

Supporting Information for

**Suzuki Polycondensation towards High Molecular Weight  
Poly(*m*-phenylene)s: Mechanistic Insights and End Functionalization**

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## 1. General

All the reactions were carried out under nitrogen by using standard Schlenk techniques. All the reagents were purchased from commercial sources and used without further purification unless noted. Solvents were dried using a SP-105 solvent purification system from LC Technology Solutions Inc. Degassing was performed by at least three consecutive freeze-pump-thaw cycles.  $\text{Pd}[\text{P}(p\text{-tol})_3]_3$  was prepared according to literature procedures.<sup>1</sup> SPhos was purchased from Sigma-Aldrich. Column chromatography was performed by using Merck silica gel Si60 (particle size 40-63  $\mu\text{m}$ ).

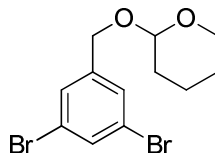
NMR was recorded with Bruker AM ( $^1\text{H}$ : 300 MHz or 700 MHz,  $^{13}\text{C}$ : 75.5 MHz) at room temperature using chloroform- $d$  as solvent. The solvent signal was used as internal standard of chemical shift ( $^1\text{H}$ :  $\delta = 7.24$  ppm,  $^{13}\text{C}$ :  $\delta = 77.00$  ppm).

High-resolution mass spectrometry (HRMS) analyses were performed by the MS-service in the laboratory of organic chemistry at ETH Zurich using an electrospray-ionization (ESI) MS spectrometer with a Quadrupole-Time-of-flight tandem mass analyzer (Q-TOF) (Bruker Daltonics maXis) or electron-impact-ionization (EI) (Micromass AutoSpec-Ultima). MALDI-TOF mass spectra were recorded using a Bruker UltraFlex II MALDI-TOF mass spectrometer (Bremen, Germany) equipped with a  $\text{N}_2$  smartbeam laser ( $\lambda = 337$  nm, 150  $\mu\text{J}$ , 3 ns) operating at a pulse rate of 100 Hz. For MALDI-TOF MS analyses, the ions were accelerated with pulsed ion extraction (PIE) by a voltage of 25 kV. The analyzer was operated in reflection mode unless otherwise stated, and the ions were detected using a microchannel plate detector. A total of 500-1000 shots were accumulated for each mass spectrum. As matrix material *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) with NaOTf or AgOTf was used.

Analytical GPC measurements were performed using a Viscotek GPC-system with chloroform eluent, equipped with a pump and a degasser (GPCmax VE2001, flow rate 1.0 ml/min), a detector module (Viscotek 302 TDA), a UV detector (Viscotek 2500,  $\lambda = 254$  nm) and three columns (1  $\times$  PLGel Mix-B and 1  $\times$  PLGel Mix-C, 7.5  $\times$  300 mm for each). Universal calibration was performed with polystyrene standards (Polymer laboratories) in the range of  $M_p$  1480 to 4340000. Prior to injection, the sample solution was filtered through a sintered stainless steel filter (pore size 2  $\mu\text{m}$ ).

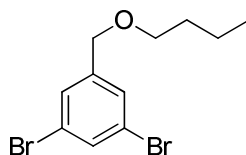
Preparative recycling GPC separation was done on a LC-9101 system from Japan Analytical Industry Co., Ltd. (JAI) with two columns (1  $\times$  JAIGEL-2H and 1  $\times$  JAIGEL-2.5H, 20  $\times$  600 mm each) using chloroform as eluent. The JAI 3702 UV detector was set to a wavelength of 285 nm.

## 2. Procedures for Monomer Synthesis



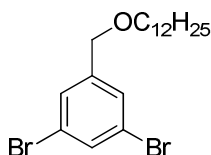
**2-(3,5-Dibromobenzoyloxy)tetrahydropyran (1a):** A stirred solution of 10 g (38 mmol) (3,5-dibromophenyl)methanol<sup>2</sup> in dichloromethane was cooled to 0 °C. 5.2 mL (56 mmol) 3,4-dihydropyran and 71 mg (0.38 mmol) 4-methylbenzensulfonic acid monohydrate was added. The mixture was allowed to warm up to room temperature overnight. The dark brown solution was quenched with triethylamine (10 mL) upon which the color changed to orange. The solvent was evaporated and the crude product was purified using medium pressure liquid chromatography (SiO<sub>2</sub>, dichloromethane/hexane, 1:1) to give 12.19 g (93%) of **1a** as a colorless liquid.

<sup>1</sup>H-NMR (300 MHz)  $\delta$ /ppm: 7.57 (s, 1 H, Ar-H); 7.44 (s, 2H, Ar-H); 4.75 – 4.62 (m, 2 H, benzyl and THP); 4.43 (d,  $J$  = 12.7 Hz, 1H, benzyl); 3.94 – 3.77 (m, 1H, THP); 3.61 – 3.46 (m, 1H, THP); 1.91 – 1.48 (m, 6H, THP). <sup>13</sup>C-NMR (75 MHz)  $\delta$ /ppm: 142.4; 132.9; 129.1; 122.8; 98.0; 67.2; 62.1; 30.4; 25.3; 19.2. ESI-MS:  $m/z$  calculated for C<sub>12</sub>H<sub>14</sub>Br<sub>2</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 370.9253, found 370.9257.



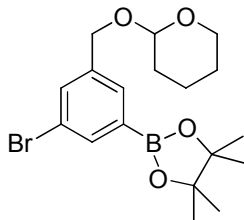
**1,3-Dibromo-5-(butoxymethyl)benzene (1b):** In an oven dried Schlenk flask 6.1 g NaH (254 mmol) was suspended in dry THF (200 mL) and kept under a N<sub>2</sub> atmosphere. A solution of 45 g (3,5-dibromophenyl)methanol<sup>2</sup> (169 mmol) in dry THF (130 mL) was slowly added. The mixture was heated to reflux whereby the solution turned orange. After 45 min 54.8 mL 1-bromobutane (508 mmol) was added in one portion. After 18 h the slightly yellow suspension was cooled to room temperature and excess NaH was quenched by adding water (300 mL). The two clear phases were separated and the aqueous phase was extracted with Et<sub>2</sub>O (3 x 150 mL). The organic phases were combined, dried over MgSO<sub>4</sub>, filtered and evaporated to give an orange oil. Vacuum distillation (0.2 mbar, 125 °C) yielded 47.9 g of **1b** (88 %) as a colorless liquid.

<sup>1</sup>H-NMR (300 MHz)  $\delta$ /ppm: 7.59 (s, 1H, Ar-H), 7.44 (s, 2H, Ar-H), 4.46 (s, 2H, Ar-CH<sub>2</sub>-), 3.50 (t,  $J$  = 6.5 Hz, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.64 (m, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.43 (m 2H, CH<sub>2</sub>-CH<sub>3</sub>), 0.96 (t,  $J$  = 7.3 Hz, 3H, -CH<sub>3</sub>). <sup>13</sup>C-NMR (75 MHz)  $\delta$ /ppm: 142.9; 132.9; 129.0; 122.9; 71.2; 70.7; 31.7; 13.3; 13.9. EI-MS:  $m/z$  calculated for C<sub>7</sub>H<sub>6</sub>Br<sub>2</sub> [M]<sup>+</sup> 319.9411, found 319.9396, calculated for C<sub>7</sub>H<sub>5</sub>Br<sub>2</sub>O [M- C<sub>4</sub>H<sub>9</sub>]<sup>+</sup> 262.8707, found 262.8703, calculated for C<sub>7</sub>H<sub>5</sub>Br<sub>2</sub> [M-C<sub>4</sub>H<sub>9</sub>O]<sup>+</sup> 246.8758, found 246.8760.



**1,3-Dibromo-5-(dodecyloxymethyl)benzene (1c):** To a stirred mixture of 20.70 g (3,5-dibromophenyl)methanol<sup>2</sup> (75.5 mmol) and 320 mg imidazole (4.7 mmol) in dry THF (200 mL) in a Schlenk tube under N<sub>2</sub> was added 5.39 g NaH (224.7 mmol). After stirring for 2 h, 72.0 mL dodecyloxymethylbromide (297.6 mmol) was added and the solution was stirred for 4 d at 40 °C. Then the reaction mixture was quenched with water (100 mL), the phases were separated and the aqueous phase was extracted with Et<sub>2</sub>O (3 x 70 mL). The combined organic phase was washed with brine (70 mL), dried over MgSO<sub>4</sub> and the solvent was evaporated. From the remaining yellow oil the excess dodecyloxymethylbromide was distilled off under reduced pressure (0.6 mbar, 92 °C). A yellowish solid precipitated overnight and was washed with an ice-cold mixture of ethanol/isopropanol (1:1) to give 23.92 g of **1c** (73%) as a white solid.

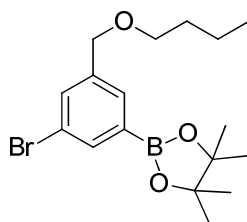
mp: 31 – 32 °C. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ/ppm: 7.57 (s, 1H, Ar-H), 7.42 (s, 2H, Ar-H), 4.43 (s, 2H, Ar-CH<sub>2</sub>-), 3.46 (t, *J* = 6.4 Hz, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.62 (quint, *J* = 5.1 Hz, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.26 (s, 18H, -(CH<sub>2</sub>)<sub>9</sub>-CH<sub>3</sub>), 0.8 (t, *J* = 6.5 Hz, 3H, -CH<sub>3</sub>). <sup>13</sup>C-NMR (75 MHz) δ/ppm: 142.9; 132.9; 129.0; 122.9; 71.2; 71.0; 31.91; 29.654; 29.636; 29.629; 29.599; 29.580; 29.43; 29.34; 26.12; 22.68; 14.11. EI-MS: *m/z* calculated for C<sub>7</sub>H<sub>6</sub>Br<sub>2</sub> [M-C<sub>12</sub>H<sub>25</sub>O]<sup>+</sup> 246.8758, found 246.8752, calculated for C<sub>7</sub>H<sub>6</sub>Br [M-C<sub>12</sub>H<sub>25</sub>BrO]<sup>+</sup> 246.8758, found 246.8752.



**2-(3-Bromo-5-((tetrahydropyranyloxy)methyl)phenyl)pinacol borane (2a):** A stirred solution of 19.5 g (55.7 mmol) (3,5-Dibromobenzyloxy)tetrahydropyran (**1a**) in dry diethyl ether (300 mL) under nitrogen atmosphere was cooled to -78 °C and 38.3 mL *n*-butyllithium (1.6 M in hexane, 61.3 mmol) was added dropwise over 45 min. After stirring the yellow mixture for 3 h, 13.6 mL isopropyl pinacol (66.8 mmol)borate was added. The mixture was stirred for 3 h and then slowly warmed up to room temperature. After stirring overnight saturated NH<sub>4</sub>Cl aq. (150 mL) was added to the white suspension and the phases were separated. The aqueous phase was extracted with diethyl ether (3 x 100 mL). The ether phases were combined, dried over MgSO<sub>4</sub> and evaporated at 0.1 mbar to give a yellow oil. The residue was recrystallized in petrol ether (b.p.: 80 – 110 °C) and again recrystallized in acetonitrile to give 16.03 g **2a** (72 %) as a white crystalline solid.

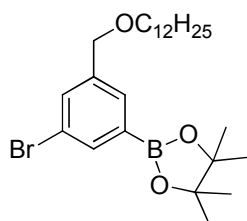
m.p.: 68 – 70 °C. <sup>1</sup>H-NMR (700 MHz) δ/ppm: 7.84 (s, 1H, Ar-H); 7.66 (s, 1H, Ar-H); 7.64 (s, 1H, Ar-H); 4.74 (d, *J* = 12.2 Hz, 1H, CH<sub>2</sub>); 4.69 (t, *J* = 3.5 Hz, 1H, THP), 4.45 (d, *J* = 12.2 Hz, 2H, Ar-CH<sub>2</sub>); 3.91 – 3.88 (m, 1H, THP); 3.56 – 3.53 (m, 1H, THP); 1.89 – 1.84 (m, 1H, THP); 1.76 – 1.72 (m, 1H, THP); 1.68 – 1.53 (m, 4H, THP); 1.34 (s, 12 H, -CH<sub>3</sub>). <sup>13</sup>C-NMR (75 MHz) δ/ppm: 140.0; 136.5; 133.4; 132.4;

122.5; 97.9; 54.1; 68.0; 62.1; 30.4; 25.4; 24.8; 19.2 (Carbon attached to boron was not observed due to quadrupolar relaxation). ESI-MS:  $m/z$  calculated for  $C_{18}H_{30}BBrNO_4$   $[M+NH_4]^+$ : 414.1446, found: 414.1448.



**2-(3-Bromo-5-(butoxymethyl)phenyl)pinacol borane (2b):** A stirred solution of 8.15 g (25.3 mmol) 1,3-dibromo-5-(butoxymethyl)benzene (**1b**) in dry diethyl ether (140 mL) under nitrogen atmosphere was cooled to -78 °C and 16.6 mL n-butyllithium (1.6 M in hexane, 26.6 mmol) was added dropwise over 20 min. After stirring the yellow mixture for 3 h, 6.2 mL isopropyl pinacol (30.4 mmol) borate was added. The mixture was stirred for 3 h and then slowly warmed up to room temperature. After stirring overnight saturated  $NH_4Cl$  aq. (100 mL) was added to the white suspension and the phases were separated. The aqueous phase was extracted with diethyl ether (3 x 100 mL). The ether phases were combined, dried over  $MgSO_4$  and evaporated. The resulting oil was purified by medium pressure liquid chromatography ( $SiO_2$ , hexane/ethyl acetate, 95:5) to give 3.4 g **2b** (35 %) as a colorless liquid.

$^1H$ -NMR (300 MHz)  $\delta$ /ppm: 7.84 (s, 1H, Ar-H), 7.64 (s, 1H, Ar-H), 7.61 (s, 1H, Ar-H), 4.45 (s, 2H, Ar-  $CH_2$ ), 3.46 (t,  $J$  = 6.6 Hz, 2H, -O- $CH_2$ - $CH_2$ -), 1.65-1.53 (m, 2H, -O- $CH_2$ - $CH_2$ -), 1.45-1.34 (m, 2H, - $CH_2$ - $CH_3$ ), 1.34 (s, 12H, pinacol), 0.92 (t,  $J$  = 7.3 Hz, 3H, - $CH_3$ ).  $^{13}C$ -NMR (75 MHz)  $\delta$ /ppm: 140.4; 136.5; 133.3; 132.2; 122.5; 84.1; 72.0; 70.5; 31.8; 24.8; 19.3; 13.9 (Carbon attached to boron was not observed due to quadrupolar relaxation). EI-MS:  $m/z$  calculated for  $C_{17}H_{26}BBrO_3$   $[M]^+$  368.1158, found 368.1157, calculated for  $C_{16}H_{23}BBrO_3$   $[M-CH_3]^+$  353.0924, found 353.0922, calculated for  $C_{13}H_{17}BBrO_2$   $[M-C_4H_9O]^+$  295.0505, found 295.0515.



**2-(3-Bromo-5-(dodecyloxymethyl)phenyl)pinacol borane (2c):** A stirred solution of 2.0 g (4.61 mmol) 1,3-dibromo-5-(dodecyloxymethyl)benzene (**1c**) in THF (50 mL) under nitrogen atmosphere was cooled to -50 °C and 3.0 mL n-butyllithium (1.6 M in hexane, 4.84 mmol) was added dropwise over 10 min. After stirring the deep red solution for 45 min, 1.4 mL isopropyl pinacol (6.91 mmol) borate was added. The yellow/orange solution was stirred for 3 h and then slowly warmed up to room temperature. After stirring overnight water (50 mL) was added to the yellow suspension and the phases were separated. The aqueous phase was extracted with diethyl ether (3 x 50 mL). The ether phases were combined, dried over  $MgSO_4$  and

evaporated. The resulting oil was purified by column chromatography (SiO<sub>2</sub>, hexane/ethyl acetate, 5:1) to give 0.71 g **2c** (32 %) as a colorless liquid.

<sup>1</sup>H-NMR (300 MHz)  $\delta$ /ppm: 7.84 (s, 1H, Ar-H), 7.64 (s, 1H, Ar-H), 7.61 (s, 1H, Ar-H), 4.46 (s, 2H, Ar-CH<sub>2</sub>-), 3.45 (t,  $J$  = 6.6 Hz, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.61 (t,  $J$  = 7.2 Hz, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34 (s, 12H, pinacol), 1.26 (s, 18H, -(CH<sub>2</sub>)<sub>9</sub>-CH<sub>3</sub>), 0.88 (t,  $J$  = 6.6 Hz, 3H, -CH<sub>2</sub>-CH<sub>3</sub>). <sup>13</sup>C-NMR (75 MHz)  $\delta$ /ppm: 140.4; 136.5; 133.3; 132.2; 122.5; 84.1; 72.0; 70.8; 31.9; 29.68; 29.65; 29.61; 29.589, 29.580, 29.46; 29.33; 26.1; 24.8; 22.7; 14.1 (Carbon attached to boron was not observed due to quadrupolar relaxation). EI-MS:  $m/z$  calculated for C<sub>25</sub>H<sub>39</sub>BBrO<sub>3</sub> [M-CH<sub>3</sub>]<sup>+</sup> 465.2176, found 465.2169, calculated for C<sub>13</sub>H<sub>17</sub>BBrO<sub>3</sub> [M-C<sub>12</sub>H<sub>25</sub>]<sup>+</sup> 311.0454, found 311.0463.

### 3. Procedures for Suzuki Polycondensation

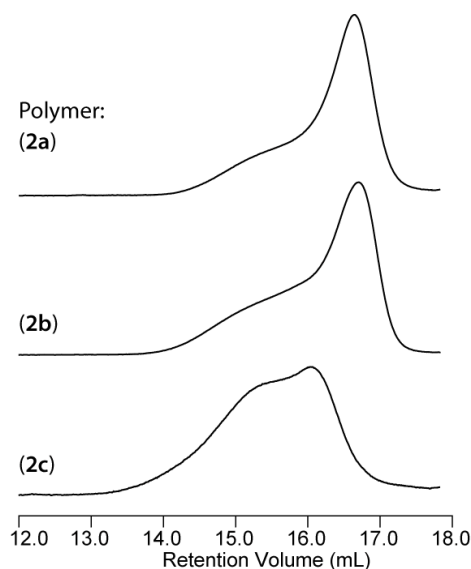
**A Typical Procedure for Suzuki Polycondensation in batch:** A Schlenk flask was charged with 750 mg monomer **1a** (1.89 mmol) and 1.05 g Cs<sub>2</sub>CO<sub>3</sub> (3.21 mmol.). The flask was evacuated and back-filled with N<sub>2</sub> for three times. In a glove box, 38 mg Pd[P(*p*-tol)<sub>3</sub>]<sub>3</sub><sup>1</sup> (2 mol%) was weighed, dissolved in degassed THF (1 mL) and added by syringe. The mixture was degassed and vigorously stirred at 70 °C under an N<sub>2</sub> atmosphere. After 3 d THF was evaporated and dichloromethane (30 mL) was added. The organic phase was washed with water (3 x 50 mL), dried over MgSO<sub>4</sub>, filtrated and evaporated to give the product as grey solid (320 mg, 89 %).

**A Typical Procedure for Suzuki Polycondensation with Slow Monomer Addition:** A Schlenk flask was charged with 7.2 mg Pd(dba)<sub>2</sub> (0.013 mmol, 0.01 eq.), 10.3 mg SPhos (0.025 mmol, 0.02 eq.), and 845 mg NaHCO<sub>3</sub> (10.1 mmol, 8 eq.). The flask was evacuated and back-filled with N<sub>2</sub> for three times. Degassed THF (10 mL) and water (10 mL) was added, the mixture was degassed again and vigorously stirred at 70 °C. A degassed solution of 500 mg monomer **1a** (1.26 mmol, 1 eq.) in THF (10 mL), was added by syringe pump at a rate of 0.74 mL/h. After the addition, stirring and heating was continued for 1 d. After cooling to room temperature, water (25 mL) and chloroform (25 mL) were added and the heterogeneous solution was stirred with NaCN (50 mg) for at least 2 h. The phases were separated and the aqueous layer was extracted with chloroform (3 x 25 mL). The organic phases were combined, dried over MgSO<sub>4</sub>, filtered and evaporated. The slightly yellow solid was dissolved in ca. 3 mL dichloromethane and slowly precipitated into 50 mL methanol at -15 °C. The precipitate was collected by filtration or centrifugation and dried *in vacuo* to afford the product (210 mg, 88 %) as an off-white powder.

**A Typical Procedure for Suzuki Polycondensation with End Capping:** A Schlenk flask was charged with 3.6 mg Pd(dba)<sub>2</sub> (6  $\mu$ mol, 0.01 eq.), 5.2 mg SPhos (13  $\mu$ mol, 0.02 eq.) and 423 mg NaHCO<sub>3</sub> (5.0 mmol, 8 eq.). The flask was evacuated and back-filled with N<sub>2</sub> for three times. Degassed THF (10 mL), water (10 mL) and 27.5 mg 4-bromofluorobenzene (0.157 mmol, 0.25 eq.) was added. Then, the mixture was degassed again and vigorously stirred at 70 °C. A degassed solution of 250 mg monomer **1a** (0.63 mmol, 1 eq.) in THF (5 mL), was added by syringe pump at a rate of 1 mL/h. After the addition, a solution of 4-anisylpinacolborane in degassed THF (2 mL) was added. Stirring and heating was continued for 1 d. After cooling to room

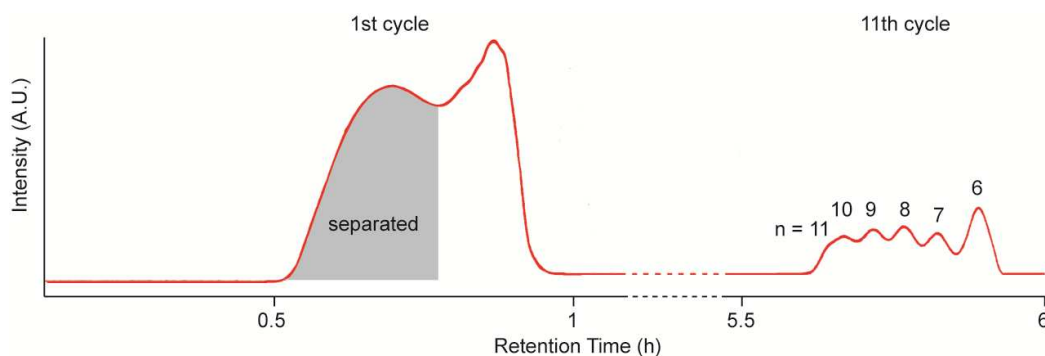
temperature, water (25 mL) and chloroform (25 mL) were added and the heterogeneous solution was stirred with NaCN (25 mg) for at least 2 h. The phases were separated and the aqueous layer was extracted with chloroform (3 x 20 mL). The organic phases were combined, dried over MgSO<sub>4</sub>, filtered and evaporated. The slightly yellow solid was dissolved in ca. 3 mL dichloromethane and slowly precipitated into 30 mL methanol at -15 °C. The precipitate was collected by filtration or centrifugation and dried *in vacuo* to afford the product (99 mg, 83 %) as an off-white powder.

#### 4. GPC Elution Curves of SPC Products with Different Side Groups



**Figure S1.** GPC elution curves obtained from SPC products with different side groups **2a-c**. The polymers were synthesized by SPC with the following reaction conditions: Pd[P(p-Tol)<sub>3</sub>]<sub>3</sub> (0.01 eq), NaHCO<sub>3</sub> (8 eq) in THF-water 3:1. The curves were recorded with a RI detector.

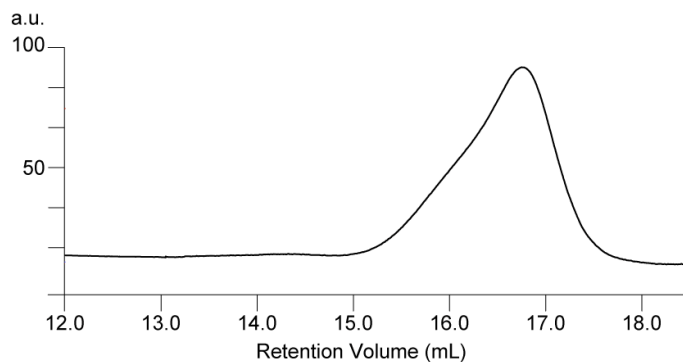
#### 5. Separation of Cyclic Oligomers by Preparative Recycling GPC



**Figure S2.** Recycling GPC elugram of polymer **2a**. The gray part was removed at the first cycle; cyclic oligomers were isolated after the 11<sup>th</sup> and subsequent cycles.

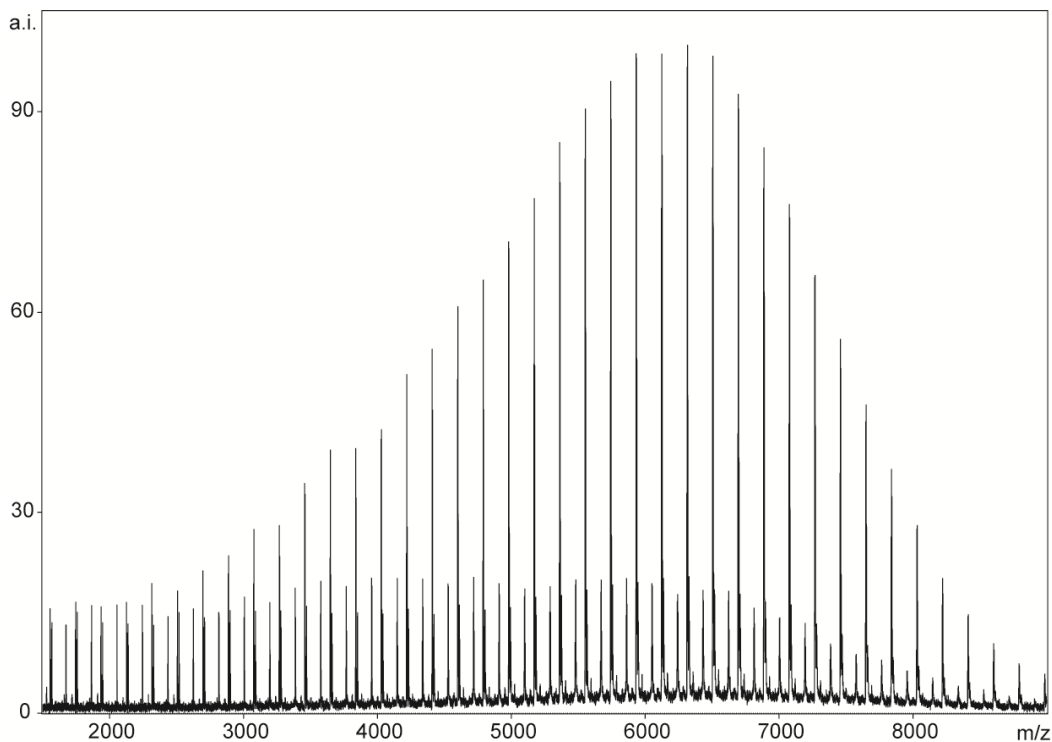


## 6. SPC using $\text{Bu}_4\text{NOH}\cdot 30\text{H}_2\text{O}$ and $\text{Pd}(\text{dba})_2/\text{SPhos}$



**Figure S3.** GPC elution curve obtained from SPC using  $\text{Pd}(\text{dba})_2$  (0.01 eq), SPhos (0.02 eq),  $\text{Bu}_4\text{NOH}\cdot 30\text{H}_2\text{O}$  (1.6 eq) in THF. The monomer was slowly added over 10 h. The average molecular weight determined by a relative method versus polystyrene standards are estimated to be  $M_w = 3.1$  kDa and  $M_n = 2.2$  kDa. The curve was recorded with a RI detector.

## 7. MALDI-TOF Mass Spectrum of SPC with $\text{Pd}(\text{OAc})_2/\text{SPhos}$



**Figure S4.** MALDI-TOF mass spectrum obtained from SPC using  $\text{Pd}(\text{OAc})_2$  (0.1 eq) as palladium source. For a magnified region with peak assignment, see Figure 11c.

## 8. References

- 1) Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669-2676.
- 2) Kissel, P.; Breitler, S.; Reinmüller, V.; Lanz, P.; Federer, L.; Schlüter, A. D.; Sakamoto, J. *Eur. J. Org. Chem.* **2009**, 2953–2955.