



## STUDY OF CATALYTIC PERSPECTIVES OF DABCO BASED ACIDIC IONIC LIQUID FOR THE SYNTHESIS OF 2-PHENYL-1,3-DITHIOLANE

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### Abstract

In this paper, DABCO based acidic ionic liquids have been used as a simple, efficient, ecofriendly, and reusable catalyst at room temperature in aqueous media for the synthesis of 1,3-dithiolane derivatives. A wide range of aldehydes and ketones were easily undergo thioacetalization with 1,2-dithiol in good to excellent yields. The synthesized compounds were characterized via FT-IR, <sup>1</sup>HNMR, <sup>13</sup>CNMR and mass spectroscopy. In comparison to ketones, the protection of carbonyl compounds was very selective towards aldehydes. The present approach highlights several merits, including an ecofriendly and inexpensive catalyst, green solvent media, shorter reaction time, good to exceptional product yields, and recyclability of the ionic liquid for subsequent reactions without a considerable reduction in activity.

**Keywords:** Ionic liquid, Carbonyl compounds, 1,2-dithiol, Thioacetalization, Catalysis, Green chemistry.

### 1. Introduction

Ionic liquids are currently receiving a lot of attention for their potential use as catalysts in a variety of chemical reactions<sup>i-iv</sup>. Ionic liquids have attracted towards research and academia, and their catalytic properties have been studied extensively in recent years because of their alluring properties, including low vapour pressure, dissolving power, non-volatility, non-flammability, and high thermal stability<sup>v-vii</sup>. From an environmental viewpoint, the quest for a variety of ionic liquids that may act as catalysts and solvents is necessary. The popularity of ionic liquids in numerous fields of sciences can be attributed to their structural flexibility such as electrochemistry, chemistry, biology, and synthetic and industrial chemistry<sup>viii-xi</sup>. The physical and chemical properties of ionic liquids are determined by the type of their cation and anion constituents. This shows that a given ionic liquid can be systematically tailored to have precise features termed as “task specific” and “designer” ionic liquids<sup>xii,xiii</sup>.

In the synthesis of natural products and polyfunctional molecules, the protection and deprotection of reactive functional groups is required. In organic synthesis, the carbonyl group is one of the most studied and highly valued functional group due to its strong reactivity and extensive variety of transformations<sup>xiv</sup>. The protection of carbonyl functionality as dithioacetals or dithioketals is a common and widely utilized strategy in organic chemistry, and it is regularly employed as a synthetic step for the synthesis of many significant natural and synthetic organic compounds<sup>xv,xvi</sup>. Dithioacetals commonly prepared by condensation of aldehydes and ketones with dithiols employing acid catalyst, including HCl<sup>xvii</sup>, ZnCl<sub>2</sub><sup>xviii</sup>, AlCl<sub>3</sub><sup>xix</sup>, BF<sub>3</sub>.OEt<sub>2</sub><sup>xx</sup>, PTSA<sup>xxi</sup>, LaCl<sub>3</sub><sup>xxii</sup>, InCl<sub>3</sub><sup>xxiii</sup>, NBS<sup>xxiv</sup>, [bmim]HSO<sub>4</sub><sup>xxv</sup>, [BEPSe]BF<sub>4</sub><sup>xxvi</sup>, SA-MNPs<sup>xxvii</sup>, CSA<sup>xxviii</sup>, SBA-15-Ph-SO<sub>3</sub>H<sup>xxix</sup>, HBA<sup>xxx</sup>, multi-functional bronsted acidic ionic liquid<sup>xxxi</sup>, [Et<sub>3</sub>NH][HSO<sub>4</sub>]<sup>xxxii</sup>, TBATB<sup>xxxiii</sup>, and Acidic Pseudo-IL<sup>xxxiii</sup>. The acquired findings were compared regarding reaction time and yield to the other reported methods for thioacetalization. (Table 1)

**Table 1:** Comparative study of different catalysts in the thioacetalization of carbonyl compounds

Entry	Reaction conditions/Catalyst	Solvent	Temperature (°C)	Time	Yield (%)	Reference
1	SA-MNPs	Solvent-free	r.t	30 min	99	[xxvii]
	CSA	Acetonitrile	r.t	26 min	94	[xxviii]
2						
3	SBA-15-Ph-SO <sub>3</sub> H	Acetonitrile	r.t.	20-90 min	80-96	[xxix]
4	HBA	Acetonitrile	r.t	1 min	95	[xxx]
5	Acidic Pseudo-IL	cyclohexane	Reflux	4 h	90-99	[xxxiii]
<b>5</b>	<b>[H<sub>2</sub>-DABCO][H<sub>2</sub>PO<sub>4</sub>]<sub>2</sub></b>	<b>H<sub>2</sub>O</b>	<b>r.t</b>	<b>1.5h</b>	<b>84</b>	<b>Present work</b>
<b>6</b>	<b>[H<sub>2</sub>-DABCO][HSO<sub>4</sub>]<sub>2</sub></b>	<b>H<sub>2</sub>O</b>	<b>r.t</b>	<b>1h</b>	<b>85</b>	<b>Present work</b>
<b>7</b>	<b>[H<sub>2</sub>-DABCO][ClO<sub>4</sub>]<sub>2</sub></b>	<b>H<sub>2</sub>O</b>	<b>r.t</b>	<b>1h</b>	<b>89</b>	<b>Present work</b>

## 2. Experimental

### Chemicals

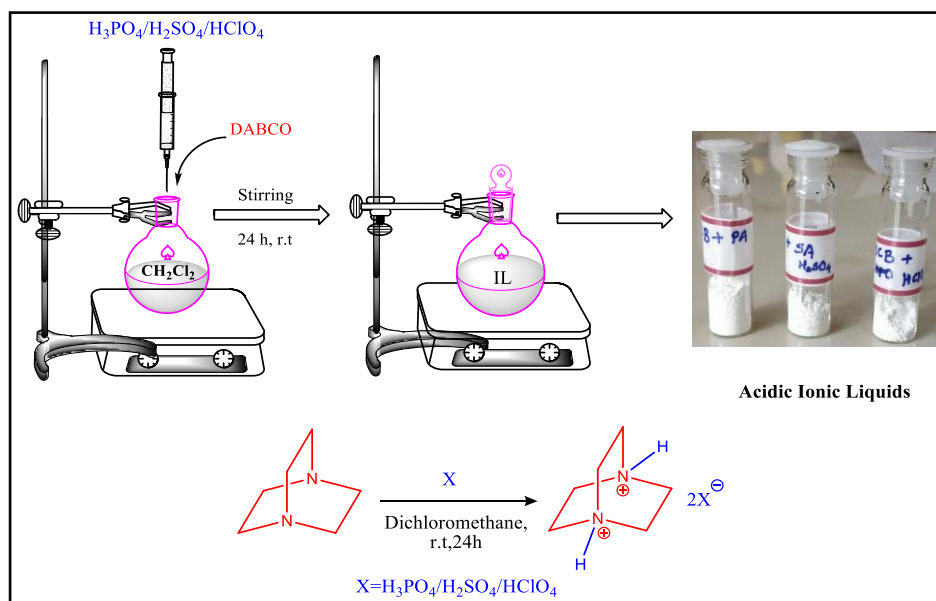
All solvents and chemical materials used in this work were acquired from Spectrochem, Merck (Mumbai), and Sigma Aldrich and used without further purification, while solvents were purified by distillation before they were used.

### Instruments

A Programmable melting point apparatus was used to record the melting points in capillary tubes and changes in chemicals were observed visually. FT-IR spectra were recorded on KBr pellets with the Perkin-Elmer spectrometer. <sup>1</sup>HNMR and <sup>13</sup>CNMR spectra were recorded on the BRUKER AVANCE NEO Spectrometer at 500MHz and 125MHz respectively, in CDCl<sub>3</sub> solvent. Mass spectra were acquired by the Maldi Synapt XS HD mass spectrometer.

### Preparation of catalyst $[\text{H}_2\text{-DABCO}][\text{H}_2\text{PO}_4]_2/[\text{H}_2\text{-DABCO}][\text{HSO}_4]_2/[\text{H}_2\text{-DABCO}][\text{ClO}_4]_2$

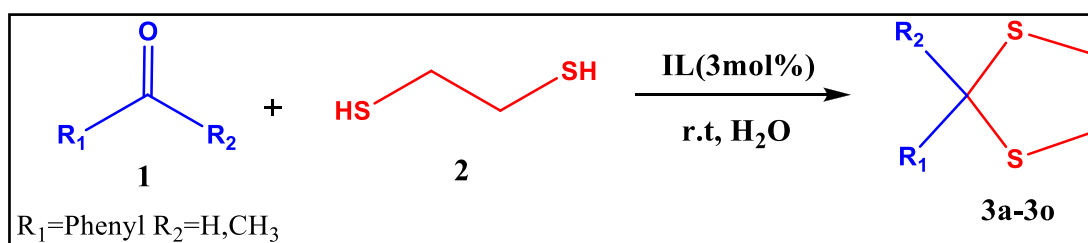
To the solution of DABCO (5 mmol) in dichloromethane (10 ml) a stoichiometric amount of phosphoric acid/sulfuric acid/perchloric acid (10 mmol) was added drop wise within 15 min. After the addition, the mixture was left for stirring at room temperature for 24 h. Then the solvent was decanted and the resulting white solid was washed with diethyl ether ( $3 \times 10$  ml) several times to obliterate non-ionic residues. Finally, the ionic liquid was vacuum dried and employed as a catalyst for subsequent reactions <sup>[xxxiv,xxxv]</sup>. (Figure 1)



**Figure 1:** A thumbnail sketch for the preparation of Acidic Ionic Liquids

### General procedure for thioacetalization of aldehydes/ketones catalyzed by Acidic Ionic Liquids

To a solution of aldehydes/ketones (1 mmol) in water, 1,2-ethanedithiol (1.2 mmol) and dicationic acidic ionic liquid (3 mol%) were added and the mixture was stirred at room temperature for an appropriate time. After completion of reaction (as determined by TLC), the reaction mixture was extracted with ethyl acetate, and the organic layer was concentrated under reduced pressure and purified the crude product by recrystallisation with methanol. Using a functional test for aldehydes or ketones, the purified product was screened qualitatively.



**Scheme 1:** Synthesis of 1,3-dithiolane

### Spectral data of representative compounds

#### **2-(anthracen-9-yl)-1,3-dithiolane (3a)**

M.P. 130-132°C FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3474, 3413, 3237, 2923, 1617, 728;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 500MHz,  $\delta$ , ppm): 8.77(d, 2H, Ar-H), 8.43(s, 1H, Ar-H), 7.97(d, 2H, Ar-H), 7.51-7.53(m, 2H, Ar-H), 7.43-7.50(m, 2H, Ar-H), 7.30(s, 1H, S-CH-S), 3.77-3.82(m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>-S), 3.56-3.62(m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>-S);  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 125MHz,  $\delta$ , ppm): 131.71, 130.67, 129.61, 129.37, 125.54, 125.36, 125.03, 124.97, 51.33, 40.55; Mass (m/z): 282[M-1]<sup>+</sup>

#### **2-(4-(benzyloxy)phenyl)-1,3-dithiolane (3b)**

M.P. 82-84°C FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3468, 3414, 2918, 1613, 1246, 1016;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 500MHz,  $\delta$ , ppm): 6.89-7.85(m, 9H, Ar-H), 5.63(s, 1H, S-CH-S), 5.05(s, 2H, CH<sub>2</sub>), 3.46-3.52(m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>-S), 3.31-3.37(m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>-S);  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 125MHz,  $\delta$ , ppm): 158.63, 136.91, 132.13, 129.18, 128.60, 127.99, 127.45, 114.81, 70.08, 56.05, 40.21; Mass (m/z): 287[M-1]<sup>+</sup>

#### **2-methyl-(2-phenyl)-1,3-dithiolane (3i)**

$^1\text{H}$ NMR ( $\text{CDCl}_3$ , 500MHz,  $\delta$ , ppm): 7.60(d, 2H, Ar-H), 7.09(d, 2H, Ar-H), 3.39-3.44(m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>-S), 3.32-3.37(m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>-S), 2.31(s, 3H, CH<sub>3</sub>), 2.12(s, 3H, CH<sub>3</sub>);  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 125MHz,  $\delta$ , ppm): 142.96, 136.83, 128.72, 126.74, 68.49, 40.36, 33.94.

#### **2-methyl-(2-(4-chlorophenyl)-1,3-dithiolane (3j)**

$^1\text{H}$ NMR ( $\text{CDCl}_3$ , 500MHz,  $\delta$ , ppm): 7.67(d, 2H, Ar-H), 7.24(d, 2H, Ar-H), 3.42-3.48(m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>-S), 3.32-3.38(m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>-S), 2.11(s, 3H, CH<sub>3</sub>);  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 125MHz,  $\delta$ , ppm): 144.75, 132.92, 128.39, 128.05, 68.03, 40.45, 33.64

### 3. Results and Discussion

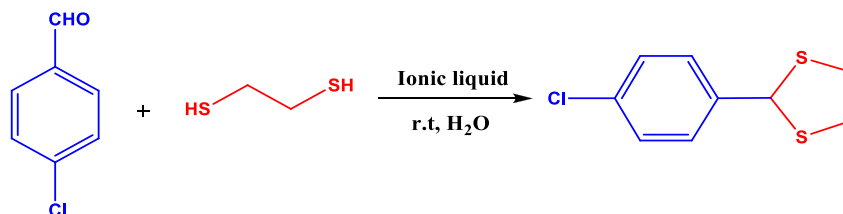
The activity and selectivity of ionic liquid can be altered through anionic modification, and is referred to as task-specific ionic liquid. In the current study, we investigate the applicability of three DABCO based acidic ionic liquids [H<sub>2</sub>-DABCO][H<sub>2</sub>PO<sub>4</sub>]<sub>2</sub>, [H<sub>2</sub>-DABCO][HSO<sub>4</sub>]<sub>2</sub>, and [H<sub>2</sub>-DABCO][ClO<sub>4</sub>]<sub>2</sub> for the synthesis of 1,3-dithiolane.

To optimize the reaction conditions, the synthesis of 2-(4-chlorophenyl)-1,3-dithiolane from 4-Cl benzaldehydes (1 mmol) and 1,2-ethanedithiol (1.2 mmol) was selected as the model reaction and it was carried out under various reaction parameters, including the solvent and amount of catalysts has been investigated and observations were recorded in Table 2. The model reaction was first carried out using several solvents such as ethanol, DMF, acetonitrile, toluene, water, and solvent free. It was found that among all solvents, water was the most efficient solvent for this reaction than other solvents in terms of both reaction time and yield of the required 2-(4-chlorophenyl)-1,3-dithiolane. The effect of varying amounts of ionic liquids on the model reaction was investigated, and it was observed that the variation of amount of ionic liquids, 3 mol% of catalyst was sufficient to carry out the reaction in good yield. The amount of catalyst was increased to 5 mol% to boost the yield of the desired product, but no significant effects were observed on the yield of 2-(4-chlorophenyl)-1,3-dithiolane. Therefore, the optimal reaction condition for the synthesis of 2-(4-chlorophenyl)-1,3-dithiolane derivatives is when the reaction is carried out by using 3mol% of catalyst at room temperature in an aqueous medium (Table 2, row 7).

We explored reactions applicability with a variety of aldehydes and ketones containing different electron withdrawing or electron donating substituents react with 1,2-ethanedithiol which gave expected products 1,3-dithiolane (Table 3) in good to high yields with high purity in aqueous media. It was observed that aromatic aldehyde with electron withdrawing groups gives the desired product faster than electron donating groups. The catalytic efficiency of DABCO based acidic ionic liquids was investigated and the finding revealed that [H<sub>2</sub>-

DABCO][ClO<sub>4</sub>]<sub>2</sub> ionic liquid promoted reaction in shorter time with a higher yield than the other mentioned DABCO based acidic ionic liquids.

**Table 2** Effect of solvent and amounts of catalyst for the synthesis of 2-(4-chlorophenyl)-1,3-dithiolane using [H<sub>2</sub>-DABCO][H<sub>2</sub>PO<sub>4</sub>]<sub>2</sub>, [H<sub>2</sub>-DABCO][HSO<sub>4</sub>]<sub>2</sub>, and [H<sub>2</sub>-DABCO][ClO<sub>4</sub>]<sub>2</sub> catalysts as A, B, and C respectively



Entry	Solvent	Catalyst (mol%)			Time (hr)			Yield (%) <sup>a</sup>		
		A	B	C	A	B	C	A	B	C
1	Ethanol	5	5	5	3	3	3	60	60	62
2	DMF	5	5	5	4	3.5	3.5	57	57	58
3	Acetonitrile	5	5	5	3	3	3	65	67	69
4	H <sub>2</sub> O	5	5	5	3	3	3	64	62	65
5	H <sub>2</sub> O	1	1	1	3	3	3	50	57	60
6	H <sub>2</sub> O	2	2	2	2	2	2	70	69	70
7	H <sub>2</sub> O	3	3	3	1	1	1	84	85	89
8	H <sub>2</sub> O	4	4	4	1	1	1	84	85	89
9	H <sub>2</sub> O	-	-	-	3	3	3	trace	trace	trace
10	Toluene	3	3	3	3	3	3	NR <sup>b</sup>	NR <sup>b</sup>	NR <sup>b</sup>
11	Solvent free	3	3	3	3	3	3	70	72	75
12	Solvent free	-	-	-	4	4	4	trace	trace	trace

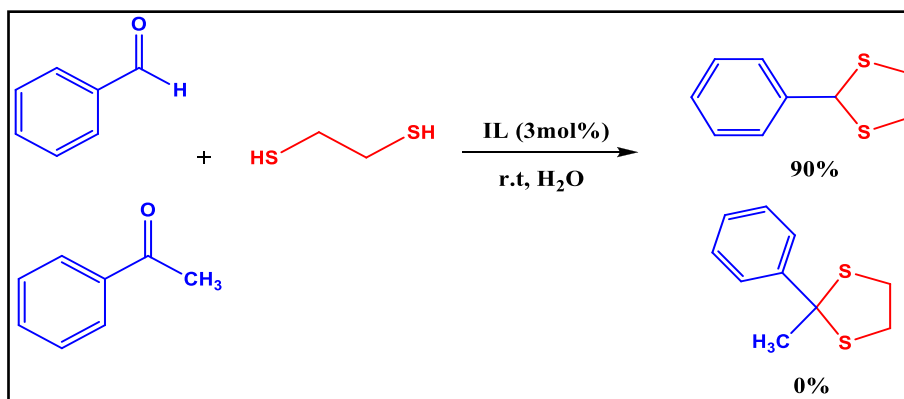
<sup>a</sup>Isolated yields

<sup>b</sup>No Reaction

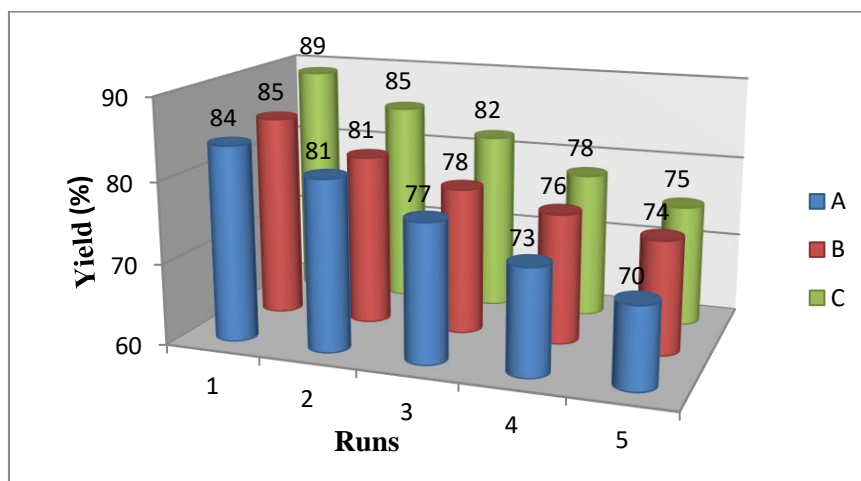
Due to the reactivity difference between aldehyde and ketone, this methodology may be used for chemoselective protection of the aldehydes in presence of ketone. For this confirmation an equimolar mixture of benzaldehydes and acetophenone was reacted with 1,2-ethanedithiol using ionic liquid (3 mol%) as a catalyst, only 2-(phenyl)-1,3-dithiolane was formed in 90% yield while 96% of acetophenone was recovered. (Scheme 2)

By periodically performing the model reaction under optimum conditions, the recyclability of ionic liquid was examined for the synthesis of 2-(4-chlorophenyl)-1,3-dithiolane (Figure 2). The product was separated after completion of reaction by extracting with ethyl acetate and separating organic and aqueous phases. The catalyst was recovered by concentrating the aqueous layer under reduced pressure, washed with hot ethanol, and reused it in the following cycle without loss of reactivity. As a consequence, it can be stated that the recovered catalyst is sufficiently stable after five cycles and used in the synthesis of 2-(4-chlorophenyl)-1,3-dithiolane.

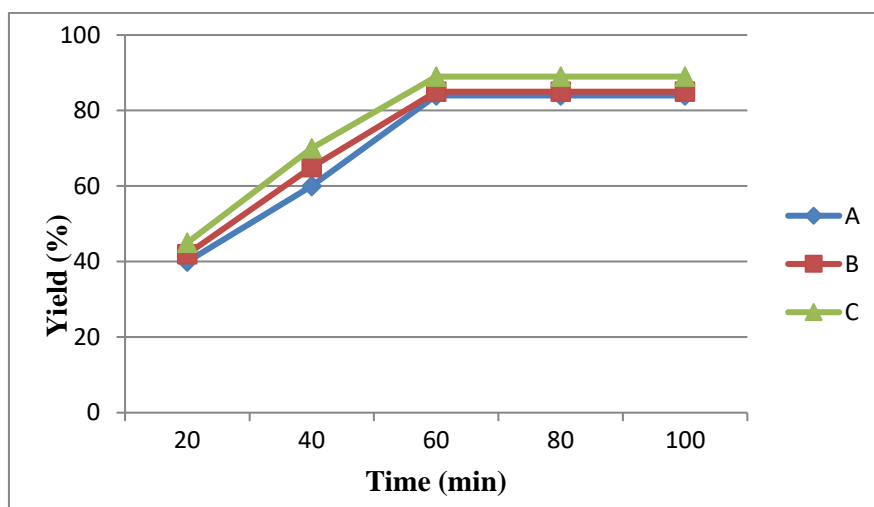
Figure 3 demonstrated the relationship between the yield of 2-(4-chlorophenyl)-1,3-dithiolane and reaction time. The yield of 2-(4-chlorophenyl)-1,3-dithiolane increased significantly between 0.1-1 h, whereas extending the reaction time had no effect, the reaction was completed in about 1 h.



**Scheme 2:** Chemoselectivity of aldehyde and ketone in presence of acidic ionic liquid

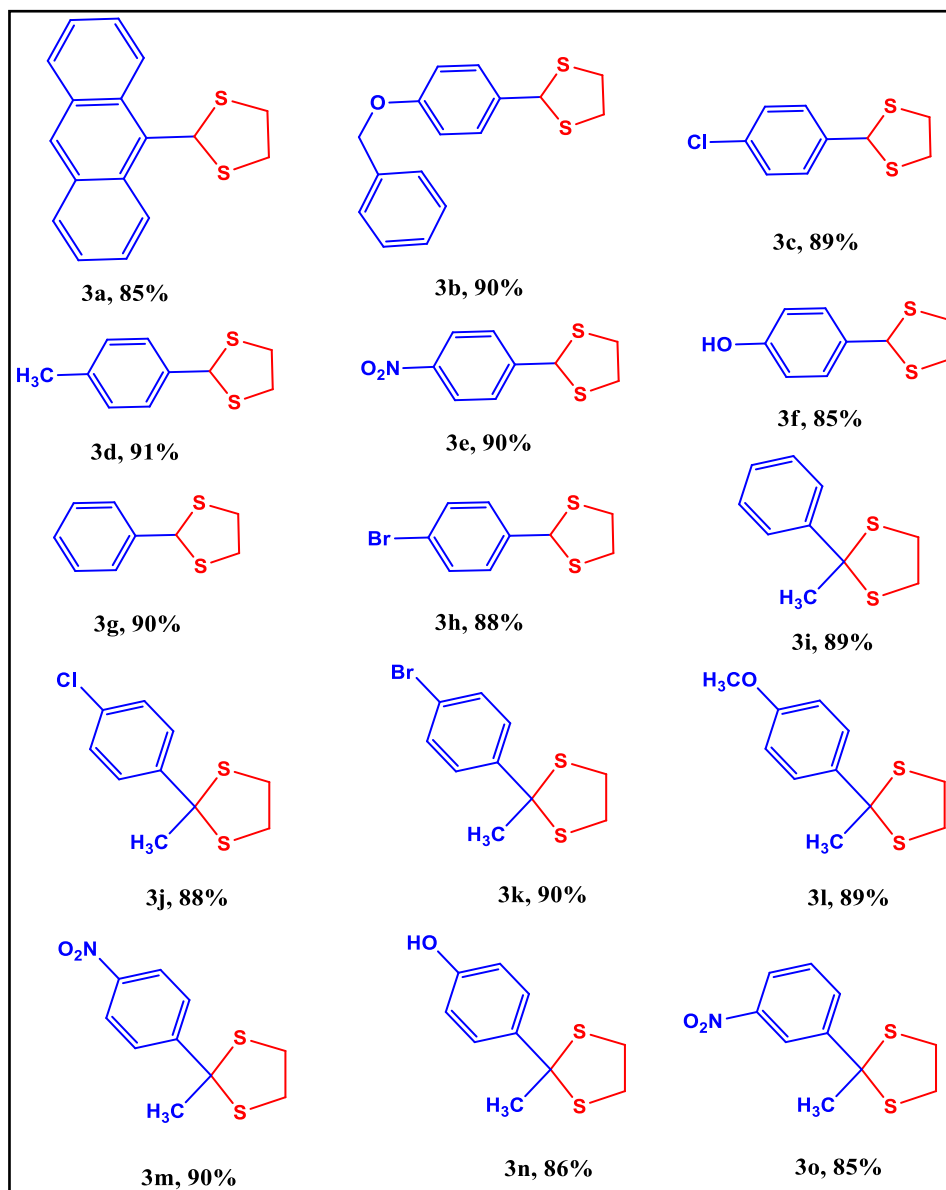


**Figure 2:** Recyclability of  $[H_2\text{-DABCO}][H_2PO_4]_2$ ,  $[H_2\text{-DABCO}][HSO_4]_2$  and  $[H_2\text{-DABCO}][ClO_4]_2$  catalyst A, B and C respectively in the synthesis of 2-(4-chlorophenyl)-1,3-dithiolane



**Figure 3:** The effect of reaction time on the yield for the synthesis of 2-(4-chlorophenyl)-1,3-dithiolane using  $[H_2\text{-DABCO}][H_2PO_4]_2$ ,  $[H_2\text{-DABCO}][HSO_4]_2$  and  $[H_2\text{-DABCO}][ClO_4]_2$  catalysts as A, B, and C respectively

**Table 3:** Synthesis of 1,3-dithiolane derivatives in the presence of acidic ionic liquid catalyst



#### 4. Conclusion

The present study shows the synthesis of 2-(phenyl)-1,3-dithiolane derivatives using DABCO based acidic ionic liquids  $[H_2\text{-DABCO}][H_2PO_4]_2$ ,  $[H_2\text{-DABCO}][HSO_4]_2$ , and  $[H_2\text{-DABCO}][ClO_4]_2$  as an eco-friendly, recyclable, non toxic, and thermally stable catalyst in an aqueous media. FT-IR, NMR, and mass spectroscopy were used to characterize the structure of synthesized compounds. In this work, the catalytic applicability of three DABCO based ionic liquids was investigated, and the results revealed that  $[H_2\text{-DABCO}][H_2PO_4]_2$  ionic liquid had lower catalytic activity whereas  $[H_2\text{-DABCO}][ClO_4]_2$  ionic liquid shows higher catalytic activity. The proposed method displayed several notable merits, including an environmental friendly and inexpensive catalyst, green solvent media, shorter reaction time, good to excellent product yield, and recyclability of the ionic liquid without a considerable reduction in activity.

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