Supplementary Information

^{13}C NMR was used to characterize each of the starting materials and the products of reaction in the absence and presence of CO_2. ^{1}H and ^{13}C NMR spectra were collected on a Bruker AMX-400. To conduct quantitative ^{13}C NMR, a complete relaxation was determined by performing an inversion recovery T1 experiment. The carbonyl peak at 159.14 ppm had the longest T1 time of 23 s. The recommended delay time is 5 times the longest T1 time and therefore a delay time of 125 s was used. A full 90° pulse was used to insure complete excitation of the nucleus, and proton decoupling was done only during the acquisition period to avoid a false and disproportional signal build-up.

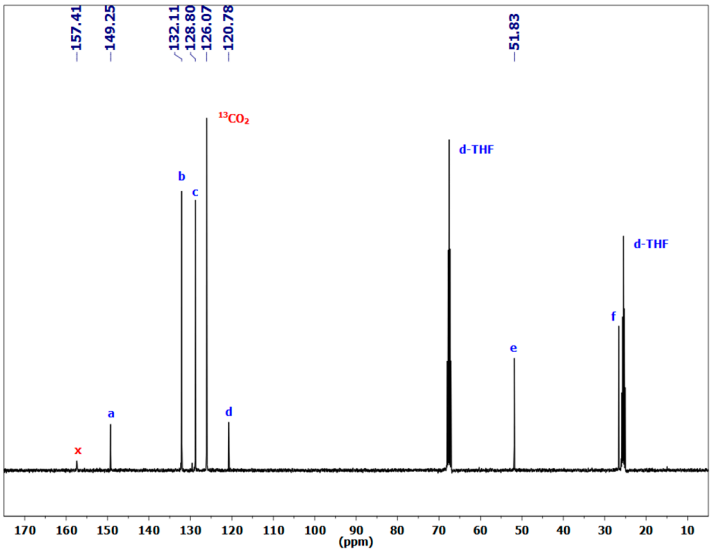

Figure S1. ^{13}C NMR of the reaction of 13C-labeled CO_2 with 4-bromo-α-methylbenzylamine (**1**) in THF at 50 °C to form ammonium carbamate salt (**2**).

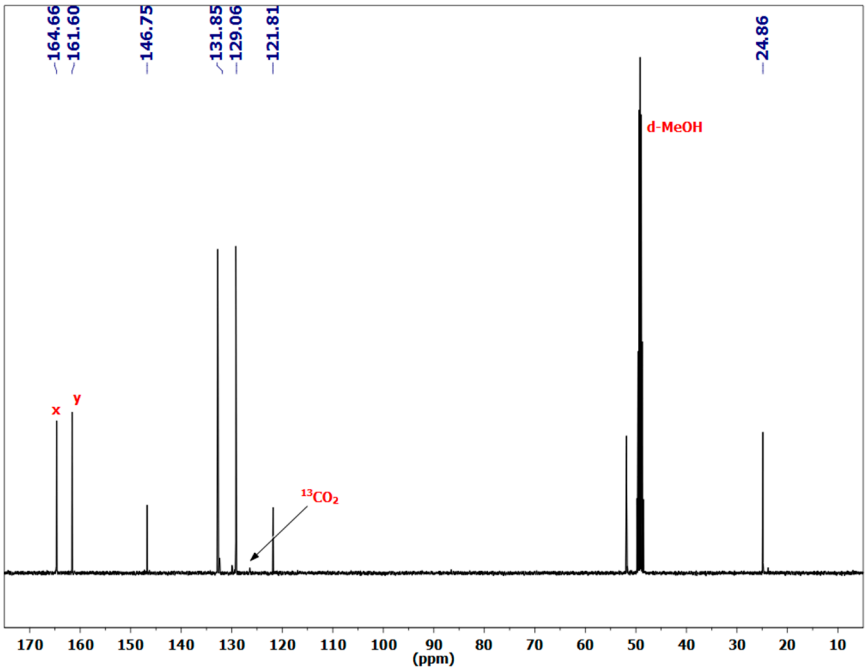

Figure S2. ^{13}C NMR spectrum for the reaction of 4-bromo-α-methylbenzylamine (**1**) with ^{13}C-labeled CO_2 at 25 °C in Methanol to form ammonium carbamate salt (**3**).

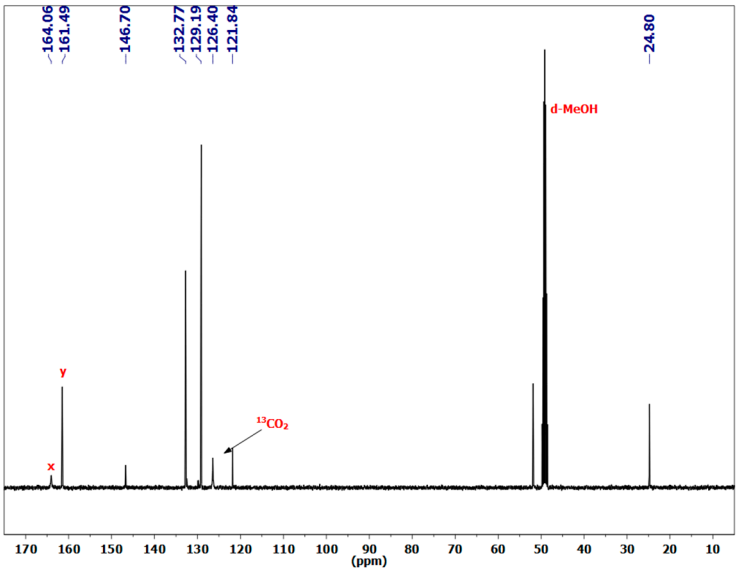

Figure S3. ^{13}C NMR spectrum for the reaction of 4-bromo-α-methylbenzylamine (**1**) with ^{13}C-labeled CO_2 at 50 °C in Methanol to form ammonium carbamate salt (**3**).

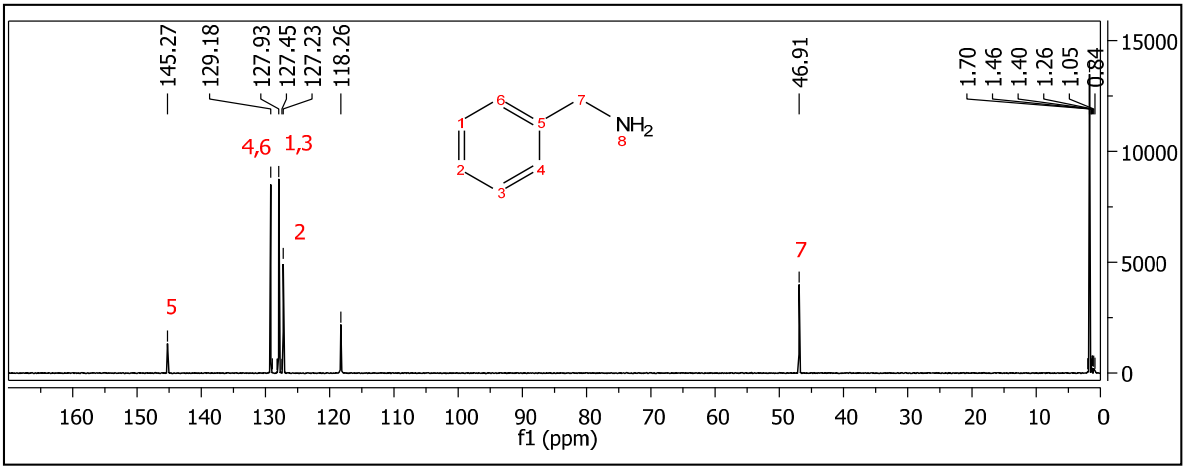

Figure S4. ^{13}C NMR spectrum of benzylamine (**4**) (BA) in deuterated acetonitrile.

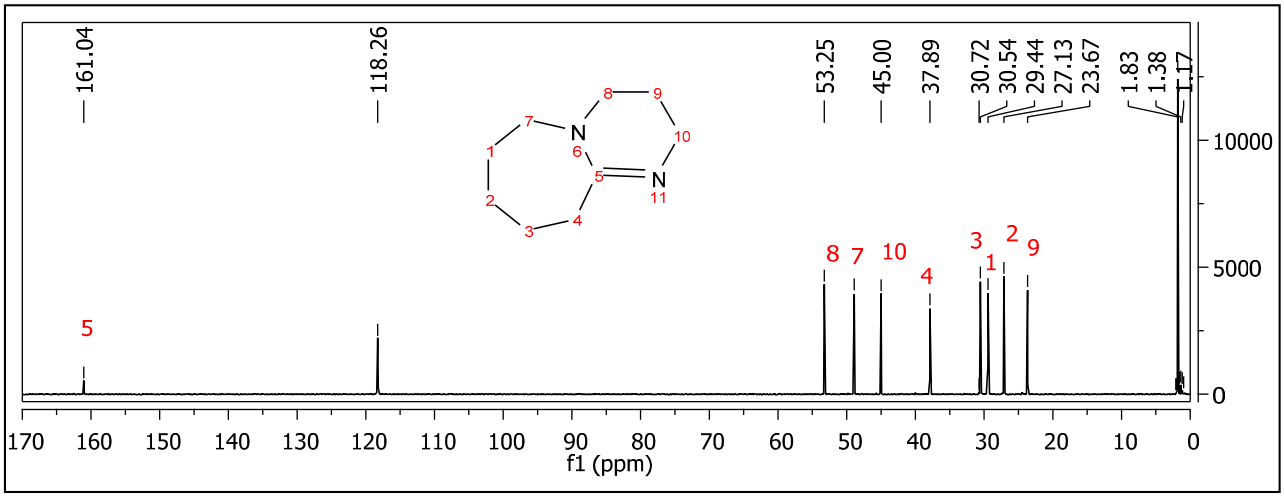

Figure S5. ^{13}C NMR spectrum of DBU (**6**) in deuterated acetonitrile.

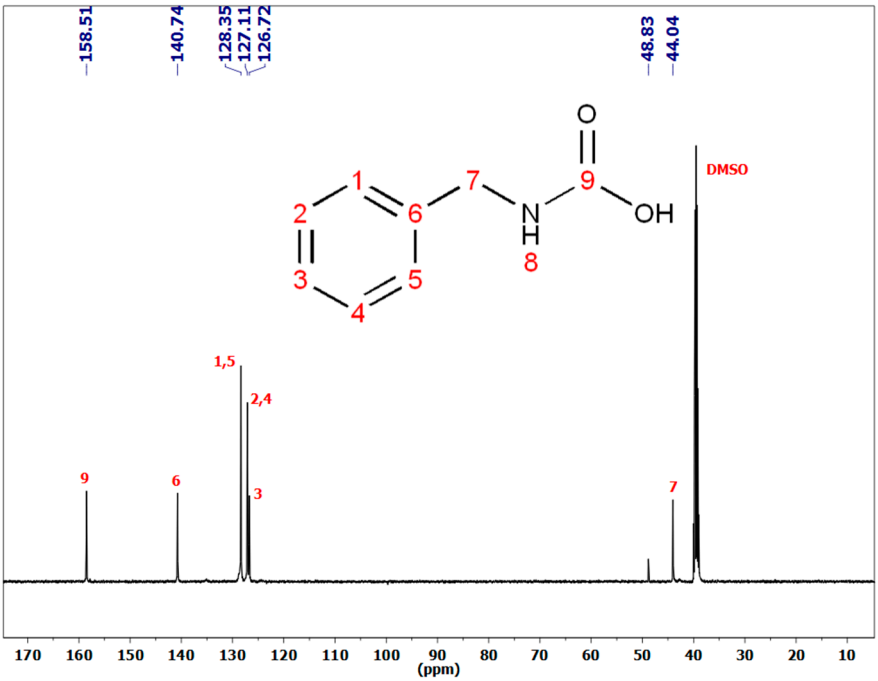

Figure S6. ^{13}C NMR spectrum for the reaction of benzylamine (**4**) with ^{13}C-labeled CO_2 in DMSO, forming the benzyl carbamic acid (**5**).

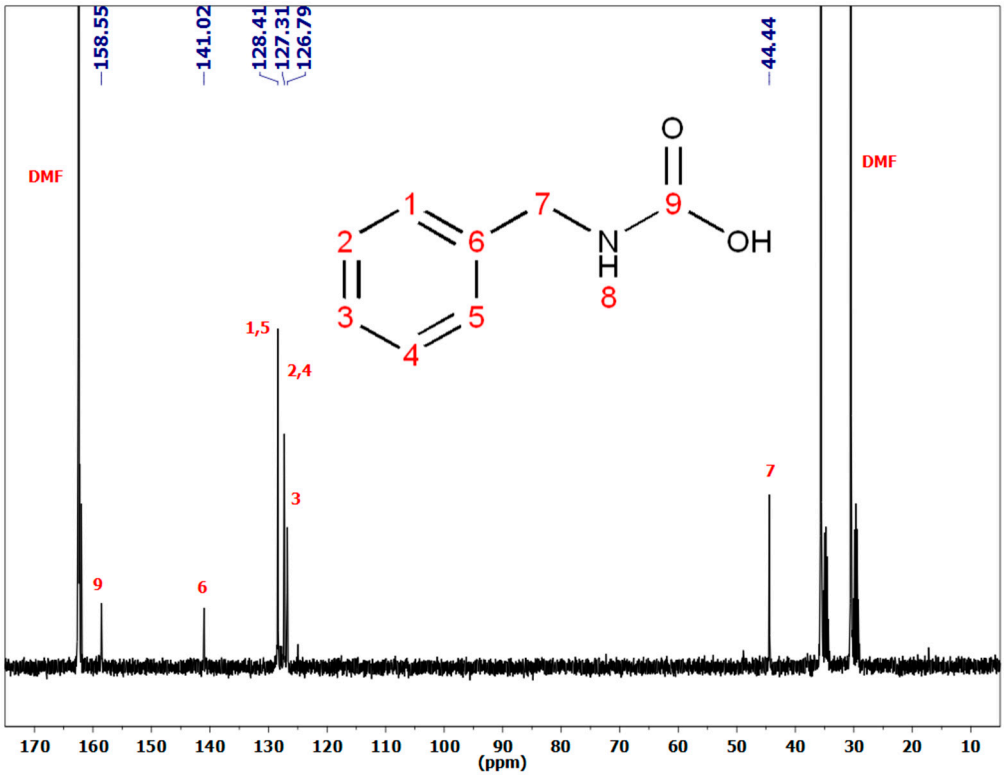

Figure S7. ^{13}C NMR spectrum for the reaction of benzylamine with ^{13}C-labeled CO_2 in DMF, forming the benzyl carbamic acid (**5**).

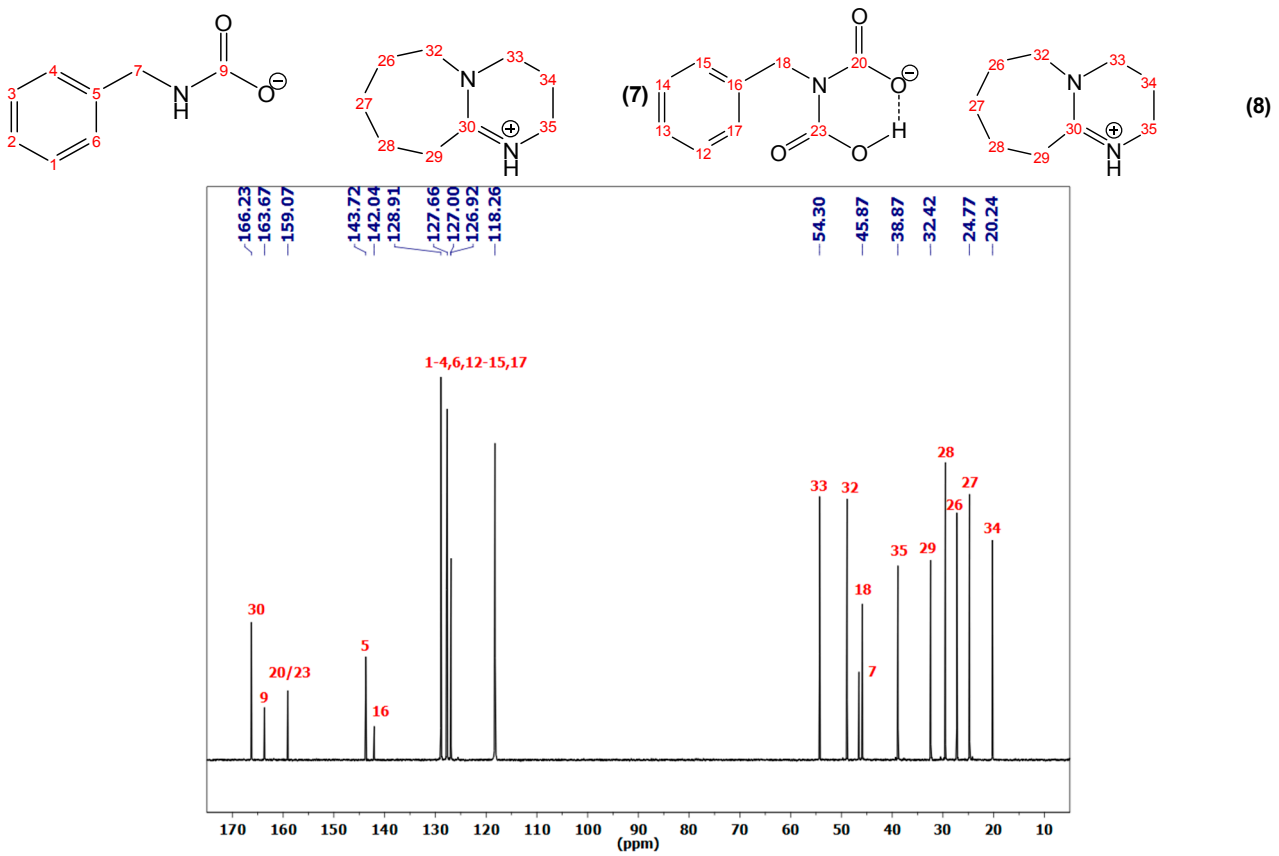

Figure S8. ^{13}C NMR of reaction of benzylamine (**4**) with CO_2 in acetonitrile in the presence of one equivalent of DBU(**6**), leading to amidiniums (**7**) and (**8**).

1. Reaction of Benzylamine with Isopropenyl Acetate in the Absence of CO_2

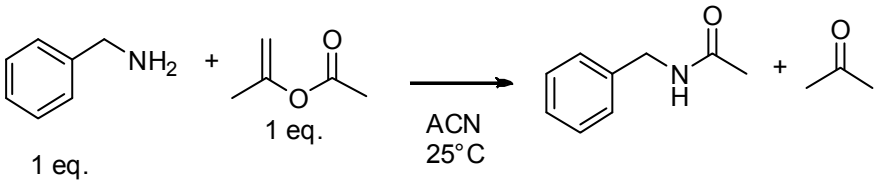

Figure S9. Control reaction of isopropenyl acetate (IPA) with benzylamine (BA).

The ^{13}C NMR spectrum of the reaction products of benzylamine (**4**) with isopropenyl acetate (**10**) in the absence of CO_2 is shown in Figure S10. The reaction was conducted under similar conditions to those employed in the reaction in the presence of CO_2 using DBU as the added base (see Figures 5 and 6). After 6 h of reaction time, significant evidence of the *N*-benzylacetamide (**12**) product was observed (see peaks labeled "16" at 170.62 ppm and "12" at 140.56 ppm in Figure S10. Unreacted isopropenyl acetate (IPA) and benzylamine are also evident (see peaks "5" and "2" at 169.77 ppm and 154.38 ppm which corresponds to IPA and peaks "23" and "25" corresponding to benzyl amine (see Figure S11).

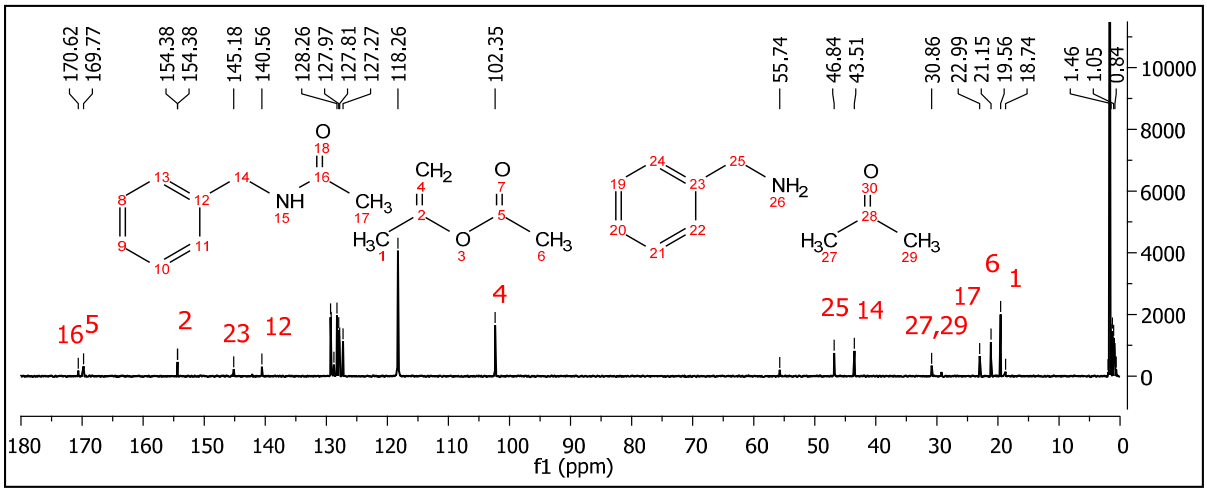

Figure S10. ^{13}C NMR control reaction of benzylamine (**4**) (BA) with isopropenyl acetate (**10**) (IPA) in the absence of CO_2.

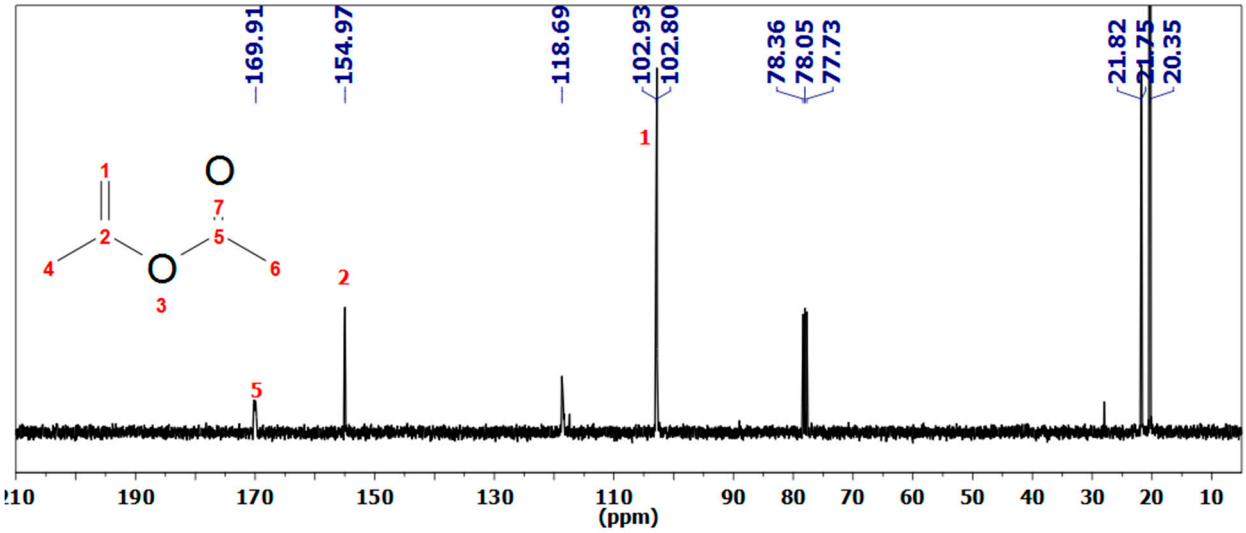

Figure S11. ^{13}C NMR of isopropenyl acetate (**10**) (IPA) in deuterated acetonitrile.

2. Reaction of Benzylamine with Isopropenyl Acetate and DBU in the Presence of CO_2

The reaction of CO_2 with benzylamine (**4**) in acetonitrile was as previously described; the molar ratio of DBU to benzylamine was 1.1. Isopropenyl acetate (**10**) (1 equivalent) was then added at room temperature and allowed to react for 6 h. No *N*-acylation was observed by ^{13}C NMR as seen in Figure S10. The peak "41" at 169.67 ppm is attributed to unreacted IPA. No trace of either *N*-acylation product (**12**) is observed; the absorptions at 170.62 ppm and ~140 ppm, observed Figure S10, are completely absent. It is concluded, therefore, that the benzylamine was protected by CO_2 as the DBU salt of carbamic acid. This carbamate is identified by peak "9" at 163.64 ppm and peak "20/23" at 159.11 ppm (see Figure 7). In addition, no reaction between DBU and isopropenyl acetate was observed.

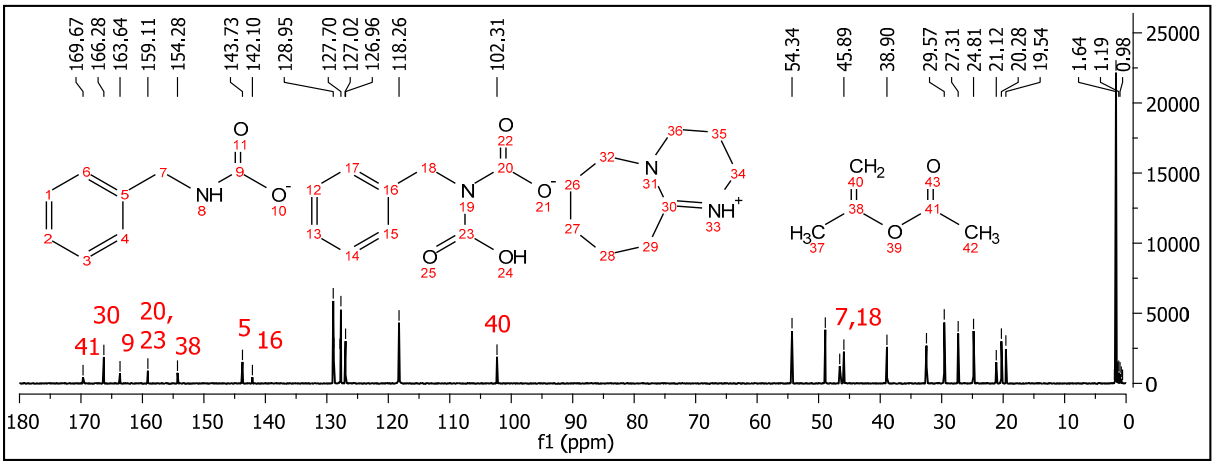

Figure S12. ^{13}C NMR of reaction investigated between CO_2-protected benzylamine (BA) using DBU and isopropenyl acetate (IPA).

Comparing Figure S10 with Figure S12 clearly shows that the CO_2-protection strategy in the presence of an added strong organic base is successful.

3. Reaction of Benzyl Alcohol with Isopropenyl Acetate in the Presence of DBU

Figure S15 shows the ^{13}C NMR from the reaction of benzyl alcohol (**11**) with IPA (**10**) in acetonitrile. *O*-acylation product (benzyl acetate (**13**)) peaks at 171.45 ppm labeled "28" and 137.58 ppm labeled "24" can be clearly identified.

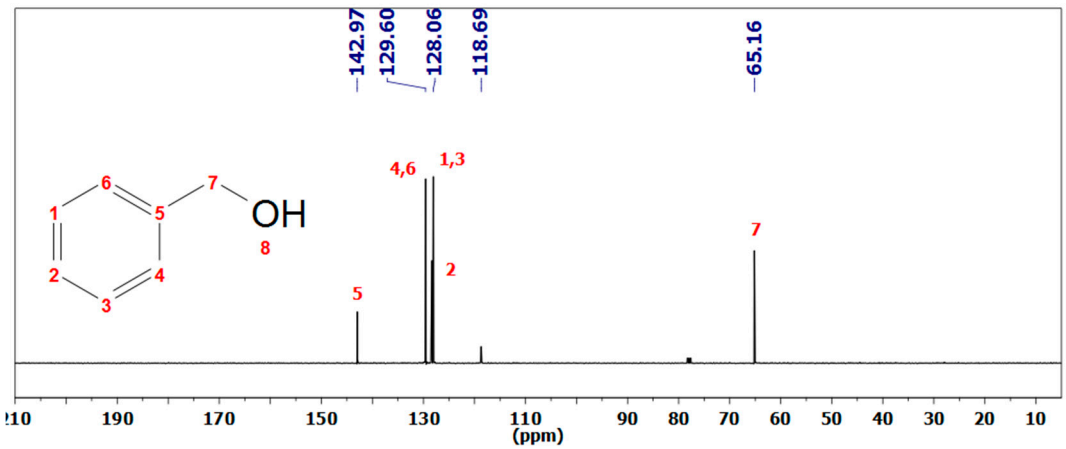

Figure S13. ^{13}C NMR of Benzyl Alcohol (**11**) (BzOH).

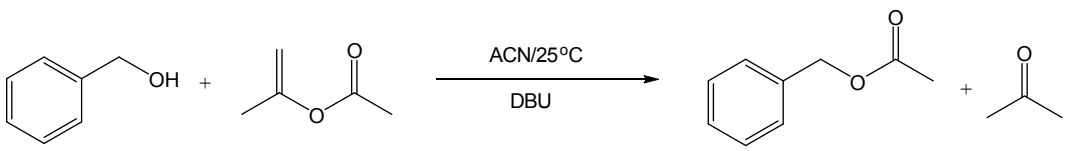

Figure S14. Reaction of isopropenyl acetate (**10**) (IPA) with benzyl alcohol (**11**) (BzOH) in the presence of DBU to form benzyl acetate (**13**).

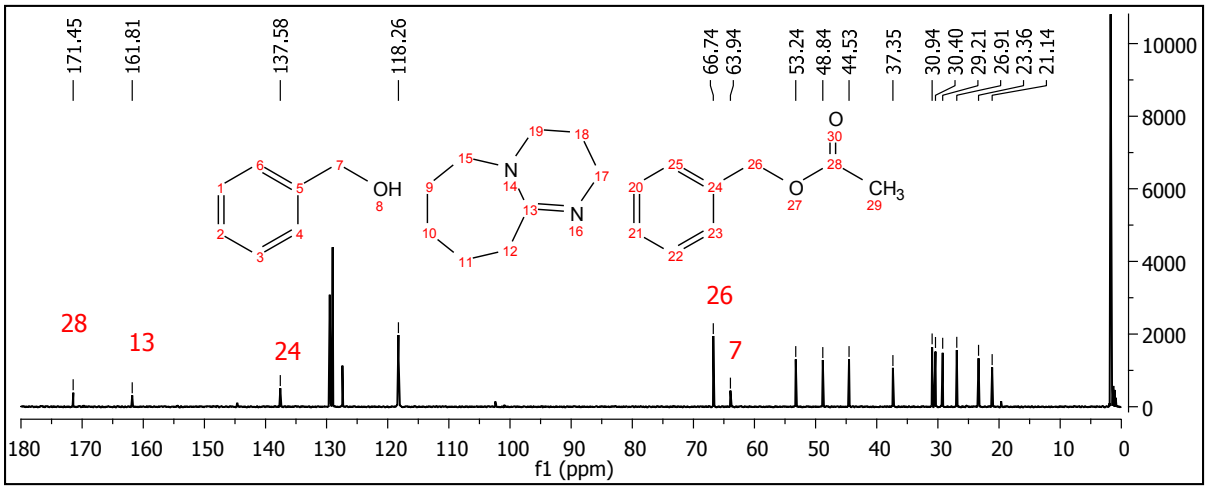

Figure S15. ^{13}C NMR showing reaction products from benzyl alcohol (BzOH) and isopropenyl acetate (IPA) in the presence of DBU (no CO_2).

4. Reaction of Equimolar Amounts of Benzyl Alcohol and Benzylamine with Isopropenyl Acetate in the Presence of DBU in the Presence of CO_2

Equimolar quantites of benzyl alcohol and benzylamine (**4**) were treated with CO_2 in the presence of DBU(**6**) in acetonitrile. The ^{13}C NMR spectrum after 6 h of reaction with isopropenyl acetate at room temperature is shown in Figure S10. No reaction of benzylamine is observed. In contrast, however, benzyl alcohol was observed to react with the isopropenyl acetate to yield benzyl acetate (**13**). More specifically, peak "39" at 171.32 ppm and peak "35" at ~137 ppm are identified as the *O*-acylation product (see Figure S15). The absorptions at ~170 ppm and ~140 ppm associated with the *N*-acylation product (Figure S10) are absent.

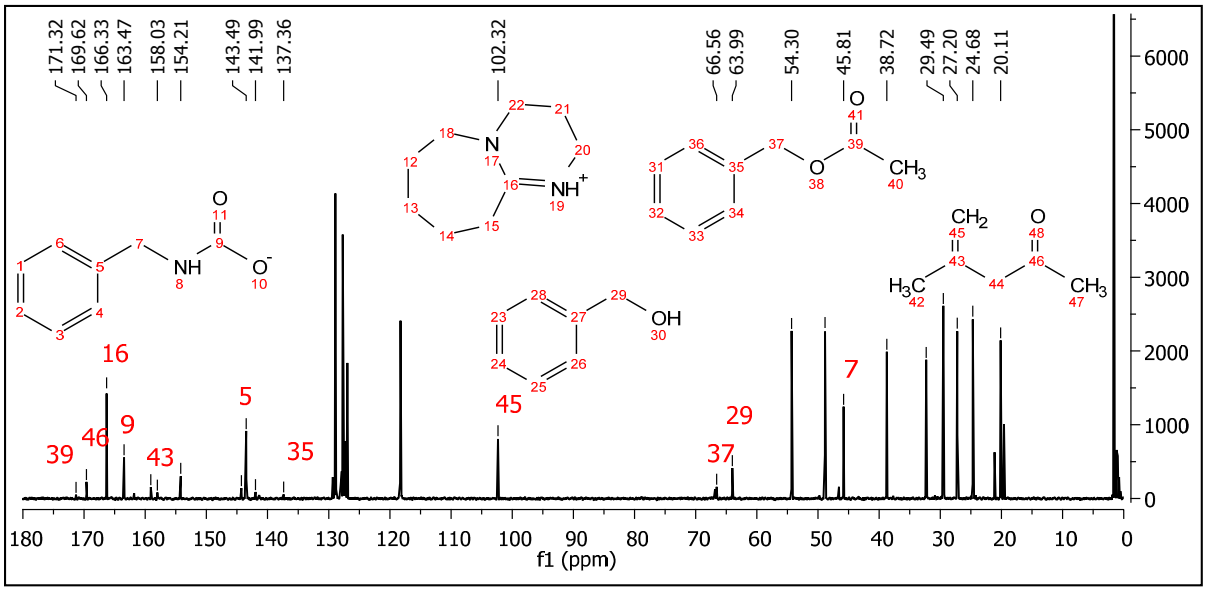

Figure S16. ^{13}C NMR of reaction of equimolar amounts of benzylamine and benzylalochol with isopropenyl acetate in the presence of DBU and CO_2.

5. Reaction 4-(aminomethyl)benzyl Alcohol with Isopropenyl Acetate and DBU in the Absence of CO_2

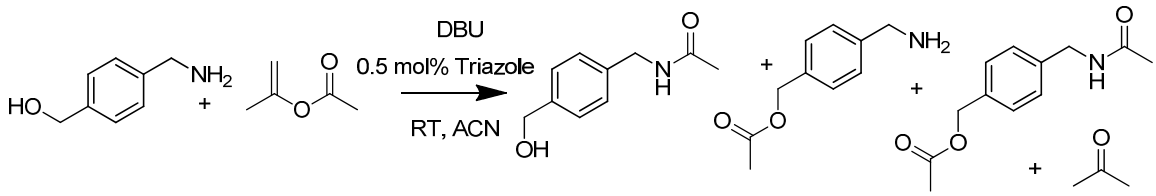

Figure S17. Reaction of 4-(aminomethyl)benzyl alcohol with isopropenyl acetate.

The reaction of the bifunctional molecule, 4-(aminomethyl)benzyl alcohol (**14**), with isopropenyl acetate (1.7 equivalents) in acetonitrile in the presence of DBU and 0.5 mol% triazole was conducted in the absence of CO_2. The ^{13}C NMR spectrum of the reaction products is shown in Figure S18. Absorptions at ~171 ppm and ~170 ppm peaks were observed which correspond to both to *O*- and *N*- acylated products. These are labeled peaks "13" and "9" respectively. It is important to note that the characteristic peaks at ~169 ppm and ~154 ppm which are attributed to the IPA (Figure S11) are not observed. This is interpreted to mean that the acylation reaction has gone to completion with amine reactivity dominating.

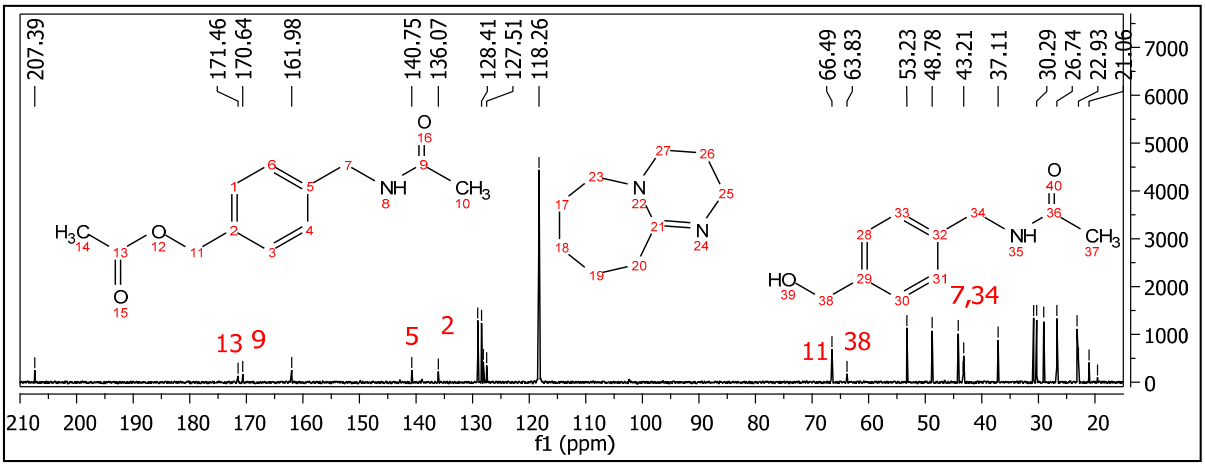

Figure S18. ^{13}C NMR control reaction of unprotected 4-(aminomethyl)benzyl alcohol with isopropenyl acetate in the presence of DBU (no CO_2).

6. Reaction of 4-(Aminomethyl)benzyl Alcohol with Isopropenyl Acetate and DBU in the Presence of CO_2

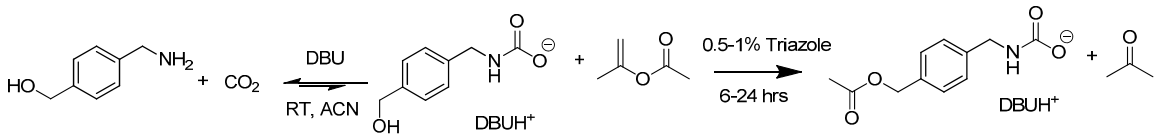

Figure S19. Reaction scheme of CO_2-protected 4-(aminomethyl)benzyl alcohol using DBU with isopropenyl acetate.

Reaction of 4-(aminomethyl)benzyl alcohol (**14**) with isopropenyl acetate in the presence of DBU and 0.5 mol % of 1,2,4-triazole as catalyst was conducted for 6 h. The ^{13}C NMR (Figure S19) showed 30% of the hydroxyl group had reacted while none of the amine reacted; it remained CO_2-protected. The reaction was also carried out at a longer time period (24 h) using 1 mol % catalyst. By NMR (Figure S20) 80% of the hydroxyl group reacted while none of the amine reacted. The amine remained CO_2-protected. This is supported by peaks"17" and "9" showing that we did create the carbamate species. More importantly, the *N*-acylation peak at ~170 ppm is not observed while the *O*-acylation at 171.46 ppm is again observed (peak "14").

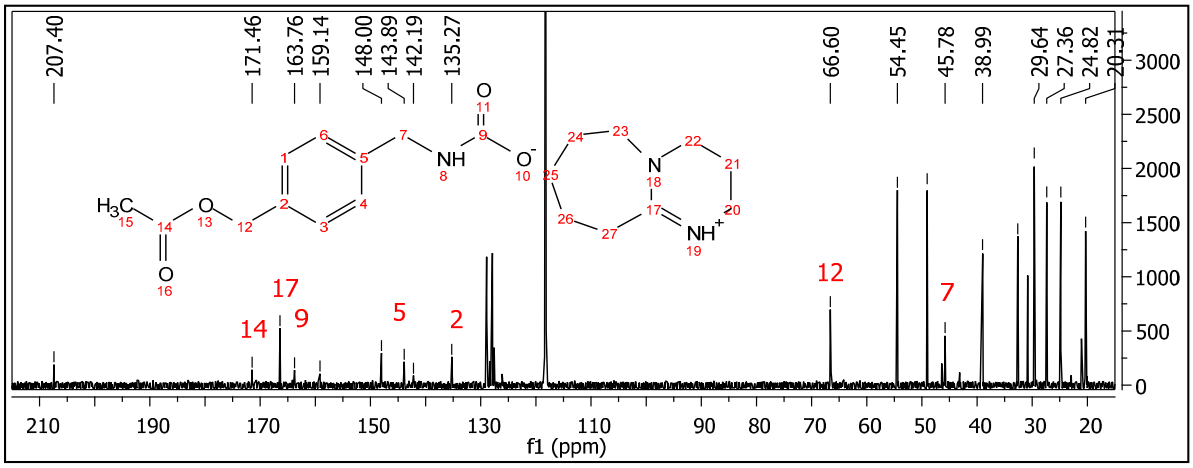

Figure S20. ^{13}C NMR of reaction of CO2-protected 4-(aminomethyl)benzyl alcohol using DBU with isopropenyl acetated in the presence of 1 mol % of 1,2,4-triazole over a reaction time of 24 h.