 27 [DABCO-$(HSO_3)_2$][$2HSO_4$] for the synthesis of pyrano[2,3-d]-pyrimidinediones

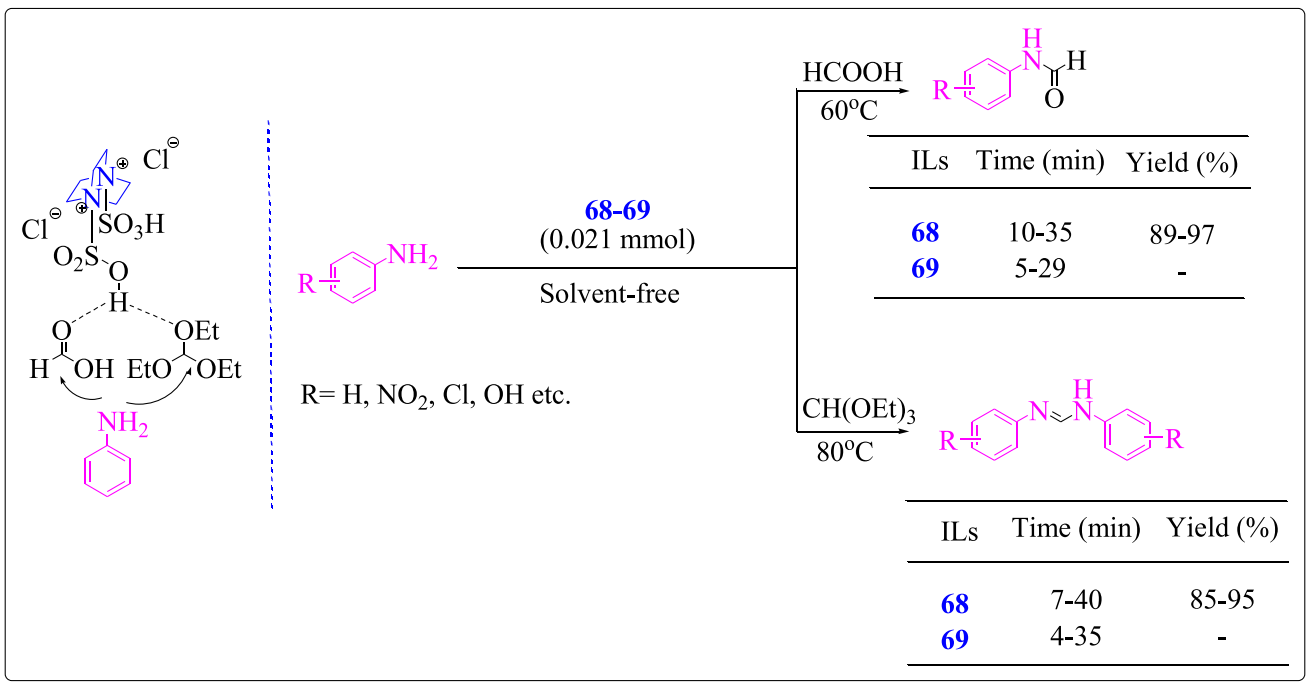


quinazolinones and [1,2,4]triazolo[1,5-a]pyrimidines with good to excellent yields via three-component reactions of aldehydes, β-diketones and 3-amino-1,2,4-triazole or 2-amino benzimidazole.

The same research group used **68** and **69** for the N-formylation of primary and secondary amines with formic acid (Hosseini Lakeh et al. 2020). They also used these ILs for the synthesis of *N*, *N*′-diarylformamidines by reacting

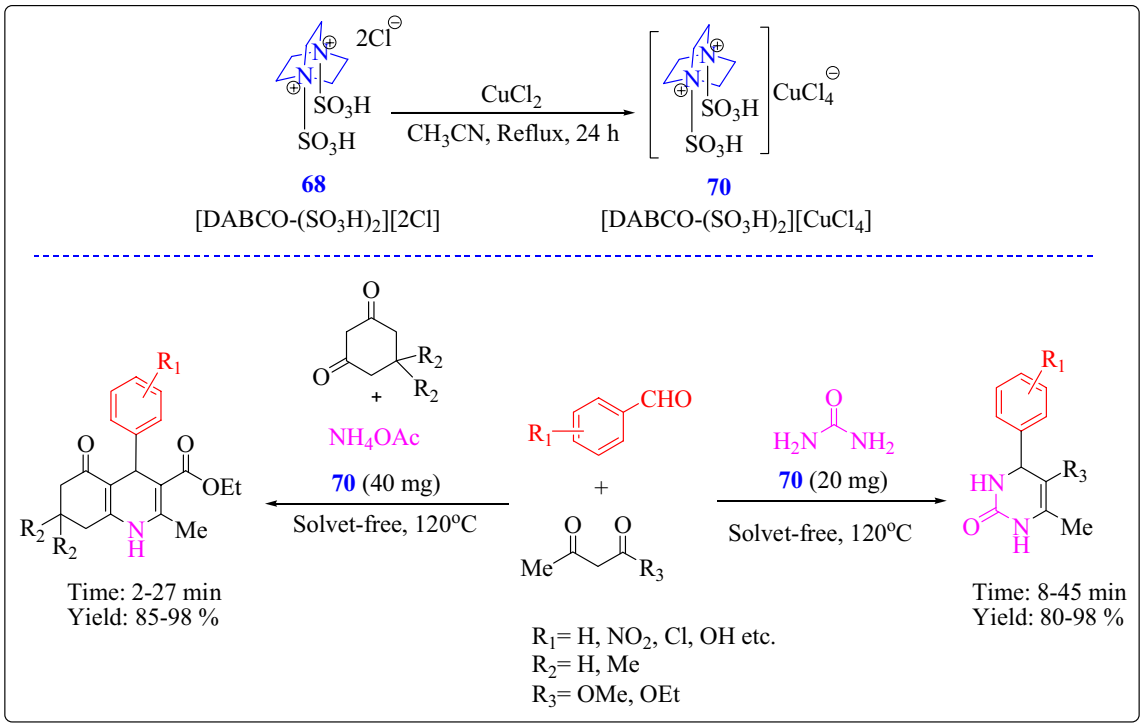


Scheme 28 Quinazolinone and pyrimidine synthesis using [DABCO-$(HSO_3)_2$][2X]

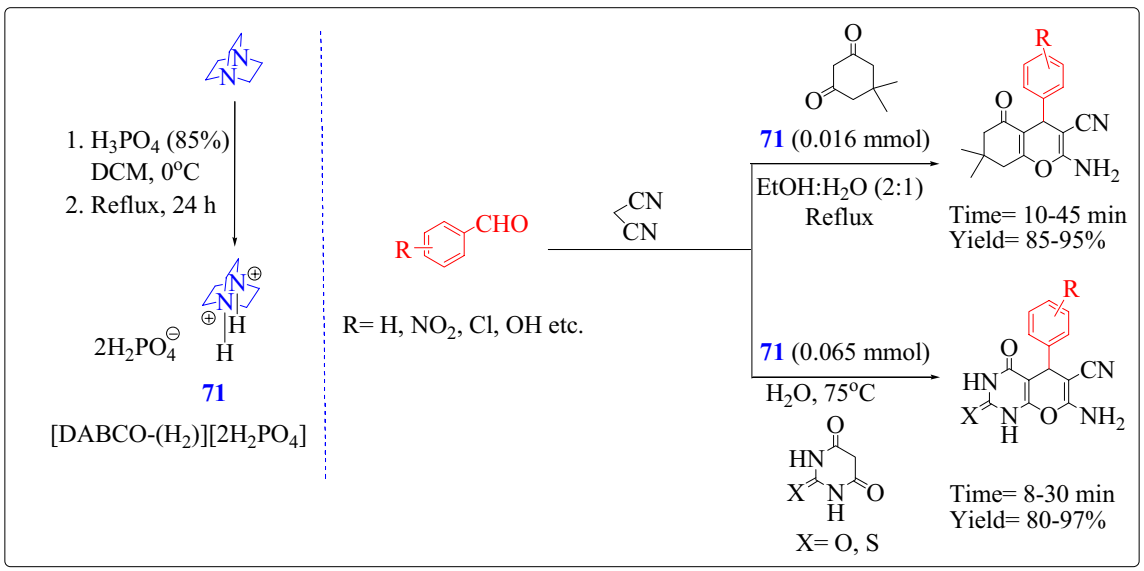


Scheme 29 Synthesis of *N*, *N*′-diarylformamidines using [DABCO-$(HSO_3)_2$][2X]

triethyl orthoformate with primary aryl amines under solvent-free conditions (Scheme 29). The **69** is more active than **68** due to its higher acidity, making it more recyclable in the N-formylation of 4-chloroaniline and the synthesis of *N*, *N*′-diaryl formamidine derivative of 4-chloroaniline. In this process, the acidic nature of the IL activates the formic acid, which the amine then attacks. Both the ILs could be recycled many times without loss in activity.

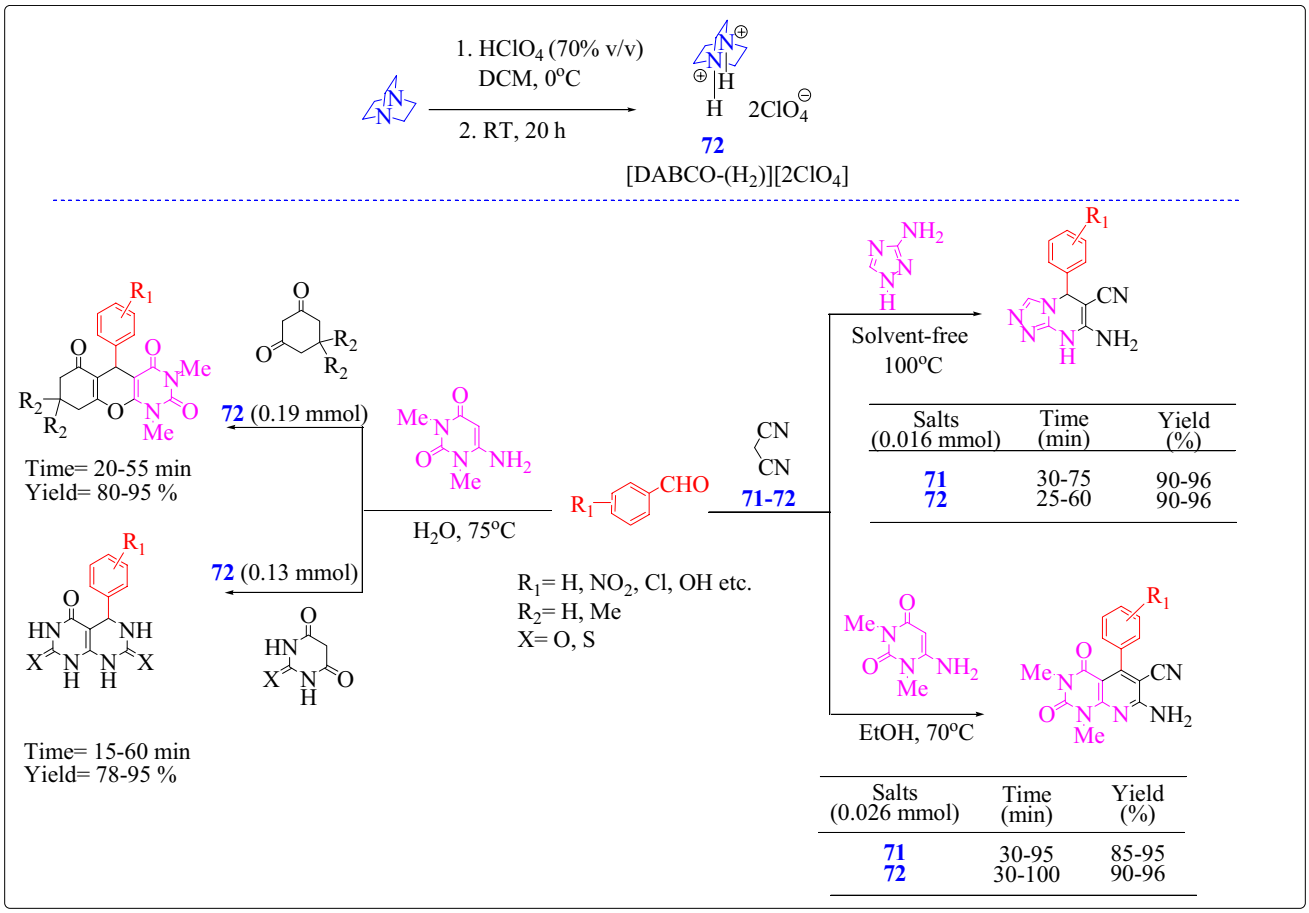


Scheme 30 [DABCO-$(HSO_3)_2$][$CuCl_4$] salt-catalyzed synthesis of 3,4-dihydropyrimidines and polyhydroquinolines



Scheme 31 [H_2-DABCO][$2H_2PO_4$] salt-catalyzed synthesis of tetrahydrobenzo[b]pyrans and pyrano[2,3-d]pyrimidinones

The Cu-based ionic salt [DABCO-$(HSO_3)_2$][$CuCl_4$] (**70**), was used as an efficient catalyst for the one-pot synthesis of 3,4-dihydropyrimidine and polyhydroquinoline derivatives (Scheme 30) (Fekrat et al. 2023). This **70** has dual acidic functionality (Brønsted and Lewis) and was synthesized by treating [DABCO-$(HSO_3)_2$][2Cl] (**68**) with $CuCl_2$ in refluxing CH_3CN. It delivered good to excellent yields of 3,4-dihydropyrimidinone derivatives in a one-pot reaction of aldehydes, ethyl acetoacetate, and urea, as well as polyhydroquinolines in a solvent-free environment at 120 °C. The salt showed up to six times reusability in the synthesis of



Scheme 32 [H_2-DABCO][$2ClO_4$] salt for the synthesis of pyrimidines and quinoline derivatives

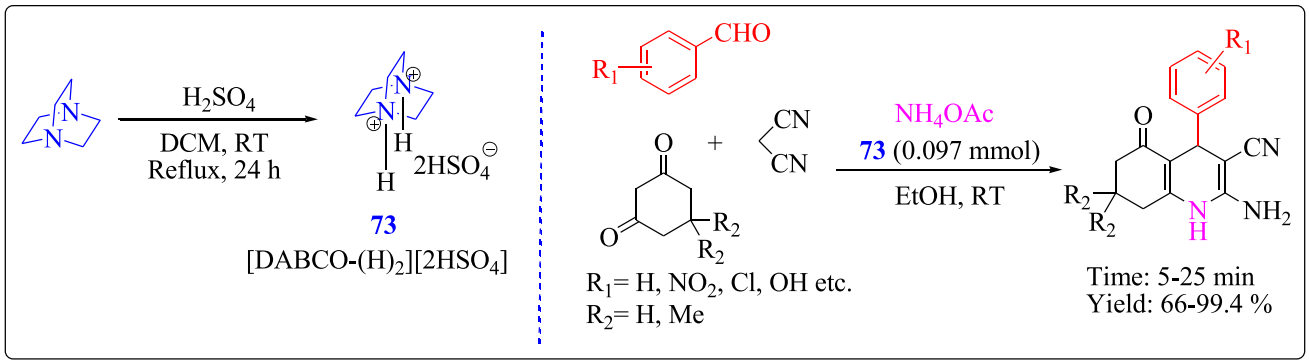
polyhydroquinoline. The salt **70** activates the carbonyl group of the aldehyde, promoting nucleophilic attack by urea.

Shirini and coworkers reported a DABCO-based [H_2-DABCO][$2H_2PO_4$] ionic salt (**71**) for the synthesis of tetrahydrobenzo[b]pyran and pyrano[2,3-d]pyrimidinone derivatives (Scheme 31) (Shirini et al. 2017). The **71** (mp = 98 °C) was synthesized by treatment of DABCO with a stoichiometric amount of phosphoric acid (85 *w/w*) in a dry DCM. The salt delivered the desired tetrahydrobenzo[b]pyrans in EtOH:H_2O (2:1) mixture at reflux and pyrano[2,3-d]pyrimidinones in water at 75 °C with good to excellent yields. The salt showed up to four times reusability with decreased yield of the products in the reactions.

Correspondingly, they synthesized a similar type of salt called [H_2-DABCO][$2ClO_4$] (**72**) (white solid, mp = 55 °C) as a new member of DABCO-based acidic ionic salt and applied for the synthesis of and 1,2,4-triazolo[4,3-a]pyrimidines and pyrido[2,3-d]pyrimidines (Jamasbi et al. 2018) as well as pyrimido[4,5-*b*]-quinoline and pyrimido[4,5-*d*]pyrimidine derivatives (Scheme 32) (Shirini et al. 2018). The **72** could be recycled at least six times with decreased product yields.

Recently, [H_2-DABCO][$2HSO_4$] salt (**73**) (mp = 85 °C) was synthesized by treatment of DABCO and a stoichiometric amount of 98% H_2SO_4 in DCM and used for the one-pot multi-component synthesis of hexahydroquinolines under ambient reaction conditions (Scheme 33) (Sahiba et al. 2023). The protocol involves the reaction of 1,3-dicarbonyls, malononitrile, and NH_4OAc with various aldehydes in the presence of 73 in EtOH affording hexahydroquinolines in good to excellent yields (76 – 100%) at RT. The salt can be recycled at least five times with decreased product yield.

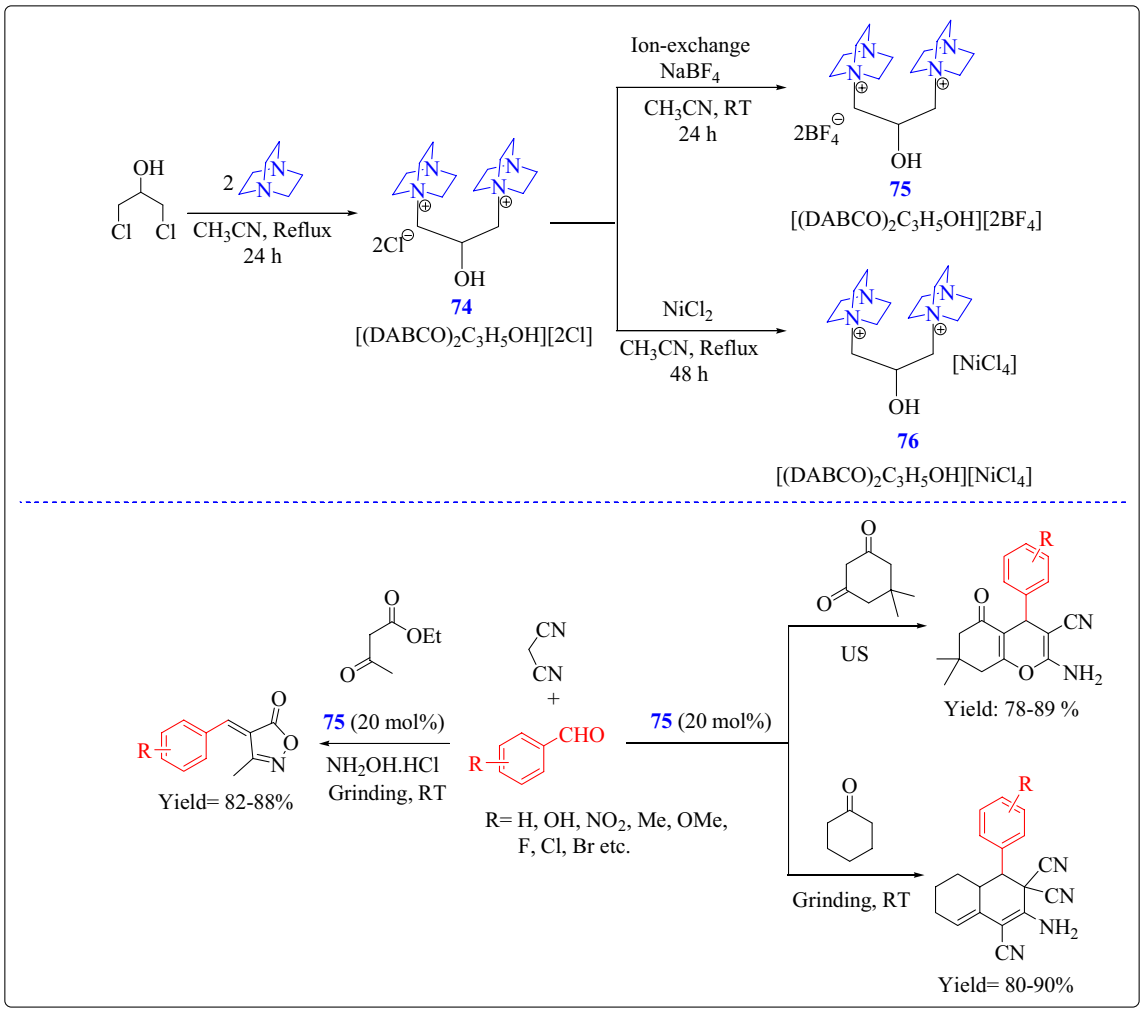
In 2016, we developed a multi-component synthesis of heterocyclic scaffolds under sustainable reaction conditions using DABCO functionalized dicationic ionic liquid (DDIL) [$(DABCO)_2C_3H_5OH$][$2BF_4$] (**75**) (Scheme 34) (Lohar et al. 2016). First, [$(DABCO)_2C_3H_5OH$][2Cl] **74** was synthesized using the reaction of DABCO with 1,3-dichloro-2-propanol, which on ion exchange with $NaBF_4$ in acetonitrile afford DDIL **75**. The **75** is compatible with the base-catalyzed one-pot multi-component synthesis of ortho-amino carbonitriles and 3-methyl-4-arylmethylene-isoxazol-5(4*H*)-ones under grinding without solvent. In addition, the activity of salt **75** was also studied for the synthesis of tetrahydrobenzo[b]



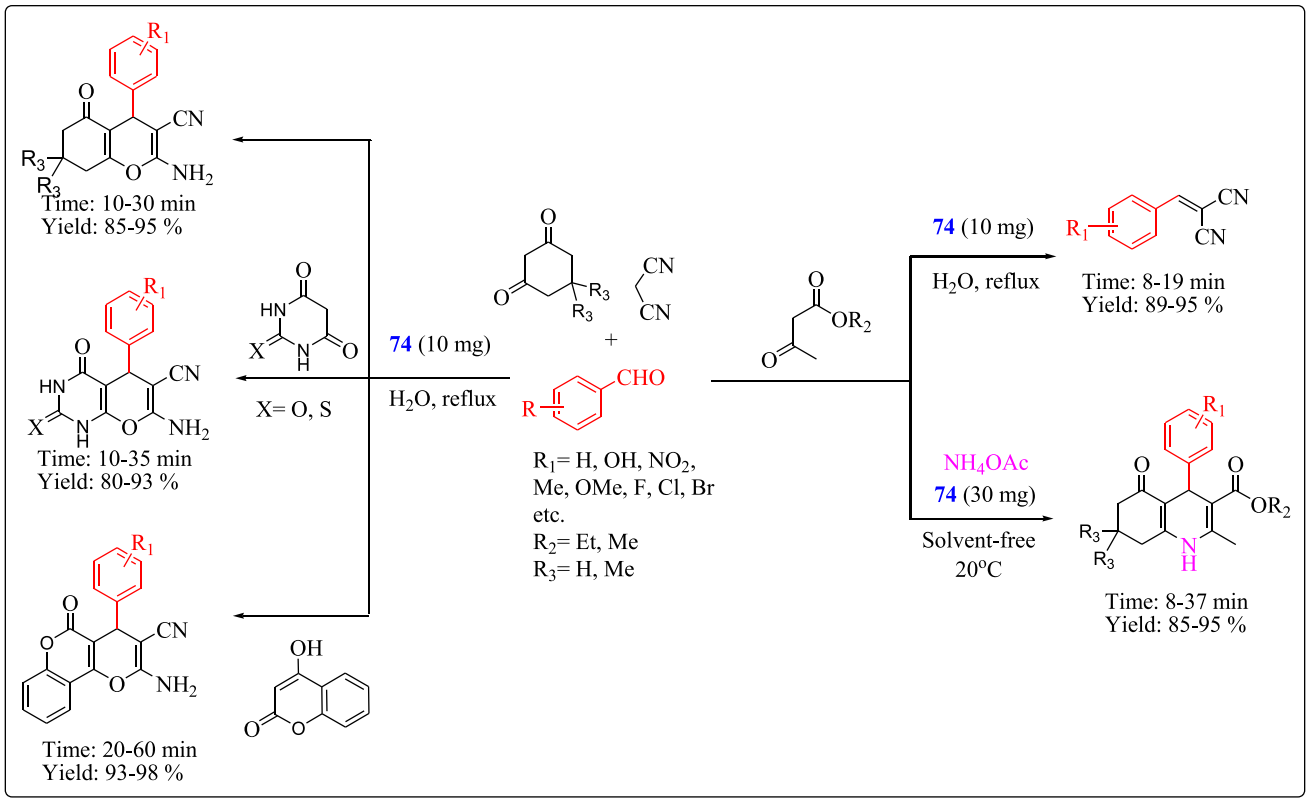
Scheme 33 [H_2-DABCO][$2HSO_4$] salt-catalyzed synthesis of hexahydroquinolines

pyrans under ultrasound irradiation in water. Furthermore, the **75** was easily recoverable and recyclable many times with a modest decrease in activity.

In connection with this, Langarudi et al. (Zabihzadeh et al. 2020) efficiently used DDIL **74** in the synthesis of arylidenemalononitrile, tetrahydrobenzo[b]pyran, pyrano[2,3-d]-pyrimidinone (thione), dihydropyrano[3,2-c] chromene, and polyhydroquinoline derivatives under various reaction conditions (Scheme 35). All the heterocycles were obtained with excellent yields under different reaction



Scheme 34 [$(DABCO)_2C_3H_5OH$][$2BF_4$] DDILs for the synthesis of heterocycles



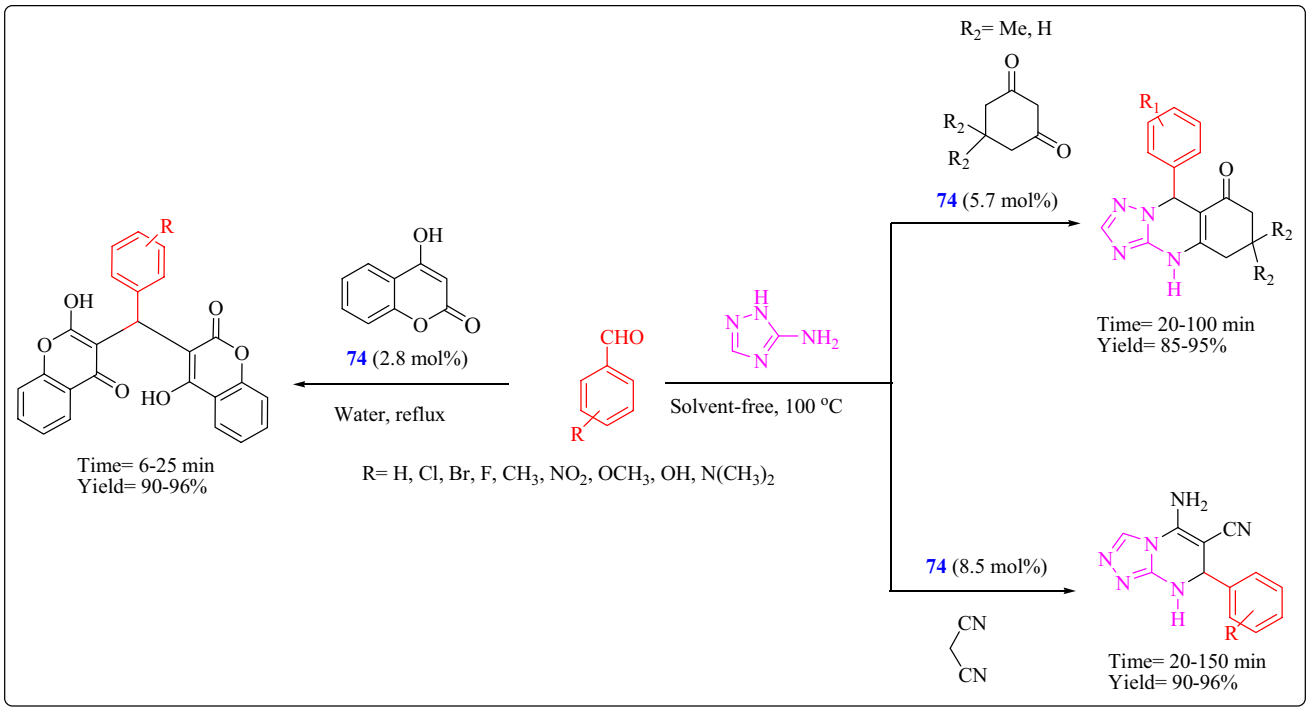
Scheme 35 $[(DABCO)_2C_3H_5OH][2Cl]$ DDILs for the synthesis of heterocycles

conditions. Furthermore, the DDIL **74** was recycled at least six times with a modest decrease in activity.

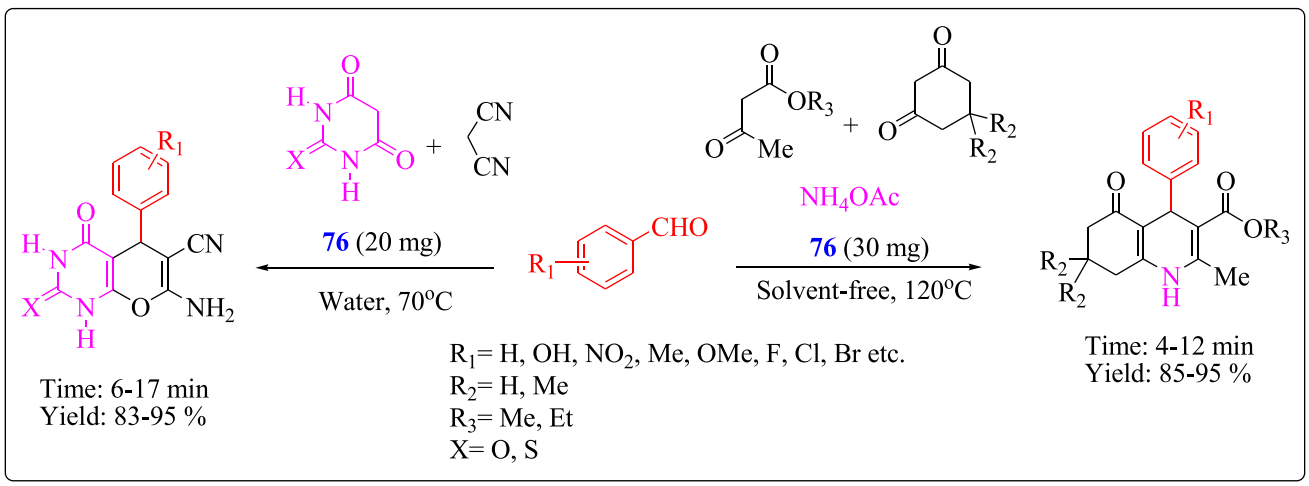
A DDIL **74** also showed excellent activity in the synthesis of 1,2,4-triazolopyrimidine, quinazolinone, and bis coumarin derivatives under green conditions (Nazari et al. 2023) (Scheme 36). All the triazolopyrimidine, quinazolinone derivatives were obtained with excellent yields under solvent-free conditions at 100 °C, while bis coumarin derivatives were obtained in water at reflux condition. The DDIL showed at least three times reusability with consistent activity.

As an extension, Ni containing DABCO ionic salt $[(DABCO)_2C_3H_5OH][NiCl_4]$ (**76**) was synthesized by treatment of **74** with $NiCl_2$ and characterized by EDX, TGA, FT-IR, ICP-AES, FE-SEM, and TEM techniques (Yarinia et al. 2022) (Scheme 35). This nanosized reagent showed efficient catalytic ability in synthesizing 1,4-dihydropyridine and pyrano[2,3-d]pyrimidinones (Scheme 37). Furthermore, salt **76** was easily recovered and recycled eight times with a modest decrease in activity.

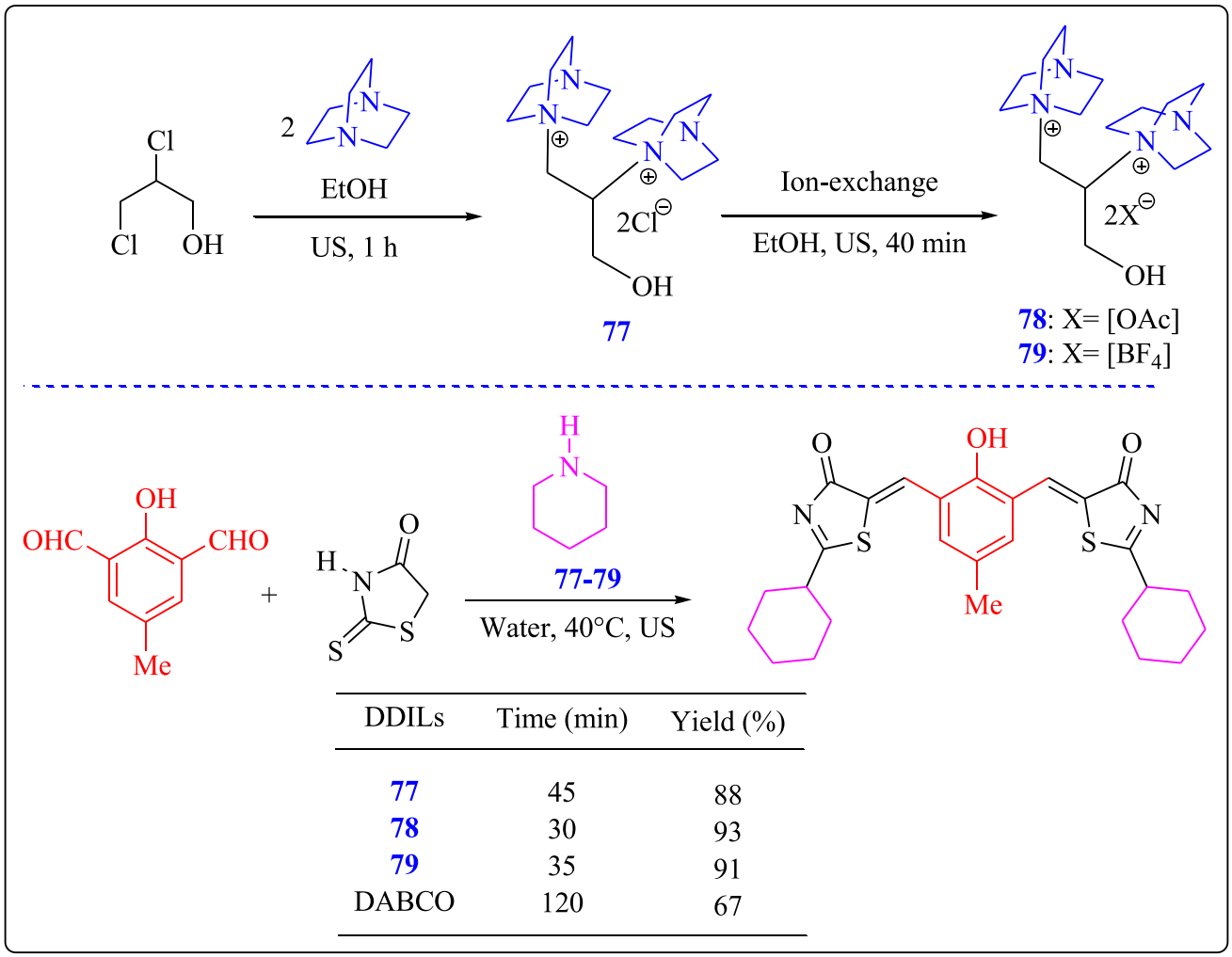
A similar type of DDILs (**77–79**) was synthesized and applied for a one-pot synthesis of bis-2-amino-5-arylidenethiazol-4-ones (Scheme 38) (Arafa and Mourad 2019). Initially, under ultrasonication (US) DABCO was quaternized with one 2,3-dichloropropan-1-ol in EtOH to afford the chloride salt (**77**), which underwent an anion exchange reaction with NaOAc or $NaBF_4$ in ethanol to afford the required dense colorless liquids (**78–79**) under US. The synthesis of heterocycle proceeds via a one-pot pseudo-five-component Knoevenagel condensation reaction of appropriate dialdehydes, rhodamine, and amines with excellent yields in a short reaction time under ultrasound. The recyclability of the **79** was also investigated with an average recovered yield of 97% for six sequential cycles without any significant loss of activity.



Scheme 36 [(DABCO)$_2$C$_3$H$_5$OH][2Cl] DDILs for the synthesis of heterocycles



Scheme 37 Ni containing DABCO salt for the synthesis of 1,4-dihydropyridines and pyrano[2,3-d]pyrimidinones



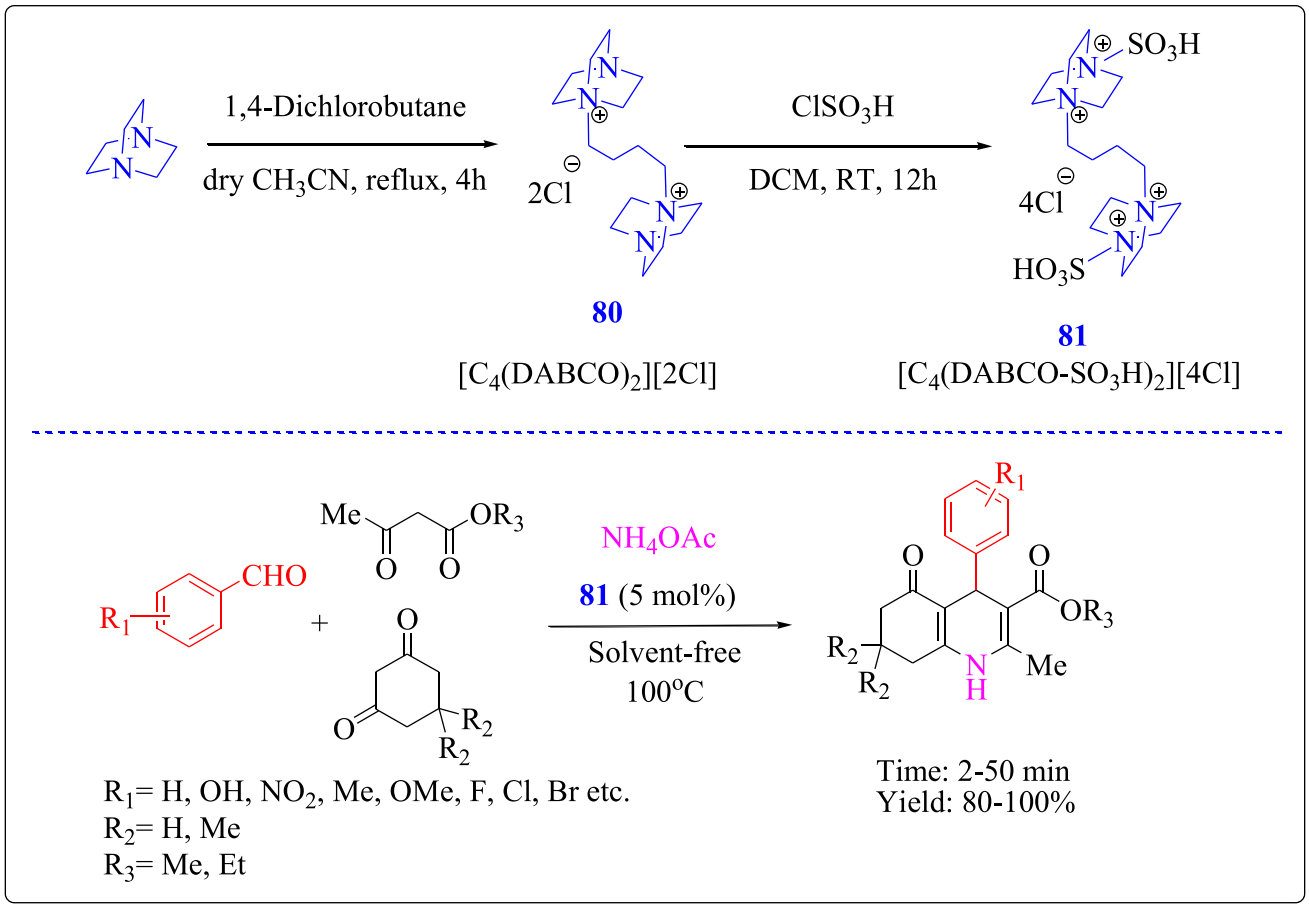
DDILs	Time (min)	Yield (%)
77	45	88
78	30	93
79	35	91
DABCO	120	67

Scheme 38 DDIL-catalyzed one-pot synthesis of bis-2-amino-5-arylidenethiazol-4-ones

Applications of tetracationic DABCO ionic salts in multi-component reactions

Shirini and coworkers synthesized a new nano-sized N-sulfonic acid tetra cationic DABCO ionic salt $[C_4(DABCO\text{-}SO_3H)_2)][4Cl]$ (**81**). The synthesis involves the first reaction of 1,4-dichlorobutane and DABCO in refluxing CH_3CN to from $[C_4(DABCO)_2][2Cl]$ (**80**) followed by reacting chlorosulfonic acid at RT (Scheme 39). The salt **81** was efficiently used for the synthesis of hexahydroquinolines via one-pot four-component condensation of aryl aldehydes, 1,3-cyclohexadiones, *β*-ketoesters, and NH_4OAc under solvent-free conditions in excellent yields in short reaction times (Goli-Jolodar et al. 2016b). The **81** was also applied for the synthesis of 2-amino-4*H*-pyrans via one-pot three-component reactions of aryl aldehydes, 1,3-cyclohexadiene derivatives, *β*-ketoesters, and NH_4OAc under solvent-free conditions with excellent yields in short reaction times (Goli-Jolodar et al. 2016a).

A similar type of salt, $[C_4(DABCO\text{-}SO_3H)_2)][4ClO_4]$ (**82**), was synthesized by reacting salt **81** with $HClO_4$, as

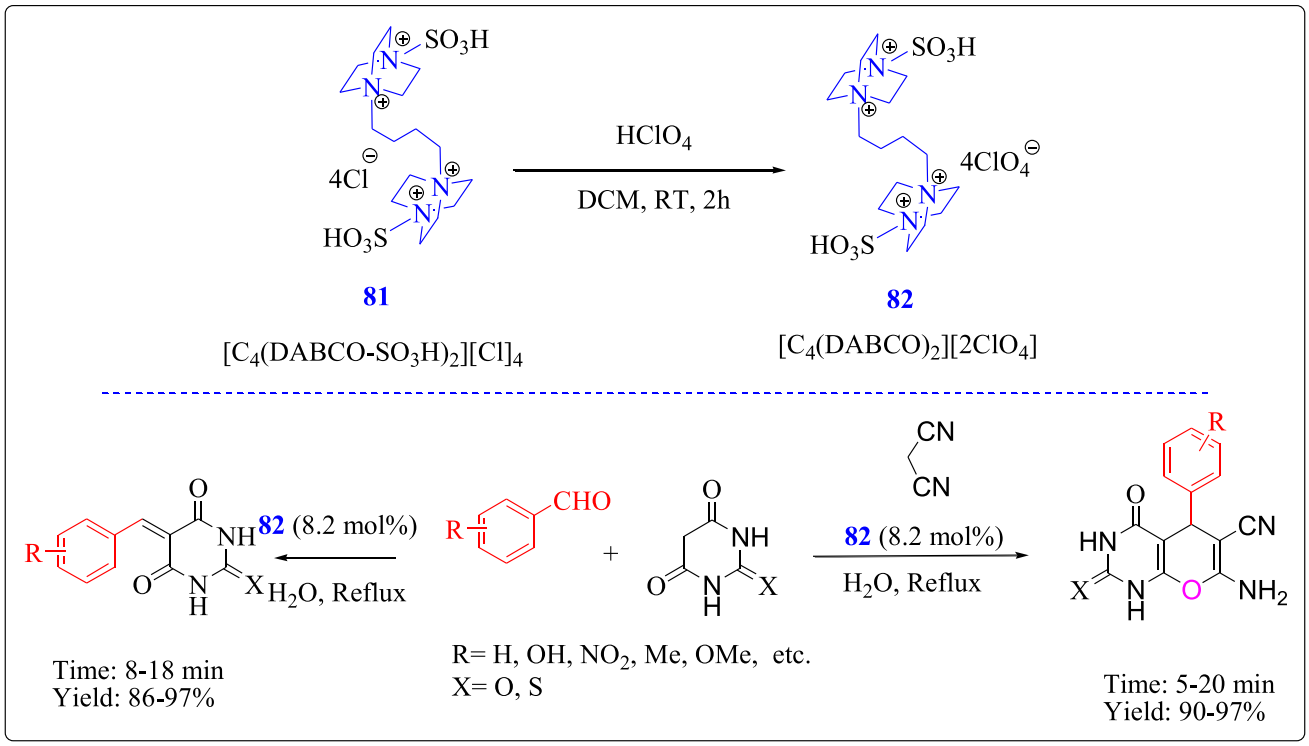


Scheme 39 Tetracationic DABCO ionic salts for the one-pot synthesis of hexahydroquinolines

reported by Sahrapeyma et al. (2023) (Scheme 40). This prepared salt was effectively used to synthesize 5-arylidene (thio)barbituric acid and pyrano[2,3-d]pyrimidinone derivatives in water. The main advantages of this method include short reaction times, straightforward work-up, easy isolation of the products from the reaction medium, high yields, and the catalyst's reusability for at least five cycles.

The $[C_3(DABCO\text{-}SO_3H)_2)][4HSO_4]$ (**84**) salt was synthesized from salt $[C_3(DABCO\text{-}SO_3H)_2)][4Cl]$ (**83**) and applied for Knoevenagel condensation of aldehydes with active cyclic methylene compounds in water at RT (Halimehjani et al. 2019) (Scheme 41). The 2,2'-(phenylmethylene) bis(3-hydroxy-5,5-dimethylcyclohex-2-enone) derivatives were obtained in 40–95% isolated yields in the reaction of aldehydes with dimedone, while the corresponding Knoevenagel adducts were obtained in 84–95% yields using 1,3-dimethylbarbituric acid.

Another type of an acidic tetra cationic salt $[C_4(H\text{-}DABCO)_2][4HSO_4]$ (**85**) was applied for the synthesis of 2*H*-indazolo[2,1-*b*]phthalazinetrione and [1,2,4]triazoloquinazolinone derivatives under solvent-free condition (Scheme 42) (Safari et al. 2020). Here the hydrogen ions loaded by $[C_4(H\text{-}DABCO)_2][4HSO_4]$ can catalyze the enolization of dimedone/cyclohexadione. It also enhancement the electrophilicity of the carbonyl group of aldehydes against the nucleophilic addition.



Scheme 40 Tetracationic DABCO ionic salts for the synthesis of 5-arylidene (thio)barbituric acid and pyrano[2,3-d]pyrimidinone derivatives in water

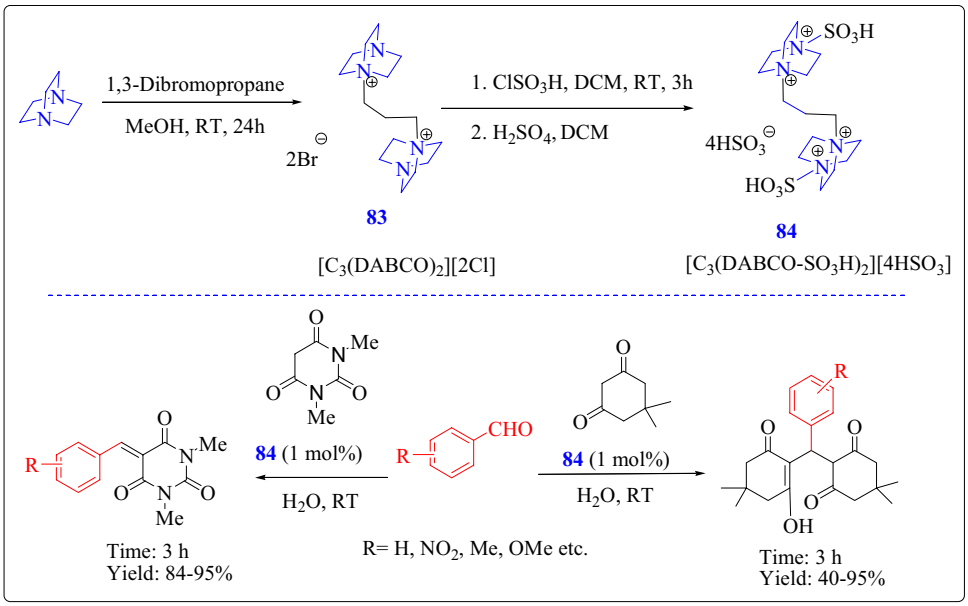
Applications of polycationic DABCO ionic liquids (PDIL) in multi-component reactions

Polycationic DABCO ionic liquid (PDIL) (**87**) was synthesized by condensation of 1,4-dichloro butane and DABCO in ethylene glycol at 110 °C to form salt **86** followed by a reaction with H_2SO_4 (Scheme 43). The **87** acts as an efficient catalyst for the one-pot preparation of 2,3-dihydro quinazoline-4-(1*H*)-ones with good to excellent yields (Mohammadi et al. 2017). The protocol involves a reaction of isatoic anhydride, aromatic aldehyde, and NH_4OAc or aniline, in the presence of **87** under solvent-free conditions at 90 °C. The catalyst was used for four subsequent cycles. A small decrease in the performance of the catalyst is observed in subsequent cycles. PDIL activates aldehyde and isatoic anhydride via protonation with the carbonyl group.

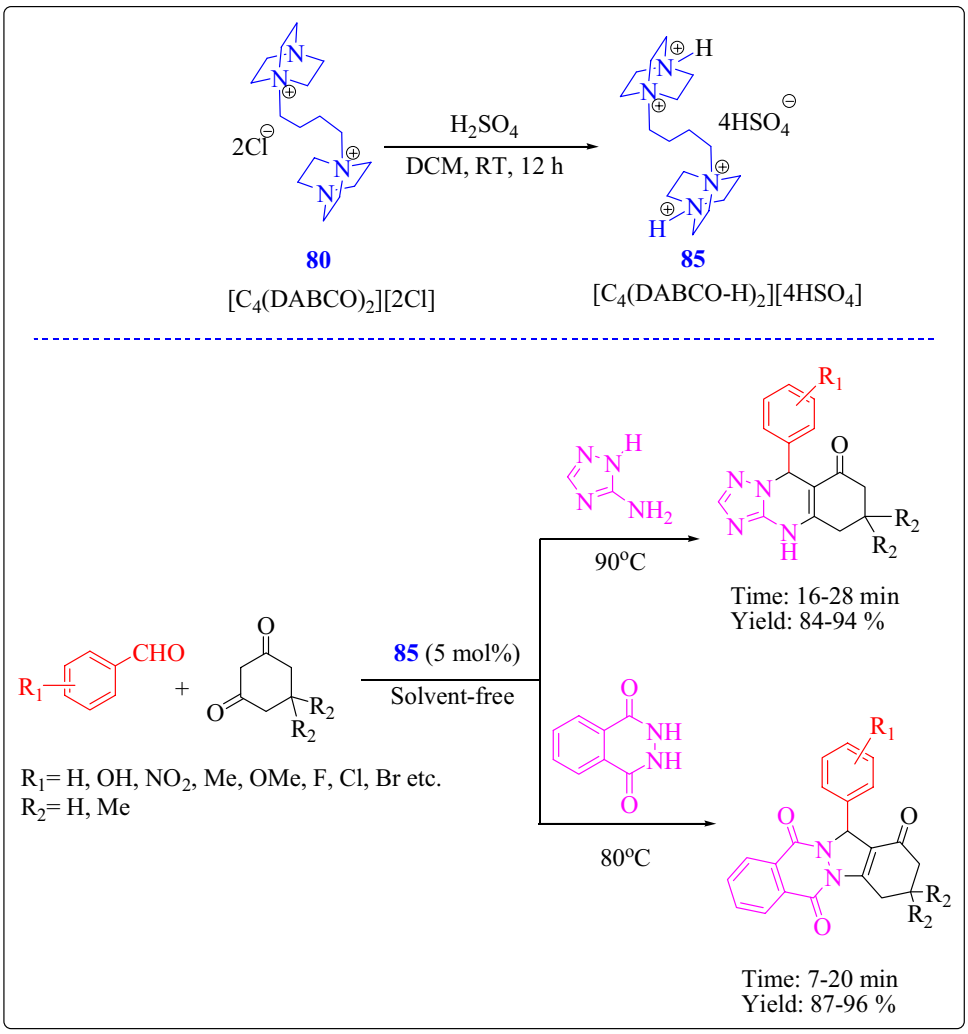
Conclusions

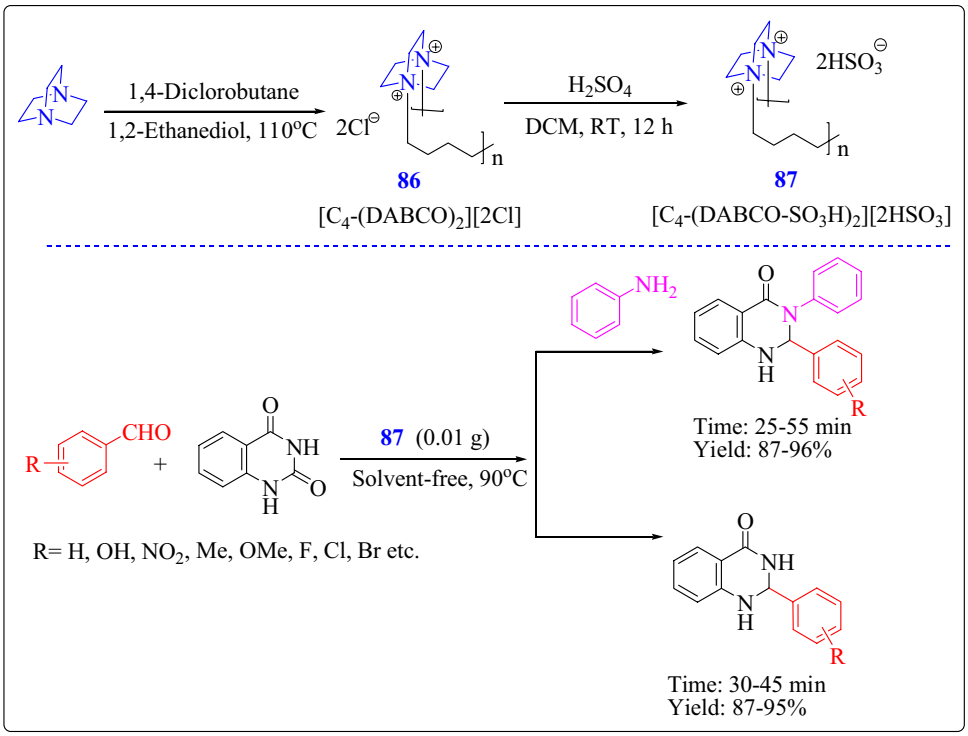
In summary, the present short review discusses the significant development in the synthesis and applications of DABCO-based ILs, mainly focusing on their role in multi-component reactions. Despite the promising potential of DABCO-based ILs, their prevalence is notably lower than

Scheme 41 Tetracationic DABCO ionic salts for the one-pot synthesis of hexahydroquinolines



Scheme 42 Tetracationic DABCO ionic salts for the synthesis of phthalazinetrione and triazoloquinazolinone derivatives





Scheme 43 DAIL-catalyzed synthesis of 2,3-dihydroquinazoline-4-(1*H*)-ones

that of imidazolium-based ILs. The unique salt formation abilities of DABCO have recently attracted considerable attention in the synthesis of task specific ILs. However, a key limitation is the lack of availability of comprehensive physical data on these ILs. While these ILs can be recycled with minimal loss of catalytic activity, the variety of DABCO-based ILs is still limited. This highlights the need for further research to expand the range of DABCO-based ILs and to gather more extensive physical and chemical data to utilize their potential fully in catalytic applications.

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