Supporting information for:

TBD catalysis with dimethyl carbonate: a fruitful and sustainable alliance

Hatice Mutlu, Johal Ruiz, Susanne C. Solleder and Michael A. R. Meier*

Karlsruhe Institute of Technology (KIT), Institute of Organic Chemistry, Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany. Email: m.a.r.meier@kit.edu; Web: www.meier-michael.com

Materials

All alcohols (analytical grade), glycerol (≥99%), dimethyl carbonate (DMC, 99%), 1,5,7-triazobicyclo[4.4.0]dec-5-ene (TBD, 98%), 1,4-benzoquinone (**BQ**, ≥98%), ethyl vinyl ether (99%), tetradecane (>99%), pyrrolidine (>99.5%), benzylidene[1,3-*bis*-(2,4,6-trimethylphenyl)imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium (second generation Grubbs catalyst, **C1**), [1,3-*bis*-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(o-isopropoxy-phenylmethylene)ruthenium (second generation Hoveyda-Grubbs catalyst, **C2**) were obtained from Aldrich. 1,3-*bis*-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-yliden[2-(isopropoxy)-5-N,N-dimethylaminosulfonyl)phenyl] methylene ruthenium (II) dichloride (Zhan catalyst, **C3**, 96%) was delivered from ABCR. Poly(ethylene glycol) methyl ether (mPEG-OH, M_n~500 Da) was purchuased from Fluka. All reagents were used without further purification. (*E*) icos-10-ene-1,20-diol (**D3**) was prepared according to the procedure reported by Meier and co-workers.[1] Solvents for chromatography were technical grade.

General Methods

Thin layer chromatography (TLC) was performed on silica gel TLC-cards (layer thickness 0.20 mm, Fluka). Preparative column chromatography or thin layer chromatography were carried out using silica gel 60 (0.063-0.200 mm, Fluka). Permanganate reagent was used as a developing solution.

All ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired in $CDCl_3$ (99.8 atom% D, Armar Chemicals) and DMSO-*d6* (99.8 atom% D, Euriso-top) as solvent using Bruker AVANCE DPX spectrometers operating at 300 MHz for ^{1}H NMR and 75.5 MHz for ^{13}C NMR. Chemical shifts (δ) are given in ppm relative to the internal standard

tetramethylsilane (TMS, δ=0.00 ppm) for ^{1}H-NMR. The ^{1}H-NMR spectra were referenced to the residual proton impurities at δH 2.50 ppm and 7.26 ppm in DMSO-*d6* and $CDCl_3$, respectively. The ^{13}C-NMR spectra were referenced at δC 39.52 and 77.00 ppm to ^{13}DMSO and $^{13}CDCl_3$, respectively. For the analysis of the polymers the relaxation time was set to 5 seconds.

Electron spray ionization mass spectra (ESI-MS) were recorded on a Micromass Q-TOF instrument and high resolution mass spectra (HRMS) with electron impact ionization (EI) were recorded on a GC-TOF. Analytical GC characterization was carried out with a Bruker 430 GC instrument equipped with a capillary column FactorFour™ VF-5 ms (30 m × 0.25 mm × 0.25 μm), using flame ionization detection. The oven temperature program was: initial temperature 95 °C, hold for 1 min, ramp at 15 °C × min^{-1} to 220 °C, hold for 4 min, ramp at 15 °C × min^{-1} to 300 °C, hold for 2 min. The injector transfer line temperature was set to 220 °C. Measurements were performed in split–split mode using hydrogen as the carrier gas (flow rate 30 mL × min^{-1}). GC-MS (EI) chromatograms were recorded using a Varian 431 GC instrument with a capillary column FactorFourTM VF-5 ms (30 m × 0.25 mm × 0.25 μm) and a Varian 210 ion trap mass detector. Scans were performed from 40 to 650 *m*/*z* at rate of 1.0 scans × s^{-1}. Method A - the oven temperature program was: initial temperature 95 °C, hold for 1 min, ramp at 15 °C × min^{-1} to 200 °C, hold for 2 min, ramp at 15 °C × min^{-1} to 325 °C, hold for 5 min. Method B - the oven temperature was: initial 35 °C, hold for 2 min, ramp at 10 °C × min^{-1} to 150 °C, hold for 1 min. The injector transfer line temperature was set to 250 °C. Measurements were performed in split–split mode (split ratio 50 : 1) using helium as the carrier gas (flow rate 1.0 mL × min^{-1}).

Average molar mass (M_n) and molar mass distribution [PDI (polydispercity index) = M_w/M_n] values of the polymers were determined from the chromatogram traces recorded by SEC (GPC) using a LC-20A system from Shimadzu equipped with an SIL-20A autosampler and an RID-10A refractive index detector in THF (flow rate 1 mL × min^{-1}) at 50 °C. The analysis were performed on column system: PLgel 5 μm MIXED-D column (Varian, 300 mm × 7.5 mm, 10 000 Å) with precolumn . All elution curves were calibrated with linear poly(methyl methacrylate) standards (Polymer Standard Service, M_P 1100-981 000 Da).

All reactions and polymerizations were perfromed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK).

Synthesis and characterization of unsymmetric organic carbonates

Tetradecane (10.0 mol% relative to the alcohol) was used as internal standard and the conversion (%), selectivity (%) and yield (%) were calculated with respect to the alcohol. In a typical procedure, a mixture of the alcohol (15.0 mmol) and the corresponding amount DMC (see Table 2 in the main text) was added to the carousel tube and stirred magnetically at 80 °C for a couple of minutes. After taking a t = 0 min sample, if not otherwise specified, 0.15 mmol TBD was added to the carousel tube (see Table 2 in the main text for additional information). The reactions were sampled and analysed by GC, GC-MS and NMR in specific time intervals, thus the product distribution and conversion being determined. After a defined time, the heating was stopped and the recation mixtures were allowed to cool to room temperature. The crude reaction mixture was purified by column chromatography to obtain the pure product. In cases when the product was a mixture of the unsymmetric and symmetric organic carbonate mixture, fractional destillation was applied.

Model compound - methyl octyl carbonate: after purification with column chromotography (*n*-hexane/ethyl acetate = 9:1) methyl octyl carbonate was obtained as colourless oil in a yield of 95%. The ^{1}H and ^{13}C NMR spectra were in accordance with the already reported one.[2]

Characterization of the unsymmetric carbonates (Table 2)

Butyl methyl carbonate (entry 1): colourless liquid, *n*-hexane/ethyl acetate = 2/1, yield = 85%. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 4.11 (m, 2H, -C*H*$_2$-O-), 3.77 (s, 3H, -O-C*H*$_3$), 1.73−1.46 (m, 2H, -C*H*$_2$-CH_2-CH_3), 1.43−1.15 (m, 2H, -CH_2-C*H*$_2$-CH_3), 0.87 (t, *J* = 6.6 Hz, 3H, -C*H*$_3$).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.7 (-O*C*O_2-), 69.1 (-*C*H_2-O-), 54.9 (-O-*C*H_3), 28.9 (-*C*H_2-CH_2-CH_3), 18.8 (-CH_2-*C*H_2-CH_3), 13.5 (-*C*H_3).

MS (EI) of $C_6H_{12}O_3$ $[M+H]^+$ calc. 133.08 found 133.2

Hexyl methyl carbonate (entry 2): colourless oil, *n*-hexane/ethyl acetate = 9/1, yield = 89%

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 4.22−3.98 (m, 2H, -C*H*$_2$-O-), 3.77 (s, 3H, -O-C*H*$_3$), 1.77−1.49 (m, 2H, aliphatic -C*H*$_2$-), 1.46−1.16 (m, 6H, aliphatic -C*H*$_2$-), 0.87 (t, *J* = 6.6 Hz, 3H, -C*H*$_3$).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.9 (-O*C*O_2-), 68.2 (-*C*H_2-O-), 54.6 (-O-*C*H_3), 31.6 (aliphatic -*C*H_2-), 28.6 (aliphatic -*C*H_2-), 25.3 (aliphatic -*C*H_2-), 22.5 (aliphatic -*C*H_2-), 13.9 (-*C*H_3).

HRMS of $C_8H_{16}O_3$ $[M+H]^+$ calc. 161.11 found 161.30

Methyl undec-10-en-1-yl carbonate (entry 3): colourless oil, *n*-hexane/ethyl acetate = 9/1, yield = 93%. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.80 (ddt, *J* = 16.9, 10.2 and 6.7 Hz, 1H, CH_2=C*H*-), 5.03–4.82 (m, 2H, C*H*$_2$=CH-), 4.11 (t, *J* = 6.7 Hz, 2H, -C*H*$_2$-O-), 2.07–1.96 (m, 2H, CH_2=CH-C*H*$_2$-), 1.69–1.57 (m, 2H, -C*H*$_2$-CH_2-O-), 1.42–1.18 (m, 12H, aliphatic -C*H*$_2$-). ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.8 (–O*C*O$_2$-), 139.1 (CH_2=*C*H-), 114.1 (*C*H_2=CH-), 68.2 (-C*H*$_2$-O-), 54.5 (-O*C*H_3), 33.8 (CH_2=CH-*C*H_2-), 29.4-25.6 (aliphatic-*C*H_2-). HRMS of $C_{13}H_{24}O_3$ $[M+H]^+$ calc. 229.18 found 229.10

3,7-dimethyloct-6-en-1-yl methyl carbonate (entry 4): colourless liquid, *n*-hexane/ethyl acetate = 9/1, yield = 94%. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.18–4.95 (m, 1H, -*H*C=C$(CH_3)_2$), 4.28–4.04 (m, 2H, -O-C*H*$_2$-), 3.86 (s, 3H, -O-C*H*$_3$), 1.94 (pt, *J* = 13.1, 6.6 Hz, 2H, -C*H*$_2$-HC=C$(CH_3)_2$), 1.78–1.08 (m, 11H), 0.91 (d, *J*=6.4 Hz, 3H, -CH(C*H*$_3$)-). ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.9 (-O*C*O$_2$-), 131.3 (-HC=*C*$(CH_3)_2$), 124.5 (-H*C*=C$(CH_3)_2$), 66.6 (-O-*C*H_2-), 54.6(O-*C*H_3), 36.9 (-*C*H_2-CH_2-HC=C$(CH_3)_2$), 35.6 (CH_3O-C(O)$_2$-CH_2-*C*H_2-), 29.3 (-CH_2-*C*H(CH_3)-CH_2-), 25.6 (-*C*$_{isomer}$$H_2$-HC=C$(CH_3)_2$), 25.3 (-*C*$_{isomer}$$H_2$-HC=C$(CH_3)_2$), 19.3 (-HC=C(*C*$H_3$)$_2$), 17.6 (-HC=C(*C*$H_3$)$_2$).

HRMS of $C_{12}H_{22}O_3$ $[M+H]^+$ calc. 215.16 found 215.20

Allyl methyl carbonate (entry 5): colourless oil, *n*-hexane/ethyl acetate = 15/1, yield = 80 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 6.06–5.77 (m, 1H, CH_2=C*H*-), 5.38–5.21 (m, 2H, C*H*$_2$=CH-), 4.60 (dd, *J* = 5.7 and 1.3 Hz, 2H, -C*H*$_2$-O-), 3.68 (s, 3H, -O-C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.7 (-O*C*O$_2$-), 131.7 (CH_2=*C*H-), 118. (*C*H_2=CH-), 68.5 (-*C*H_2-O-), 54.9 (-O-*C*H_3).

MS (EI) of $C_{12}H_{22}O_3$ $[M+H]^+$ calc. 117.05 found 117.20

Methyl *trans*-2-hexen-1-yl carbonate (entry 6): colourless oil, *n*-hexane/ethyl acetate = 9/1, yield = 92%. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.97–5.32 (m, 2H, -C*H*=C*H*-), 4.54 (ddd, *J* = 19.6, 10.3, 4.2 Hz, 2H, -C*H*$_2$-O-), 3.76 (s, 3H, -O-C*H*$_3$), 2.17–1.87 (m, 2H, -C*H*$_2$-CH=CH-), 1.50–1.27 (m, 2H, -C*H*$_2$-CH_2-CH=CH-), 0.90 (t, 3H, -C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.8 (-O*C*O$_2$-), 137.4 (-CH=*C*H-CH_2-O*C*O$_2$-), 123.5 (-*C*H=CH-CH_2-O*C*O$_2$-), 68.9 (-*C*H_2-O-), 54.8 (-O-*C*H_3), 34.4 (-*C*H_2-CH=CH-), 22.1 (-CH_2-CH_2-CH=CH-), 13.7 (CH3-).

HRMS of $C_8H_{12}O_3$ $[M]^+$ calc. 158.09 found 158.20

Methyl *trans*-2,4-hexadien-1-yl carbonate (entry 7): colourless oil, *n*-hexane/ethyl acetate = 9/1, yield = 89%. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 6.40–5.93 (m, 2H, -CH=C*H*-C*H*=CH-), 5.86–5.54 (m, 2H, -C*H*=CH-CH=C*H*-), 4.72–4.52 (m, 2H, -C*H*$_2$-O-) 3.77 (s, 3H, -

O-C*H*$_3$), 1.87–1.65 (m, 3H, -C*H*$_3$).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.6 (-O-*C*H_3), 135.5 (-CH=*C*H-CH=CH-CH_3), 131.6 (-CH=CH-CH=*C*H-CH_3), 130.3 (-CH=CH-CH=*C*H-CH_3), 122.9 (*C*H=CH-CH=CH-CH_3), 68.2 (-*C*H_2-O), 54.7 (-O-*C*H3), 18.1 (-*C*H_3).

HRMS of $C_8H_{12}O_3$ $[M]^+$ calc. 156.08 found 156.10

Methyl propargyl carbonate (entry 8): yellowish oil, *n*-hexane/ethyl acetate = 15/1, yield = 75%. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 4.68–4.64 (m, 2H, -C*H*$_2$-O-), 3.75 (s, 3H, -O-C*H*$_3$), 2.52-2.48 (m, 1H, *H*C≡C-).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.1 (-O*C*O_2-), 76.9 (HC≡*C*-, overlapping with $CDCl_3$), 75.6 (HC≡C-), 55.1 (-*C*H2-O-), 55.0 (-O-*C*H3).

MS (EI) $C_5H_6O_3$ $[M+H]^+$ calc. 115.04 found 115.20

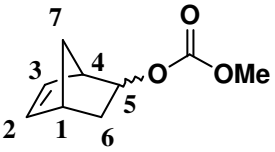
Methyl poly(ethylene glycol) methyl ether carbonate (entry 9): excess of DMC carbonate was removed *via* extraction of the crude reaction mixture with hexane; the highly viscous product was dried under vacuum thus yielding 94% viscous colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 4.30- 4.20 (m, 2H, -C*H*$_2$-O-C(O)O-$CH_{3\,end\ group}$), 3.76 (s, 1H, -CH_2-O-C(O)O-C*H*$_{3\,end\ group}$), 3.72-3.49 (m, repeating unit -O-C*H*$_2$-C*H*$_2$-O-), 3.35 (s, 3H, -CH_2-O-C*H*$_{3\,end\ group}$).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 156.8 (-O*C*O_2-), 71.9 (-O-CH_2-*C*H_2-O-$CH_{3\,end\ group}$), 70.6 (repeating unit -O–*C*H_2-*C*H_2-O-), 70.4 (-O-*C*H_2-CH_2-O-$CH_{3\,end\ group}$), 68.9 (-*C*H_2-CH_2-O-C(O)O-$CH_{3\,end\ group}$), 66.9 (-*C*H_2-O-C(O)O-$CH_{3\,end\ group}$), 58.9 (-CH_2-O-*C*$H_{3\,end\ group}$), 54.6 (-C(O)O-*C*$H_{3\,end\ group}$).

Cyclohexyl methyl carbonate (entry 10): colourless liquid, *n*-hexane/ethyl acetate = 9/1, yield = 93%. Spectroscopic properties were in agreement with those reported in the literature.[3]

Bicyclo[2.2.1]hept-5-en-2-yl methyl carbonate (entry 11): colourless liquid, *n*-hexane/ethyl acetate = 4/1, yield = 95%.



^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 6.36–6.27 (m, 1H, H^2), 6.00–5.92 (m, 1H, H^3), 5.25–5.15 (m, 1H, H^5), 3.72 (s, 3H, -OC*H*$_3$), 3.18–3.12 (m, 1H, H^4), 2.85–2.78 (m, 1H, H^1), 2.16–2.08 (m, 1H, H^6), 1.48–1.43 (m, 1H, H^7), 1.29 (d, *J* = 8.9 Hz, 1H, $H^{7´}$), 1.03–0.95 (m, 1H, $H^{6´}$).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 154.2 (-O*C*O_2-), 139.9 ($C^{2´}$), 137.3 (C^2), 130.9 ($C^{3´}$), 129.8 (C^3), 77.54 ($C^{5´}$), 77.2 (C^5), 53.0 (OMe´), 52.9 (O*C*H_3), 46.1 (C^7), 45.9 ($C^{7´}$), 44.7 ($C^{4´}$), 44.3 (C^4), 40.8 (C^1), 39.1 ($C^{1´}$), 33.0 (C^6, $C^{6´}$).

HRMS of $C_{12}H_{18}O_3$ $[M]^+$ calc. 168.08 found 168.80

2-Adamantyl methyl carbonate (entry 12): recrystalized from MeOH, yield = 93%. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 4.86–4.67 (m, 1H, -C*H*-O-C(O)O-), 3.76 (s, 3H, C*H*$_3$-O-C(O)O-), 2.17–1.96 (m, 2H), 1.92–1.66 (m, 8H), 1.53 (t, *J* = 16.1 Hz, 4H).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.3 (-O*C*O_2-), 81.1 (-C*H*-O-C(O)O-), 54.4 (-O-*C*H_3), 37.3 (2C), 36.3 (2C), 31.8, 31.5, 28.8, 27.1, 26.9.

HRMS of $C_{12}H_{18}O_3$ $[M+H]^+$ calc. 211.13 found 211.00

Methyl-1,4-pentadien-3-yl carbonate (entry 13): colourless oil, *n*-hexane/ethyl acetate = 15/1, yield = 89%. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.94–5.69 (m, 2H, CH_2=C*H*-), 5.46 (dt, *J*=11.6 and 8.3 Hz, 1H, -C*H*-O-), 5.38–5.13 (m, 4H, C*H*$_2$=CH-), 3.75 (s, 3H, -O-C*H*$_3$).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 156.4 (-O*C*O_2-), 134.6 (CH_2=*C*H-), 118.1 (*C*H_2=CH-), 79.1 (-*C*H_2-O-), 54.8 (-O-*C*H_3).

Benzyl methyl carbonate (entry 14): colourless oil, *n*-hexane/ethyl acetate = 9/1, yield = 93%. Spectroscopic properties were in agreement with those reported in the literature.[4]

Methyl (1-phenylbut-3-en-1-yl) carbonate (entry 15): colourless oil, *n*-hexane/ethyl acetate = 5/1, yield = 90%. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 7.49–7.27 (m, 10H, aromatic –C*H*-), 5.87–5.57 (m, 1H, CH_2=C*H*-), 5.29–4.99 (m, 3H, C*H*$_2$=CH- and CH_2=CH-CH_2-C*H*-), 3.69 (s, 3H, -OC*H*$_3$), 2.99–2.42 (m, 2H, CH_2=CH-C*H*$_2$-CH-).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.0 (-O*C*O_2-), 139.4 (aromatic –*C*H-), 132.8 (CH_2=*C*H-), 128.4 (aromatic –*C*H-), 128.1 (aromatic –*C*H-), 126.4 (aromatic –*C*H-), 118.3 (*C*H_2C=H-), 79.3 (-*C*H-O-), 54.6 (-*C*H_2-O-), 40.7 (CH_2=CH-*C*H_2-).

HRMS of $C_{12}H_{14}O_3$ $[M+H]^+$ calc. 207.10 found 207.10

***tert*-Butyl methyl carbonate (entry 16):** colourless liquid, *n*-hexane/ethyl acetate = 10/1, yiled = 82%. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 3.74 (s, 3H, -O-C*H*$_3$), 1.43 (s, 9H, C-(C*H*$_3$)$_3$).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.6 (–O*C*O_2-), 81.1 (-*C*-(CH_3)$_3$), 55.9 (-C*H*$_2$-O-), 28.4 (-C-(*C*H_3)$_3$).

MS (EI) of $C_6H_{12}O_3$ $[M+H]^+$ calc. 133.08 found 133.10

Glycerol carbonate (entry 17): colourless oil, *n*-hexane/ethyl acetate = 1/25, yield = 95%. ^{1}H NMR (300 MHz, DMSO-$_{d6}$, δ in ppm): 5.28 (dd, *J* = 7.2, 3.8 Hz, 1H, *H*O-CH$_2$-CH-) 4.80 (ddd, *J* = 11.6, 5.9, 3.0 Hz, 1H, HO-CH$_2$-C*H*-), 4.49 (td, *J* = 8.3, 2.9 Hz, 1H, -O-C*H*$_2$-CH-), 4.28 (dd, *J* = 8.1, 5.8 Hz, 1H, -O-C*H*$_2$-CH-). 3.67 (ddd, *J* = 12.6, 5.4, 2.7 Hz, 1H, HO-C*H*$_2$-CH-), 3.50 (ddd, *J* = 12.6, 5.6, 3.3 Hz, 1H, HO-C*H*$_2$-CH-).

^{13}C NMR (75 MHz, DMSO-$_{d6}$, δ in ppm): 155.3 (-O*C*O$_2$-), 77.1 (HO-CH$_2$-*C*H-), 65.9 (HO-*C*H$_2$-CH-), 60.6 (-O-*C*H$_2$-CH-).

MS (EI) of $C_4H_6O_4$ $[M+H]^+$ calc. 119.03 found 119.01

One pot two-step polymerization via TBD mediated polycondesation

Polymers in Table 3 and 4 were synthesized following a two-step polycondensation of DMC with **D1**, **D2** and **D3** (Scheme 2 in the main text), respectively, in the melt. In a typical experiment 2.7 gr (35.0 mmol) of DMC and 1.0 equvialent (17.5 mmol) of the corresponding "potential" green diols (**D1**, **D2** or **D3**) were introduced into a carousel tube. The reaction was equipped with magnetic stirring and a screw cap with a septum. The mixture was homogenized at room temperature for 10 min and the specific amount of TBD (0.1, 0.5, 1.0 and 5.0 mol% to the alcohol) was added, then the reaction which was equipped with argon purge and heated at 80 °C. Once the sufficient amount of oligomers was obtained, vacuum was applied (10^{-2} bar) and the temperature was increased to 90 °C to facilitate the polymerization by removing both unreacted DMC and methanol released in the condensation reactions. The reactions were kept at 90 °C for 1 h except for **D1**. The temperature of the reactions for **D2** and **D3** were gradually increased to 150 °C over a period of *ca* 3 h and maintained at this temperature for 1 h to allow complete removal of the methanol and DMC. The reaction of **D1** was kept at 90 °C at continuous vacuum for 3 h in total. After completion, the reaction mixtures were dissolved in THF and the obtained polymers were precipitated in ice cold MeOH in yields ranging from 75 to 95%.

P3 (89%): ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.41–5.28 (m, -C*H*=C*H*-), 4.11 (t, *J* = 6.7 Hz, -C*H*$_2$-O-), 1.98 (t, *J* = 14.6 Hz, -CH=CH-C*H*$_2$-), 1.72–1.53 (m, -C*H*$_2$-CH$_2$-O-), 1.40–1.21 (m, aliphatic -C*H*$_2$-).

P5 (82%): ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 4.25–4.03 (m, -O-C*H*$_2$-CH$_2$-C*H*$_2$-O-), 3.66–3.56 (m, -O*H*$_{end\ group}$), 2.03–1.87 (m, H, -O-CH$_2$-C*H*$_2$.CH$_2$-O-), 1.85–1.72 (m, 1H).

P6 (89%):^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 4.19–3.92 (m, -O-C*H*$_2$-), 1.73–1.48 (m, -CH$_2$-C*H*$_2$-CH$_2$-CH$_2$-C*H*$_2$-CH$_2$-), 1.47–1.21 (m, -CH$_2$-CH$_2$-C*H*$_2$-C*H*$_2$-CH$_2$-CH$_2$-).

Synthesis and characterization of the symmetrical organic carbonates

Reactions were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). Tetradecane (10.0 mol% relative to the alcohol) was used as internal standard, and the conversion (%), selectivity (%) and yield (%) were calculated with respect to the limiting reactant (in this case: DMC)

Typical procedure:

Diallyl carbonate (entry 1): 871 mg of allyl alcohol (15.0 mmol) was mixed with 643 mg of DMC (7.14 mmol) into a carousel reaction tube. To this mixture, 10.0 mg of TBD (1.0 mol%) was added at 80 °C. The reaction was stirred under contionuos argon purge until completion as confirmed by TLC. The heating was stopped and the reaction mixtures were allowed to cool to room temperature. The crude reaction mixture was filtered through a short pad of silica gel with *n*-hexane/ethyl acetate = 9/1 to give a light yellow liquid in 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.94 (ddd, *J* = 16.2, 11.0, 5.8 Hz, 2H, CH_2=C*H*-), 5.42–5.19 (m, 4H, CH_2=CH-), 4.64 (dd, *J* = 5.7 and 1.3 Hz, 4H, -CH_2-O-).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.7 (-O*C*O_2-), 131.7 (CH_2=*C*H-), 118.1 (*C*H_2=CH-), 68.5 (-*C*H_2-O-).

MS (EI) of $C_7H_{10}O_3$ $[M]^+$ calc. 142.06 found 142.10

Characterization of the unsymmetric carbonates in Table 5

Di(undec-10-en-1-yl) carbonate (M1, entry 2): purified over short pad of silica with *n*-hexane to give a colourless liquid in 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.80 (ddt, *J* = 16.9, 10.2 and 6.7 Hz, 2H,CH_2=C*H*-), 5.03–4.82 (m, 4H, CH_2=CH-), 4.11 (t, *J* = 6.7 Hz, 4H, -CH_2-O-), 2.07–1.96 (m, 4H, CH_2=CH-CH_2-), 1.69–1.57 (m, 4H, -CH_2-CH_2-O-), 1.42–1.18 (m, 24H, aliphatic -CH_2-).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.4 (–O*C*O_2-), 139.1 (CH_2=*C*H-), 114.1 (*C*H_2=CH-), 67.9 (-CH_2-O-), 33.8 (CH_2=CH-*C*H_2-), 29.4–25.7 (aliphatic -*C*H_2-).

HRMS of $C_{23}H_{42}O_3$ $[M+H]^+$ calc. 367.32 found 367.30

Di(3,7-dimethyloct-6-en-1-yl) carbonate (M2, entry 3): purified over short pad of silica (*n*-hexane/ethyl acetate = 9/1), colourless oil in 94% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.08 (t, *J* = 7.0 Hz, 2H, -*H*C=C$(CH_3)_2$), 4.25–4.07 (m, 4H, -O-CH_2-), 1.94 (pt, *J* = 13.1, 6.6 Hz, 4H, -CH_2-HC=C$(CH_3)_2$), 1.77–1.53 (m, 16H), 1.53–1.11 (m, 6H), 0.91 (d, *J* = 6.4 Hz, 6H-CH(CH_3)-).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.4 (-O*C*O_2-), 131.3 (-HC=*C*$(CH_3)_2$), 124.5 (-H*C*=C$(CH_3)_2$), 66.4 (-O-*C*H_2-), 37.0 (-*C*H_2-CH_2-HC=C$(CH_3)_2$), 35.5 (CH_3O-C(O)$_2$-CH_2-*C*H_2-), 29.2 (-CH_2-*C*H(CH_3)-CH_2-), 25.7 (-$C_{isomer}H_2$-HC=C$(CH_3)_2$), 25.3 (-$C_{isomer}H_2$-HC=C$(CH_3)_2$), 19.3 (-HC=C(*C*$H_3)_2$), 17.6 (-HC=C(*C*$H_3)_2$).

HRMS of $C_{21}H_{38}O_3$ $[M+H]^+$ calc. 339.29 found 339.20

Dibenzyl carbonate (entry 4): purified with extraction using *n*-hexane to yield a solid at RT (93%). ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 7.54–7.30 (m, 10H), 5.22 (s, 4H).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.0 (-O*C*O_2-), 135.12 (aromatic *C*H), 128.4 (aromatic *C*H), 69.6(-*C*H_2-O-).

HRMS of $C_{15}H_{14}O_3$ $[M+H]^+$ calc. 243.10 found 243.10

Di(1-phenylbut-3-en-1-yl) carbonate (entry 5): purified over short pad of silica (*n*-hexane/ethyl acetate = 5/1); colourless oil in 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 7.49–7.27 (m, 10H, aromatic C*H*), 5.87–5.57 (m, 2H, CH_2=C*H*-), 5.29–4.99 (m, 6H, C*H*$_2$=CH- and CH_2=CH-CH_2-C*H*-), 2.99–2.42(m, 4H, CH_2=CH-C*H*$_2$-CH-).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 153.9 (-O$C_{isomer}O_2$-), 153.8 (-O$C_{isomer}O_2$-), 139.4 (aromatic *C*H), 139.3 (aromatic CH), 132.8 (CH_2=C_{isomer}H-), 132.7 (CH_2=C_{isomer}H-), 128.4-126.3 (aromatic *C*H), 118.2 ($C_{isomer}H_2$C=H-), 118.1 ($C_{isomer}H_2$C=H-), 79.2 (-C_{isomer}H-O-), 79.1 (-C_{isomer}H-O), 40.7 (CH_2=CH-$C_{isomer}H_2$-), 40.6 (CH_2=CH-$C_{isomer}H_2$-).

HRMS of $C_{21}H_{22}O_3$ $[M+H]^+$ calc. 323.16 found 323.20

ADMET polymerization of M1 with different metathesis catalysts

Reactions were carried out in parallel using a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). In a representative polymerization 500 mg (1.37 mmol) of **M1** and 0.4 mol % **BQ** were added to a carousel tube equipped with a screw at reaction temperature of 80°C and let to stir magnetically for 10 min. Then, 0.2 mol% of the corresponding ruthenium catalyst (**C1**, **C2** or **C3**) was added to the reaction mixture. After 1 h reaction under continuous vacuum, the reaction mixtures were allowed to cool to room temperature, the residue was dissolved in THF and the metathesis reaction was stopped by adding ethyl vinyl ether (500-fold excess to the catalyst) and stirring for 30 minutes (at room temperature). Polymers were precipitated in cold MeOH on ice bath.

P10 (85%): ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.44–5.30 (m, -C*H*=C*H*-), 4.12 (dt, *J* = 9.7, 6.5 Hz, -CH_2-O-), 2.05–1.87 (m, -CH=CH-CH_2-), 1.73–1.54 (m, aliphatic -CH_2-), 1.27 (s, aliphatic -CH_2-).

ADMET polymerization of M2

Reactions were carried out in parallel using a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). In a representative polymerization 500 mg (1.48 mmol) of **M2** and different amounts of **C3** (see Table 7 in the main text) were added separately to a carousel tube equipped with a screw at 90 °C. The influence of the amount of the **BQ**, added 10 min prior to the catalyst addition, on the obtained molecular weight was studied. After 4 h reaction under continuous vacuum, the reaction mixtures were allowed to cool to room temperature, then the residue was dissolved in THF and the metathesis reaction was stopped by adding ethyl vinyl ether (500-fold excess to the catalyst) and stirring for 30 minutes (at room temperature). Polymers were precipitated in ice cold MeOH.

In addition, it was observed that the high loadings of the catalyst (**C3**) in the presence of 2.0 mol% **BQ** (relative to the **M2)** were reason for the olefin isomerization of the terminal double bond as shown below in Figure 1. Thus high loadings of **BQ** (4.0 mol% relative to **M2**) were required. However, this was not efficient to prevent completely the isomerization.

P14 (75%) ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.46-4.96 (m, -C*H*=C*H*-), 4.14 (dt, *J* = 13.3, 6.6 Hz, -CH_2-O-), 2.48-2.15 (m, -CH=CH-C$_{isomerized}H_2$-), 2.14-1.80 (m, -CH=CH-CH_2-), 1.80-1.40 (m, aliphatic -CH_2-), 1.38-1.04 (m, aliphatic -CH_2-), 1.04-0.72 (m, -CH_3).

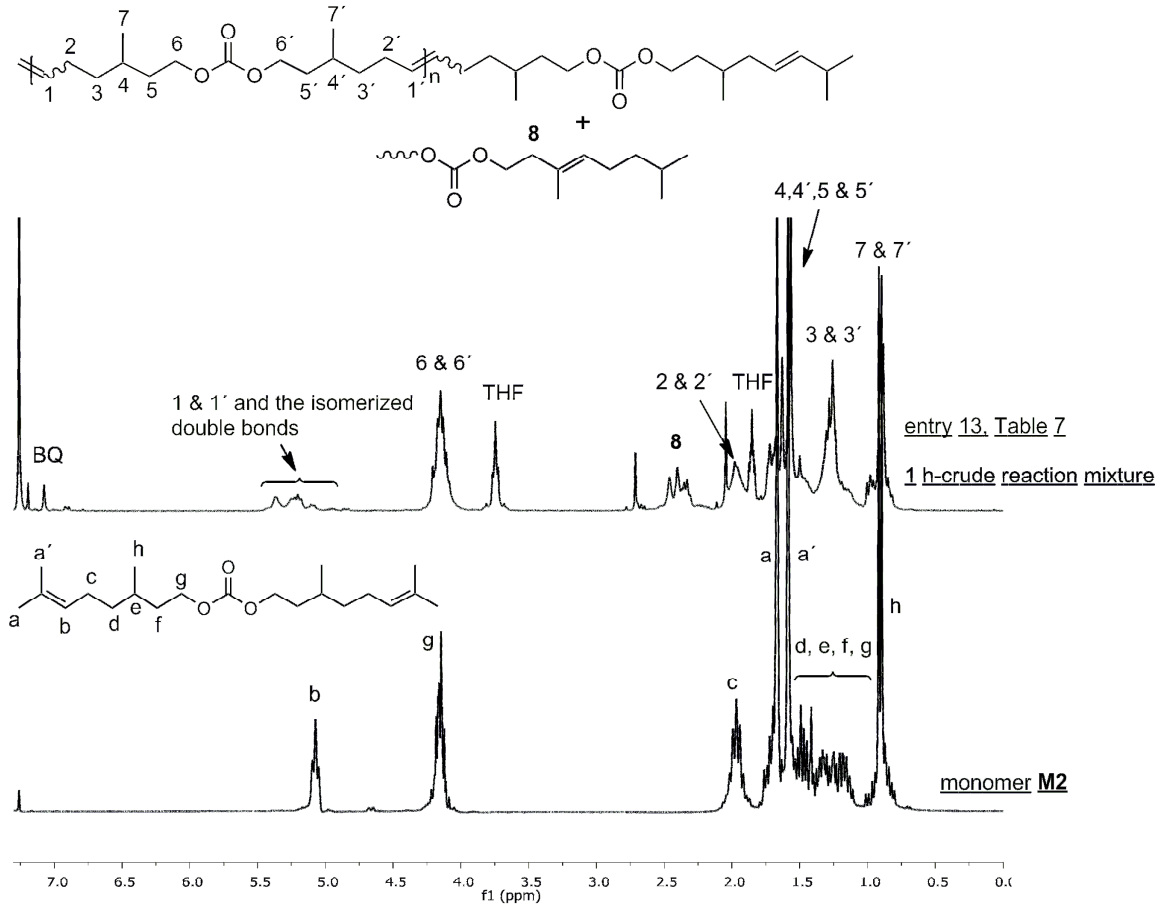


Fig.1-SI Olefin isomerization observed during the polymerization of **M2** in the presence of **C3**.

References

1 M. Firdaus, L. Montero de Espinosa and M. A. R. Meier, *Macromolecules,* 2011, **44**, 7253.

2 P. Tundo, F. Aricò, A. E. Rosamilia and Sofia Memoli, *Green Chem.* 2008, **10**, 1182.

3 Y.Terui, K. Tori, N. Tsuji, *Tetrahedron Lett.,* 1976, **17**, 621.

4 M. Selva, C. A. Marques, P. Tundo, *J. Chem. Soc., Perkin Trans.* I, 1995, 1889-1893.