Supporting Information

Homogeneous and Heterogenised Masked *N*-Heterocyclic Carbenes for Bio-based Cyclic Carbonate Synthesis

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Experimental

Materials

Diglycerol (>80%) was purchased from ABCR. GC analysis showed it to contain 86 wt.% diglycerol, 9 wt.% glycerol and the remaining 5 wt.% was made up of higher oligomers. Dimethyl carbonate (≥99%) was purchased from Merck. Imidazole (≥99.5%), 1-methylimidazole (>99%), 1-butylimidzole (98%), 1,2-dimethylimidazole (98%), sodium hydride (95%), *p*-toluenesulphonylmethyl isocyanide (98%), acetaldehyde (99.5%), benzaldehyde (>99.5%), valeraldehyde (97%), 1-methyl-5-nitroimidazole (97%), 5-chloro-1-methylimidazole (98%), bromohexane (98%), bromodecane (98%), anisole (>99%), 1,3-propanediol (≥99%), 1,2-butanediol (98%), potassium bis(trimethylsilylamide) (99%), (3-chloropropyl)triethoxysilane (95%), 1,3,5-trimethylbenzene (98%), tetraethyl orthosilicate (≥ 99%), Pluronic P123, anisole (>99%), chlorotrimethylsilane (≥98%) and 1-dodecanol (≥98%) were all purchased from Sigma Aldrich. 1-butyl-3-methylimidazolium bromide (99%) was purchased from Io-li-tec. 1-methylbenzimidazole (99%) was purchased from Alfa Aesar. Dry THF and diethyl ether were obtained from a SPS system. Glycerol (99+%), 1,2-propanediol (99+%), 1,3-butanediol (99%), 1,1,1,3,3,3-hexadimethydilsilizane (98%) and 2,3-butanediol (98%) were purchased from Acros. Ethylene alcohol (>99.5%) was purchased from Fluka. Crude glycerol containing 83.3wt% glycerol, with the remaining being made up of soaps, water and esters was obtained from DOW chemicals. All reagents were used as received.

Instrumentation

DRIFTS measurements were performed on a Bruker Tensor 37 in a range from 600 cm^{-1} to 4000 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans at room temperature. The spectra were analysed with OPUS software. Thermal gravimetric analysis was performed on a Q50 from TA Instruments with a heating rate of 5 K/min from 25 °C to 600 °C under nitrogen atmosphere. At 120 °C the temperature was held for 15 min. An amount of around 15 mg was usually analysed. Gas chromatography analysis was performed on a Varian GC equipped with a VF-ms capillary column and a FID detector. ^{1}H-NMR spectra were obtained from a Varian 400 MHz spectrometer. Solid state ^{13}C-NMR was carried out at 500 MHz with a double 4.0 mm double resonance MAS probe head at room temperature using a Bruker Advance III spectrometer. The MAS rate was 13.3 kHz in all experiments. ^{1}H-^{13}C cross-polarisation (CP) spectra were acquired using 30000 scans, a recycle delay of 5 s and a Hartmann-Hahn contact time of 2000 µs. Three other ^{1}H-^{13}C CP experiments were carried out on the unwashed **IL2** using contact times of 750, 250 and 75 µs. The ^{13}C chemical shifts were referenced to adamantane by the substitution method where the $–CH_2$- peak in adamantane was set to be at 38.48 ppm.[1] Experimental analyses were performed from by Mikroanalytisches Laboratory Kolbe (Germany). N_2-physisorption isotherms were recorded with a Micromeritics Tristar 3000 at -196 °C. The samples were initially dried at 80 °C under vacuum, before a further drying step prior to performing the measurements for at least 16 h at 100 °C in a N_2 flow. The surface area was determined using the Brunauer-Emmett-Teller (BET) theory. The total pore volume was defined as the single-point pore volume at $p/p_o = 0.95$.

Substituted imidazole and imidazolium-2-carboxylate syntheses

Those 1-alkylimidazoles that could not be purchased were synthesised using a previously published alkylation reaction.[2] In a typical reaction 1.2 eq. of sodium hydride were dissolved in 50

mL dry dimethyl formamide (DMF) and the temperature lowered to 0 °C. 1 eq. imidazole was added and the solution was allowed to stir under an argon atmosphere for 45 min, during which evolution of bubbles was observed. 1.05 eq. bromoalkane was added and the reaction stirred for a further 18 h at room temperature. On completion of the reaction, DMF was removed *in vacuo*. The resulting residue was dissolved in a 1:1 mixture of water and ethyl acetate. The solution was washed with brine solution and the product extracted in ethyl acetate. The organic solution was dried over sodium sulphate and concentrated *in vacuo*. The crude product was purified using column chromatography and analysed by ^{1}H NMR. The recorded spectra were compared with known literature examples.

1-hexylimidazole ($CDCl_3$, 400 MHz): δ = 7.46 (s, 1H, NC*H*N), 7.05 (s, 1H, NC*H*CH), 6.90 (s, 1H, NCHC*H*), 3.92 (t, 2H, NC*H*$_2$CH$_2$(CH$_2$)$_3$CH$_3$), 1.77 (quint., 2H, NCH$_2$C*H*$_2$(CH$_2$)$_3$CH$_3$), 1.30 (m, 6H, NCH$_2$CH$_2$(C*H*$_2$)$_3$CH$_3$), 0.88 (t, 3H, NCH$_2$CH$_2$(CH$_2$)$_3$C*H*$_3$) ppm.

1-decylimidazole ($CDCl_3$, 400 MHz): δ = 7.47 (s, 1H, NC*H*N), 7.06 (s, 1H, NC*H*CH), 6.90 (s, 1H, NCHC*H*), 3.92 (t, 2H, NC*H*$_2$CH$_2$(CH$_2$)$_7$CH$_3$), 1.77 (quint., 2H, NCH$_2$C*H*$_2$(CH$_2$)$_7$CH$_3$), 1.29-1.25 (m, 14H, NCH$_2$CH$_2$(C*H*$_2$)$_7$CH$_3$), 0.88 (t, 3H, NCH$_2$CH$_2$(CH$_2$)$_7$C*H*$_3$) ppm.[3]

1,5-substituted imidazoles were synthesised using a van Leusen synthesis.[4] In a typical reaction, methylamine hydrochloride (3 eq.) and sodium hydroxide (3 eq.) were dissolved in 30 mL methanol and stirred for 5 min at room temperature. 1.5 eq. of the relevant aldehyde was added and the reaction stirred for a further 3 h. *p*-Toluenesulphonylmethyl isocyanide (1 eq.), dissolved in a 1:1 mixture of dichloromethane and methanol, was then added to the reaction and the reaction mixture was stirred for 18 h at room temperature. On completion of the reaction, solvent was removed *in vacuo*. The resulting residue was dissolved in a 1:1 mixture of water and ethyl acetate, washed with brine solution and the product extracted in ethyl acetate. The organic solution was dried over sodium sulphate and concentrated. The crude product was purified using column chromatography and analysed by ^{1}H NMR. The recorded spectra were compared with known literature examples.

5-phenyl-1-methylimidazole (**8**) ($CDCl_3$, 400 MHz): δ = 7.47 (s, 1H, NC*H*N,7.38 (m, 5H, NCHC(C$_6$*H*$_5$)), 7.05 (s, 1H, NC*H*C(C$_6$H$_5$)), 3.62 (s, 3H, CHNC*H*$_3$) ppm.[4]

1,5-dimethylimidazole (**9**) ($CDCl_3$, 400 MHz): δ = 7.40 (s, 1H, NC*H*N), 6.78 (s, 1H, NC*H*C(CH$_3$)), 3.52 (s, 3H, CHNC*H*$_3$), 2.16 (s, 3H, NCHC(C*H*$_3$)) ppm.[5]

5-*n*-butyl-1-methylimidazole (**10**) ($CDCl_3$, 400 MHz): δ = 7.38 (s, 1H, NC*H*N), 6.77 (s, 1H, NC*H*C(C*H*$_2$CH$_2$CH$_2$CH$_3$)), 3.54 (s, 3H, CHNC*H*$_3$), 2.52 (t, 2H, NCHC(C*H*$_2$CH$_2$CH$_2$CH$_3$)), 1.61 (q, 2H, NCHC(CH$_2$C*H*$_2$CH$_2$CH$_3$)), 1.40 (q, 2H, NCHC(CH$_2$CH$_2$C*H*$_2$CH$_3$)), 0.95 (t, 3H, NCHC(CH$_2$CH$_2$CH$_2$C*H*$_3$)) ppm. HRMS (ESI) Theoretical 139.1235 Found 139.1225, $C_8H_{15}N_2$ ($M+H^+$).

1,3-dimethyl-imidazolium-2-carboxylate (**1**) was synthesised with an adapted literature method.[6, 7] In a screw-top pressure tube 2 mL 1-methylimidazole was combined with 3 mL dimethyl carbonate and stirred for 24 h at 90 °C. The reaction mixture, a white solid in an orange-brown supernatant, was filtered and the resulting white crystals washed with dichloromethane (3 x 15 mL), acetone (3 x 15 mL) and diethyl ether (2 x 15 mL). The solid was dried under vacuum at ambient

temperature to give an isolated yield of 87%. The solid was characterised by HR-MS and ^{1}H NMR, with the spectrum being consistent with literature data.[7]

^{1}H NMR (D_2O, 400 MHz): δ = 3.99 (s, 6H, N-C<u>*H*₃</u>), 7.37 (s, 2H, C4-<u>*H*</u> and C5-<u>*H*</u>) ppm. HRMS (ESI) Theoretical: 141.0664. Found: 141.1226, $C_6H_8N_2O_2$ ($M+H^+$).

1-butyl-3-methylimidazolium-2-carboxylate (**2**) was synthesised with an adapted literature method.[8] Into an oven-dried flask under argon, 0.60 g 1-butyl-3-methylmidazolium bromide and 0.60 g potassium bis(trimethylsilylamide) (KHMDS) were added. 40 mL dry THF was added under stirring at -80 °C. The solution was allowed to slowly come to room temperature and was stirred for a further 40 hours. The subsequent white precipitate was filtered under argon and the transparent orange solution was collected. A balloon of CO_2 was then introduced and the solution became opaque. This solution was stirred for 1 h, after which the opaque solution was concentrated *in vacuo* to yield an orange-yellow solid. The solid was washed with dry diethyl ether and dried *in vacuo* yielding the desired product (14% isolated yield), which was characterised by ^{1}H and ^{13}C NMR, with the spectra being in accordance with literature.[7]

^{1}H NMR (D_2O, 400 MHz): δ = 0.90 (t, 3H, C<u>*H*₃</u>), 1.29 (m, 2H, C<u>*H*₂</u>), 1.80 (m, 2H, C<u>*H*₂</u>), 3.96 (s, 3H, N-C<u>*H*₃</u>), 4.40 (t, 2H, N-C<u>*H*₂</u>), 7.39 (d, 1H, C5-<u>*H*</u>), 7.43 (d, 1H, C4-<u>*H*</u>) ppm. ^{13}C NMR (D_2O, 400 MHz): δ = 12.54 (CH_2-<u>*C*</u>H_3), 18.70 (CH_3-<u>*C*</u>H_2), 31.76 (CH_2-<u>*C*</u>H_2), 36.31 (N-<u>*C*</u>H_3), 49.24 (N-<u>*C*</u>H_2), 121.63 (<u>*C*</u>*H*), 122.98 (<u>*C*</u>*H*), 139.88 (<u>*C*</u>-*CO*$_2$), 158.44 (C-<u>*C*</u>O_2) ppm

1,2,3-trimethyl-imidazolium-4-carboxylate (**3**) was synthesised with an adapted literature method.[6, 7] In a screw-top pressure tube 1 mL 1,2-dimethylimidazole was combined with 2 mL dimethyl carbonate and stirred for 23 h at 84 °C. The reaction mixture, a white solid in an orange-brown supernatant, was filtered and the resulting white crystals washed with dichloromethane (3 x 15 mL), acetone (3 x 15 mL) and diethyl ether (2 x 15 mL). The solid was dried under vacuum at ambient temperature to give an isolated yield of 3%. The solid was characterised by ^{1}H NMR and ^{13}C NMR.

^{1}H NMR (D_2O, 400 MHz): δ = 2.56 (s, 3H, C-C<u>*H*₃</u>), 3.76 (s, 6H, N-C<u>*H*₃</u>), 7.28 (s, 1H, C5-<u>*H*</u>) ppm. ^{13}C NMR (D_2O, 400 MHz): δ = 8.51 (C-<u>*C*</u>H_3), 34.41 (N-<u>*C*</u>H_3), 121.63 (<u>*C*</u>*H*), 144.60 (<u>*C*</u>-CH_3), 160.24 (C-<u>*C*</u>*O*$_2$), 221.80 (<u>*C*</u>-CO_2)

1,3-dimethyl-imidazolium-4-carboxylate (**4**) was synthesised with an adapted literature method.[6, 7] In a screw-top pressure tube 2 mL 1-methylimidazole was combined with 3 mL dimethyl carbonate and stirred for 40 h at 120 °C. The reaction mixture, a white solid in an orange-brown supernatant, was filtered and the resulting white crystals washed with dichloromethane (3 x 15 mL), acetone (3 x 15 mL) and diethyl ether (2 x 15 mL). The solid was dried under vacuum at ambient temperature to give an isolated yield of 79%. The solid was characterised by ^{1}H NMR, with the spectra being consistent with literature data.[7]

^{1}H NMR (D_2O, 400 MHz): δ = 3.89 (s, 3H, N-C<u>*H*₃</u>), 4.01 (s, 3H, N-C<u>*H*₃</u>), 7.71 (s, 1H, C5-<u>*H*</u>) ppm. ^{13}C NMR (D_2O, 400 MHz): δ = 35.56 (C-<u>*C*</u>H_3), 35.65 (N-<u>*C*</u>H_3), 126.13 (<u>*C*</u>*H*), 130.61 (<u>*C*</u>*H*), 138.10(<u>*C*</u>-*CO*$_2$), 163.26 (C-<u>*C*</u>O_2) ppm. HRMS (ESI) Theoretical 141.0664. Found 141.1219, $C_6H_8N_2O_2$ ($M+H^+$).

Reaction analysis

All products of the catalytic reactions have previously been reported in literature. The ^{1}H NMR data listed below was used to identify the species present in our reaction mixtures. ^{1}H NMR analysis was chosen due to the thermal instability of the product (DGDC), which rules out the possibility of gas chromatography analysis. Carbon balance is defined as amount of total carbon of the starting substrate and detected products divided by the total amount of carbon of the substrate at the beginning of the reaction, as a percentage.

glycerol carbonate: ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 5.29 (t, 1H, O*H*), 4.80 (m, 1H, C*H*), 4.49 (dd, 1H, C*H*$_2$(O)CH), 4.28 (dd, 1H, C*H*$_2$(O)CH), 3.65 (ddd, 1H, C*H*$_2$OH), 3.50 (ddd, 1H, C*H*$_2$OH) ppm.[9]

diglycerol dicarbonate: ^{1}H NMR (DMSO-d_6, 400 MHz,) δ = 4.94 (*m,* 2H) C*H*(CH$_2$)$_2$O, 4.52 (*t,* 2H) and 4.23 (*q, 2H*) C*H*$_2$(O)CH, 3.73 (*m,* 4H) C*H*$_2$(O)CH ppm.[10]

ethylene carbonate ([1,3]-Dioxolan-2-one): ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 4.48 (s, 4H, C*H*$_2$) ppm.[11]

1,2-propylene carbonate (4-Methyl-[1,3]-Dioxolan-2-one): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.79 (m, 1H, C*H*), 4.50 (m, 1H, C*H*$_2$), 3.97 (m, 1H, C*H*$_2$), 1.43 (dd, 3H, C*H*$_3$) ppm.[12]

1,2-butylene carbonate (4-Ethyl-[1,3]-Dioxolan-2-one): ^{1}H NMR (CD_3OD, 400 MHz): δ = 4.63 (p, 1H, C*H*), 4.48 (t, 1H, C*H*$_2$), 4.04 (t, 1H, C*H*$_2$), 1.76 (m, 2H, C*H*$_2$), 1.00 (t, 3H, C*H*$_3$) ppm.[12]

propane 1,3-carbonate ([1,3]-Dioxan-2-one) (**12**): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.25 (t, 4H, C*H*$_2$), 2.07 (q, 2H, C*H*$_2$) ppm.[13]

3-methoxycarbonyloxypropan-1-ol (**13**): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.24 (t, 2H, C*H*$_2$), 3.73 (s, 3H, C*H*$_3$), 3.67 (t, 2H), 2.54 (t, 1H), 1.86 (q, 2H, C*H*$_2$) ppm.[13]

propane-1,3-diyl dimethyl dicarbonate (**14**): ^{1}H NMR ($CDCl_3$,400 MHz) δ = 4.24 (t, J = 6.2 Hz, 4H, C*H*$_2$), 3.78 (s, 6H, C*H*$_3$), 2.04 (m, J = 6.2 Hz, 2H, C*H*$_2$) ppm.[14]

butane 1,3-carbonate (1-methyl-trimethylene carbonate) (**15**): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.90 (m, 1H), 4.22 (m, 2H), 1.96 (m, 2H), 1.35 (d, 3H) ppm.[13]

3-methoxycarbonyloxybutan-1-ol (**17**): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.39 (m, 1H), 4.26 (m, 1H), 3.96 (m, 1H), 3.80 (s, 3H), 2.00 (d, 1H), 1.85 (m, 1H), 1.76 (m, 1H), 1.25 (d, 3H) ppm.[13]

butane-1,3-diyl dimethyl dicarbonate (**18**): ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 4.94–4.84 (m, 1H), 4.21 (t, J = 6.3 Hz, 2H), 3.78 (s + s, 6H), 2.05–1.87 (m, 2H), 1.32 (d, J =6.3 Hz, 3H) ppm.[13]

butane-2,3-carbonate:[15]

(*R,R*) and (*S,S*)-4,5-dimethyl-1,3-dioxolan-2-one: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.30 (m, 2H), 1.42 (d, 6H) ppm.

meso-4,5-dimethyl-1,3-dioxolan-2-one: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.80 (m, 2H), 1.33 (d, 6H) ppm.

Mechanistic study: Reactions were run between $^{13}C_3$-Dimethyl carbonate and 1,3-dimethylimidazolium-2-carboxylate in a 1.5:1 molar ratio in DMSO-d_6 at 74 ^{o}C for 18 h. ^{1}H, ^{13}C and HMBC NMR experiments were run and signal assignments made.

Silylation of the sample

For gas chromatography analysis, it is necessary to silylate samples in order to detect both glycerol and glycerol carbonate, as well as any other alcohol group containing by-products. To the reaction mixtures of 0.1 g scale with respect to glycerol, 2 mL of pyridine stock containing 5 wt.% dodecanol as standard was added This was allowed to stir at room temperature overnight to ensure full solubility of the compounds. 1.60 mL of 1,1,1,3,3,3-hexamethyldisilazane and 0.80 mL of chlorotrimethylsilane were then added and this mixture was then stirred for an hour at 70 °C.

Table S1: Influence of dimethyl carbonate/diglycerol ratio on diglycerol dicarbonate yield.

DMC/DG Molar ratio	Di-cyclic Yield (%)	Di-cyclic Selectivity (%)	Mono-cyclic carbonate Yield (%)	Mono-cyclic carbonate Selectivity (%)	C-balance (%)
3	64	85	6	8	94
6	78	94	8	9	103
9	63	83	13	18	99

Conditions: 2.0 g diglycerol, 5 mol% 1,3-dimethylimidazolium-2-carboxylate synthesised *in situ*, 74 ^{o}C, 18 h.

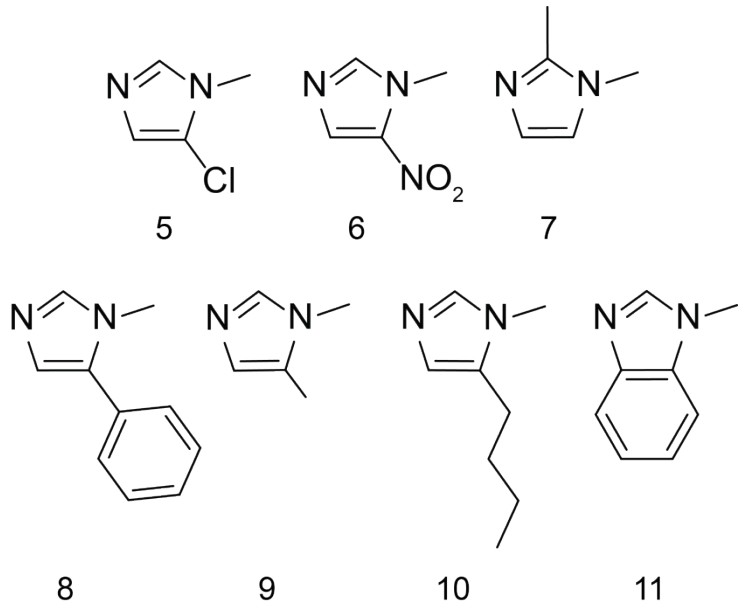
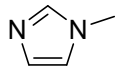
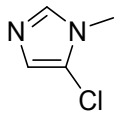
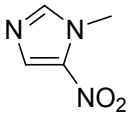
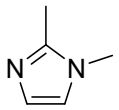
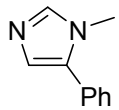
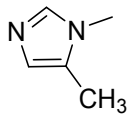
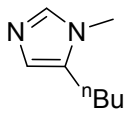
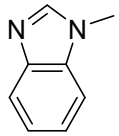


Figure S1: Substituted 1-methylimidazoles tested as catalyst precursors for diglycerol cyclocarbonation.

Table S2: Activity of 2- or 5-substituted 1-methylimidazoles for the conversion of diglycerol.

Catalyst precursor	Conversion (%)	Di-cyclic Yield (%)	Di-cyclic Selectivity (%)	Mono-cyclic carbonate Yield (%)	Mono-cyclic carbonate Selectivity (%)	C-balance (%)
	97	78	94	8	9	103
	13	0	-	4	40	92
	5	0	-	4	98	100
	29	3	11	16	67	94
	6	0	-	5	91	99
	14	0	-	9	70	96
	18	0	-	8	56	92
	6	0	-	5	98	100

Conditions: 0.5 g diglycerol, 5 mol% precursor, 74 °C, 18 h, DMC:DG 6:1.

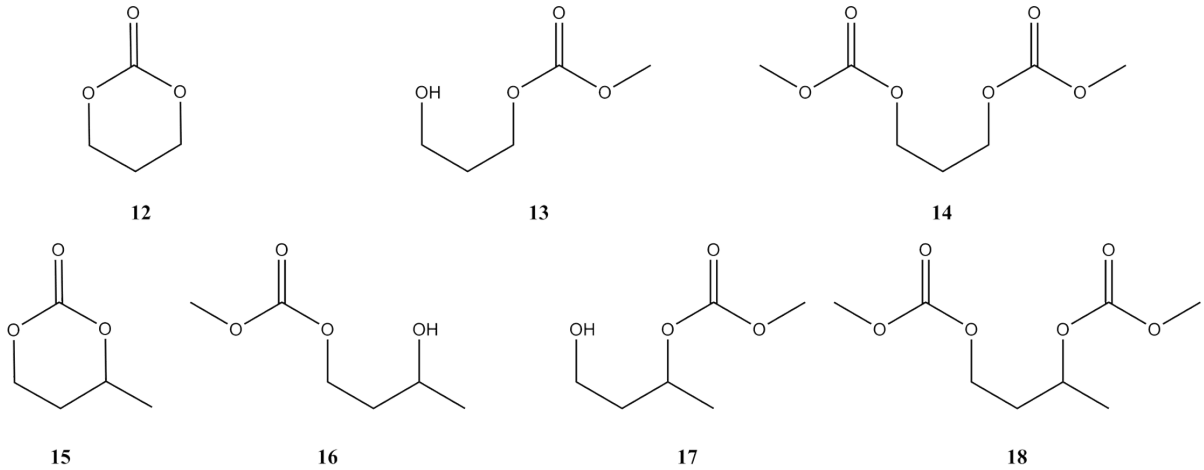


Figure S2: Potential products of 1,3-diols for the reaction with DMC.

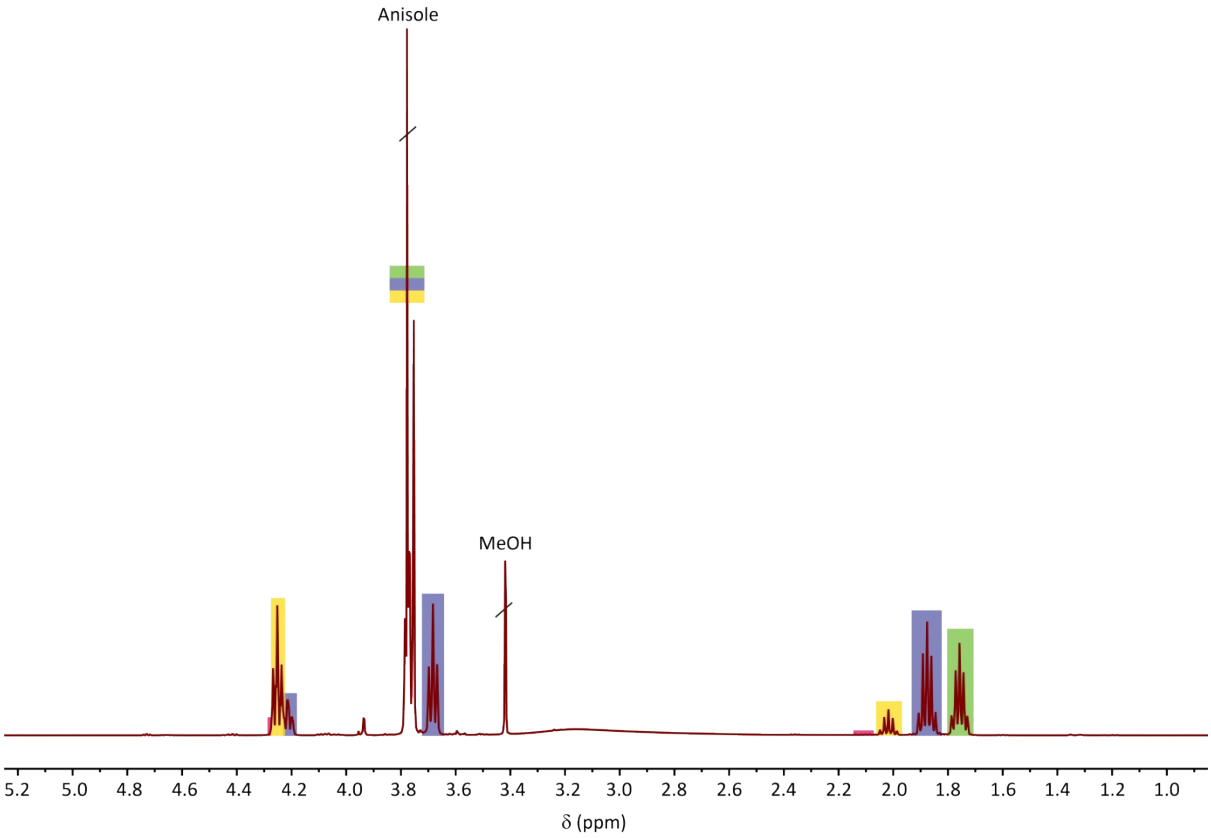


Figure S3: ^{1}H NMR spectra in $CDCl_3$ of reaction between 1,3-PD and DMC, with **1** as catalyst. Anisole was used as an internal standard. The mixture contains 1,3-PD (green), **13** (purple), **14** (yellow) and **12** (red). Stacked colours around 3.75 ppm is due to overlap of a number of compounds.

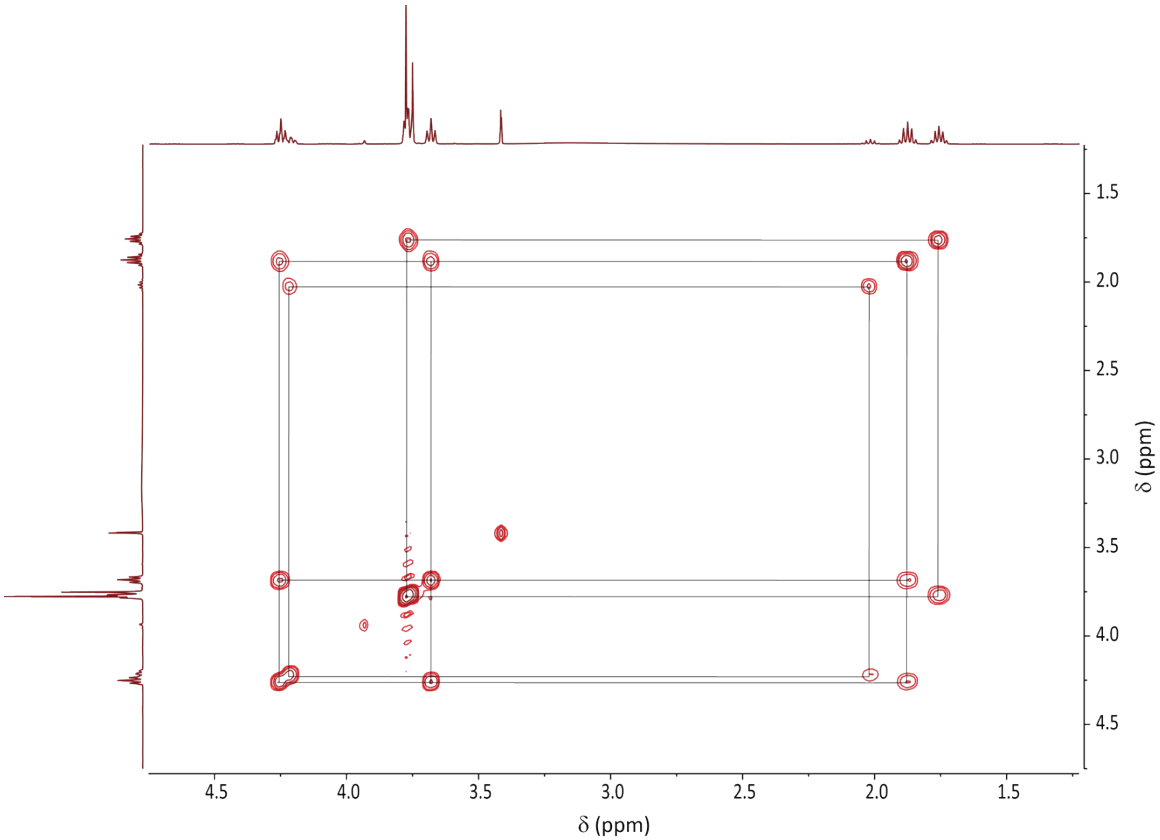


Figure S4: ^{1}H-^{1}H TOCSY MR spectra in $CDCl_3$ of reaction between 1,3-PD and DMC, with **1** as catalyst.

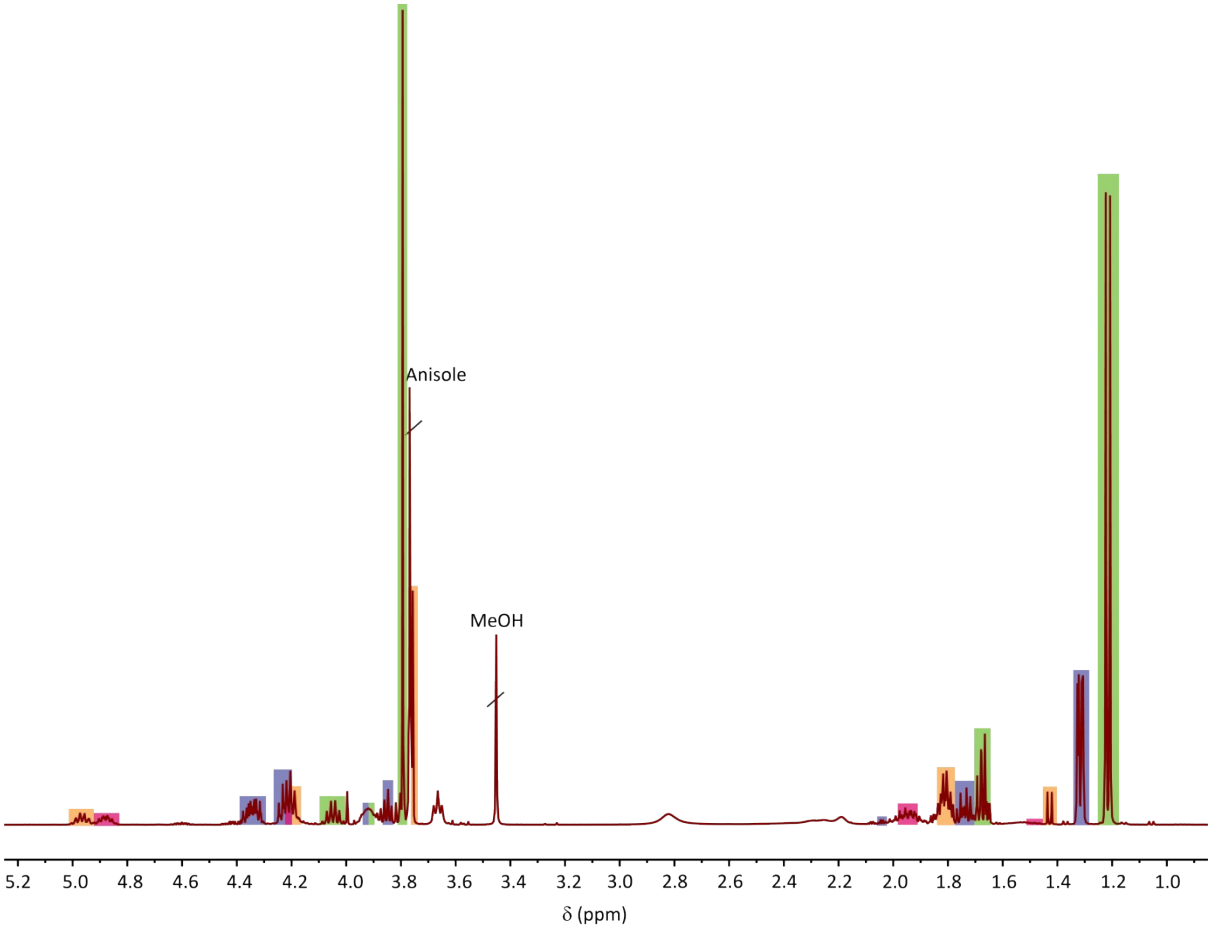


Figure S5: ^{1}H NMR spectra in $CDCl_3$ of reaction between 1,3-BD and DMC, with **1** as catalyst. Anisole was used as an internal standard. The mixture contains 1,3-BD (green), **16** (purple), **18** (orange) and **15** (red). The mixture also contains **17**, which is not fully distinguishable with ^{1}H-NMR.

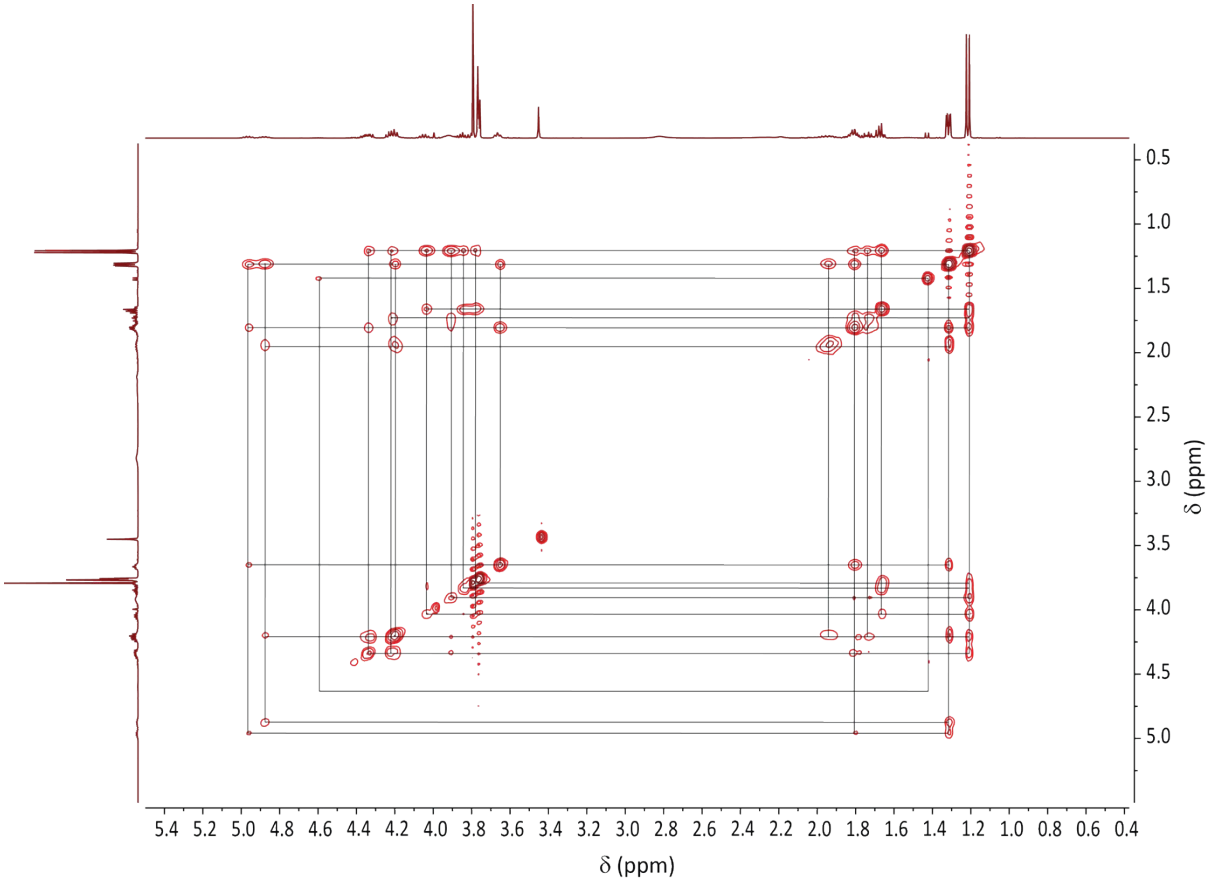


Figure S6: ^{1}H-^{1}H TOCSY NMR spectra in $CDCl_3$ of reaction between 1,3-BD and DMC, with **1** as catalyst.

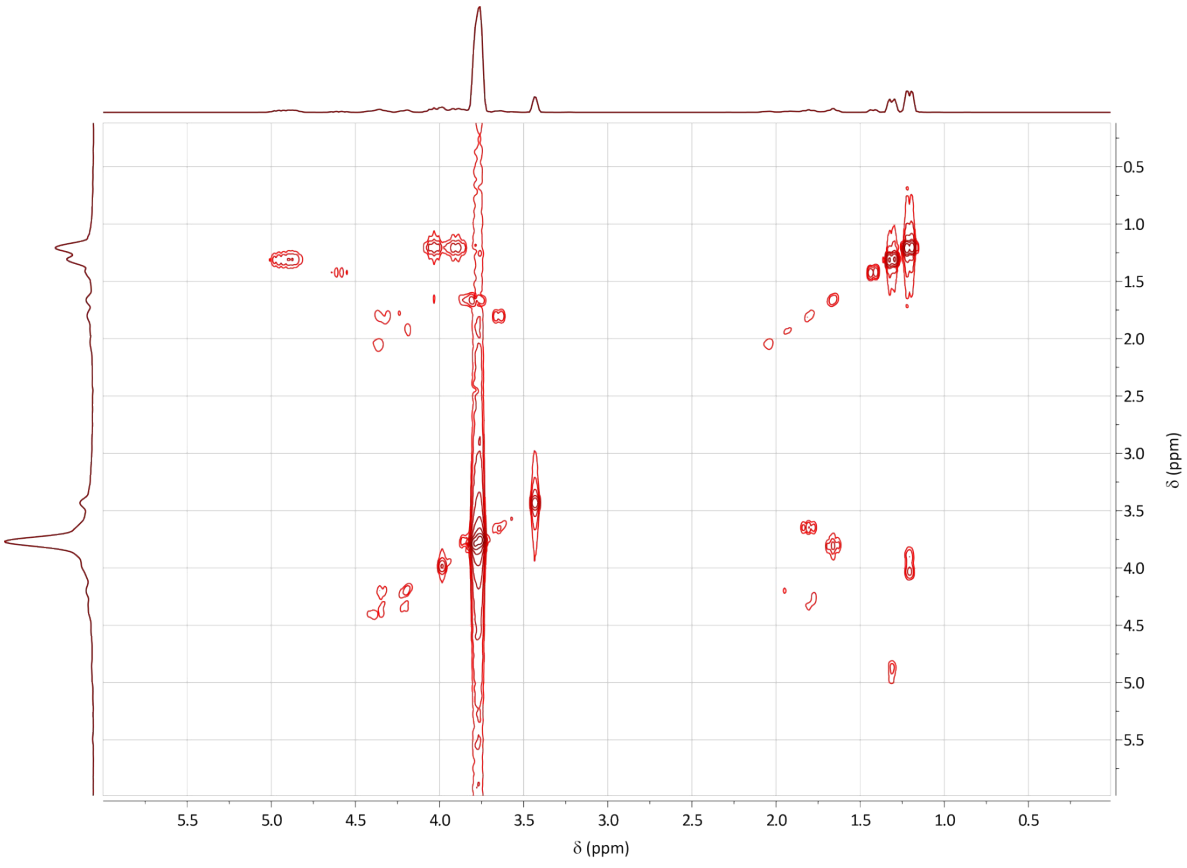


Figure S7: ^{1}H-^{1}H COSY NMR spectra in $CDCl_3$ of reaction between 1,3-PD and DMC, with **1** as catalyst.

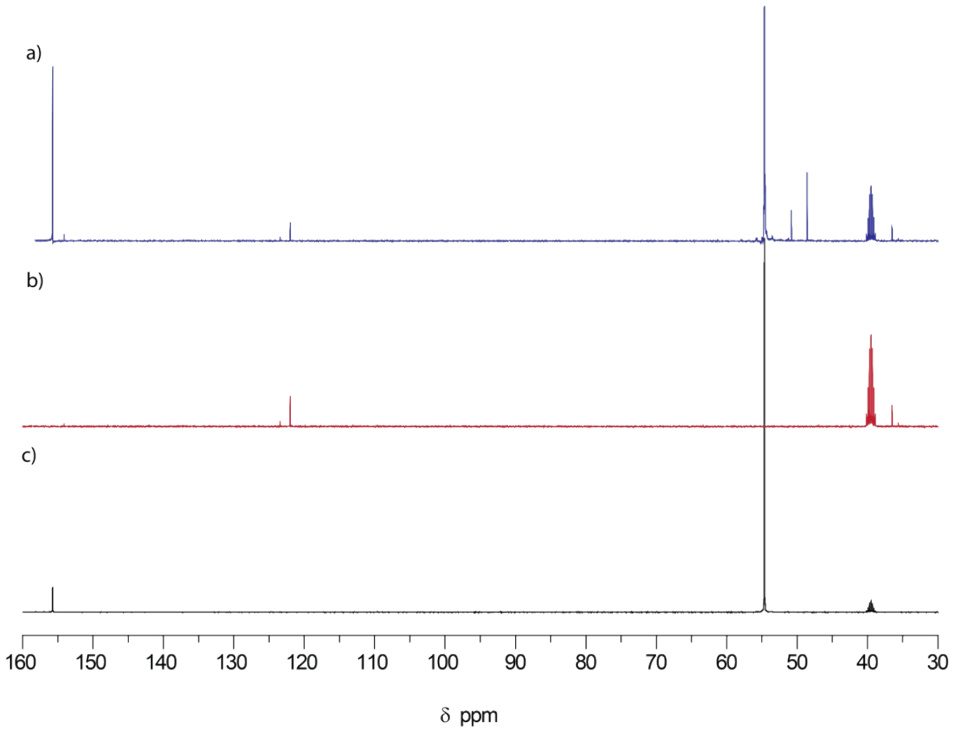


Figure S8: ^{13}C-NMR comparison of a) Reaction between $^{13}C_3$-DMC and **1**, b) **1** and c) $^{13}C_3$-DMC all in DMSO-d_6.

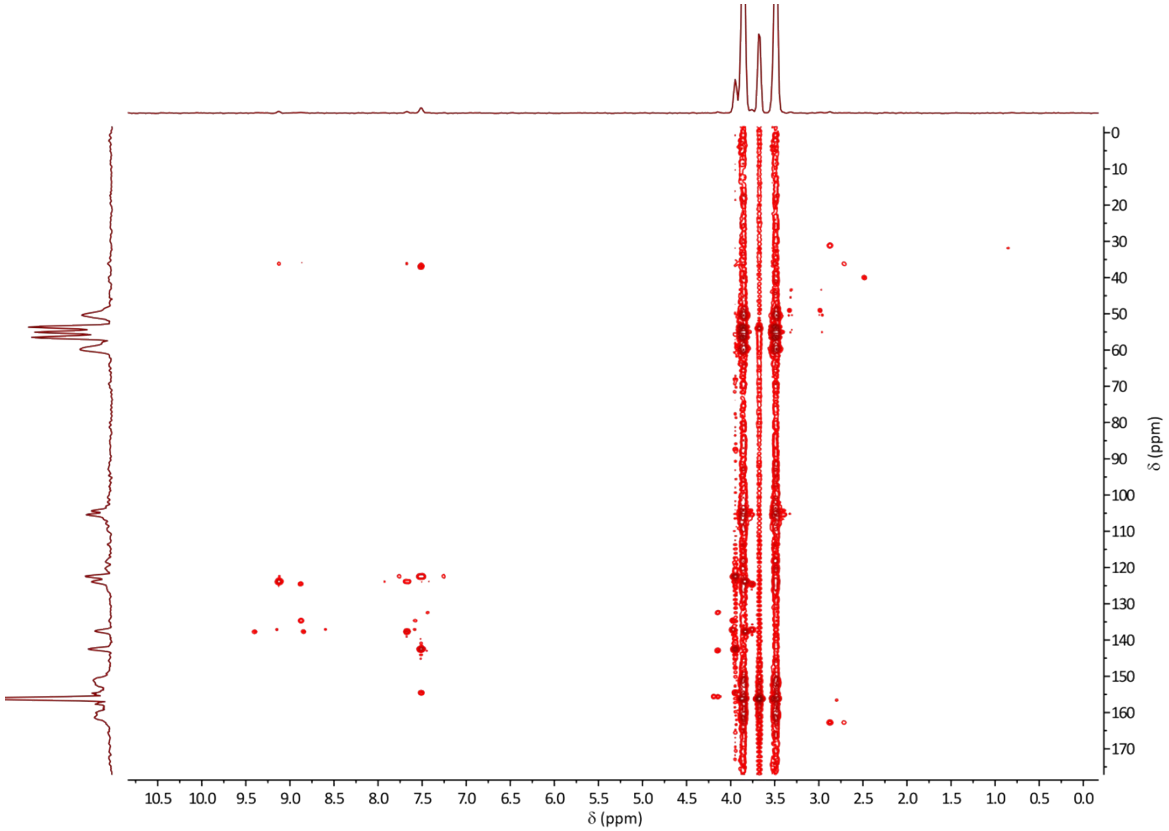


Figure S9: ^{1}H-^{13}C HMBC NMR spectra in DMSO-d_6 of **1** and $^{13}C_3$-DMC.

Heterogenised organocatalyst

MCF synthesis

A modified MCF synthesis was employed.[16] 4 g of Pluronic P123 were dissolved in an acidic solution of 20 mL conc. HCl (37 wt.%) and 130 mL deionized H_2O in a PE-bottle. The mixture was stirred overnight at room temperature. 4 g 1,2,3-trimethylbenzene (TMB) were added dropwise and the resulting solution was heated to 34.2 °C with vigorous stirring for 4 h. 9.2 mL of tetraethyl orthosilicate (TEOS) was then added at once and the solution was stirred for 5 min. After removing the stir bar the solution was aged at 39 °C for 20 h under static conditions. A total of 46 mg NH_4F were dissolved in 5 mL HCl (37%) and added dropwise to the PE-bottle under stirring. The molar ratio was 1 TEOS : 0.0167 P123 : 0.808 TMB : 0.030 NH_4F : 6.150 HCl : 175.29 H_2O. The mixture was then hydrothermally treated at 90 °C for 24 h. The mixture was cooled down under ambient conditions. The precipitate was then filtered and washed with deionised water until reaching a neutral pH value (>500 mL) and then with ethanol. The solid was dried at 60 °C overnight. The white solid was calcined in air at 550 °C for 6 h with a ramp of 5 °C/min. The mesoporous material yielded was characterised by DRIFTS (cm^{-1}): 3747, 1988, 1878, 1625, 1363, 1206, 1058, 976, 829. The specific surface area was evaluated from nitrogen physisorption data using Brunauer-Emmett-Teller method.

MCF functionalisation

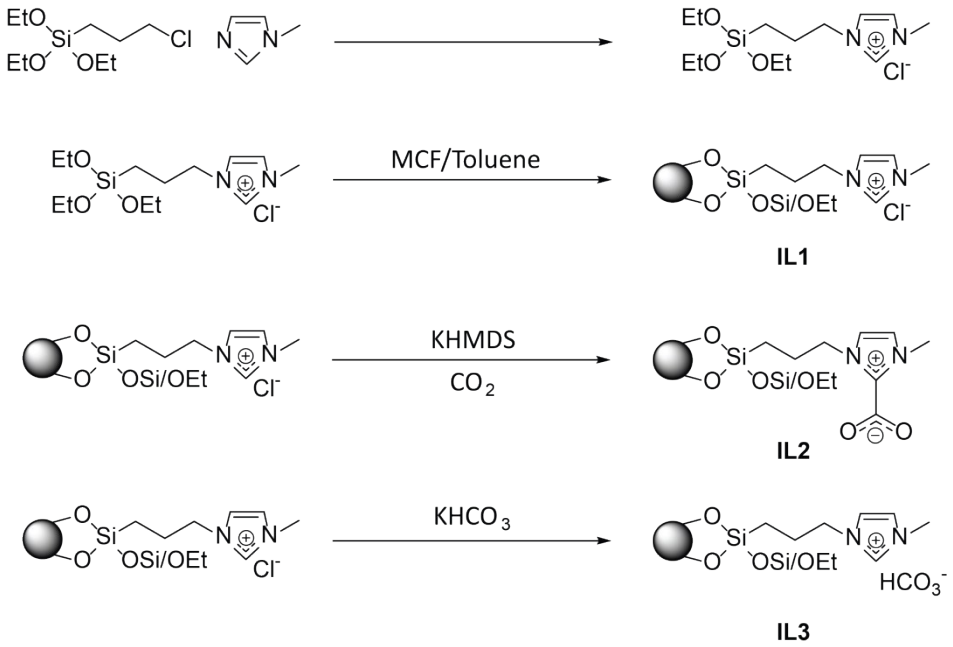


Figure S10: Synthesis of functionalised MCF; targeted products: **IL1** – imidazolium chloride, **IL2** – imidazolium-2-carboxylate, **IL3** – Imidazolium hydrogen carbonate.

1-methyl-3-(3-triethoxysilylpropyl) imidazolium chloride was synthesised in accordance with literature.[17] 1-methylimidazole (2.5 mL) and (3-chloropropyl)triethoxysilane (20 mL) were mixed in a dry 100 mL flask under argon. The mixture was stirred at 70 °C for 48 h. The reaction mixture was cooled and the mixture washed with dry diethyl ether to remove unreacted reactants, before being dried under vacuum.

1-methyl-3-(3-triethoxysilylpropyl) imidazolium chloride: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.58 (m, 2H, 1.18 (t, 9H), 1.98 (m, 2H), 3.79 (q, 6H), 4.09 (s, 3H), 4.30 (t, 2H), 7.32 (s, 1H), 7.62 (s, 1H), 10.58 (s, 1H) ppm.

A typical functionalisation procedure is as follows. 1 g of MCF was dried under vacuum at 200 °C. Upon cooling, 100 mL anhydrous toluene was added before 3 mmol of 1-methyl-3-(3-triethoxysilylpropyl) imidazolium chloride was added. The mixture was then refluxed for 24 h under argon. The resultant product (**IL1**) was filtered and washed with dichloromethane before being dried under vacuum at 80 °C. The functionalised mesoporous material was characterised; by DRIFTS: 3155, 3106, 2982, 2937, 2900, 1991, 1876, 1631, 1574, 1457, 1282, 1070, 944, 817, 623 cm^{-1}; by ^{13}C MAS-NMR: 137, 124, 59, 52, 36, 24, 17, 9 ppm; by TGA: the difference in weight loss observed above 180 °C with that of pristine silica was used to determine the extent of functionalisation.

Typical CO_2 protection of the catalyst is as follows. 0.5 g **IL1** was dried under vacuum at 80 °C. Once cooled, 1.05 eq. (with respect to the amount of functionalisation) of KHMDS was added, followed by 75 mL of anhydrous THF. The mixture was stirred for 3 h under argon, after which a balloon of CO_2 was introduced and bubbled through the solution while stirring. After 6 h, the mixture was filtered under argon and washed with methanol. The resulting CO_2-protected functionalised silica (**IL2**) was then dried at 65 °C under vacuum, and stored under argon.[18] The functionalised mesoporous material was characterised; by DRIFTS: 3155, 3116, 2962, 2932, 2874, 1983, 1868, 1633, 1579, 1525, 1459, 1352, 1238, 1053, 959, 866, 844, 807, 623 cm^{-1}; by ^{13}C MAS-NMR: 162, 138, 124, 62, 51, 37, 24, 10, -1 ppm; by TGA: the difference in weight loss observed above 180 °C with that of pristine silica was used to determine the extent of functionalisation.

The HCO_3 protected pre-catalyst was typically as follows. 0.5 g **IL1** was dried under vacuum at 80 °C. Once cooled, 100 mL deionised water was added followed by 1.02 eq. (with respect to the amount of functionalisation) dried $KHCO_3$.[19] The suspension was stirred at room temperature for 24 h, after which it was filtered and the silica washed with 250 mL deionised water. The resulting (H)HCO_3-protected carbene functionalised silica (**IL3**) was then dried at 65 °C under vacuum, and stored under argon.[19] The functionalised mesoporous material was characterised; by DRIFTS : 3158, 3119, 2966, 2938, 2899, 2878, 1994, 1871, 1642, 1576, 1460, 1309, 1207, 1061, 959, 815, 624 cm^{-1}; by ^{13}C MAS-NMR: 136, 123, 51, 36, 24, 8 ppm; by TGA: the difference in weight loss observed above 180 °C with that of pristine silica was used to determine the extent of functionalisation. Elemental analysis showed 80% of ion exchange.

For TGA, each sample was initially heated to 120 °C and held at this temperature for 15 min to ensure the loss of adsorbed solvents and water, this is observed in Figure S11 as the distinct peak at 120 °C in the weight loss derivative graph. The samples were then heated at a constant rate of 5 °C/min to 600 °C. For the pristine MCF sample, a very small percentage, 1.85%, was lost at higher temperatures and attributed to trapped template from the synthesis procedure.

For DRIFTS analysis, the broad band between 2900-3400 cm^{-1} and band at 1670 cm^{-1} are due to adsorbed water on the silica. The samples presented in Figure S12 were not dried, however drying under vacuum at 120 °C only slightly reduced this signal. As heating to higher temperatures may cause loss of functionalisation, it was chosen to present the results for the non-dried samples.

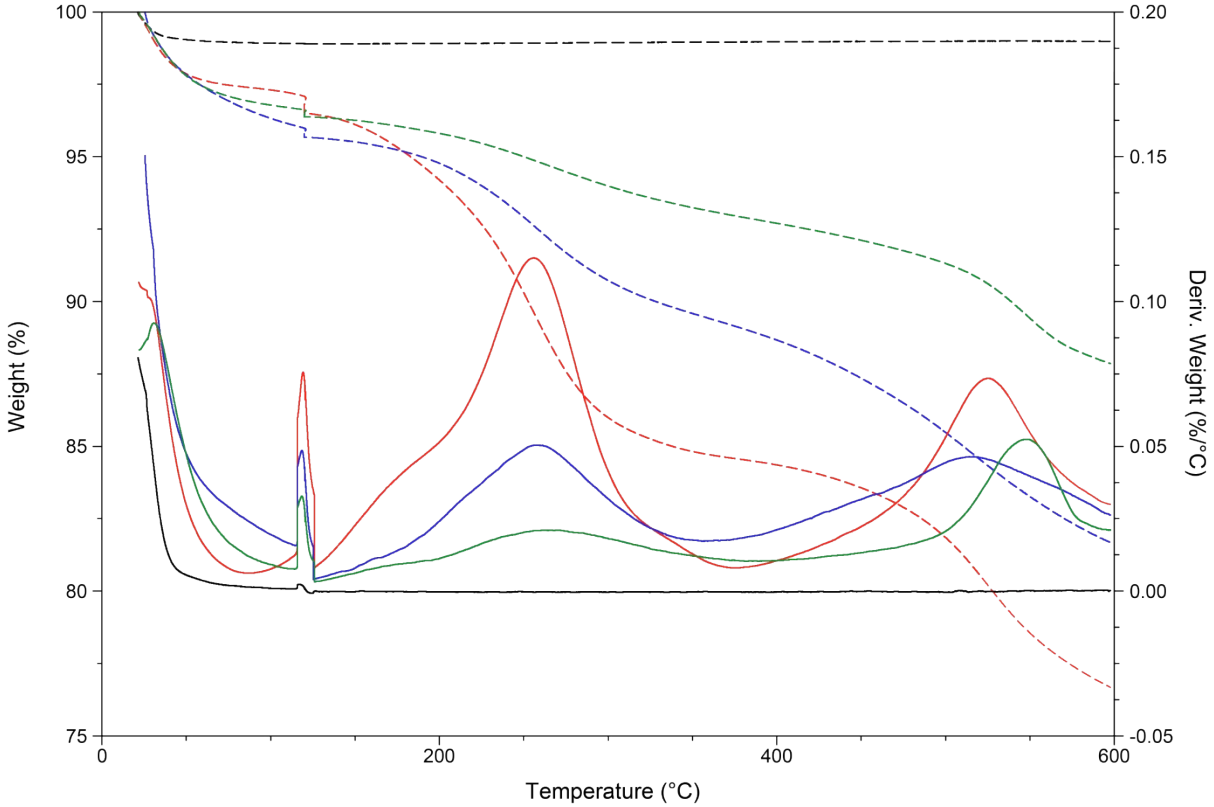


Figure S11: TGA of pristine MCF (black), **IL1** (red), **IL2** (blue) and **IL3** (green) showing the percentage weight loss and the weight loss derivative.

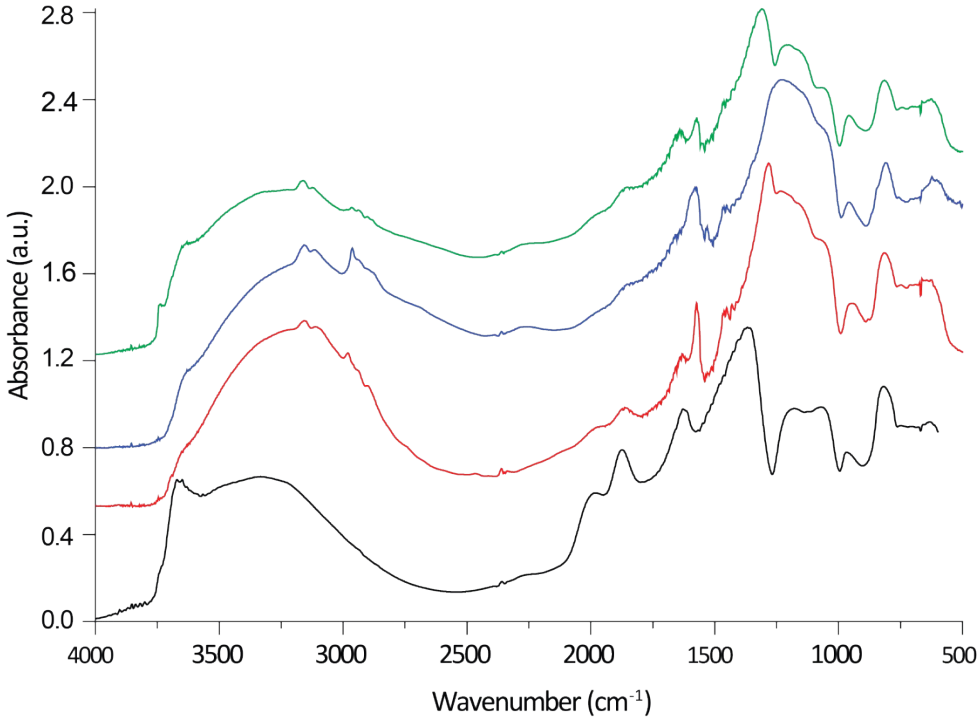


Figure S12: DRIFTS analysis of pristine MFC silica (black), **IL1** (red), **IL2** (blue) and **IL3** (green). The spectra are offset for clarity.

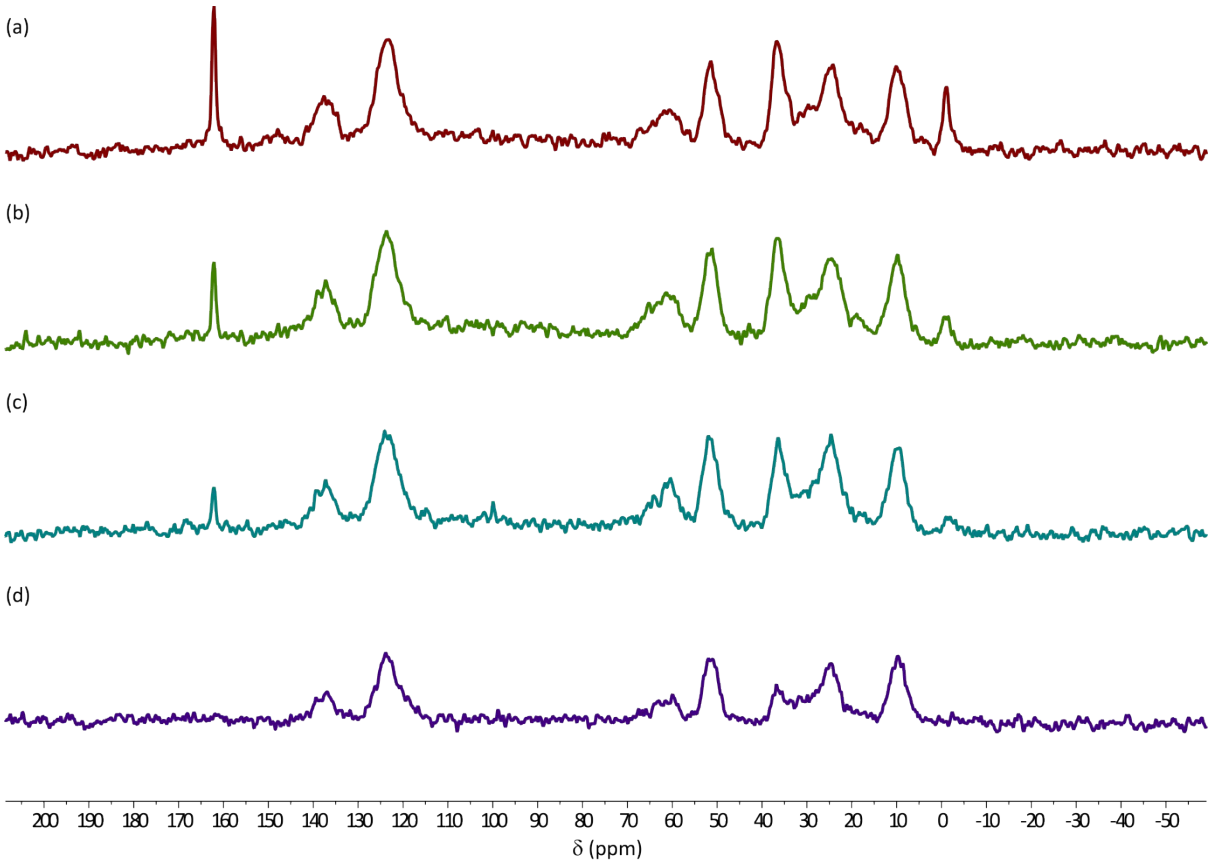


Figure S13: ^{1}H-^{13}C cross polarisation (CP) experiments of **IL2** with varying contact time; (a) 2000 µs, (b) 750 µs, (c) 250 µs, (d) 75 µs.

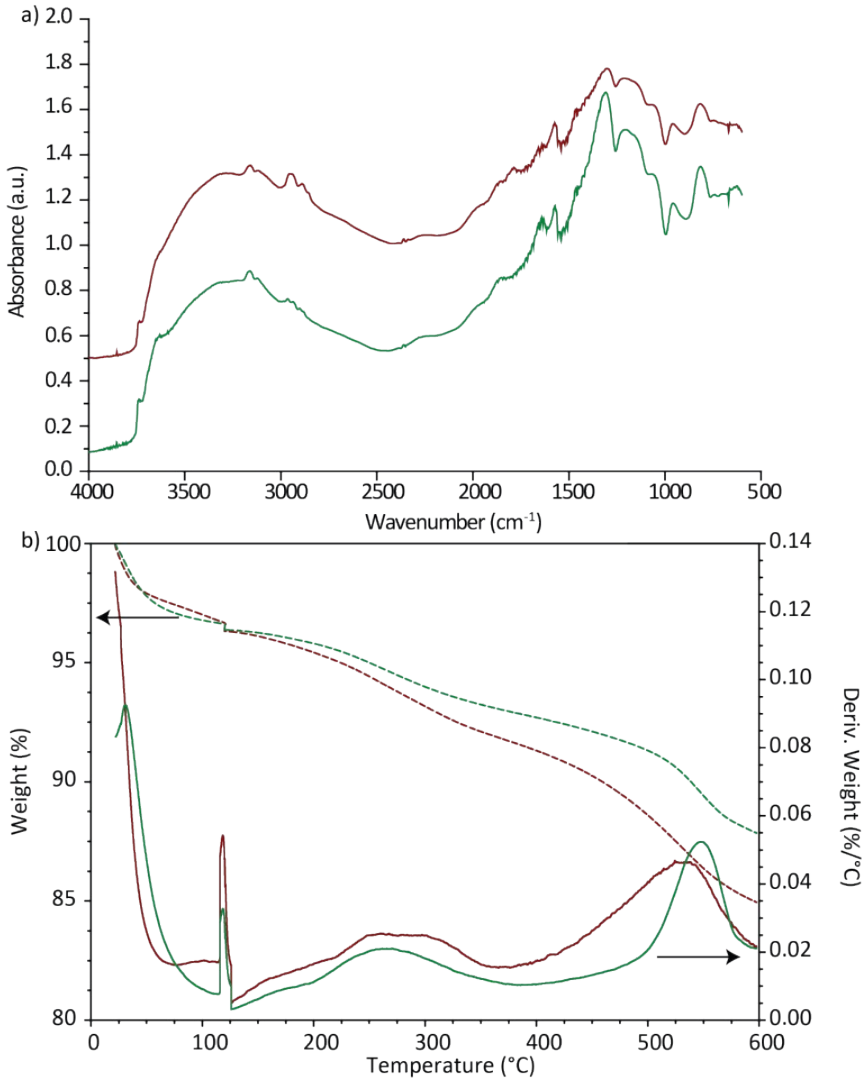


Figure S14: a) DRIFTS and b) TGA analysis of fresh and spent **IL3**, showing percentage weight loss and weight loss derivative. The spectra have been translated vertically for clarity.

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