Advanced Synthesis & Catalysis

Supporting Information

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An efficient synthesis of organic carbonates using nanocrystalline magnesium oxide

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General Remarks

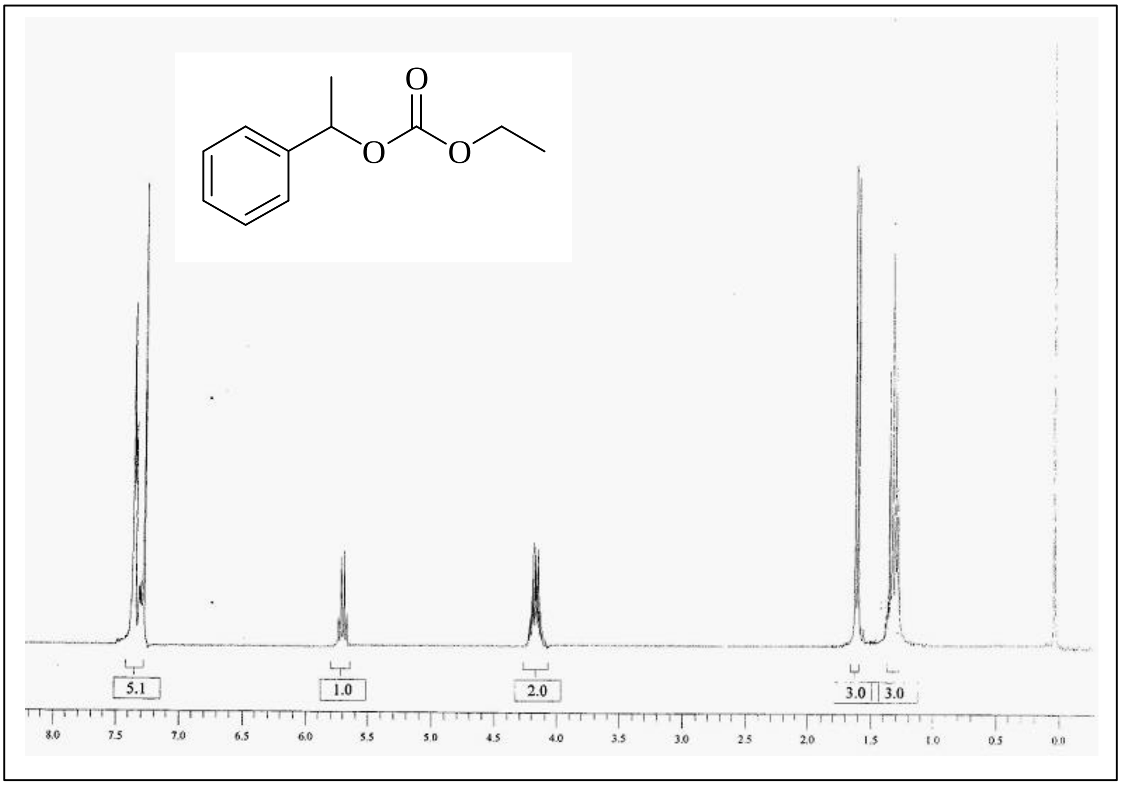
Commercial magnesium oxide (CM-MgO, S.A: 25 m^2/g) was purchased from Aldrich. The conventionally prepared magnesium oxide (NanoActive^{TM} MgO abbreviated as NA-MgO S.A: 252 m^2/g) and Aerogel prepared magnesium oxide (NanoActive^{TM} MgO Plus abbreviated as NAP- MgO, S.A: 590 m^2/g) samples were purchased from Nano Scale Materials Inc, Manhattan, KS 66502, USA. All the fresh catalysts were activated at 500 °C before use. All chemicals were purchased from Aldrich and were used as received. All solvents used were analytical grade and were used as received from Merck India Pvt. Ltd. Silylated NAP-MgO, NA-MgO were prepared according to the literature.[1] All products are characterized by ^{1}H NMR, and EI-MS. ^{1}H NMR spectra were recorded at room temperature on Bruker, Avance 300, and Gemini 200 MHz instrument with respect to TMS.

General Information: NMR spectra data for all compounds are given below. ACME SILICA GEL (100-200 mesh) was used for column chromatography and thin layer chromatography was performed on Merck precoated silica gel 60-F254 plates. Optical rotations were obtained on an automated JASCO P-1020 polarimeter, and the values were reported in absolute rotations: $[a]_D^T$ [concentration *c* in g/100 mL of solvent].The absolute stereochemistry was assigned by comparing the optical rotation with the literature values. X-ray photoemission spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα anode. The pressure in spectrometer was about 10^{-9} Torr. For energy calibration, we have used the carbon 1s photoelectron line. The carbon 1s binding energy was taken to be 285.0 eV. Spectra were deconvoluted using the Sun Solaris based Vision 2 curve resolver. The location and the full width at half maximum (FWHM) for a species were first determined using the spectrum of a pure sample. The location and FWHM of the products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible to within ± 0.1 eV. GC analysis was done by GC-2010, Gas Chromatograph Shimadzu, with ZB5 capillary column and dodecane (0.05 ml) was used as an internal standard, internal diameter 0.53 mm, film thickness 1.50 μm, length 30 m, initial temperature 70 ^{0}C (hold 2 minutes), ramp 7 ^{0}C/min ? 279 ^{0}C (hold 7 min), injection temperature 250 ^{0}C, detector temperature 280 ^{0}C (FID). TGA-DTA-MS thermograms were recorded on Mettler-Toledo TGA/SDTA 851^{e} instrument coupled to MS Balzers Thermostar GSD 300T using open alumina crucibles, containing 8-10 mg of the sample with a linear heating in the temperature range of 25 -1000 ^{0}C at a rate of 10 ^{0}C/min in nitrogen atmosphere.

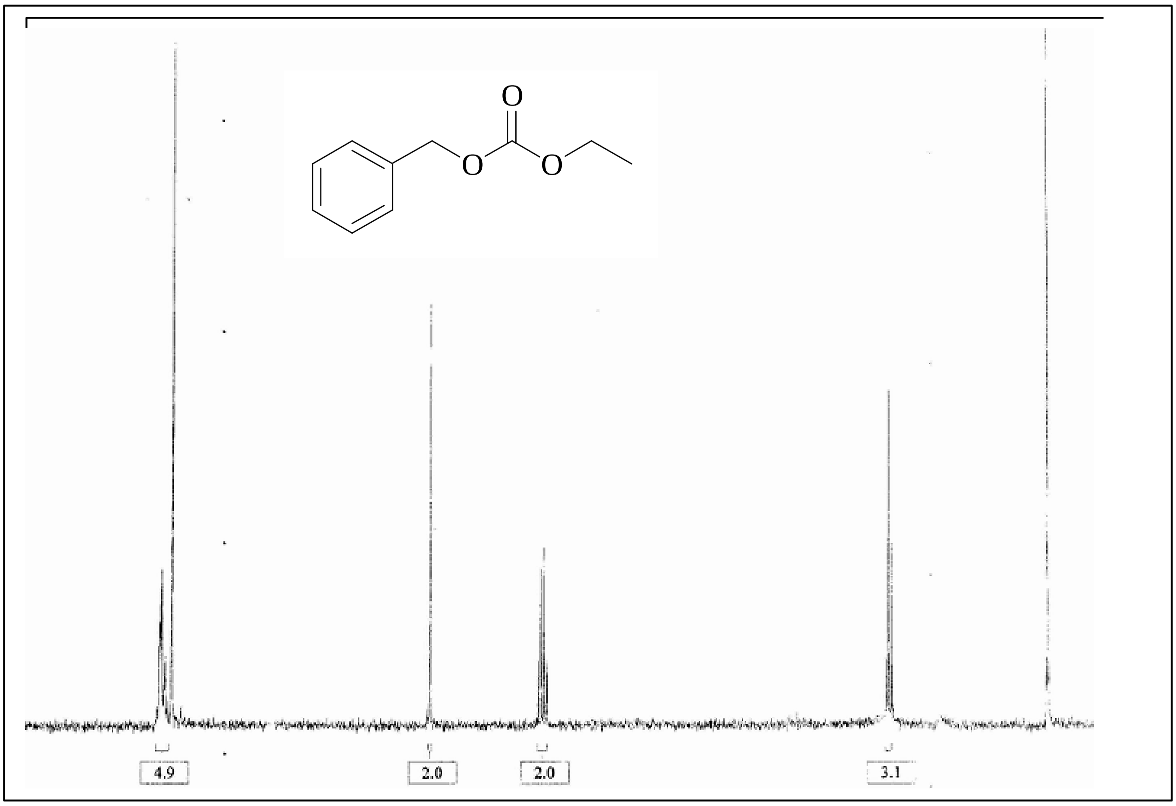
General procedure for the synthesis of unsymmetrical organic carbonates: A dry and nitrogen flushed 25 mL two neck flask, equipped with a magnetic stirring bar, reflux condenser and oil bath, was charged with an excess of DEC (33 mmol, 4 mL) and alcohol (2 mmol) at 125 ^{0}C and the mixture was stirred at the same temperature till the completion of reaction. After completion of the reaction, (monitored by TLC and GC), the reaction mixture was centrifuged to separate the catalyst and washed several times with ether. The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel: 100-200 mesh using ethyl acetate and hexane) to give the corresponding organic carbonate.

Characterization of Products:

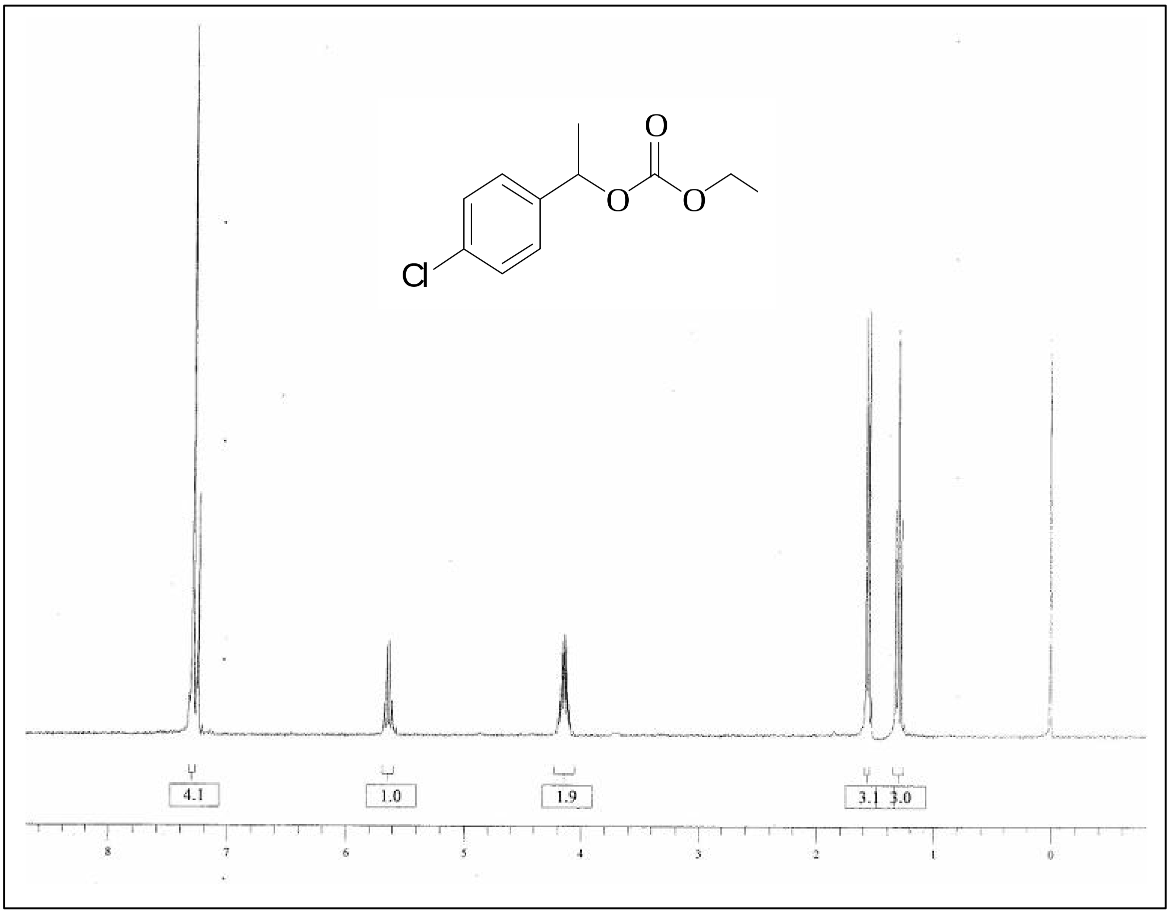
[1-(Phenyl)ethyl] ethyl carbonate (Table 2, entry 1): ^{1}H NMR (300MHz,CDCl$_3$) d1.30 (t, 3H, J=6.8 Hz), 1.59 (d, 3H, J= 6.8 Hz), 4.20-4.08 (m, 2H), 5.68 (q, 1H, J=6.8 Hz), 7.38-7.22 (m, 5 H); EIMS m/z (%) 196, (M$^+$+2, 7); 123 (15); 106 (100); 105 (85); 78 (60); 43 (50). A copy of the ^{1}H NMR spectra is provided.



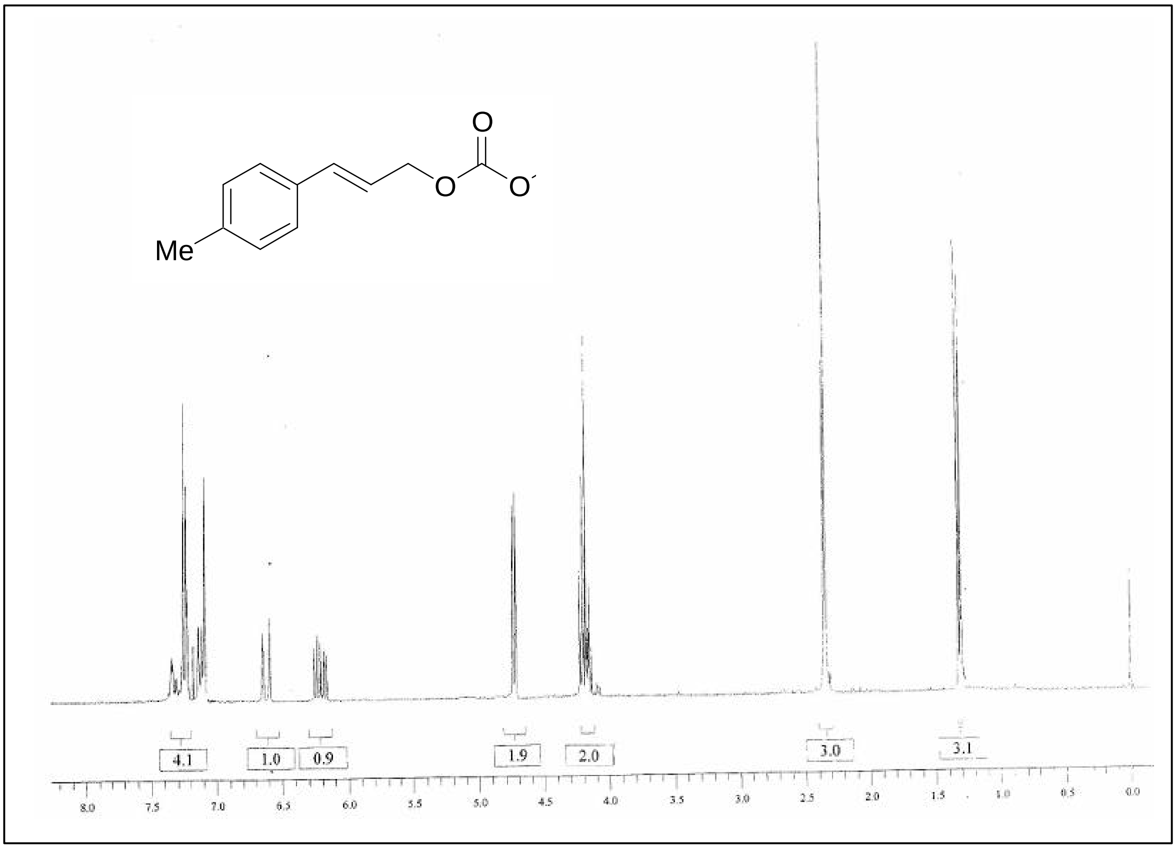
Benzyl ethyl carbonate (Table 2, entry 2): ^{1}H NMR (300MHz,$CDCl_3$) d 1.32 (t, 3H, J= 6.8 Hz), 4.19 (q, 2H, J= 6.8 Hz), 5.12 (s, 2H), 7.36-7.26 (m, 5 H); EIMS m/z (%) 182 (M+2, 25), 181 (M^++1, 13); 156 (7); 142 (27); 109 (35); 108 (45), 92 (100); 80 (50). A copy of the ^{1}H NMR spectra is provided.



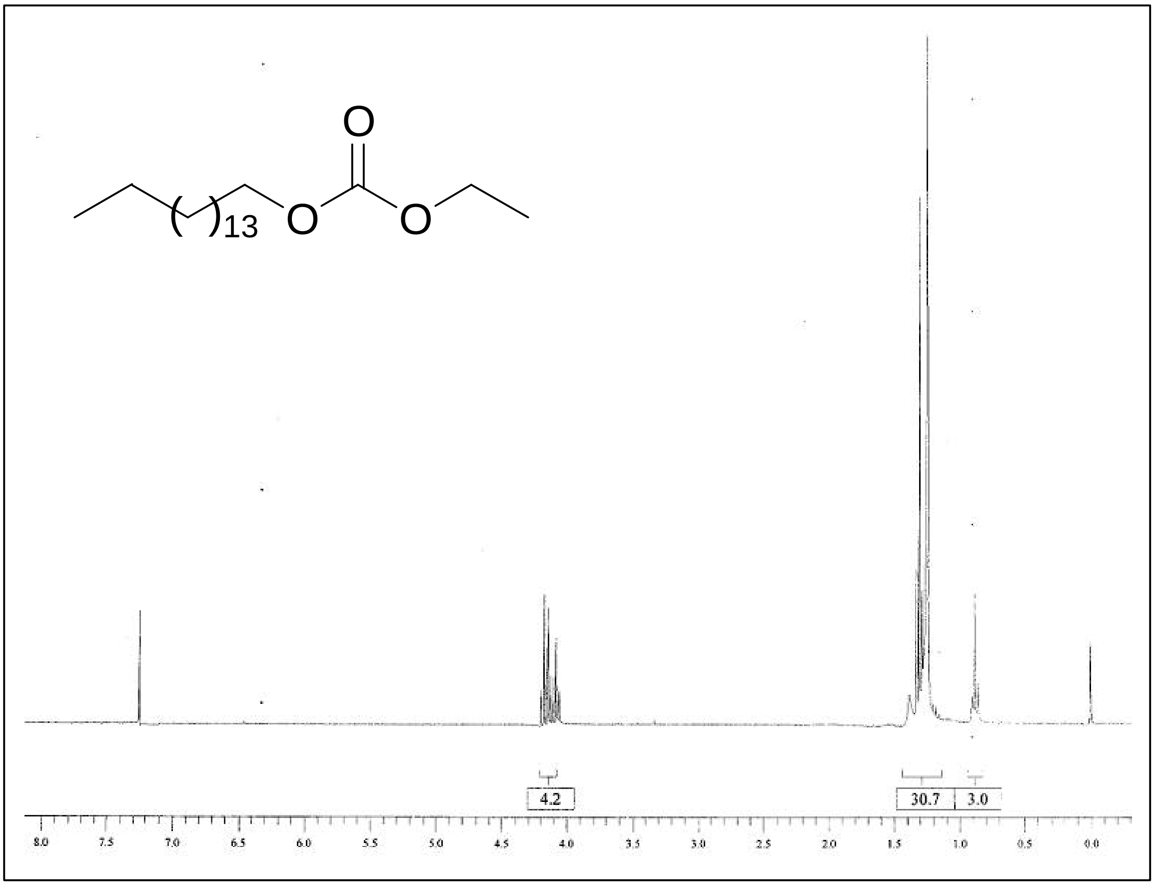
[1-(4-Chlorophenyl)ethyl] ethyl carbonate (Table 2, entry 3): ^{1}H NMR (300MHz, $CDCl_3$) d 1.30 (t, 3H, J=6.8 Hz), 1.56 (d, 3H, J= 6.8 Hz), 4.20-4.08 (m, 2H), 5.64 (q, 1H, J=6.8 Hz), 7.35-7.20 (m, 4 H). A copy of the ^{1}H NMR spectra is provided.



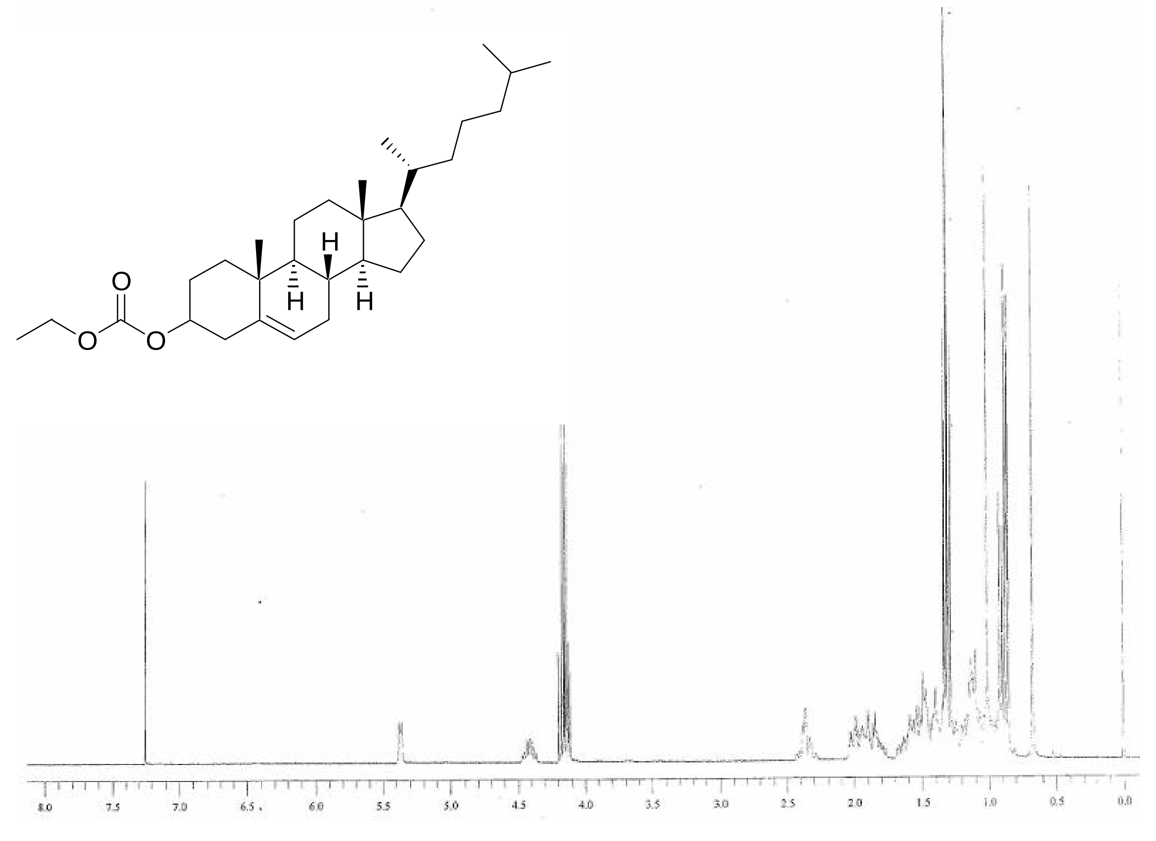
3-(4-Methylphenyl)-(E)-2-propenyl ethyl carbonate (Table 2, entry 4): ^{1}H NMR (300MHz, $CDCl_3$) d 1.33 (t, 3H, J= 6.8 Hz), 2.33 (s, 3H), 4.23-4.13 (m, 2H), 4.73 (dd, 2H, J= 6.7, 1.5 Hz), 6.20 (dt, 1H, J= 15.9, J=6.8Hz), 6.62 (d, 1H, J= 15.9 Hz), 7.36-704 (m, 4H). A copy of the ^{1}H NMR spectra is provided.



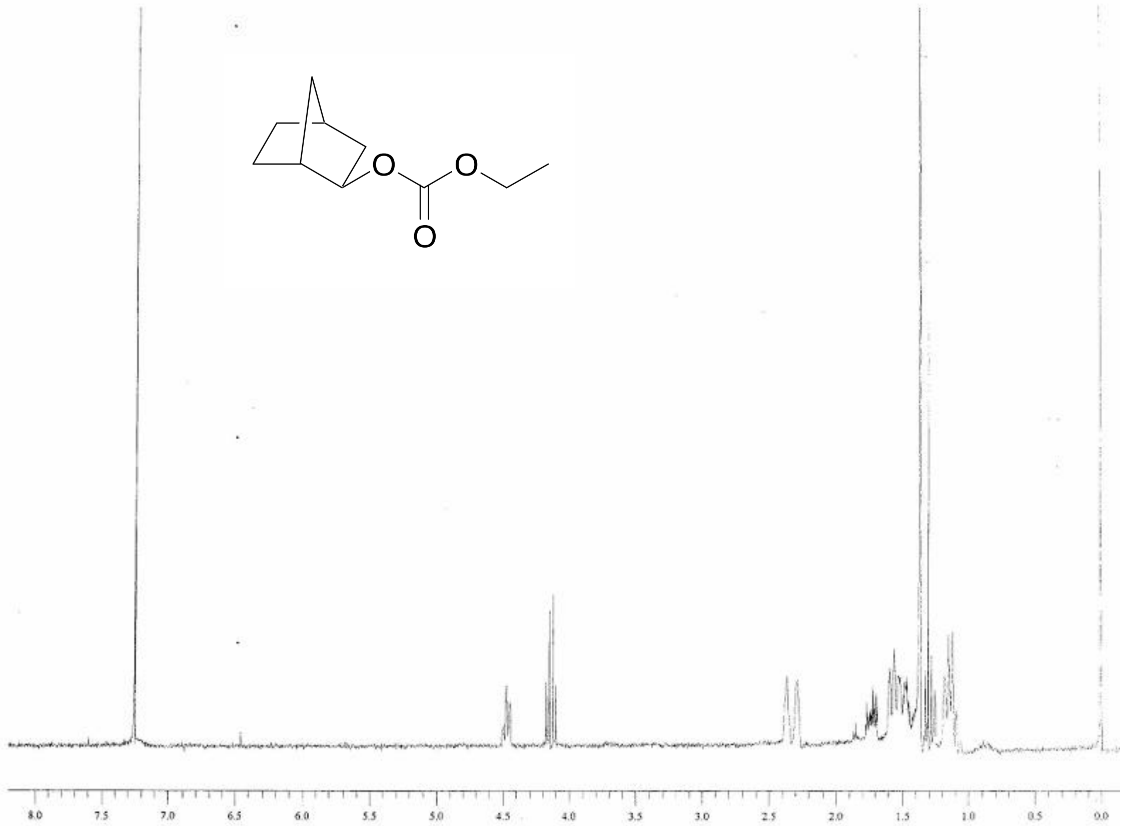
Ethyl hexadecyl carbonate (Table 2, entry 5): ^{1}H NMR (300MHz, $CDCl_3$) d 0.88 (t, 3H, J=6.8Hz) 1.4-1.24 (m, 31H), 4.20-4.04 (m, 4H). A copy of the ^{1}H NMR spectra is provided.



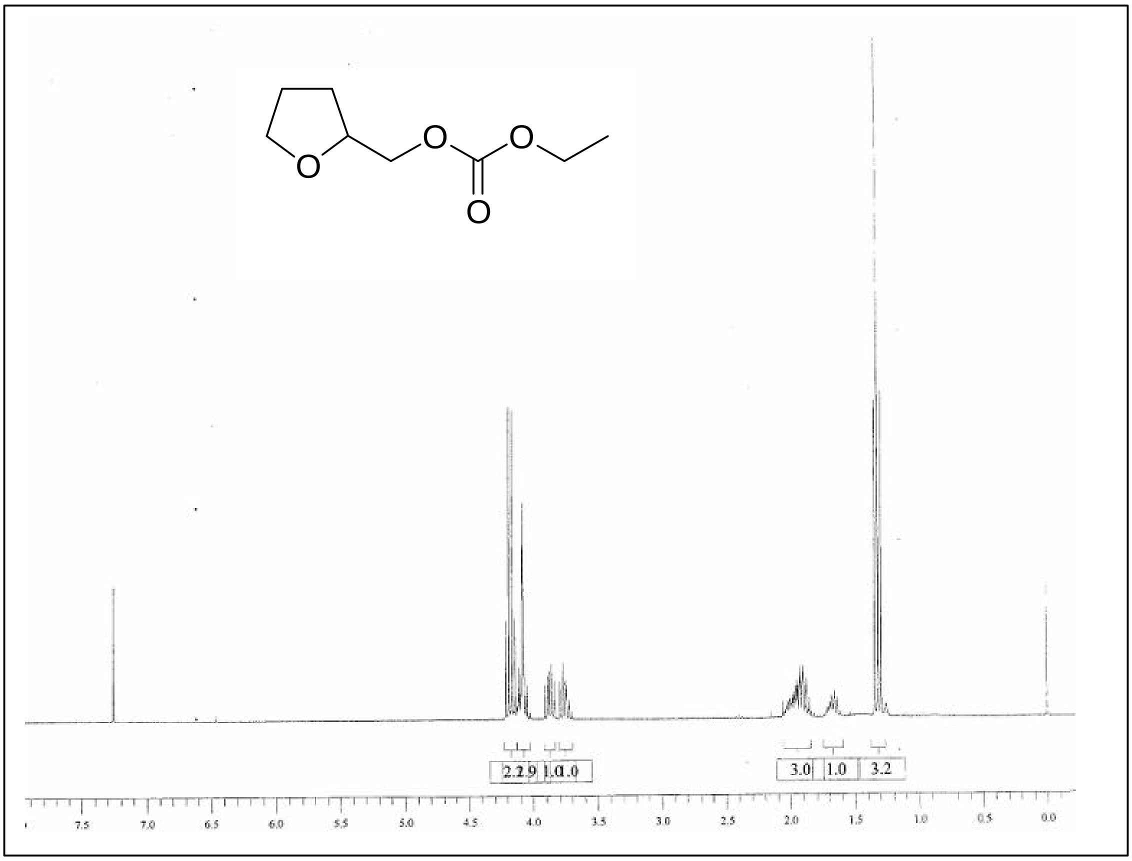
Cholesterol ethyl carbonate (Table 2, entry 6): ^{1}H NMR (300MHz, $CDCl_3$) d 2.4-0.6 (m, 46H), 4.18 (q, 2H, J= 7.2 Hz), 4.47-4.36 (m, 1H), 5.39-5.34 (m, 1H). EIMS m/z (%) 457 (M^+-1, 5); 440 (5); 385 (20); 369 (100); 353 (10); 255 (20); 213 (12); 199 (10); 173 (20); 159 (35); 105 (42); 95 (60); 81 (60); 69 (45); 55 (50). A copy of the ^{1}H NMR spectra is provided.



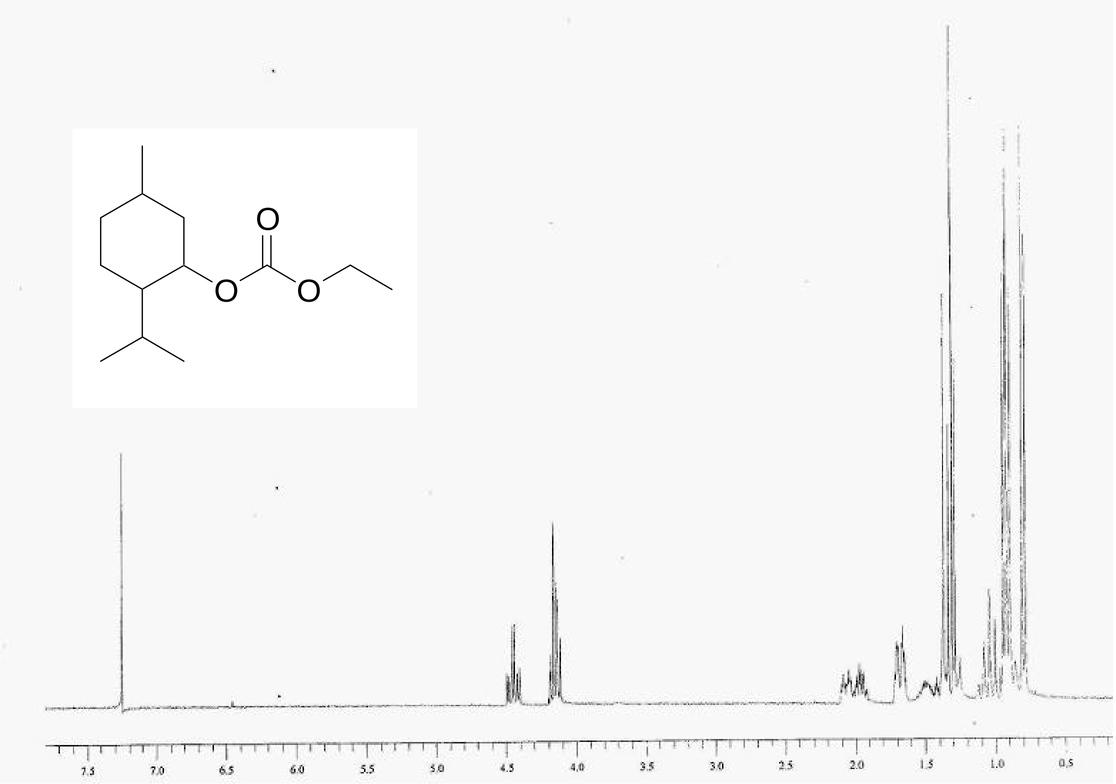
Bicyclo[2.2.1] heptanyl ethyl carbonate (Table 2, entry 7): ^{1}H NMR (300MHz, $CDCl_3$) d 1.76-1.04 (m, 11H), 2.32-2.26 (m, 1H), 2.40-2.33 (m, 1H), 4.13 (q, 2H, J= 6.8 Hz), 4.51-4.43 (m, 1H). EIMS m/z (%) 184 (M^+, 5); 182 (M-2 8); 171 (7); 156 (30); 142 (90); 124 (25); 108 (40); 106 (90); 105 (100); 95 (93); 80 (70); 67 (65); 52 (25); 43 (50). A copy of the ^{1}H NMR spectra is provided.

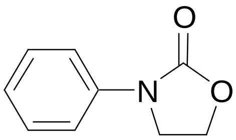


(3-Tetrahydro-2-furanyl)-methyl ethyl carbonate (Table 2, entry 8): ^{1}H NMR (300MHz, $CDCl_3$) d1.32 (t, 3H, J= 7.2 Hz), 1.73-1.60 (m, 1H), 2.07-1.82 (m, 3H), 3.80-3.70 (m, 1H), 3.91-3.83 (m, 1H), 4.12-4.02 (m, 3H), 4.18 (q, 2H, J= 7.2 Hz). A copy of the ^{1}H NMR spectra is provided.

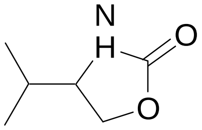


2-Isopropyl-5-methyl-1-cyclohexanyl ethyl carbonate (Table 2, entry 9): ^{1}H NMR (300MHz, $CDCl_3$) d 1.55-0.75 (m, 17H), 1.73-1.63 (m, 2H), 2.12-1.90 (m, 2H), 4.15 (q, 2H, J= 6.8 Hz), 4.45 (dt, 1H, J= 4.5 Hz, J= 10.6 Hz). A copy of the ^{1}H NMR spectra is provided.

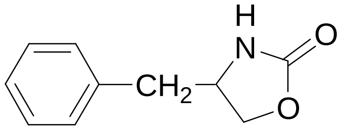




Scheme 2, compound 1(3-Phenyl-oxazolidin-2-one): ^{1}H NMR 200MHz, (200MHz, $CDCl_3$) d 7.58-7.05 (m, 5H), 4.55-4.41 (m, 2H), 4.12-3.99 (m, 2H). EIMS m/z (%) 163 (M^+, 25), 141 (10); 131 (12); 112 (40); 104 (80); 95 (35); 91 (30), 77 (100); 57 (32); 51 (60).



Scheme 3, compound (a) (4-Isopropyl-oxazolidin-2-one): ^{1}H NMR (300MHz,CDCl$_3$) d 0.91 (d, 3H, J= 6.8 Hz), 0.98 (d, 3H, J= 6.8 Hz), J= 8.3 Hz), 1.80-1.64 (m, 1H), 3.64-3.56 (m, 1H), 4.07(dd, 1H, J= 9.1 H, 4.42 (dd, 1H, J= 9.1 Hz, J= 8.3 Hz), 7.39 (s, 1H).



Scheme 3, compound (b) (4-Benzyl-oxazolidin-2-one): ^{1}H NMR (300MHz, CDCl$_3$) d2.95-2.78 (m, 2H), 4.15-4.00 (m, 2H), 4.46-4.37 (m, 1H), 5.65 (s, 1H), 7.35-7.12 (m, 5H). EIMS m/z (%) 177 (M$^+$, 7); 92 (100); 91 (100); 86 (100); 77 (25); 65 (85); 42 (99).

The results of different MgO samples were checked by gas chromatography with a GC-2010, Gas Chromatograph Shimadzu equipped with ZB5 capillary column. NAP-MgO shows full conversion in short time while NA-MgO afforded undesirable by-products along with carbonate product and CM-MgO gave very low conversion. High surface area of NAP-MgO has high surface concentrations of edge/corner and various exposed crystal planes (such as 002, 001, 111), which leads to inherently high surface reactivity per unit area. Thus NAP-MgO indeed display highest activity compared to that of NA-MgO and CM-MgO. Accordingly, the number of active sites are more with higher surface area, hence the yield of products will also be high in case of NAP-MgO compared to NA-MgO and CM-MgO. NAP-MgO has three-dimensional structure and defined size and shape, which are likely to be considered for higher selectivity. Although both the NAP-MgO and NA-MgO possess defined shapes and the same average concentrations of surface –OH groups, a possible rationale for the display of higher yield by the NAP-MgO is that the –OH groups present on edge and corner sites on the NAP-MgO are more isolated and accessible for the reactants, whereas on NA-MgO relatively large portions of the –OH's are situated on flat planes in closer proximity with each other and thus are hindered. Conversely, CM-MgO, which showed almost no activity, has assorted crystals.

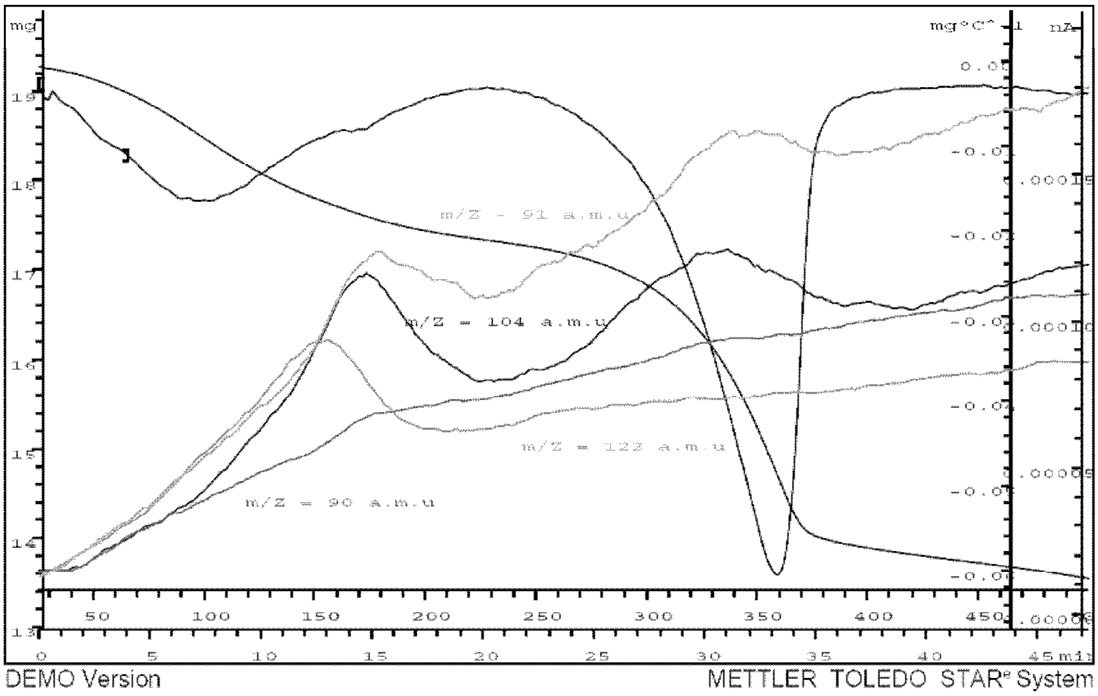


Figure 3. TGA-DTA-MS of 1-pheynylethanol treated NAP-MgO.

XPS high resolution narrow scan for Mg 2p in the fresh NAP-MgO exhibits one line at 48.7 eV (Figure 2). XPS specturm of the 1-phenylethanol treated NAP-MgO for the Mg 2p exhibit two lines at 48.7 and 50.7 eV, which can be attributed to magnesium in NAP-MgO and Ph-CH(Me)-O-MgO respectively (Figure 2, main text). This provides evidence that in the proposed mechanism, O^{2-}/O^{-} of NAP-MgO abstracts an acidic proton of the 1-phenylethanol, giving a Ph-CH(Me)-O^{-}, which forms a complex with the unsaturated Mg^{+} site (Lewis acid-type) of NAP-MgO (Scheme 4, main text). Ph-CH(Me)-O-MgO is subjected to TGA-DTA-MS to detect the evolved gas fragments as a function of temperature. The observed m/Z values of the fragments for Ph-CH(Me)-O^{-}-NAP-MgO are 90, 91, 104 and 122 amu that correspond to C_7H_6, C_7H_7, C_8H_8 and $C_8H_{10}O$, respectively. The major fragment, m/Z = 91 amu observed corresponds to the benzyl radical cation of the surface transient organometallic intermediate, (SI, Figure 3) further supports the proposed mechanism.

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Reuse of the catalysts:

After completion of the reaction, the catalyst was recovered by centrifugation and activated under nitrogen flow for 1 h at 250 ^{0}C for further reuse. NAP-MgO shows consistent activity for five cycles under the same reaction conditions. (Table 4, entry 1), The reusability of NAP-MgO catalyst is summarized in SI (Figure 4).

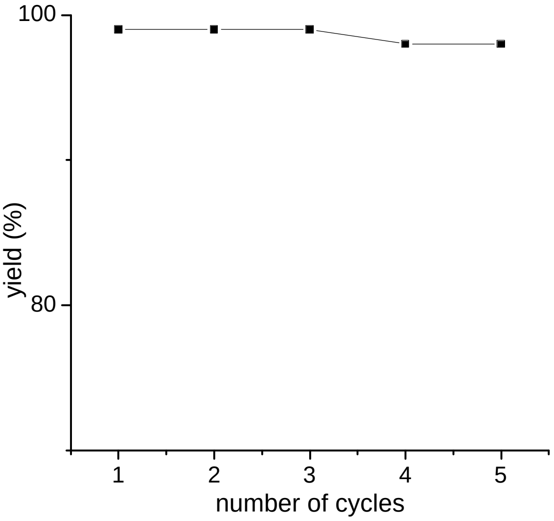

Figure 4. Yields obtained in multiple uses of NAP-MgO catalyst for the synthesis of organic carbonates using 1-phenyl ethanol and DEC as a model reaction.

References

[1] B. M. Choudary, R. S. Mulukutla, K. J. Klabunde, *J. Am. Chem. Soc*. **2003**, *125*, 2020.

[2] B. M. Choudary, S. Madhi, M. L. Kantam, B. Sreedhar, Y. Iwasawa, *J. Am. Chem. Soc*. **2004**, *126*, 2292.

[3] K. J. Klabunde, J. Stark, O. Koper, C. Mohs, D. G. Park, S. Decker, Y. Jiand, I. Lagadic, D. Zhang, *J. Phys. Chem*. **1996**, *100*, 12142.