Electronic Supplementary Information (ESI) for:

3-Methoxybutan-2-one as a sustainable bio-based alternative to chlorinated solvents

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1 ^{1}H NMR, GC-MS and UV-vis. spectrum

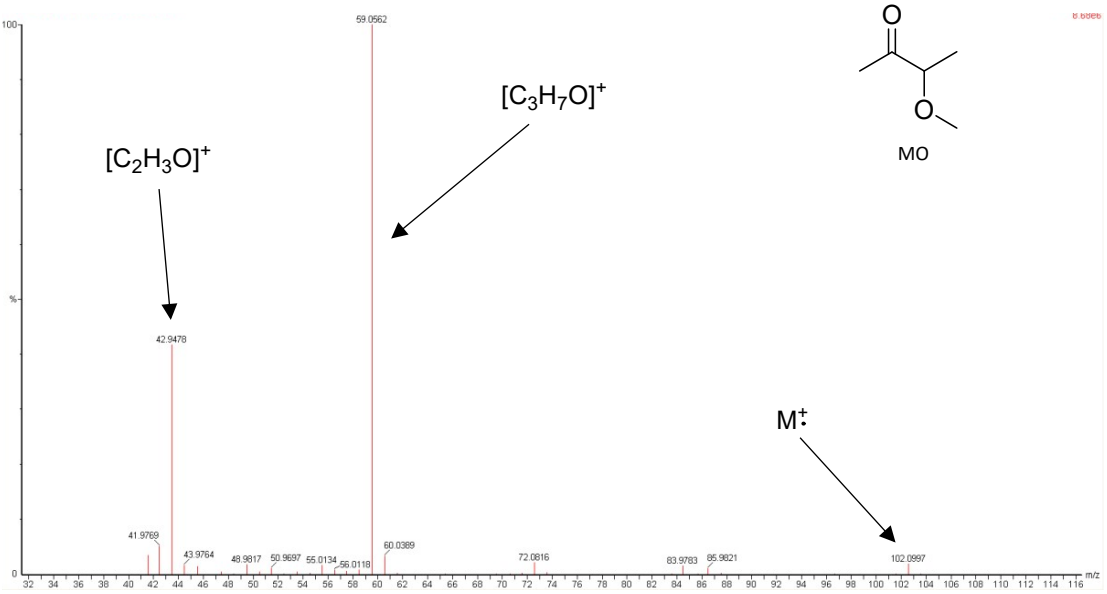

Fig. S1. Mass spectrum (EI) of MO.

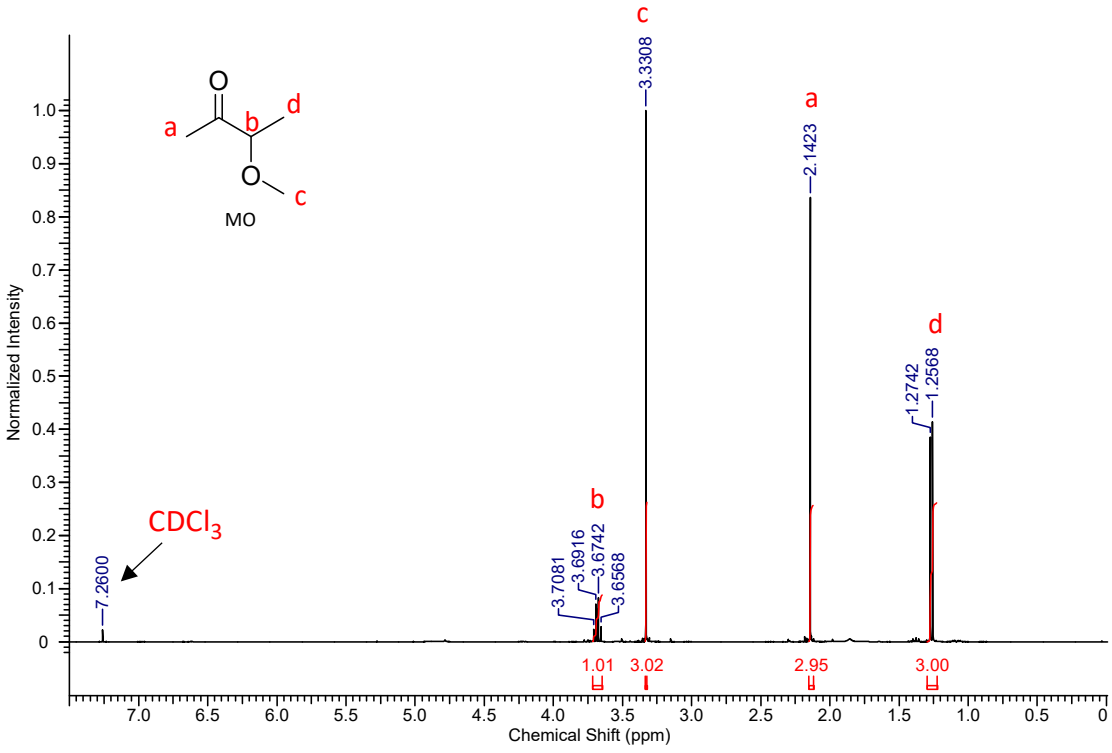

Fig. S2. ^{1}H NMR of MO.

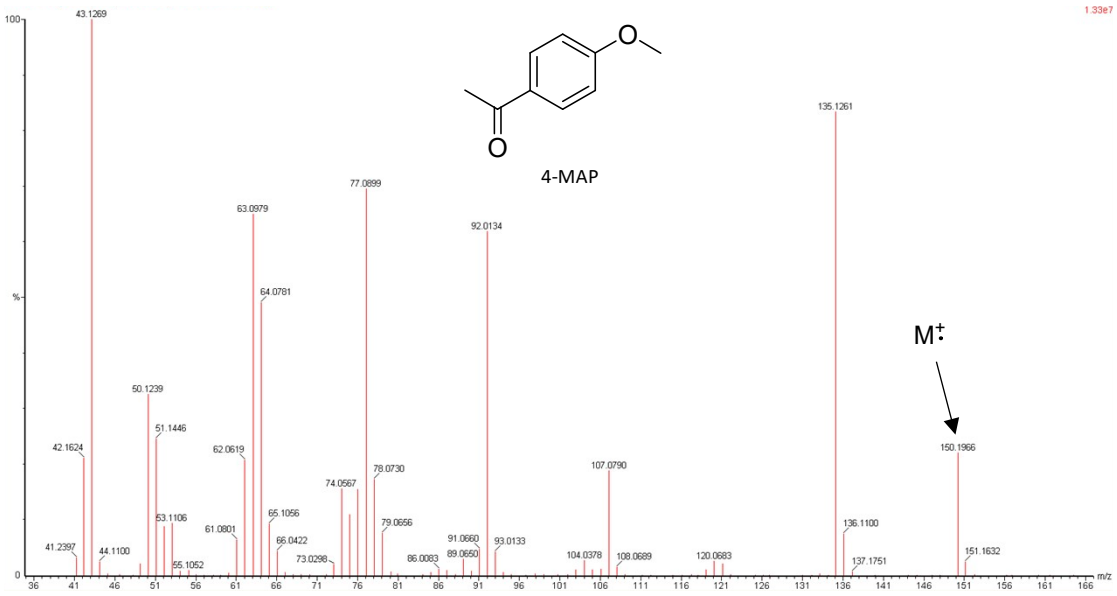

Fig. S3. Mass spectrum (EI) of 4-MAP.

This mass spectrum (EI) of 4-MAP obtained in this experiment was also in accordance with the standard mass spectrum.

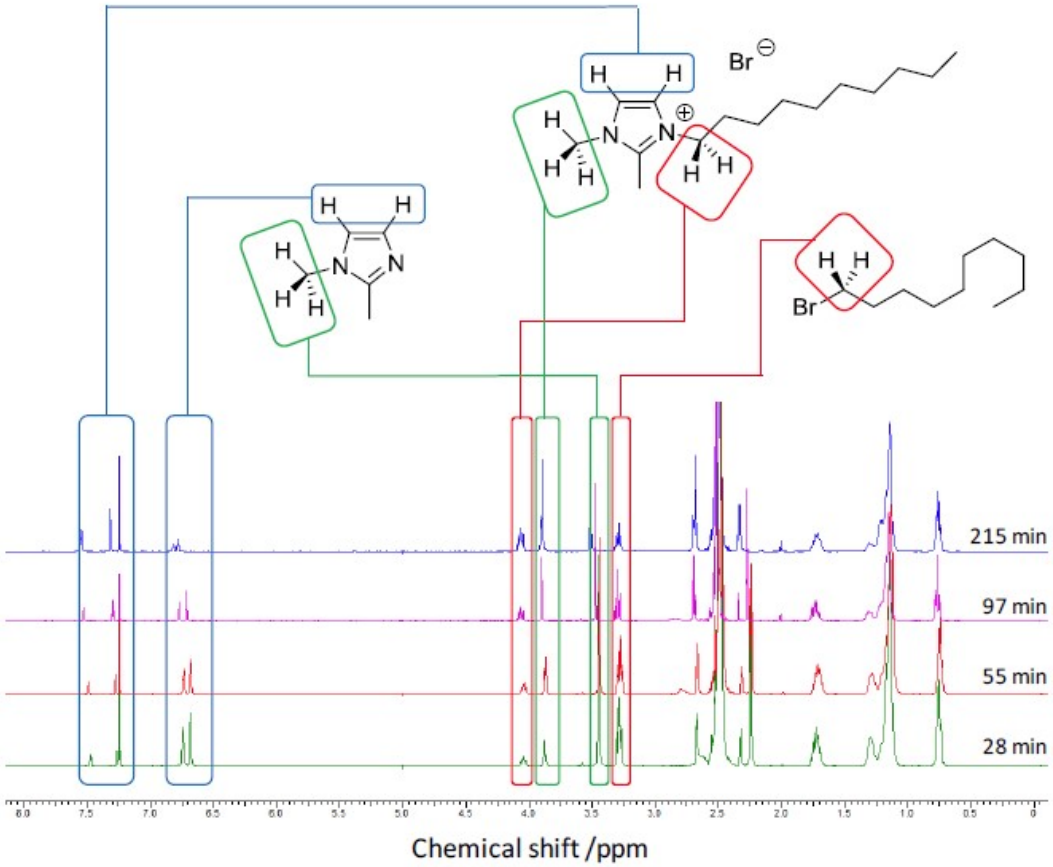

Fig. S4. Annotated 1H NMR spectrum of a representative Menschutkin reaction in DMSO, demonstrating part way through the for the formation of 1-decyl-2,3-dimethylimidazolium bromide.[1]

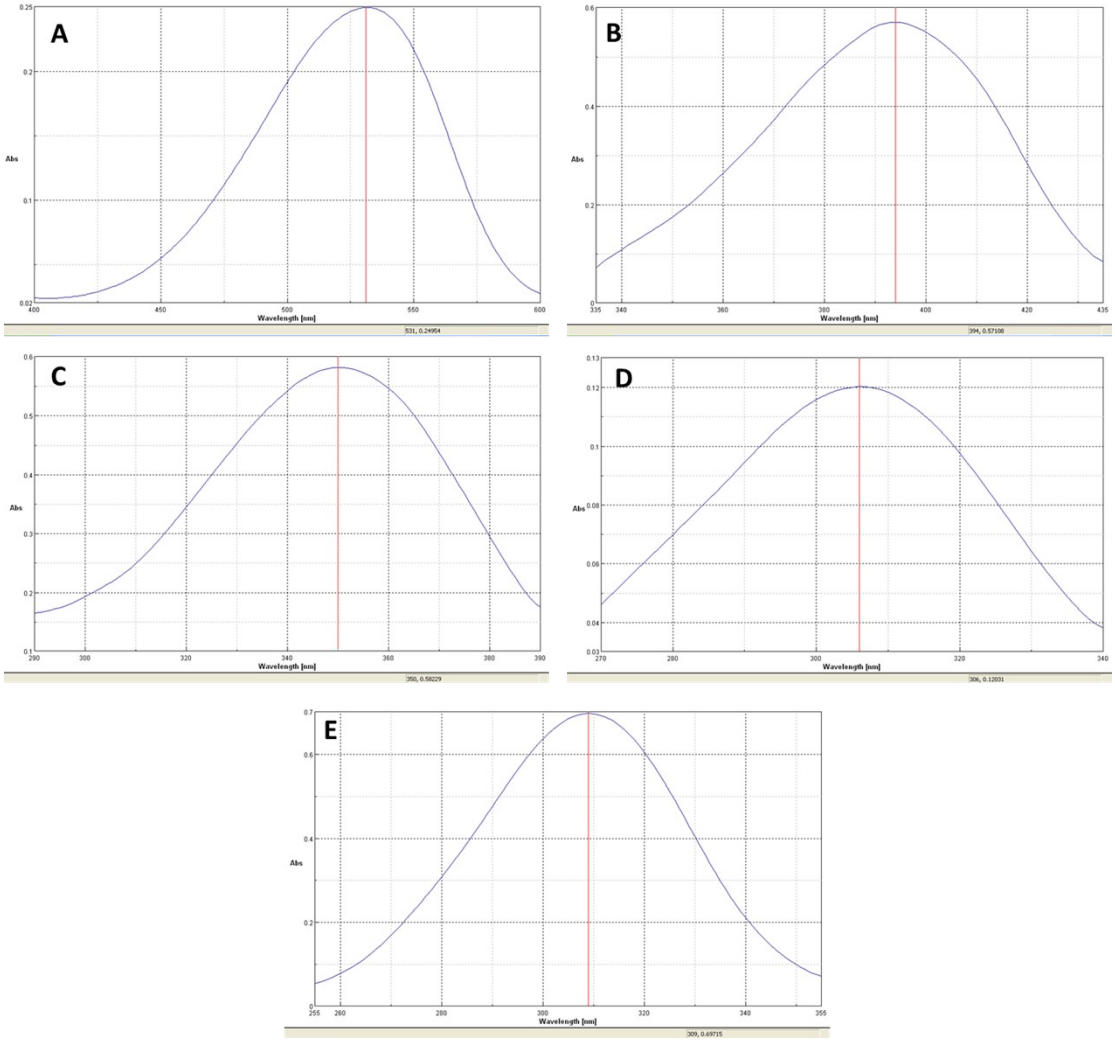

Fig. S5. The UV-vis. spectrum of A) Nile red (NR) dissolved in MO (λ_{max} = 531 nm), B) *N,N*-diethyl-4-nitroaniline (NN) dissolved in MO (λ_{max} = 394 nm), C) 4-nitroaniline (NA) dissolved in MO (λ_{max} = 350 nm), D) 4-nitrophenol (NP) dissolved in MO (λ_{max} = 306 nm) and E) 4-nitroanisole (NS) dissolved in MO (λ_{max} = 309 nm)

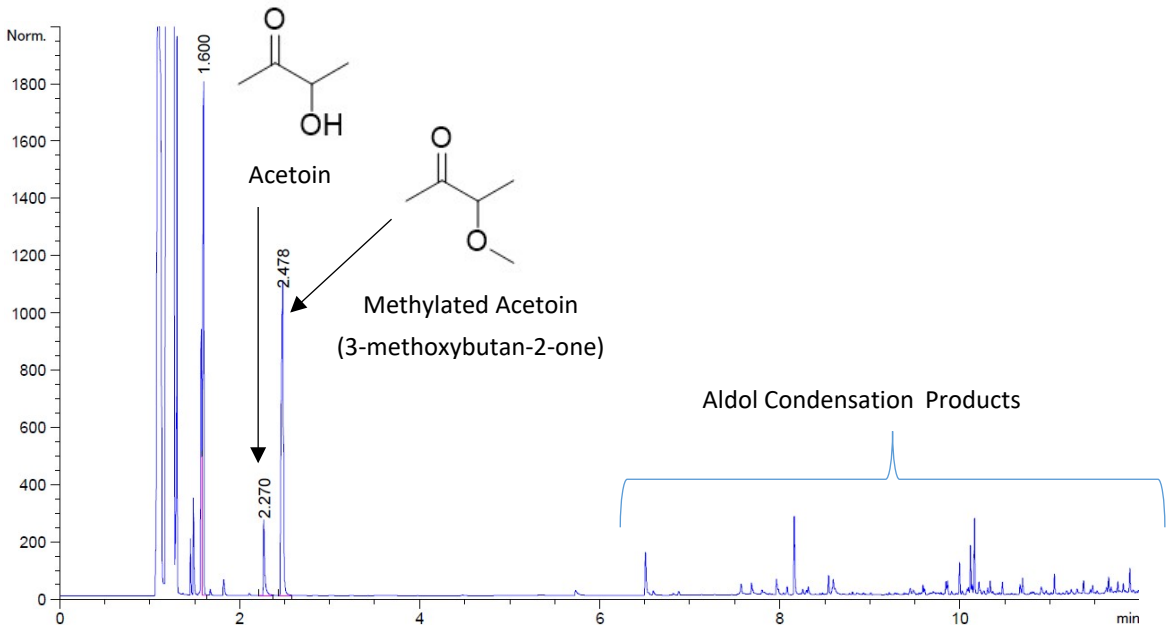

Fig. S6. GC spectrum of crude product from methylation of acetoin with DMC using p-TSA in catalyst screen

2 Optimisation of reaction time

In order to optimise the yield of MO synthesised from the reaction of dimethyl carbonate (DMC) with acetoin (catalysed by *p*-toluenesulphonic acid at 160 °C), the effect of reaction time was investigated. A molar ratio of 1:8 of acetoin to DMC was selected. The results indicated the highest NMR yield (95%) of MO is obtained after 100 min (shown in Table S1). This result demonstrates that higher isolated yield can be achieved by better distillation methodology, and currently the improvement of isolated yield of MO is still in progress.

Table S1. Yields study of MO by ^{1}H NMR at the condition of 1 : 8 of mole ratio of acetoin to DMC[a]

Entry	Reaction time (min)[b]	Yield (%) of MO by ^{1}H NMR[c]
1	10	0
2	20	13%
3	30	58%
4	40	86%
5	50	90%
6	60	93%
7	70	93%
8	80	94%
9	90	94%
10	100	95%
11	110	95%
12	120	95%

[a] Reaction conditions: acetoin/DMC/PTSA = 0.5 mol : 4 mol : 0.025 mol; *T* = 160 °C. [b] Reaction time 0 min is defined at when the reaction temperature just reached 90 °C. [c] Selectivity > 99% in all reaction time towards MO calculated by ^{1}H NMR.

Table S2: Catalyst screening under conventional heating.

Catalyst	Reaction Type	Duration	NMR % Conversion
p-TSA monohydrate	Reaction Vessel	1 Hour	76
Sulphuric Acid	Reaction Vessel	1 Hour	85
Hydrochloric Acid	Reaction Vessel	1 Hour	39
Aluminium (III) Chloride	Reaction Vessel	1 Hour	11
Iron (III) Chloride	Reaction Vessel	1 Hour	22
Montmorillonite K10	Reaction Vessel	1 Hour	5
Al-Pillared Montmorillonite	Reaction Vessel	1 Hour	6
Zeolite	Reaction Vessel	1 Hour	1
Starbon A450	Reaction Vessel	1 Hour	74
Boron Trifluoride	Reaction Vessel	1 Hour	13

Methanesulphonic Acid	Reaction Vessel	1 Hour	85
Oxalic Acid	Reaction Vessel	1 Hour	2
Phosphoric Acid	Reaction Vessel	1 Hour	66
Trifluoroacetic Acid	Reaction Vessel	1 Hour	0
Calcium Carbonate	Reaction Vessel	1 Hour	0
H-Y Zeolite	Reaction Vessel	1 Hour	0
β-Zeolite, Ammonium	Reaction Vessel	1 Hour	0
Nafion SAC-13	Reaction Vessel	1 Hour	33
Tungstosilicic Acid Hydrate	Reaction Vessel	1 Hour	0

Table S3: Catalyst screening under microwave heating.

Catalyst	Reaction Type	Duration	NMR %Conversion
p-TSA monohydrate	Microwave	20 Mins	100
Sulphuric Acid	Microwave	5 Mins	100
Phosphoric Acid	Microwave	1 Hour	66
Starbon A450	Microwave	1 Hour	87
Methanesulphonic Acid	Microwave	1 Hour	89
Tungstosilicic Acid Hydrate	Microwave	10 Mins	79
H-Y Zeolite	Microwave	1 Hour	31
β-Zeolite, Ammonium	Microwave	1 Hour	61
Nafion SAC-13	Microwave	1 Hour	77
Tungstosilicic Acid Hydrate	Microwave	1 Hour	86
p-TSA monohydrate	Microwave	20 Mins	100
Sulphuric Acid	Microwave	5 Mins	100

References

1 J. Sherwood, PhD Thesis, University of York, 2013.