Supporting Information

Catalytic Conversions of Isocyanate to Urea and Glucose to Levulinate Esters over Mesoporous α-$Ti(HPO_4)_2.H_2O$ in Green Media

Arpita Hazra Chowdhury,[a] Ipsita Hazra Chowdhury,[a] Surajit Biswas,[a] Pekham Chakrabortty,[a] and Sk. Manirul Islam[a]*

Department of Chemistry, University of Kalyani, Kalyani, Nadia, 741235, W.B., India

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Materials

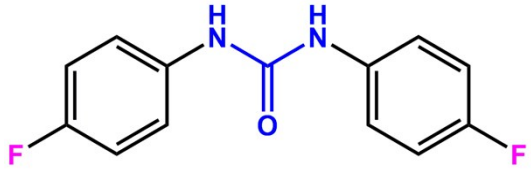
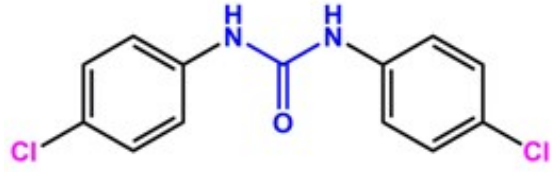
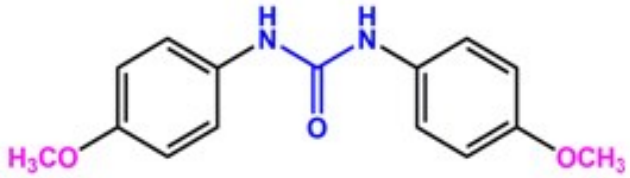
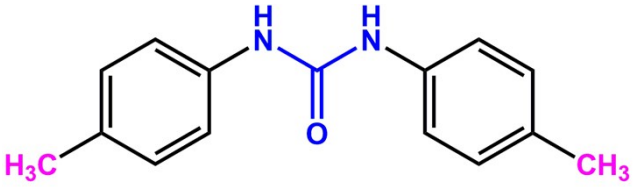
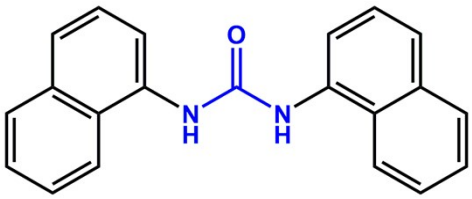
Titanium isopropoxide and isocyanates were purchased from Aldrich, phosphoric acid, 85% (w/w), all the alcohols of AR grade each were purchased from Merck, India. Deionized (DI) water was used throughout the experiment.

Instrumentation

PXRD study of the sample was performed by Cu-Ka radiation (Ni-filtered) (k = 0.15418 nm) using Philips X'Pert Pro powder diffractometer (PW 3050/60). The UV–Vis spectra of the $Ti(HPO_4)_2.H_2O$ sample was obtained from a UV–vis–NIR spectrophotometer (UV-3101PC, Shimadzu). The FESEM study of the $Ti(HPO_4)_2.H_2O$ material was performed to know about the morphological data of the sample by Zeiss, Supra™ 35VP instrument (Oberkochen, Germany). Transmission electron microscope (JEOL JEM 2010) was engaged to do the TEM study of the sample. To know about the elements present in the material EDS was done, which was coupled with TEM. ASIQ MP BET analyzer (Quantachrome Instruments, USA) was used to do the N_2 adsorption-desorption study of $Ti(HPO_4)_2.H_2O$ sample. The pore size distribution of the

phosphate material was estimated by BJH method. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer.

^{1}H NMR of isolated urea products:

1,3-Bis(4-fluorophenyl)urea[1] 	White solid, **^{1}H NMR (400 MHz, DMSO-D6)** δ 7.09 (t, *J*=8.8 Hz, 4H), 7.43-7.47 (m, 4H), 8.69 (s, 2H) ppm.
1,3-Bis(4-chlorophenyl)urea[1] 	White solid, **^{1}H NMR (400 MHz, DMSO-D6)** δ 7.38-7.41 (m, 4H), 7.52-7.56 (m, 4H), 8.92 (s, 2H) ppm.
1,3-Bis(4-methoxyphenyl)urea[1] 	White solid, **^{1}H NMR (400 MHz, DMSO-D6)** δ 3.87 (s, 6H), 6.90 (dd, *J*=5.6 Hz, 8.4 Hz, 4H), 7.36 (t, *J*=8.8 Hz, 4H), 8.44 (s, 2H) ppm.
1,3-Bis(4-methylphenyl)urea[2] 	White solid, **^{1}H NMR (400 MHz, DMSO-D6)** δ 2.42 (s, 6H), 7.11 (t, *J*=8.8 Hz, 4H), 7.32 (m, 4H), 8.55 (s, 2H) ppm.
1,3-Di(naphthalen-1-yl)urea[1] 	White solid, **^{1}H NMR (400 MHz, DMSO-D6)** δ 7.48-7.67 (m, 8H), 7.95 (d, *J*=8.0 Hz, 2H), 8.06 (d, *J*=7.2 Hz, 2H), 8.23 (d, *J*=8.4 Hz, 2H), 9.19 (s, 2H) ppm.

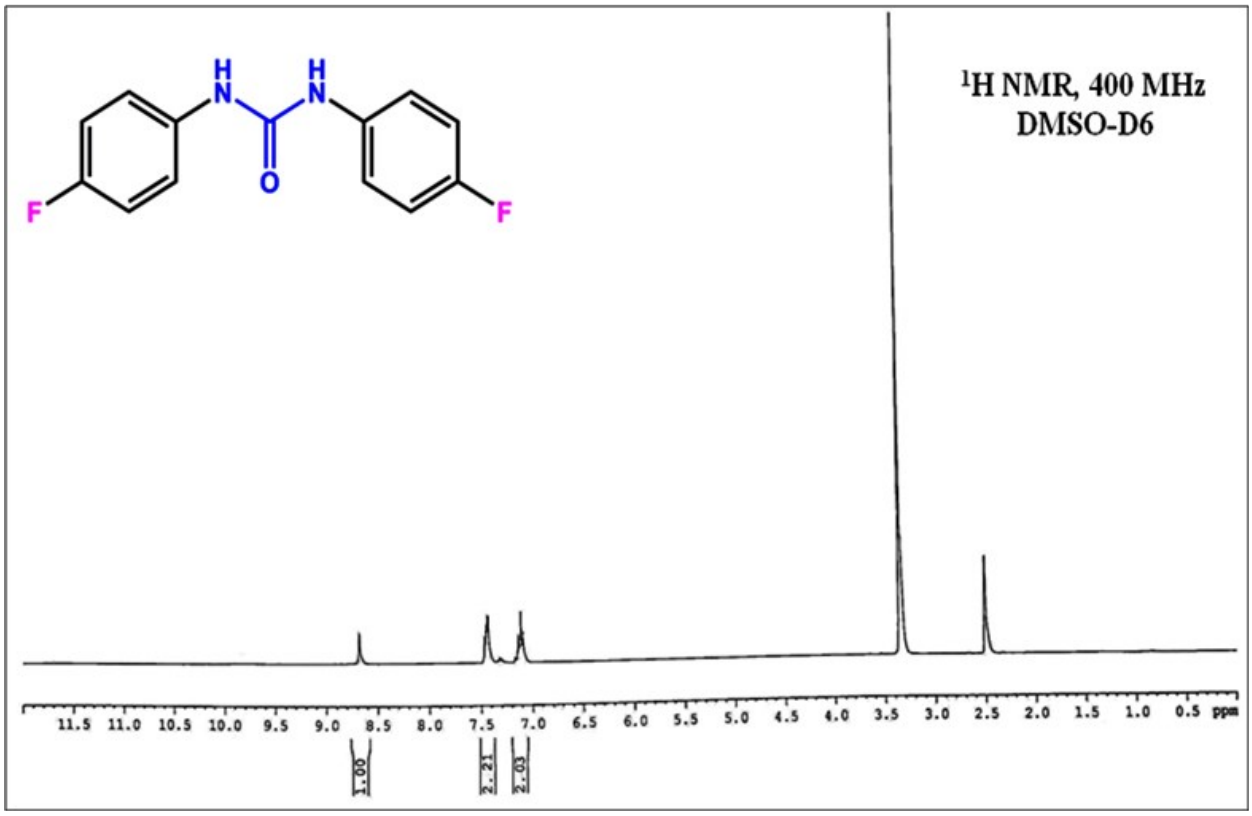


Fig S1: ^{1}H NMR spectra of 1,3-Bis(4-fluorophenyl)urea.

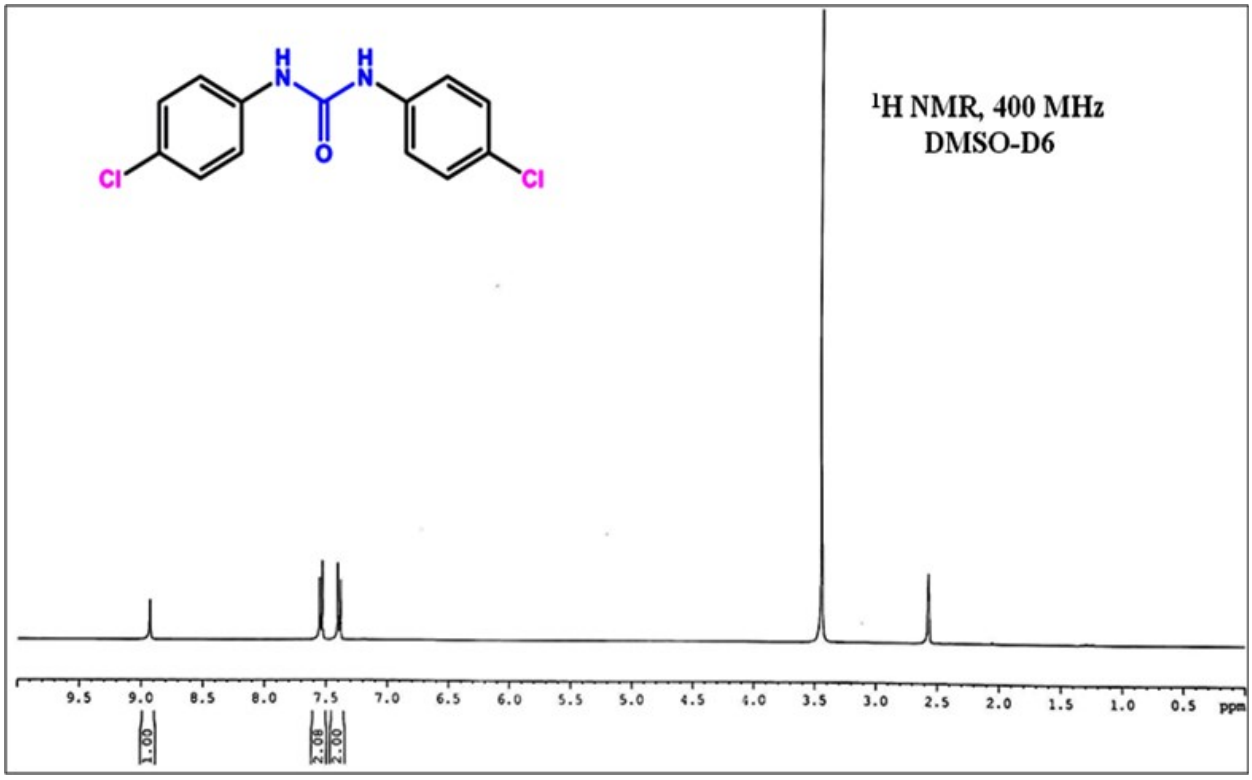


Fig S2: ^{1}H NMR spectra of 1,3-Bis(4-chlorophenyl)urea.

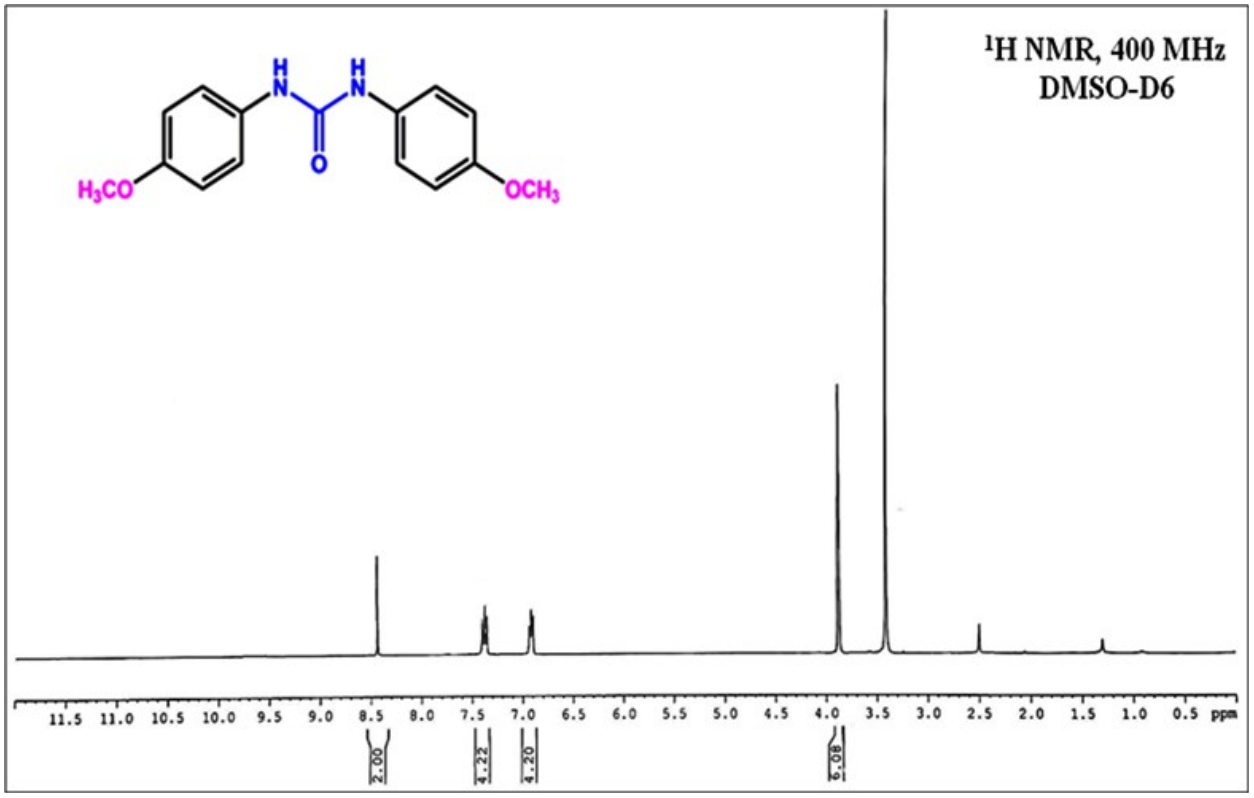


Fig S3: ^{1}H NMR spectra of 1,3-Bis(4-methoxyphenyl)urea.

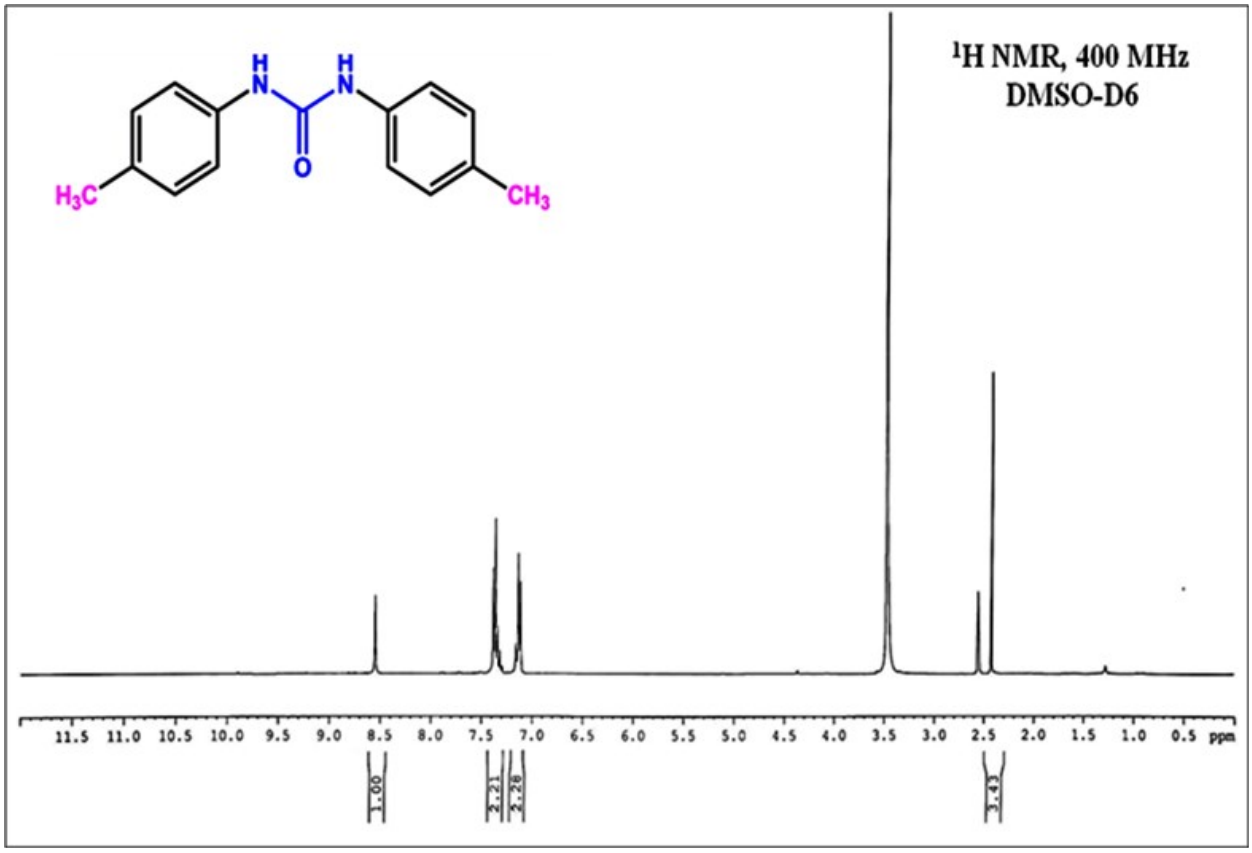


Fig S4: ^{1}H NMR spectra of 1,3-bis(4-methylphenyl)urea.

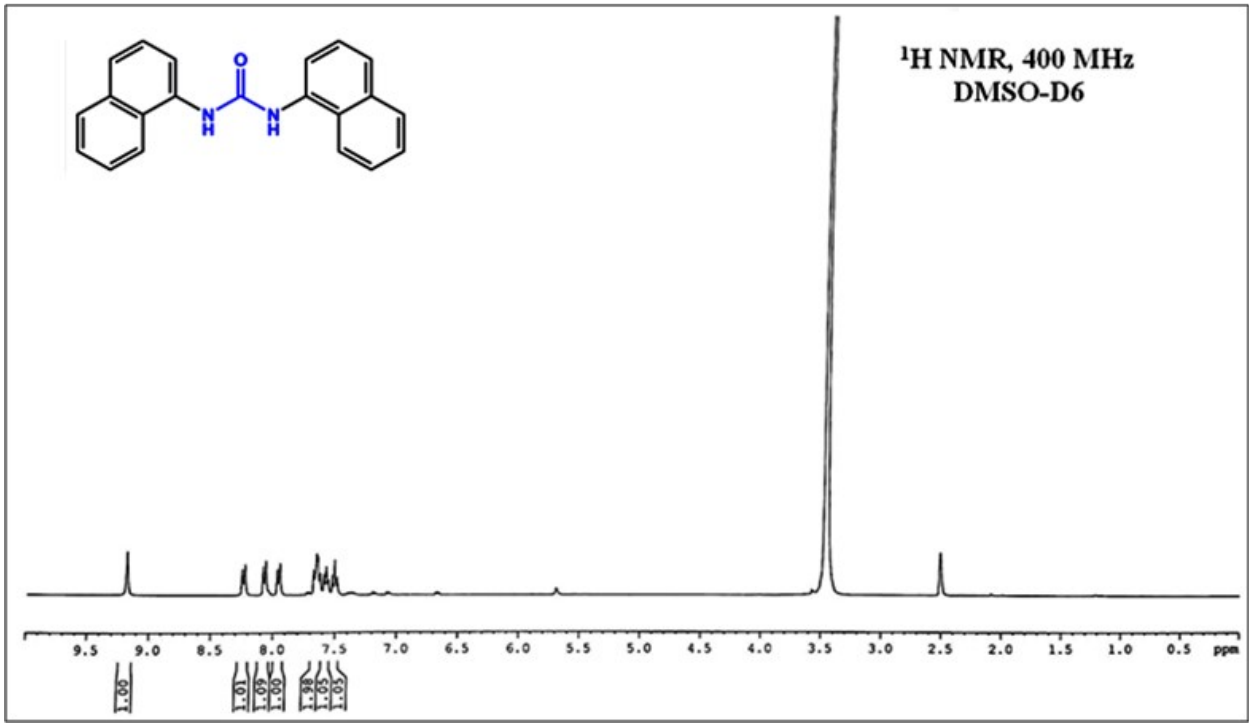
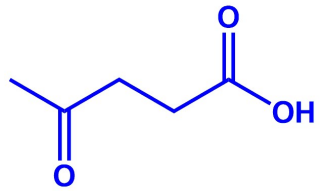
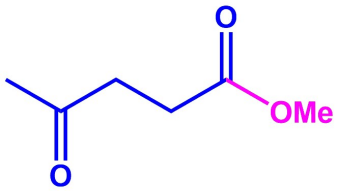
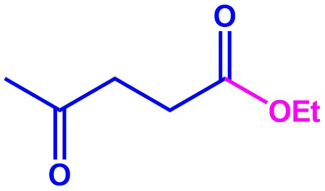
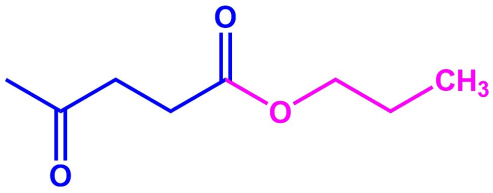
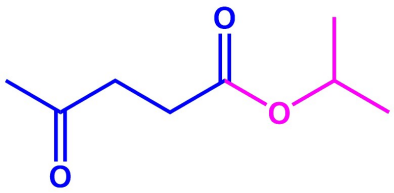
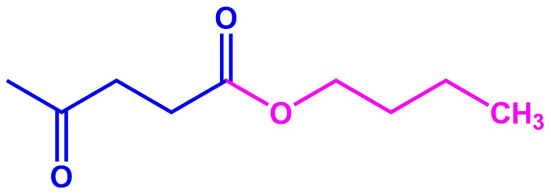


Fig S5: ^{1}H NMR spectra of 1,3-di(naphthalen-1-yl)urea.

^{1}H NMR of isolated LA and levulinate ester proucts:

Levulinic acid[3] 	Yellowish oil, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 2.20 (s, 3 H), 2.59 (t, *J*=6.0 Hz, 2H), 2.74 (t, *J*=6.4 Hz, 2H) ppm.
Methyl levulinate[4] 	Colourless liquid, **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.12 (s, 3H), 2.49-2.539 (m, 2H), 2.67-2.71 (m, 2H), 3.59 (s, 3H) ppm.
Ethyl levulinate[4] 	Colourless liquid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.18 (t, *J*=6.4 Hz, 3H), 2.13 (s, 3H), 2.53 (t, *J*=6.0 Hz, 2H), 2.67 (t, *J*=6.4 Hz, 2H), 4.06-4.11 (t, *J*=6.4 Hz, 2H) ppm.
Propyl levulinate[4] 	Colourless liquid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 0.76 (t, *J*=7.6 Hz, 3H), 1.46-1.52 (m, 2H), 2.04 (s, 3H), 2.40-2.46 (m, 2H), 2.59 (t, *J*=6.8 Hz, 2H), 3.86 (t, *J*=6.4 Hz, 2H) ppm.
Isopropyl levulinate[4] 	Colourless liquid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.83(t, *J*=6.4 Hz, 6H), 2.13 (s, 3H), 2.54 (t, *J*=6.0 Hz, 2H), 2.67 (t, *J*=6.8 Hz, 2H), 4.81-4.85 (m, 1H) ppm.
Butyl levulinate[4]	Colourless liquid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ

	0.83 (t, *J*=7.6 Hz, 3H), 1.29 (t, *J*=7.6 Hz, 2H), 1.51-1.51 (t, *J*=8.0 Hz, 2H), 2.12 (s, 3H), 2.48-2.55 (m, 2H), 2.66-2.70 (m, 2H), 3.98 (t, *J*=6.8 Hz, 2H) ppm.

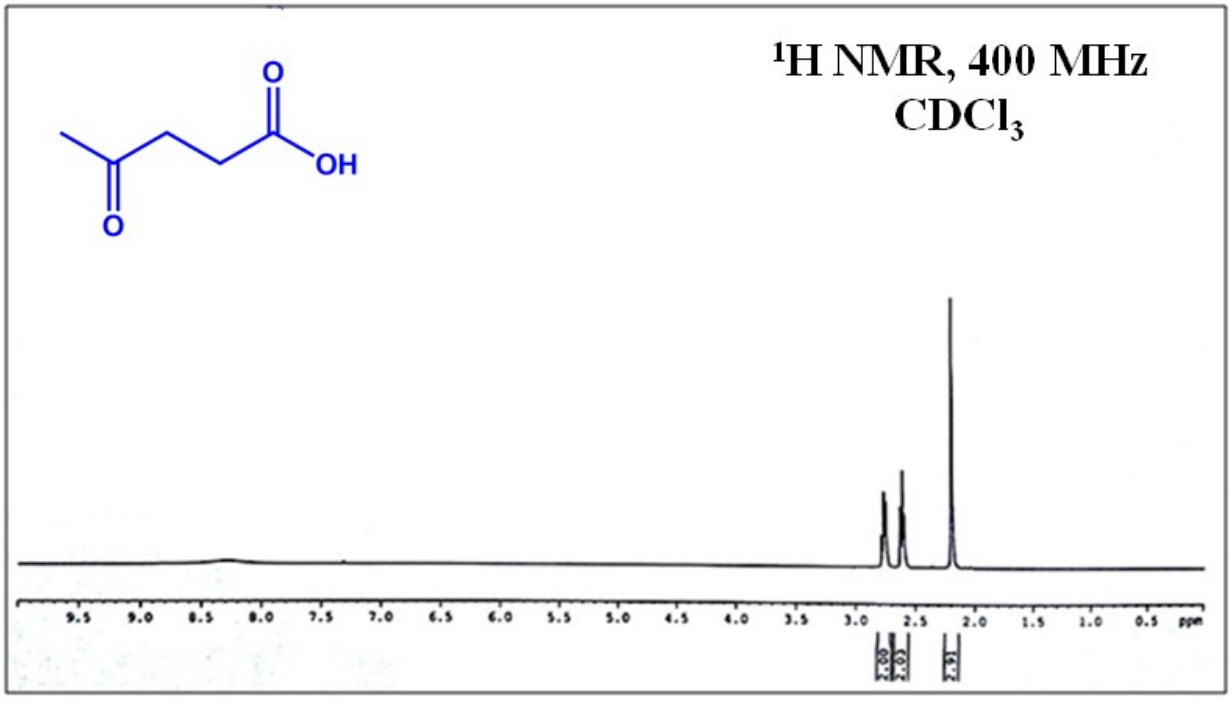


Fig S6: ^{1}H NMR spectra of levulinic acid.

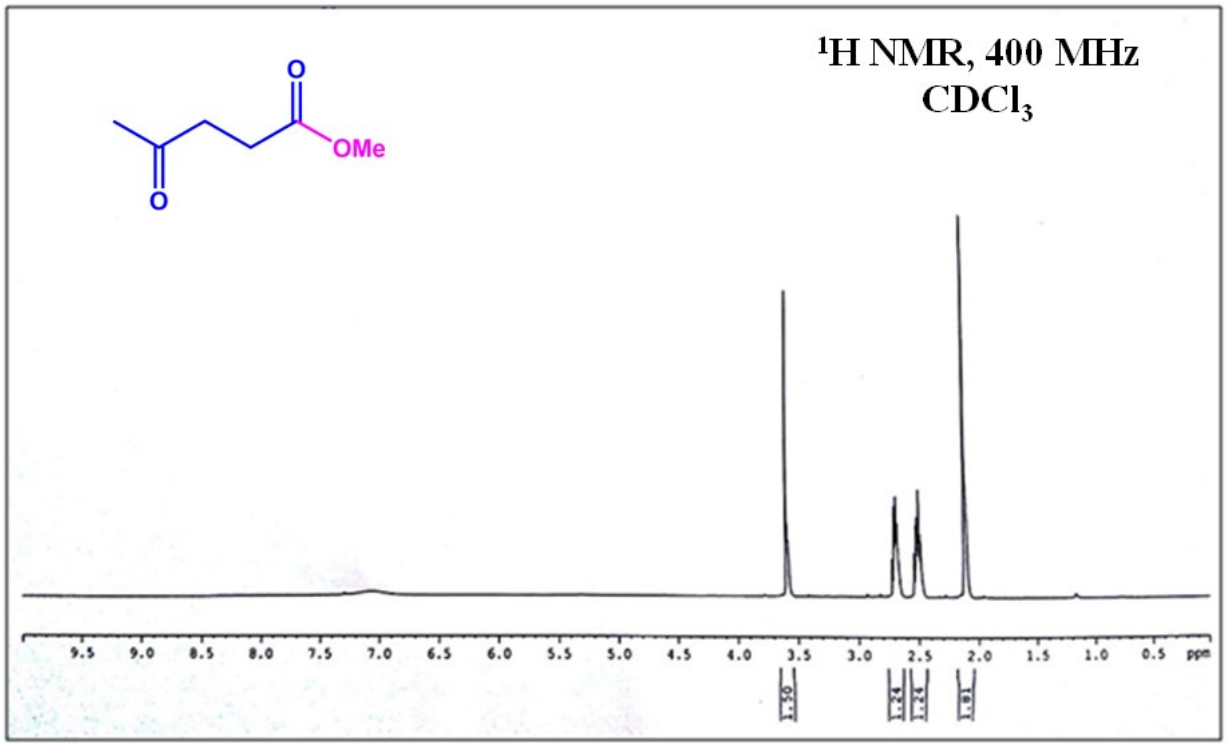


Fig S7: ^{1}H NMR spectra of methyl levulinate.

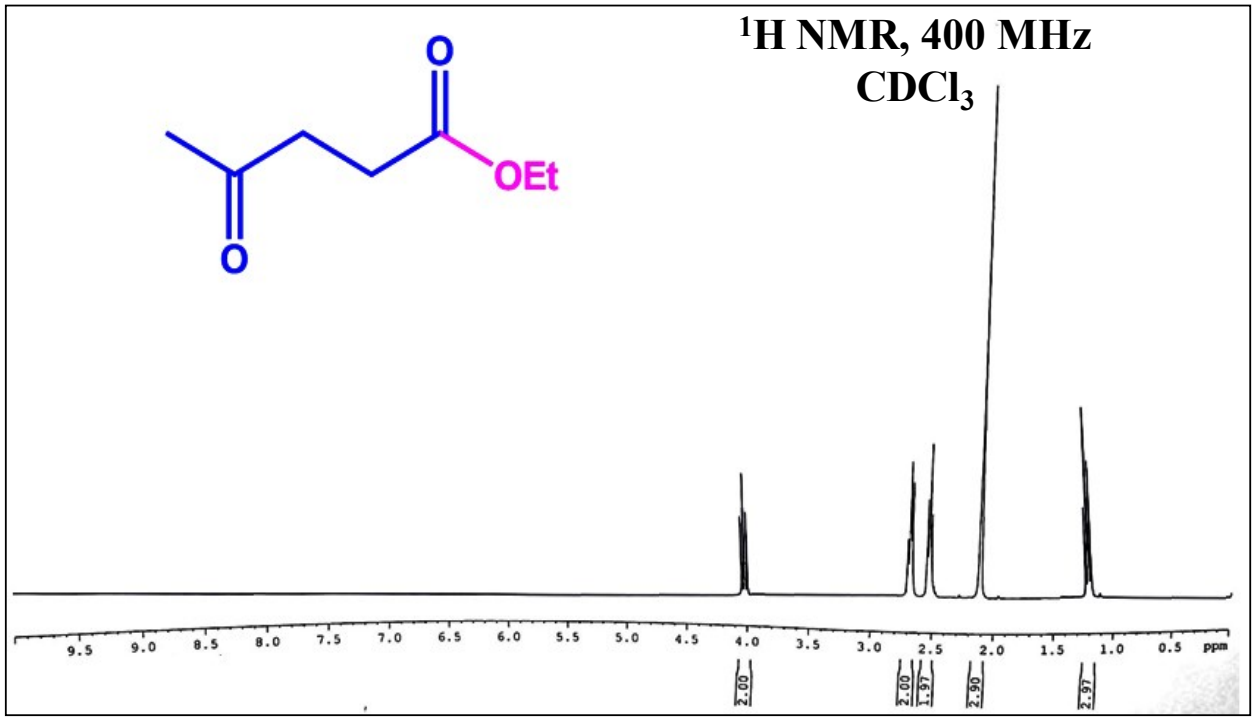


Fig S8: ^{1}H NMR spectra of ethyl levulinate.

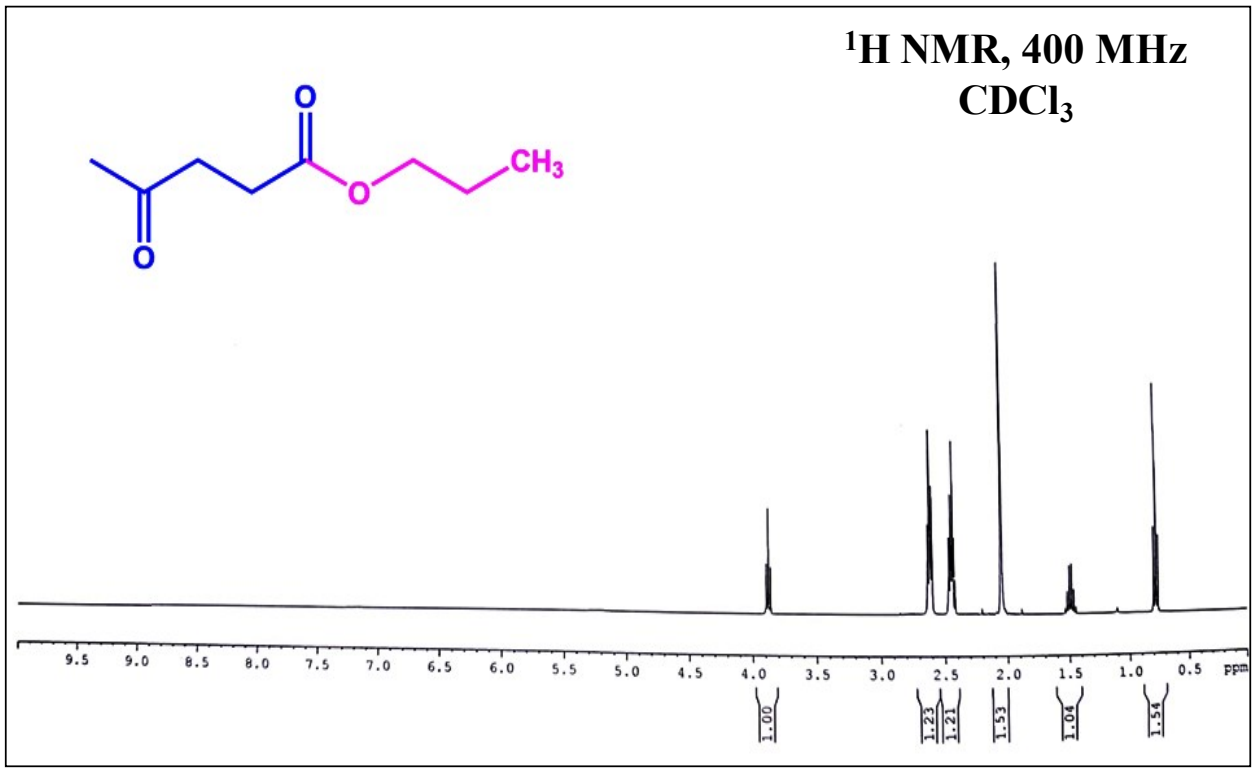


Fig S9: ^{1}H NMR spectra of propyl levulinate.

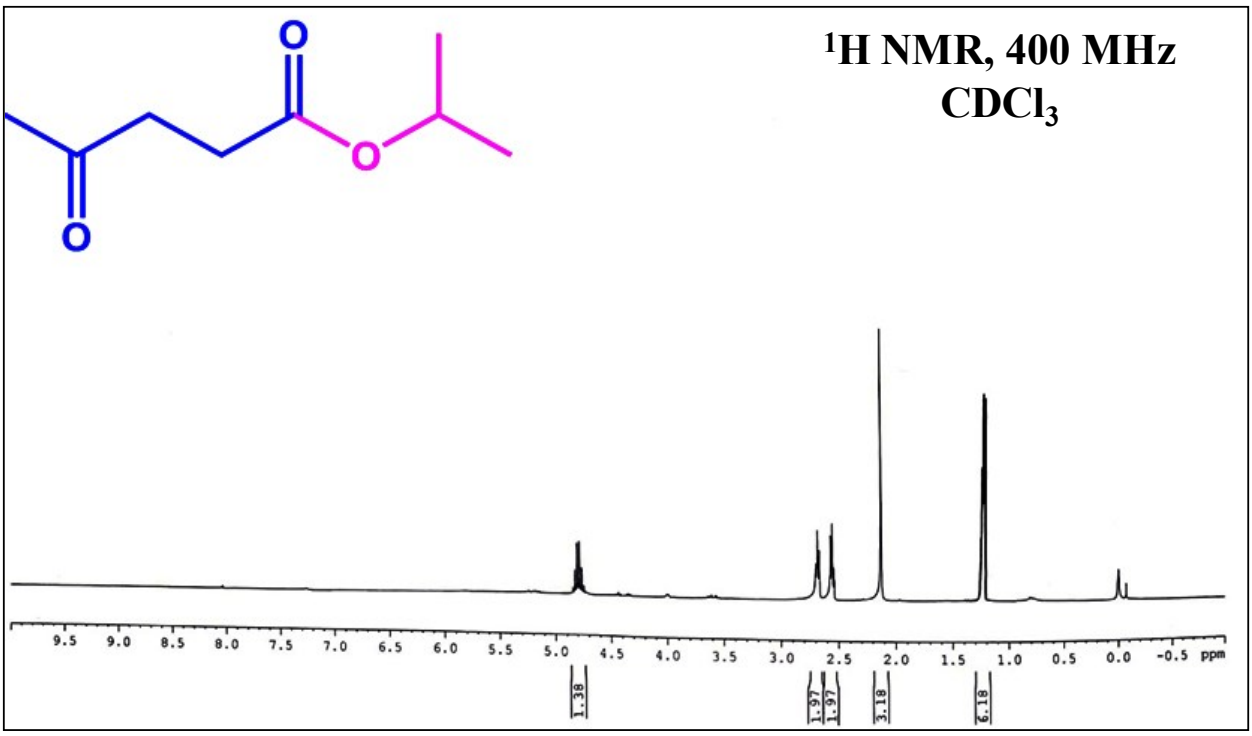


Fig S10: ^{1}H NMR spectra of isopropyl levulinate.

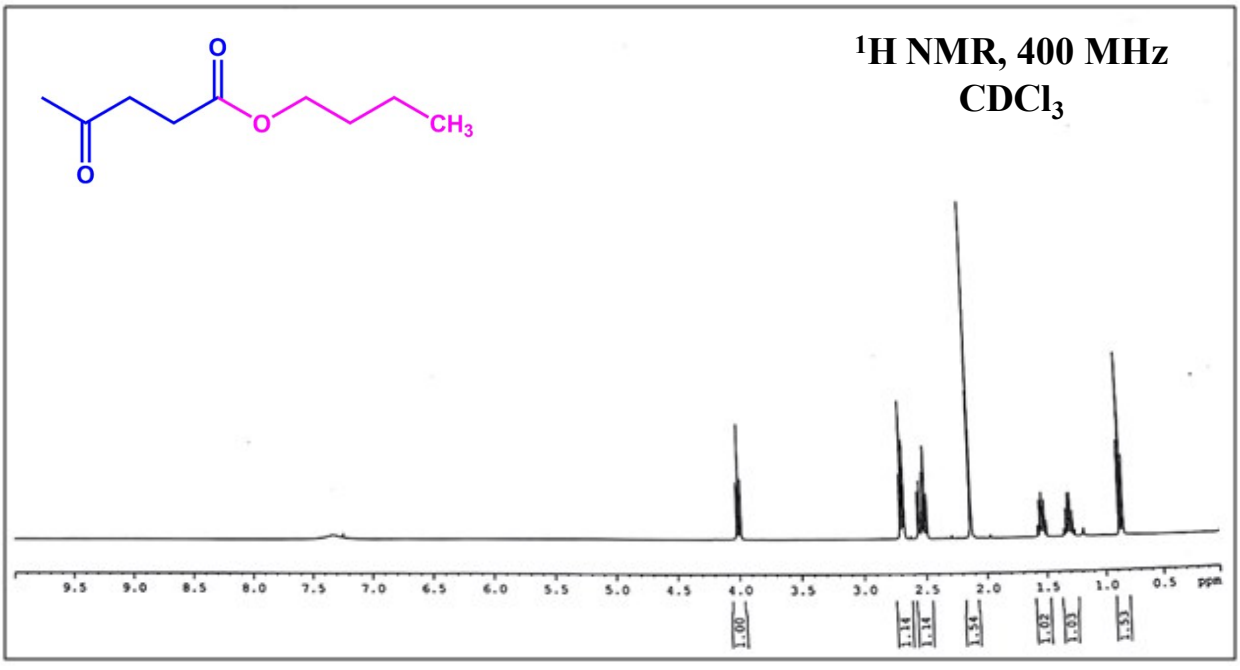


Fig S11: ^{1}H NMR spectra of butyl levulinate.

References:

1 L. Wang, H. Wang, G. Li, S. Min, F. Xiang, S. Liu, and W. Zheng, *Adv. Synth. Catal*. 360 (2018) 4585 – 4593.

2 M. Xu, A. R. Jupp, M. S. E. Ong, K. I. Burton, S. S. Chitnis, and D. W. Stephan, *Angew. Chem. Int. Ed*., 58 (2019) 5707-5711.

3 A. Victor, I. N. Pulidindi , A. Gedanken, *RSC Adv.*, 4 (2014) 44706-44711

4 T. K. Dey, P. Bhanja, P. Basu, A. Ghosh, S. M. Islam, *ChemistrySelect*, 4 (2019) 14315-14328.