Supporting information

Title: One-Pot and Metal-Free Synthesis of Dimethyl Carbonate From CO_2 at Room Temperature

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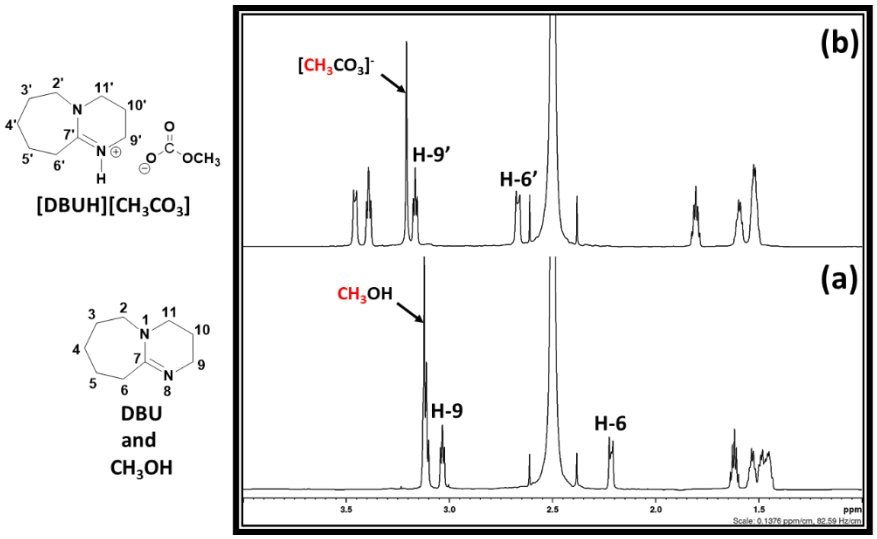

Figure S1. ^{1}H NMR spectra of (a) DBU and methanol and (b) [DBUH][CH_3CO_3] (NMR analysis with D_2O capillary).

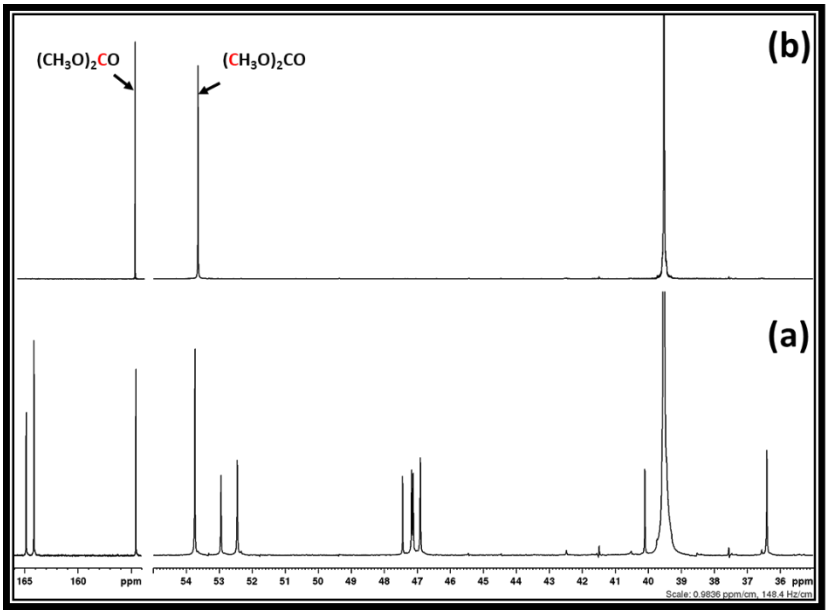

Figure S2: ^{13}C NMR spectra of the (a) reaction mixture after addition of 1 equivalents of CH_3I in DMSO solution of [DBUH][CH_3CO_3] and (b) commercially available DMC (NMR analysis with D_2O capillary).

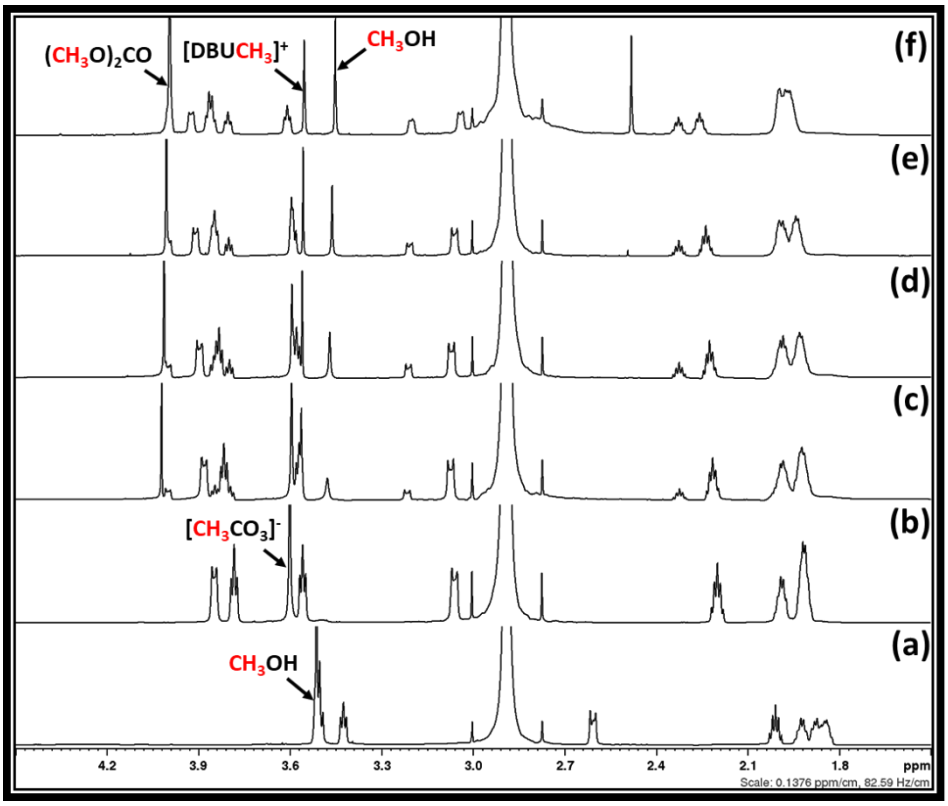

Figure S3. ^{1}H NMR spectra for the synthesis of DMC from [DBUH][$MeCO_3$] and CH_3I in DMSO. (a) DBU and methanol, (b) [DBUH][CH_3CO_3], reaction mixture after addition of (c) 0.25, (d) 0.50, (e) 0.75, and (f) 1 equivalents of CH_3I in DMSO solution of [DBUH][CH_3CO_3] (NMR analysis with D_2O capillary).

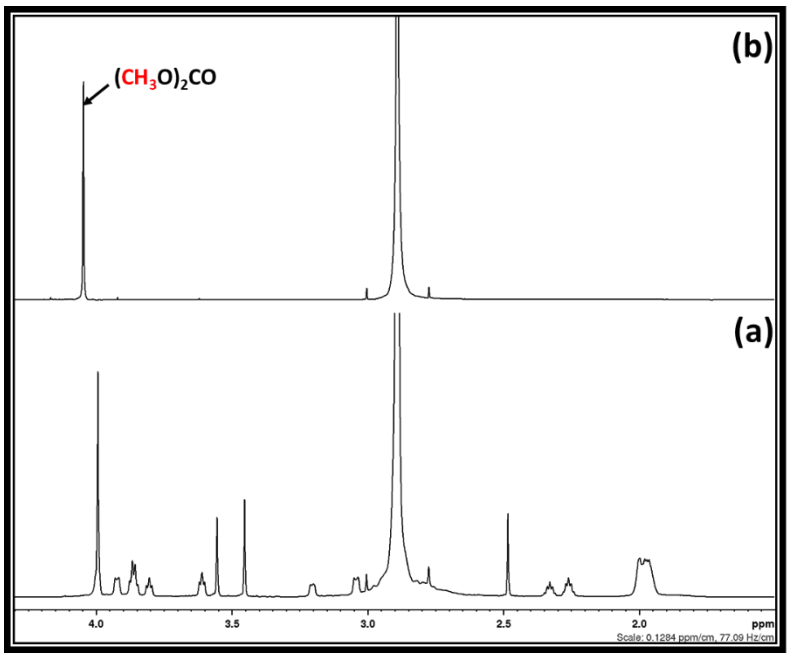

Figure S4. ^{1}H NMR of the (a) reaction mixture after addition of 1 equivalent of CH_3I in DMSO solution of [DBUH][CH_3CO_3] and (b) commercially available DMC (NMR analysis with D_2O capillary).

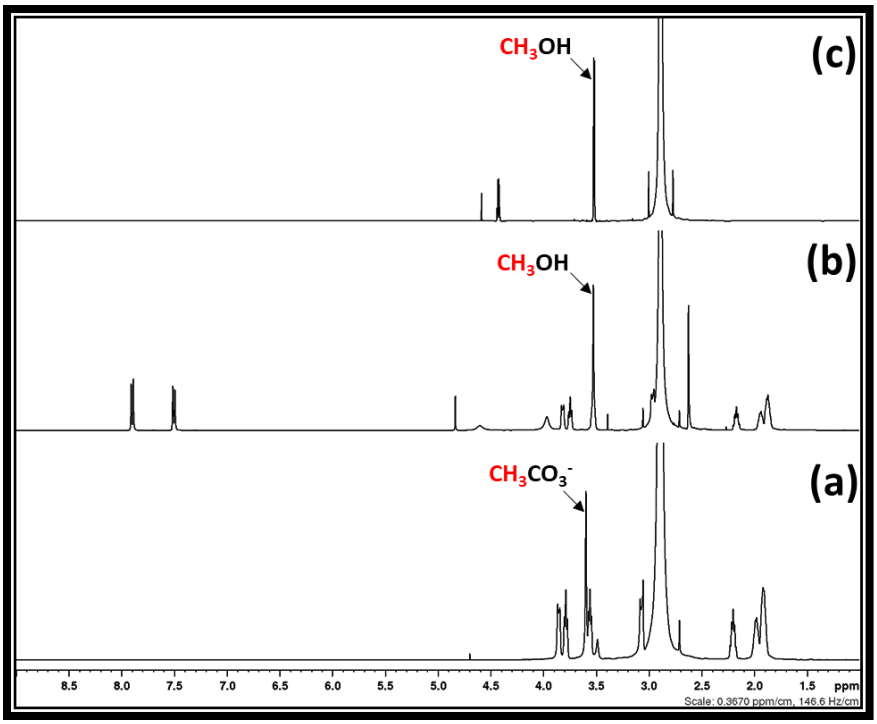

Figure S5. ^{1}H NMR spectra of the reaction mixture (a) containing [DBUH][CH_3CO_3] in DMSO and (b) after addition of *p*-toluene sulfonic acid in DMSO solution of [DBUH][CH_3CO_3] (NMR analysis with D_2O capillary), and (c) methanol in DMSO (NMR analysis with D_2O capillary).

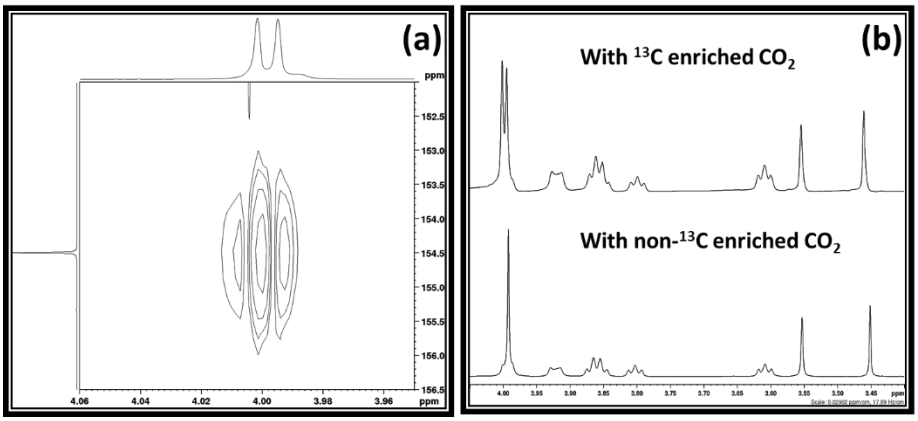

Figure S6. (a) ^{1}H-^{13}C HMBC spectra of the reaction mixture after addition of 1 eq. of CH_3I in DMSO solution of [DBUH][$CH_3{}^{13}CO_3$] and (b) ^{1}H NMR spectra of the reaction mixtures where 'normal' and ^{13}C-enriched CO_2 were used (NMR analysis with D_2O capillary).

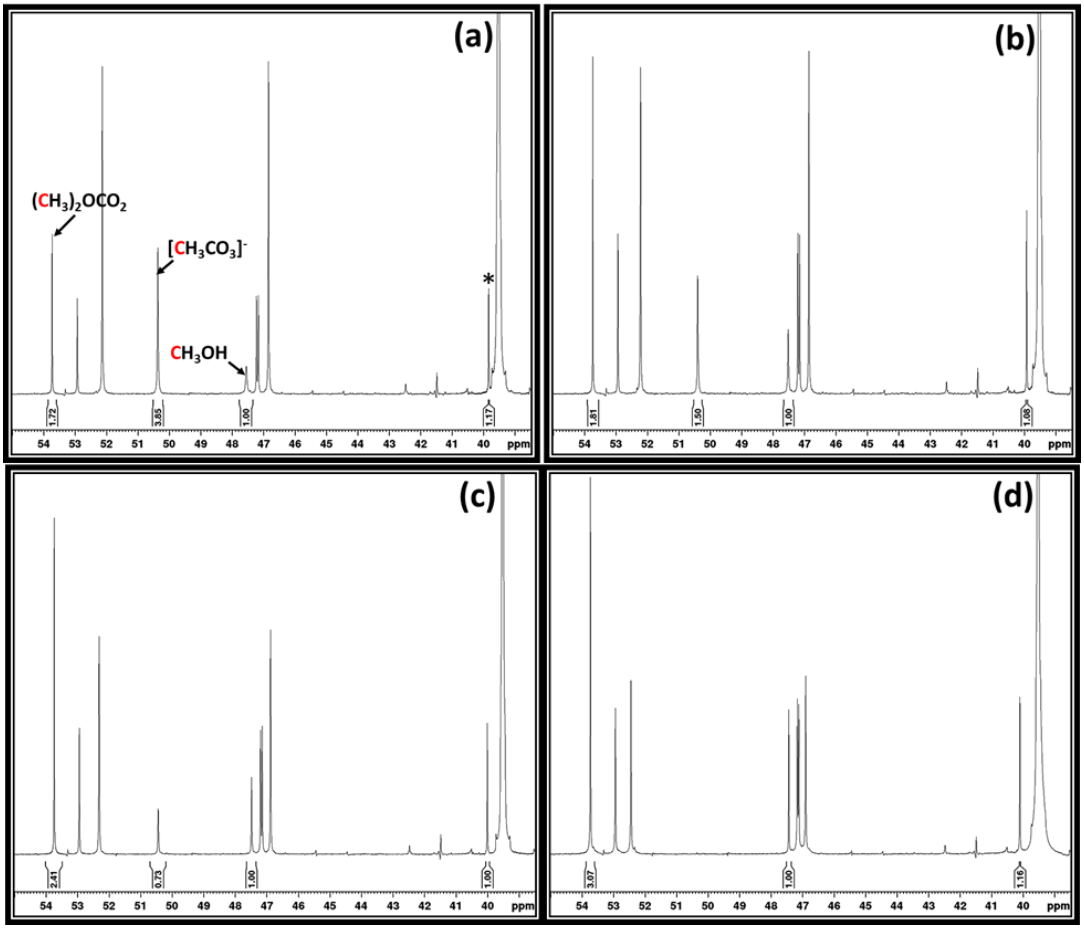

Figure S7. Integration of characteristic peaks in the ^{13}C NMR spectra of the reaction mixture after addition of different equivalents of CH_3I in DMSO solution of [DBUH][CH_3CO_3] (a) 0.25, (b) 0.50, (c) 0.75, and 1 eq. of CH_3I (NMR analysis with D_2O capillary).

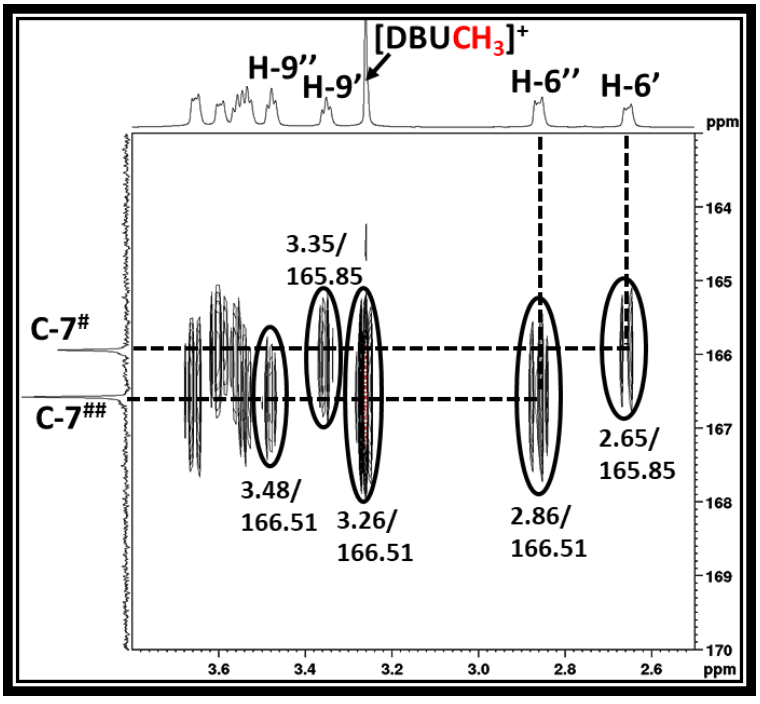

Figure S8. ^{1}H-^{13}C HMBC spectra of recovered DBU salts, [DBUH][I] and [DBUCH_3][I] (NMR analysis with D_2O. As the neat D_2O used for analysis, the mentioned chemical shifts values are different compared to the values obtained when D_2O capillary used during analysis.).

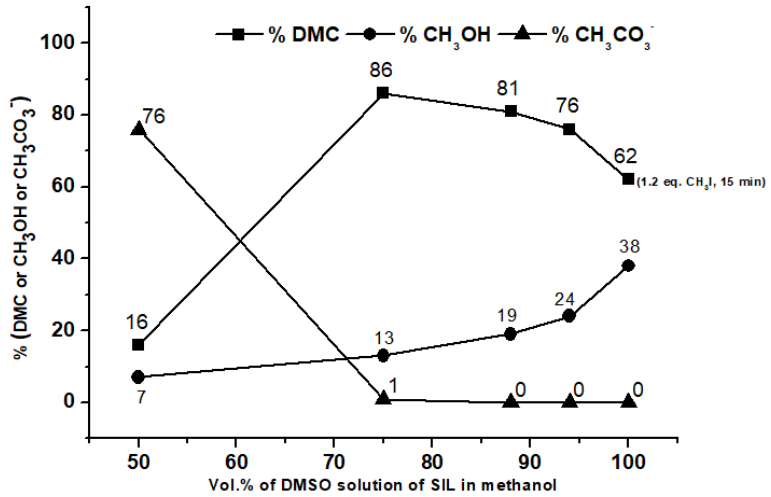

Figure S9. Amounts (%) of DMC, CH_3OH. and $CH_3CO_3^-$ anions in the reaction mixture containing different amounts of methanol or DMSO solution of SIL; 3 eq. of CH_3I was added (based on the amounts of DBU), 1h of reaction time.

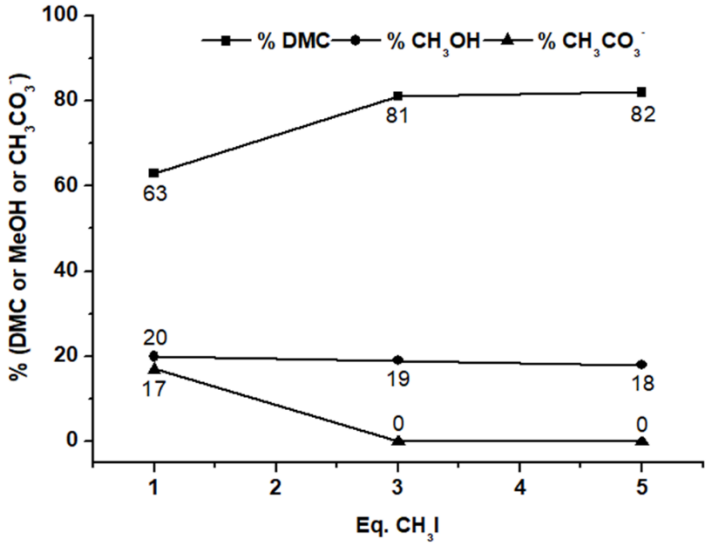

Figure S10. Amounts (%) of DMC, CH_3OH, and [CH_3CO_3]- anions in the reaction mixture after addition of different amounts of CH_3I (1, 2, and 5 eq. based on amount of DBU). The reaction performed with 12 vol.% of methanol with 88 vol.% of SIL in DMSO for 1h.

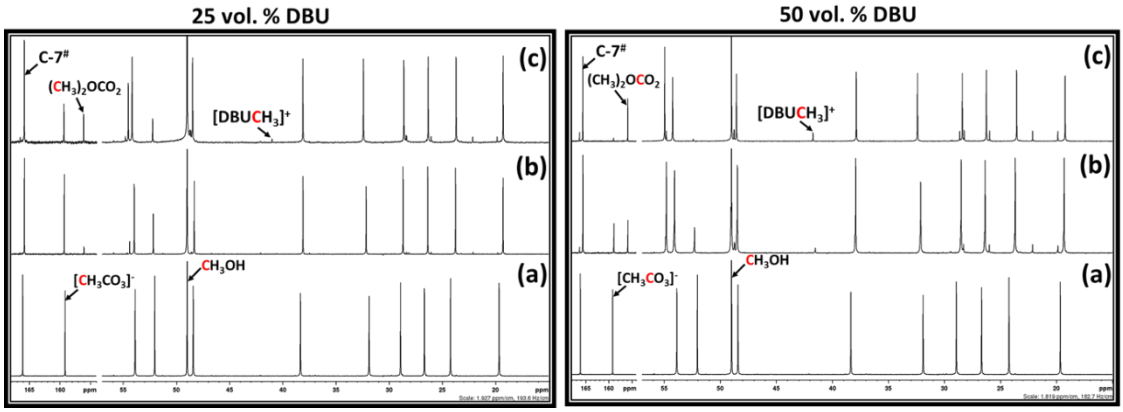

Figure S11. ^{13}C NMR spectra of the reaction mixture for the different reaction times after addition of 3 eq. of CH_3I (based on amount of DBU) in the solution of SIL ([DBUH][CH_3CO_3]) in methanol. The 25 or 50 vol.% of DBU in methanol was taken during SIL synthesis, (a) 0 h (only SIL in methanol), (b) 1h, and (c) 5h (NMR analysis with D_2O capillary).

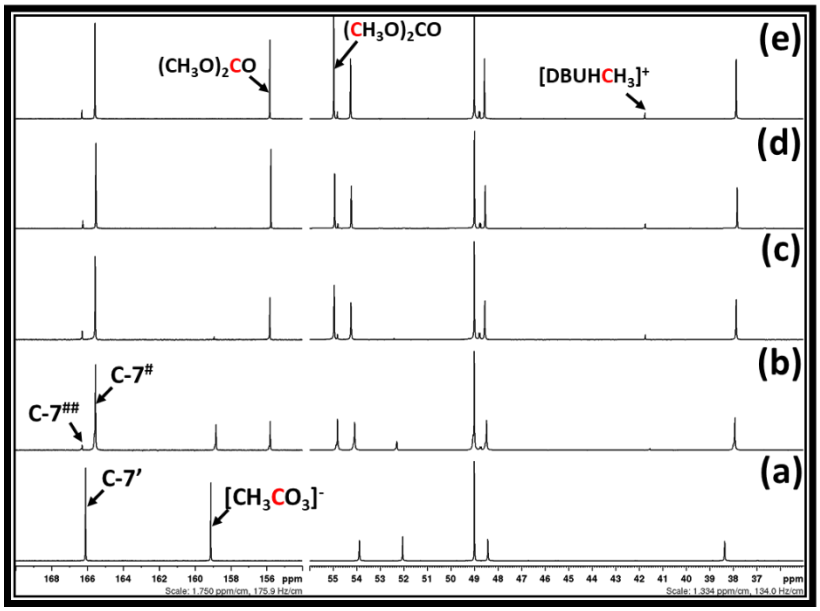

Figure S12. ^{13}C NMR spectra for the synthesis of DMC in reaction mixtures with 50 vol.% of DBU in alcoholic solution with different reaction times: (a) 0 h (only SIL in methanol), (b) 1h, (c) 5h, (d) 7h, and (e) 10h; 3 eq. of CH_3I was added (NMR analysis with D_2O capillary).

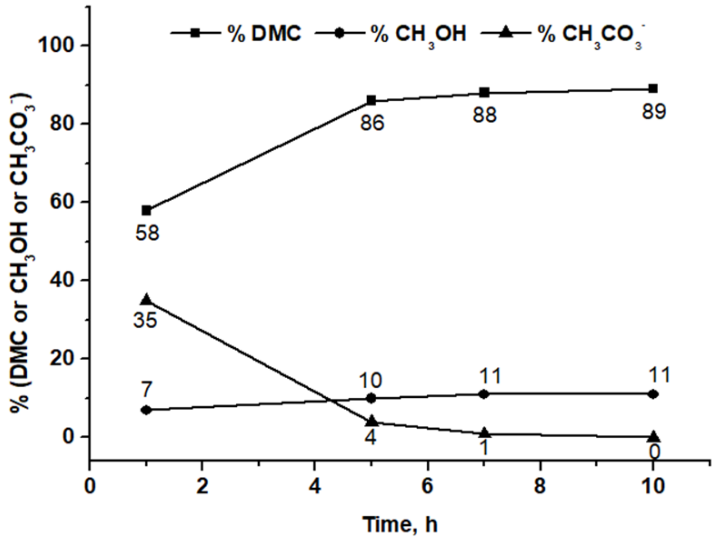

Figure S13. Amounts of DMC, methanol, and [$CH_3CO_3^-$] anions formed in the reaction mixture with different reaction times with reaction composition having 50 vol.% of DBU in alcoholic solution; 3 eq. of CH_3I was added.

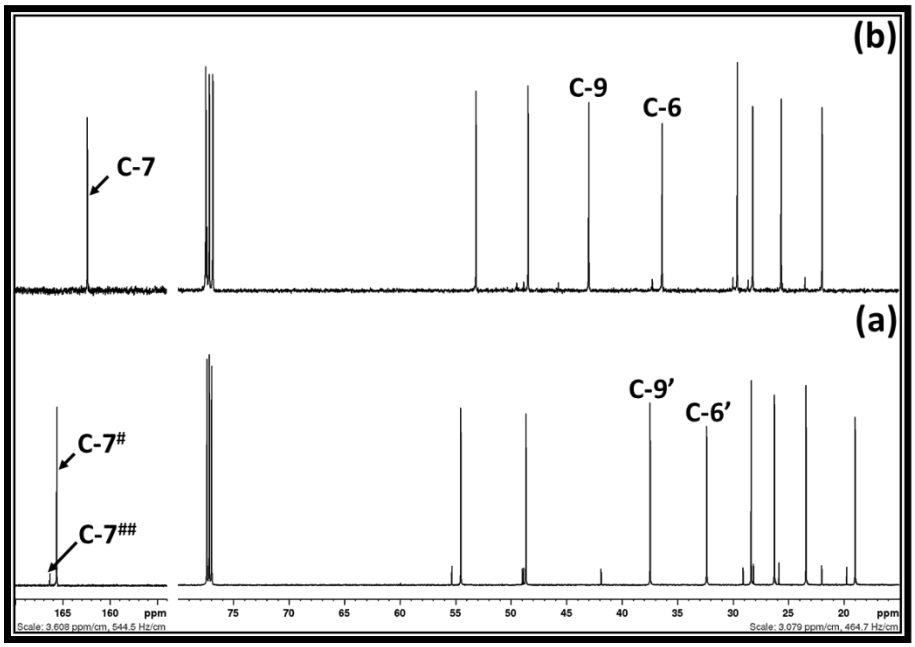

Figure S14. ^{13}C NMR spectra of the (a) recovered DBU salts, [DBUH][I] and [$DBUCH_3$][I], and (b) recovered DBU (NMR analysis with $CDCl_3$).