ChemInform Abstract: Eco-Efficient Synthesis of Cyclic Carbamates/Dithiocarbonimidates from Cyclic Carbonates/Trithiocarbonate and Aromatic Amines Catalyzed by Ionic Liquid BmimOAc…

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Eco-Efficient Synthesis of Cyclic Carbamates/Dithiocarbonimidates from Cyclic Carbonates/Trithiocarbonate and Aromatic Amines Catalyzed by Ionic Liquid BmimOAc

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Abstract: We have investigated the reactions of cyclic carbonates/trithiocarbonate and aromatic amines in the presence of a basic ionic liquid, 1-butyl-3-methylimidazolium acetate (BmimOAc), which produced various cyclic carbamates/dithiocarbonimidates in fairly good to excellent yields. The use of BmimOAc as catalyst here not only offers an effective approach to the synthesis of the target compounds, but also avoids the use of conventional toxic materials. By means of the reactions of cyclic carbonates and aromatic amines, 3-aryloxazolidin-2-ones, 3,3′-aryldioxazolidin-2-ones and 3-aryl[1,3]oxazinan-2-ones could be synthesized. NMR spectroscopy and DFT calculations revealed that both the cation and the anion of BmimOAc activate cooperatively the substrates in these reactions by means of inducing hydrogen bonding. In addition, condensation reactions of ethylene trithiocarbonate and aromatic amines also proceeded very well in the presence of the BmimOAc catalyst, which opened a hitherto unreported route to [1,3]dithiolan-2-ylidene-arylamine derivatives in a straightforward way.

Keywords: cyclic carbamates; cyclic dithiocarbonimidates; green chemistry; ionic liquids

Introduction

Cyclic carbamates/dithiocarbonimidates are important heterocyclic compounds, which have attracted much attention in the past decades because of their biological activity. For example, 3-aryloxazolidin-2-ones exhibit selective and reversible inhibition of monoamine oxidase A, an important enzyme responsible for the degradation of various amine neurotransmitters. They also have potent activities against Gram-positive bacterial pathogens including methicillin-resistant *Staphylococcus aureas* (MRSA) and vancomycin-resistant Enterococci (VRE).[1] 3-Aryl[1,3]oxazinan-2-ones have quite recently displayed potency against 11β-hydroxysteroid dehydrogenase type 1 (11β-HSD1) in humans.[2]

Conventionally, these cyclic carbamates/dithiocarbonimidates are prepared from toxic phosgene[3] or isocyanates/isothiocyanates.[4] However, these processes suffer from the utilization of toxic materials and have other drawbacks like a heavy reliance on expensive metal catalysts, long reaction times or tedious steps. In addition, alternative methods for the synthesis of cyclic carbamates by reactions of CO_2 and aziridines have also been reported.[5]

Recently, we reported a method for the preparation of 3-phenyloxazolidin-2-one by using an ionic liquid as catalyst and ethylene carbonate/aniline as substrates.[6] Imidazolium-based ionic liquids exhibited a high catalytic activity, which was ascribed to a cooperative cation-anion effect in the reaction. Herein, in continuation of our studies on reactions involving organic carbonates,[6,7] we wish to report our recent re-

Scheme 1. The reaction of cyclic carbonates and aromatic amines catalyzed by BmimOAc.

sults on the use of cyclic carbonates for the carbonylation of aromatic amines by using 1-butyl-3-methylimidazolium acetate (BmimOAc) as an eco-efficient catalyst. Various cyclic carbamates including 3-aryloxazolidin-2-ones, 3,3′-aryldioxazolidin-2-ones and 3-aryl-[1,3]oxazinan-2-ones were synthesized in fairly good to excellent yields (Scheme 1). Moreover, an unexpected condensation reaction of ethylene trithiocarbonate and aromatic amines was also observed in the presence of BmimOAc as catalyst, which produced [1,3]dithiolan-2-ylidene-arylamines in good yields.

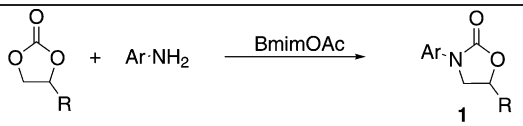
Results and Discussion

Synthesis of 3-Aryloxazolidin-2-ones from Cyclic Carbonates and Aromatic Amines in the Presence of BmimOAc

Imidazolium-based ionic liquids proved to be effective catalysts for the reaction of cyclic carbonates and aniline.[6] However, only simple carbonates and anilines have been examined before. In order to gain as much benefit as possible from the ionic liquid catalyst, we have now used it in the reactions of substituted cyclic carbonates with N-heterocyclic aromatic amines, in which various 3-aryloxazolidin-2-ones (**1**) will hopefully generated.

Initially, ethylene carbonate was employed as substrate to react with various anilines. As shown in Table 1, many substituted anilines were converted smoothly to **1a**–**1g** in the presence of a catalytic amount of BmimOAc in good to excellent yields (Table 1, entries 1–7). Naphthalen-1-ylamine and dibenzofuran-2-ylamine gave **1h** and **1i** in 80% and 78% yields, respectively (Table 1, entries 8 and 9). Notably, N-heterocyclic aromatic amines, such as pyridin-2-ylamine, pyrimidin-2-ylamine and 6-methoxy-2-methylpyridin-3-ylamine, were also applicable in this system, and can be successfully converted to the corresponding products **1j**–**1l** in yields of 71–95%. Reactions of propylene carbonate with aromatic amines also proceeded very well in the presence of BmimOAc, which afforded the corresponding products, **1m**–**1p**, in yields ranging from 70% to 99% (Table 1, entries 13–16). This system is also suitable for the reactions of 4-phenoxymethylethylene carbonate, which afforded **1q**–**1s** in yields of 51–85%

Table 1. Reaction of cyclic carbonates and aromatic amines catalyzed by BmimOAc.[a]



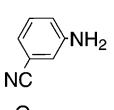
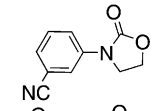
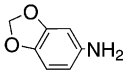
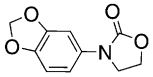
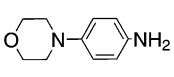
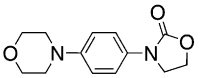
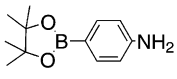
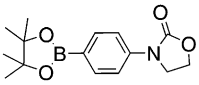
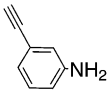
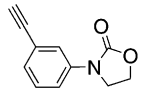
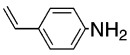
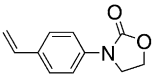
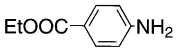
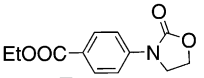
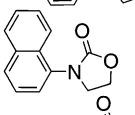
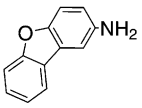
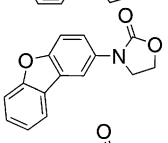
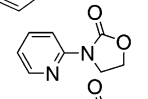
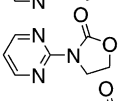
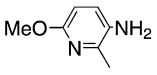
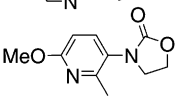
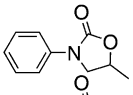
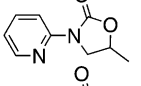
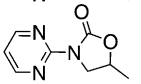
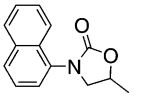
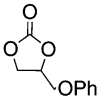
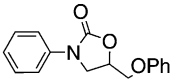
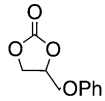
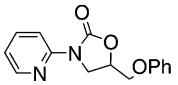
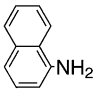
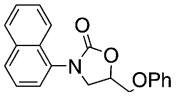
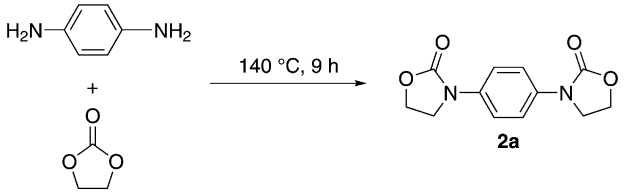
Entry	Cyclic carbonate	Aromatic amine	Product		Yield[b] [%]
1				**1a**	91
2				**1b**	93
3				**1c**	83
4				**1d**	65
5				**1e**	63
6				**1f**	54
7				**1g**	47
8				**1h**	80
9				**1i**	78
10				**1j**	95
11				**1k**	83
12				**1l**	71
13				**1m**	99[c]
14				**1n**	91
15				**1o**	70
16				**1p**	78

Table 2. (Continued)

Entry	Cyclic carbonate	Aromatic amine	Product		Yield[b] [%]
17				**1q**	80
18				**1r**	85
19				**1s**	51

[a] *Reaction conditions:* cyclic carbonate (10 mmol), aromatic amine (2 mmol), BmimOAc (0.2 mmol), 9 h, 130 °C.
[b] Isolated yield.
[c] 140 °C, ref.[6b]

Table 2. Reaction of ethylene carbonate and benzene-1,4-diamine catalyzed by various ionic liquids.[a]



Entry	Ionic liquid	Yield[b] [%]
1	BmimOAc	79
2	BmmimOAc	53
3	BmimCl	6
4	BmimBr	5
5	$BmimBF_4$	3

[a] *Reaction conditions:* ethylene carbonate (10 mmol), benzene-1,4-diamine (2 mmol), ionic liquid (0.2 mmol), 140 °C, 9 h.
[b] Isolated yield.

(Table 1, entries 17–19). The above-mentioned results also allowed us to draw the conclusion that, when the same amine was used, the reactivity of these cyclic carbonates decreased according to the following order: ethylene carbonate > propylene carbonate > 4-phenoxymethylethylene carbonate, which is consistent with the order of substituent size. It indicated that steric hindrance of the substrate influenced, to some extent, the reactivity of the substrates.

Synthesis of 3,3′-Aryldioxazolidin-2-ones from Cyclic Carbonates and Aromatic Diamines in the Presence of BmimOAc

The synthesis of 3,3′-aryldioxazolidin-2-ones was first reported by Braun et al., who utilized 1,4-diisocyanatoarenes and epoxides as starting materials.[4b] However, the toxicity of 1,4-diisocyanatoarenes limited the application of this method. Nandakumar reported an alternative method for the synthesis of 3,3′-aryldioxazolidin-2-ones, which is based upon a C–N coupling reaction of oxazolidin-2-one and diiodobenzene catalyzed by transition metal complexes in the presence of stoichiometric amounts of an inorganic base.[8] Taking advantage of our protocol for the preparation of 3-aryloxazolidin-2-ones, we then explored the feasibility of synthesizing 3,3′-(1,4-phenylene)dioxazolidin-2-one (**2a**) from ethylene carbonate and benzene-1,4-diamine using BmimOAc as catalyst.

As shown in Table 2, BmimOAc effectively catalyzed the reaction to afford **2a** in 79% yield (Table 2, entry 1). However, when 1,2-dimethyl-3-butylimidazolium acetate (BmmimOAc), in which the C-2 proton of the imidazolium ring was replaced by a methyl group, was applied the yield dropped to 53% (Table 2, entry 2). These results indicate that the C-2 proton of the imidazolium ring plays an important role in the catalysis. Moreover, the yields obtained with BmimCl, BmimBr and $BmimBF_4$ were rather poor (Table 2, entries 3–5). These results imply that the acetate anion is also an indispensable factor to ensure a good performance of the ionic liquid in this reaction.

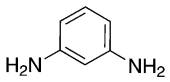
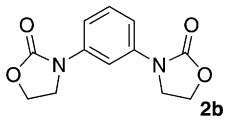
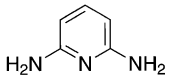
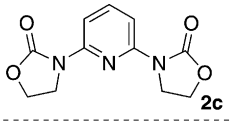
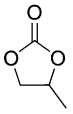
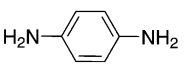
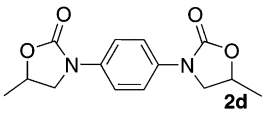
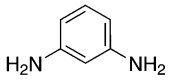
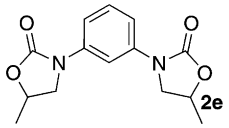
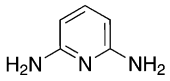
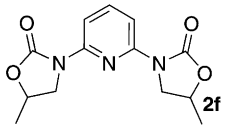
Then various 3,3′-aryldioxazolidin-2-ones were synthesized with the aid of BmimOAc as catalyst (Table 3). Ethylene carbonate smoothly reacted with benzene-1,3-diamine and pyridine-2,6-diamine to form the corresponding dioxazolidin-2-ones **2b** and **2c** in 67% and 60% yields, respectively (Table 3, entries 1 and 2). Propylene carbonate can also react with aromatic diamines to form the expected products **2d–2f** in fairly good yields (Table 2, entries 3–5). The obtained results also demonstrate that the reactivity of ethylene carbonate is slightly higher than that of propylene carbonate in the present reaction.

Mechanistic Studies

To rationalize the role of BmimOAc in the reactions of cyclic carbonates with aromatic amines, the interaction between BmimOAc and the substrates was studied by NMR spectroscopy and DFT calculations. In these studies, propylene carbonate and aniline were selected as model substrates.

NMR spectroscopy has been widely used to study the hydrogen bonding interactions of organic molecules.[9] Some intrinsic advantages of this method, such as accuracy, reliability and easy operation prompted us to use it to shed light on the mechanism associated with the BmimOAc catalyst. Initially, ^1H NMR titration experiments based on the addition

Table 3. Reaction of cyclic carbonates and aromatic diamines catalyzed by BmimOAc.[a]

Entry	Cyclic carbonate	Aromatic diamine	Product	Yield[b] [%]
1			 **2b**	67
2			 **2c**	60
3			 **2d**	76
4			 **2e**	55
5			 **2f**	50

[a] *Reaction conditions:* cyclic carbonate (10 mmol), aromatic diamine (2 mmol), BmimOAc (0.2 mmol), 140 °C, 9 h.
[b] Isolated yield.

of aliquots propylene carbonate to BmimOAc were carried out. As shown in Figure 1, the C-2 proton of imidazolium was shifted upfield step by step when propylene carbonate was added. After addition of 5 equivalents of propylene carbonate, the resonance of the C-2 proton moved from $\delta = 10.20$ to $\delta = 10.08$. This may result from a change of the hydrogen bond donor-acceptor pair. In BmimOAc, besides an electrostatic interaction, the C-2 proton of the imidazolium cation also acts as a hydrogen bond donor to interact with the acetate anion which, in turn, acts as a hydrogen bond acceptor. After addition of propylene carbonate into BmimOAc, the intramolecular hydrogen bond interaction is weakened, and an intermolecular hydrogen bond interaction between imidazolium and propylene carbonate plays a predominant role (equilibrium shown in Figure 1). These results imply that the carbonyl group of propylene carbonate could be activated by the C-2 proton of imidazolium. The activation of the carbonyl group by the C-2 proton had also been reported by us and others.[7a,10] The interaction between aniline and BmimOAc was also investigated by ^{1}H NMR. Upon addition of 3 equivalents of BmimOAc, the N–H proton of aniline undergoes a downfield shift (from $\delta = 4.09$ to $\delta = 4.59$ ppm) with peak broadening (Figure 2), which indicates the formation of hydrogen bonding between aniline and acetate. This demonstrates that aniline could be activated by the acetate through hydrogen bonding. These NMR studies have illustrated that BmimOAc could cooperatively activate cyclic carbonates and aromatic amines by hydrogen bonding to promote the reactions efficiently.

The interactions between BmimOAc and the model substrates, aniline and propylene carbonate, were also investigated by DFT calculations. The optimized geometrical structures of propylene carbonate, the complex of propylene carbonate with BmimOAc, aniline, and the complex of aniline with BmimOAc were simulated at the B3LYP/6-31G level (Figure 3). The bond length of the C-1–O-1 of propylene carbonate was elongated from 1.2130 Å to 1.2584 Å after complexation with BmimOAc, and hydrogen bond O-1–H-1 was formed with a bond length of 1.3830 Å. These results imply that propylene carbonate is acti-

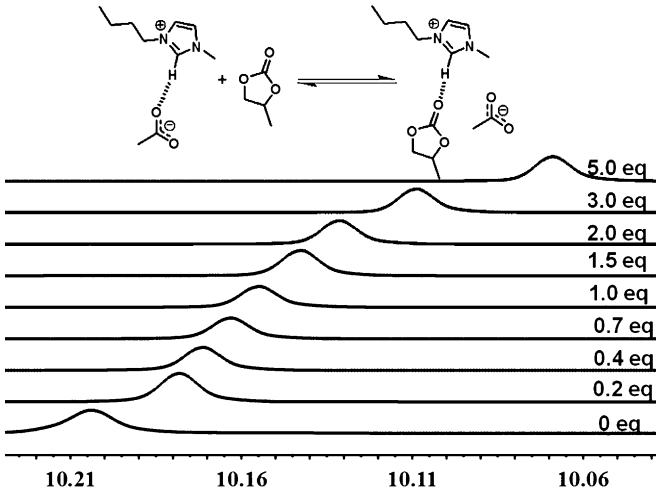


Figure 1. ^{1}H NMR spectra of the C-2 proton of imidazolium on addition of propylene carbonate in CD_3CN.

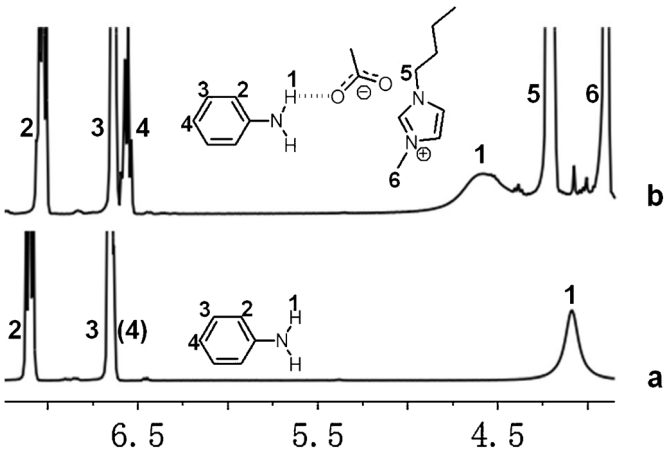


Figure 2. Partial ^{1}H NMR spectra of (a) aniline only, (b) 1:3 complex of aniline with BmimOAc.

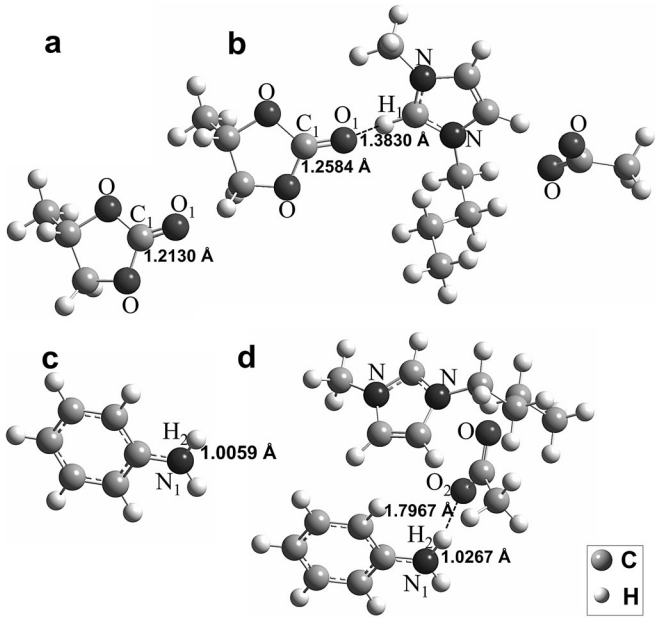


Figure 3. DFT optimized geometry of (a) propylene carbonate, (b) the complex of propylene carbonate with BmimOAc, (c) aniline and (d) the complex of aniline with BmimOAc.

vated by a hydrogen bonding interaction between the carbonyl group and the imidazolium. Meanwhile, the length of N-1–H-2 bond of aniline was elongated from 1.0059 Å to 1.0267 Å after complexation with BmimOAc, and the hydrogen bond H-2–O-2 was formed with a bond length of 1.7967 Å. This demonstrates that aniline is activated by hydrogen bonding with acetate. The DFT calculations also indicated that the cation and anion of BmimOAc cooperatively activated the substrates *via* formation of hydrogen bonds.

After completion of the reaction of propylene carbonate and aniline, ^{1}H NMR spectra of the reaction mixture clearly show that an equivalent of **1m** and propane-1,2-diol are generated, accompanied by consumption of two equivalents of propylene carbonate. Based on this result and our previous work,[7e] a reaction course is proposed: firstly one equivalent of propylene carbonate reacts with aniline to afford the intermediate 1-(phenylamino)propan-2-ol and CO_2. Then another equivalent of propylene carbonate further reacts with the intermediate 1-(phenylamino)propan-2-ol to yield **1m** and the by-product – propane-1,2-diol (see the Supporting Information).

Stability and Reusability of BmimOAc

The stability of BmimOAc under the reaction conditions of the present study was investigated by ^{1}H NMR spectroscopy *via* a modification of a recently reported approach.[11] A thermal treatment at 140 °C did not make the BmimOAc decompose even after 100 h (see the Supporting Information). Additionally, ^{1}H NMR spectra of the mixture after completion of the reaction showed that the structure of BmimOAc was not significantly affected although its signals partially overlapped with resonances of the products (see the Supporting Information), which also confirmed the high stability of BmimOAc.

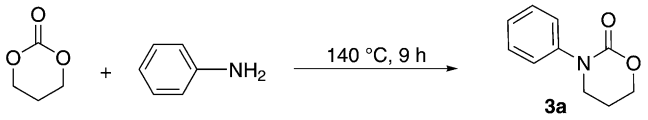
The recycling ability of the ionic liquid catalyst was also examined in the reaction of ethylene carbonate with benzene-1,4-diamine. After completion of the reaction, BmimOAc was recovered through a procedure involving extraction with methanol, evaporation, washing with toluene, and desiccation under vacuum. However, with the recovered BmimOAc catalyst, the yield in the second run dropped from 79% to 58%. In the third run, only a 21% yield was obtained. The decrease of the yields in the second and third runs could be ascribed to the contamination by the ethylene glycol by-product (detected by GC and ^{1}H NMR spectroscopy, see the Supporting Information) in the recovered ionic liquid catalyst, which was difficult to separate from BmimOAc. The existence of the ethylene glycol by-product inhibited the reaction. This can be verified by a control experiment. In the reaction of ethylene carbonate with benzene-1,4-diamine, **2a** was obtained in only 21% yield in the presence of 2 equivalents of ethylene glycol under otherwise identical conditions.

Synthesis of 3-Aryl[1,3]oxazinan-2-ones from Trimethylene Carbonate and Aromatic Amines in the Presence of BmimOAc

The most synthetic routes to access 3-aryl-[1,3]oxazinan-2-ones were established by reactions of toxic isocyanates with oxetane,[12] or tributyltin γ-iodopropoxide.[4c] Two-step reactions of dialkyl carbonates, 1,3-diols and aromatic amines have been developed aiming at avoiding the use of toxic isocyanates.[13] However, these approaches are plagued by a tedious operational procedure. The synthesis of 3-phenyl-[1,3]oxazinan-2-one (**3a**) through the reaction of trimethylene carbonate with aniline, if established, would be a huge incentive for us as the reaction has many salient features, such as environmentally benign reagents and good availability of starting materials. Due to these considerations, we studied the feasibility of this reaction by employing BmimOAc as a catalyst.

As shown in Table 4, the reaction proceeded smoothly with the aid of BmimOAc as catalyst, and **3a** was obtained in 62% yield after 9 h of reaction in 140 °C (Table 4, entry 1). The reaction with BmmimOAc as catalyst only afforded **3a** in 14% yield (Table 4, entry 2). Additionally, in this reaction, the catalytic activities of imidazolium-based ionic liquids

Table 4. Reaction of trimethylene carbonate and aniline catalyzed by various ionic liquids.[a]



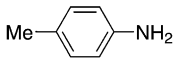
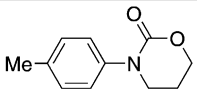
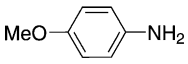
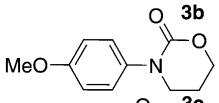
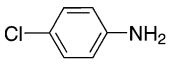
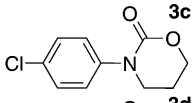
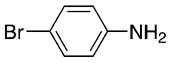
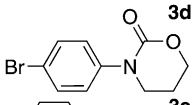
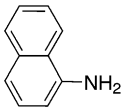
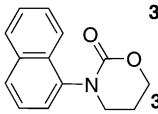
Entry	Ionic liquid	Yield[b] [%]
1	BmimOAc	62
2	BmmimOAc	14
3	BmimCl	42
4	BmimBr	16
5	$BmimBF_4$	0
6	NaOAc	0

[a] *Reaction conditions:* trimethylene carbonate (5 mmol), aniline (1 mmol), ionic liquid (0.1 mmol).
[b] GC yield.

decreased according to the following order: OAc > Cl > Br > BF_4, which is consistent with the order of the hydrogen bond acceptor ability of the anions of the ionic liquids (Table 4, entries 1, 3–5).[6a] Also NaOAc did not show any catalytic activity for the reaction (Table 4, entry 6).

The effects of some parameters, such as reaction time, temperature and catalyst amount, on the reaction of trimethylene carbonate with aniline have also been investigated, and the optimal conditions are 9 h, 140 °C, and 10 mol% of BmimOAc catalyst (see the Supporting Information). Then various aromatic amines were used as substrates in this reaction (Table 5). *para*-Tolylamine, 4-methoxyphenylamine, 4-chlorophenylamine and 4-bromophenylamine gave desired products **3b**–**3e** in yields ranging from 59% to 75% (Table 5, entries 1–4). Naphthalen-1-ylamine afforded the corresponding product **3f** in 48% yield (Table 5, entry 5).

Table 5. Reaction of trimethylene carbonate and aromatic amines catalyzed by BmimOAc.[a]

Entry	Aromatic amine	Product	Yield[b] [%]
1		 **3b**	75
2		 **3c**	59
3		 **3d**	63
4		 **3e**	65
5		 **3f**	48

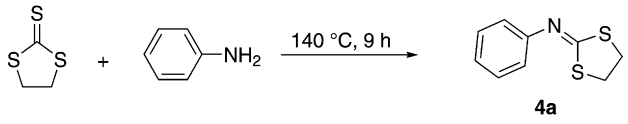
[a] *Reaction conditions:* trimethylene carbonate (10 mmol), aromatic amine (2 mmol), BmimOAc (0.2 mmol), 9 h, 140 °C.
[b] GC yield.

Synthesis of [1,3]Dithiolan-2-ylidene-arylamines from Ethylene Trithiocarbonate and Aromatic Amines in the Presence of BmimOAc

Proceeding on the same lines, we then examined the reaction of ethylene trithiocarbonate with aniline. To our surprise, this reaction produced [1,3]dithiolan-2-ylidene-phenylamine (**4a**) instead of 3-phenylthiazolidine-2-thione. It should be noted that [1,3]dithiolan-2-ylidene-arylamines, as bioactive cyclic dithiocarbonimidates, are effective anti-inflammatory analgesics with low ulcerogenicity.[14] The known methods for the synthesis of [1,3]dithiolan-2-ylidene-arylamines involve the use of toxic isothiocyanates.[4d,15] An alternative method established by the reaction of aromatic amines, carbon disulfide and dibromoethane has also been reported.[16] However, it suffered from a tedious and wasteful multi-step operational procedure. To the best of our knowledge, this is the first report on the preparation of [1,3]dithiolan-2-ylidene-arylamines from ethylene trithiocarbonate and aromatic amines. Because both ethylene trithiocarbonate and aromatic amines are readily available today, this reaction thus holds a great potential to be applied in organic synthesis.

Table 6 shows the catalytic activities of various ionic liquids for the reaction of ethylene trithiocarbonate with aniline. Both BmimOAc and BmmimOAc gave **4a** in relatively high yields (Table 6,

Table 6. Reaction of ethylene trithiocarbonate and aniline catalyzed by various ionic liquids.[a]



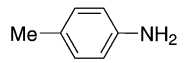
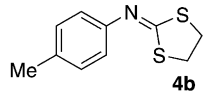
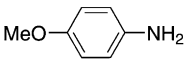
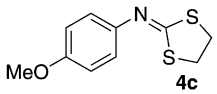
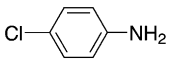
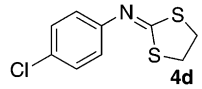
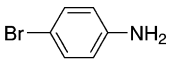
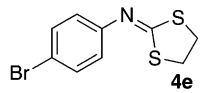
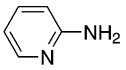
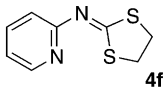
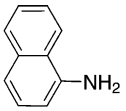
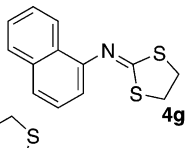
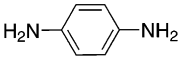
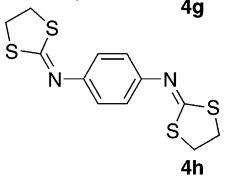
Entry	Ionic liquid	Yield[b] [%]
1	BmimOAc	85
2	BmmimOAc	89
3	BmimCl	64
4	BmimBr	56
5	$BmimBF_4$	52
6	NaOAc	43
7	–	43

[a] *Reaction conditions:* ethylene trithiocarbonate (10 mmol), aniline (2 mmol), ionic liquid (0.2 mmol).
[b] GC yield.

entries 1 and 2). It seems that the C-2 proton of the imidazolium ring does not play a dominating catalytic role in the reaction. Compared with BmimOAc, other ionic liquids, such as BmimCl, BmimBr and $BmimBF_4$, afforded lower yields, respectively, which implies that the high catalytic activities of the ionic liquids BmimOAc and BmmimOAc may be related to acetate anion (Table 6, entries 3–5). However, NaOAc showed very low catalytic activity for the reaction, probably owing to its low solubility (Table 6, entries 6 and 7).

After optimizing the reaction temperature (see the Supporting Information), various aromatic amines were used as substrates in this reaction (Table 7). *para*-Tolylamine, 4-methoxyphenylamine, 4-chlorophenylamine and 4-bromophenylamine could all be converted to the expected products, **4b**–**4e**, in moderate to good yields (Table 7, entries 1–4). Pyridin-2-ylamine and naphthalen-1-ylamine can also be used, providing the desired products, **4f** and **4g**, in 88% and 37% yields, respectively (Table 7, entries 5 and 6). Furthermore, benzene-1,4-diamine gave *N,N′*-bis-[1,3]dithiolan-2-ylidene-benzene-1,4-diamine (**4h**) in 40% yield (Table 7, entry 7). The structure of **4h** was also confirmed by an X-ray single-crystal diffraction study, an ORTEP diagram is shown in Figure 4.

Table 7. Reaction of ethylene trithiocarbonate and aromatic amines catalyzed by BmimOAc.[a]

Entry	Aromatic amine	Product	Yield[b] [%]
1		 **4b**	79
2		 **4c**	81
3		 **4d**	50
4		 **4e**	48
5		 **4f**	88
6		 **4g**	37
7		 **4h**	40[c]

[a] *Reaction conditions:* ethylene trithiocarbonate (10 mmol), aromatic amine (2 mmol), BmimOAc (0.2 mmol), 140 °C, 9 h.
[b] GC yield.
[c] Isolated yield.

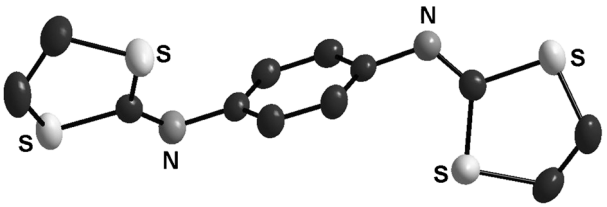


Figure 4. ORTEP diagram (50% probability) of **4h**. Hydrogen atoms are omitted for clarity.

Conclusions

In summary, a convenient method for the preparation of biologically active cyclic carbamates/dithiocarbonimidates has been developed with the aid of the ionic liquid BmimOAc. Starting from easily available cyclic carbonates and aromatic amines, various 3-aryloxazolidin-2-ones, 3,3′-aryldioxazolidin-2-ones and 3-aryl-[1,3]oxazinan-2-ones have been synthesized in moderate to high yields. NMR spectroscopy and DFT calculations have revealed that the cation and anion of BmimOAc can cooperatively activate cyclic carbonates and aromatic amines to effect these reactions. Furthermore, by using ethylene trithiocarbonate and aromatic amines as starting materials, a hitherto unreported and environmentally benign protocol for synthesizing [1,3]dithiolan-2-ylidene-arylamines has also be developed with the aid of the same ionic liquid catalyst.

Experimental Section

General Information

All ionic liquids were supplied by Centre for Green Chemistry and Catalysis, LICP, CAS. Ethylene carbonate and propylene carbonate were supplied by Sigma–Aldrich. Ethylene trithiocarbonate was supplied by TCI. The other compounds were supplied by Sinopharm. All chemicals were used without further purification.

GC analysis was performed on a Shimadzu GC-14B equipped with a capillary column DM-1701 30 m × 0.32 mm × 0.25 μm using a flame ionization detector. NMR spectra were recorded on Bruker Ascend400 and Bruker DRX500 instruments with tetramethylsilane as the internal standard. Melting points were determined using a Beijing Tech instrument X-4 apparatus and are uncorrected. HR-

MS analyses were measured on a Bruker Microtof II instrument. FT-IR spectra were recorded on a Nicolet nexus 670 instrument. Elemental analysis was done on an Elementar III analyzer.

General Procedure for the Synthesis of 3-Aryl-oxazolidin-2-ones/3,3′-Aryldioxazolidin-2-ones from Cyclic Carbonates and Aromatic Amines/Aromatic Diamines Catalyzed by BmimOAc

The reaction was carried out in a 5-mL round-bottomed flask equipped with a magnetic stirrer under a nitrogen atmosphere. Cyclic carbonate (10.0 mmol), aromatic amine/aromatic diamine (2.0 mmol) and BmimOAc (0.040 g, 0.2 mmol) were mixed together and heated to the desired temperature for 9 h. After completion of the reaction, the pure product was obtained by chromatography on silica gel and structurally characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, HR-MS.

Characterization Data of the New Compounds

3-(3-Isocyanophenyl)oxazolidin-2-one (1a): White solid; mp 56–58 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.87$ (s, 1H), 7.82 (d, $J = 8.4$ Hz, 1H), 7.49 (t, $J = 8.0$ Hz, 1H), 7.41 (d, $J = 7.6$ Hz, 1H), 4.54 (t, $J = 8.0$ Hz, 2H), 4.09 (t, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.9$, 139.1, 130.0, 127.3, 122.0, 121.0, 118.4, 113.1, 61.5, 44.8; IR (KBr): $\nu = 1050$, 1222, 1412, 1486, 1580, 1741, 1803, 2228, 2850, 2920 cm^{-1}; HR-MS (ESI): $m/z = 211.0479$, calcd. for $C_{10}H_8N_2O_2$ $[M+Na]^+$: 211.0478.

3-Benzo[1,3]dioxol-5-yl-oxazolidin-2-one (1b): Brown solid; mp 58–60 °C, ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 7.29$ (d, $J = 2.0$ Hz, 1H), 6.87–6.94 (m, 2H), 6.02 (s, 2H), 4.40 (t, $J = 8.0$ Hz, 2H), 4.00 (t, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 155.5$, 147.9, 143.9, 133.5, 111.9, 108.5, 101.7, 101.3, 61.8, 45.9; IR (KBr): $\nu = 1040$, 1231, 1454, 1502, 1635, 1729, 2850, 2919, 2994, 3368 cm^{-1}; HR-MS (ESI): $m/z = 230.0430$, calcd. for $C_{10}H_9NO_4$ $[M+Na]^+$: 230.0424.

3-(4-Morpholin-4-yl-phenyl)-oxazolidin-2-one (1c): Yellow solid; mp 142–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.42$ (d, $J = 8.8$ Hz, 2H), 6.91 (d, $J = 8.8$ Hz, 2H), 4.44 (t, $J = 8.0$ Hz, 2H), 4.00 (t, $J = 8.0$ Hz, 2H), 3.85 (t, $J = 4.6$ Hz, 4H), 3.11 (t, $J = 4.8$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.6$, 148.1, 131.0, 119.9, 116.3, 66.9, 61.4, 49.6, 45.6; IR (KBr): $\nu = 1047$, 1120, 1236, 1478, 1517, 1609, 1726, 1770, 2840, 2909 cm^{-1}; HR-MS (ESI): $m/z = 249.1234$, calcd. for $C_{13}H_{16}N_2O_3$ $[M+H]^+$: 249.1234.

3-[4-(4,4,5,5-Tetramethyl[1,3,2]dioxaborolan-2-yl)phenyl]-oxazolidin-2-one (1d): Yellow solid; mp 120–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.82$ (d, $J = 8.8$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.55 (d, $J = 8.8$ Hz, 1H), 7.40 (d, $J = 8.4$ Hz, 1H), 4.49 (t, $J = 8.6$ Hz, 2H), 4.08 (t, $J = 8.0$ Hz, 2H), 1.33–1.35 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.2$, 135.9, 135.8, 129.1, 118.4, 118.3, 117.1, 83.9, 83.6, 61.4, 45.1, 24.9; IR (KBr): $\nu = 1091$, 1145, 1362, 1402, 1530, 1607, 1663, 1747, 1807, 2924, 2978, 3043, 3109, 3195, 3363 cm^{-1}; HR-MS (ESI): $m/z = 312.1377$, calcd. for $C_{15}H_{20}BNO_4$ $[M+Na]^+$: 312.1378.

3-(3-Ethynylphenyl)oxazolidin-2-one (1e): Light yellow solid; mp 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.67$ (d, $J = 8.0$ Hz, 1H), 7.58 (s, 1H), 7.34 (t, $J = 8.0$ Hz, 1H), 7.27 (t, $J = 3.8$ Hz, 1H), 4.50 (t, $J = 8.0$ Hz, 2H), 4.05 (t, $J = 8.0$ Hz, 2H), 3.09 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.1$, 138.4, 129.2, 127.7, 122.9, 121.3, 118.8, 83.1, 77.7, 61.3, 45.0; IR (KBr): $\nu = 1118$, 1396, 1439, 1571, 1634, 1730, 2200, 3230, 3359 cm^{-1}; HR-MS (ESI): $m/z = 210.0529$, calcd. for $C_{11}H_9NO_2$ $[M+Na]^+$: 210.0525.

3-(4-Vinylphenyl)oxazolidin-2-one (1f): Yellow solid; mp 52–54 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.50$ (d, $J = 8.8$ Hz, 2H), 7.41 (d, $J = 8.8$ Hz, 2H), 6.68 (dd, $J_1 = 17.6$ Hz, $J_2 = 10.8$ Hz, 1H), 5.70 (d, $J = 17.6$, 1H), 5.22 (d, $J = 10.8$ Hz, 1H), 4.46 (t, 8.0 Hz, 2H), 4.03 (t, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.2$, 137.8, 135.9, 133.4, 126.8, 118.2, 113.4, 61.4, 45.2; IR (KBr): $\nu = 1222$, 1408, 1516, 1645, 1733, 1807, 2254, 2979, 3045, 3467 cm^{-1}; HR-MS (ESI): $m/z = 212.0686$, calcd. for $C_{11}H_{11}NO_2$ $[M+Na]^+$: 212.0682.

4-(2-Oxooxazolidin-3-yl)benzoic acid ethyl ester (1g): White solid; mp 217–219 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.06$ (d, $J = 8.8$ Hz, 2H), 7.63 (d, $J = 8.8$ Hz, 2H), 4.52 (t, $J = 8.0$ Hz, 2H), 4.37 (q, $J = 7.2$ Hz, 2H), 4.11 (t, $J = 8.0$ Hz, 2H), 1.40 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 166.1$, 154.9, 142.1, 130.7, 125.7, 117.2, 61.4, 45.0, 30.9, 14.4; IR (KBr): $\nu = 1186$, 1210, 1399, 1516, 1606, 1697, 1746, 1804, 2921, 2963, 2988, 3364 cm^{-1}; HR-MS (ESI): $m/z = 258.0736$, calcd. for $C_{12}H_{13}NO_4$ $[M+Na]^+$: 258.0737.

3-Dibenzofuran-2-yloxazolidin-2-one (1i): Light grey solid; mp 215–217 °C; ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 8.09$–8.14 (m, 2H), 7.96 (s, 1H), 7.61–7.70 (m, 2H), 7.38–7.51 (m, 2H), 4.50 (t, $J = 7.4$ Hz, 2H), 4.18 (t, $J = 7.4$ Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 156.4$, 156.3, 155.4, 138.8, 127.4, 123.9, 123.7, 121.7, 121.2, 119.5, 114.1, 112.0, 101.8, 62.0, 45.7; IR (KBr): $\nu = 1052$, 1119, 1503, 1581, 1635, 1739, 1905, 2919, 3088, 3359 cm^{-1}; HR-MS (ESI): $m/z = 276.0634$, calcd. for $C_{15}H_{11}NO_3$ $[M+Na]^+$: 276.0631.

3-Pyrimidin-2-yloxazolidin-2-one (1k): White solid; mp 171–173 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.69$ (d, $J = 4.8$ Hz, 2H), 7.07 (t, $J = 4.8$ Hz, 1H), 4.51 (t, $J = 7.9$ Hz, 2H), 4.29 (t, $J = 7.9$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 158.2$, 156.9, 153.1, 116.4, 61.6, 44.8; IR (KBr): $\nu = 1214$, 1415, 1564, 1765, 2923, 2986 cm^{-1}; HR-MS (ESI): $m/z = 188.0431$, calcd. for $C_7H_7N_3O_2$ $[M+Na]^+$: 188.0430.

3-(6-Methoxy-2-methylpyridin-3-yl)oxazolidin-2-one (1l): Yellow solid; mp 54–56 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.42$ (d, $J = 8.8$ Hz, 1H), 6.61 (d, $J = 8.8$ Hz, 1H), 4.51 (t, $J = 4.0$ Hz, 2H), 3.87–3.92 (m, 5H), 2.42 (s, 3H); $_{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 162.6$ 156.9, 154.1, 137.4, 125.4, 108.9, 62.3, 53.7, 47.7, 20.6; IR (KBr): $\nu = 1230$, 1292, 1583, 1646, 1753, 1806, 3395, 3489 cm^{-1}; HR-MS (ESI): $m/z = 209.0924$, calcd. for $C_{10}H_{12}N_2O_3$ $[M+H]^+$: 209.0921.

5-Methyl-3-pyridin-2-yloxazolidin-2-one (1n): White solid; mp 56–57 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.31$–8.32 (m, 1H), 8.21 (d, $J = 8.5$ Hz, 1H), 7.68–7.71 (m, 1H), 7.01–7.04 (m, 1H), 4.79–4.83 (m, 1H), 4.35–4.39 (m, 1H), 3.81–3.85(m, 1H), 1.53 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.7$, 151.1, 147.6, 137.8, 119.1, 113.1, 70.4, 50.8, 20.8; IR (KBr): $\nu = 1440$, 1475, 1591, 1765, 2895, 2986 cm^{-1}; HR-MS (ESI): $m/z = 201.0654$, calcd. for $C_9H_{10}N_2O_2$ $[M+Na]^+$: 201.0634.

5-Methyl-3-pyrimidin-2-yloxazolidin-2-one (1o): White solid; mp 136–137 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.67$ (d, $J = 4.7$ Hz, 2H), 7.05 (t, $J = 4.7$ Hz, 1H), 4.77–4.81 (m, 1H), 4.34 (t, $J = 9.1$ Hz, 1H), 3.81–3.84 (m, 1H), 1.53 (d, $J =$

6.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.2, 156.9, 152.8, 116.3, 69.9, 51.4, 20.5; IR (KBr): ν = 1210, 1449, 1566, 1777, 2897, 2991 cm^{-1}; HR-MS (ESI): m/z = 202.0592, calcd. for $C_8H_9N_3O_2$ $[M+Na]^+$: 202.0587.

3,3′-(Pyridine-2,6-diyl)dioxazolidin-2-one (2c): White solid; mp 255–257 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, J = 8.1 Hz, 2H), 7.74 (t, J = 8.1 Hz, 1H), 4.49 (t, J = 8.1 Hz, 4H), 4.23 (t, J = 8.1 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.7, 149.1, 139.9, 107.4, 61.9, 43.8; IR (KBr): ν = 1250, 1402, 1456, 1587, 1755, 2924, 2996 cm−1; HR-MS (ESI): m/z = 272.0642, calcd. for $C_{11}H_{11}N_3O_4$ $[M+Na]^+$: 272.0642.

3,3′-(1,4-Phenylene)bis(5-methyloxazolidin-2-one) (2d): Brown solid, decomposition at 360 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.55 (s, 4H), 4.78–4.80 (m, 2H), 4.15 (t, J = 8.6 Hz, 2H), 3.64–3.67 (m, 2H), 1.42 (d, J = 6.2 Hz, 6H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 164.0, 143.8, 128.1, 79.2, 60.7, 29.7; IR (KBr): ν = 1221, 1513, 1559, 1631, 2979 cm^{-1}; HR-MS (ESI): m/z = 299.0986, calcd. for $C_{14}H_{16}N_2O_4$ $[M+Na]^+$: 299.1002.

3,3′-(1,3-Phenylene)bis(5-methyloxazolidin-2-one) (2e): Brown solid; mp 134–135 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (s, 1H), 7.28–7.34 (m, 3H), 4.76–4.80 (m, 2H), 4.11–4.15 (m, 2H), 3.62–3.66 (m, 2H), 1.53 (d, J = 6.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.8, 139.1, 129.4, 113.2, 107.8, 69.6, 51.8, 20.6; IR (KBr): ν = 1219, 1474, 1503, 1607, 1738, 2902, 2983 cm^{-1}; HR-MS (ESI): m/z = 299.1031, calcd. for $C_{14}H_{16}N_2O^4$ $[M+Na]^+$: 299.1002.

3,3′-(Pyridine-2,6-diyl)bis(5-methyloxazolidin-2-one) (2f): White solid; mp 179–180 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (d, J = 8.1 Hz, 2H), 7.71 (t, J = 8.1 Hz, 1H), 4.77–4.81 (m, 2H), 4.29–4.34 (m, 2H), 3.74–3.78 (m, 2H), 1.53 (d, J = 6.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.3, 149.1, 139.8, 107.3, 70.2, 50.5, 20.6; IR (KBr): ν = 1244, 1402, 1454, 1587, 1765, 2909, 2987 cm^{-1}; HR-MS (ESI): m/z = 300.0981, calcd. for $C_{13}H_{15}N_3O_4$ $[M+Na]^+$: 300.0955.

General Procedure for the Synthesis of 3-Aryl[1,3]-oxazinan-2-ones/[1,3]Dithiolan-2-ylidene-arylamines from Trimethylene Carbonate/Ethylene Trithiocarbonate and Aromatic Amines Catalyzed by BmimOAc

The reaction was carried out in a 5-mL round-bottomed flask equipped with a magnetic stirrer under a nitrogen atmosphere. Trimethylene carbonate/ethylene trithiocarbonate (10.0 mmol), aromatic amine (2.0 mmol) and BmimOAc (0.040 g, 0.2 mmol) were mixed together and heated to 140 °C for 9 h. After completion of the reaction, the reaction mixture was analyzed by GC using *n*-dodecane as the internal standard. The pure product was obtained by chromatography on silica gel and structurally characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, HR-MS, and elemental analysis.

Characterization Data of the New Compounds

3-(4-Methoxyphenyl)-[1,3]oxazinan-2-one (3c): White solid; mp 102–104 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 4.41 (t, J = 5.3 Hz, 2H), 3.80 (s, 3H), 3.67 (t, J = 6.1 Hz, 2H), 2.18–2.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3 153.2, 136.0, 127.3, 114.6, 67.0, 55.6, 49.3, 22.6; IR (KBr): 1081, 1436, 1479, 1521, 1680, 2835, 2907, 2950 cm^{-1}; HR-MS (ESI): m/z = 230.0797, calcd. for $C_{11}H_{13}NO_3$ $[M+Na]^+$: 230.0788.

3-(4-Bromophenyl)-[1,3]oxazinan-2-one (3e): Light yellow solid; mp 114–116 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50–7.51 (m, 2H), 7.21–7.23 (m, 2H), 4.42 (t, J = 5.4 Hz, 2H), 3.70 (t, J = 6.1 Hz, 2H), 2.20–2.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 142.1, 132.3, 127.5, 120.2, 67.1, 48.7, 22.6; IR (KBr): ν = 1395, 1433, 1488, 1671, 2969 cm^{-1}; HR-MS (ESI): m/z = 277.9779, calcd. for $C_{10}H_{10}NO_2Br$ $[M+Na]^+$: 277.9787.

(4-Bromophenyl)-[1,3]dithiolan-2-ylidene-amine (4e): Yellow solid; mp 81–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, J = 7.9 Hz, 2H), 6.84 (d, J = 7.8 Hz, 2H), 3.49–3.59 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.5, 151.1, 132.1, 122.1, 117.6, 38.0, 35.3; IR (KBr): ν = 1206, 1471, 1586, 2923 cm^{-1}; HR-MS (ESI): m/z = 273.9367, calcd. for $C_9H_8BrNS_2$ $[M+H]^+$: 273.9354.

[1,3]Dithiolan-2-ylidene-pyridin-2-ylamine (4f): Light yellow solid; mp 77–78 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.47–8.49 (m, 1H), 7.68–7.71 (m, 1H), 7.18 (d, J = 8.1 Hz, 1H), 7.04–7.07 (m, 1H), 3.45–3.54 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.7, 158.6, 146.9, 137.9, 120.4, 120.2, 38.7, 33.2; IR (KBr): ν = 1245, 1279, 1423, 1453, 1526, 1565, 2915 cm^{-1}; anal. calcd. for $C_8H_8N_2S_2$ (196.01): C 48.95, H 4.11, N 14.27; found: C 48.82, H 4.11, N 14.24; HR-MS (ESI): m/z = 197.0229, calcd. for $C_8H_8N_2S_2$ $[M+H]^+$: 197.0202.

[1,3]Dithiolan-2-ylidene-naphthalen-1-ylamine (4g): Light yellow solid; mp 86–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, J = 7.6 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.40–7.48 (m, 3H), 6.98 (d, J = 7.2 Hz, 1H), 3.51 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.4, 149.2, 134.1, 127.8, 126.3, 125.7, 125.6, 124.6, 123.5, 114.3, 37.6, 35.3; IR (KBr): ν = 1277, 1389, 1426, 1510, 1596, 2927, 3050 cm^{-1}; HR-MS (ESI): m/z = 246.0419, calcd. for $C_{13}H_{11}NS_2$ $[M+H]^+$: 246.0406.

***N,N′*-Bis[1,3]dithiolan-2-ylidene-benzene-1,4-diamine (4h):** Light yellow solid; mp 218–220 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98 (s, 4H), 3.50–3.60 (m, 8H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.4, 148.4, 120.8, 37.8, 34.8; IR (KBr): ν = 1213, 1279, 1489, 1574, 1580, 2929, 3032 cm^{-1}; HR-MS (ESI): m/z = 312.9958, calcd. for $C_{12}H_{12}N_2S_4$ $[M+H]^+$: 312.9956.

Typical Procedure for ^{1}H NMR Titration

The ^{1}H NMR titration experiments were performed on a Bruker Ascend400 (400 MHz) at 298 K. A solution (100 mM) of BmimOAc in CD_3CN was titrated with small aliquots from a stock solution of propylene carbonate (5000 mM) in the same solvent. The changes in the chemical shift of the C-2 proton of the imidazolium moiety in the BmimOAc were monitored.

Computational Calculations

The calculations of optimal structures were performed by the DFT method with Becke's three-parameter exchange functional in combination with the Lee, Yang and Parr correlation functional (B3LYP) using the 6–31G basis set as implemented in the Gaussian 09 program package. Vibrational frequency calculations, from which the zero-point energies were derived, have been performed for each optimized

structure at the same level to identify the natures of all the stationary points.

X-Ray Structure Determination

A crystal of **4h** suitable for X-ray diffraction studies was obtained by slow evaporation of concentrated solutions of **4h** in CH_2Cl_2/CH_3CN. X-ray diffraction data from suitable crystals were collected on a Bruker Apex-II CCD area detector equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied using the SADABS program. The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2, with all non-hydrogen atoms refined with the anisotropic thermal parameters. All the hydrogen atoms attached to carbon atoms were placed in calculated positions and refined using the riding model. All calculations were carried out with the SHELXTL software. CCDC 993136 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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