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Highly efficient synthesis of cyclic carbonates from carbon dioxide and epoxides catalyzed by ionic liquid [Heemim][ZrCl₅]

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A facile and efficient synthesis of cyclic carbonates by cycloaddition reaction is described. Treatment of epoxides with carbon dioxide in the presence of [Heemim][ZrCl₅] under solvent- and additive-free conditions gives the corresponding cyclic carbonates in good to high yields and selectivity. Furthermore, the catalyst can be recycled or reused without any significant loss of catalytic activity. Additionally, the possible mechanism of cycloaddition in the catalytic system is also proposed.

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Introduction

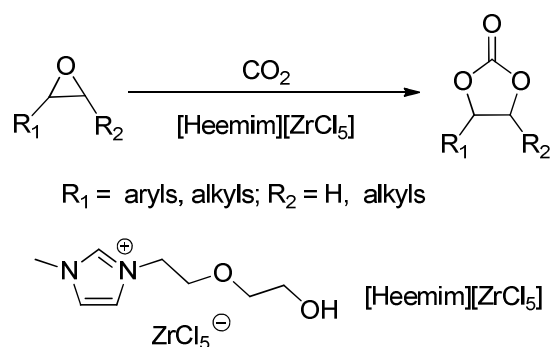
Carbon dioxide (CO₂) is an abundant, environmentally benign, economical, and renewable C1 source that have been used extensively as building block in the preparation of a variety of organic chemicals, materials, cyclic carbonates, etc.¹ Up to now, many publications in the open literature have been found in synthesis of these type of compounds using CO₂ as raw material, and one of the most interesting protocols constitutes the synthesis of cyclic carbonates via cycloaddition of CO₂ to epoxides.² The common methods for

performing such a transformation generally involve the use of stoichiometric amount of alkali metal catalysts (e.g. MoCl_5 , AlCl_3 , sodium iodide dihydrate, NaBr , NbCl_5 , etc),³ and suffer from considerable drawbacks such as harsh reaction condition, low yield, and a large amount of waste byproducts. Various reagents employed as the catalysts have been developed for this cycloaddition include $\text{Sc}(\text{OTf})_3/\text{CTAB}$,⁴ PPN salts,⁵ $\text{ZnBr}_2\text{-Ph}_4\text{PI}$,⁶ supported imidazole,⁷ organometallic complexes,⁸ organic base niobate salts,⁹ imidazolium bromides,¹⁰ $\text{ZnCl}_2/\text{mp-C}_3\text{N}_4$,¹¹ MCM-41-Imi/Br ,¹² $\text{ECS-Ni}(\text{acac})_2/\text{TBAB}$,¹³ ZIF-8 ,¹⁴ organocatalysts,¹⁵ and other complexes.¹⁶ However, some of these procedures are invariably associated with one or more disadvantages such as the low activity, rigorous reaction conditions, high cost, unsatisfactory stability, environmental hazards, and difficulties in recycling of the catalyst.

Ionic liquids (ILs) have received considerable attention as alternatives to the traditional organic solvents. Because of their interesting physical and chemical properties, such as negligible vapor pressure, unique permittivity, high thermal stability, good solvents for both organic and inorganic substances, high electrical conductivity and wide electrochemical window,^{17,18} ionic liquids have found an application in many chemical reactions¹⁹ and processes including extraction and separation.²⁰ Up to now, examples of their application as catalysts in the cycloaddition of CO_2 to epoxides were also reported.²¹ However, these reported protocols are still associated with one or more disadvantages, such as low catalyst activity, water or air sensitivity, and the requirement for transition metal additives. Consequently, search for new and environmentally benign synthetic methodologies for the synthesis of cyclic carbonates that address these drawbacks is still highly required.

Considering the good physical and toxicological properties of ILs, the main aim of this work is to establish a green, efficient protocol for synthesis of cyclic carbonates in the presence of ionic liquid. Herein, we report a new, efficient and environmentally friendly protocol for the cycloaddition reaction of

epoxides to cyclic carbonates with CO₂ catalyzed by ionic liquid 1-[2-(2-hydroxyethoxy)ethyl]-3-methylimidazolium zirconium chloride ([Heemim][ZrCl₅]) under mild conditions (Scheme 1). In addition, the catalytic system can be easily recovered and reused without any significant loss of catalytic activity.



Scheme 1 Synthesis of cyclic carbonates from epoxides and CO₂.

Results and discussion

The initial study was carried out using propylene oxide and CO₂ as the model substrates to optimize the reaction conditions, and the results are summarized in Table 1. At first, the cycloaddition in the presence of the catalytic amount of a series of ILs based on Heemim⁺, Hmim⁺, Bmim⁺ or Bmpy⁺ cation and CuCl₂[−], ZnCl₃[−], ZrCl₅[−], CoCl₃[−], TiCl₅[−], AlCl₄[−], Cl[−], Br[−], BF₄[−] or PF₆[−] anion (Table 1, entries 1–13). The results showed that the kinds of cations or anions of ILs have great influences on the cycloaddition, and it was observed that the Heemim⁺ cation and ZrCl₅[−] anion demonstrated the best performance. Therefore, [Heemim][ZrCl₅] was identified as the most effective ionic liquid catalyst (Table 1, entry 3), and was thus chosen as the model catalyst for further investigation. The different effects of ILs in the reaction may be attributed to their different abilities of stabilizing and dissolving propylene oxide and CO₂. Under the same conditions, the IL who stabilizes and dissolves them more easily will leads to a larger increase in the effective reactant concentration, which increases the encounter probabilities between the substrate and

reactive species, and so the higher rate or yield of the reaction is observed.

Table 1 Optimization of the conditions for the synthesis of propylene carbonate^a

Entry	Catalyst	Time / h	Yield / (%) ^b	Selectivity / (%) ^c
1	[Heemim][CuCl ₂]	5	62	75
2	[Heemim][ZnCl ₃]	3	69	80
3	[Heemim][ZrCl ₅]	3	96	> 99
4	[Heemim][CoCl ₃]	5	65	78
5	[Heemim][TiCl ₅]	3	84	92
6	[Heemim][AlCl ₄]	3	72	85
7	[Heemim]Cl	8	68	83
8	[Heemim]Br	8	65	76
9	[Heemim][BF ₄]	8	48	54
10	[Heemim][PF ₆]	8	32	57
11	[Hmim][ZrCl ₅]	3	81	90
12	[Bmim][ZrCl ₅]	3	78	88
13	[Bmpy][ZrCl ₅]	3	70	85

^a The reactions were carried out with propylene oxide (10 mmol), IL (2 mmol) , and CO₂ (1 MPa) at 120 °C. ^b Isolated yield. ^c Isolated selectivity.

The cycloaddition reaction of propylene oxide with CO₂ was then tested at 120 °C in the presence and absence of [Heemim][ZrCl₅]. Reaction screening led to disappointing results in the absence of ionic liquid, and no product was detected after 24 h (Table 2, entry 1). When the reaction was performed in the presence

of the ionic liquid [Heemim][ZrCl₅], the product propylene carbonate could be obtained in a higher yield 48% or selectivity 82% in a shorter time (5 h) when only 0.5 mmol of [Heemim][ZrCl₅] was used (Table 2, entry 2). The yield and selectivity improved with increasing amount of [Heemim][ZrCl₅] (Table 2, entries 2–6), and reached maximum with 2.0 mmol of [Heemim][ZrCl₅] (Table 2, entry 6). However, further addition the amount of [Heemim][ZrCl₅], under the same conditions, the yield and selectivity were not enhanced significantly (Table 2, entry 7). In addition, the thermal property of [Heemim][ZrCl₅] was investigated by means of TGA. As depicted in Fig. 1a, the pyrolysis temperature of [Heemim][ZrCl₅] is above 250 °C. The mass loss might be due to the decomposition of [Heemim][ZrCl₅], which caused cleavage of the chains. From the curve depicted in Fig. 1b, one can see that [Heemim][ZrCl₅] is thermally stable at 120 °C. The good thermal stability of [Heemim][ZrCl₅] may be beneficial to the recycling experiments, and the IL could be typically recovered and reused with no appreciable decrease in yields and reaction rates (Table 2, entries 8 and 9).

Table 2 Screening of the reaction condition for the synthesis of propylene carbonate^a

Entry	Ionic liquid / mmol	Time / h	Yield / (%) ^b	Selectivity / (%) ^c
1	0	24	0	0
2	0.5	5	48	82
3	1.0	5	75	90
4	1.5	3	86	95
5	1.8	3	91	98
6	2.0	3	96	> 99
7	2.5	3	96	99
8 ^d	2.0	3	96	> 99

9^e

2.0

3

95

> 99

^a The reactions were carried out with propylene oxide (10 mmol), [Heemim][ZrCl₅] (2 mmol), and CO₂ (1 MPa) at 120 °C. ^b Isolated yield. ^c Isolated selectivity. ^d The first run. ^e The second run.

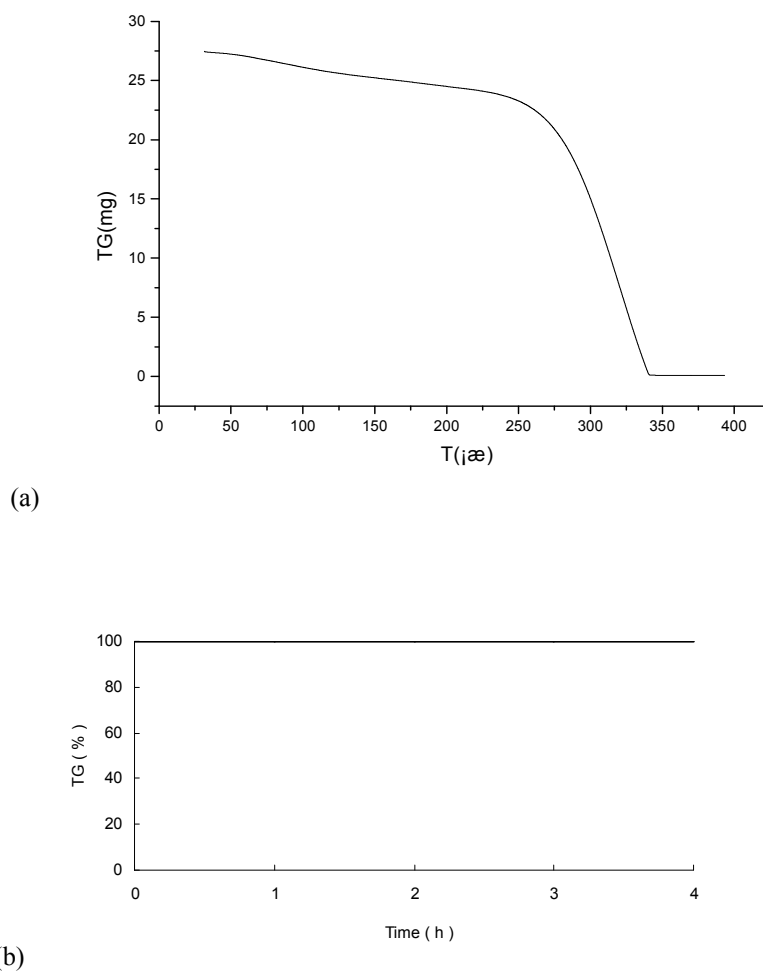


Fig. 1 TGA curves of [Heemim][ZrCl₅] with a heating rate of 15 K/min in dynamic argon atmosphere, approximately 27 mg sample was used. The curves were shifted vertically for clarity. (a) The sample was heated from 30 to 390 °C; (b) the same sample was kept at 120 °C for 4 h.

It was found that the yield of propylene carbonate was strongly affected by the reaction temperature. As shown in Fig. 2, the yield and selectivity of propylene carbonate increased with the reaction temperature

up to 120 °C, whereas further increase in the temperature caused a decrease in the yield and selectivity, possibly due to side-products formed at the higher temperature, such as, the isomerization and the ring opening of propylene oxide. These results show that the optimal temperature, such as 120 °C enhanced the cycloaddition.

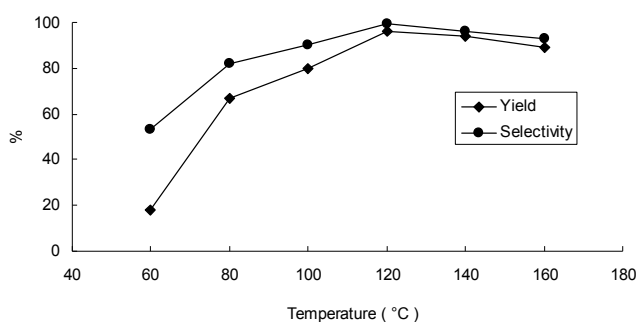


Fig. 2 Influence of temperature on the synthesis of propylene carbonate. Reaction conditions: propylene oxide (10 mmol), [Heemim][ZrCl₅] (2 mmol), CO₂ (1 MPa), 3 h.

Depicted in Fig. 3 is the plot of propylene carbonate yield and selectivity versus CO₂ pressure. As can easily be seen, an almost quantitative yield together with excellent selectivity could be retained at a low CO₂ pressure, demonstrating the preferential effect of the cation and anion of [Heemim][ZrCl₅] for promoting the reactivity of CO₂. The catalytic activity increased with the CO₂ pressure to 1 MPa, however, the yield and selectivity were decreased with the further increase of CO₂ pressure. Too high CO₂ pressure may retard the interaction between propylene oxide and the catalyst, and could cause a low concentration of propylene oxide in the vicinity of the catalyst, thus resulting in a low yield and selectivity. Therefore, the suitable CO₂ pressure would be 1 MPa.

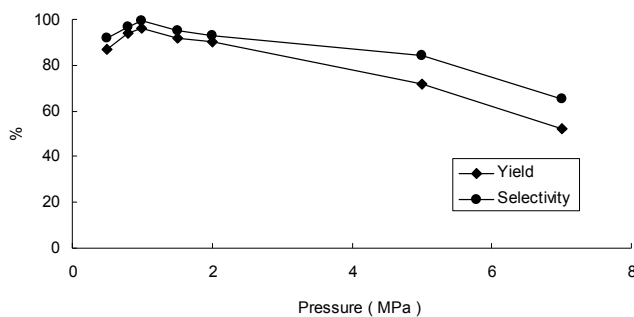
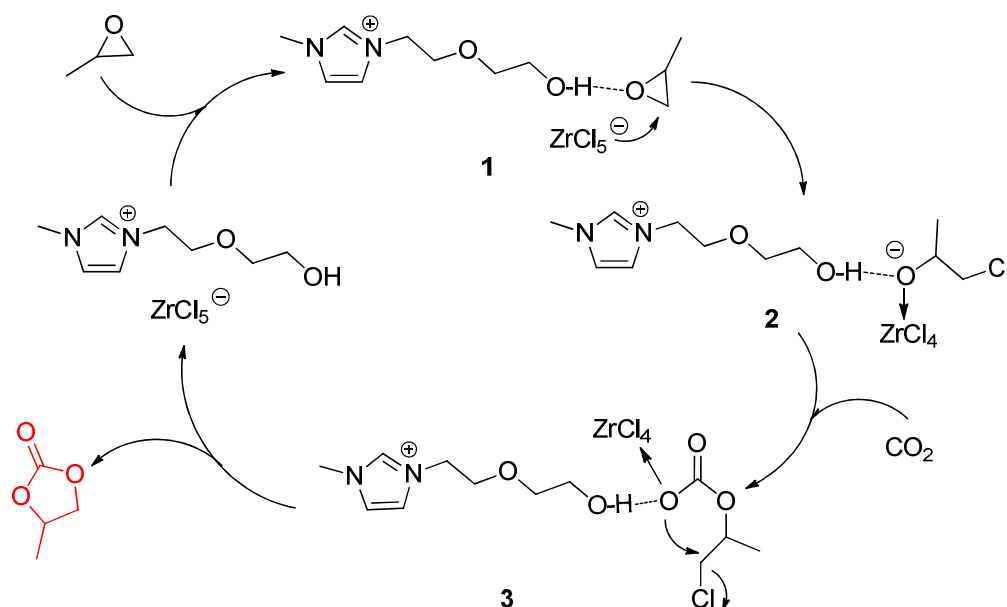


Fig. 3 Influence of CO₂ pressure on the synthesis of propylene carbonate. Reaction conditions: propylene oxide (10 mmol), [Heemim][ZrCl₅] (2 mmol), 120 °C, 3 h.


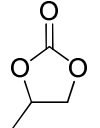

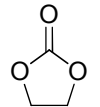
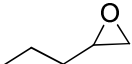
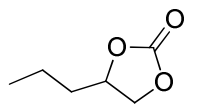
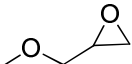
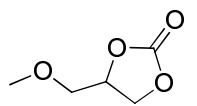
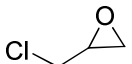
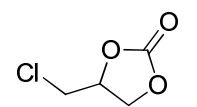
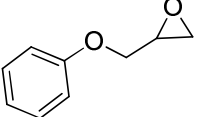
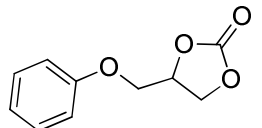
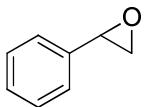
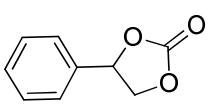
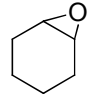
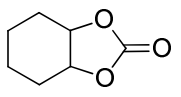
According to the literatures²² and the observations in our reactions, taking the cycloaddition of propylene oxide with CO₂ as an example, a possible mechanism is proposed (Scheme 2). In the reaction, the coordination of H atoms in the –OH groups with the O atom of propylene oxide through a hydrogen bond resulted in the polarization of C–O bonds (**1**), and the ZrCl₅ anion made a nucleophilic attack on the less sterically hindered carbon atom of propylene oxide at the same time. As a result, the ring of propylene oxide was opened to form transition state **2**. Then, the interaction occurred between the oxygen anion and CO₂, forming an alkylcarbonate anion **3**, which would be transformed into the desired product by the intramolecular substitution of the halide in the next step. It looks like that the formations of **2** from **3** are the rate-determining steps.



Scheme 2 Possible mechanism for the cycloaddition.

The above results indicated that [Heemim][ZrCl₅] is an effective, stable and reusable catalyst for the cycloaddition of CO₂ to propylene carbonate. In order to investigate the applicability of [Heemim][ZrCl₅], the catalyst was tested for the synthesis of cyclic carbonates from different epoxides (Table 3). Under the adopted conditions, the corresponding cyclic carbonates are obtained in good to high isolated yield using the catalytic protocol (Table 3, entries 1-8). The epoxides such as propylene carbonate, oxirane, 2-propyloxirane, 2-(methoxymethyl)oxirane, 2-(chloromethyl)oxirane, 2-(phenoxymethyl)oxirane, and 2-phenyloxirane were the preferred substrates for the reaction and these reactions could be completed in no more than 3 h (Table 3, entries 1-7). While cyclohexene oxide, which needs 12 h to reach 81% yield due to the higher hindrance originated from the two rings (Table 3, entry 8). The selectivity of all the reactions to the cyclic carbonates was more than 98%.

Table 3 Catalytic cycloaddition of epoxides and CO₂ to cyclic carbonates^a

Entry	Substrate	Product	Time / h	Yield / (%) ^b	Selectivity / (%) ^c
1			3	96	> 99
2			3	98	> 99
3			3	95	98
4			3	96	98
5			2	97	99
6			2	98	99
7			3	97	99
8			12	81	98

^a The reactions were carried out with epoxide (10 mmol), [Heemim][ZrCl₅] (2 mmol), and CO₂ (1 MPa) at 120 °C. ^b Isolated yield. ^c Isolated selectivity.

Conclusions

In conclusion, we have developed a new and highly efficient procedure for the synthesis of cyclic carbonates under mild conditions. Catalysts with different cation and anion of IL had a remarkable influence on the reaction. Among all the IL catalysts investigated, [Heemim][ZrCl₅] was the most effective.

The catalyst could be applicable to a series of epoxides with good activities. Mild reaction conditions,

simplicity of operation, high yields, stability, and excellent recyclability of the catalyst are the attractive features of this methodology. The scope, definition of the mechanism and synthetic application of this reaction are currently under study in our laboratory.

Experimental

All the chemicals were from commercial sources without any pretreatment. All reagents were of analytical grade. The ionic liquids were synthesized according to the literature procedures.¹⁸ NMR spectra were recorded on a Bruker 500-MHz spectrometer using CDCl₃ as the solvent with tetramethylsilane (TMS) as an internal standard. GC analysis were performed on a Shimadzu-14B gas chromatography equipped with HP-1 capillary column. Thermogravimetric analysis (TGA) was carried out using TG 209 F3 thermobalance (Netzsch Geratebau GmbH). Elemental analysis were performed on a Vario EL III instrument (Elementar Analysensysteme GmbH, Germany).

General procedure for cycloaddition of epoxide with CO₂

The cycloaddition reaction was carried out in a stainless-steel reactor equipped with a magnetic stirrer and automatic temperature control system. [Heemim][ZrCl₅] (2 mmol) and epoxide (10 mmol) were charged into the reactor. CO₂ was charged in the reactor and the pressure was adjusted to 1 MPa at 120 °C. The reactor was heated at 120 °C for an appropriate time (Table 3), and the pressure was kept constant during the reaction. The progress of the reaction was monitored by GC. Then the reactor was cooled to ambient temperature, and then the excess of CO₂ was vented. The resulting mixture was transferred to a round bottom flask and the residue was purified by distillation under vacuum to afford the desired pure product. The rest of the ionic liquid was recovered and reused directly without further treatment. Fresh substrates and CO₂ were then recharged to the recovered catalyst and then recycled under identical reaction

conditions. The target substrates were characterized by Elemental analysis, NMR spectra or compared with their authentic samples. Spectroscopic data for selected products is as follows.

4-Propyl-1,3-dioxolan-2-one (Table 3, entry 3)

^1H NMR: δ 0.85 (t, CH_3 , 3H), 1.35 (m, CH_2 , 2H), 1.59 (dd, CH_2 , 2H), 4.11 (m, CH, 1H), 4.51 (t, CH_2 , 1H), 4.69 (t, CH_2 , 1H). ^{13}C NMR: δ 14.2, 21.8, 36.7, 68.5, 76.4, 155.2. Anal. Calcd. for $\text{C}_6\text{H}_{10}\text{O}_3$: C, 55.34; H, 7.71; O, 36.85. Found: C, 55.37; H, 7.74; O, 36.88.

4-(Methoxymethyl)-1,3-dioxolan-2-one (Table 3, entry 4)

^1H NMR: δ 3.46 (s, CH_3 , 3H), 3.72-3.87 (dd, CH_2 , 2H), 4.17 (t, CH_2 , 1H), 4.56 (t, CH_2 , 1H), 4.78 (m, CH, 1H). ^{13}C NMR: δ 60.4, 67.9, 74.9, 78.5, 155.9. Anal. Calcd. for $\text{C}_5\text{H}_8\text{O}_4$: C, 45.43; H, 6.08; O, 48.41. Found: C, 45.46; H, 6.10; O, 48.44.

4-(Chloromethyl)-1,3-dioxolan-2-one (Table 3, entry 5)

^1H NMR: δ 3.73-3.82 (dd, CH_2 , 2H), 4.36 (dd, CH_2 , 1H), 4.57 (dd, CH_2 , 1H), 4.89 (m, CH_2 , 1H). ^{13}C NMR: δ 44.2, 67.3, 73.9, 155.1. Anal. Calcd. for $\text{C}_4\text{H}_5\text{ClO}_3$: C, 35.16; H, 3.67; Cl, 25.94; O, 35.11. Found: C, 35.19; H, 3.69; Cl, 25.97; O, 35.15.

4-Phenoxymethyl-1,3-dioxolan-2-one (Table 3, entry 6)

^1H NMR: δ 4.12-4.25 (m, CH_2 , 2H), 4.54-4.65 (m, CH_2 , 2H), 4.98 (m, CH, 1H), 6.94-7.05 (m, Ar-H, 3H), 7.36 (m, Ar-H, 2H). ^{13}C NMR: δ 66.3, 67.8, 75.6, 115.2, 122.4, 155.1, 157.3. Anal. Calcd. for $\text{C}_{10}\text{H}_{10}\text{O}_4$: C, 61.83; H, 5.18; O, 32.94. Found: C, 61.85; H, 5.19; O, 32.96.

4-Phenyl-1,3-dioxolan-2-one (Table 3, entry 7)

^1H NMR: δ 4.35 (t, CH_2 , 1H), 4.76 (t, CH_2 , 1H), 5.63 (t, CH_2 , 1H), 7.32-7.46 (m, Ar-H, 5H). ^{13}C NMR: δ 69.5, 75.6, 125.5, 128.9, 130.5, 134.8, 155.4. Anal. Calcd. for $\text{C}_9\text{H}_8\text{O}_3$: C, 65.83; H, 4.87; O, 29.22. Found: C, 65.85; H, 4.91; O, 29.24.

Acknowledgements

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