Supporting Information
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Experimental Section.

All experiments were carried out under an argon atmosphere using dried glassware. Chemicals were purchased from commercial suppliers and used as received unless otherwise noted. Benzaldehyde was freshly distilled prior to use. Dry CH$_2$Cl$_2$ was purchased from Sigma-Aldrich and dried via a Solvent Purification System MB-SPS 800 from MBraun. Column chromatography was performed on Merck Silica Gel 60 (230-400 mesh). Ultrafiltration was performed with a 300 mL solvent-resistant stirred cell with regenerated cellulose membranes (molecular weight cutoff 5000 g mol$^{-1}$), both from Millipore. $^1$H-, $^13$C- and $^{31}$P-NMR spectra were recorded at room temperature using a Jeol ECX 400 and Bruker AV 700. 2D spectra were recorded on a Jeol Eclipse 500. Chemical shifts ($\delta$) were reported in parts per million (ppm) relative to tetramethylsilane and coupling constants ($J$) in Hertz (Hz). The spectra were referenced against the internal solvent (CDCl$_3$, $^1$H = 7.26 ppm, $^{13}$C = 77.0 ppm). O-Mesylpolyglycerol was synthesized according to the literature procedure.$^{1}$

Polyglycerylmethylamine (2). O-Mesylpolyglycerol (4.4 g, 28.6 mmol mesyl groups) was dissolved in p.a. DMF (20 mL) in a 48 mL ACE pressure tube using ultrasonication. In the next step, 15 mL methylamine gas was condensed into the tube and sealed afterwards. The mixture was stirred and heated up to 60 °C for 24 h. For workup the mixture was diluted with methanol and filtered using a glass frit. The dissolved crude product was further purified by ultrafiltration with methanol as solvent and 2 mL triethylamine as an additive in the first run. After the third run the filtrate became colorless. The solvent was evaporated and a brown honey-like product was obtained. Yield: 95%, 8 mmol methylamine-groups per gram polymer; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 3.87–3.16 (br m, PG-backbone), 2.77–2.62 (m, functionalized PG groups), 2.42–2.17 (br m, NCH$_3$); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 78.6–68.7 (PG), 62.0–46.0 (functionalized PG groups); 43.0-34.0 (NHMe).

PG-Hexamethylphosphoramide (4). Polyglycerylmethylamine (2) (1 g, 8 mmol) was dissolved in dry THF (20 mL) in a 50 mL Schlenk tube. The clear yellow solution was cooled to -78 °C and after 30 min, N$_2$N,N$'$,N$''$-tetramethylphosphoro-diamidic chloride (8 mmol, 1.2 mL) was added dropwise by syringe. The reaction was warmed to room temperature overnight and then quenched by addition of methanol. The crude product was purified by ultrafiltration (membrane: 5kDa, solvent: methanol). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 3.85–3.28 (br m, PG-backbone), 2.65–2.16 (br m, NCH$_3$); $^{31}$P-NMR (121.5 MHz, CDCl$_3$): $\delta$ = 26.0, 27.4 ppm. Loading: 1 mmol HMPA per gram polymer; determined by addition of tritylphosphine oxide as internal standard, followed by integration in the $^{13}$P spectra.

General procedure for the catalyzed aldol reaction with slow addition of aldehyde.$^{15, 16}$ The catalyst PG-HMPA (50 mg, 0.05 mmol, 0.1 equiv.) was dissolved in CH$_2$Cl$_2$ (0.5 mL), and the solution was cooled to -78 °C. 1-Cyclohexenylhexachlorosilane (100 $\mu$L, 0.55 mmol, 1.1 equiv.) was added dropwise. A solution of benzaldehyde (50 $\mu$L, 0.5 mmol, 1.0 equiv.) in CH$_2$Cl$_2$ (0.2 mL) was then added dropwise to the first solution with the help of a syringe pump (speed: 0.3 mL/1 h). During the addition the temperature remained constant at -78 °C. The reaction mixture was stirred at -78 °C for an additional 60 min and then quickly poured into a cold (2 °C) saturated aqueous solution of sodium bicarbonate (2 mL). The mixture was allowed to warm to rt. The phases were separated, and the aqeous phase was washed with CH$_2$Cl$_2$ (2 x 10 mL). The organic phases were combined, dried over MgSO$_4$ and the solvent was removed in vacuo. The crude product was analyzed by $^1$H NMR. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.36–7.28 (m, 5 H, HC(Aryl)), 5.86–5.76 (m, 1 H, HC-3), 5.18–5.13 (m, 2 Ph), 2.58–2.53 (m, 2 H, H$_2$C-4), 4.78 (dd, $J = 7.3, 5.5$ Hz, 1 H, HC-1), 2.57–2.45 (m, 1 H, HC-2), 2.05 (br s, 1 H, OH).