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Co-catalyst and solvent free nitrogen rich triazole based organocatalysts for cycloaddition of CO_2 into epoxide

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ABSTRACT

A general synthesis of triazole-based catalysts remains a significant challenge. Consequently, triazole-based catalysts are rarely studied. Herein, the first report is presented for the construction of cyclic carbonates using triazole-based organocatalysts, which is a crucial technology to a genuinely sustainable and atom-efficient economy. A series of triazole-based organocatalysts was synthesized, entirely characterized by FTIR, NMR, mass spectrometry, and elemental analysis. This work is mainly based on the construction of nucleophilic-electrophilic bifunctional catalysts (N-rich triazole ring-carboxylic group) combined with substituents, which evaluate the vital effect of substituents for the catalytic cycloaddition reaction of CO_2 into epoxide. In general, various systems required the Lewis basic site in the form of cocatalyst or solvent to be optimally effective. However, our designed catalyst contained Lewis basic and acidic sites. It, therefore, can catalyze the reaction proficiently without the aid of solvent, cocatalysts and can perform at ambient pressure of CO_2 (1 bar) to produce different cyclic carbonates. Moreover, the catalyst is reusable, maintaining the same activity along with remarkable catalyst stability.

1. Introduction

Utilization of CO_2 being abundant, inexpensive, C1 carbon, and a renewable source has great importance for the synthesis of cyclic carbonates. The ultimate aim of CO_2 fixation is, to reduce the emission of carbon dioxide in the atmosphere, generated from fossil fuels. Therefore, the title reaction plays an important role in decreasing the rising level of greenhouse gases, especially CO_2. As cyclic carbonate can be synthesized on a low scale; however, it is an attractive means of chemically fixing CO_2 due to the widespread utility of cyclic carbonates. Such as polar aprotic solvents, cosmetics, intermediates for the preparation of pharmaceuticals and fine chemicals, as electrolytes in lithium-ion batteries, and as raw materials for polymers. [1–7] Cyclic carbonates are also applied as intermediate in Asahi-Kasei synthesis of polycarbonates and as intermediates in Shell's Omega process for the production of glycols [8,9]. Indeed on the significant application of cyclic carbonates, this reaction has been extensively investigated using a long series of catalysts, including both homogeneous and heterogeneous catalysts.

These catalytic systems include ionic liquids [10–13], metal complexes [14–22], metal oxide [23], alkali metal halides and carbonates [24–26], phosphonium salts/quaternary ammonium [27,28], functional polymer [29,30], mesoporous materials [31,32], MOFs [33–35], COFs [25,36] and core-shell of organic-inorganic hybrid microspheres [37]. Including metal-based catalysts, transition metal-based catalysts coupled with a quaternary ammonium salt as a cocatalyst exhibited excellent catalytic activity for the synthesis of cyclic carbonate at mild conditions [38–40]. However, the metal-based synthetic procedure is complex, costly, consists of multi-steps, and needs high pressure and hence limits its application on an industrial scale. In recent years,

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metal-free catalysts have attracted more attention for the synthesis of cyclic carbonates, because of the remarkable feature of organocatalysts such as less toxic, more sustainable, easy accessibility, cost-effective and more important easily to handle [41,42]. So far, several metal-free catalysts have been developed for the title reaction by various researchers. Metal-free catalytic systems including ammonium salts [43], phosphonium salts [44,45], and imidazolium salts [46,47] have been reported to generate cyclic carbonates. In addition, two-component systems containing quaternary ammonium salts and a polyol have also been studied. However, halides, as part of the system, may limit the use of these catalysts due to their corrosive nature towards the steel reactors [48]. Shen et al. reported 4-dimethyl aminopyridine (DMAP) conjunction with salen ligands for the chemical fixation of CO_2 and epoxide into cyclic carbonates at 120 °C and 35 bar. [49] Additionally, Hydrogen-Bond-Donation (HBD) catalysis has attracted much attention as a greener alternative along with good to excellent yields of cyclic carbonate from CO_2 and epoxide under mild conditions. Several examples of HBD organocatalysts have been reported such as 2-pyridinemethanol/(n-tetrabutylammonium iodide) TBAI, [50] graphene oxides/dimethylformamide (DMF) [51], ascorbic acid/TBAI [52], squaramide/TBAI, [53] *etc*. More recently, North and co-workers developed salophen organocatalytic systems for the insertion of CO_2 into epoxides at high temperature, 120 °C, along with solvent (2-Me THF) under 30 bar pressure. [54] However, still, the use of solvents, additives, high pressure, and high temperature are required. One important point related to the sustainability of the process is the high-temperature value, which is a great problem in the balance of utilization/emission of CO_2. Therefore, there is a high demand to develop an effective catalytic protocol such as metal-free, cocatalyst free, and mainly working at low temperature and ambient pressure of CO_2. Here, keeping these concerns in mind, we designed nitrogen-rich triazole based organocatalysts, the green candidate for the generation of cyclic carbonates. This work is based on a detailed study of N-rich triazole organocatalysts and its substituents effect, which points out the important role of substituents for cycloaddition reaction of CO_2 into epoxide catalysis. The specially designed organocatalytic system, bearing CO_2 activation sites, brönsted acidic center, and nucleophilic center, (Fig.1) helps to construct cyclic carbonate under solvent-free, cocatalyst-free and at low-pressure *i-e.,* 1 bar. The catalyst synthesis is facile, cost-effective, and more delightfully reusable and stable. Till now, from the best of our knowledge, we report for the first time the triazole organocatalysts, which displays interesting results for the title reaction. These organocatalysts will open a new gateway for non-redox catalytic CO_2 fixation in cyclic carbonates.

2. Experimental section

2.1. Synthesis and characterization of catalysts

The compounds **A–D** were synthesized by the reported system, [55] with some modifications. In a typical procedure, sodium ascorbate (0.32 mmol) and $CuSO_4{\cdot}5H_2O$ (0.16 mmol) were dissolved in 1.0 mL H_2O poured into a two-necked flask equipped with Ar atmosphere (the click catalyst). Then, a series of compounds such as 2-azido-1,3,5-trimethyl benzene, azidobenzene, fluorobenzene, nitrobenzene (3.26 mmol, 1.0 equiv.) and propiolic acid (3.92 mmol, 1.2 equiv.) were carefully added in 0.5 mL *ter*-BuOH and injected to the already prepared click catalyst solution. Under inert atmosphere and at room temperature, the reaction mixture was stirred for 24 h. After that, 15 mL saturated $NaHCO_3$ solution was added to quench the reaction, and the desired precipitate was washed twice with ether and filtered. Subsequently 100 mL H_2SO_4 solution was added to the desired product, followed by extraction with ethyl acetate. The anhydrous Na_2SO_4 was used for drying the organic fractions and then filtered. The obtained filtrate was evaporated and dried under vacuum at 30 − 40 °C.

2.2. Compound (A) Yield: 73 %

^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.84 (s, 2 H), 2.33 (s, 6 H), 2.26 (s, 3 H); ^{13}C-NMR (126 MHz, CDCl3) δ 135.3, 134.3, 131.8, 129.5, 20.7, 18.0.

Elemental Analysis: Calcd for $C_{12}H_{13}N_3O_2$: C, 62.33; H, 5.67; N, 18.17; O, 13.84. Found: C, 62.73; H, 6.07; N, 18.57; **FTIR (neat):** $\nu_{\mathbf{max}}$ = 3149, 3110, 2958, 2920, 2647, 2569, 1689, 1538, 1503, 1409, 1355, 1245, 1191, 1035, 930, 852, 770, 584, 544 cm^{-1}; **The HR-ESI -MS (positive)** of catalyst A exposed to molecular ion peak at *m/ z* = 210.100 correspond to $[C_{12}H_{13}N_3O_2+Na^+]^+$, [56] almost analogue to $[C_{12}H_{13}N_3O_2]$.

2.3. Compound (B) Yield

71 %: ^{1}H NMR (500 MHz, Chloroform-d) δ 8.64 (s, 1 H), 7.80 (d, J =7.8 Hz, 2 H), 7.60 (d, J =8.1 Hz, 2 H), 7.55 (t, J =7.4 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.53, 139.89, 136.25, 130.06, 126.25, 120.92, 76.77. **Elemental Analysis:** Calcd for $C_9H_7N_3O_2$: C, 57.14; H, 3.73; N, 22.21; O, 16.91. Found: C, 57.54; H, 4.13; N, 22.61; **FTIR (neat):** $\nu_{\mathbf{max}}$ = 3479, 3136, 2894, 2806, 2727, 2634, 2557, 1988, 1809, 1697, 1652, 1596, 1552, 1504, 1404, 1321, 1251, 1168, 1041, 991, 918, 850, 761, 683, 567, 507, 428 cm^{-1}; **The HR-ESI-MS (positive):** *m*/*z* calcd. for $C_9H_7N_3O_2$: 189.17; Found = 190.061.

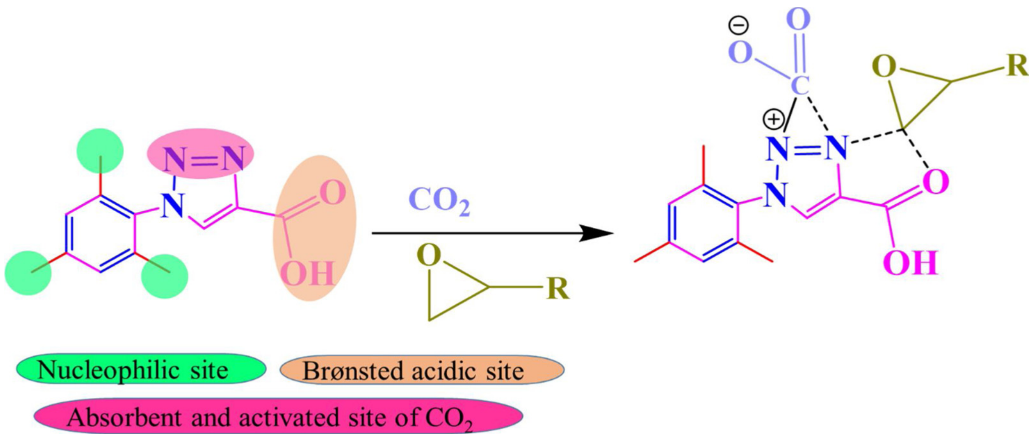
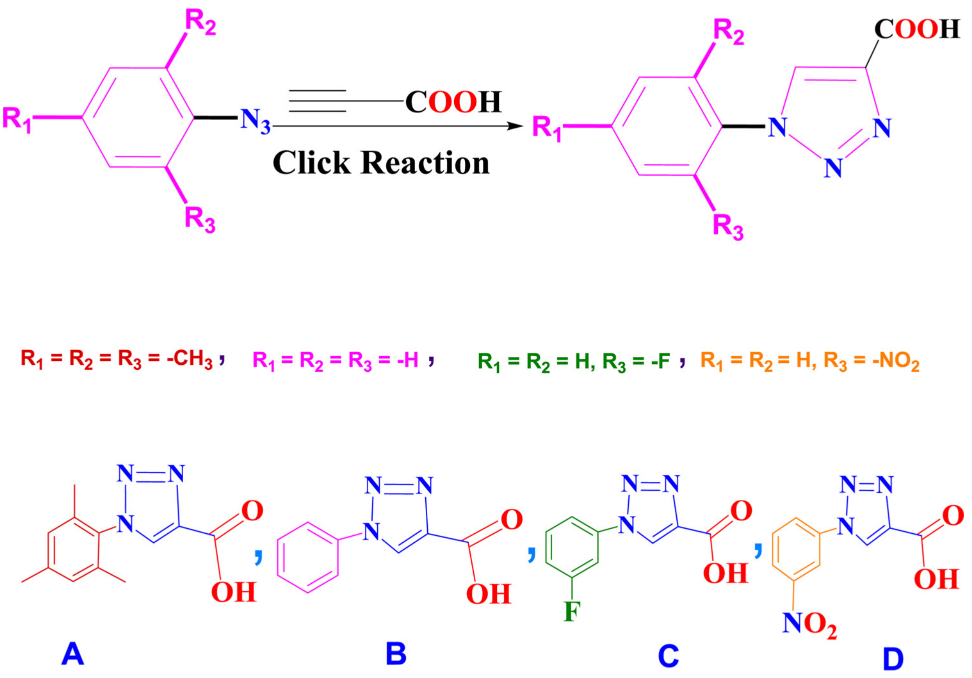
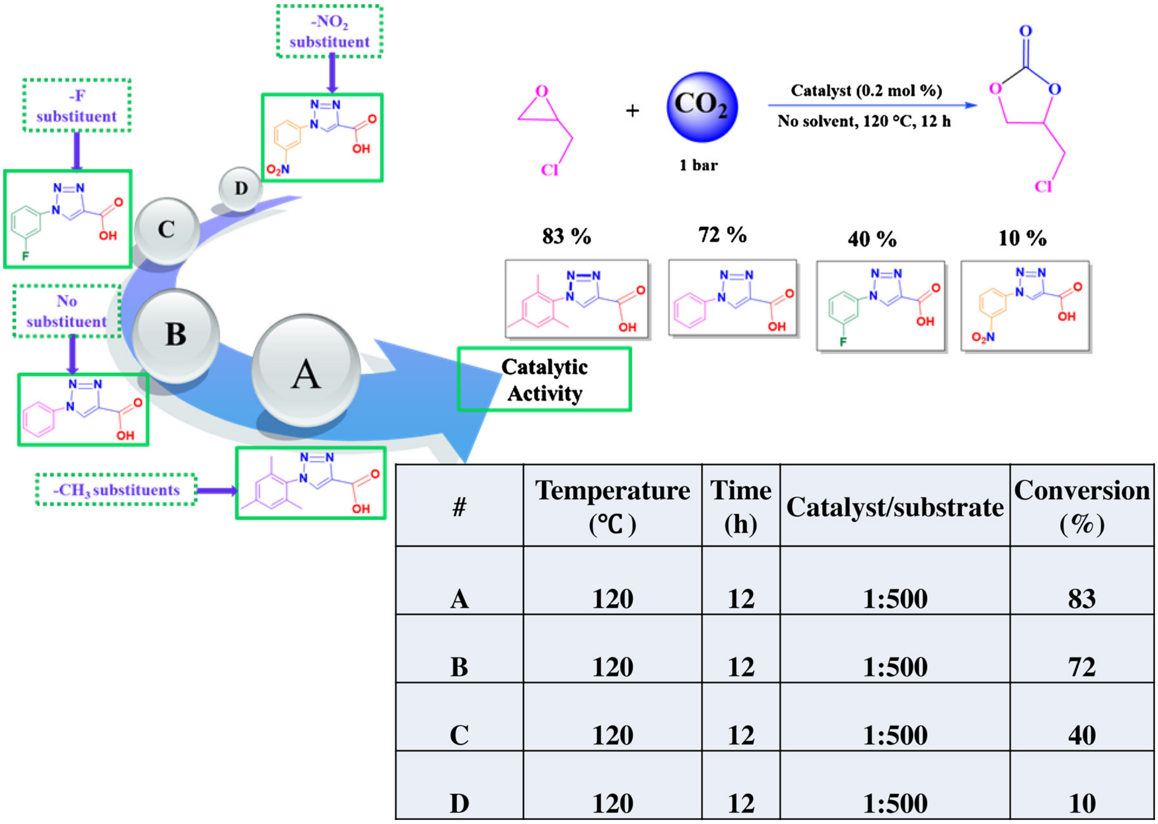


Fig. 1. Triazole organocatalysts design along with active sites.



Scheme 1. General procedure for the synthesis of catalysts **(A-D)**.

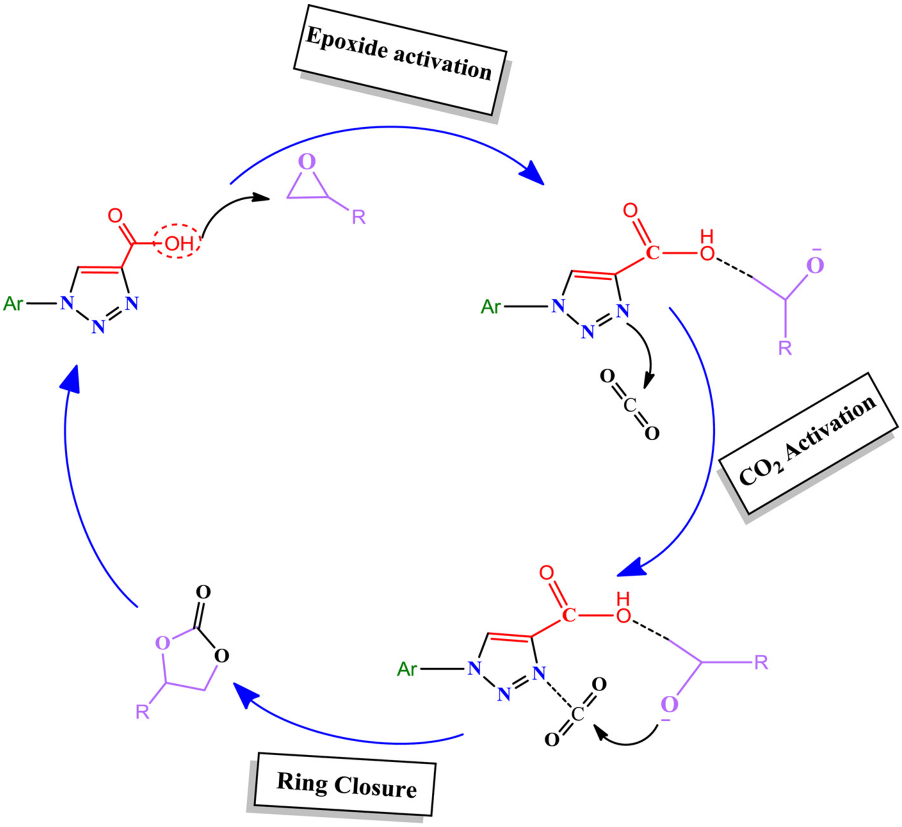


#	Temperature (℃)	Time (h)	Catalyst/substrate	Conversion (%)
A	120	12	1:500	83
B	120	12	1:500	72
C	120	12	1:500	40
D	120	12	1:500	10

Fig. 2. Catalytic activities for triazole-based organocatalysts. Reaction conditions: Epichlorohydrin 10 mmol, Catalyst 0.02 mmol, Pressure 1 bar, Temperature 120 °C, time 12 h.

2.4. Compound (C) Yield: 68 %

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.16 (d, J = 1.6 Hz, 1 H), 7.90 – 7.85 (m, 1 H), 7.69 – 7.63 (m, 1 H), 7.63 – 7.56 (m, 1 H), 7.47 (t, J = 7.6 Hz, 1 H); ^{13}C NMR (126 MHz, DMSO) δ 161.83, 155.64, 140.70, 132.43, 130.82, 126.94, 117.52, 39.83, 39.49. **Elemental Analysis:** Calcd for $C_9H_6FN_3O_2$: C, 52.18; H, 2.92; F, 9.17; N, 20.28; O, 15.45 Found: C, 52.58; H, 3.32; N, 20.68; **FTIR (neat):** ν_{max} = 3427, 3176, 3091, 2958, 2920, 2850, 2758, 2694, 2653, 2580, 1716, 1697, 1600, 1560, 1544, 1508, 1473, 1419, 1350, 1288, 1267, 1247, 1218, 1174, 1110, 1035, 987, 925, 846, 817, 759, 669, 628, 570, 545, 514, 468; **The HR-ESI-MS (positive):** m/z calcd. for $C_9H_6FN_3O_2$: 207.16; Found



Scheme 2. Proposed catalytic mechanism for cyclic carbonate synthesis catalyzed by A.

$[C_9H_6FN_3O_2 + Na^+]^+$: 230.033.

2.5. Compound (D) Yield

75 %: ^{1}H NMR (500 MHz, DMSO-d6) δ 9.62 (s, 1 H), 8.82 (s, 1 H), 8.47 (s, 1 H), 8.35 (s, 1 H), 7.94 (s, 1 H); ^{13}C NMR (126 MHz, DMSO) δ 161.78, 148.96, 141.43, 137.28, 132.00, 128.21, 127.10, 124.11, 115.90, 40.16. **Elemental Analysis:** Calcd for $C_9H_6N_4O_4$: C, 46.16; H, 2.58; N, 23.93; O, 27.33. Found: C, 46.56; H, 2.98; N, 24.33; **FTIR (neat):** $\nu_{\mathbf{max}}$ = 3572, 3151, 3097, 2873, 2777, 2586, 2534, 2362, 1701, 1535, 1438, 1406, 1350, 1294, 1253, 1184, 1089, 1043, 979, 898, 873, 808, 779, 740, 669, 574, 528, 453 cm^{-1}; **HR- ESI-MS (positive):** *m/z* calcd. for $C_9H_6N_4O_4$: 234.17; Found $[C_9H_6N_4O_4 + Na^+]^+$: 257.028.

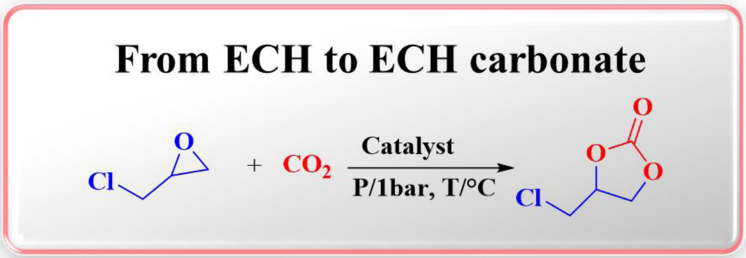
2.6. General procedure for CO_2 fixation into epoxides

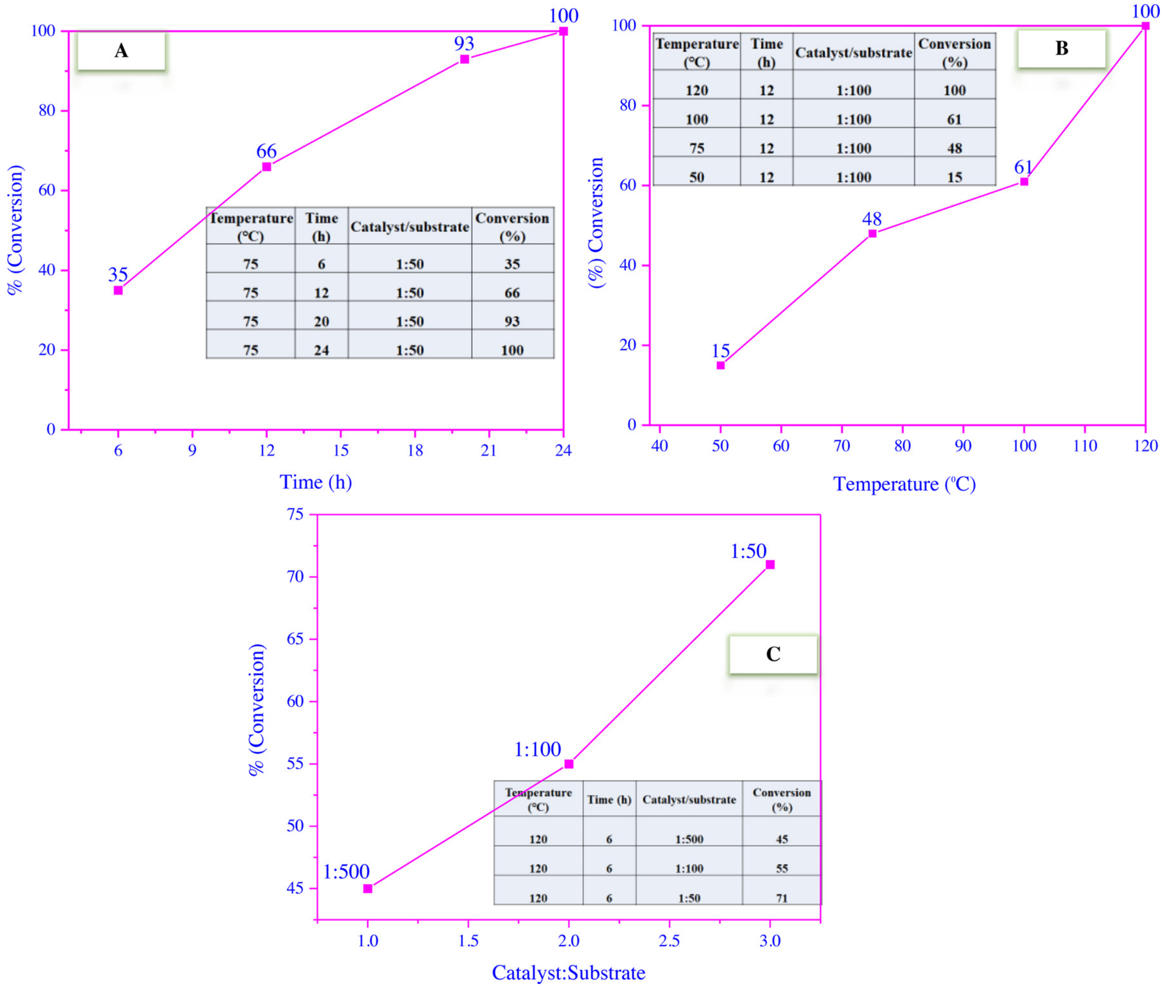
The catalyst (4.62 mg, 0.02 mmol) along with 2 mmol of epoxides were added in a 30 mL stainless-steel autoclave equipped with a magnetic stirring bar. The reaction mixture in the autoclave was purged with carbon dioxide gas at room temperature. After that, the reactor was dipped in the preheated oil bath, and then pressurized to low atmospheric pressure i-e 1 bar of CO_2. After a particular time, the reaction was stopped, cooled the reactor slowly to room temperature. An aliquot of the reaction mixture was analyzed using ^{1}H-NMR to determine the conversion of epoxides.

3. Results and discussion

For industrial applications, designing an effective catalyst to generate cyclic carbonate at ambient pressure is quite demandable in terms of negative emission technology. This requires well-developed and easy to synthesize homogeneous organocatalysts with excellent reusability and recoverability bearing acidic/basic site and which mainly facilitate the target reaction at ambient pressure without any solvents and co-catalysts. A simple and straightforward, well-designed series of triazole ring containing compounds bearing maximum basicity and competence to adsorb CO_2 were designed, demonstrating an incredible feature for using a substituted triazole ring as a bidentate ligand. Triazole based organocatalysts **(**A–D in Scheme 1**)** were achieved in good yields and synthesized according to a reported method. [57,58] A series of bidentate ligands such as 1-mesityl-*1H*-1,2,3-triazole-4-carboxylic acid, 1-phenyl-*1H*-1,2,3-triazole-4-carboxylic acid, 1-(3-fluorophenyl)-*1H*-1,2,3-triazole-4-carboxylic acid and 1-(3-nitrophenyl)-*1H*-1,2,3-triazole-4-carboxylic acid was synthesized by copper-catalyzed azide-alkyne click cycloaddition reaction of propiolic acid and aryl azides (Scheme 1 A). The structures of these organocatalysts were established based on NMR (S1-S4), HR-ESI-MS (S5-S6), elemental analysis, and FTIR (S7-S8). The HR-ESI-MS of catalysts A, C, and D revealed molecular ion peaks at *m/z* = 210.10, 207.16, and 234.17 corresponding to [Catalysts A, B, C + Na], respectively. The structure of these organocatalysts demonstrates two significant functions, Lewis acidic and Brønsted acidic sites, for the efficient chemical fixation of CO_2 to epoxides. These two important functions encouraged us to investigate the utility of the newly developed catalysts for the generation of cyclic carbonate at ambient pressure of CO_2.

Their activity was tested determine the most efficient catalyst by selecting the standard reaction conditions (ECH = 10 mmol, 120 °C, Catalyst = 0.02 mmol, 1 bar pressure of CO_2, and 12 h). The results revealed that the presence of electron-donating groups ($-CH_3$) in $[C_{12}H_{13}N_3O_2]$, significantly enhances the organocatalyst activity for the formation of cyclic carbonates compared to those with electron-withdrawing groups, e.g.-F, and -NO_2. This behavior is quite expected and can be explained based on the nucleophilicity of the triazole nitrogen, where the presence of a carboxylic group on triazole moiety decreases its nucleophilicity, and decrease its ability to activate CO_2 molecule. Thus, the presence of an electron-donating group such as three methyls





Temperature (°C)	Time (h)	Catalyst/substrate	Conversion (%)
75	6	1:50	35
75	12	1:50	66
75	20	1:50	93
75	24	1:50	100

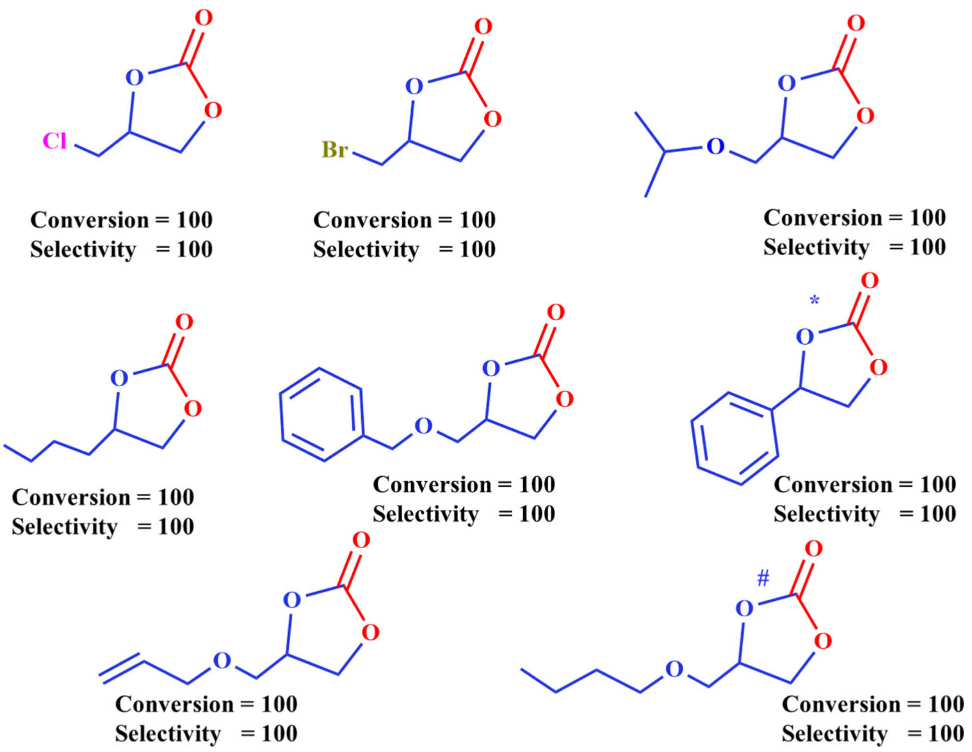
Temperature (°C)	Time (h)	Catalyst/substrate	Conversion (%)
120	12	1:100	100
100	12	1:100	61
75	12	1:100	48
50	12	1:100	15

Temperature (°C)	Time (h)	Catalyst/substrate	Conversion (%)
120	6	1:500	45
120	6	1:100	55
120	6	1:50	71

Fig. 3. Optimizing of the reaction conditions for the cycloaddition of CO_2 in the presence of epichlorohydrin. Conversion is based on ^{1}H-NMR on the crude reaction mixture.

on the phenyl moiety in catalyst A will significantly increase the electron density on the triazole ring and enhance its nucleophilicity. The decreasing order in catalytic activity for cycloaddition reaction of CO_2 to epoxide is –mesitylene > phenyl > -F > -NO_2 (Fig. 2). The NO_2-substituted compound exhibits a lower catalytic activity than the F-substituted compound since NO_2 is a more electron-withdrawing group as compared to F. (Scheme 2)

Once the model catalyst was carefully chosen, then different parameters such as reaction time, temperature, and catalyst loading at a low pressure of CO_2 were explored. Increasing the reaction time played a critical role in the formation of cyclic carbonate, with an increment of time, a 100 % conversion within 24 h was obtained (Fig. 3A). Under these reaction conditions at 120 °C, a complete synthesis of the ECH carbonate product was received. However, at lower temperature a decrease of activity was observed, indicating the critical role of the temperature (Fig. 3B). Increasing the catalyst to substrate ratio significantly enhance the yield, whereas the maximum product (71 % yield) is achieved using a catalyst-to- substrate ratio of 1:50 for 6 h at 120 °C (Fig. 3C). Therefore, the overall optimized reaction condition is 0.02 mmol of the catalyst, 2 mmol of the substrate, temperature 75 – 100 °C and time is 24 – 48 h under mild pressure of CO_2. A series of epoxides were investigated towards the transformation of cyclic carbonates based on the obtained optimized reaction conditions. The catalyst showed unusual activity for the epoxides bearing electron-withdrawing substituents (Figure S10-S114, S16), as evidenced by the conversion in 24 h. However, for substrates such as styrene oxide (Figure S15) and 1,2 epoxy hexane (Figure S17), the conversion rises by prolonging the reaction time (48 h) and clearly shows that such effect is



Scheme 3. Catalytic efficiency of catalyst A for chemical fixation of CO_{2}/.
Reaction conditions: Catalyst 1 mol %, Pressure 1 bar, Time 24 h, Temperature 75 °C.
*, # Temperature 100 °C and *, # Time 48 h. Conversion determined by NMR.

due to the steric hindering during the reaction as shown in (Scheme 3).

It is worth noting that no side products were observed, hence the catalyst gave > 99 % selectivity for the development of cyclic carbonates. The catalyst was also investigated to its performances towards internal epoxides, and unluckily the catalyst showed an inferior conversion for internal epoxides using the optimized reaction conditions (Scheme 3).

Additionally, we applied the standard deviation (S.D) to investigate the mean and accuracy of the conversion data. Noticeably, each substrate was tested three times to obtain data of S. D. (± 1 %) The standard deviation was calculated using the following formula:

$$\text{Standard Deviation } = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}$$

Where

x_i = Value of the i^{th} point in the data set.

$\bar{x}$ = Then mean value of the data set.

n = The number of data points in the data set.

On the bases of industrial importance, green and economic processes, the reusability and, more significantly, the stability of the catalyst play a vital role. The reusability and stability of catalyst **A** were examined for the cycloaddition of CO_2 into ECH using the optimal conditions (1 mol % catalyst, 1 bar, 24 h, and 75 °C). As the catalyst is homogeneous, the catalyst was loaded once in the first run, afterward, in each consecutive run, the precise amount of fresh substrate (ECH) was added, to examine the reusability of the catalyst up to five runs. To our delight, the catalyst possesses incredible reusability until five successive runs to generate ECH carbonate (Figure S9 A). The catalyst was successfully separated from the reaction mixture, using column chromatography, packed with silica and ethyl acetate/petroleum ether mixture (1:3) as eluent. In this procedure, the cyclic carbonate is separated first, followed by the desired catalyst. The catalyst is then recovered from the column, using methanol. Next, the recovered catalyst was analyzed by ^{1}H-NMR and FTIR (Figure S9 B, C), which indicates that the catalyst retained its stability.

The mechanistic details are apprehended based on previously reported literature for the catalytic cycloaddition of CO_2 [51,53,59–61]. The nucleophilic hydroxyl group of the bifunctional catalyst might activate the epoxide ring leading to the epoxy ring-opening through the less hindered side and forming an oxy-anion species. In the next step, the already formed catalyst-bound alkoxide ion acts as a nucleophile and, in turn, activates CO_2. as a result, closure of the ring will lead to the formation of the final product *i.e.*, cyclic carbonate.

4. Conclusion

In conclusion, we have successfully studied substituent effects n the triazole-ring on the catalytic activity for the construction of cyclic carbonates. From the investigation, we observed that the catalytic activity toward CO_2 transformation significantly enhances with electron-donating groups in [$C_{12}H_{13}N_3O_2$]. The N-rich centers and the carboxylic functional group combined with electron donating substituent assist in the cyclic carbonates synthesis, operating at ambient pressure (1 bar) under solvent-free and cocatalyst free conditions. Significantly, the catalyst is reusable, and more interestingly retained its stability during the recycling. Therefore, the designed catalyst is highly vital to fix CO_2 into cyclic carbonates with attractive industrial importance.

CRediT authorship contribution statement

Suleman Suleman: Investigation, Writing - original draft. **Hussein A. Younus:** Conceptualization, Methodology. **Zafar A.K. Khattak:** Methodology. **Habib Ullah:** Investigation. **Mirella Elkadi:** Validation, Writing - review & editing. **Francis Verpoort:** Conceptualization, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.111071.

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