Electronic Supplementary Informations
for

Synthesis of Dibenzyl carbonate: Towards a Sustainable Catalytic Approach

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Materials and Methods

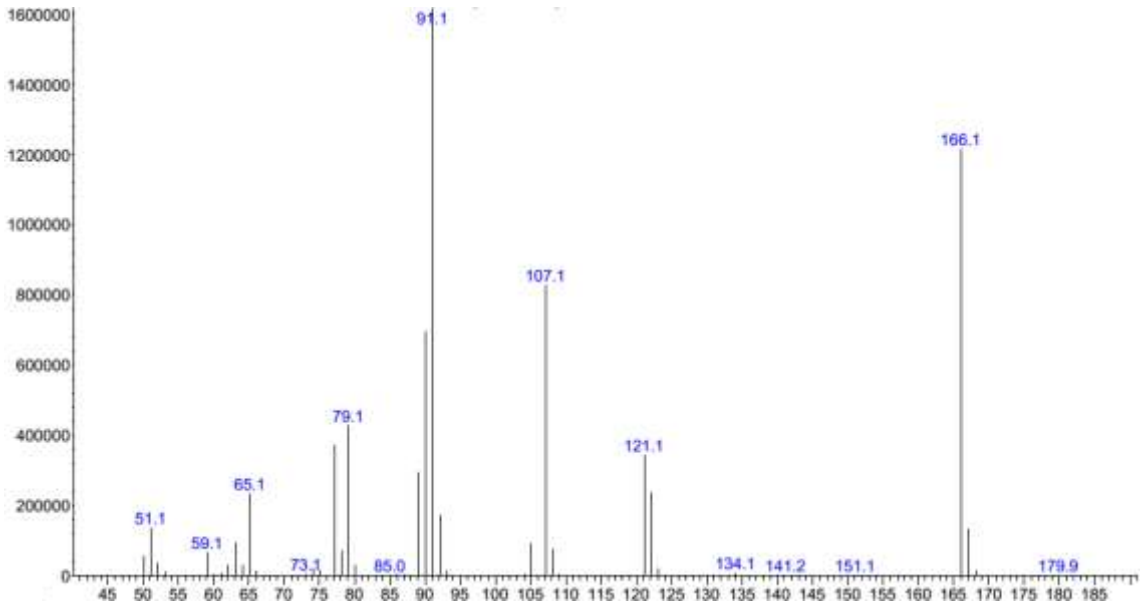
All reagents were ACS grade and were purchased from Sigma Aldrich. Except for benzyl alcohol, they were used without further purification.
Before use, benzyl alcohol (BnOH) was analysed by GC before to estimate the presence of benzaldehyde impurities. When benzaldehyde was detected in an amount > 1 %, BnOH was purified by vacuum distillation.[1]
Doubly distilled MilliQ was employed throughout this study.
GC-MS (EI, 70 eV) analyses were performed with a HP5890 gas chromatograph equipped with a HP-5 MS capillary column (30 m x 0,25 mm; coating thickness 0,25 µm) and a HP 5970 quadrupole mass detector (EI, 70 eV). NMR spectra were recorded using a Varian Unity 400 MHz spectrometer, $CDCl_3$ was used as a solvent, the residual signal of the deuterated solvent was used as internal reference. FT-IR spectra were recorded with a Perkin Elmer Spectrum One Instrument on KBr pellets. Melting points were collected by a Scott Scientific melting point apparatus. Ion-chromatography analyses were carried out at 30 °C, using an IonPac AS23 Anion-Exchange column (4 x 40 mm) and an aqueous solution of Na_2CO_3 and $NaHCO_3$ (4.5 mM and 0.8 mM, respectively) as an eluant (1 mL/min).

Catalysts preparation

The homogeneous transesterification catalyst methyltrioctylphosphoniummethylcarbonate, $[P_{1,8,8,8}]][O(CO)OCH_3]$ was synthesized and characterized according to previously published literature procedures.[2]
The heterogeneous transesterification catalyst, $CsF/\alpha\text{-}Al_2O_3$ (1 mmolCsF/g) was synthesized according to previously reported protocols.[3]

Benzyl methyl carbonate (BnMC)

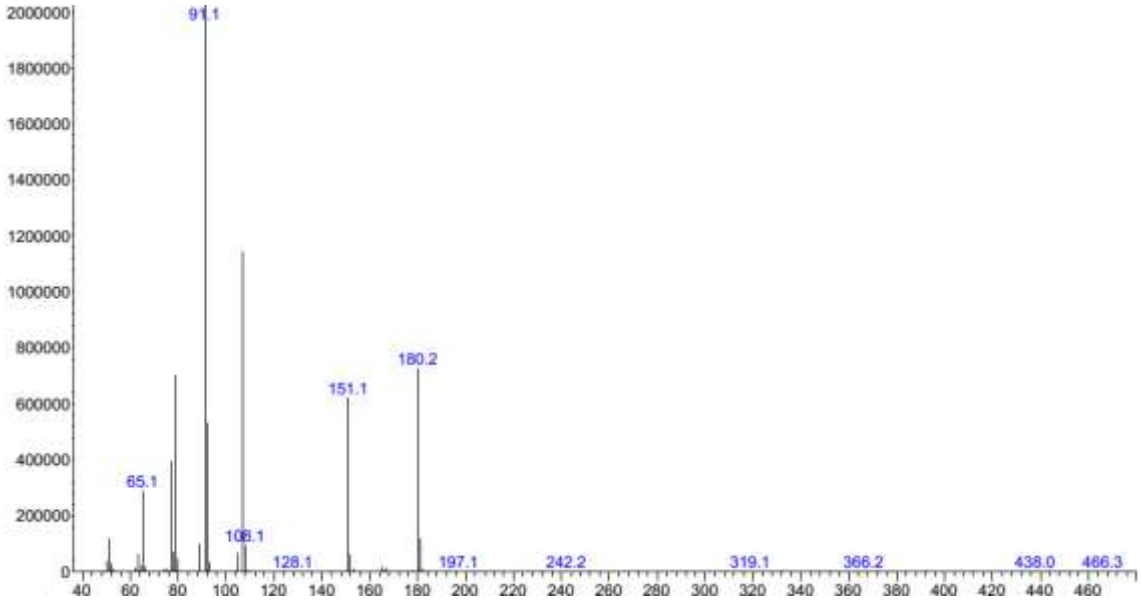
GC-MS spectrum



EI-MS (70 eV): 166 [M+] (23), 121 (13), 107 (42), 92 (11); 91 (100); 90 (47); 89 (21); 79 (33); 77 (32); 65 (25); 63 (10); 51 (20); 50 (10).[4]

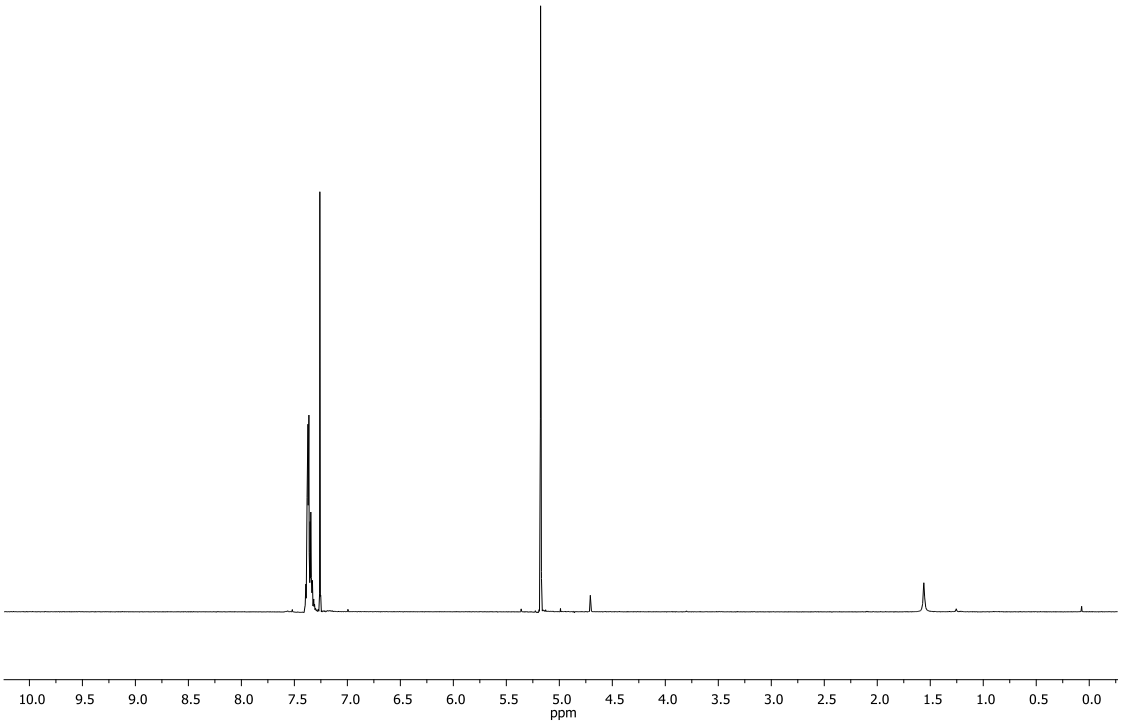
Dibenzylcarbonate (DBnC)

GC-MS spectrum



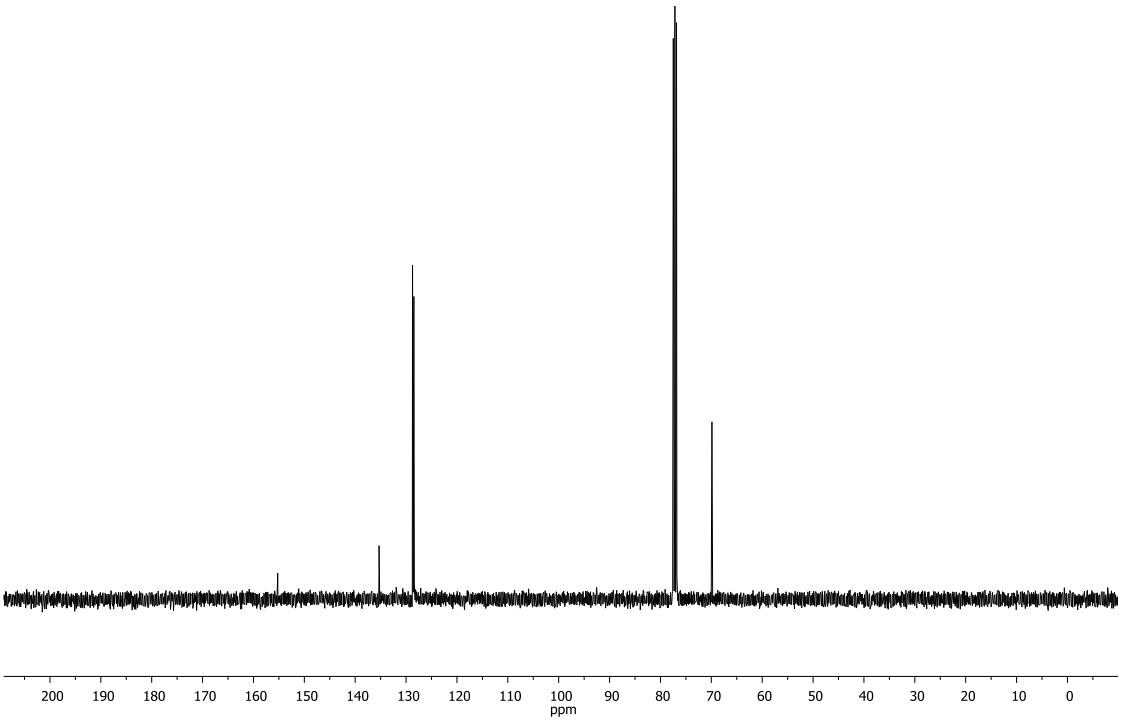
EI-MS (70 eV): 180 [M+- 62] (10); 151 (12); 107 (41); 92 (24); 91 (100); 79 (40); 77 (24); 65 (22); 51 (13).[5]

^{1}H NMR spectrum



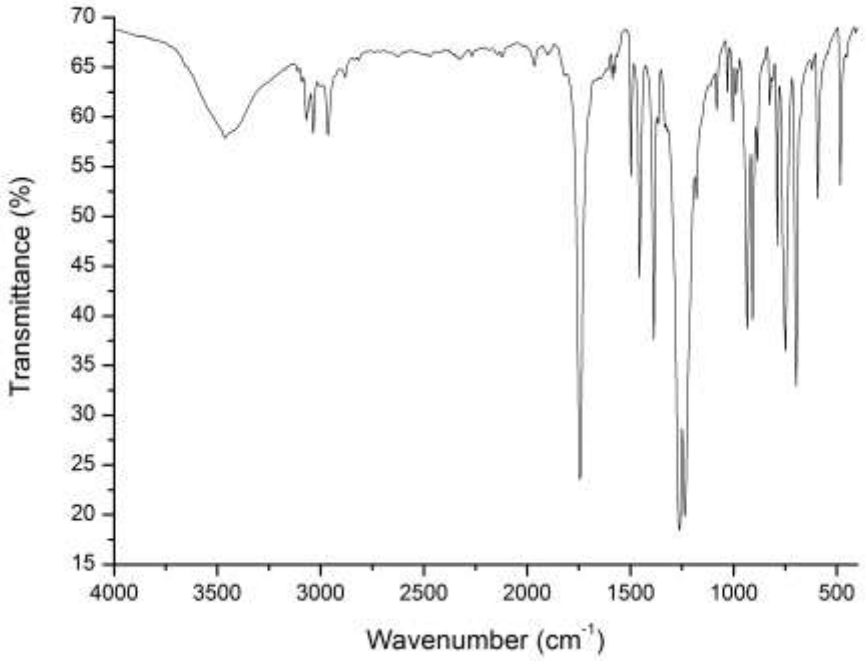
^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ): 7.41–7.30 (m, 10H), 5.18 (s, 4H).[6]

^{13}C NMR spectrum



^{13}C NMR (101 MHz, $CDCl_3$, 298 K, δ): 155.23, 135.31, 128.73, 128.68, 128.47, 69.88.[6]

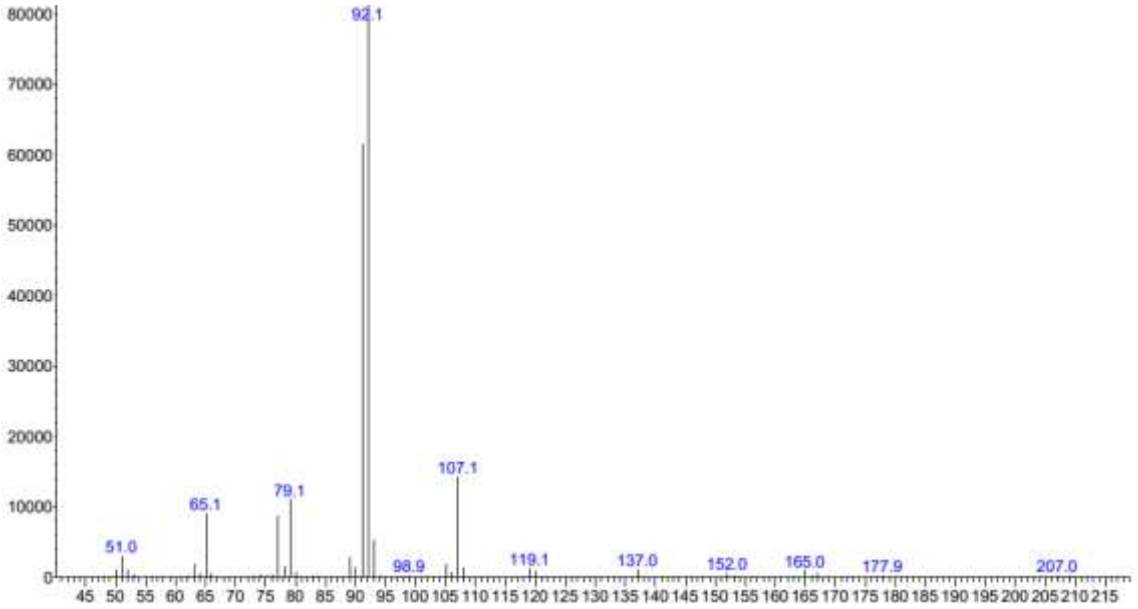
FT-IR (KBr Pellets)



IR (KBr): 1744 (br);1456 (sh); 1385 (sh); 1259 (br);1224 (br); 934 (sh); 907 (sh); 788 (sh); 747 (sh); 695 (sh); 591 (sh); 482 (sh).[7]

Dibenzyl Ether (DBnE)

GC-MS Spectrum



EI-MS (70 eV): 107 [M+- 91] (14); 92 (100); 91 (89); 79 (16); 77 (21); 65 (24); 51 (14); 44 (10). Database NIST: Ref. #118448, match quality 94%.

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