Electronic Supplementary Material (ESI) for New Journal of Chemistry.


# SUPPORTING INFORMATION

**AgNPs supported over porous organic polymers for the fixation of $CO_2$ on propargyl alcohols and amines under solvent free conditions**

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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***

A D8 Advance SWAX diffractometer from Bruker-AXS utilizing a constant current (40 mA) and voltage (40 kV) was used to obtain the powder XRD pattern of the AgNPs@TzTa-POP catalyst. The XRD machine was calibrated with silicon sample utilizing Ni-filtered Cu $K_{\alpha}$ radiation ($\lambda$=0.15406 nm). On a Perkin–Elmer FTIR 783 spectrophotometer the Fourier transform infrared (FTIR) spectra of the catalysts were recorded from 400 to 4000 $cm^{-1}$ using KBr pellets. Scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility was used to measure surface morphology of the AgNPs@TzTa-POP. BET surface area and porosity of these materials were estimated from the respective $N_2$ sorption isotherms at 77 K by using a Quantachrome Instruments Autosorb-1C surface area analyzer. The samples were activated at 403 K under high vacuum for 12 h before the $N_2$ adsorption−desorption analysis. TEM images were recorded using FEI Tecnai G2 F20 X-TWIN TEM at an accelerating voltage of 200 kV. HR-TEM, 5 mg of the AgNPs@TzTa-POP catalyst was dispersed into absolute EtOH under the application of sonication for 30 min, followed by the sample coating on a carbon coated copper TEM grid and dried in air. All spectra were taken at 400 MHz for $^1H$ NMR. Using Bruker DPX-400 in $CDCl_3$ instrument with TMS as internal standard the products was confirmed by $^1H$ spectroscopy.

***Characterisations***

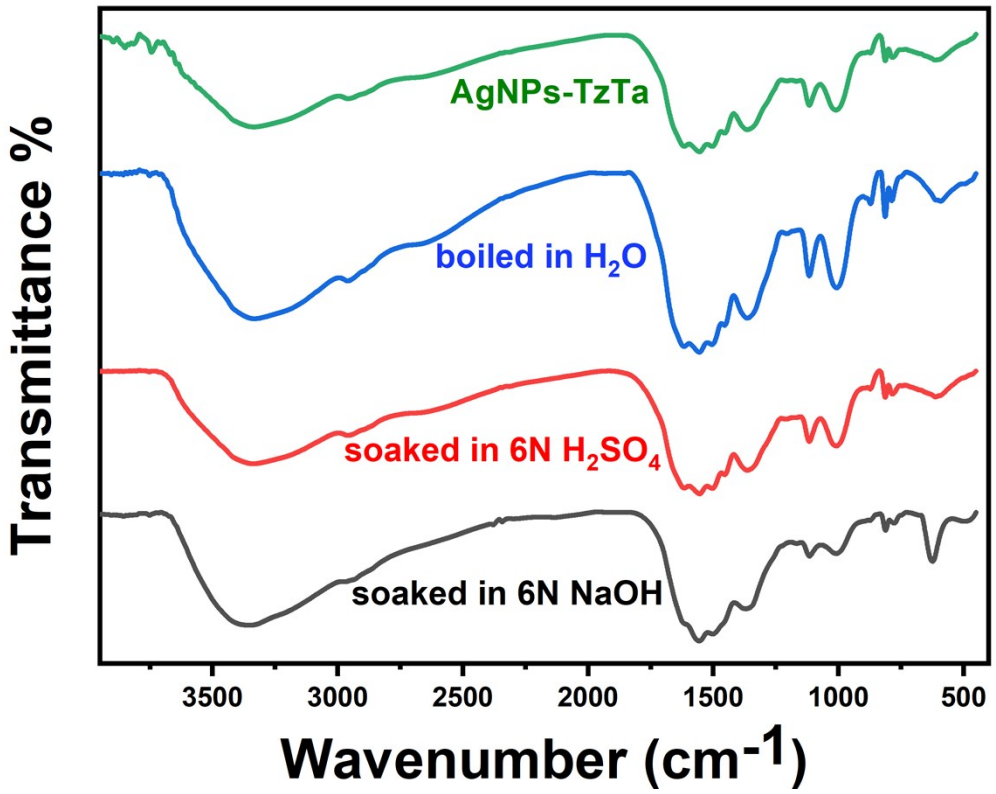


**Fig. S1: IR of catalyst under different medium**

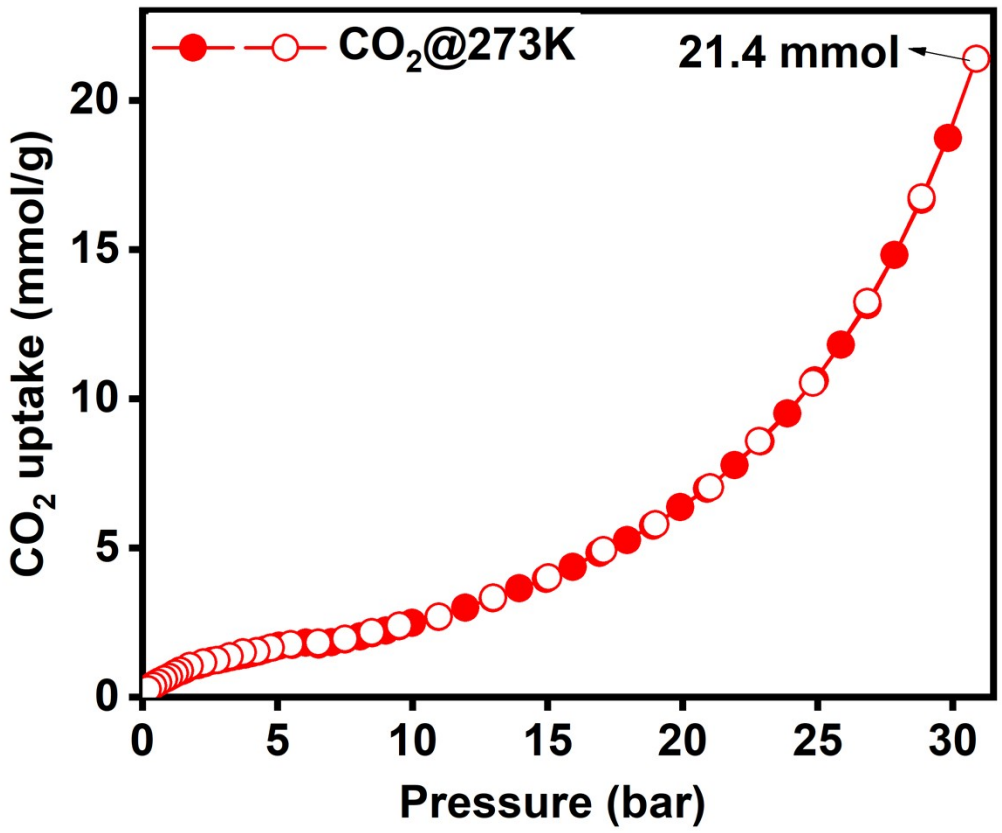


**Fig. S2:** $CO_2$ adsorption-desorption profile of AgNPs@TzTa-POP.

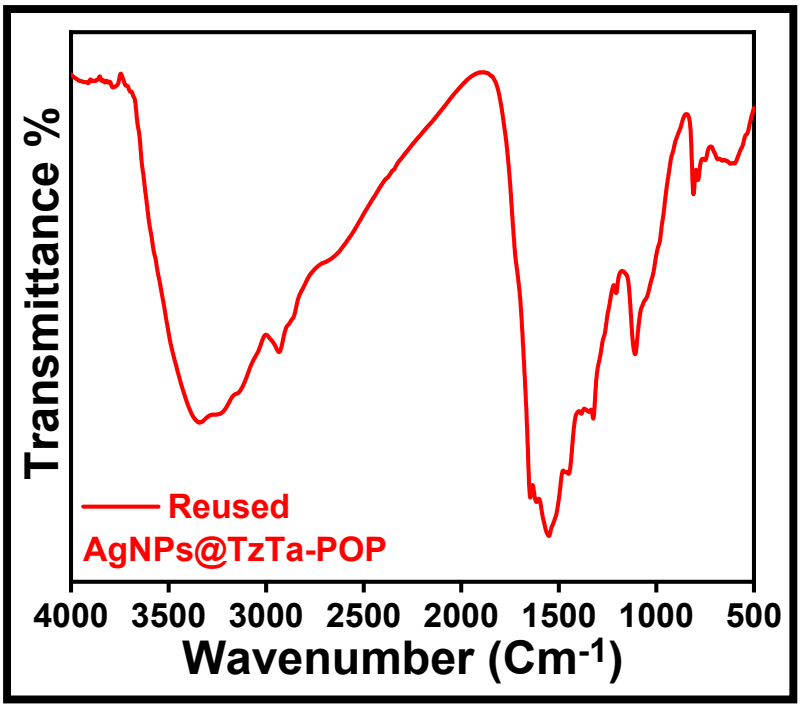


**Fig. S3 :** IR of reused catalyst AgNPs@TzTa-POP.

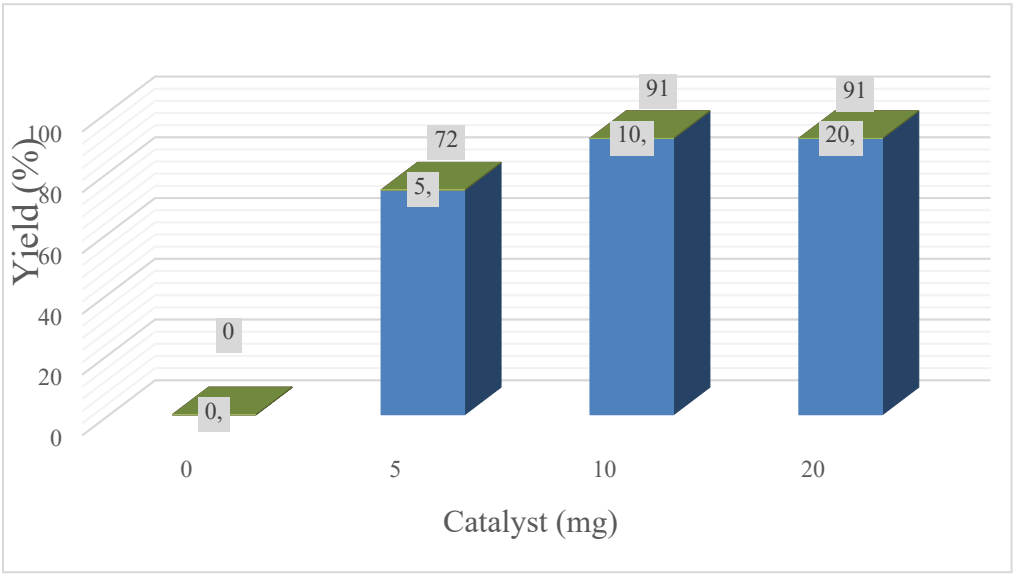


**Fig. S4:** Variation of catalyst loading on the carbamates formation reaction (reaction conditions: benzylamine (6 mmol), iodopropane (6 mmol), $Cs_2CO_3$ (1.5 eq.), $CO_2$ balloon, RT, 8h) (Edit the figure: write Catalyst (mg) in X-axis and place the Yield (%) in Y-axis properly).

***SEM of reused catalyst AgNPs@TzTa-POP***

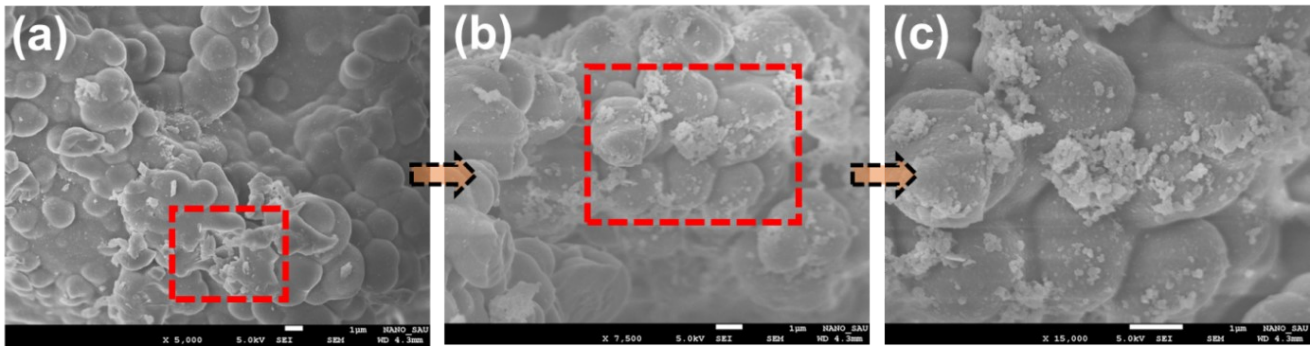


**Fig S5 :** SEM of reused catalyst AgNPs@TzTa-POP.

**Characterizations data of respective *α*-alkylidene cyclic carbonates.[1]**

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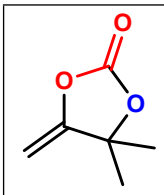
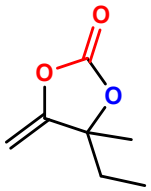
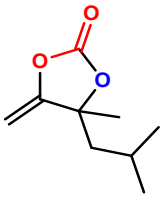
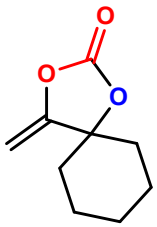
|  2a | **[4,4-dimethyl-5-methylene-1,3-dioxolan-2-one]**: $^1$H NMR (400 MHz, $CDCl_3$): *δ* (in ppm) 1.184 (s, 6H), 4.366 (d, *J* = 5.6 Hz, 1H), 4.663 (d, *J* = 5.6 Hz, 1H). |
|  2c | **[4-ethyl-4-methyl-5-methylene-1,3-dioxolan-2-one]**: $^1$H NMR (400 MHz, $CDCl_3$): *δ* (in ppm) 1.183 (t, *J* = 4.0, 3H), 1.476 (s, 3H), 1.678-1.712 (m, 2H), 4.297 (d, *J* = 4.0 Hz, 1H), 4.608 (d, *J* = 4.0 Hz, 1H). |
|  2d | **[4-isobutyl-4-methyl-5-methylene-1,3-dioxolan-2-one]:** $^1$H NMR (400 MHz, CDCl3): *δ* (in ppm) 0.913-0.963 (m, 6H), 1.536 (s, 3H), 1.754-1.780 (m, 1H), 1.836-1.874 (m, 2H), 4.347 (d, *J* = 4.8 Hz, 1H), 4.683 (d, *J* = 4.8 Hz, 1H). |
|  2e | **[4-methylene-1,3-dioxaspiro[4.5]decan-2-one]:**$^1$H NMR (400 MHz, CDCl3): *δ* (in ppm) 1.183-1.956 (m, 10H), 4.213 (d, *J*= 3.6Hz, 1H), 4.689 (d, *J*= 4.0 Hz, 1H). |

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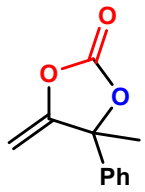
|  2f | **[4-methyl-5-methylene-4-phenyl-1,3-dioxolan-2-one]:** $^1$H NMR (400 MHz, CDCl3): $\delta$ (in ppm)1.936 (s, 3H), 4.391 (d, *J*= 3.6Hz,1H), 4.878 (d, *J*= 3.6Hz, 1H), 7.183 (d, *J*=8.0 Hz, 1H), 7.435-7.458 (m, 2H), 7.812 (d, *J* = 8.0 Hz, 2H). |

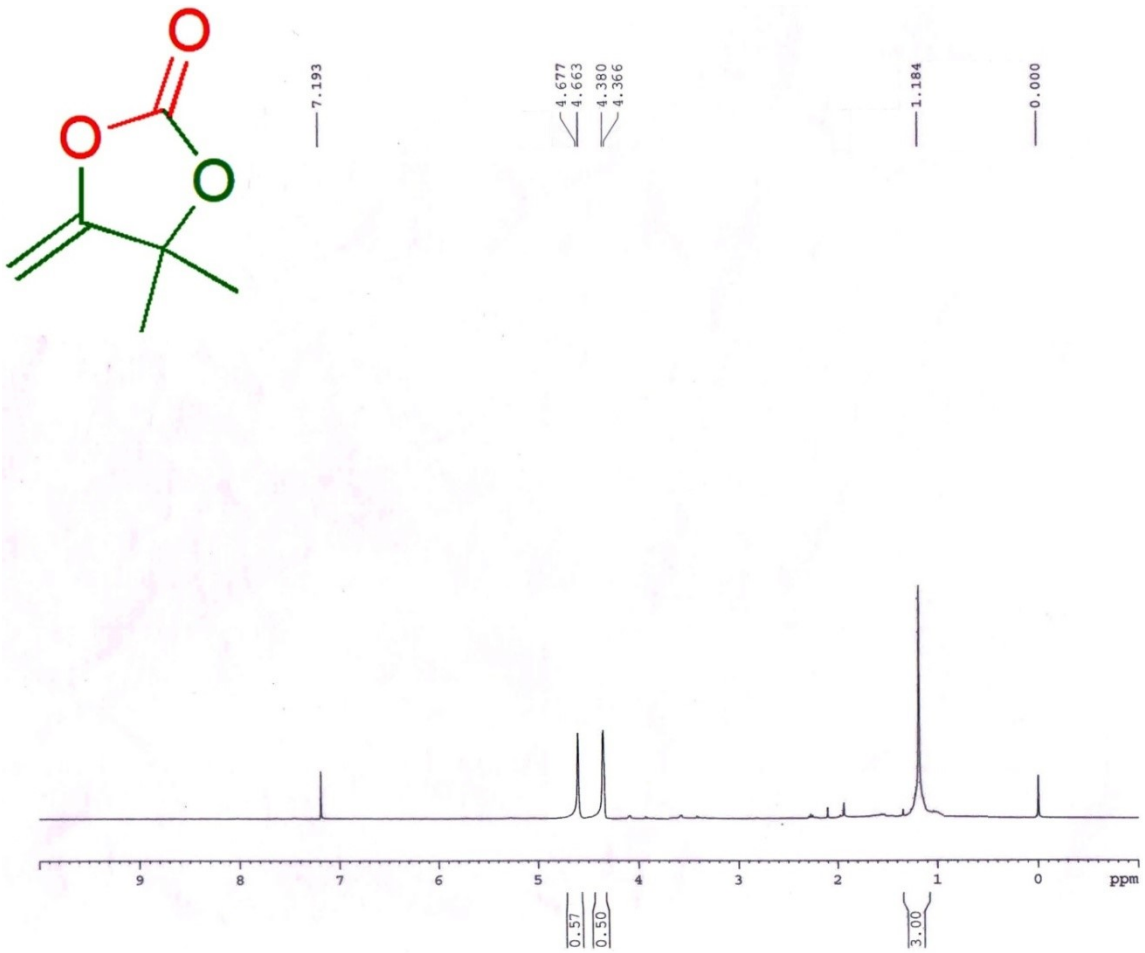



**Fig S6:** $^1$H NMR of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one.

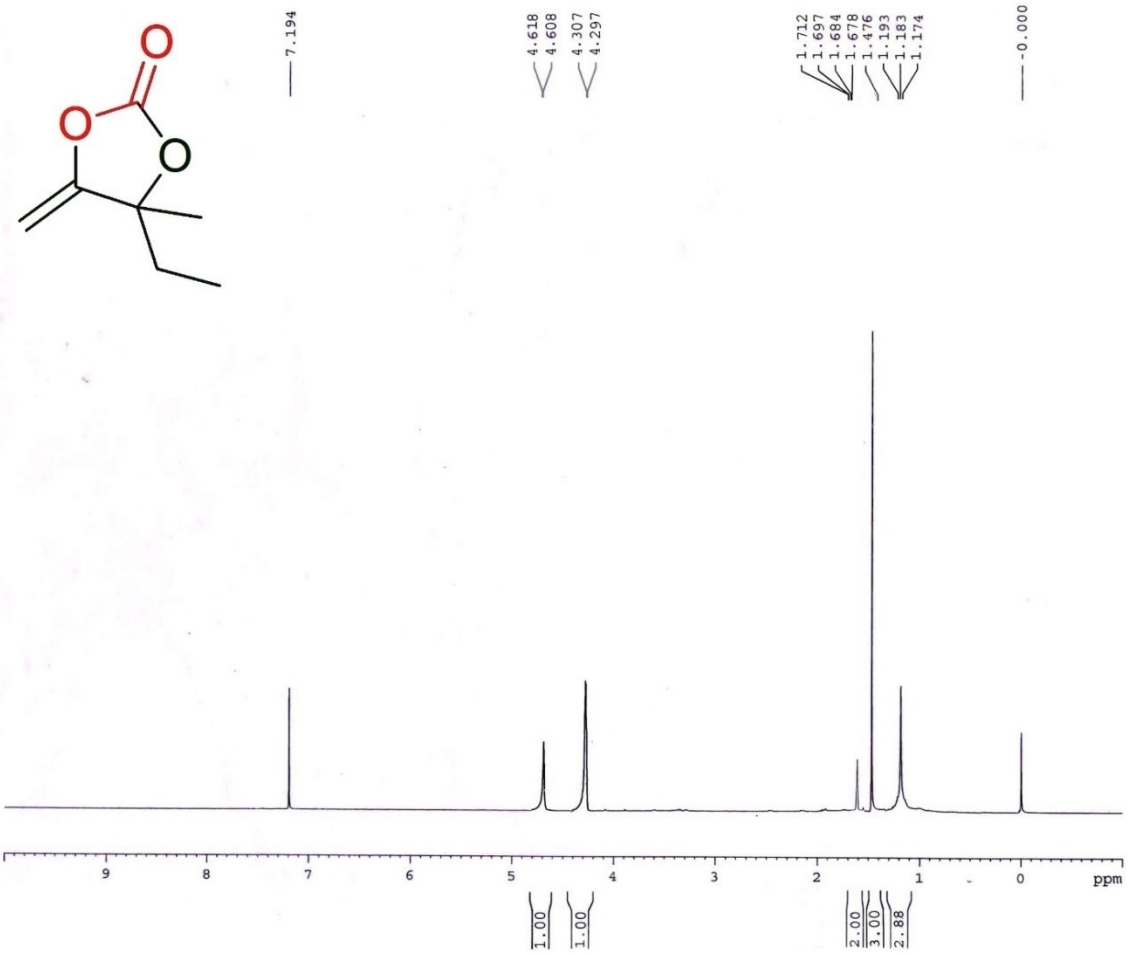



**Fig S7:** $^{1}$H NMR of 4-ethyl-4-methyl-5-methylene-1,3-dioxolan-2-one.

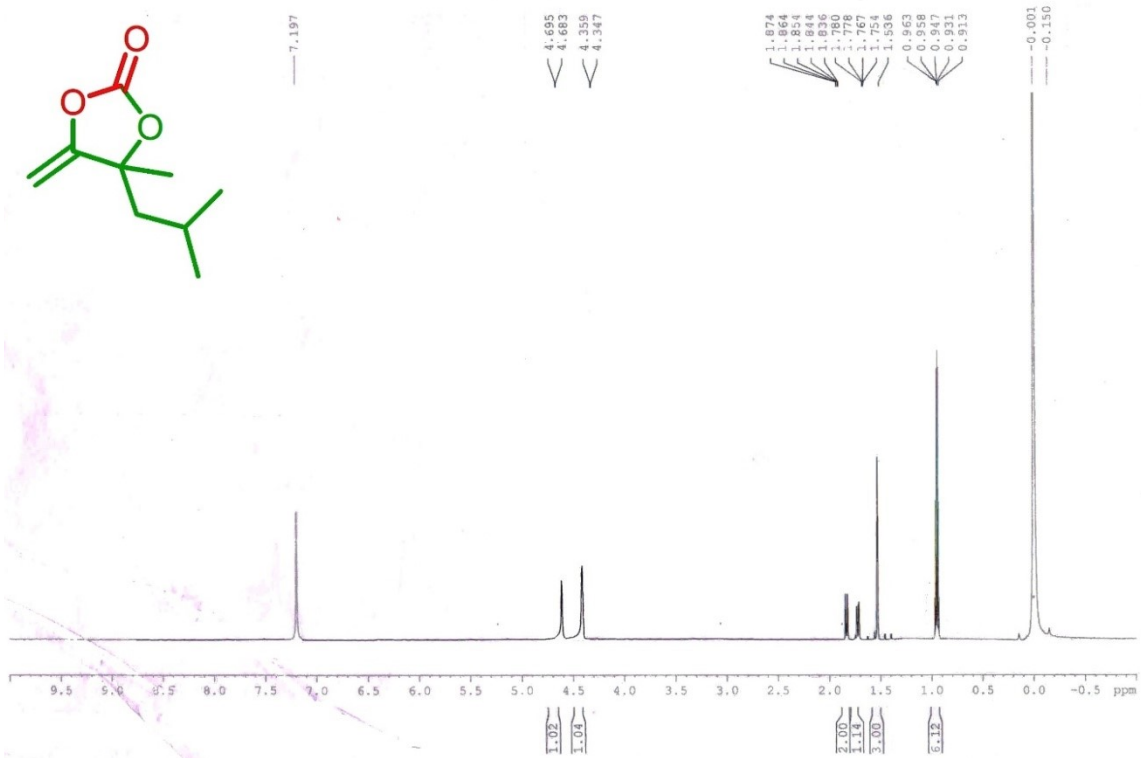


**Figure S8:** $^{1}$H NMR of 4-ethyl-4-methyl-5-methylene-1,3-dioxolan-2-one.

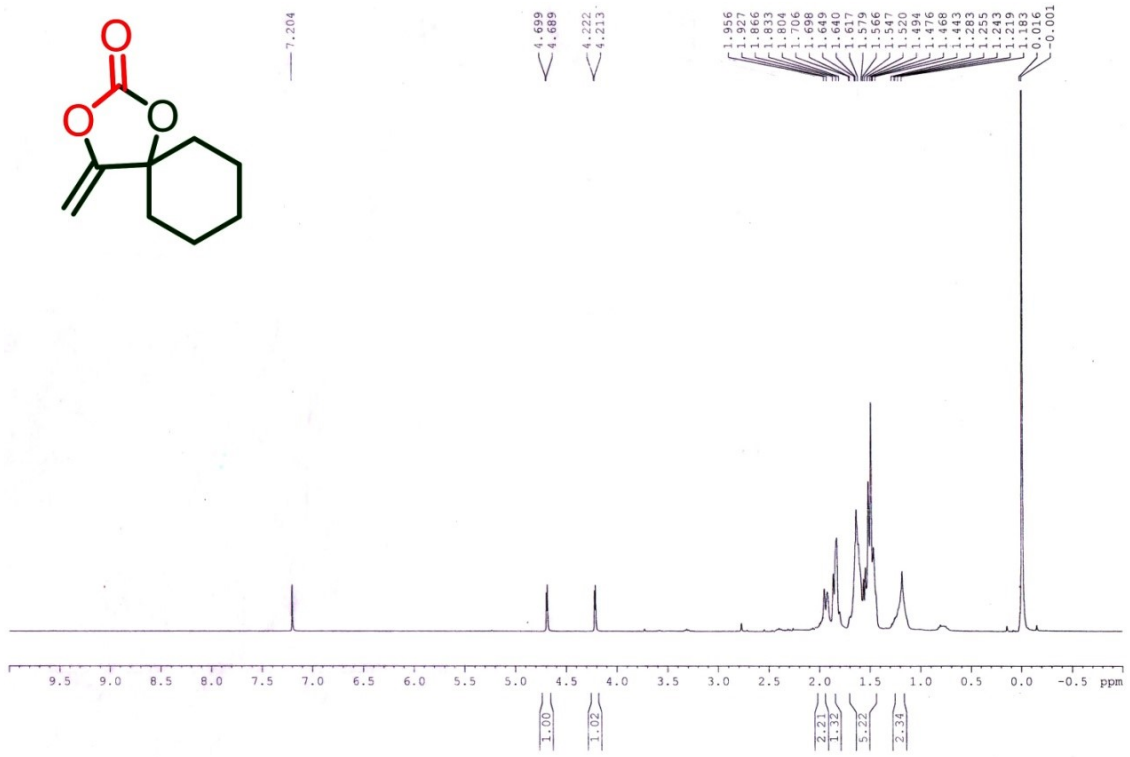


**Fig S9:** $^{1}$H NMR of 4-methylene-1,3-dioxaspiro[4.5]decan-2-one.

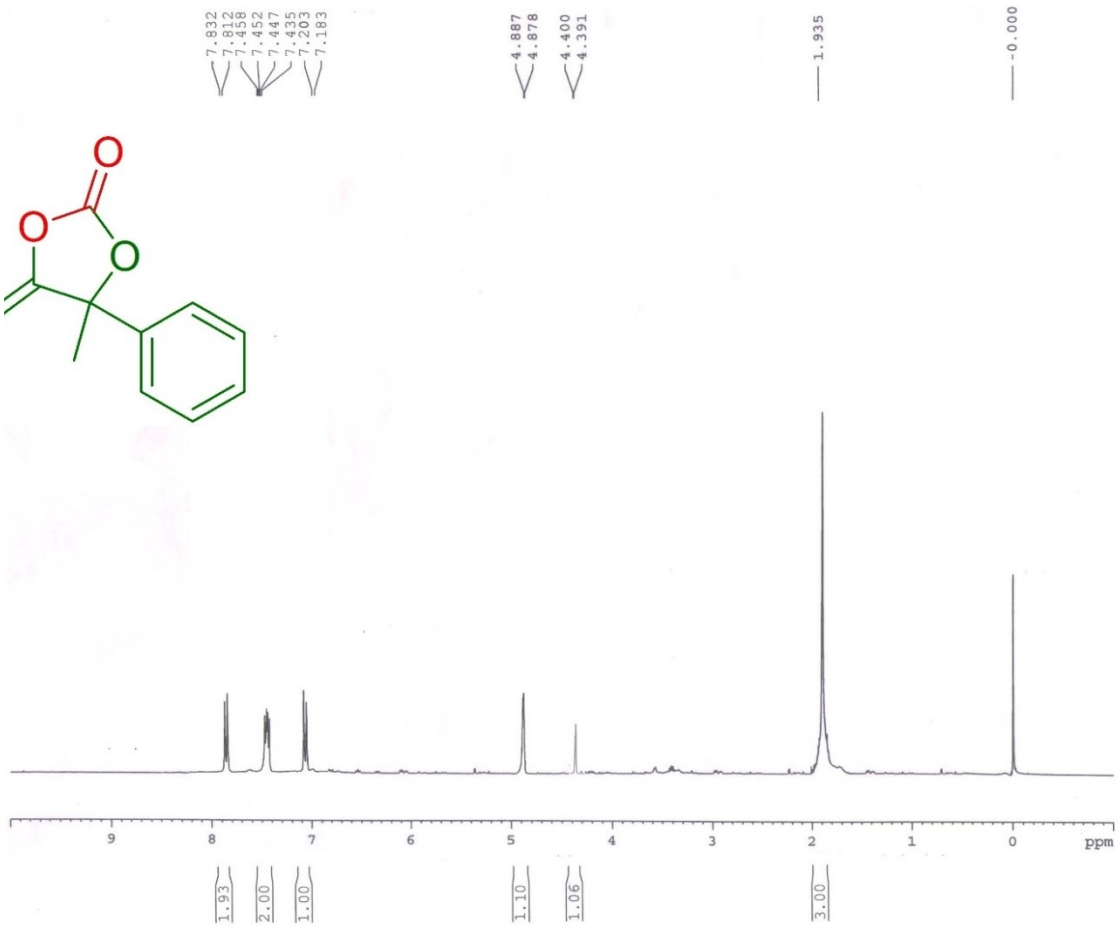



**Fig S10:** $^{1}$H NMR of 4-methyl-5-methylene-4-phenyl-1,3-dioxolan-2-one.

**Characterizations data of respective isolatedcarbamatesfrom amines, halides and $CO_2$.[2]**

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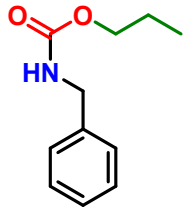
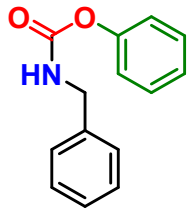
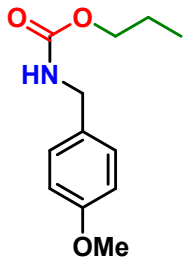
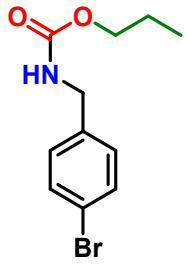
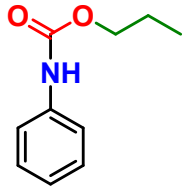
|  5a | **Benzyl-carbamic acid propyl ester**:$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm)1.541 (t, *J*= 6.8Hz, 3H), 3.101 (s, 2H), 3.997-4.030 (m, 2H), 4.306 (t,*J*=6.8Hz,2H), 5.938 (s, 1H), 7.268-7.382 (m, 2H), 7.640-7.690 (m, 1H), 7.778-7.802 (m,2H). |
|  5b | **Benzyl-carbamic acid phenyl ester:**$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm)4.291 (d, *J*= 6.0 Hz, 2H), 4.938 (s, 1H), 6.501-6.616 (m, 6H), 7.062-7.135 (m, 4H). |
|  5c | **Propyl (4-methoxybenzyl) carbamate**: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 1.388 (t, *J*= 6.8 Hz, 3H), 2.44-2.269 (m, 2H), 2.900 (t, *J*= 6.8 Hz, 2H), 3.561 (s, 3H), 4.104 (s, 2H), 4.669 (s, 1H), 7.229 (t, *J*= 7.6Hz, 2H), 7.761 (t, *J*= 7.6 Hz, 2H). |
|  5d | **Propyl (4-bromobenzyl)carbamate:**$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm)1.522 (t, *J*= 7.2Hz, 3H), 3.004 (t,*J*=7.2Hz, 2H), 3.156 (t,*J*= 7.6Hz,2H), 4.178 (s, 2H), 4.813 (s, 1H), 6.524-6.562 (m, 2H), 7.096-7.134 (m, 2H). |
|  5e | **Phenyl-carbamic acid propyl ester**: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm)0.904 (t, *J*= 6.8Hz, 3H), 1.587-1.659 (m, 2H), 4.048 (t, *J*= 6.8Hz, 2H), 7.156-7.248 (m, 4H), 7.920 (s, 1H). |

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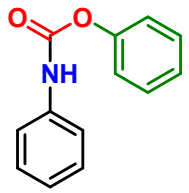
|  5f | **Phenyl phenylcarbamate**: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm)4.613 (s, 1H), 6.732-6.821 (m, 3H), 7.085-7.167 (m, 3H), 7.596 (d, *J*= 8.8Hz, 2H), 8.183 (s, 2H). |

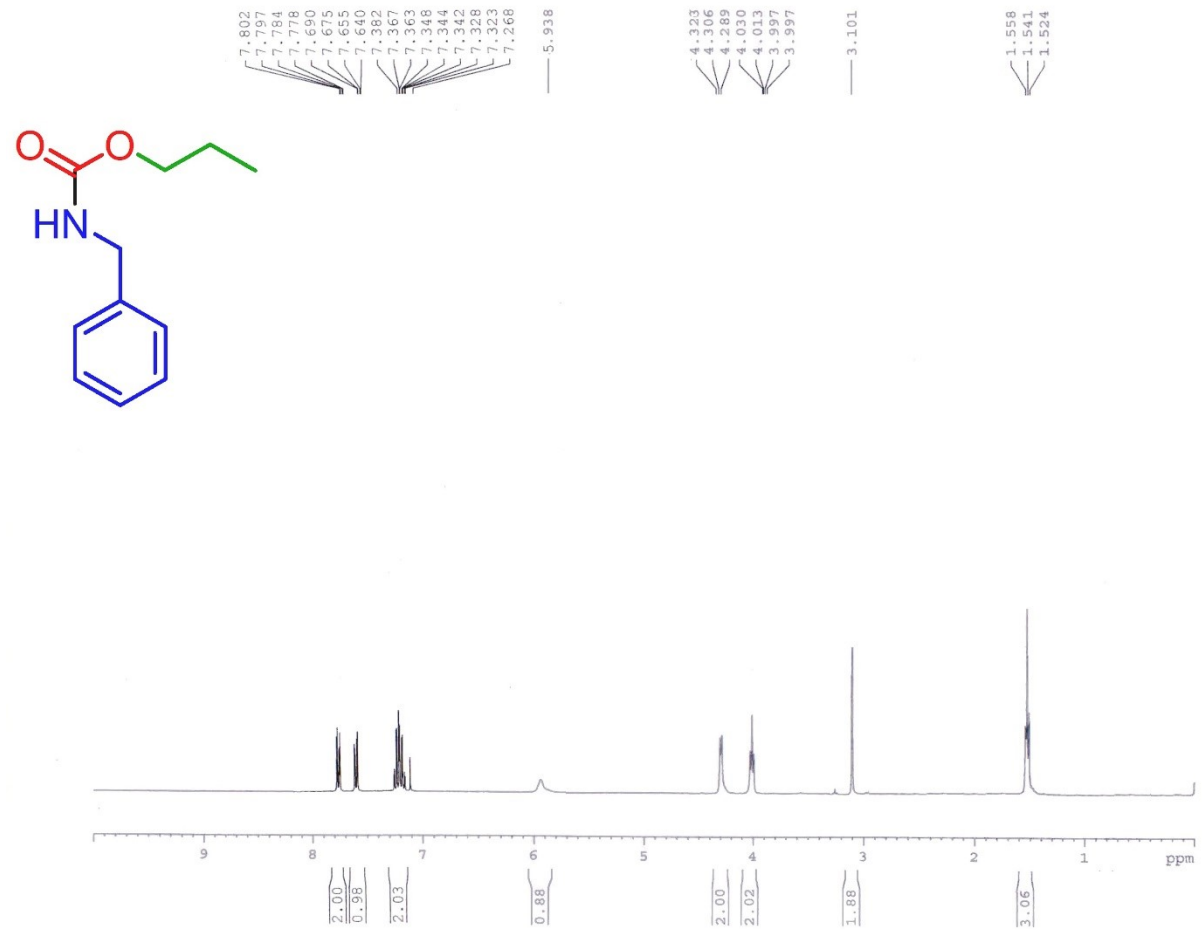



**Fig S11:** $^1$H NMR of Benzyl-carbamic acid propyl ester.

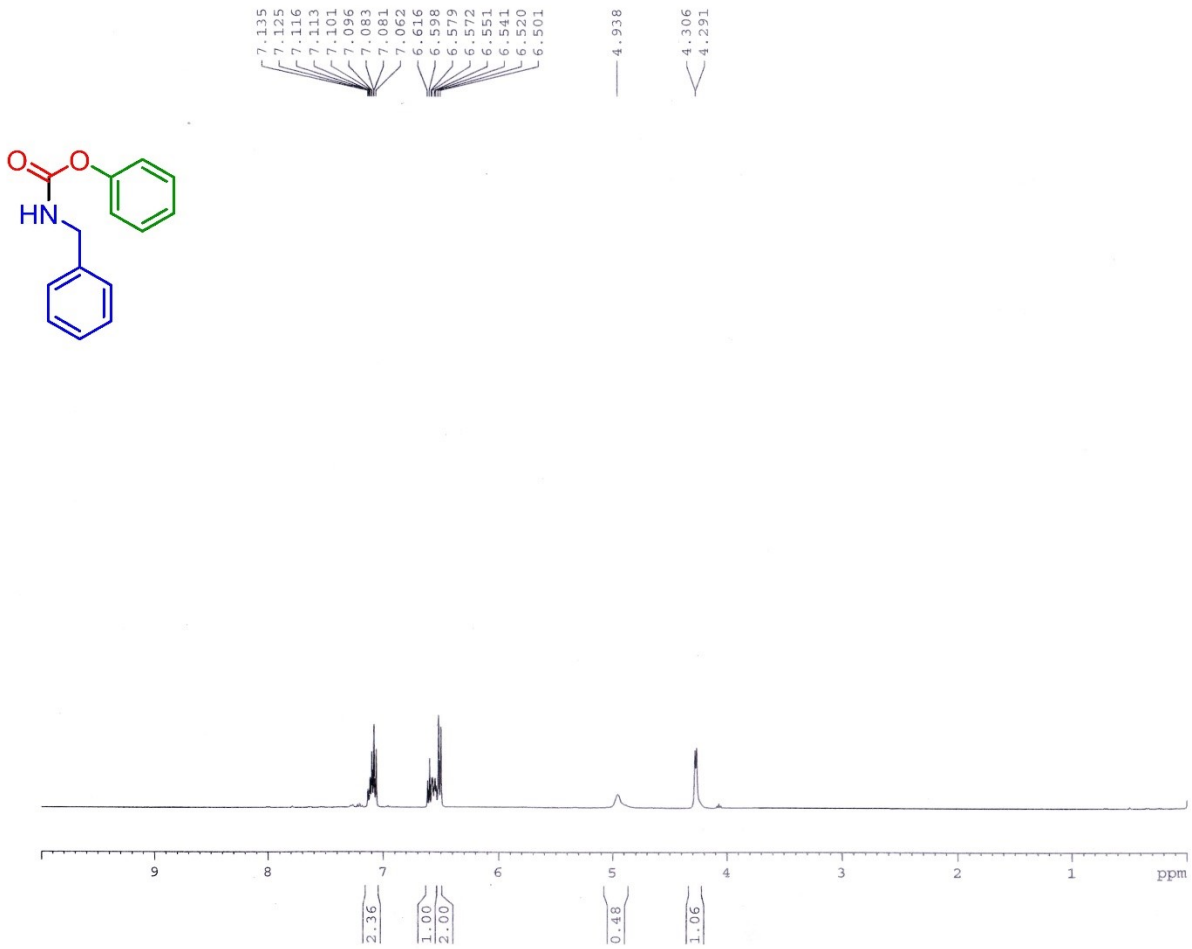



**Fig S12:** $^{1}$H NMR of Benzyl-carbamic acid phenyl ester.

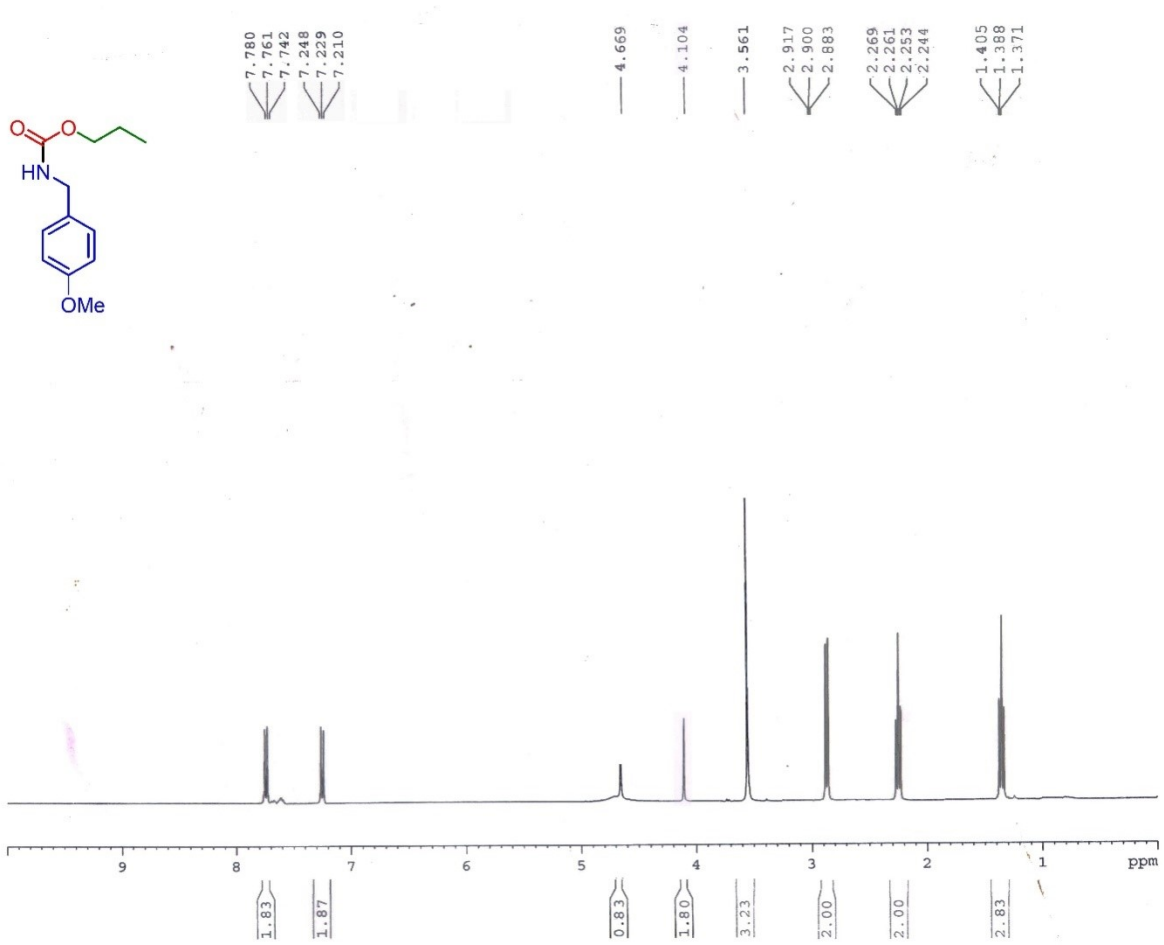



**Fig S13:** $^{1}$H NMR of Propyl (4-methoxybenzyl) carbamate.

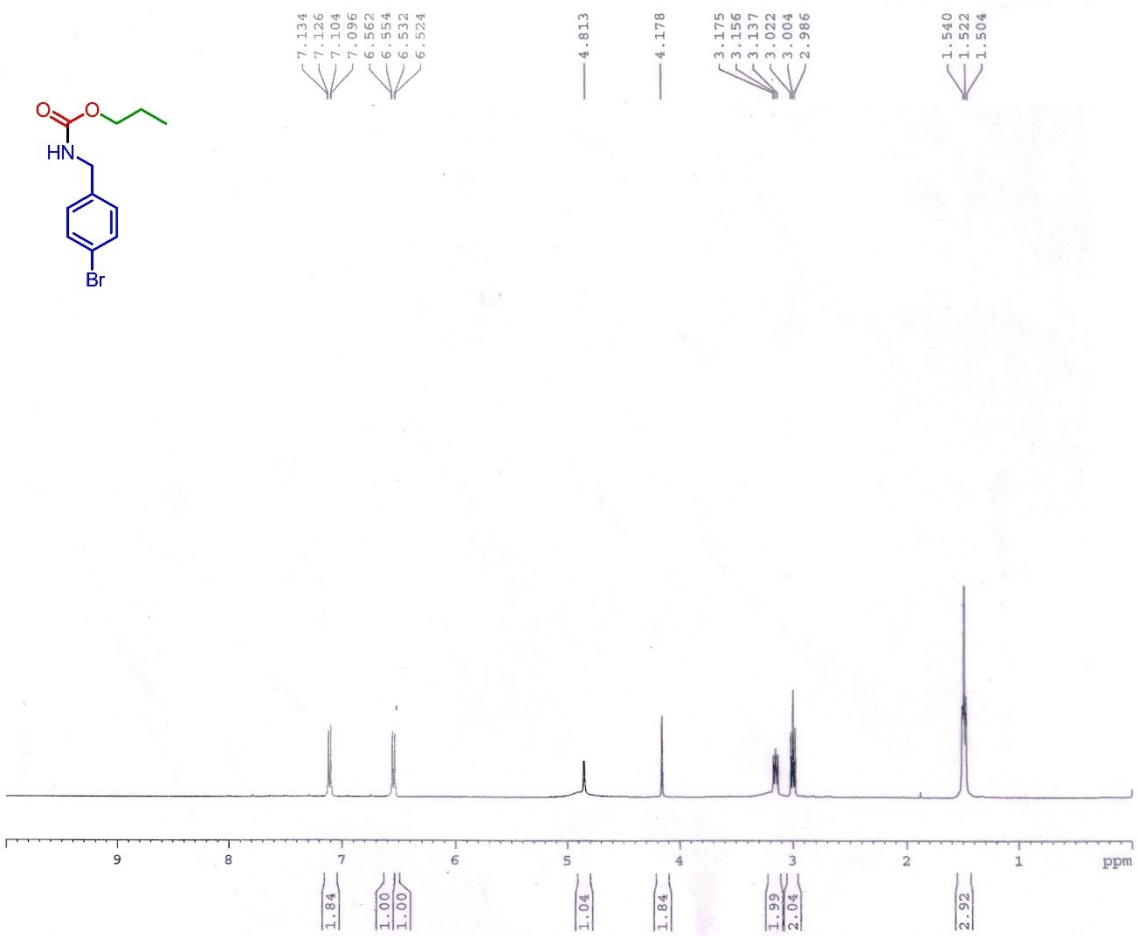



**Fig S14:** $^{1}$H NMR of Propyl (4-bromobenzyl) carbamate.

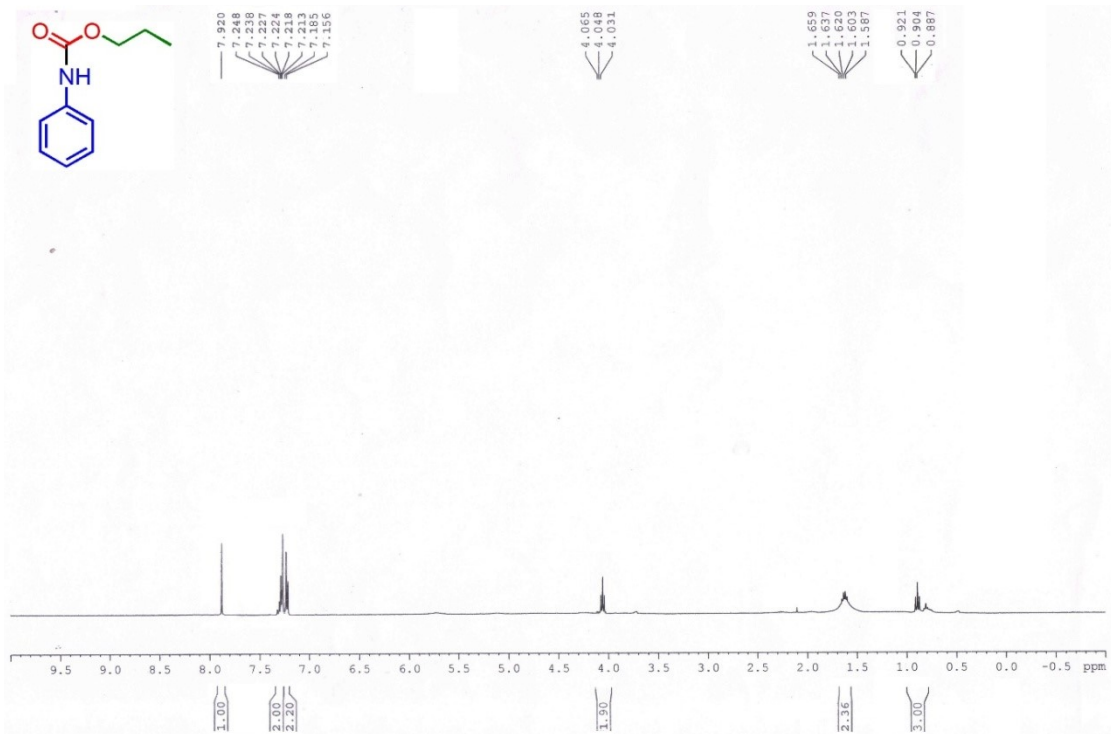



**Fig S15:** $^{1}$H NMR of Phenyl-carbamic acid propyl ester.

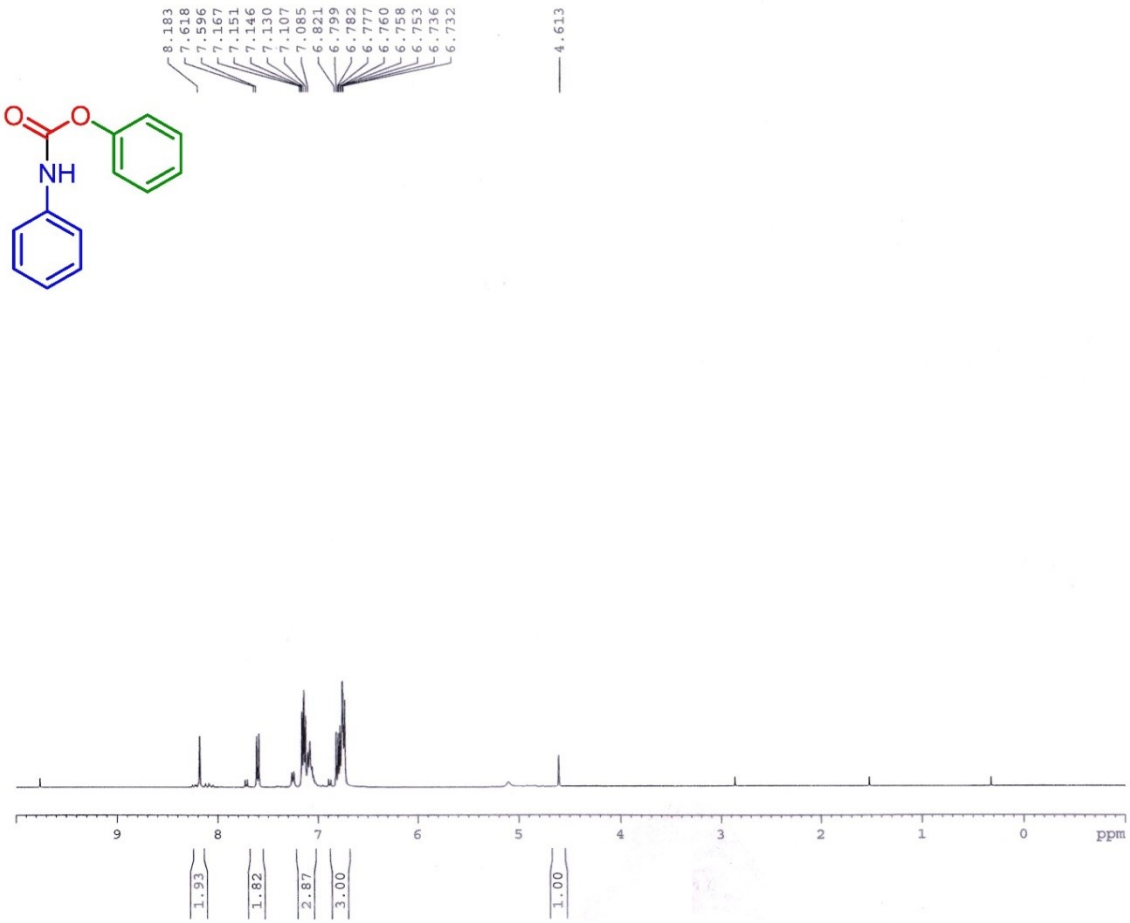



**Fig S16:** $^{1}$H NMR of Phenyl phenylcarbamate.

## References

[1] Z. Wu, X. Lan, Y. Zhang, M. Lia and G. Bai, *Dalton Trans.*,2019, **48**, 11063-11069.

[2] R. Khatun, S. Biswas, S. Islam, I. H. Biswas, S. Riyajuddin, K. Ghosh, and S. M. Islam, *ChemCatChem.*,2019,**11,** 1303–1312.