Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supplementary Information

“Is the DBU-CO_2 Adduct Stable in Ionic Liquid Media?”

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Experimental part

The ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][TFSI], 99%) and butyltrimethylammonium bis(trifluoromethylsulfonyl)imide ([Btma][TFSI], 99.5%) were provided by Ionic Liquids Technologies GmbH. They were vacuum dried for at least overnight prior to their use. The water content measured by Karl Fischer for [Emim][TFSI] was < 50.0 ppm. DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, 98%, from Sigma Aldrich) was used as received and only manipulated in a dry nitrogen or argon atmosphere. The absorption of ultrapure CO_2 (>99.99%; from Oxilumen Gases) was carried out in both open and closed systems. For the open system, a glass flask with a septum lid was employed, where two needles were inserted, one to purge CO_2 over and the other to release excess pressure from the flask. This setup was utilized under ambient conditions, enabling an environment with the presence of air and moisture. For the closed system, solutions were pressurized with CO_2 at 1.1 bar in high pressure NMR tubes connected to a pressure gauge thoroughly purged and evacuated at least five times, to ensure a dry and anaerobic environment. The addition of labelled $^{13}CO_2$ (99 atom % ^{13}C; from Sigma Aldrich) was conducted under ambient conditions.

The attenuated total reflectance Fourier transform infrared (ATR-FT-IR) spectra were acquired in a Vertex-80v spectrometer from Bruker, with 128 scans and a resolution of 2 cm^{-1}, using an ATR-Platinum module equipped with a diamond crystal, under a N_2 atmosphere at approximately 1 bar. The spectral region of interest is within the medium-infrared range (MIR, 400 – 4000 cm^{-1}) and hence, KBr beamsplitter and DLaTGS detector were selected.

The ^{13}C Nuclear Magnetic Resonance (NMR) spectra were collected in a spectrometer Inova 300 MHz from Varian provided with broadband 2-channel console or in a 400 MHz Bruker Avance III spectrometer equipped with a broadband probe BBO. HMBC (Heteronuclear Multiple Bond Correlation) experiments were carried out in the Bruker equipment. All spectra were recorded with a capillary containing DMSO-d6 as the internal reference.

To access the infrared spectrum of the system DBU-water, an equimolar mixture of the superbase with deionized water was prepared. To obtain protonated DBU (DBUH), HCl 38% (provided by Labsynth) was added in neat DBU at around 6 ^{o}C, with an excess of 25 % in mass of acid. A colorless liquid was obtained. The ATR-FT-IR spectra were registered for both systems, as well as for neat DBU.

Computational Analysis

Geometry optimizations were performed at the CAM-B3LYP/6-311++G(d,p) level of Density Functional Theory in [Emim][TFSI] SMD continuum solvation model environment, employing D3 Grimme's dispersion corrections with Becke-Johnson damping (GD3BJ).[1, 2] Ultrafine integration grid was used. Single-point energies of the optimized structures were obtained through second-order Møller-Plesset perturbation theory, at MP2/Def2TVZPP level, in the same [Emim][TFSI] environment, in order to compute the interaction energy between the DBU-CO_2 adduct and water. Counterpoise correction was performed to estimate basis set superposition error on the interaction energy value. The obtained BSSE-corrected value of −19.29 kJ.mol^{-1} was calculated as shown in Equation 1 below. The raw values of energy are exhibited in Table S3. All aforementioned computational procedures were performed using Gaussian16.

$$E_{int} = E_{adduct-H_2O} - E_{adduct} - E_{H_2O} + E_{BSSE} \qquad (1)$$

Table S1. Assignment of the ^{13}C NMR peaks observed for bicarbonate, carbonate, DBU (C_7) and CO_2 in the DBU-CO_2 adduct in [Emim][TFSI] medium.

Species	**^{13}C peak / ppm**
HCO_3^-	162.6
CO_3^{2-}	175.5
CO_2 (DBU-CO_2 adduct)	160.3
DBU C_7 ($DBUH^+$)	165.3
DBU C_7 (DBU-CO_2 adduct)	165.0

Table S2. Natural charges obtained through Natural Population Analysis of the optimized geometry DBU-CO_2-H_2O for carbons, nitrogens, and oxygens of the adduct. Atom labels in the structure are shown.

Atom	**Natural Charge**
C_7	0.64614
N_1	–0.39240
C_{11}	–0.17269
N_8	–0.52074
C_9	–0.17882
C_5	–0.37946
C_4	–0.40469
C_3	–0.40278
C_2	–0.18254
C_6	–0.46741
C_{10}	–0.42132
C_{12}	0.97865
O_{13}	–0.62226
O_{14}	–0.70906

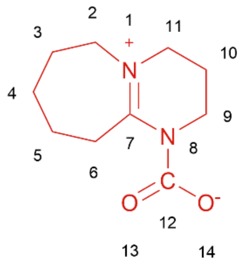

Table S3. Computed values of total electronic energy used to calculate the interaction energy.

Energy	Value / Hartree
$E_{adduct-H2O}$	–725.786645
E_{adduct}	–649.444993
E_{H2O}	–76.332185
E_{BSSE}	0.002121
E_{int}	–0.007346

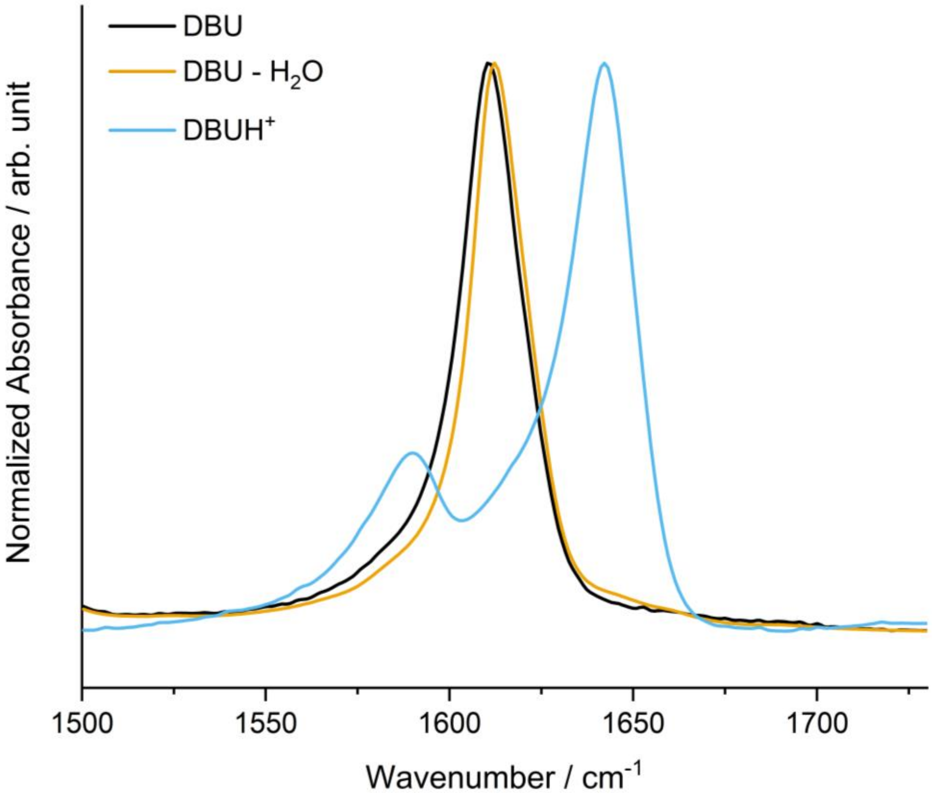

Figure S1. Spectral region (1500 – 1730 cm^{-1}) of the C=N symmetric stretching from DBU, $\nu(C{=}N)_{DBU}$, in the ATR-FT-IR spectra of neat DBU (in black), an equimolar mixture DBU:H_2O (in yellow), and [$DBUH^+$][Cl^-] (in blue).

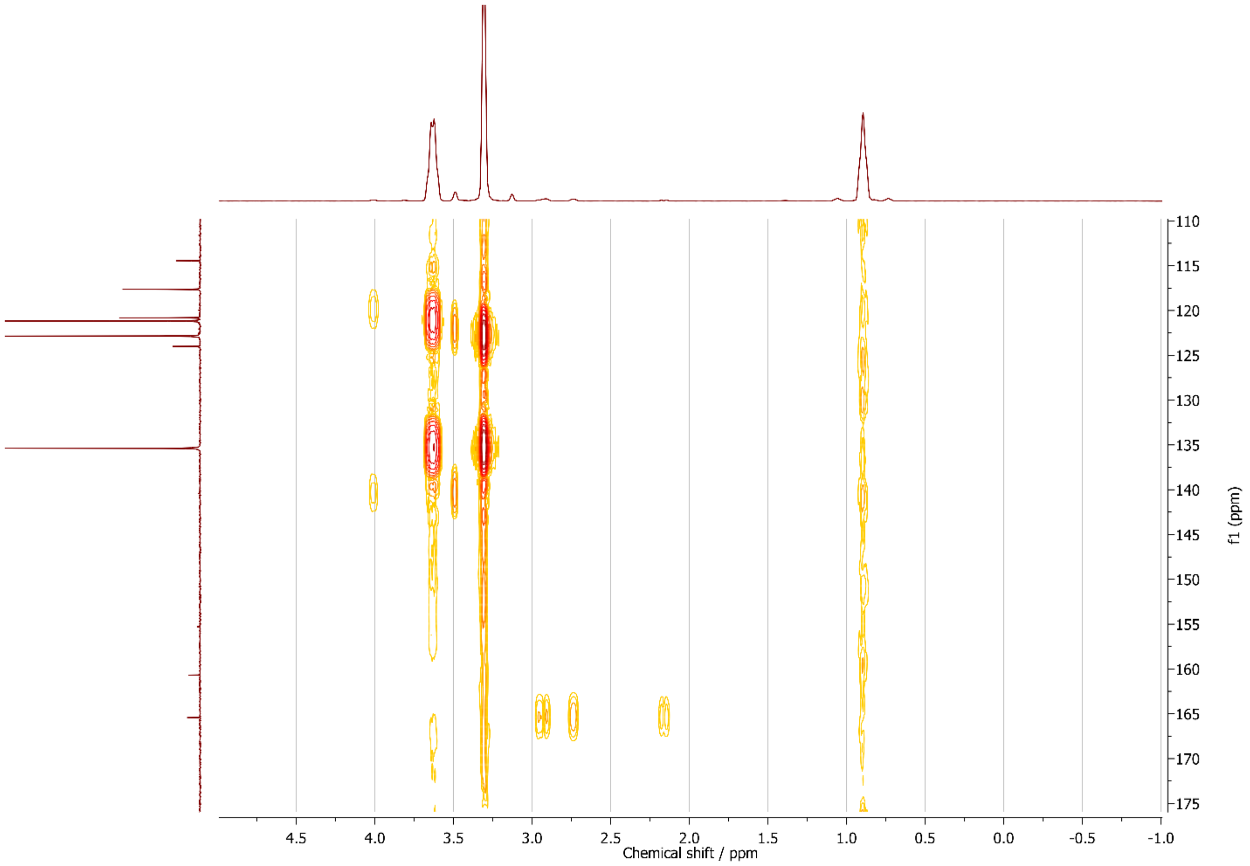

Figure S2. HMBC spectrum of the DBU solution in [Emim][TFSI] at mole ratio 1:10 (DBU:IL) with CO_2 absorbed under open-system conditions. The cross-peaks of the 165.1 ppm signal (DBU C_7) are correlated with DBU hydrogens. The ranges are -1.0 to 4.8 ppm and 110.0 to 175.0 ppm.

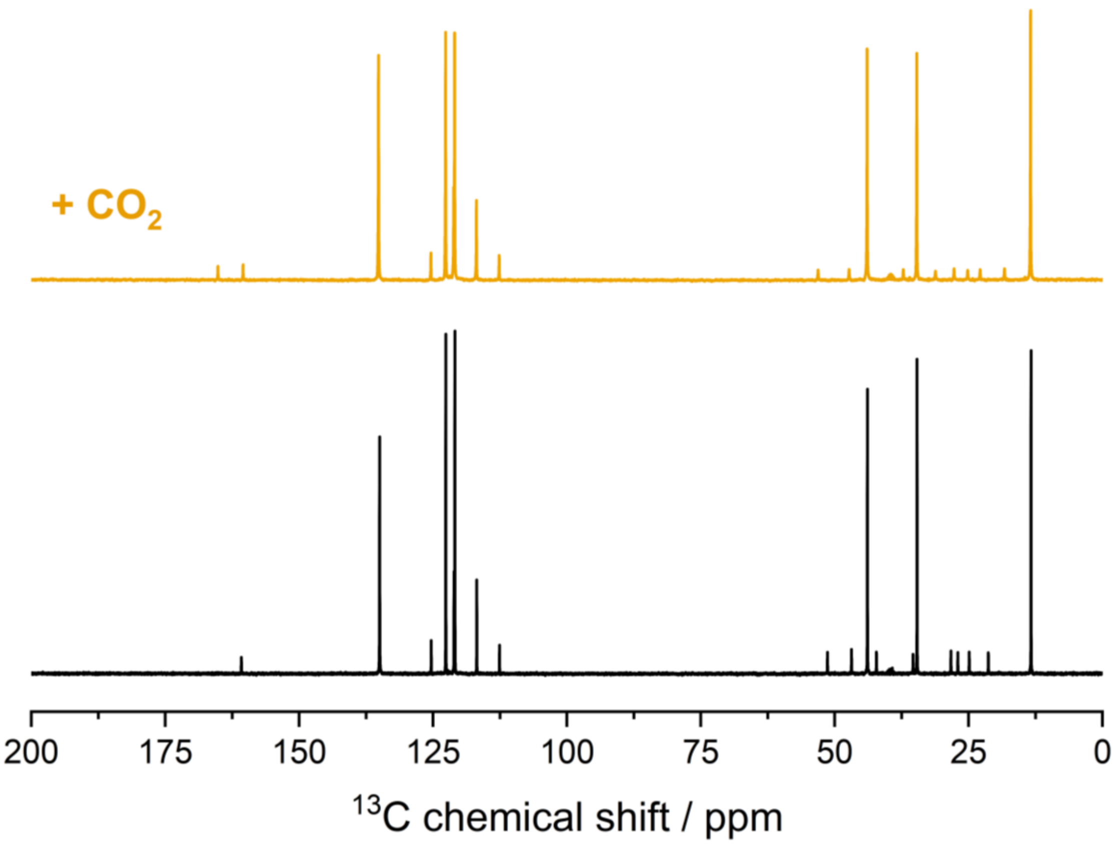

Figure S3. ^{13}C NMR spectrum of the system DBU:[Emim][TFSI] (1:10) without (in black) or with CO_2 absorbed under open-system conditions (in yellow).

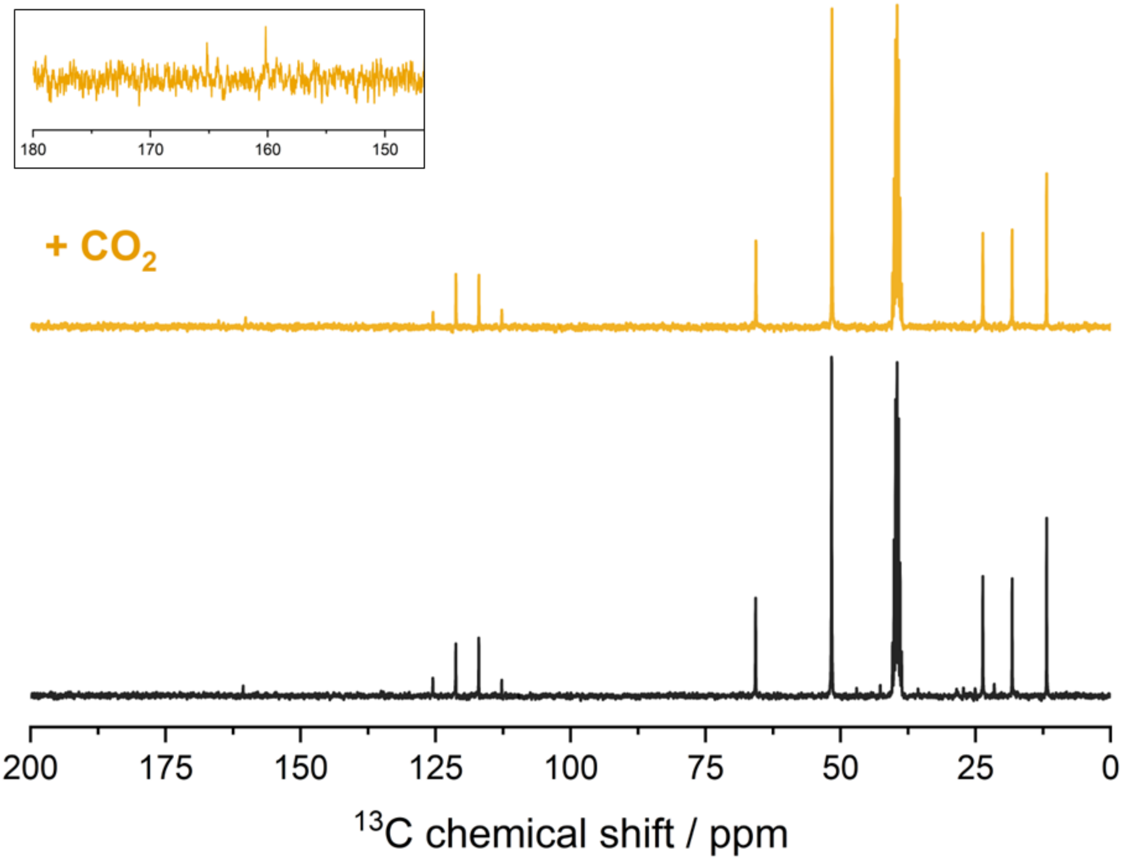

Figure S4. ^{13}C NMR spectrum of the system DBU:[Btma][TFSI] (1:10) without (in black) or with CO$_2$ absorbed under open-system conditions (in yellow).

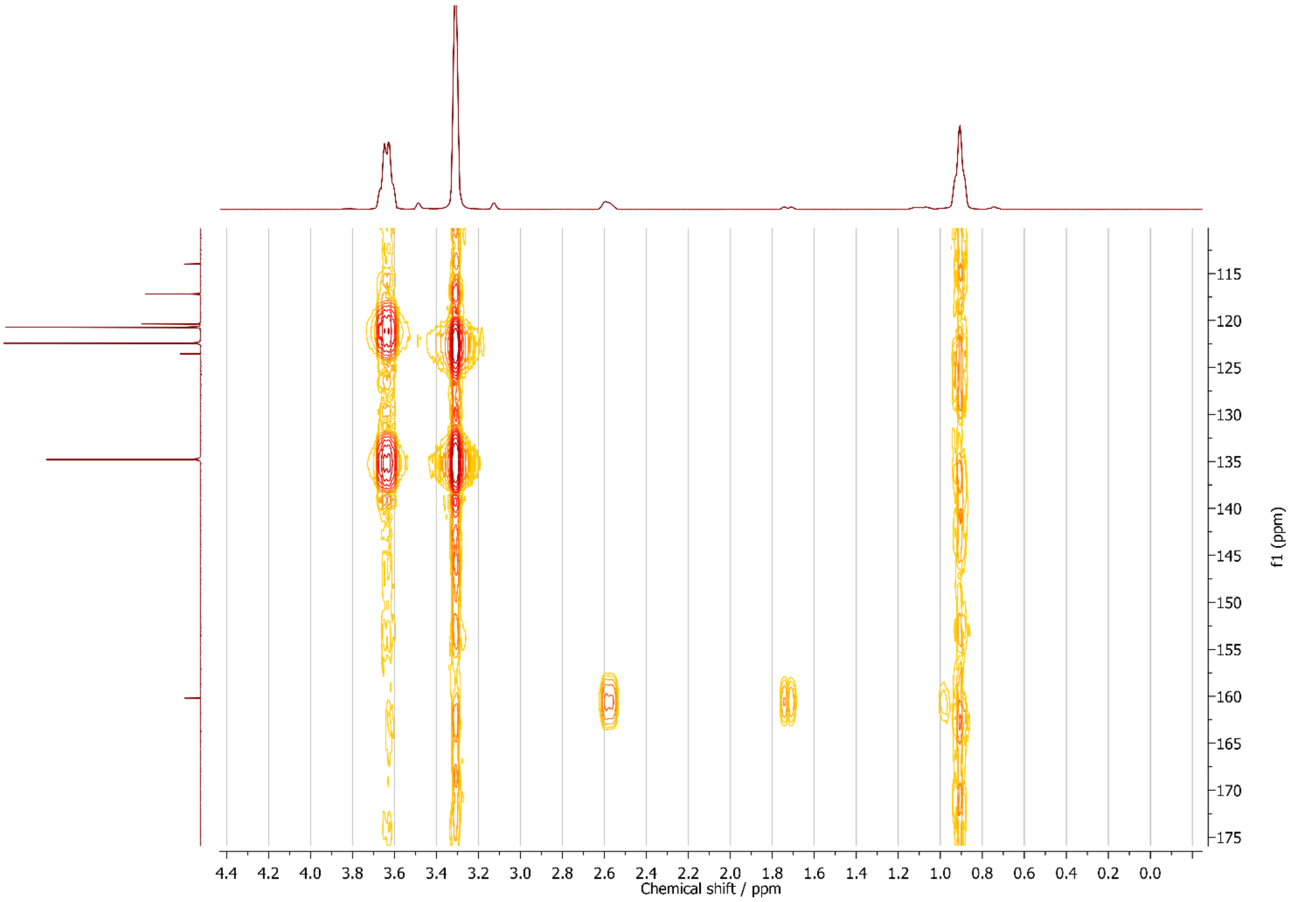

Figure S5. HMBC spectrum of the DBU solution in [Emim][TFSI] at mole ratio 1:10 (DBU:IL). The cross-peaks of the 160.8 ppm signal (DBU C_7) are correlated with DBU hydrogens. The ranges are -0.3 to 4.4 ppm and 109.0 to 175.0 ppm.

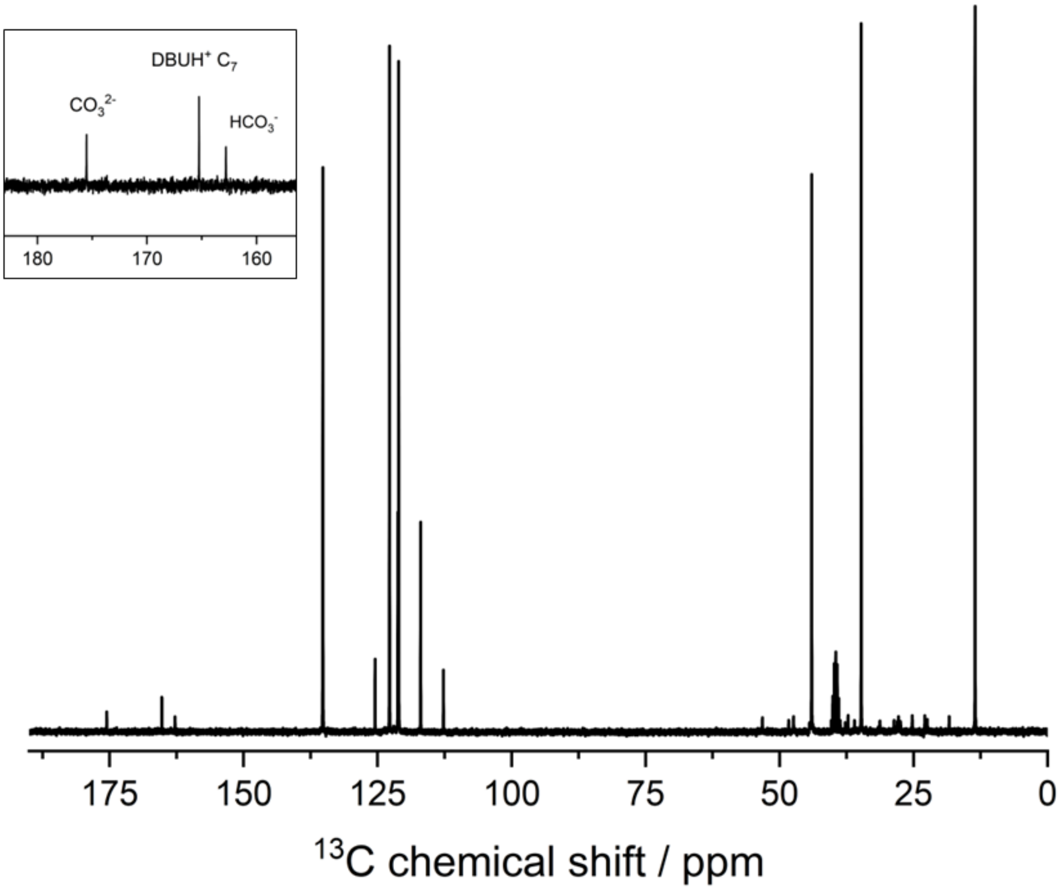

Figure S6. ^{13}C NMR spectrum of the DBU solution in [Emim][TFSI] at mole ratio 1:10 (DBU:IL) with CO_2 and K_2CO_3 added.

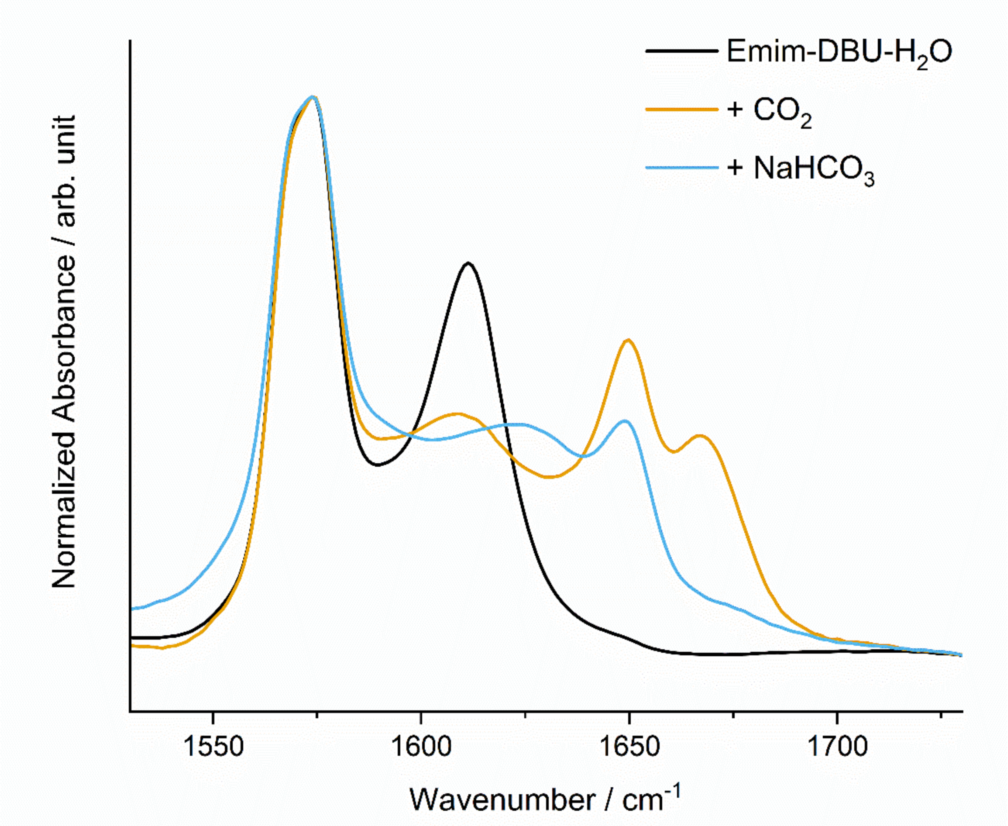

Figure S7. ATR-FT-IR spectra at 1530 – 1730 cm^{-1} spectral range of the DBU-H_2O mixture in [Emim][TFSI] at mole ratio 1:1:10 (DBU:H_2O:IL) without CO_2, in black; in the presence of CO_2, in yellow; and with $NaHCO_3$ added to the system in the presence of CO_2, in blue.

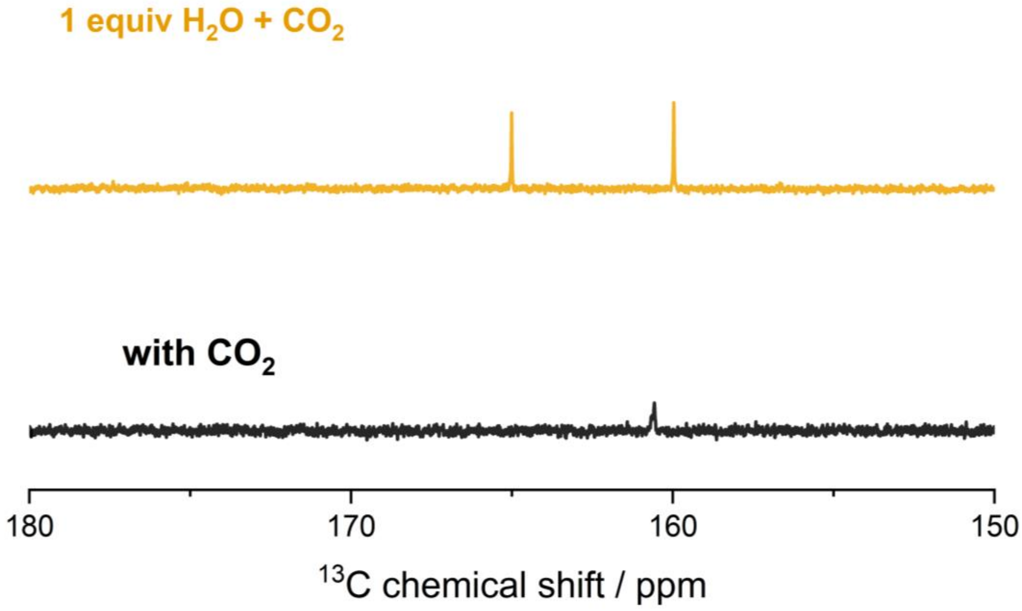

Figure S8. ^{13}C NMR spectra in the 150.0 – 180.0 ppm range of the system DBU:[BtmaTFSI] at mole ratio 1:10 with CO_2, in black, and the ternary DBU:H_2O: [BtmaTFSI] system at mole ratio 1:1:10 with CO_2, in yellow. The absorption of CO_2 was carried out under 1.1 bar in an anaerobic and dry environment.

References

1. V. S. Bernales, A. V. Marenich, R. Contreras, C. J. Cramer and D. G. Truhlar, *The Journal of Physical Chemistry B*, 2012, **116**, 9122-9129.
2. S. Grimme, S. Ehrlich and L. Goerigk, 2011, **32**, 1456-1465.