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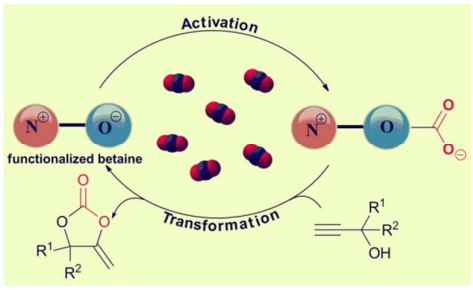

Alkoxide-functionalized imidazolium betaines (AFIB) functioned as organocatalyst for coupling CO_2 with propargylic alcohols to valuable cyclic carbonates *via* AFIB-CO_2 adduct.

Alkoxide-Functionalized Imidazolium Betaine for CO_2 Activation and Catalytic Transformation

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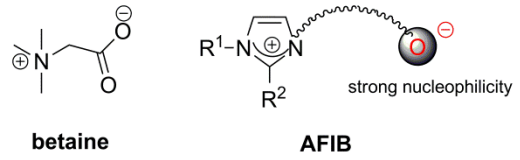
Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

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 to moisture 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 became 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 η^1 or η^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, expectantly 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].



betaine AFIB

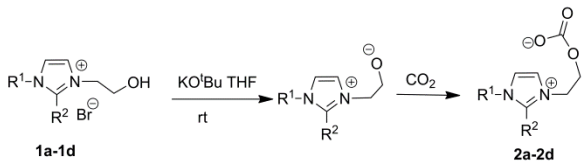
Scheme 1 The structures of betaine and alkoxide-functionalized imidazolium betaine (AFIB)

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 [7b]. Notably, Arnold group has successfully synthesized various copper, potassium and silver complexes bearing alkoxide-functionalized *N*-heterocyclic carbene as ligands[9]. 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[7a]. 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.

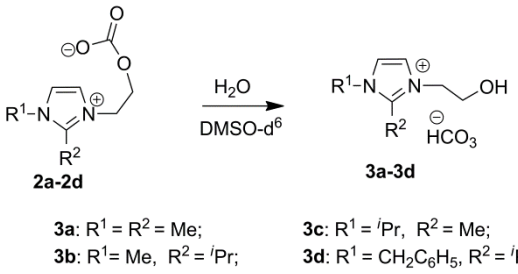
Results and Discussion

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 ^1H 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].



Scheme 2 The synthesis of AFIB-CO_2 adducts

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 ^1H 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 ^1H NMR spectra, the value of which was nearly the same as the corresponding 2-methene in compound **1c**. Meanwhile, a new signal at 158.7 ppm in the ^{13}C NMR spectra ascribes to C=O of hydrogen carbonate salt [10]. Compound **2c** was almost transformed to hydrogen carbonate salt **3c** overnight. The crystal structure of compound **3c** is decribed in Figure 1. The detail spectra difference between **2a-2b, 2d** and **3a-3b, 3d** were shown in supporting information Figure S3.



Scheme 3 The transformation of **2a-2d** to **3a-3d** in the presence of H_2O

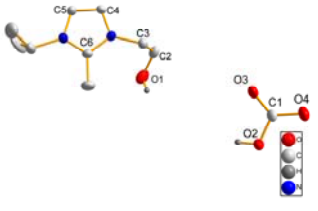
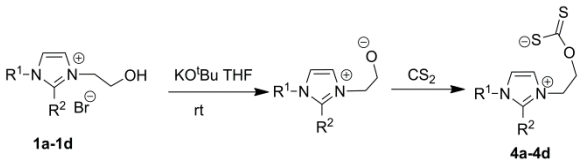


Fig. 1 Molecular structures of **3c** with thermal ellipsoids drawn at 30% probability. Selected Bond Lengths (Å) and Angles (deg) in Complexes **3c** as follow: **3c** O(1)-C(2) 1.415(6), O(2)-C(1) 1.326(4), O(3)-C(1) 1.255(4), O(4)-C(1) 1.246(4), O(2)-C(1)-O(3) 117.9(3), O(2)-C(1)-O(4) 116.9(3), O(3)-C(1)-O(4) 125.2(3).



Scheme 4 The synthesis of AFIB-CS_2 adducts

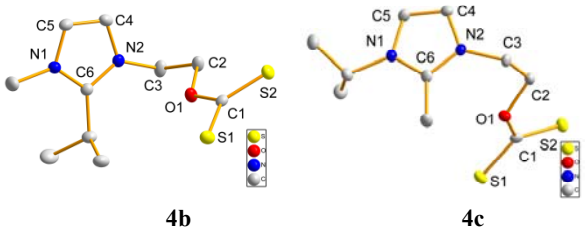


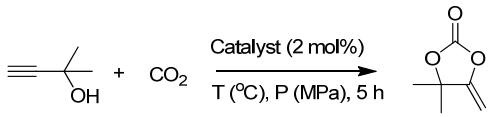
Fig. 2 Molecular structures of **4b** and **4c** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms have been omitted for clarity. Selected Bond Lengths (Å) and Angles (deg) in Complexes **4b** and **4c** as follow: **4b** S(1)-C(1) 1.687 (2), S(2)-C(1) 1.676(2), O(1)-C(1) 1.363(2), O(1)-C(2) 1.442(2), S(2)-C(1)-S(1) 126.6(1). **4c** S(1)-C(1) 1.665(3), S(2)-C(1) 1.692(3), O(1)-C(1) 1.372(3), O(1)-C(2) 1.444(3), S(1)-C(1)-S(2) 126.9(2).

It is generally known that CS_2 has higher electroaffinity than CO_2, while their structures are nearly same in the both

ground and activation states. Therefore, we reasonably assume that the structure of AFIB-CS_2 adduct should reflect that of the corresponding AFIB-CO_2 adduct. Various AFIB-CS_2 adducts **4a-4d** were synthesized by the reaction of CS_2 with compounds **1a-1d** pretreated by KO^{t}Bu in THF solution at ambient temperature (Scheme 4). They are more stable towards moisture than the corresponding AFIB-CO_2 adducts . Moreover, the structures of compounds **4b** and **4c** were clearly characterized by X-ray crystallography (Figure 2). The bent geometry of the binding CS_2 was revealed in the dithiocarboxylates zwitterions with a S–C–S angle of 126.6~126.9º. These results indirectly confirm the structures of the AFIB-CO_2 adducts in hand.

The successful synthesis of these AFIB-CO_2 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 CO_2 is the synthesis of alkylidene cyclic carbonates through the coupling reaction with propargylic alcohol with CO_2. Although this coupling reaction can be smoothly carried out by the aid of metal catalysts of Ag[11],Cu[12],Pd[13],Co[14] and Ru[15], the use of organocatalysts for this transforamtion is very limited. It has been reported to use NHC[16], NHO[4], tertiary phosphines[17] and guanidine[18] as catalysts for selective synthesis of various alkylidene cyclic carbonates. As a result, we are of great interest to investigate these AFIB-CO_2 adducts for catalyzing the coupling reaction of propargylic alcohols with CO_2. Initially, we attempted the coupling reaction of 2-methylbut-3-yn-2-ol (**5a**) with CO_2 using 2 mol% **2a** under the solvent-free reaction conditions, giving the desired product **6a** in 87 % yield under 80 °C within 5 h (Table 1, entry 1). Encouraged by the above result, further condition optimization shown that reaction temperature has a profound impact on the efficiency of this reaction and the better yield of 90% was obtained at 60 °C (Table 1, entry 2). However, A lower catalyst loading or decrease in CO_2 pressure led to a decreased yield (Table 1, entries 4 and 5). It is interesting that the structures of AFIB-CO_2 have an important influence on the catalytic activity. The results from Table 1 exhibited that *N*-isopropyl-substituted AFIB-CO_2 adduct showed slightly higher catalytic activity than *N*-methyl-substitued (Table 1, entries 2 and 7). Surprisingly, 2-isopropyl-substitued AFIB-CO_2 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].

Table 1. Optimization of Reaction Conditions for the Carboxylative Cyclization of 2-methylbut-3-yn-2-ol (5a) with CO_2[a]



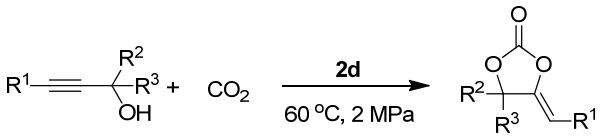
5a **6a**

Entry	Cat	T(°C)	P(MPa)	Yield(%)[b]
1	**2a**	80	2	87
2	**2a**	60	2	90
3	**2a**	40	2	34
4[c]	**2a**	60	2	76
5	**2a**	60	0.5	64
6	**2b**	60	2	82
7	**2c**	60	2	92
8	**2d**	60	2	97

[a] Reaction conditions: substrate **5a** (3 mmol), 5 h. [b] Yield determined by ^{1}H-NMR spectroscopy, using durene as an internal standard. [c] 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 CO_2 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 cyclopentanol **5e** gave inferior results relative to 1-ethynyl cyclohexanol **5d** (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 propargylic 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.

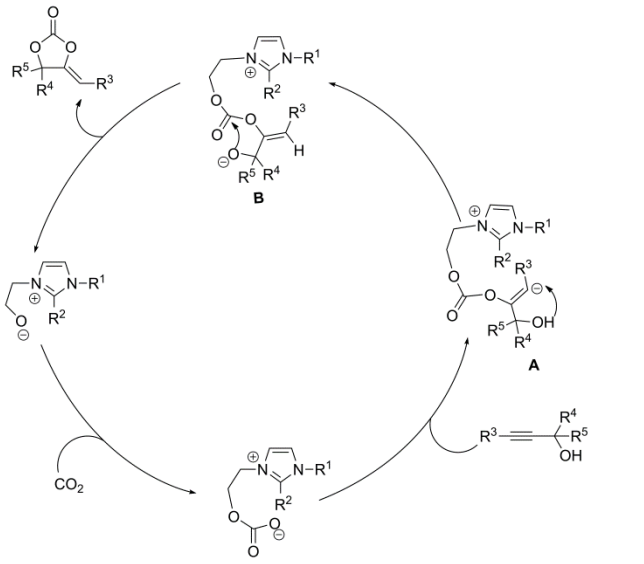
Table 2. Carboxylative Cyclization of Various Propargylic Alcohols with CO_2 to Give α-Alkylidene Cyclic Carbonates by 2d[a]



5b-5i **6b-6i**

Entry	Substrate	R^1	R^2	R^3	Yield[b]
1	**5b**	H	Me	Et	94
2	**5c**	H	Me	Ph	88
3	**5d**	H	-$(CH_2)_5$-		75
4	**5e**	H	-$(CH_2)_4$-		8
5[c]	**5e**	H	-$(CH_2)_4$-		87
6[c]	**5f**	H	Me	Hex	94
7[c]	**5g**	H	Et	Et	92
8[c]	**5h**	H	Me	^{i}Pr	35
9[c]	**5i**	Ph	Me	Me	30

[a]Reaction conditions: substrate **5** (3 mmol), catalyst **2d** (2 mol%), 60 °C, 2 MPa CO_2, 5 h. [b]Yield determined by ^{1}H-NMR spectroscopy, using durene as an internal standard. [c]The reaction was carried out under a enhanced catalyst loading of 5 mol% **2d** for 24 h.



Scheme 5 Plausible Mechanisms for Carboxylative Cyclization of Propargylic Alcohols with CO_2 Catalyzed by AFIB-CO_2 adducts

On the basis of the above results and previous work [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 sequestration, affording a CO_2 or CS_2 adduct (AFIB–CO_2 or AFIB–CS_2), in which the binding CS_2 exhibits a bent geometry with an S–C–S angle of 126.6~126.9º. AFIB-CO_2 adducts as organocatalysts could effectively catalyze the coupling reaction of propargylic alcohols with CO_2 under mild and solvent-free reaction conditions, selectively affording the functionalized cyclic carbonates.

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 AvanceII 400M type (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz) spectrometer. High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometry (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 phosphorus pentoxide under N_2 atmosphere. DMSO-d_6 was distilled from calcium hydride under reduced pressure and stored over 4A molecular sieves. Commercially available terminal propargylic alcohols were used without further purification. Internal propargylic alcohol (**5i**) was prepared by Sonogashira coupling reaction of corresponding 2-Methyl-3-butyn-2-ol with iodobenzene according to the literature methods with modifications [20].

Preparation of 1-(2-Hydroxyethyl)-2,3-disubstitutedimidazoli -um bromine (1a-1d)

The synthesis of 1a: To a three-neck round-bottomed flask containing 1, 2-dimethyl imidazole (3.84 g, 40 mmol) was added acetonitrile (20 mL) and 2-bromoethanol (7.50 g, 60 mmol). The mixture was heated to 80 ^{o}C 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. **1a**: **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.65 (d, 1H, J = 2.4 Hz, NC*H*), 7.63 (d, 1H, J = 2.4 Hz, NC*H*), 5.09 (t, 1H, J = 1.2 Hz, CH_2OH), 4.20 (t, 2H, J = 5.2 Hz, CH_2CH_2), 3.78 (s, 3H, NCH_3), 3.68 (q, 2H, CH_2CH_2), 2.60 (s, 3H, CCH_3). **^{13}C NMR** (100 MHz, DMSO-d_6): δ =145.3, 122.6, 121.7, 60.1, 50.7, 35.3, 10.5. **HRMS** (ESI, *m*/*z*) calcd. for $C_7H_{13}BrN_2$ $[M\text{-}Br]^+$: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)[21] to give complex **1b** as a white solid in 71 % yield. **1b**: **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.69 (d, 1H, J = 2.4 Hz, C*H*=CH), 7.67 (d, 1H, J = 2.4 Hz, CH=C*H*), 5.14 (t, 1H, J = 2.4 Hz, CH_2OH), 4.27 (t, 2H, J = 5.2 Hz, CH_2CH_2), 3.89 (s, 3H, NCH_3), 3.68 (m, 3H, CH_2CH_2 and $CH(CH_3)_2$), 1.36 (d, 3H, J = 7.2 Hz, $CH(CH_3)_2$). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 149.4, 123.4, 121.5, 59.6, 50.4, 35.9, 24.1, 18.4. **HRMS** (ESI, *m*/*z*) calcd. for $C_9H_{17}BrN_2$ $[M\text{-}Br]^+$: 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)[4] to give complex **1c** as a white solid in 77 % yield. **1c**: **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.87 (d, 1H, J = 1.6 Hz, C*H*=CH), 7.71 (d, 1H, J = 1.6 Hz, CH=C*H*), 5.11 (s, 1H, CH_2OH), 4.69 (m, 1H, $CH(CH_3)_2$), 4.20 (t, 2H, J = 4.8 Hz, CH_2CH_2), 3.71 (m, 2H, CH_2CH_2), 2.66 (s, 3H, CCH_3), 1.43 (d, 3H, J = 6.4 Hz, $CH(CH_3)_2$). **^{13}C NMR** (100 MHz, DMSO-d_6): δ =144.2, 122.8, 118.3, 60.1, 50.8, 50.6, 22.6, 10.4. **HRMS**

(ESI, *m/z*) calcd. for $C_9H_{17}BrN_2$ $[M-Br]^+$: 169.1337, found: 169.1341.

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[21] to give **1d** as a white solid in 63 % yield. **1d**: **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.80 (d, 1H, J = 1.6 Hz, C*H*=CH), 7.76 (d, 1H, J = 1.6 Hz, CH=C*H*), 7.24-7.43 (m, 5H, Ph) 5.58 (s, 2H, CH_2Ph), 5.21 (t, 2H, J = 6.4 Hz, O*H*), 4.30 (m, 2H, J = 5.2 Hz, CH_2CH_2), 3.69-3.78 (m, 3H, CH_2CH_2 and $CH(CH_3)_2$), 1.26 (d, 6H, J = 7.2 Hz, $CH(CH_3)_2$). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 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 KO^{t}Bu (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 equipped with a CO_2 and the flask was degassed at -78 °C in vacuo, filled with 1 atm CO_2. The solution was stirred to room temperature for 2 hours. The precipitate was formed and collected via filtration. Subsequent the solid was washed with THF (2×10 mL), Et_2O (2×10 mL) to afforded the corresponding AFIB-CO_2 adducts and then pumped to dryness.

2a, white powder, 87 % yield. **^{1}H NMR** (400 MHz, DMSO-d_6): δ =7.60 (s, 1H, C*H*=C*H*), 7.59 (s, 1H, C*H*=C*H*), 4.20 (t, 2H, J= 5.6 Hz, CH_2CH_2), 3.89 (t, 2H, J = 5.6 Hz, CH_2CH_2), 3.76 (s, 3H, NCH_3), 2.59 (s, 3H, CCH_3). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 153.3, 144.7, 122.1, 121.3, 61.3, 48.6, 34.6, 9.22. **IR** (KBr) 1671 cm^{-1} (vs).

2b, white powder, 82 % yield. **^{1}H NMR** (400 MHz, DMSO-d_6): δ= 7.60 (s, 1H, C*H*=C*H*), 7.59 (s, 1H, C*H*=C*H*), 4.27 (t, 2H, J= 4.8 Hz, CH_2CH_2), 3.89-3.91 (m, 5H, CH_2CH_2 and NCH_3), 3.63 (m, 1H, $CH(CH_3)_2$), 1.39 (d, 6H, J = 6.4 Hz, CCH_3). **^{13}C NMR** (100 MHz, DMSO-d_6): δ= 153.3, 149.4, 123.3, 121.6, 61.4, 48.7, 35.8, 24.2, 18.3. **IR** (Film) 1682 cm^{-1} (vs).

2c, white powder, 85 % yield. **^{1}H NMR** (400 MHz, DMSO-d_6): δ= 7.83 (d, 1H, J = 1.2 Hz, C*H*=CH), 7.66 (d, 1H, J = 1.2 Hz, CH=C*H*), 4.68 (m, 1H, NC*H*$(CH_3)_2$), 4.20 (t, 2H, J = 4.8 Hz, CH_2CH_2), 3.89 (t, 2H, J = 4.8 Hz, CH_2CH_2), 3.64 (s, 3H, CCH_3), 1.41 (d, 6H, J = 6.4 Hz, $CH(CH_3)_2$). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 153.3, 143.5, 122.2, 117.4, 61.2, 49.8, 48.5, 21.9, 9.2. **IR** (Film) 1686 cm^{-1} (vs).

2d, white powder, 80 % yield. **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.71 (d, 1H, J = 1.6 Hz, C*H*=CH), 7.68 (d, 1H, J = 1.6 Hz, CH=C*H*), 7.22-7.43 (m, 5H, Ph), 5.54 (s, 2H, CH_2Ph), 4.31 (m, 1H, J = 5.2 Hz, CH_2CH_2), 3.97 (t, 2H, J = 5.2 Hz, CH_2CH_2), 3.67 (m, 1H, $CH(CH_3)_2$), 1.28 (d, 6H, J = 7.2 Hz $CH(CH_3)_2$). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 153.4, 149.7, 135.2, 128.9, 128.2, 127.0, 122.6, 122.5, 61.3, 51.0, 49.0, 24.3, 18.8. **IR** (Film) 1694 cm^{-1} (vs).

The synthesis of 4a-4d: 1-(2-Hydroxyethyl)-2,3-disubstituted imidazolium bromine (2 mmol) and KO^{t}Bu (2.4 mmol, 0.27g) 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, CS_2 (6 mmol, 0.46 g) was added into the yellow filtrate. The precipitate was formed immediately and was collected via filtration. The pure **4a** and **4b** were obtained by washing the yellow precipitate with cold methanol (2×10 mL). Washing the yellow precipitate with cold acetonitrile (2×10 mL) afforded pure **4c**. The pure **4d** was obtained by washing the precipitate with THF (2×10 mL).

4a, yellow powder, 35% yield. **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.62 (s, 1H, C*H*=CH), 4.56 (t, 2H, J = 4.8Hz, CH_2CH_2), 4.31 (t, 2H, J = 4.8Hz, CH_2CH_2), 3.76 (s, 3H, NCH_3), 2.68 (s, 3H, CCH_3). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 228.3, 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. **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.64 (d, 1H, J = 2.0Hz, C*H*=CH), 7.63 (d, 1H, J = 2.0Hz, CH=C*H*), 4.56 (t, 1H, J = 4.8Hz, CH_2CH_2), 4.49 (t, 2H, J = 4.8Hz, $CH(CH_3)_2$). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 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. **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.82 (d, 1H, J = 2.0Hz, C*H*=CH), 7.67 (d, 1H, J = 2.0Hz, CH=C*H*), 4.67 (m, 1H,C*H*$(CH_3)_2$), 4.59 (t, 2H, J = 4.8Hz, CH_2CH_2), 4.42 (t, 2H, J = 4.8Hz, CH_2CH_2), 2.72 (s, 3H, CCH_3), 1.41 (d, 6H, J = 6.8Hz, $CH(CH_3)_2$). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 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. **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.77 (d, 1H, J = 1.6Hz, C*H*=CH), 7.72 (d, 1H, J = 1.6Hz, CH=C*H*), 7.23-7.43 (m, 5H, Ph), 5.57 (s, 2H, CH_2Ph), 4.67 (t, 2H, J = 4.8Hz, CH_2CH_2), 4.56 (t, 2H, J = 4.8Hz, CH_2CH_2), 3.73 (m, 1H, C*H*$(CH_3)_2$),1.33 (d, 6H, J = 7.2Hz, $CH(CH_3)_2$). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 228.5, 150.0, 135.0, 128.9, 128.3, 127.0, 122.7, 122.5, 67.9, 51.1, 47.5, 24.4, 19.1. **IR** (KBr) 1070 cm^{-1} (vs).

Representative experimental procedure for carboxylation cyclization 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 ^{1}H NMR analysis.

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

4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (6a). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.78 (d, J = 4.0 Hz, 1H, C*H*=CH), 4.32 (d, J = 4.0 Hz, 1H, CH=C*H*), 1.62 (s, 6H, CH_3). **^{13}C NMR** (100

MHz, $CDCl_3$): δ = 158.8, 151.4, 85.4, 84.7, 27.7. IR (cm^{-1}) (Film) 1824, 1684. **HRMS** (ESI, *m/z*) calcd. for $C_6H_8O_3Na$ $[M+Na]^+$: 151.0371, found: 151.0368.

4-methyl-4-ethyl-5-methylene-1,3-dioxolan-2-one (6b). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.82 (d, 1H, *J* = 4.0 Hz, C*H*=CH), 4.27 (d, 1H, *J* = 4.0 Hz, CH=C*H*), 1.87-1.96 (m, 1H, CH_2CH_3), 1.70-1.77 (m, 1H, CH_2CH_3), 1.59 (s, 3H, CCH_3), 0.99 (t, 3H, *J* = 4.0 Hz, CH_2CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 157.6, 151.7, 87.6, 85.7, 33.5, 26.1, 7.5. IR (cm^{-1}) (Film) 1832, 1687. **HRMS** (ESI, *m/z*) calcd. for $C_7H_{10}NaO_3$ $[M+Na]^+$: 165.0528, found: 165.0533.

4-methyl-5-ethylene-4-phenyl-1,3-dioxolan-2-one (6c). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.47-7.49 (m, 2H, C_6H_5), 7.38-7.44 (m, 3H, C_6H_5), 4.95 (d, 1H, *J* = 4.0 Hz, CH=C*H*), 4.47 (d, 1H, *J* = 4.0 Hz, CH=C*H*), 1.97 (s, 6H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 157.5, 151.3, 139.3, 129.3, 129.0, 124.8, 88.3, 87.3, 27.6. **IR** (cm^{-1}) (Film) 1821, 1686. **HRMS** (ESI, *m/z*) calcd. for $C_{11}H_{10}O_3Na$ $[M+Na]^+$: 213.0528, found: 213.0534.

5-ethylene-1,3-dioxaspiro[4.5]decan-2-one (6d). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.76 (d, *J* = 4.0 Hz, 1H, CH=C*H*), 4.29, (d, *J* = 4.0 Hz, 1H, CH=C*H*), 2.62 (t, *J* = 7.6 Hz, 2H), 1.99-2.06 (m, 2H), 1.58-1.73 (m, 7H), 1.26-1.38 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 158.8, 151.6, 86.5, 85.6, 36.6, 24.4, 21.7. **IR** (cm^{-1}) (Film) 1838, 1814, 1682. **HRMS** (ESI, *m/z*) calcd. for $C_9H_{12}O_3Na$ $[M+Na]^+$: 191.0684, found: 191.0680.

4-methylene-1,3-dioxaspiro[4.4]nonan-2-one (6e). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.80 (d, *J* = 4.0 Hz, 1H, CH=C*H*), 4.34, (d, *J* = 4.0 Hz, 1H, CH=C*H*), 2.18-2.25 (m, 2H), 1.85-1.95 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 157.9, 151.6, 94.4, 85.5, 40.8, 24.4. **IR** (cm^{-1}) (Film) 1824, 1685. **HRMS** (ESI, *m/z*) calcd. for $C_8H_{10}NaO_3$$[M+Na]^+$: 177.0528, found: 177.0529.

4-hexyl-4-methyl-5-methylene-1,3-dioxolan-2-one (6f). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.80 (d, *J* = 4.0 Hz, 1H, CH=C*H*), 4.26, (d, *J* = 4.0 Hz, 1H, CH=C*H*), 1.82-1.90 (m, 1H), 1.66-1.74 (m, 1H), 1.58 (s, 3H, CCH_3), 1.28-1.42 (m, 8H), 0.88 (t, 3H, *J* = 4.0 Hz, CH_2CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 157.3, 151.7, 87.4, 85.6, 40.6, 31.6, 29.1, 26.5, 23.1, 22.6, 14.1. **IR** (cm^{-1}) (Film) 1828, 1685. **HRMS** (ESI, *m/z*) calcd. for $C_{11}H_{18}NaO_3$ $[M+Na]^+$: 221.1154, found: 221.1147.

4,4-diethyl-5-methylene-1,3-dioxolan-2-one (6g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.87 (d, *J* = 4.0 Hz, 1H, CH=C*H*), 4.23, (d, *J* = 4.0 Hz, 1H, CH=C*H*), 1.89-1.98 (m, 2H, CH_2CH_3), 1.67-1.76 (m, 2H, CH_2CH_3), 0.98 (t, 3H, *J* = 7.2 Hz, CH_2CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 156.1, 152.0, 91.0, 86.0, 32.0, 7.2. **IR** (cm^{-1}) (Film) 1837, 1685. **HRMS** (ESI, *m/z*) calcd. for $C_8H_{12}NaO_3$ $[M+Na]^+$: 179.0684, found: 179.0684.

4-methyl-4-isopropyl-5-methylene-1,3-dioxolan-2-one (6h). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.83 (d, *J* = 4.0 Hz, 1H, C*H*=CH), 4.28 (d, 1H, *J* = 4.0 Hz, CH=C*H*), 1.95(m, 1H, $CH(CH_3)_2$), 1.58 (s, 6H, CCH_3), 1.03 (d, 3H, *J* = 6.8 Hz, CH_2CH_3), 1.01 (d, 3H, *J* = 6.8 Hz, CH_2CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 157.2, 151.8, 90.0, 86.4, 37.1, 24.2, 16.5, 16.2. **IR** (cm^{-1}) (Film) 1820, 1682. **HRMS** (ESI, *m/z*) calcd. for $C_8H_{12}NaO_3$ $[M+Na]^+$: 179.0684, found: 179.0688.

(Z)-5-benzylidene-4,4-dimethyl-1,3-dioxolan-2-one (6i). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.53-7.55 (m, 2H, C_6H_5), 7.23-7.37 (m, 3H, C_6H_5), 5.50 (s, 1H, C=C*H*), 1.68 (s, 6H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ =151.4, 150.8, 132.5, 128.7, 128.6, 127.7, 101.6, 85.7, 27.8. **IR** (cm^{-1}) (Film) 1835, 1814, 1701. **HRMS** (ESI, *m/z*) calcd. for $C_{12}H_{12}NaO_3$ $[M+Na]^+$: 227.0684, found: 227.0676.

Notes and references

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† Electronic Supplementary Information (ESI) available: Crystallography and Copies of NMR. See DOI: 10.1039/b000000x/

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