This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Alkoxide-functionalized imidazolium betaines (AFIB) functioned as organocatalyst for coupling CO$_2$ with propargylic alcohols to valuable cyclic carbonates via AFIB-CO$_2$ adduct.
Alkoxide-Functionalized Imidazolium Betaine for CO$_2$ Activation and Catalytic Transformation

Yan-Bo Wang, Dong-Sheng Sun, Hui Zhou, Wen-Zhen Zhang, and Xiao-Bing Lu*

Xth XXXXXXXXXXX 200X, Accepted Xth XXXXXXXXXXX 200X
First published on the web Xth XXXXXXXXXXX 200X
DOI: 10.1039/b000000x

Alkoxide-functionalized imidazolium betaines (AFIB), including an alkoxide anion and an imidazolium cation, were synthesized by treating potassium tert-butoxide with 1-(2-hydroxyethyl)-2,3-disubstituted imidazolium bromide. The novel betaines were able to fast capture CO$_2$, affording the carboxylate zwitterions (AFIB-CO$_2$ adducts). In the presence of adventitious water, the transformation of AFIB-CO$_2$ adducts into the corresponding bicarbonate salts was observed by $^1$H and $^13$C NMR spectroscopy. The structure of AFIB bicarbonate salts was solved using single crystal X-ray crystallography. Furthermore, the dithiocarboxylates zwitterions (AFIB-CS$_2$ adducts), which are more stable in comparison with their CO$_2$ adducts, were prepared by reacting CS$_2$ with the corresponding betaines. X-ray single crystal analysis revealed the bent geometry of the binding CS$_2$ in the dithiocarboxylates zwitterions with a S–C–S angle of 126.6–126.9º, which indirectly confirm the structure of the AFIB-CO$_2$ adducts in hand. These AFIB-CO$_2$ adducts were found to be functioned as organocatalysts for the coupling reaction of propargylic alcohols with CO$_2$ for selectively producing the valuable cyclic carbonates under mild and solvent-free reaction conditions.

Introduction

The use of CO$_2$ as a C1 feedstock for preparing useful fine chemicals has become a flourishing area of research in the past decades[1]. However, the biggest obstacle for transforming CO$_2$ into value-added chemicals lies in its remarkable thermodynamic and kinetic stability, since CO$_2$ is at the highest oxidation state of carbon. Perspective to the discrepancy of electronegativity between the carbon and oxygen atoms, CO$_2$ prevalently behaves as an electrophile, and thus easily being activated by strong nucleophiles or low-valent metal reagents. Generally, CO$_2$ as a $\eta^1$ or $\eta^2$ ligand could coordinate towards various low-valent metal complexes, demonstrated by several research groups[2]. On the other hand, a variety of metal-free activation systems based on carbon and nitrogen atom as nucleophiles were reported. The former mainly referred to the study of N-heterocyclic carbene (NHC)[3] or N-heterocyclic olefin (NHO)[4]. The later concerned amidines or guanidines compounds containing nitrogen heterocyclic, which were described to react with CO$_2$, expectingly affording zwitterionic adducts.[5] However, in most cases bicarbonate salts were unexpectedly produced owing to the presence of adventitious water. More recently, a new concept of frustrated Lewis pair (FLP) introduced by Stephan et al. represents a fundamental and novel strategy to straightforwardly sequester CO$_2$[6]. Although considerable progress on CO$_2$ activation by carbon or nitrogen atom as nucleophilic site has been achieved, oxygen atom as nucleophilic position is poorly explored[7].

It is generally known that a betaine shown in Scheme 1, named as N,N,N-trimethylglycine, consists of an quaternary ammonium positive ion center bearing no hydrogen atom and a carboxylate anionic moiety that is not adjacent to the cationic site. On the whole, betaine could be regarded as a neutral compound. In view of the special structure, much effort for establishing a reasonable chemical circumstance between the cationic and anionic centres was conducted for achieving Lewis acid-base synergistic effect. Ooi and co-workers have demonstrated the great potential of betaines as catalysts for asymmetric reactions[8]. The synthesis of cyclic carbonates through the coupling reaction between epoxides with CO$_2$ using betaines as catalyst has been described by Sakai et al.[9]. Notably, Arnold group has successfully synthesized various copper, potassium and silver complexes bearing alkoxide-functionalized N-heterocyclic carbene as ligands[10]. Furthermore, Rossi and colleagues have shown that the reaction of commercially available tetrabutylammonium methoxide or ethoxide as intermolecular ion pairs with carbon dioxide yields the corresponding methyl and ethyl tetrabutylammonium carbonates[11]. Based on the above studies, great interest has been aroused to explore alkoxide-functionalized imidazolium betaine for CO$_2$ activation and further transformation, since the alkoxide anion has enough potential nucleophilicity for CO$_2$ sequestration. Herein we first describe the syntheses of various CO$_2$ adducts and CS$_2$ adducts of alkoxide-functionalized imidazolium betaine.
(AFIB) and further explore these AFIB-CO$_2$ adducts serve as effective organocatalysts for CO$_2$ transformation to valuable chemicals.

5 Results and Discussion

To avoid the interference of reactive hydrogen atoms on the deprotonation step in preparing AFIB, compounds 1a-1d (Scheme 2) with methyl or iso-propyl substituted at 2 position of the imidazolium ring were used for synthesizing AFIB by the reaction with potassium tert-butoxide under anhydrous conditions. The resultant AFIB solution was covered with an atmosphere of CO$_2$, resulting in immediate precipitation of the white solid 2. The obvious differences in chemical shift were observed in the $^1$H and $^{13}$C NMR spectra of compounds 1 and 2 (See supporting information, Figure S1). In comparison with the 2-methylene adjacent to alcoholic hydroxyl group of compounds 1a-1d, chemical shift of methylene at the same position in 2a-2d clearly moves toward downfield. Meanwhile $^{13}$C NMR spectra of compounds 2a-2d show strong carboxylate carbon signals at 153.3-153.4 ppm. Dependent on the substituent groups in the imidazolium ring, the C=O stretching frequencies of the carboxylates in the FTIR spectra of 2a-2d change from 1671 cm$^{-1}$ to 1694 cm$^{-1}$, similar with that of methyl and ethyl tetrabutylammonium carbonates (1670 cm$^{-1}$)[7a].

Although much effort was paid to cultivate the single crystal of the AFIB-CO$_2$ adducts 2a-2d in hand, we failed to isolate them, perhaps due to their sensitivities towards water. Therefore, the stability of all the AFIB-CO$_2$ adducts towards water was further studied (Scheme 3). Take compound 2c for example, when trace water was introduced to a DMSO-d$_6$ solution of 2c, obvious changes in chemical shift at the $^1$H and $^{13}$C NMR spectra were observed within minutes (See supporting information, Figure S2). A new signal appears at 3.71 ppm attributable to chemical shift of the methene adjacent to the alcoholic hydroxyl group in the FTIR spectra of 2a-2d change from 1671 cm$^{-1}$ to 1694 cm$^{-1}$, similar with that of methyl and ethyl tetrabutylammonium carbonates (1670 cm$^{-1}$)[7a].
ground and activation states. Therefore, we reasonably assume that the structure of AFIB-CS₂ adduct should reflect that of the corresponding AFIB-CO₂ adduct. Various AFIB-CS₂ adducts 4a-4d were synthesized by the reaction of CS₂ with compounds 1a-1d pretreated by KO(Bu) in THF solution at ambient temperature (Scheme 4). They are more stable towards moisture than the corresponding AFIB-CO₂ adducts. Moreover, the structures of compounds 4b and 4c were clearly characterized by X-ray crystallography (Figure 2). The bent geometry of the binding CS₂ was revealed in the dithiocarbamates zwitterions with a S–C–S angle of 126.6°–126.9°. These results distinctly confirm the structures of the AFIB-CS₂ adducts in hand. The successful synthesis of these AFIB-CS₂ adducts may afford the opportunity to examine the catalytic performance referred to the transformations of carbon dioxide into desirable, high value-added chemicals. We note that one of the most promising routes that effectively utilizes CO₂ is the synthesis of alkylidene cyclic carbonates. As a result, we are of great interest to investigate these AFIB-CS₂ adducts towards moisture than the corresponding AFIB-CO₂ adducts. However, AFIB-CS₂ adducts showed slightly lower catalytic activity than AFIB-CS₂ adducts. Surprisingly, 2-isopropyl-substituted AFIB-CS₂ adduct showed slightly decreased yield (Table 1, entries 4 and 5). It is interesting that the structures of AFIB-CS₂ have an important influence on the catalytic activity. The results from Table 1 exhibited that N-isopropyl-substituted AFIB-CS₂ adduct showed slightly higher catalytic activity than N-methyl-substituted (Table 1, entries 2 and 7). Surprisingly, 2-isopropyl-substituted AFIB-CS₂ adduct represented lower catalytic activity than 2-methyl-substituted (Table 1, entries 2 and 6). It was found that the use of 2d provided the best yield of 97%, possibly due to its good solubility (Table 1, entries 8) [19].

![Diagram](GreenChemistry.png)

**Table 1. Optimization of Reaction Conditions for the Carboxylative Cyclization of 2-alkylidene-3-yn-2-ol (5a) with CO₂**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat</th>
<th>T(°C)</th>
<th>P(MPa)</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2a</td>
<td>80</td>
<td>2</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>2a</td>
<td>60</td>
<td>2</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>2a</td>
<td>40</td>
<td>2</td>
<td>34</td>
</tr>
<tr>
<td>4</td>
<td>2a</td>
<td>60</td>
<td>2</td>
<td>76</td>
</tr>
<tr>
<td>5</td>
<td>2a</td>
<td>60</td>
<td>0.5</td>
<td>64</td>
</tr>
<tr>
<td>6</td>
<td>2b</td>
<td>60</td>
<td>2</td>
<td>82</td>
</tr>
<tr>
<td>7</td>
<td>2c</td>
<td>60</td>
<td>2</td>
<td>92</td>
</tr>
<tr>
<td>8</td>
<td>2d</td>
<td>60</td>
<td>2</td>
<td>97</td>
</tr>
</tbody>
</table>

*Reaction conditions: substrate 5a (3 mmol), 5 h. Yield determined by 1H-NMR spectroscopy, using durene as an internal standard.¹ mol% 2a.

With the optimized conditions established, we further investigated the reaction using a variety of propargylic alcohols as the substrates, and the results are outlined in Table 2. The coupling reaction of most propargyl alcohols with CO₂ proceeded smoothly to give the corresponding α-alkylidene cyclic carbonates in good to excellent yields. The reaction activity was depended on the substitute of propargylic alcohols. Surprisingly, the 1-ethynyl cyclohexanol 5e gave inferior results relative to 1-ethynyl cyclohexan-1-ol (Table 2, entry 3 vs 4). StERICally hindered substrates 5f-5h could yield the desired products at a higher catalyst loading and prolonged reaction time. However, in the case of internal propargyl alcohol 5i as substrate (Table 2, entry 9), α-alkylidene cyclic carbonate 6i was obtained at a low yield. These results reflected that the present catalyst system seemed to be more favorable for terminal propargylic alcohols than internal propargylic alcohols.

**Table 2. Carboxylative Cyclization of Various Propargylic Alcohols with CO₂ to Give α-Alkylidene Cyclic Carbonates by 2d**

<table>
<thead>
<tr>
<th>Entry</th>
<th>substrate</th>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5b</td>
<td>H</td>
<td>Me</td>
<td>Et</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>5e</td>
<td>H</td>
<td>Me</td>
<td>Ph</td>
<td>88</td>
</tr>
<tr>
<td>3</td>
<td>5d</td>
<td>H</td>
<td>-(CH₂)₂</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5e</td>
<td>H</td>
<td>-(CH₂)₂</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5e</td>
<td>H</td>
<td>-(CH₂)₂</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5f</td>
<td>H</td>
<td>Me</td>
<td>Hex</td>
<td>94</td>
</tr>
<tr>
<td>7</td>
<td>5g</td>
<td>H</td>
<td>Et</td>
<td>Et</td>
<td>92</td>
</tr>
<tr>
<td>8</td>
<td>5h</td>
<td>H</td>
<td>Me</td>
<td>Pr</td>
<td>35</td>
</tr>
<tr>
<td>9</td>
<td>5i</td>
<td>Ph</td>
<td>Me</td>
<td>Me</td>
<td>30</td>
</tr>
</tbody>
</table>

*Reaction conditions: substrate 5 (3 mmol), catalyst 2d (2 mol%), 60 °C, 2 MPa CO₂, 5 h. Yield determined by 1H-NMR spectroscopy, using durene as an internal standard. The reaction was carried out under an enhanced catalyst loading of 5 mol% 2d for 24 h.
On the basis of the above results and previous work \cite{4,16,17}, a possible mechanism was proposed and shown in Scheme 5. CO$_2$ was firstly activated by AFIB to form AFIB-CO$_2$ adduct in which the carboxylate anion moiety could firstly attack the triple bond of propargylic alcohol to form intermediate A. Then the new intermediate B was produced by hydrogen migration from the hydroxyl group of alcohol. Finally, the alkoxide anion of intermediate B attacked the carbonyl carbon to release the desired product and AFIB, which rapidly captures free CO$_2$ to regenerate AFIB-CO$_2$ adduct for finishing a catalyst cycle.

**Conclusions**

In summary, alkoxide-functionalized imidazolium betaine (AFIB) bearing an alkoxide anion and an imidazolium cation was found to be shown strong tendency for CO$_2$ or CS$_2$ (AFIB) bearing an alkoxide anion and an imidazolium cation to release the desired product and AFIB, which rapidly captures free CO$_2$ to regenerate AFIB-CO$_2$ adduct for finishing a catalyst cycle.

**Acknowledgment**

This work was financially supported by the National Natural Science Foundation of China (U1162101), and Program for Changjiang Scholars and Innovative Research Team in University (IRT13008). X.-B. Lu gratefully acknowledges the Chang Jiang Scholars Program (No. T2011056) from Ministry of Education, People’s Republic of China.

**Experimental**

Unless otherwise statement, all manipulations were performed using standard Schlenk techniques under a dry nitrogen atmosphere. NMR spectra were recorded on a Bruker Avance 400M type (1H NMR, 400 MHz; 13C NMR, 100 MHz) spectrometer. High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometer (Micromass, Wythenshawe, UK) equipped with Z-spray ionization source. Infrared spectra (IR) was measured using a Nicolet NEXUS FT-IR spectrophotometer. Carbon dioxide (99.999%) was used as received without further purification. Tetrahydrofuran, diethyl ether and hexane were distilled from sodium/benzophenone under N$_2$ atmosphere. CS$_2$ and acetonitrile was distilled from 45 mmol). The mixture was heated to 80 oC under N$_2$ and stirred for 24 h and then cooled to room temperature. After the solvent was removed under the reduced pressure, the residue was washed with THF (3×20 mL). The product 1a was isolated as a white solid in 88 % yield. 1H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.65 (d, 1H, J = 2.4 Hz, NCH$_3$), 7.63 (d, 1H, J = 2.4 Hz, CH$_2$:CH$_2$), 4.20 (t, 2H, J = 5.2 Hz, CH$_2$:CH$_2$), 3.78 (s, 3H, NCH$_3$), 3.68 (q, 2H, CH$_2$:CH$_2$), 2.60 (s, 3H, CCH$_3$). 13C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 145.3, 122.6, 121.7, 60.1, 50.7, 35.3, 10.5. HRMS (ESI, $m/z$) calcd. for C$_7$H$_{13}$BrN$_2$ [M-Br]: 141.1028, found: 141.1026.

Complex 1b was synthesized by the same manner with 1a starting from 1-methyl-2-isopropyl imidazole (2.48 g, 20 mmol)\cite{21} to give complex 1b as a white solid in 71 % yield. 1H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.69 (d, 1H, J = 2.4 Hz, CH$_2$:CH$_2$), 7.67 (d, 1H, J = 2.4 Hz, CH$_2$:CH$_2$), 7.54 (t, 1H, J = 2.4 Hz, CH$_2$:CH$_2$), 4.27 (t, 2H, J = 5.2 Hz, CH$_2$:CH$_2$), 3.89 (s, 3H, NCH$_3$), 3.68 (m, 3H, CH$_3$:CH$_2$ and CH$_2$:CH$_2$), 1.36 (d, 3H, J = 7.2 Hz, CH$_2$:CH$_2$). 13C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 149.4, 123.4, 121.5, 59.6, 50.4, 35.9, 24.1, 18.4. HRMS (ESI, $m/z$) calcd. for C$_7$H$_{14}$BrN$_2$ [M-Br]: 169.1341, found: 169.1343.

Complex 1c was synthesized by the same manner with 1a starting from 1-isopropyl-2-methyl imidazole (2.48 g, 20 mmol)\cite{20} to give complex 1c as a white solid in 77 % yield. 1H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.87 (d, 1H, J = 1.6 Hz, CH=CH$_3$), 7.71 (d, 1H, J = 1.6 Hz, CH=CH$_3$), 5.11 (s, 1H, CH$_2$:OH), 4.69 (m, 1H, CH(=CH$_2$)), 4.20 (t, 2H, J = 4.8 Hz, CH$_2$:CH$_2$), 3.71 (m, 2H, CH$_2$:CH$_2$), 2.66 (s, 3H, CCH$_3$), 1.43 (d, 3H, J = 6.4 Hz, CH(=CH$_2$)$_2$). 13C NMR (100 MHz, DMSO-$d_6$): $\delta$ =144.2, 122.8, 113.8, 60.1, 50.8, 50.6, 22.6, 10.4. HRMS
Compound 1d was synthesized in the same manner with 1a starting from 1-benzyl-2-isopropyl imidazole (4.00 g, 20 mmol) according to the reported synthesis method of 1-isopropyl-2-methyl imidazole with modifications\(^\text{[21]}\) to give 1d as a white solid in 63 % yield. 1d: \(^\text{1H NMR}\) (400 MHz, DMSO-\(d_6\)): \(\delta = 7.80\) (d, 1H, J = 1.6 Hz, CH=C), 7.76 (d, 1H, J = 1.6 Hz, CH=CH), 7.24-7.43 (m, 5H, Ph) 5.58 (s, 2H, CH2Ph), 5.21 (t, 2H, J = 6.4 Hz, H2, CH=C), 4.30 (m, 2H, J = 5.2 Hz, CH2CH3), 3.69-3.78 (m, 3H, CH2CH3 and CH2CH2), 1.26 (d, 6H, J = 7.2 Hz, CH2CH2). \(^\text{13C NMR}\) (100 MHz, DMSO-\(d_6\)): \(\delta = 150.4, 135.6, 129.4, 128.8, 127.6, 123.0, 122.9, 59.9, 51.5, 51.1, 24.8, 19.4.\) HRMS (ESI, m/z) calcd. For C\(_{15}\)H\(_{21}\)BrN\(_2\) [M-Br]+: 245.1662, found: 245.1654.

**Preparation of AFIB-CO\(_2\) adducts (2a-2d) and AFIB-CS\(_2\) adducts (4a-4d)**

The synthesis of 2a-2d: 1-(2-Hydroxyethyl)-2,3-disubstituted imidazolium bromine (2 mmol) and KOtBu (2.4 mmol, 0.27 g) were added to a solution of THF (15 mL) and the mixture was stirred at ambient temperature for 2 h. During the reaction course, the solution was changed to yellow gradually. After filtration to remove the salt, the yellow filtrate filled in anti-pressure Schlenk flask was transferred to the Schlenk line and was vented slowly. The yields of target products were determined as white powder, 82 % yield.

**Characterization of alkylidene cyclic carbonates (6a-6i).**

1H NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 7.62\) (s, 1H, CH=CH), 4.56 (t, 2H, J = 4.8Hz, CH2CH3), 4.31 (t, 2H, J = 4.8Hz, CH2CH3), 3.76 (s, 3H, NCH3), 2.68 (s, 3H, CH3). \(^\text{13C NMR}\) (100 MHz, DMSO-\(d_6\)): \(\delta = 122.8, 145.0, 122.3, 121.3, 67.7, 47.2, 34.7, 9.5.\) IR (KBr) 1093, 1075 cm\(^{-1}\) (vs).

4b, yellow powder, 41% yield. 1H NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 7.64\) (d, 1H, J = 2.0Hz, CH=C), 7.63 (d, 1H, J = 2.0Hz, CH=C), 4.56 (t, 1H, J = 4.8Hz, CH2CH3), 4.49 (t, 2H, J = 4.8Hz, CH2CH3), 2.72 (s, 3H, CH3). \(^\text{13C NMR}\) (100 MHz, DMSO-\(d_6\)): \(\delta = 228.9, 150.1, 124.1, 122.0, 68.7, 47.7, 36.4, 24.6, 19.1.\) IR (KBr) 1082, 1067 cm\(^{-1}\) (vs).

4c, yellow powder, 38 % yield. 1H NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 7.82\) (d, 1H, J = 2.0Hz, CH=C), 7.67 (d, 1H, J = 2.0Hz, CH=C), 4.67 (m, 1H, CH(=CH2)), 4.59 (t, 2H, J = 4.8Hz, CH2CH3), 4.42 (t, 2H, J = 4.8Hz, CH2CH3), 2.72 (s, 3H, CH3). \(^\text{13C NMR}\) (100 MHz, DMSO-\(d_6\)): \(\delta = 228.3, 143.9, 122.1, 117.6, 67.5, 49.9, 47.0, 21.9, 9.5.\) IR (KBr) 1080, 1066 cm\(^{-1}\) (vs).

4d, yellow powder, 90 % yield. 1H NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 7.77\) (d, 1H, J = 1.6Hz, CH=C), 7.72 (d, 1H, J = 1.6Hz, CH=C), 7.23-7.43 (m, 5H, Ph), 5.57 (s, 2H, CH2Ph), 4.67 (t, 2H, J = 4.8Hz, CH2CH3), 4.56 (t, 2H, J = 4.8Hz, CH2CH3), 3.73 (m, 1H, CH(=CH2)),1.33 (d, 6H, J = 6.4Hz, CH3). \(^\text{13C NMR}\) (100 MHz, DMSO-\(d_6\)): \(\delta = 228.5, 150.0, 135.0, 128.9, 128.3, 127.0, 122.7, 67.9, 51.1, 47.5, 24.4, 19.1.\) IR (KBr) 1070 cm\(^{-1}\) (vs).

**Representative experimental procedure for carboxylation of propargylic alcohols with CO\(_2\).**

A 10 mL oven dried autoclave containing a stir bar was charged 5a (0.25 g, 3 mmol), 2a (11 mg, 0.06 mmol) after purging the autoclave with CO\(_2\) three times. The sealed autoclave was pressurized to 2 MPa CO\(_2\). The reaction mixture was stirred at 60 °C for 5 h, then the autoclave was cooled to room temperature and the remaining CO\(_2\) was vented slowly. The yields of target products were determined by 1H NMR analysis.

**Characterization of alkyldiene cyclic carbonates (6a-6i).**

4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (6a). 1H NMR (400 MHz, CDCl3): \(\delta = 4.78\) (d, J = 4.0 Hz, 1H, CH=CH), 4.32 (d, J = 4.0 Hz, 1H, CH=CH), 1.62 (s, 6H, CH3). \(^\text{13C NMR}\) (100
Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry

Page 7 of 8

Green Chemistry Accepted Manuscript

Page 7 of 8

Green Chemistry
This journal is © The Royal Society of Chemistry [year]

Journal Name, [year], [vol], 00–00 | 7