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SUPPORTING INFORMATION

SO_3H-group anchored Covalent Organic Frame work for the synthesis of hydroxyl-carbamate in a single step utilizing CO_2

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Materials

All chemicals were purchased from commercially available sources and used as received without further purification. Solvents were distilled and dried through standard methods before use.

Characterization Techniques

Fourier-transform infrared spectroscopy was carried out on a Perkin-Elmer FTIR 783 spectrophotometer using KBr pellets. Bruker D8 Advance X-ray diffractometer using Cu-$K_\alpha$radiation (λ = 1.5418 Å) operating at 40 kV and 40 mA was utilized to record powder X-ray diffraction (PXRD) data of samples. Bruker AMX- 400 instrument was operates for ^{1}H NMR spectra. Transmission Electron Microscope (TEM) [JEOL JEM 2100] was used obtain the morphological information of the sample. The N_2 adsorption-desorption analysis of catalyst sample was conducted by using a BET Surface Analyzer [QUANTACHROME ASIQCOV602-5]. X-ray photoelectron spectroscopy was executed by using an Omicron Nanotechnology GmbH XPS machine.

Experimental Section:

Synthesis of TpPa-SO_3H:

The TpPa-SO_3H COF was synthesized by condensation reaction, under solvothermal condition, between 1,3,5-triformylphloroglucinol (Tp) and 2,5-diaminobenzenesulfonic acid (Pa-SO_3H). A 3mL mixture of solution was made by 1,4-dioxane and mesitylene were taken in 1:4 ratio in a round bottom flask, followed by the addition of 1,3,5-triformylphloroglucinol (Tp) (0.3 mmol, 63 mg) and 2,5-diaminobenzenesulfonic acid (Pa-SO_3H) (0.45mmol, 84.6mg). After degassing the whole mixture for 30 min, it was stirred at 120 °C for 3 days in an inert atmosphere (using N_2 gas atmosphere). A red coloured solid was obtained which was collected by filtration and washed with ethanol and tetrahydrofuran for three times, respectively. The obtained red crystallite product was dried at 100 °C for another 24 h to get the as mentioned TpPa-SO_3H (66.7 mg). The amount of yield obtained is 82%.

General Procedure of catalytic synthesis of hydroxyl-carbamate:

In this reaction, epoxide and amine have been taken in a fixed ratio into a round bottom flask. Then, 30 mg of TpPa-SO_3H has been taken as a catalyst and 10 mL chloroform as solvent. The whole mixture has been degassed. Now, the reaction mixture has been refluxed under nitrogen atmosphere at 80 °C for 8 h.

After completion of the reaction, it has been extracted with ethyl acetate and washed for several times. Finally, a N.M.R. spectrum has been done with the obtained product to confirm its structure.

FTIR Spectrum of reused catalyst:

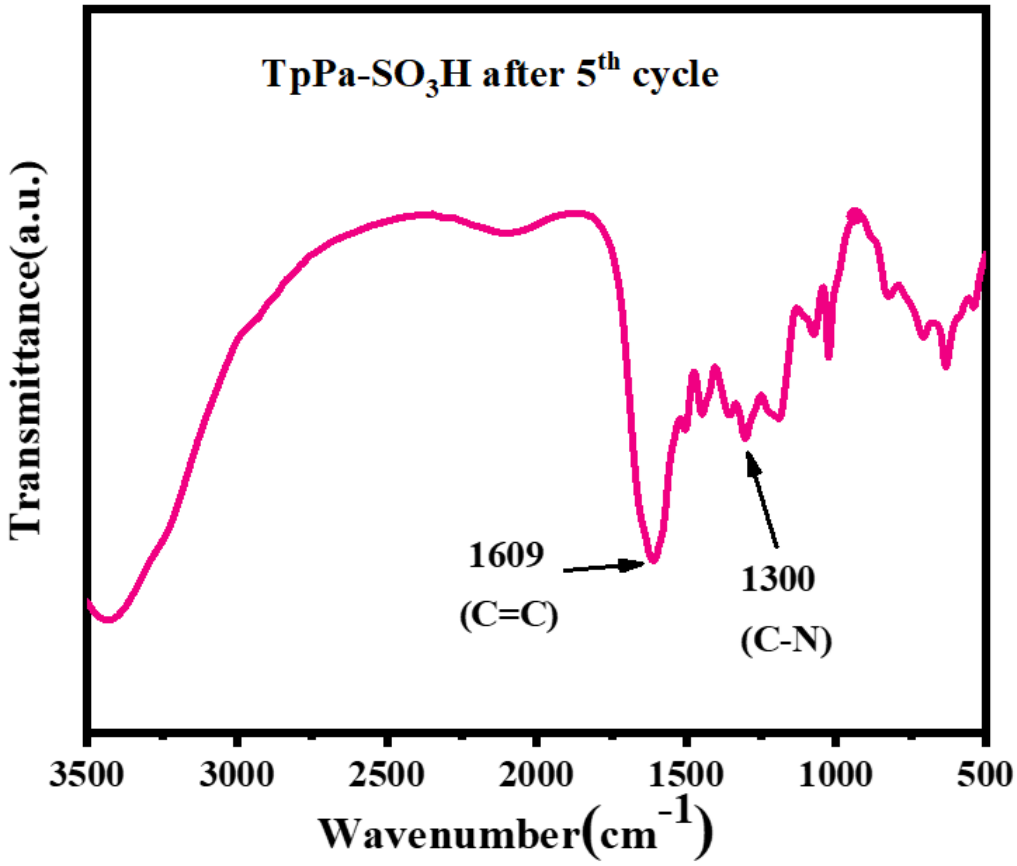

Figure S1. FTIR Spectrum of reused catalyst.

NMR data of N-methylated products

2-hydroxy-3-isopropoxypropyl phenylcarbamate:

(Hydroxyl carbamate formed from Table 5, entry 1)

^{1}H-NMR data:

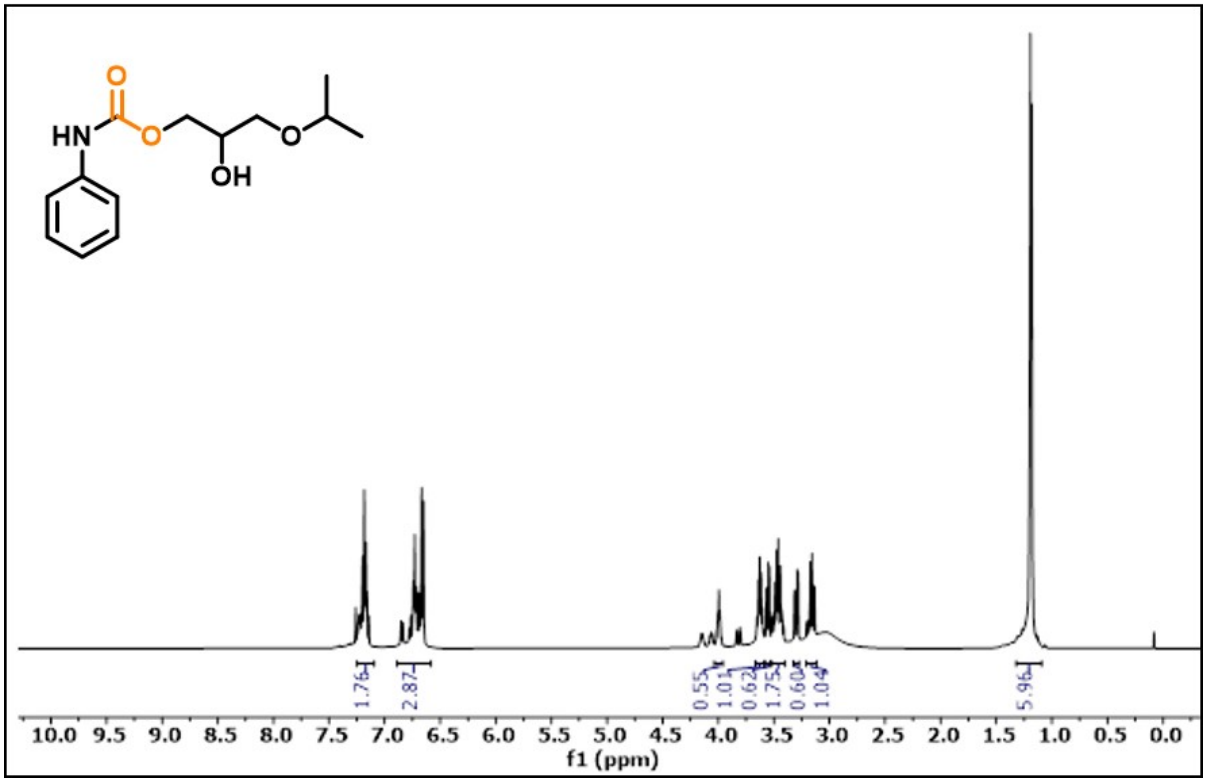

Figure S2. ^{1}H-NMR data of 2-hydroxy-3-isopropoxypropyl phenylcarbamate.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.09 (m, 2H), 6.89 – 6.58 (m, 3H), 4.02 – 3.97 (m, 1H), 3.67 – 3.59 (m, 1H), 3.55 (dd, *J* = 9.4, 3.9 Hz, 1H), 3.47 (dt, *J* = 9.5, 6.9 Hz, 2H), 3.30 (dd, *J* = 12.6, 4.3 Hz, 1H), 3.15 (dd, *J* = 12.8, 7.1 Hz, 1H), 1.19 (dt, *J* = 6.0, 1.8 Hz, 6H).

(Hydroxyl carbamate formed from Table 5, entry 1)

^{13}C NMR spectra:

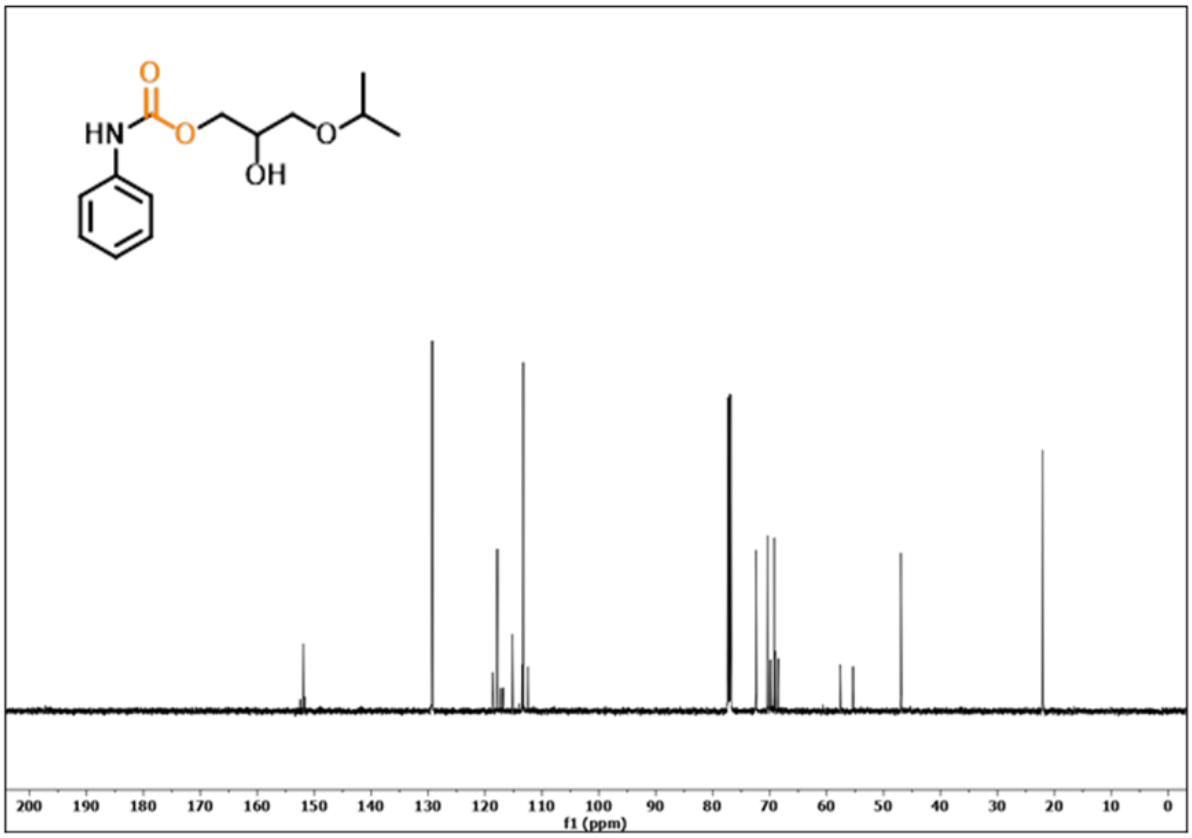

Figure S3. ^{13}C-NMR data of 2-hydroxy-3-isopropoxypropyl phenylcarbamate.

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.25, 129.27, 117.83, 115.20, 113.30, 72.39, 70.36, 69.19, 57.61, 55.35, 46.95, 22.07.

2-hydroxypropyl phenylcarbamate[1]:

(Hydroxyl carbamate formed from Table 5, entry 2)

^{1}H-NMR data:

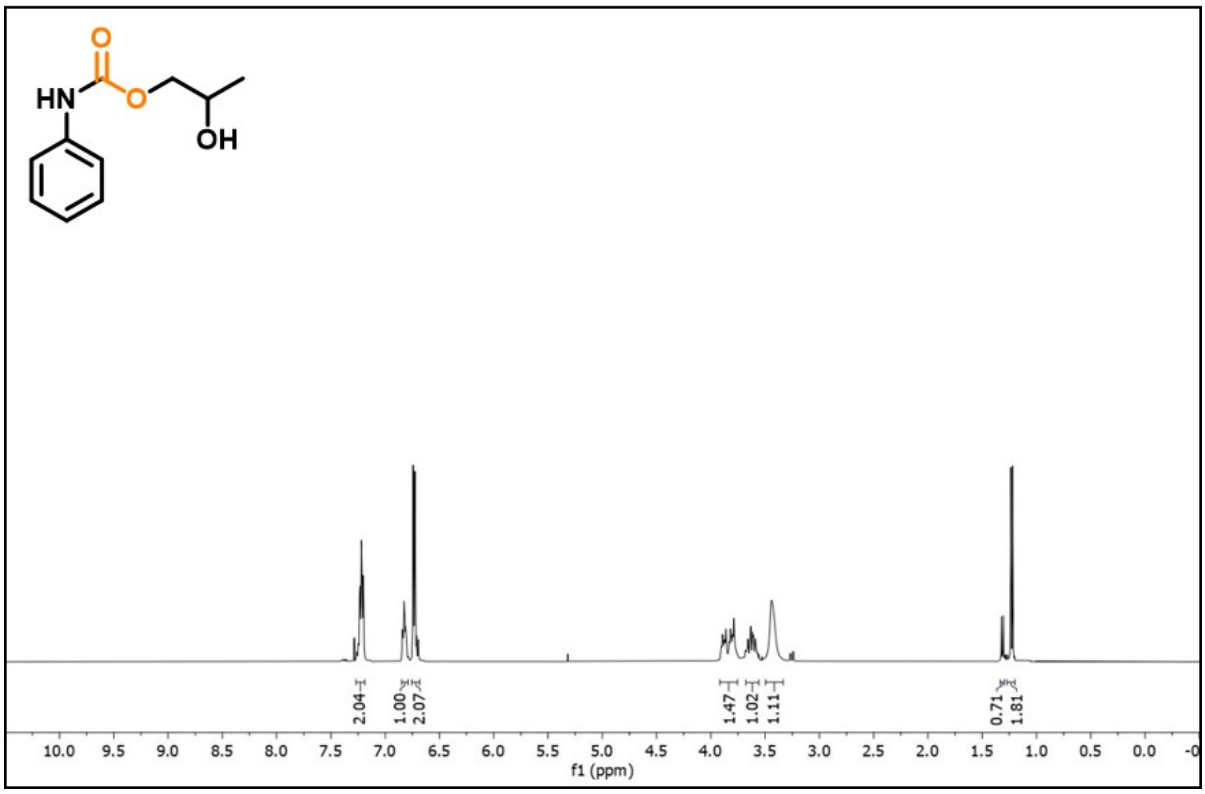

Figure S4. ^{1}H-NMR data of 2-hydroxypropyl phenylcarbamate.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.19 (m, 2H), 6.82 (m, *J* = 7.0, 1H), 6.76 – 6.68 (m, 2H), 3.91-3.75 (m, 2H), 3.70-3.55 (m, 1H), 3.40 (brs, 1H), 1.31 – 1.20 (d, 3H).

2-hydroxycycloheptyl phenylcarbamate:

(Hydroxyl carbamate formed from Table 5, entry 3)

^{1}H-NMR data:

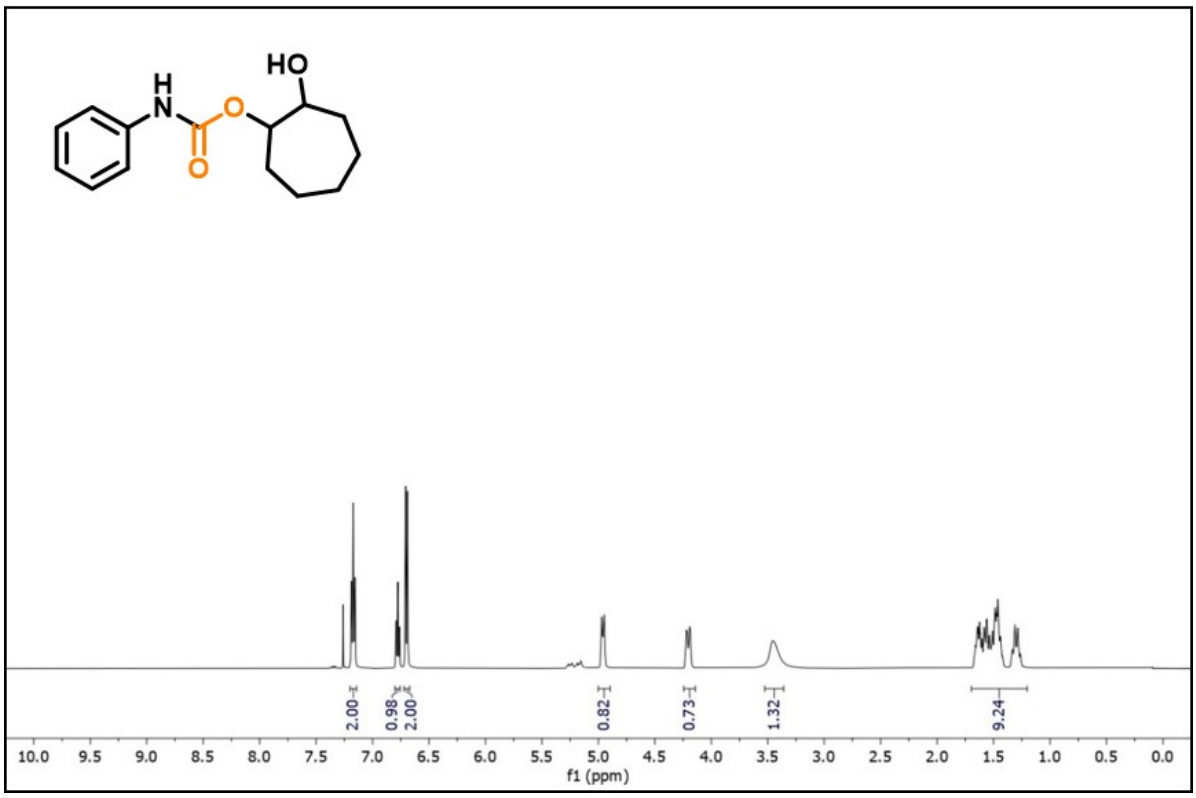

Figure S5.^{1}H-NMR data of 2-hydroxycycloheptyl phenylcarbamate.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (ddt, *J* = 8.6, 6.7, 1.4 Hz, 2H), 6.78 (td, *J* = 7.3, 1.2 Hz, 1H), 6.72 – 6.67 (m, 2H), 4.98-4.94 (d, 1H), 4.22-4.18 (m, 1H), 3.44 (s, 1H), 1.43 – 1.20 (m, 10H).

(Hydroxyl carbamate formed from Table 5, entry 3)

^{13}C NMR spectra:

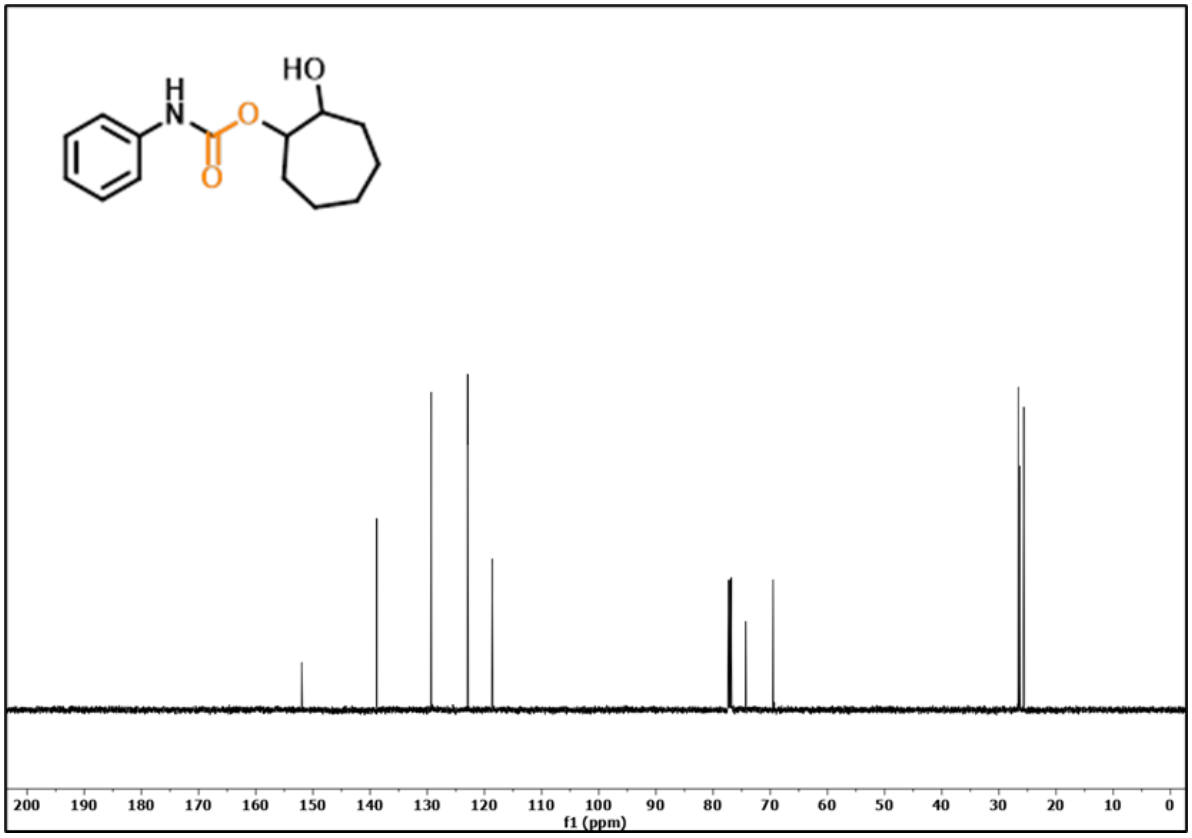

Figure S6. ^{13}C-NMR data of 2-hydroxycycloheptyl phenylcarbamate.

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.79, 139.35, 129.32, 123.11, 118.62, 72.35, 69.83, 26.59, 26.32, 25.62.

2-hydroxy-3-isopropoxypropyl benzylcarbamate:

(Hydroxyl carbamate formed from Table 5, entry 4)

^{1}H-NMR data:

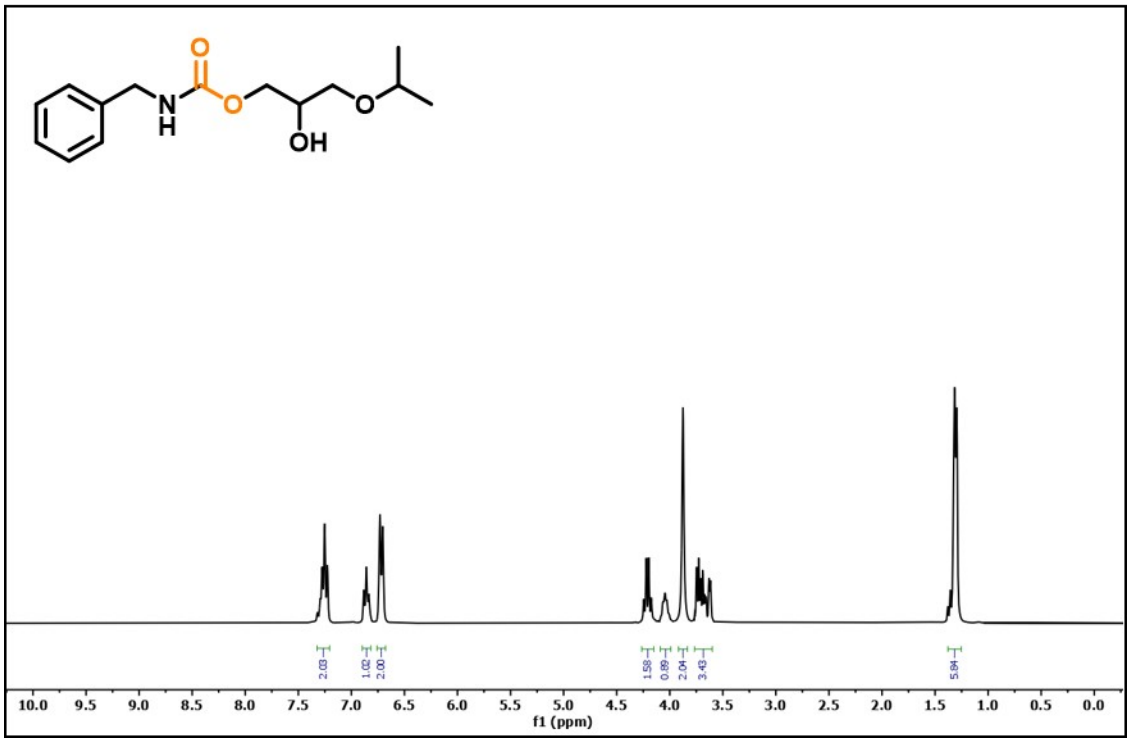

Figure S7.^{1}H-NMR data of 2-hydroxy-3-isopropoxypropyl benzylcarbamate.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (m, 2H), 6.85(m, 1H), 6.70(m, 2H), 4.20 (m, 2H), 4.05 (m, 1H), 3.83(s, 2H), 3.75-3.57(m, 3H) 1.40 – 1.25(m, 6H).

(Hydroxyl carbamate formed from Table 5, entry 4)

^{13}C NMR spectra:

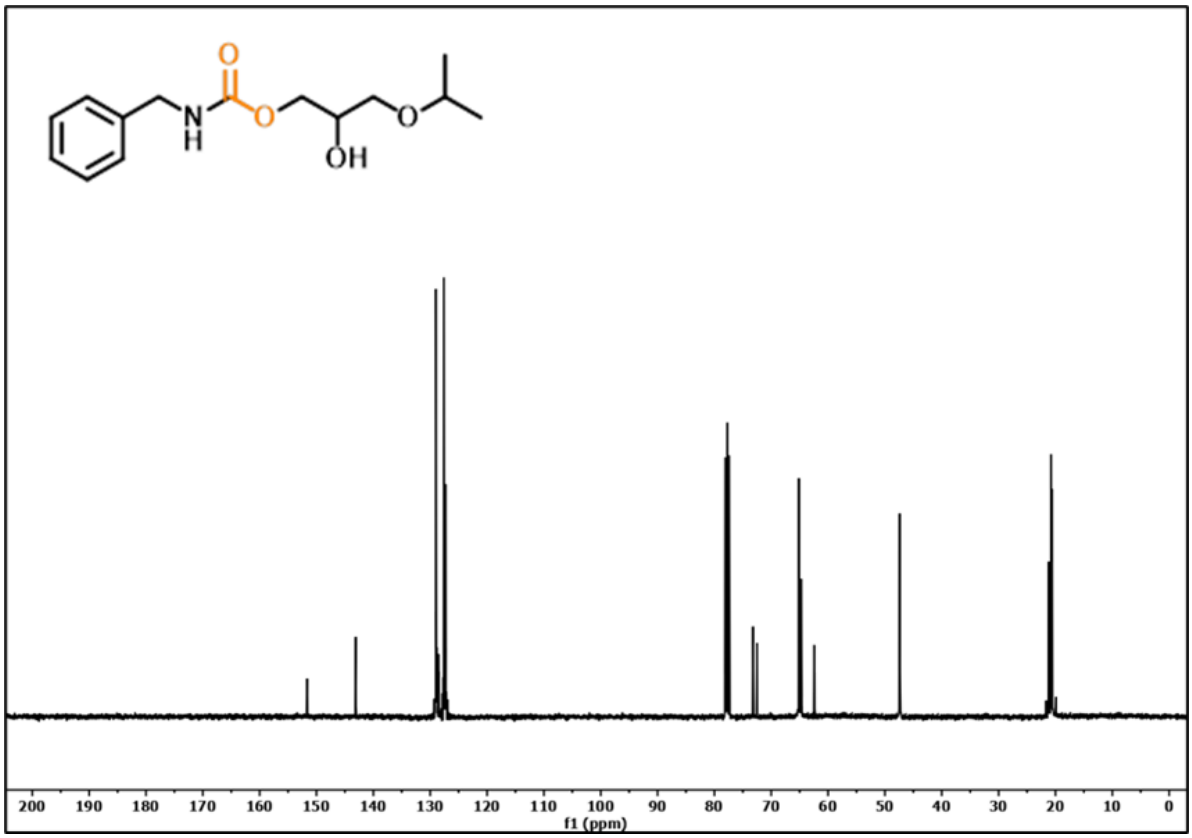

Figure S8. ^{13}C-NMR data of 2-hydroxy-3-isopropoxypropyl benzylcarbamate.

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.18, 143.11, 128.55, 127.12, 126.80, 73.20, 72.50, 65.12, 63.16, 47.12, 20.85.

3-chloro-2-hydroxypropyl benzylcarbamate[2]:

(Hydroxyl carbamate formed from Table 5, entry 5)

[1]H-NMR data:

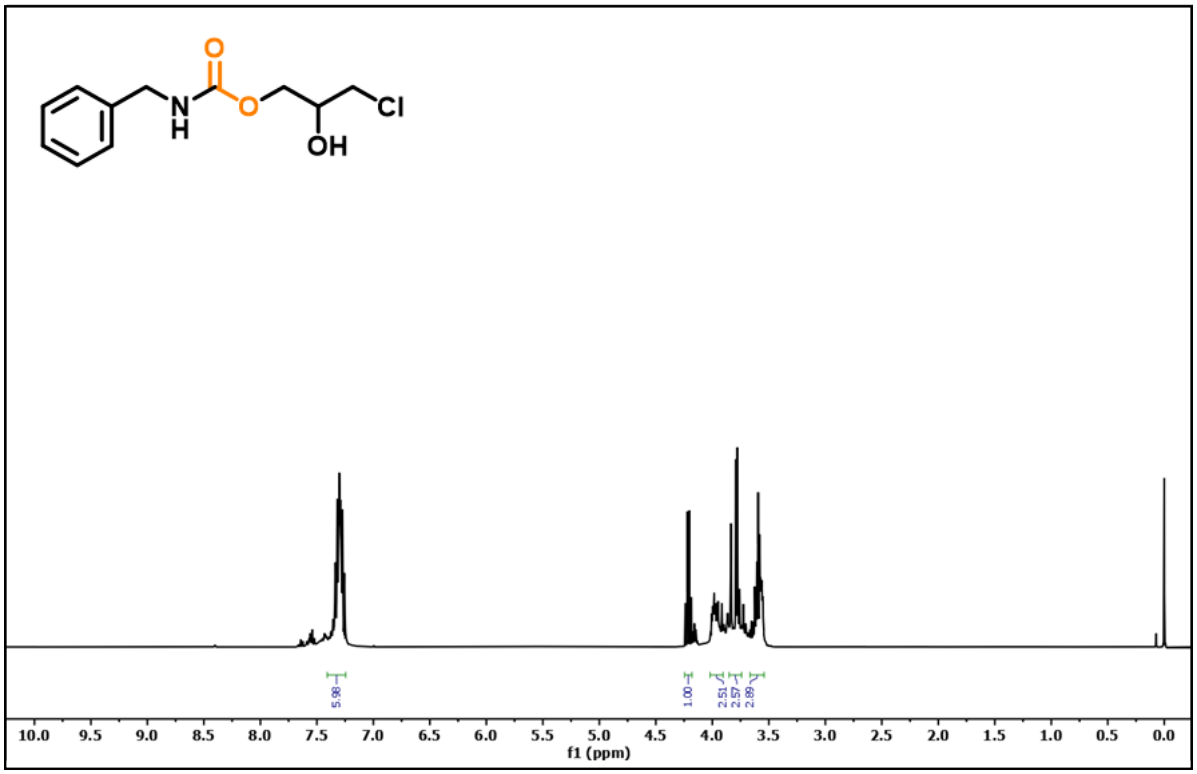

Figure S9.[1]H-NMR data of 3-chloro-2-hydroxypropyl benzylcarbamate.

[1]H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.18 (m, 5H), 4.22 – 4.15 (m, 1H), 3.94 – 3.85 (m, 2H), 3.78 – 3.75 (m, 2H), 3.56 (m, 2H).

2-hydroxypropyl benzylcarbamate[2]:

(Hydroxyl carbamate formed from Table 5, entry 6)

[1]H-NMR data:

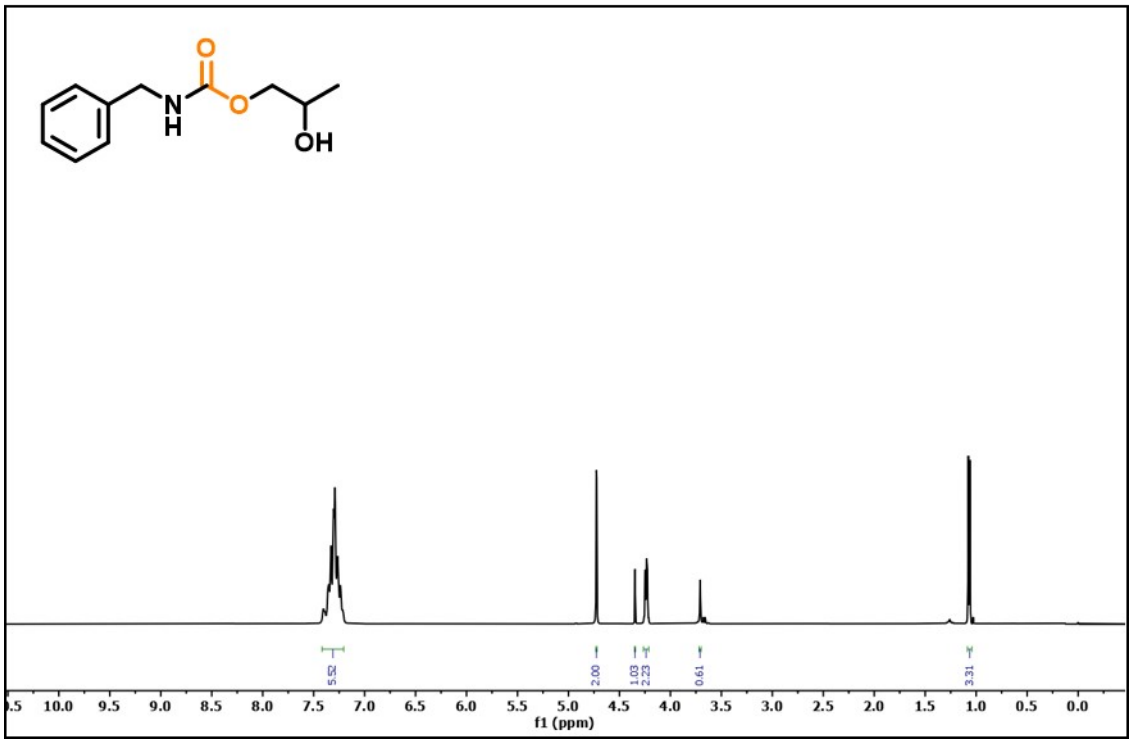

Figure S10.[1]H-NMR data of 2-hydroxypropyl benzylcarbamate.

[1]H NMR (400 MHz, $CDCl_3$): 7.45 – 7.15 (m, 5H), 4.73 (d, *J* = 1.5 Hz, 2H), 4.32-4.29 (m, 1H), 4.27-4.22(m, 2H), 3.71 (s, 1H), 1.06 (d, *J* = 6.2 Hz, 3H).

2-hydroxy-3-isopropoxypropyl diethylcarbamate:

(Hydroxyl carbamate formed from Table 5, entry 7)

^{1}H-NMR data:

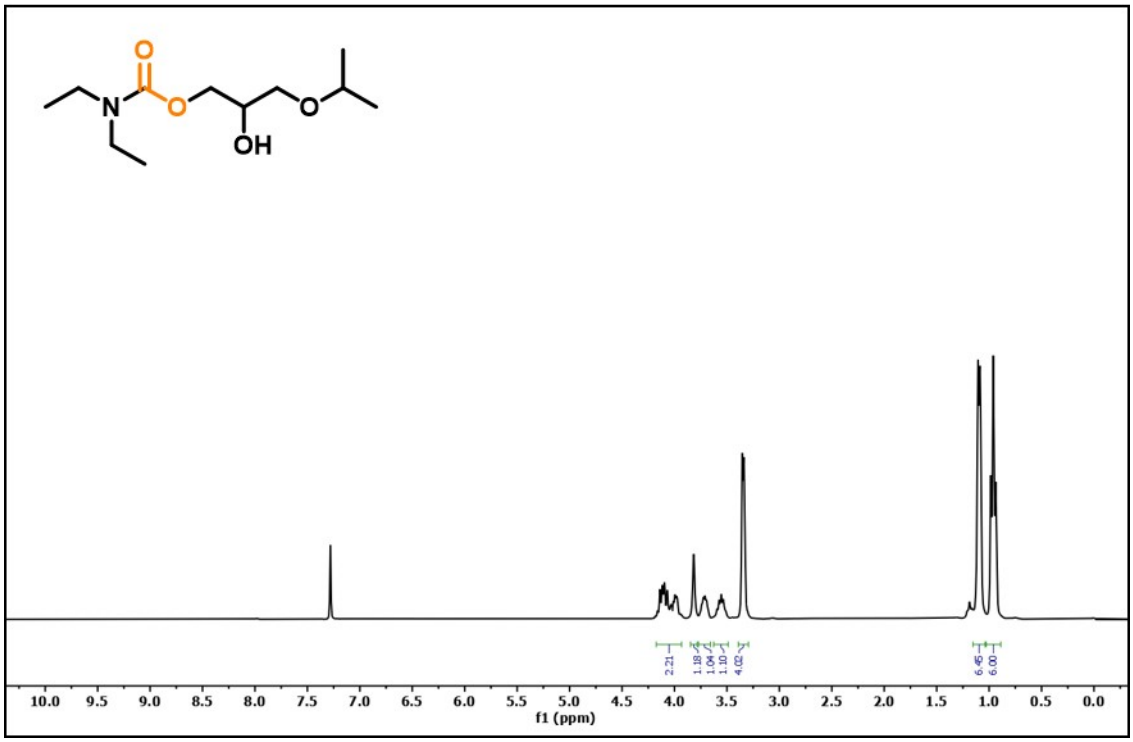

Figure S11. ^{1}H-NMR data of 2-hydroxy-3-isopropoxypropyl diethylcarbamate.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.17 – 3.89(m, 2H), 3.80 (m, 2H), 3.72 (m, 1H), 3.56 (m, 1H), 3.32 (m, 4H), 1.15 – 1.04 (m, 6H), 0.96 (m, 6H).

(Hydroxyl carbamate formed from Table 5, entry 7)

^{13}C NMR spectra:

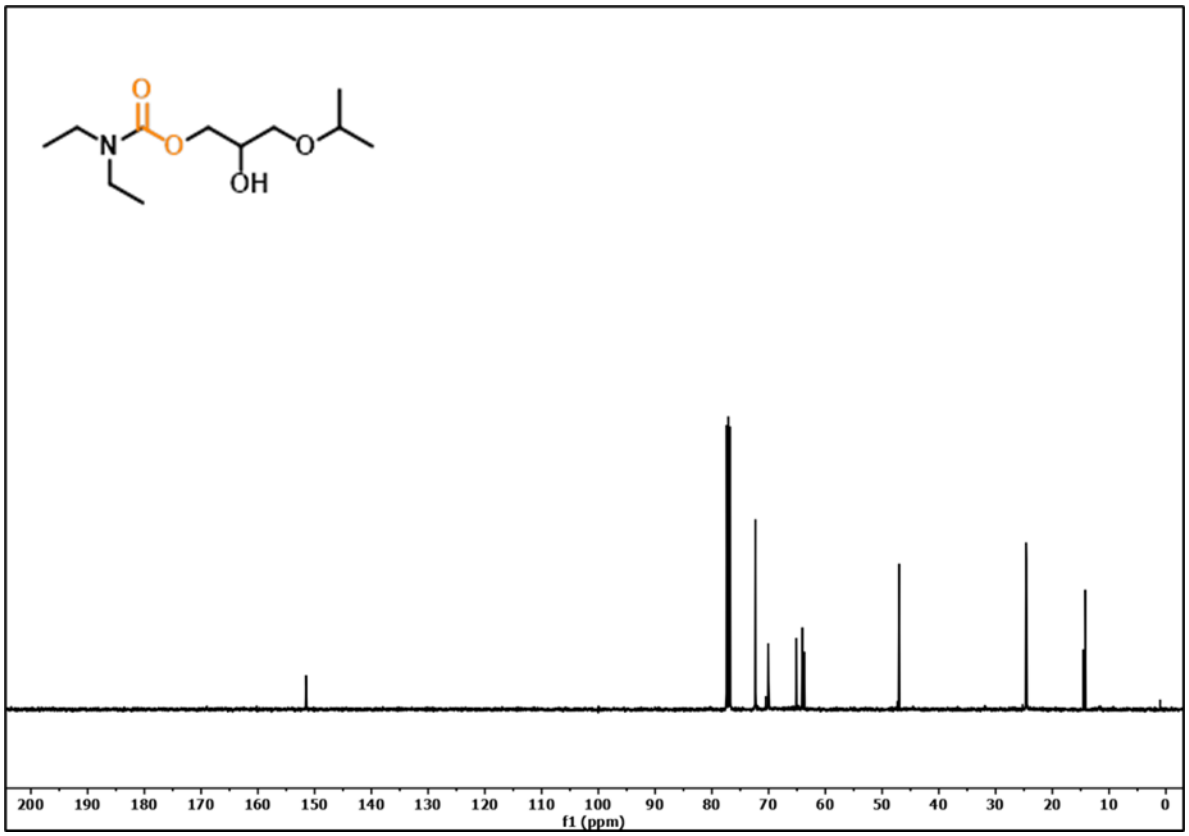

Figure S12. ^{13}C-NMR data of 2-hydroxy-3-isopropoxypropyl diethylcarbamate.

^{13}C NMR (100 MHz, CDCl3): δ 151.81, 72.32, 70.04, 65.04, 63.88, 47.02, 24.62, 14.11.

2-hydroxy-3-isopropoxypropyl dibutylcarbamate:

(Hydroxyl carbamate formed from Table 5, entry 8)

1H-NMR data:

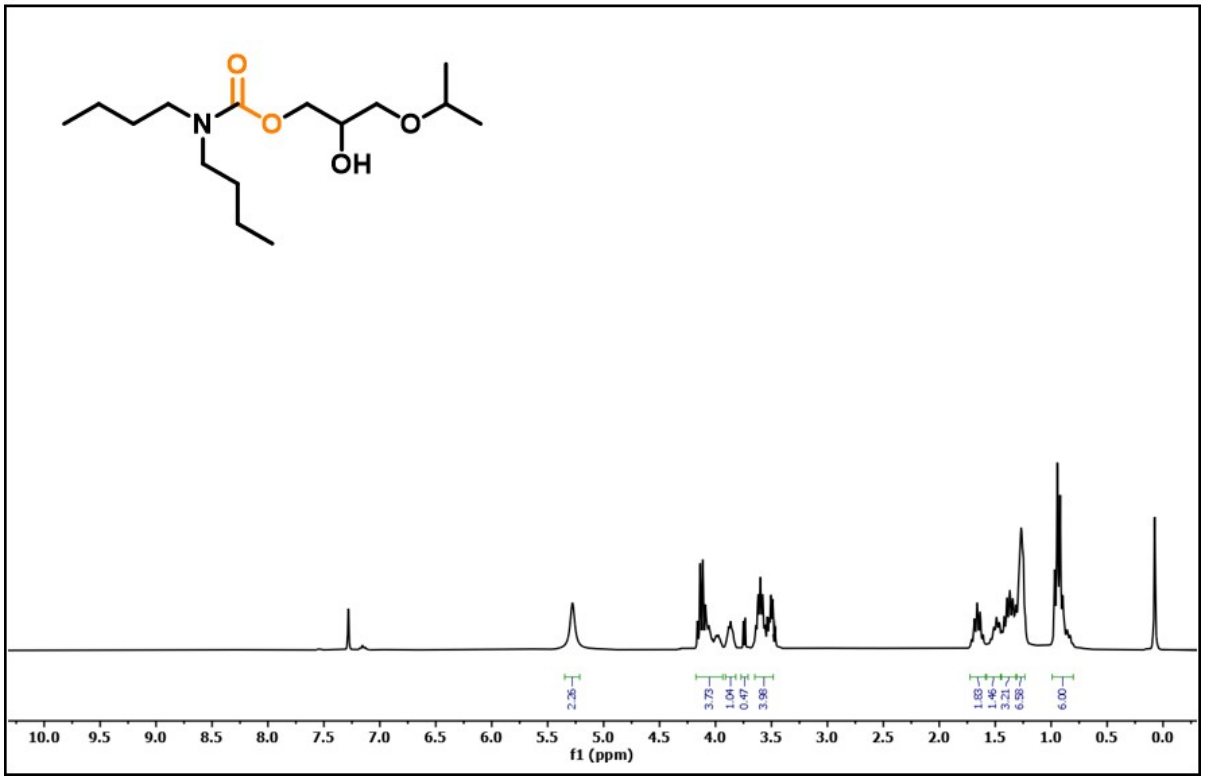

Figure S13. ^{1}H-NMR data of 2-hydroxy-3-isopropoxypropyl dibutylcarbamate.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.26 (s, 1H), 4.15 – 3.91 (m, 4H), 3.85 (m, 1H), 3.75 (m, 1H), 3.60 – 3.47 (m, 4H), 1.70 – 1.40 (m, 4H), 1.42 – 1.24 (m, 10H), 1.00 – 0.80 (m, 6H).

(Hydroxyl carbamate formed from Table 5, entry 8)

^{13}C NMR spectra:

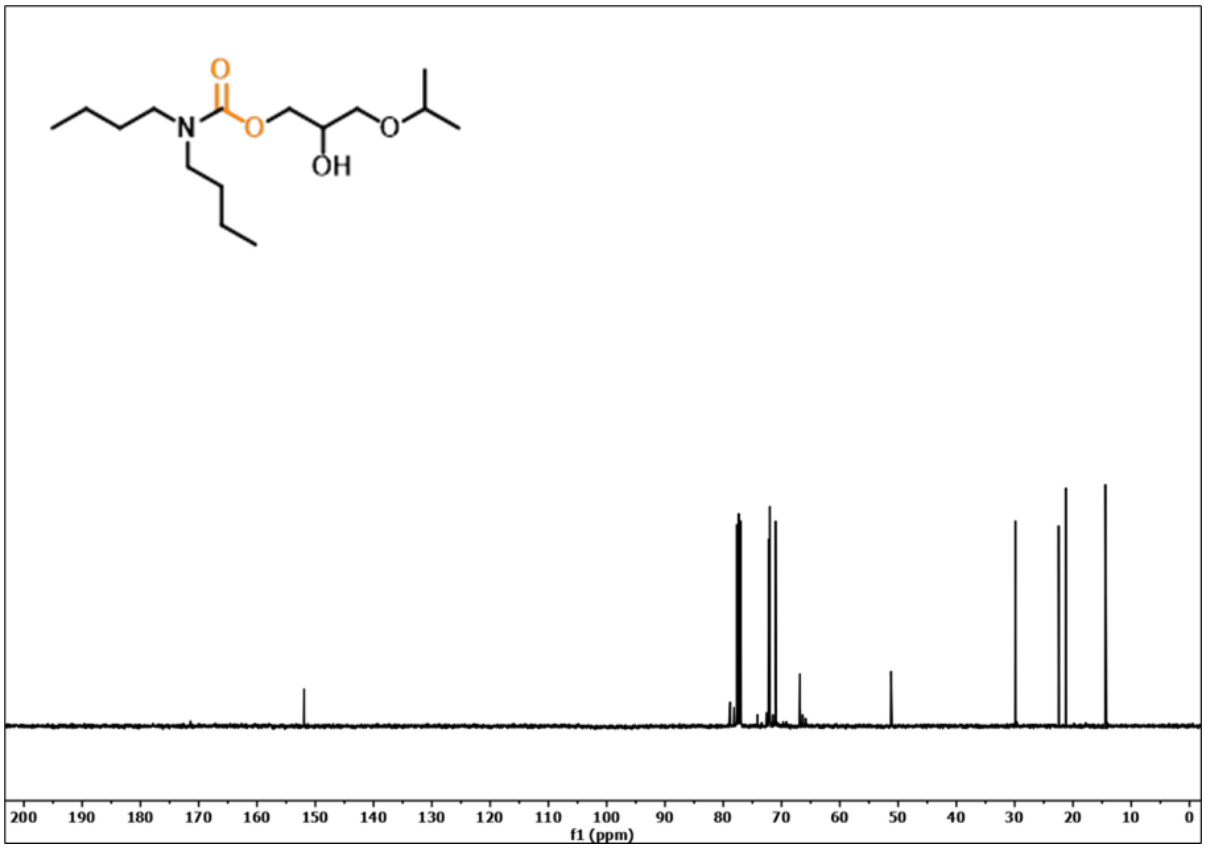

Figure S14. ^{13}C-NMR data of 2-hydroxy-3-isopropoxypropyl dibutylcarbamate.

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.47, 72.09, 71.02, 70.41, 66.85, 51.22, 29.92, 22.76, 21.18, 14.35.

Reference:

(S1) Guo, W.; Gónzalez-Fabra, J.; Bandeira, N. A.; Bo, C.; Kleij, A. W. A metal-free synthesis of N-aryl carbamates under ambient conditions. *Angewandte Chemie* **2015,***127* (40), 11852.

(S2) Shang, J.; Guo, X.; Li, Z.; Deng, Y. CO_2 activation and fixation: highly efficient syntheses of hydroxy carbamates over Au/Fe_2O_3. *Green Chemistry* **2016,***18* (10), 3082.