Supplementary Information for

# Orthogonal C–B Bond Transformation as an Approach for Versatile Synthesis of End-Functionalized Polymers

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#### 1 General

All reactions were carried out under an atmosphere of nitrogen or argon with magnetic stirring. <sup>1</sup>H NMR spectra were recorded on a JEOL JNM-ECA500 operating at 500.16 MHz (1H) and at ambient temperature. 1H NMR data were reported on the basis of the chemical shift in ppm downfield from tetramethylsilane ( $\delta$  scale). The number-average molecular weight  $(M_n)$  and  $M_w/M_n$  ratio of polymers were measured by size exclusion chromatography (SEC) at 40 °C in THF as an eluent on two polystyrene-gel columns (TOSOH TSKgel Super Multipore HZ-M or Shodex LF-404). The columns were calibrated against standard polystyrene samples (TOSOH PStQuick series or Polymer Laboratories;  $M_n = 625-1250000$ ;  $M_w/M_n = 1.02-1.30$ ). Preparative SEC was performed using JAIGEL-2.5HR or Shodex KF-5001 columns (CHCl<sub>3</sub>). For MWCO1000 (Spectra/PorVR7, diameter 11.5 dialysis, mm) was used. MALDI-TOF-MS analyses were performed on an ultraflex III (MALDI-TOF mass spectrometer, Bruker Daltonics) equipped with a 337 nm nitrogen laser with trans-2-[3-(4-tert-Butylphenyl)- -2-methyl2-propenylidene] malononitrile (DCTB) as the matrix and sodium trifluoroacetate as the cationizing agent.

2-propenylboronic acid pinacol ester (IPBpin), and tetralin were purified by distillation prior to use. Azobisisobutyronitrile (AIBN), 2-Cyano-2-propyl dodecyl (CPDT), tetraphenylporphyrin trithiocarbonate cobalt(II) (Co(TPP)),methyl-4-bromobenzoate, 4-bromoanisole, 4-Bromobenzotrifluoride, *p*-Bromonitrobenzene, *N*-methyl 4-bormobenzamide, 1-Bromo-2-fluorobenzene, 3-Bromo-4-fluoroanisole, [1,1'-Bis(diphenylphosphino)ferrocene] 4-Bromotoluene, palladium(II) Dichloride Dichloromethane Adduct  $[PdCl_2(dppf) \cdot CH_2Cl_2],$ Tetrakis(triphenylphosphine) palladium(0), cesium carbonate, N-benzylmaleimide, tert-Butylboroniac acid pinacol ester, aqueous hydrogen peroxide (30wt%), sodium hydroxide, deoxygenated THF, deoxygenated toluene, methanol (MeOH), chloroform and dichloromethane were purchased from the commercial sources and were used without further 7-Nitro-3,4-dihydronaphthalen-1-yl purification. trifluoromethanesulfonate was synthesized according to the literature.<sup>1</sup> Xylene was dried using molecular sieves and bubbled with N<sub>2</sub> for more than 15 min prior to use.

#### **2** Experimental Procedures

Typical procedure for RAFT polymerization of IPBpin and Co-catalyzed olefination of  $\omega$ -end: Synthetic procedure was basically the same to our previous report.<sup>2</sup> AIBN (63.1 mg, 384 µmol, 0.8 equiv to CPDT) was placed in a Schlenk tube. After filling with Ar, CPDT (165.9 mg, 480 µmol), toluene (1221 µL), tetraline (100 µL, internal standard), and IPBpin (4511 µL, 4033.0 mg, 24 mmol) were added. The reaction mixture was stirred at 60 °C in an oil bath. The polymerization was monitored by <sup>1</sup>H NMR and SEC. After 24 h, the Schlenk tube was taken out from oil bath, and the polymerization solution was diluted with toluene (18.0 ml, three times volume of reaction solution). Then, 0.5 wt% Co(TPP) solution in toluene (64 µL, 0.48 µmol, 0.001 equiv to CPDT) were added into the reaction mixture, followed by heating to 60 °C. After 24 h, the reaction was stopped by cooling. The crude product was then dissolved in chloroform and purified by preparative SEC to give the end-olefinated poly(IPBpin). The series of end-olefinated poly(IPBpin)s were prepared in the same manner.

Typical procedure of end-selective Suzuki-Miyaura cross coupling (SMC) on poly(IPBpin): The end-olefinated poly(IPBpin) (71.8 mg, 10 µmol) and cesium carbonate (26.1mg, 80 µmol) were placed in a Schlenk tube. After filling with Ar, PdCl<sub>2</sub>(dppf) (2.4 mg, 3.0 µmol), methyl-4-bromobenzoate (5.4 mg, 25 µmol) and THF (833 µL) were added. Water (bubbled with N<sub>2</sub> in advance, 167 µL) was then added, and the reaction mixture was stirred at 70 °C in an oil bath. After 24 h, the Schlenk tube was taken out from oil bath, and the reaction mixture was evaporated under reduced pressure to remove THF. The crude product was dissolve in dichloromethane and washed with water three times. The organic layer was collected to concentrate under reduced pressure. The crude product was then dissolved in chloroform and purified by preparative SEC to give the end-arylated poly(IPBpin) (25 mg). The series of end-functionalized poly(IPBpin)s with various aryl bromide were synthesized in the same manner.

Double functionalization at  $\omega$ -end of poly(IPBpin) through SMC and Diels-Alder cycloaddition: The end-olefinated poly(IPBpin) (223.4 mg, 30  $\mu$ mol) and cesium carbonate (78.2mg, 240  $\mu$ mol) were placed in a Schlenk tube. After filling with Ar,

9.0 7-Nitro-3,4-dihydronaphthalen-1-yl  $PdCl_2(dppf)$ (7.5)μmol), mg, trifluoromethanesulfonate (32.3 mg, 75 µmol) and THF (2.5 mL) were added. Water (bubbled with N<sub>2</sub> in advance, 5 mL) was then added, and the reaction mixture was stirred at 70 °C in an oil bath. After 24 h, the Schlenk tube was taken out from oil bath, and the reaction mixture was evaporated under reduced pressure to remove THF. The crude product was dissolve in dichloromethane and washed with water three times. The organic layer was collected to concentrate under reduced pressure. The crude product was then dissolved in chloroform and purified by preparative SEC to give poly(IPBpin) bearing diene structure (89 mg). The diene-containing poly(IPBpin) (26.2 mg, 3.5 µmol) and N-benzylmaleimide (2.2 mg, 8.8 µmol) were placed in a Schlenk tube. After filling with Ar, xylene (350 µL) was added. The reaction mixture was stirred at 140 °C in an oil bath (reflux condition). After 1 week, the Schlenk tube was taken out from oil bath, and the reaction mixture was evaporated under reduced pressure to remove xylene. The crude product was then dissolved in chloroform and purified by preparative SEC to give the poly(IPBpin) functionalized with N-benzylmaleimide (19.1 mg).

Synthesis of end-functionalized poly( $\alpha$ -methyl vinyl alcohol) though oxidation of boronyl pendants: The poly(IPBpin) bearing 2-fluoro-5-methoxyphenyl group at ω-end (40.3 mg), was dissolved in THF (11.4 mL). Ethanol (1.2 mL), an aqueous solution of NaOH (6 M, 1.2 mL), and an aqueous solution of H<sub>2</sub>O<sub>2</sub> (35wt%, 2.4 mL) were added. The reaction solution was stirred at room temperature under air. After 24 h, the volume of the solution was reduced to 8 mL by evaporation. The dialysis was repeated with varying the solvent (water/MeOH = 50/50 (v/v)  $\rightarrow$  water/MeOH = 50/50 $(v/v) \rightarrow MeOH \rightarrow MeOH$ , and it afforded poly( $\alpha$ -methyl vinyl alcohol) (PMVA, 7.2 mg) which bears the corresponding aryl group. The series of end-functionalized PMVAs were synthesized in the same manner. The quantitative conversion of Bpin pendants confirmed in all and the yields of **PMVAs** were cases. bearing 2-fluoro-5-methoxyphenyl, 4-N-methyl benzamide, and 4-trifluoromethyl phenyl group were 52%, 73%, and quant. (>95%), respectively.

## **3** Structural Characterization of End-Olefinated poly(IPBpin)



**Figure S1.** Structural information of end-olefinated poly(IPBpin). (a) <sup>1</sup>H NMR spectrum and (b) SEC curve after Co-catalyzed elimination of trithiocarbonate group. Polymerization: [IPBpin]/[AIBN]/[CPDT] = 4000/64/80 mM in Toluene at 60 °C, End-olefination: [CPDT]<sub>0</sub>/[Co(TPP)] = 20/2 mM in Toluene at 60 °C.

# 4 Evaluation of selective SMC at ω-end of poly(IPBpin)



**Figure S2.** <sup>1</sup>H NMR measurement for evaluation of SMC efficiency using  $Pd(PPh_3)_4$  catalyst (30mol%). [poly(IPBpin)]/[methyl-4-bromobenzoate]/[Pd(PPh\_3)\_4]/[Cs\_2CO\_3] = 10/25/3/80 mM in THF/water at 70 °C.



**Figure S3.** <sup>1</sup>H NMR measurement for evaluation of SMC efficiency using  $PdCl_2(dppf)$  catalyst (5mol%). [poly(IPBpin)]/[methyl-4-bromobenzoate]/[PdCl<sub>2</sub>(dppf)]/[Cs<sub>2</sub>CO<sub>3</sub>] = 10/25/0.5/80 mM in THF/water at 70 °C.



Figure S4. Structural characterization of end-functionalized of poly(IPBpin) obtained by SMC using PdCl<sub>2</sub>(dppf) (30 mol%). (a) <sup>1</sup>H NMR spectrum, (b) SEC curve and (c) MALDI-TOF-MS spectrum, [poly(IPBpin)]/[methyl-4-bromobenzoate]/[PdCl<sub>2</sub>(dppf)]/ [Cs<sub>2</sub>CO<sub>3</sub>] = 10/25/3/80 mM in THF/water at 70 °C.



Figure S5. Evaluation of SMC efficiency on poly(IPBpin) of higher molecular weight  $(M_n = 8,900)$ . (a) <sup>1</sup>H NMR spectra and (b) SEC curves before and after SMC: [poly (IPBpin)]/[methyl-4-bromobenzoate]/[PdCl<sub>2</sub>(dppf)]/[Cs<sub>2</sub>CO<sub>3</sub>] = 10/25/3/80 mM in THF/water at 70 °C.



**Figure S6.** Change in <sup>1</sup>H NMR spectra during SMC using *tert*-alkyl boronic acid pinacol ester as the model substrate of repeating units in poly(IPBpin): [t-BuBpin)]/ [methyl-4-bromobenzoate]/[PdCl<sub>2</sub>(dppf)]/[Cs<sub>2</sub>CO<sub>3</sub>] = 100/150/30/300 mM in THF/ water at 70 °C, 24 h (Identification of each <sup>1</sup>H NMR peak is based on previous reports.<sup>3</sup>).



Figure S7. Structural characterization of end-functionalized poly(IPBpin) obtained by SMC using 4-bromobenzotrifluoride as the coupling partner. (a) <sup>1</sup>H NMR spectrum, (b) SEC curve and (c) MALDI-TOF-MS spectrum, [poly(IPBpin)]/[4-bromobenzotri fluoride]/[PdCl<sub>2</sub>(dppf)]/[Cs<sub>2</sub>CO<sub>3</sub>] = 10/25/3/80 mM in THF/water at 70 °C.



**Figure S8.** Structural characterization of end-functionalized poly(IPBpin) obtained by SMC using 4-Bromonitrobenzene as the coupling partner. (a) <sup>1</sup>H NMR spectrum, (b) SEC curve and (c) MALDI-TOF-MS spectrum, [poly(IPBpin)]/[4-bromonitrobenzene]/ [PdCl<sub>2</sub>(dppf)]/[Cs<sub>2</sub>CO<sub>3</sub>] = 10/25/3/80 mM in THF/water at 70 °C.



Figure S9. Structural characterization of end-functionalized of poly(IPBpin) obtained by SMC using *N*-methyl 4-bormobenzamide as the coupling partner. (a) <sup>1</sup>H NMR spectrum, (b) SEC curve and (c) MALDI-TOF-MS spectrum, [poly(IPBpin)]/[*N*methyl-4-bormobenzamide]/[PdCl<sub>2</sub>(dppf)]/[Cs<sub>2</sub>CO<sub>3</sub>] = 10/25/3/80 mM in THF/ water at 70 °C.



**Figure S10.** Structural characterization of end-functionalized poly(IPBpin) obtained by SMC using 1-Bromo-2-fluorobenzene as the coupling partner. (a) <sup>1</sup>H NMR spectrum, (b) SEC curve and (c) MALDI-TOF-MS spectrum, [poly(IPBpin)]/[1-Bromo-2-fluorobenzene]/[PdCl<sub>2</sub>(dppf)]/[Cs<sub>2</sub>CO<sub>3</sub>] = 10/25/3/80 mM in THF/water at 70 °C.



Figure S11. <sup>1</sup>H NMR measurement for evaluation of SMC efficiency using 4-bromotoluene as the coupling partner. [poly(IPBpin)]/[4-bromotoluene]/ $[PdCl_2(dppf)]/[Cs_2CO_3] = 10/25/3/80$  mM in THF/water at 70 °C.



Figure S12. <sup>1</sup>H NMR measurement for evaluation of SMC efficiency using 4-bromoanisole as the coupling partner. [poly(IPBpin)]/[4-bromoanisole]/[PdCl<sub>2</sub>(dppf)] /[Cs<sub>2</sub>CO<sub>3</sub>] = 10/25/3/80 mM in THF/water at 70 °C.



Figure S13. Structural characterization of end-functionalized poly(IPBpin) obtained by SMC using 3-Bromo-4-fluoroanisole as the coupling partner. (a) <sup>1</sup>H NMR spectrum, (b) SEC curve and (c) MALDI-TOF-MS spectrum, [poly(IPBpin)]/[3-Bromo-4-fluoro anisole]/[PdCl<sub>2</sub>(dppf)]/[Cs<sub>2</sub>CO<sub>3</sub>] = 10/25/3/80 mM in THF/water at 70 °C.



### **5** Double Functionalization through SMC and Diels-Alder Reaction

**Figure S14.** Change of <sup>1</sup>H NMR spectra during double functionalization at  $\omega$ -end of poly(IPBpin). (a) end-olefinated poly(IPBpin), (b) formation of diene structure by SMC with alkenyl triflate: [poly(IPBpin)]/ [7-Nitro-3,4-dihydronaphthalen-1-yl trifluoro methanesulfonate]/[PdCl<sub>2</sub>(dppf)]/ [Cs<sub>2</sub>CO<sub>3</sub>] = 10/25/3/80 mM in THF/water at 70 °C, and (c) second functionalization by Diels-Alder reaction: [poly(IPBpin)]/[*N*-benzyl maleimide] = 10/25 mM in xylene (reflux).



**Figure S15.** Structural characterization of double functionalized  $\omega$  -end in poly(IPBpin) by <sup>1</sup>H NMR measurement in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure S16.** MALDI-TOF-MS spectrum after SMC of poly(IPBpin) with 7-Nitro-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate.



Figure S17. MALDI-TOF-MS spectrum after Diels-Alder reaction of poly(IPBpin).





**Figure S18.** Change of <sup>1</sup>H NMR spectra during orthogonal transformation of  $\omega$ -end and repeating unit in poly(IPBpin). (a) end-olefinated poly(IPBpin), (b) terminal selective arylation by SMC with 3-Bromo-4-fluoroanisole: [poly(IPBpin)]/[3-Bromo-4-fluoroanisole]/[PdCl<sub>2</sub>(dppf)]/ [Cs<sub>2</sub>CO<sub>3</sub>] = 10/25/4/80 mM in THF/water at 70 °C, (c) oxidation of repeating unit for synthesis of end-functionalized PMVA.



**Figure S19.** MALDI-TOF-MS spectrum of PMVA bearing 2-fluoro-5-methoxyphenyl group.



**Figure S20.** Change of <sup>1</sup>H NMR spectra during orthogonal transformation of  $\omega$ -end and repeating unit in poly(IPBpin). (a) end-olefinated poly(IPBpin), (b) terminal selective arylation by SMC with *N*-methyl-4-bromobenzamide: [poly(IPBpin)]/[*N*-methyl 4-bormobenzamide]/[PdCl<sub>2</sub>(dppf)]/ [Cs<sub>2</sub>CO<sub>3</sub>] = 10/25/4/80 mM in THF/water at 70 °C, (c) oxidation of repeating unit for synthesis of end-functionalized PMVA.



Figure S21. MALDI-TOF-MS spectrum of PMVA bearing 4-*N*-methyl benzamide group.



**Figure S22.** Change of <sup>1</sup>H NMR spectra during orthogonal transformation of  $\omega$ -end and repeating unit in poly(IPBpin). (a) end-olefinated poly(IPBpin), (b) terminal selective arylation by SMC with 4-Bromobenzotrifluoride: [poly(IPBpin)]/[4-Bromobenzo trifluoride]/[PdCl<sub>2</sub>(dppf)]/ [Cs<sub>2</sub>CO<sub>3</sub>] = 10/25/4/80 mM in THF/water at 70 °C, (c) oxidation of repeating unit for synthesis of end-functionalized PMVA.



Figure S23. MALDI-TOF-MS spectrum of PMVA bearing 4-trifluoromethyl phenyl group.

## 7 References

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