

Supporting Information

Figure S1. ^1H NMR (200 MHz, CDCl_3 , 23 °C) spectrum of $\text{TMC}(\text{OMe})_2$.

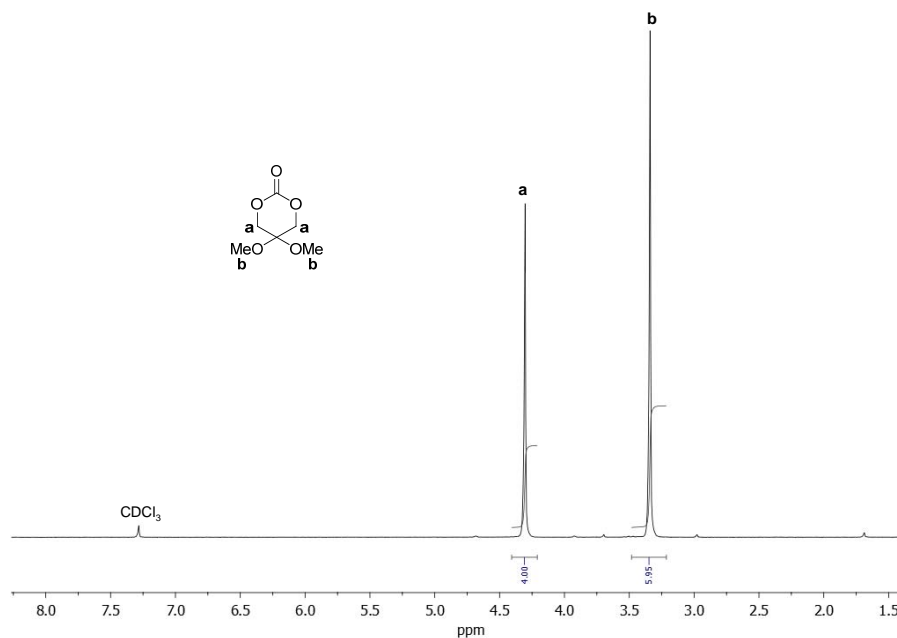
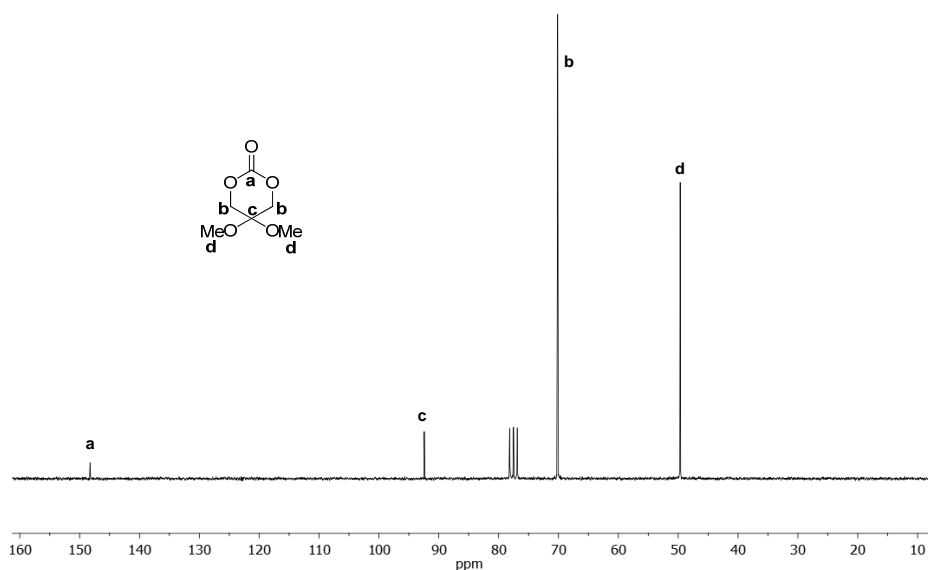


Figure S2. ^{13}C NMR (50 MHz, CDCl_3 , 23 °C) spectrum of $\text{TMC}(\text{OMe})_2$.



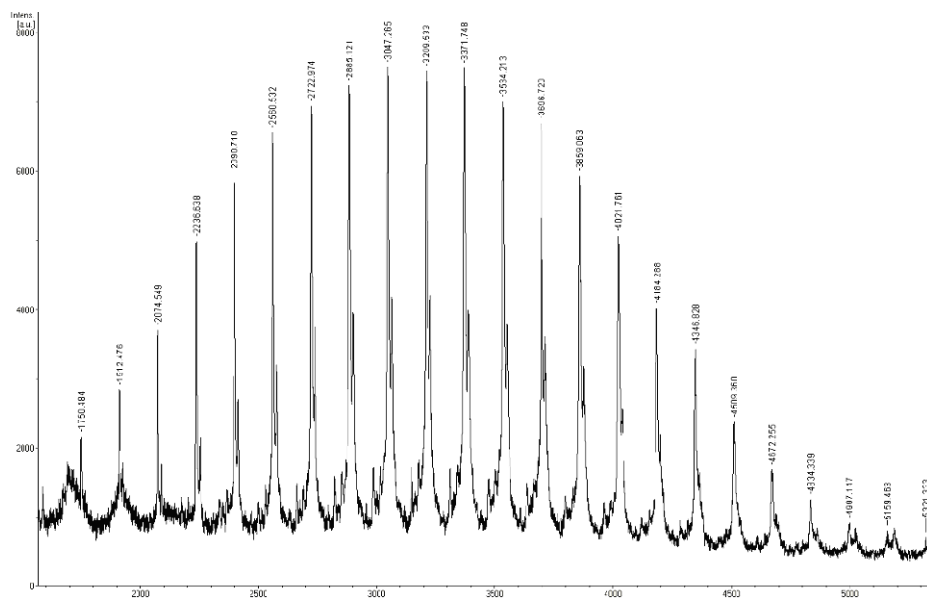
NMR Data of H-P(TMC(OMe)₂)-OBn

¹H NMR (500 MHz, CDCl₃) δ 7.39 (m, 5H, C₆H₅), 5.19 (s, 2H, C₆H₅CH₂), 4.24 (s, (4n+2)H, ({C(O)OCH₂C(OCH₃)₂CH₂}; CH₂C(OCH₃)₂CH₂OH)), 3.87 (s, 2H, HOCH₂C(CH₃)₂CH₂), 3.30 (s, (6n+6)H, {C(O)OCH₂C(OCH₃)₂CH₂}, HOCH₂C(CH₃)₂CH₂). ¹³C{¹H} NMR (50 MHz, CDCl₃) δ 155.3 ({C(O)OCH₂C(OCH₃)₂CH₂}), 138.9 (C_{6ortho}H₅), 129.0 (C_{6meta}H₅), 128.1 (C_{6para}H₅), 102.3 (HOCH₂C(OCH₃)₂CH₂OC(O)), 99.8 ({C(O)OCH₂C(OCH₃)₂CH₂}), 72.7 (PhCH₂OC(O)), 67.9 ({C(O)OCH₂C(OCH₃)₂CH₂}), 51.0({C(O)OCH₂C(OCH₃)₂CH₂}).

NMR Data of H-P(TMC(OMe)₂)-H

¹H NMR (500 MHz, CDCl₃) δ 4.24 (s, (4n+4)H, ({C(O)OCH₂C(OCH₃)₂CH₂}, HOCH₂C(OCH₃)₂CH₂), 3.78 (m, 4H, (OCH₂CH₂CH₂O)), 3.63 (s, 4H, (HOCH₂C(OCH₃)₂CH₂), 3.31 (s, (6n+6)H, {C(O)OCH₂C(OCH₃)₂CH₂}, HOCH₂C(OCH₃)₂CH₂), 1.88 (m, 2H, (OCH₂CH₂CH₂O)). ¹³C{¹H} NMR (50 MHz, CDCl₃) δ 155.2 ({C(O)OCH₂C(OCH₃)₂CH₂}), 102.6 (HOCH₂C(OCH₃)₂CH₂), 99.8 ({C(O)OCH₂C(OCH₃)₂CH₂}), 69.0 ({C(O)OCH₂C(OCH₃)₂CH₂}), 63.3 (OCH₂CH₂CH₂O), 50.8 ({C(O)OCH₂C(OCH₃)₂CH₂}), 26.9 (OCH₂CH₂CH₂O).

Figure S3. MALDI-ToF mass spectrum of a H-PTMC(OMe)₂-OBn sample (\overline{M}_n SEC = 3 130 g.mol⁻¹; Table 1, entry 7).**Error! Bookmark not defined.**^e



The most intense signal detected, m/z : 3209.5 g.mol⁻¹, corresponds to the sodium species H-[TMC(OMe)₂]₁₉-OCH₂Ph.Na⁺ containing 19 monomer units (calculated isotopic mass for ¹²C₁₂₁¹H₁₉₈²³Na₁¹⁶O₉₆: 3 210 g.mol⁻¹) and benzyloxy and hydroxyl end groups. The minor second distribution (m/z : [M+Na]⁺ + 16 = [M+K]⁺) corresponds to the analogous H-P(TMC(OMe)₂)-OCH₂Ph.K⁺ series with a similar repeat unit.

Table S1. Thermal properties of the polycarbonates

	\bar{M}_n^a (g.mol ⁻¹)	T_g^b (°C)	T_d^c (°C)
PTMCErrror!			
Bookmark not defined.	8 100-457 000	-15/-20	+ 230
P(TMC(OMe) ₂)	38 800	39	225

^[a] Molar mass value determined by SEC. ^[b] Glass transition temperature determined by DSC. ^[c] Degradation temperature determined by TGA.