Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for:

Stereoselective Polymerization of Epoxide Using Organoboron Catalysts

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Chemicals

Propylene oxide (PO), tetrahydrofuran (THF), acetonitrile, *n*-hexane, methanol, ethyl acetate, pyridine, ethyl ether, and toluene were purchased from Sinopharm Chemical Reagent Co., Ltd. and Shanghai Titan Scientific Co., Ltd. Sodium hydride (NaH), calcium hydride (CaH_2) and *n*-butyllithium (*n*-BuLi) were purchased from Meryer Co. Deuterated solvents were purchased from Cambridge Isotope Laboratories. THF, *n*-hexane, ethyl ether, and toluene were distilled over sodium/benzophenone. PO was first dried over NaH overnight, followed by vacuum distillation, and then distilled over *n*-BuLi under nitrogen and stored in the glovebox. All the raw materials for catalysts preparation in this work including 9-borabicyclo[3.3.1]nonane (9-BBN), allyl bromide, chloromethyl methyl ether, 1,3-bis(diphenylphosphino)propane nickel(II) chloride($NiCl_2$(dppp)), methylmagnesium bromide, 1,2-dibromotetrachloroethane, triflic anhydride were purchased from Energy Chemical Co. and Meryer Co. and used without further purification. $CDCl_3$ was distilled over CaH_2 for 12 h and then stored over activated Davison 4 Å molecular sieves.

Characterizations

NMR

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE III 400 spectrometer (^{1}H NMR 400 MHz, ^{13}C NMR 101 MHz) or a Bruker AVANCE III 500 spectrometer (^{1}H NMR 500 MHz, ^{13}C NMR 126 MHz) or Agilent DD2-600 type spectrometer (^{1}H NMR 600 MHz, ^{13}C NMR 151 MHz) at 25 °C. ^{1}H NMR and ^{13}C NMR spectra were referenced using the internal or external standard shifts or the residual solvent signals [^{1}H: TMS in $CDCl_3$ = 0 ppm, residual CH_2Cl_2 = 5.30 ppm, residual H_2O = 1.56 ppm; ^{13}C: $CDCl_3$ = 77.16 ppm; Data are reported as follows: Chemical shift in ppm,

multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, etc.), coupling constant *J* in Hz, integration, and (where applicable) interpretation.

HRMS

High resolution mass spectral analysis of the products were measured on an Agilent 6545 Q-TOF instrument using ESI ionization.

GPC

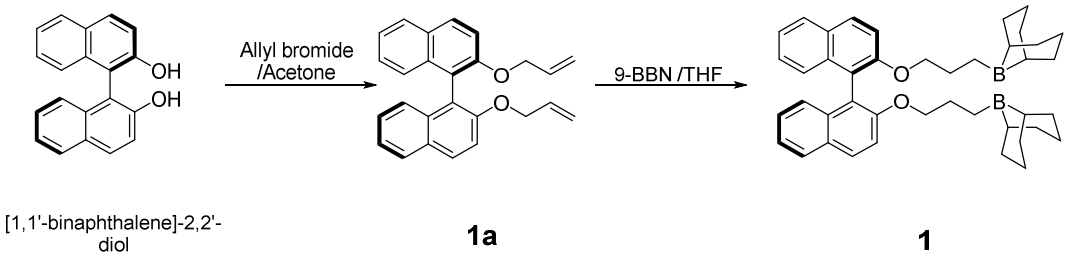
Gel permeation chromatography (GPC) was conducted on a system equipped with a Waters Chromatography, Inc. model 1515 isocratic pump, a model 2414 differential refractometer, and a three-column set of Polymer Laboratories, Inc. Styragel columns (PLgel 5 μmMixed C, 500 Å, and 104 Å, 300×7.5 mm columns). The system was equilibrated at 35 °C in THF, which served as the elute solvent with a 1.00 mL/min flow rate. Calibration was done with a series of narrowly dispersed polystyrene (PS) standards to obtain apparent number-average molar mass (M_n) and $Đ$ of the polymers. Polymer solutions were prepared at a concentration of 5 mg/mL and an injection volume of 100 μL was used.

MALDI-TOF

MALDI-TOF-MS analyses were performed on a Bruker Daltonics UltrafleXtreme system. Crude polymer samples were dissolved in THF at a concentration of 10 $mg \cdot mL^{-1}$ and CF_3COONa (2 $mg \cdot mL^{-1}$) was added for ion formation. The matrix was chosen as 2,5-dihydroxybenzoic acid (DHB). The resulting spectra were analyzed using the Bruker Daltonics flexAnalysis 3.4 software package.

Procedural Information

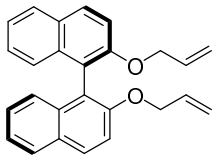
Synthesis of organoboron catalyst 1



Scheme S1. Synthesis of organoboron catalyst 1.

The syntheses of compounds **1a** and **1** began with commercially available starting materials (R)-(+)-1,1′-bi(2-naphthol).

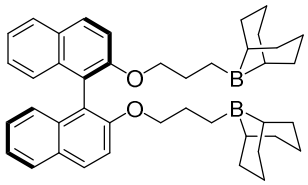
2,2'-bis(allyloxy)-1,1'-binaphthalene(1a)



A round bottom flask equipped with stir bar was charged with a solution of (R)-2,2'-dihydroxy-1,1'-binaphthyl (10.0 g, 1.0 equiv) and K_2CO_3 (14.2g, 3.0 equiv) in acetonitrile, allyl bromide (9.3 g, 2.2 equiv) was added via a dropping funnel over 30 min under nitrogen. The reaction mixture was then heated under reflux overnight before cooling to room temperature. After filtering, the reaction mixture was then concentrated in vacuo to afford the crude product that was further purified by washing with *n*-hexane for three times. The white solid was obtained (11.5 g, 90% yield) by vacuum filtration and was dried for 12 h in vacuo at 45 °C. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.91 (d, J = 9.0 Hz, 2H), 7.84 (dt, J = 8.2, 1.0 Hz, 2H), 7.37 (s, 2H), 7.30 (ddd, J = 8.1, 6.5, 1.4 Hz, 2H), 7.22 – 7.17 (m, 2H), 7.15 (dd, J = 8.5, 1.2 Hz, 2H), 5.73 (ddt, J = 17.2, 10.6, 4.8 Hz, 2H), 5.14 – 4.87 (m, 4H),

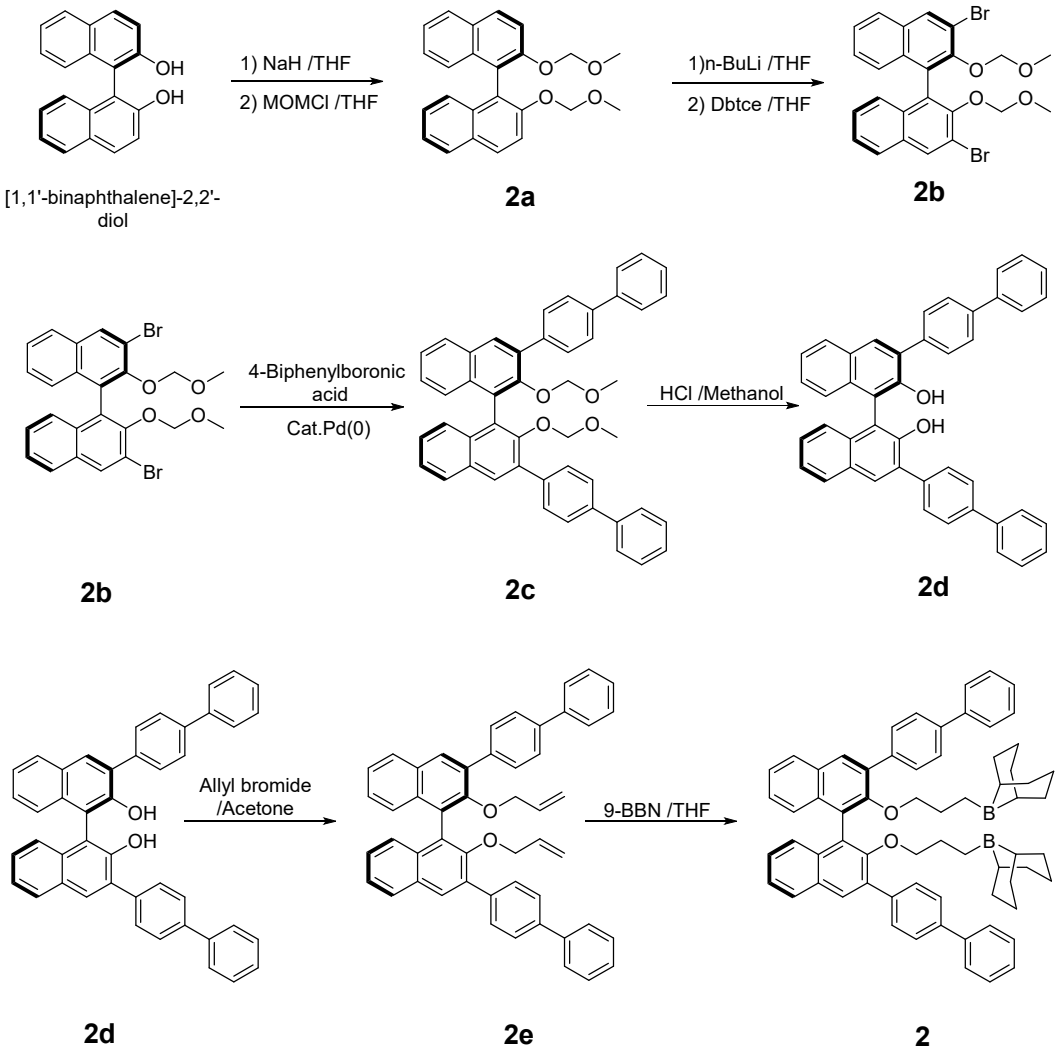
4.50 (dt, J = 4.9, 1.7 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-d) δ 154.18, 134.28, 133.87, 129.46, 129.24, 127.96, 126.30, 125.61, 123.69, 120.57, 116.47, 115.86, 70.10.

2,2'-bis(3-((1s,5s)-9-borabicyclo[3.3.1]nonan-9-yl)propoxy)-1,1'-binaphthalene (1)



To an oven dried Schlenk flask equipped with stir bar was added the 2,2'-bis(allyloxy)-1,1'-binaphthalene(**1a**, 1.0 g 1.0 equiv). The flask was placed under nitrogen, the 9-borabicyclo[3.3.1]nonane (9-BBN) in THF (0.5 M) was added via cannula(11.2 ml, 2.0 equiv). The reaction mixture was then heated to 60 °C for 12 h before cooling to room temperature. The reaction mixture was concentrated in vacuo to afford the crude solid product that was further purified by washing with *n*-hexane for three times. The white solid product was finally obtained (1.66 g, 100% yield) after dring for 8 h in vacuo at 30 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.91 (d, J = 8.9 Hz, 2H), 7.83 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 9.0 Hz, 2H), 7.29 (ddd, J = 8.1, 5.6, 2.4 Hz, 2H), 7.24 – 7.12 (m, 4H), 3.94 (ddt, J = 32.7, 9.2, 6.6 Hz, 4H), 1.87 – 1.66 (m, 12H), 1.65 – 1.56 (m, 4H), 1.48 (s, 12H), 1.16 – 1.04 (m, 4H), 1.02 – 0.92 (m, 4H). ^{13}C NMR (151 MHz, Chloroform-d) δ 157.32, 136.93, 131.95, 131.67, 130.40, 128.66, 128.23, 126.03, 123.50, 118.79, 74.78, 35.66, 33.44, 27.16, 25.79. ^{11}B NMR (400 MHz, Chloroform-d) δ 86.16. HRMS (ESI): calc. for $C_{42}H_{52}B_2O_2$ = 610.42, found $C_{42}H_{52}B_2O_2Na^+$: 633.36.

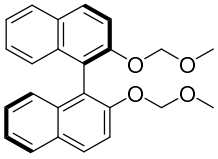
Synthesis of organoboron catalyst 2



Scheme S2. Synthesis of organoboron catalyst **2**.

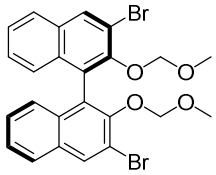
The syntheses of compounds **2a**, **2b**, **2c**, **2d**, **2e**, and **2** began with commercially available starting materials (R)-(+)-1,1′-bi(2-naphthol).

2,2'-Bis(methoxymethoxy)-1,1'-Binaphthyl (2)



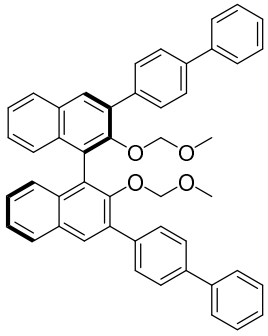
2a was synthesized according to literature procedures[1]. A white crystalline product was obtained in quantitative yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.96 (d, J = 9.0 Hz, 2H), 7.91 – 7.85 (m, 2H), 7.58 (d, J = 9.0 Hz, 2H), 7.35 (ddd, J = 8.1, 6.6, 1.3 Hz, 2H), 7.23 (ddd, J = 8.1, 6.6, 1.3 Hz, 2H), 7.16 (dt, J = 8.5, 1.1 Hz, 2H), 5.09 (d, J = 6.8 Hz, 2H), 4.98 (d, J = 6.8 Hz, 2H), 3.15 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 152.78, 134.14, 130.00, 129.47, 127.95, 126.37, 125.64, 124.14, 121.42, 117.38, 95.30, 55.84.

3,3'-Dibromo-2,2'-Bis(methoxymethoxy-1,1'-binaphthyl (2b)



2b was synthesized according to literature procedures[1]. A white crystalline product was obtained in 78% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.27 (s, 2H), 7.81 (d, J = 8.2 Hz, 2H), 7.44 (ddd, J = 8.2, 6.9, 1.2 Hz, 2H), 7.31 (ddd, J = 8.3, 6.8, 1.3 Hz, 2H), 7.23 – 7.15 (dt, 2H), 4.92 – 4.73 (m, 4H), 2.57 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 150.17, 133.13, 133.02, 131.52, 129.46, 127.39, 126.91, 126.56, 126.06, 117.41, 99.16, 56.31.

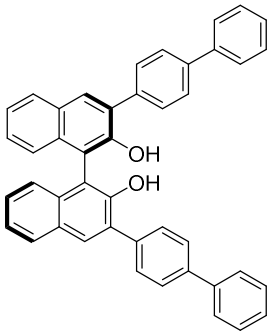
3,3'-di([1,1'-biphenyl]-4-yl)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene(2c)



The preparation of **2c** followed literature procedures[1] with some modifications. 3,3'-dibromo-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (**2b**, 1.0 g, 1 equiv) and $Pd(PPh_3)_4$ (0.22 g, 0.1 equiv) were mixed in DME (12.6 ml) in a round bottom flask at room temperature under an argon atmosphere. To the mixture, with stirring, were added 4-

biphenylboronic acid (1.30 g, 3.5 equiv) and 2 M aqueous Na2CO3 solution (5 ml, 5.2 equiv). The resulting mixture was stirred and heated to reflux for 10 h, cooled to room temperature, and passed through a pad of Celite. The organic solution was evaporated to give a residue. The residue was dissolved in CH_2Cl_2, washed with saturated aqueous NH_4Cl, water, brine, dried over Na_2SO_4, and concentrated to give a crude product. Further purification was carried by column chromatography (EtOAc/hexane: 1/10) to give a crystalline product (±)-3d (0.82 g) in 65% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.02 (s, 2H), 7.92 (d, J = 8.2 Hz, 2H), 7.89 – 7.84 (m, 4H), 7.75 – 7.71 (m, 4H), 7.70 – 7.65 (m, 5H), 7.48 (dd, J = 8.6, 6.8 Hz, 5H), 7.45 – 7.41 (m, 2H), 7.40 – 7.37 (m, 2H), 7.34 – 7.30 (m, 4H), 4.50 – 4.42 (m, 4H), 2.38 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 151.46, 140.81, 140.15, 138.11, 135.10, 133.73, 130.96, 130.57, 130.07, 128.87, 127.94, 127.41, 127.11, 127.06, 126.65, 126.50, 126.41, 125.27, 98.67, 55.96.

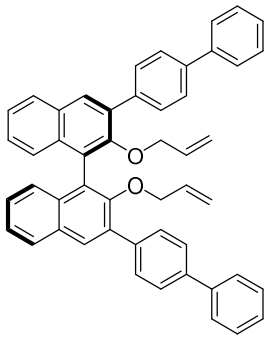
3,3'-di([1,1'-biphenyl]-4-yl)-[1,1'-binaphthalene]-2,2'-diol(2d)



2d was synthesized according to literature procedures[2] with some modifications. To a methanol and THF mixed solution (10 mL and 30 ml) of 3,3'-di([1,1'-biphenyl]-4-yl)-[1,1'-binaphthalene]-2,2'-diol (**2d**) (0.4 g, 0.59 mmol) was added conc. HCl (1.2 mL). After stirring the mixture for 2 h, saturated aqueous $NaHCO_3$ was added to quench the reaction. The organic phase was separated and the aqueous phase was extracted with ethyl acetate (50 mL). The combined organic phase was washed with water (50 mL) and brine and then dried over Na2SO4. After removal of the solvent, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (10:1) as the eluent to give 3,3'-

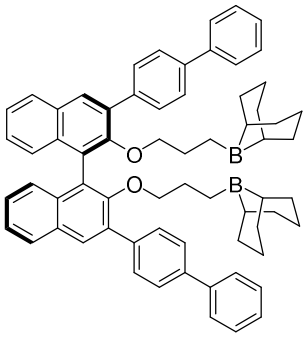
di([1,1'-biphenyl]-4-yl)-[1,1'-binaphthalene]-2,2'-diol (**2d**) as a white solid (0.32 g, 91% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.10 (s, 2H), 7.95 (d, J = 8.0 Hz, 2H), 7.87 – 7.82 (m, 4H), 7.75 – 7.71 (m, 4H), 7.70 – 7.65 (m, 4H), 7.51 – 7.31 (m, 12H), 5.43 (s, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 149.22, 139.70, 139.55, 135.39, 131.91, 130.35, 129.22, 128.98, 128.47, 127.78, 127.45, 126.40, 126.37, 126.15, 126.10, 123.37, 123.23, 111.29.

3,3'-di([1,1'-biphenyl]-4-yl)-2,2'-bis(allyloxy)-1,1'-binaphthalene(2e)



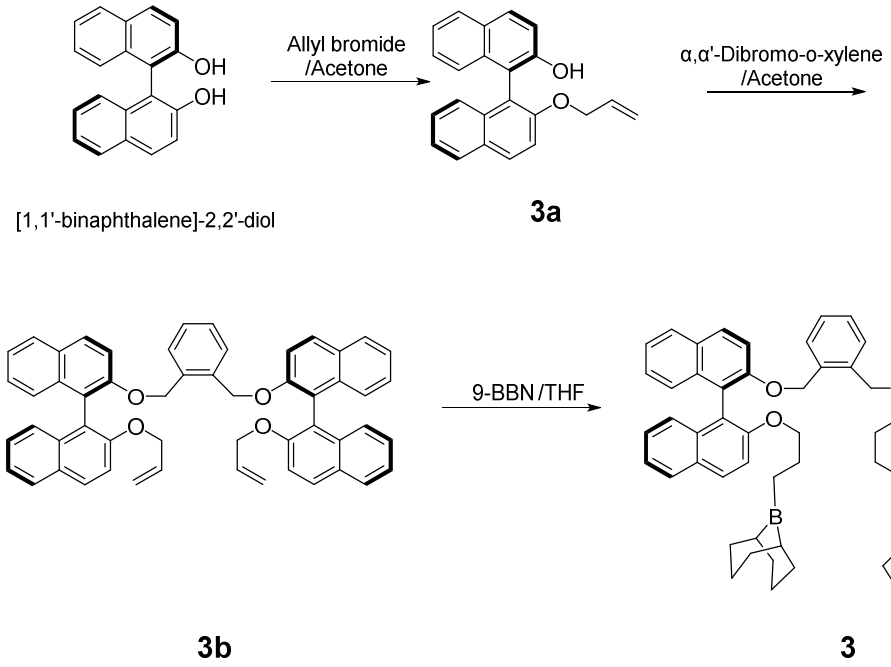
2e was synthesized according to **1a** procedure. **2e** was finally obtained as a white crystalline product in quantitative yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.03 (s, 2H), 7.94 (d, J = 8.2 Hz, 2H), 7.90 – 7.82 (m, 4H), 7.71 (dd, J = 8.6, 6.8 Hz, 8H), 7.52 – 7.35 (m, 8H), 7.28 (d, J = 3.9 Hz, 4H), 5.29 (ddt, J = 16.0, 10.7, 5.5 Hz, 2H), 4.69 (dd, J = 10.4, 1.7 Hz, 2H), 4.61 (dq, J = 17.2, 1.8 Hz, 2H), 4.04 (ddt, J = 12.2, 5.5, 1.5 Hz, 2H), 3.79 (ddt, J = 12.1, 5.6, 1.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 153.42, 140.88, 140.07, 138.08, 135.01, 133.87, 133.77, 130.88, 130.26, 129.91, 128.86, 128.08, 127.37, 127.10, 126.97, 126.42, 126.29, 126.04, 125.04, 116.32, 73.79.

(1s,1's,5s,5's)-9,9'-(((3,3'-di([1,1'-biphenyl]-4-yl)-[1,1'-binaphthalene]-2,2'-diyl)bis(oxy))bis(propane-3,1-diyl))bis(9-borabicyclo[3.3.1]nonane)(2)



2 was synthesized according to **1** procedure. **2** was finally obtained as a white crystalline product in quantitative yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.00 (s, 2H), 7.91 (d, J = 8.2 Hz, 2H), 7.89 – 7.84 (m, 4H), 7.75 – 7.64 (m, 8H), 7.47 (dd, J = 8.3, 7.0 Hz, 4H), 7.38 (dddd, J = 14.8, 7.4, 5.6, 1.8 Hz, 4H), 7.30 – 7.23 (m, 4H), 3.54 (dt, J = 8.7, 6.3 Hz, 2H), 3.20 (dt, J = 8.7, 6.8 Hz, 2H), 1.75 – 1.54 (m, 12H), 1.43 – 1.29 (m, 12H), 1.24 – 1.14 (m, 4H), 0.99 (dq, J = 11.5, 7.0, 5.4 Hz, 4H), 0.78 (ddd, J = 17.7, 9.3, 6.4 Hz, 2H), 0.56 (ddd, J = 17.4, 9.5, 6.1 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-d) δ 156.61, 143.56, 142.52, 140.97, 137.81, 136.58, 133.42, 132.74, 132.49, 131.46, 130.64, 129.94, 129.72, 129.51, 129.46, 129.10, 128.74 (d, J = 6.1 Hz), 127.41, 78.00, 35.57, 35.55, 33.30, 27.50, 25.74. ^{11}B NMR (400 MHz, Chloroform-d) δ 85.72. HRMS (ESI): calc. for $C_{66}H_{68}B_2O_2$ = 914.54, found $C_{66}H_{68}B_2O_2Na^+$: 937.53.

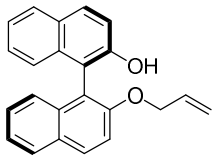
Synthesis of organoboron catalyst 3



Scheme S3. Synthesis of organoboron catalyst **3**.

The syntheses of compounds **3a**, **3b**, and **3** began with commercially available starting materials (R)-(+)-1,1´-bi(2-naphthol).

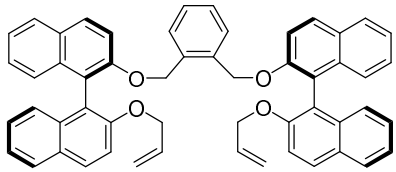
2'-(allyloxy)-[1,1'-binaphthalen]-2-ol (3a)



A round bottom flask equipped with stir bar was charged with a solution of (R)-2,2'-dihydroxy-1,1'-binaphthyl (10.0 g, 1.0 equiv) and K_2CO_3 (4.7 g, 1.0 equiv) in acetonitrile, allyl bromide (4.2 g, 1.0 equiv) was slowly added via a dropping funnel over 30 min under nitrogen. The reaction mixture was then heated under reflux overnight before cooling to room temperature. After filtering, the reaction mixture was then concentrated in vacuo to afford the crude product that was further purified by column chromatography on silica gel

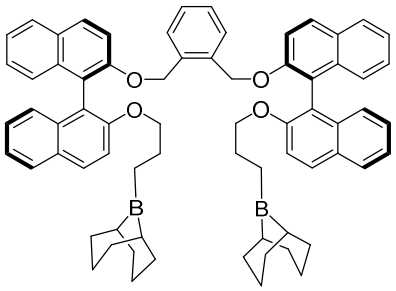
using petroleum ether/EtOAc (10:1). The product was obtained (5.8 g, 45% yield) as a white crystalline solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.02 (d, J = 9.0 Hz, 1H), 7.94 – 7.83 (m, 3H), 7.47 – 7.26 (m, 5H), 7.25 – 7.19 (m, 2H), 7.07 (d, J = 8.4 Hz, 1H), 5.82 – 5.71 (m, 1H), 5.10 – 5.02 (m, 2H), 4.95 (s, 1H), 4.62 – 4.50 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 153.95, 150.22, 133.05, 132.78, 132.09, 129.72, 128.71, 128.62, 128.10, 127.08, 127.03, 126.21, 125.29, 124.01, 123.89, 123.31, 122.14, 116.47, 116.12, 115.59, 114.77, 114.08, 68.97.

1-((((S)-2'-(allyloxy)-[1,1'-binaphthalen]-2-yl)oxy)methyl)-2-(((2'-(allyloxy)-[1,1'-binaphthalen]-2-yl)oxy)methyl)benzene (3b)



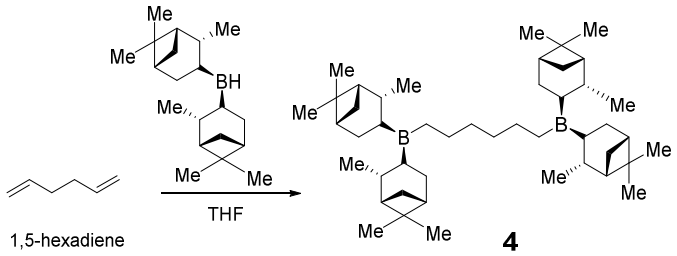
A round bottom flask equipped with stir bar was charged with a solution of **3a** (0.5 g, 2.0 equiv) and K_2CO_3 (0.2 g, 2.0 equiv) in acetonitrile, 1,2-bis(bromomethyl)benzene (0.2 g, 1.0 equiv) in acetonitrile was slowly added via a dropping funnel over 30 min under nitrogen. The reaction mixture was then heated under reflux overnight before cooling to room temperature. After filtering, the reaction mixture was then concentrated in vacuo to afford the crude product that was further purified by column chromatography on silica gel using petroleum ether/EtOAc (10:1). The product was obtained (0.4 g, 69% yield) as a white crystalline solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 – 7.76 (m, 8H), 7.34 – 7.28 (m, 4H), 7.24 (d, J = 1.3 Hz, 4H), 7.22 – 7.05 (m, 10H), 6.96 – 6.84 (m, 4H), 5.77 – 5.54 (m, 2H), 4.91 (dq, J = 6.9, 1.7 Hz, 2H), 4.87 (t, J = 1.7 Hz, 2H), 4.75 (d, J = 13.0 Hz, 2H), 4.65 (d, J = 13.1 Hz, 2H), 4.39 (dq, J = 5.0, 1.7 Hz, 4H). ^{13}C NMR (126 MHz, Chloroform-d) δ 152.92, 152.71, 134.05, 133.13, 133.05, 132.58, 128.25, 128.17, 128.07, 126.85, 126.84, 126.78, 126.29, 125.20, 125.11, 124.99, 124.43, 124.35, 122.54, 122.50, 119.39, 119.09, 115.30, 114.68, 114.39, 68.61, 67.61. HRMS (ESI): calc. for $C_{54}H_{42}O_4$ = 754.31, found $C_{54}H_{43}O_4^+$: 755.32.

1-((((S)-2'-(3-(9-borabicyclo[3.3.1]nonan-9-yl)propoxy)-[1,1'-binaphthalen]-2-yl)oxy)methyl)-2-(((2'-(3-(9-borabicyclo[3.3.1]nonan-9-yl)propoxy)-[1,1'-binaphthalen]-2-yl)oxy)methyl)benzene (3)



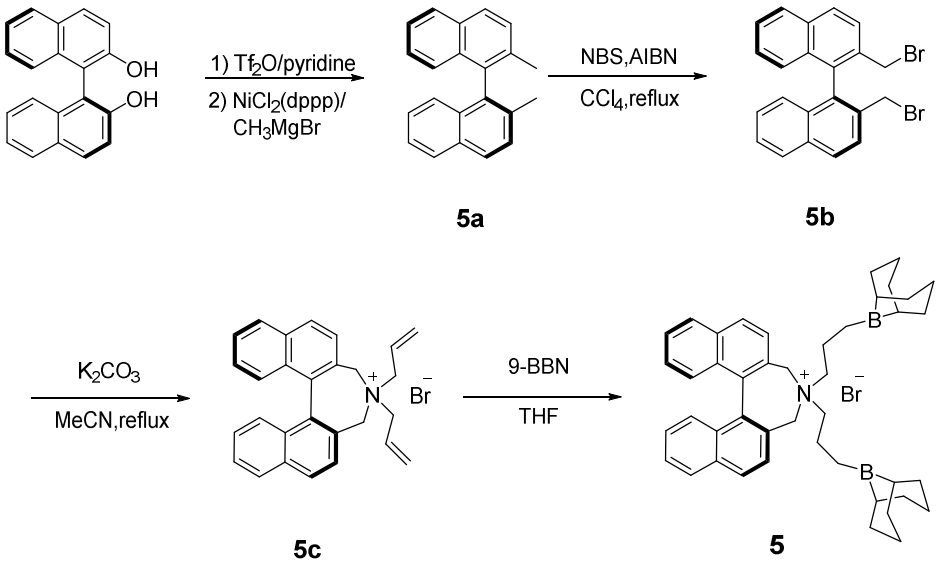
3 was synthesized according to **1** procedure. **3** was finally obtained as a yellow crystalline product in quantitative yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.80 (ddd, J = 17.0, 8.8, 6.1 Hz, 8H), 7.40 – 7.26 (m, 6H), 7.26 – 7.21 (m, 2H), 7.19 – 7.08 (m, 10H), 6.92 – 6.83 (m, 4H), 4.77 (d, J = 13.1 Hz, 2H), 4.63 (d, J = 13.1 Hz, 2H), 3.93 – 3.77 (m, 4H), 1.83 – 1.65 (m, 14H), 1.57 – 1.49 (m, 4H), 1.49 – 1.31 (m, 16H), 1.06 (dt, J = 15.1, 5.9 Hz, 4H). ^{13}C NMR (151 MHz, Chloroform-d) δ 157.27, 156.37, 137.80, 136.87, 136.85, 131.97, 131.92, 131.89, 131.82, 131.55, 130.52, 130.50, 130.38, 129.87, 128.80, 128.69, 128.21, 128.06, 126.16, 126.04, 123.42, 122.90, 118.43 (d, J = 6.1 Hz), 74.37, 71.22, 35.63, 33.41, 27.11, 25.77. ^{11}B NMR (400 MHz, Chloroform-d) δ 85.97. HRMS (ESI): calc. for $C_{70}H_{72}B_2O_4$ = 998.56, found $C_{70}H_{73}B_2O_4^+$: 999.57.

Synthesis of organoboron catalyst 4



Scheme S4. Synthesis of organoboron catalyst **4**.

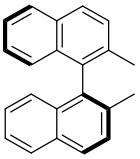
Synthesis of organoboron catalyst 5



Scheme S5. Synthesis of organoboron catalyst **5**.

The syntheses of compounds **5a**, **5b**, **5c**, **5d** and **5** began with commercially available starting materials (s)-(+)-1,1′-bi(2-naphthol). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.16 – 7.91 (m, 6H), 7.61 – 7.29 (m, 6H), 5.19 (dd, J = 50.9, 12.7 Hz, 2H), 4.00 – 3.71 (m, 2H), 3.64 (dd, J = 31.9, 13.3 Hz, 2H), 3.20 (dt, J = 51.2, 11.4 Hz, 2H), 2.28 – 1.91 (m, 4H), 1.81 – 1.60 (m, 16H), 1.59 – 1.30 (m, 14H), 1.29 – 1.06 (m, 6H). ^{13}C NMR (151 MHz, Chloroform-d) δ 139.16, 137.02, 133.84, 132.78, 131.28, 130.97, 130.18, 130.14, 129.79, 129.41, 65.76, 64.26, 35.74, 35.71, 33.12, 26.35, 25.88.

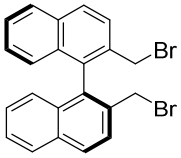
2,2'-dimethyl-1,1'-binaphthalene (5a)



5a was synthesized according to literature procedures[3]. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.94 – 7.84 (m, 4H), 7.51 (d, J = 8.4 Hz, 2H), 7.40 (ddd, J = 8.1, 6.7, 1.2 Hz, 2H), 7.21 (ddd, J = 8.2, 6.7, 1.3 Hz, 2H), 7.05 (dd, J = 8.5, 1.1 Hz, 2H), 2.04 (s, 6H).

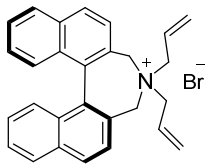
13C NMR (101 MHz, Chloroform-d) δ 134.08, 133.18, 131.73, 131.18, 127.64, 126.86, 126.38, 125.02, 124.57, 123.83, 18.94.

2,2'-bis(bromomethyl)-1,1'-binaphthalene (5b)



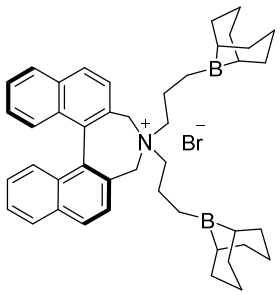
5b was synthesized according to literature procedures[3]. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.03 (d, J = 8.5 Hz, 2H), 7.93 (d, J = 7.8 Hz, 2H), 7.75 (d, J = 8.6 Hz, 2H), 7.54 – 7.44 (m, 2H), 7.28 (dd, J = 8.5, 1.4 Hz, 2H), 7.07 (d, J = 9.6 Hz, 2H), 4.26 (s, 4H). ^{13}C NMR (126 MHz, Chloroform-d) δ 134.21, 134.11, 133.28, 132.53, 129.40, 128.05, 127.77, 126.87, 126.84, 126.82, 32.66.

Binaphthyl quaternary ammonium salt (5c)



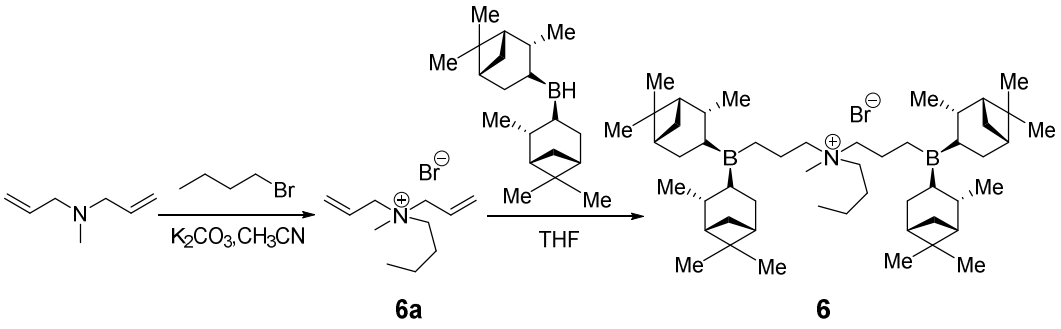
5c was synthesized according to literature procedures[4]. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.12 (d, J = 8.3 Hz, 2H), 8.01 (dd, J = 21.9, 8.3 Hz, 4H), 7.61 (ddd, J = 8.2, 6.5, 1.5 Hz, 2H), 7.45 – 7.31 (m, 4H), 6.28 (ddt, J = 17.2, 10.2, 7.3 Hz, 2H), 5.78 – 5.67 (m, 4H), 5.08 (d, J = 13.0 Hz, 2H), 4.58 (dd, J = 13.7, 7.6 Hz, 2H), 4.12 (dd, J = 13.7, 6.9 Hz, 2H), 3.76 (d, J = 13.0 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 136.48, 134.27, 131.13, 130.04, 128.56, 128.36, 128.28, 127.46, 127.37, 127.00, 126.59, 124.97, 62.43, 62.13. ^{13}C NMR (101 MHz, Chloroform-d) δ 136.48, 134.27, 131.13, 130.04, 128.56, 128.36, 128.28, 127.46, 127.37, 127.00, 126.59, 124.97, 62.43, 62.13.

Organoboron catalyst 5



5 was synthesized according to **1** procedure. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 8.08 (d, J = 8.4 Hz, 2H), 7.98 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.31 – 7.20 (m, 2H), 7.16 (d, J = 8.6 Hz, 2H), 4.52 (d, J = 13.0 Hz, 2H), 3.71 (d, J = 13.0 Hz, 2H), 3.35 (dt, J = 12.7, 6.1 Hz, 2H), 2.88 (t, J = 12.1 Hz, 2H), 1.64 – 1.42 (m, 16H), 1.32 (d, J = 11.0 Hz, 14H), 1.21 (d, J = 6.5 Hz, 4H), 1.12^{+} 1.03 (m, 6H). ^{13}C NMR (151 MHz, Chloroform-d) δ 139.16, 137.02, 133.84, 132.78, 131.28, 130.97, 130.25, 130.14, 129.79, 129.41, 65.76, 64.26, 35.71, 33.12, 29.42, 25.88. HRMS (ESI): calc. for $C_{44}H_{56}B_2N^+$ [M - Br] $^+$ = 620.46, found 620.46.

Synthesis of organoboron catalyst 6

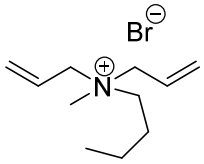


6a **6**

Scheme S6. Synthesis of organoboron catalyst **6**.

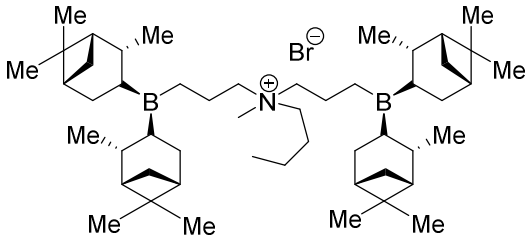
The syntheses of compounds **6a** and **6** began with commercially available starting material diallylmethylamine.

N,N-diallyl-N-methyl-N-butylammonium bromide(6a)



A round bottom flask equipped with stir bar was added potassium carbonate (1.5 equiv) and then a solution of diallylmethylamine (1.0 equiv) in acetonitrile, related bromobutane (1.0 equiv) was added via a dropping funnel over 10 min. The reaction mixture was then heated to 96 °C for 24 h before cooling to room temperature. The reaction mixture was concentrated in vacuo to afford the crude product that was further purified by washing with a mixed solvent (ethyl acetate: n-hexane = 1:1) for three times. The white solid was isolated by vacuum filtration was dried for 12 h in vacuo at 45 °C. The product was isolated as a white solid in 99% yield. ^{1}H NMR (600 MHz, Chloroform-d) δ 6.04 – 5.94 (m, 2H), 5.89 – 5.83 (m, 2H), 5.78 – 5.73 (m, 2H), 4.31 (ddd, J = 45.6, 13.2, 7.2 Hz, 4H), 3.42 – 3.35 (m, 2H), 3.30 (s, 3H), 1.82 – 1.75 (m, 2H), 1.48 – 1.38 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 129.72, 124.22, 63.54, 60.69, 47.77, 24.29, 19.66, 13.63 ppm.

Organoboron catalyst 6



To a mixture of N,N-diallyl-N-methyl-N-butylammonium bromide **6a** (1mol) in THF was slowly added (-)-diisopinocampheyl borane (2.1 equiv.) via a cannula at room temperature under argon atmosphere. Subsequently, the reaction was heated to 60 °C until the ^{1}H NMR spectrum of the reaction solution showed material was fully converted. Then the solution was concentrated in vacuo and washed with n-hexane to give chiral

organoboron catalyst **6** as white solid (yield: 99%).^{1}H NMR (400 MHz, Chloroform-d) δ 3.38 – 3.03 (m, 6H), 2.88 – 2.71 (m, 8H), 2.70 – 2.63 (m, 3H), 2.15 – 2.07 (m, 1H), 2.06 – 1.97 (m, 2H), 1.96 – 1.86 (m, 4H), 1.85 – 1.72 (m, 3H), 1.41 – 1.28 (m, 6H), 1.27 – 1.22 (m, 2H), 1.21 – 1.16 (m, 6H), 1.11 – 1.06 (m, 9H), 1.05 – 1.01 (m, 9H), 0.99 – 0.90 (m, 24H), 0.89 – 0.84 (m, 2H), 0.83 – 0.70 (m, 4H). ^{13}C NMR (151 MHz, Chloroform-d) δ 69.06, 68.34, 57.78, 53.03, 50.03, 45.54, 42.43, 39.96, 32.15, 31.46, 28.07, 24.55, 23.32, 22.63, 19.91. HRMS (ESI): calc. for $C_{51}H_{92}B_2N^+[M - Br]^+$ = 740.74, found 740.74.

Initiators prepared by salt metathesis

PPN-BA: To a solution of PPNCl (1.0 g, 1.74 mmol, 1 eq) in dichloromethane (10 mL), sodium benzoate (2.51 g, 17.4 mmol, 10 eq) was added. The resulting mixture was added H_2O and stirred for 1 h at room temperature. After completion, the reaction mixture was extracted with dichloromethane three times. The organic layer was collected and dried over with Na_2SO_4 and evaporated at reduced pressure. The crude product was purified by recrystallization from diethyl ether/dichloromethane three times (0.87 g, 76% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.14 – 8.18 (m, 2H), 7.25 – 7.75 (m, 30H), 7.18 – 7.22 (m, 3H).

PPN-PA: To a solution of PPNCl (1.0 g, 1.74 mmol, 1 eq) in dichloromethane (10 mL), sodium pivalate (3.24 g, 26.1 mmol, 15 eq) was added. The resulting mixture was added H_2O and stirred for 1 h at room temperature. After completion, the reaction mixture was extracted with dichloromethane three times. The organic layer was collected and dried over with Na_2SO_4 and evaporated at reduced pressure. The crude product was purified by recrystallization from diethyl ether/dichloromethane three times (0.67 g, 60% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.33 – 7.83 (m, 30H), 1.65 (s, 9H).

PPN-EHA: To a solution of PPNCl (1.0 g, 1.74 mmol, 1 eq) in dichloromethane (10 mL), sodium 2-ethylhexanoic acid (1.44 g, 8.7 mmol, 5 eq) was added. The resulting mixture was added H_2O and stirred for 1 h at room temperature. After completion, the reaction

mixture was extracted with dichloromethane three times. The organic layer was collected and dried over with Na_2SO_4 and evaporated at reduced pressure. The crude product was purified by recrystallization from diethyl ether/dichloromethane three times (1.04 g, 88% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.29 – 7.81 (m, 30H), 2.35 (dd, J = 8.3, 4.5 Hz, 1H), 1.58 (dq, J = 14.7, 7.3 Hz, 2H), 1.10 – 1.44 (m, 7H), 0.85 (t, J = 7.4 Hz, 3H), 0.75 (t, J = 7.1 Hz, 3H).

PPN-MOPA: To a solution of PPNCl (1.0 g, 1.74 mmol, 1 eq) in dichloromethane (10 mL), sodium pivalate (1.1 g, 8.7 mmol, 5 eq) was added. The resulting mixture was added H_2O and stirred for 1 h at room temperature. After completion, the reaction mixture was extracted with dichloromethane three times. The organic layer was collected and dried over with Na_2SO_4 and evaporated at reduced pressure. The crude product was purified by recrystallization from diethyl ether/dichloromethane three times (1.02 g, 91% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.28 – 7.81 (m, 30H), 3.92 (q, J = 6.4 Hz, 1H), 3.37 (d, J = 15.5 Hz, 3H), 1.36 (d, J = 6.6 Hz, 3H).

Representative procedure for ROP of PO

A typical procedure of entry 2 in Table 1 is as follows. A 20 mL vial equipped with magnetic stirrer was added catalyst ***(R)*-1** (18.0 mg, 30 μmol) and TBAB (4.8 mg, 15 μmol) in the glove box chamber. After keeping under -20 °C for 1 h, PO (0.43 g, 7.5 mmol) was added and the reaction vial was sealed and moved into a cold bath (-20 °C). The polymerization was carried out at this temperature for 1 h. After then, the reaction was quenched by addition of a drop of acetic acid. An aliquot was taken from the resulting crude product to determine the conversion of PO by ^{1}H NMR spectrum. The conversion can also be determined gravimetrically by removing the unreacted PO monomer under vacuum at 45 °C for 2 h, the result is same to that of received by ^{1}H NMR spectrum.

General Procedure for Kinetic Analysis

The reaction order in PO was determined by ^{1}H NMR analysis of aliquots in neat enantiomeric PO at -20 °C with PO/(***R***)-**2**/TBAB = 500/2/1 collected at different reaction times, yielding the conversion at different reaction times. The linear fit of the conversion of PO with respect to reaction time indicates the polymerization is quasi-zero-order with respect to PO.

The order in catalyst was determined by applying four different concentrations of **2** (0.16, 0.24, 0.32, 0.40 mol%) at -20 °C in neat PO. In all four cases, the linear fit of the conversion of PO with respect to reaction time yielded an initial rate coefficient. The linear fit of k_{obs} to catalyst loading indicates a first-order dependence on **2**.

Polymerization of PO in diluted conditions

Table S1 The results of ROP of PO using TBAB/**2** in diluted conditions[a]

entry	solvent	c (mol/L)	T (°C)	t (h)	Conv.[b] (%)	M_n [c] (kg/mol)	$Đ$[c]	m[d] (%)
1	THF	3	25	6	>99	18.4	1.14	76.3
2	TOL	3	25	6	44.9	5.4	1.27	69.9
3	DCM	3	25	6	<1	/	/	/
4	THF	3	-20	6	74.2	11.0	1.16	76.1
5	DME	3	-20	6	79.3	11.8	1.15	74.2
6[e]	TEGDME	3	-20	6	-[e]	-[e]	-[e]	79.2
7	n-HEX	3	-20	6	<1	/	/	/
8	THF	3	-20	2	16.4	3.0	1.13	82.1
9	DME	3	-20	2	19.8	3.4	1.15	76.3
10	THF	1	-20	36	86.3	13.7	1.20	79.2
11	THF	1	-20	12	37.3	7.9	1.11	84.8
12	DME	1	-20	12	42.9	8.1	1.13	79.2

[a] All the polymerizations were carried out using TBAB as the initiator and **(*R*)-2** as the catalyst at a Cat./I/M loading of 2/1/500. [b] Conv. = conversion; calculated by weight measurement. [c] Determined by GPC in THF with polystyrene standard, n.d. = not detected. [d] Calculated by ^{13}C NMR, where $m = A_m / (A_m + A_r)$. [e] Due to the high boiling point of TEGDME (15 Torr, 160 – 167 °C), its removal inevitably leads to the decomposition of the polyether, the molecular weight and dispersities of the product remained unmeasured.

Polymerization of other epoxides

Table S2 The results of ROP of other epoxides using TBAB/**2**[a]

entry	Monomer	Conv.[b] (%)	$M_{n(theo.)}$[c] (kg/mol)	M_n [d] (kg/mol)	$Đ$	m[e] (%)
1	BO	14.3	5.2	2.7	1.14	76.3
2	SO	<1	/	/	/	/

[a] All the polymerizations were carried out in bulk at -20 °C for 1 hour using TBAB as the initiator and **2** as the catalyst at a Cat./I/M loading of 2/1/500. [b] Conv. = conversion; calculated by ^1H NMR. [c] Theo. = theory; $M_{theo} = M_{epoxide} \times 500 \times Conv.$ [d] Determined by GPC in THF with polystyrene standard. [e] Calculated by ^{13}C NMR, where $m = A_m / (A_m + A_r)$.

Analysis of ^{13}C NMR spectra of resultant polymers

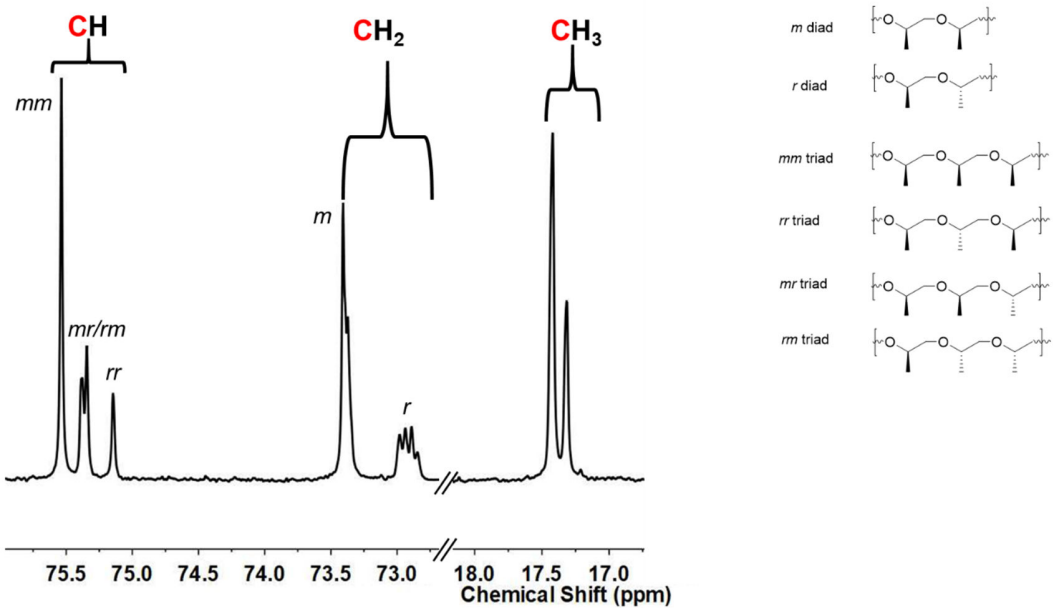


Figure S1. ^{13}C NMR spectrum of resultant PPO and the assignment of its carbon atoms

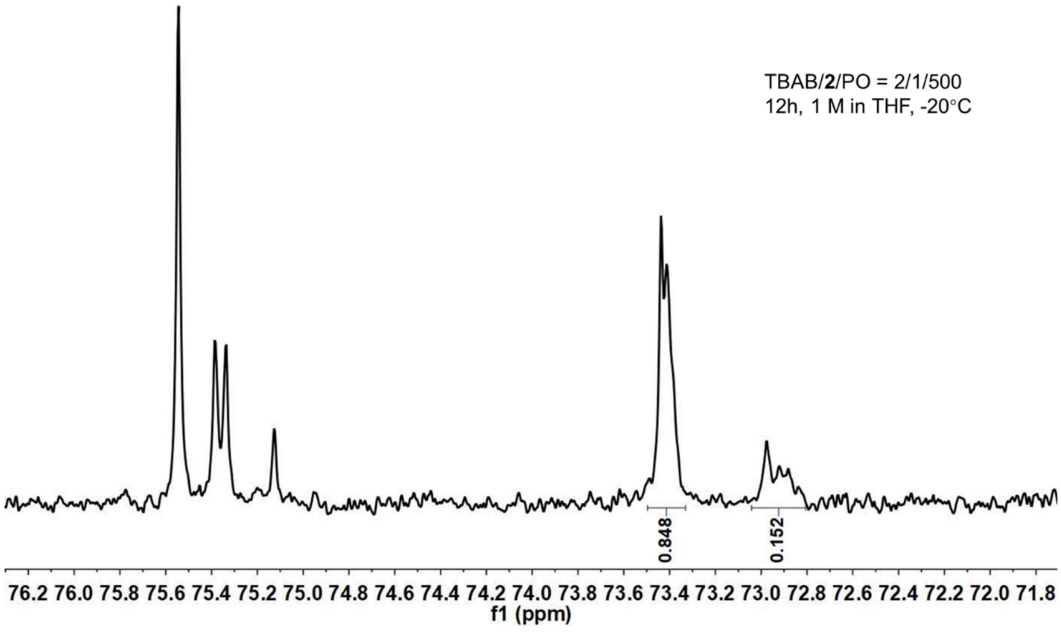


Figure S2. ^{13}C NMR spectrum of the PPO with *m* = 84.8%

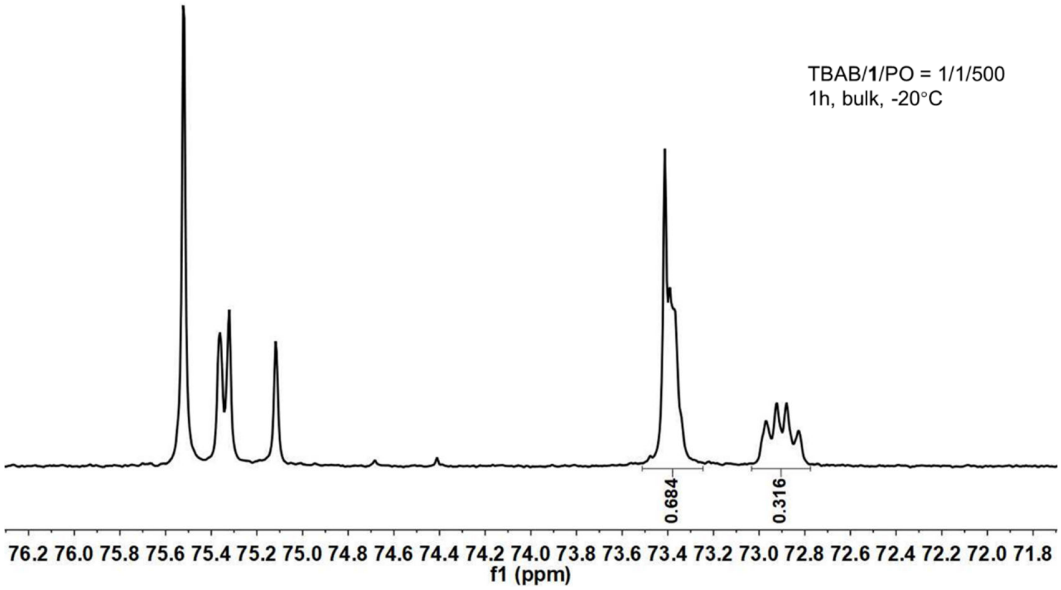


Figure S3. ^{13}C NMR spectrum of the PPO with *m* = 68.4%

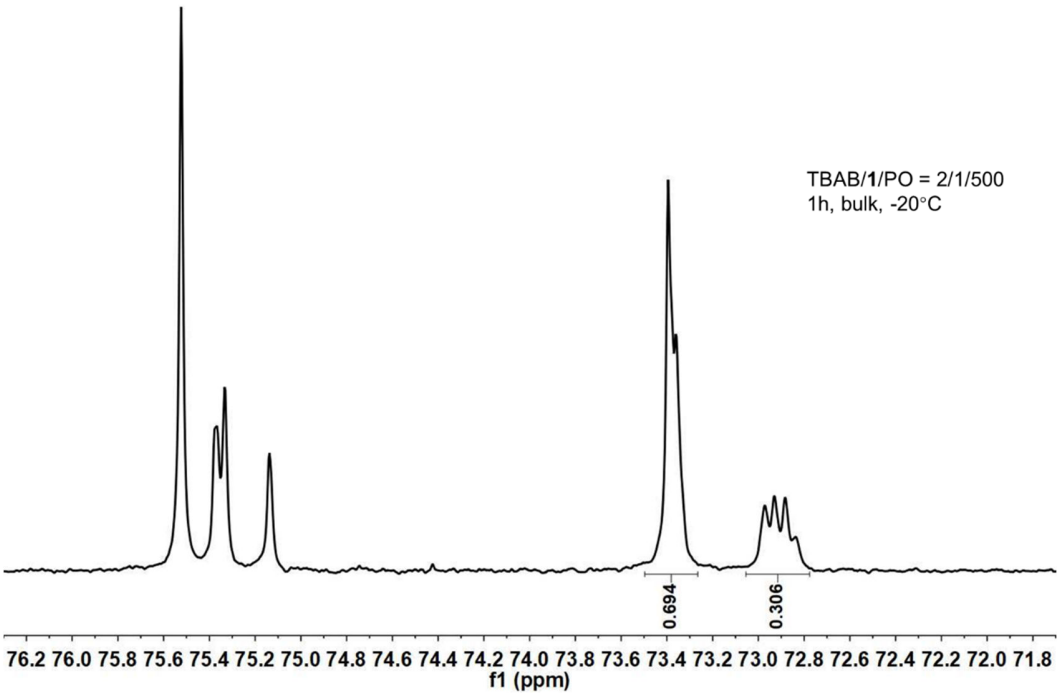


Figure S4. ^{13}C NMR spectrum of the PPO with *m* = 69.4%

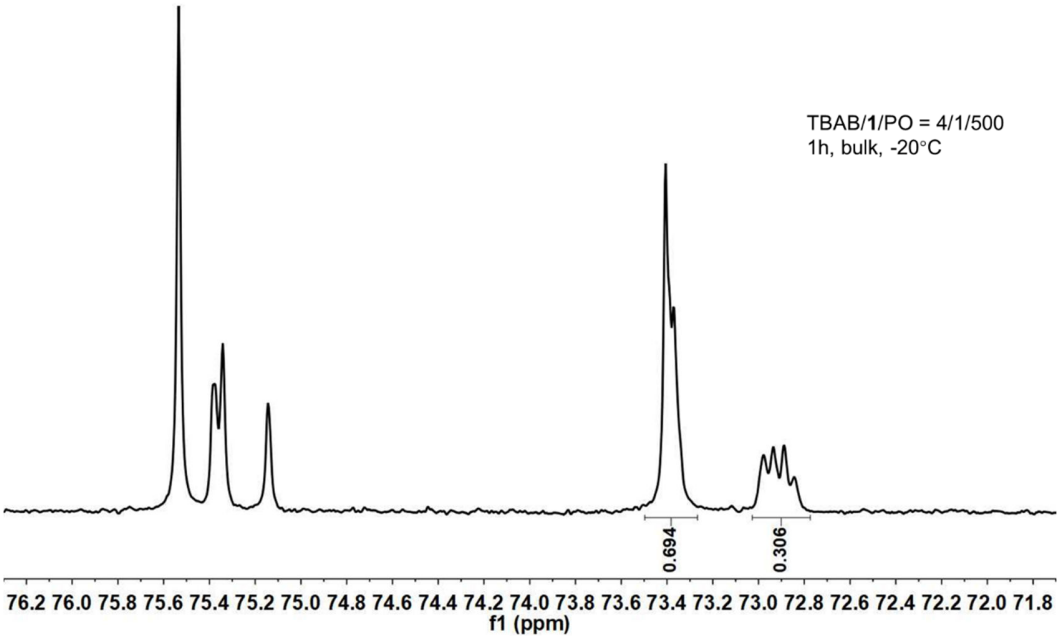


Figure S5. ^{13}C NMR spectrum of the PPO with *m* = 69.4%

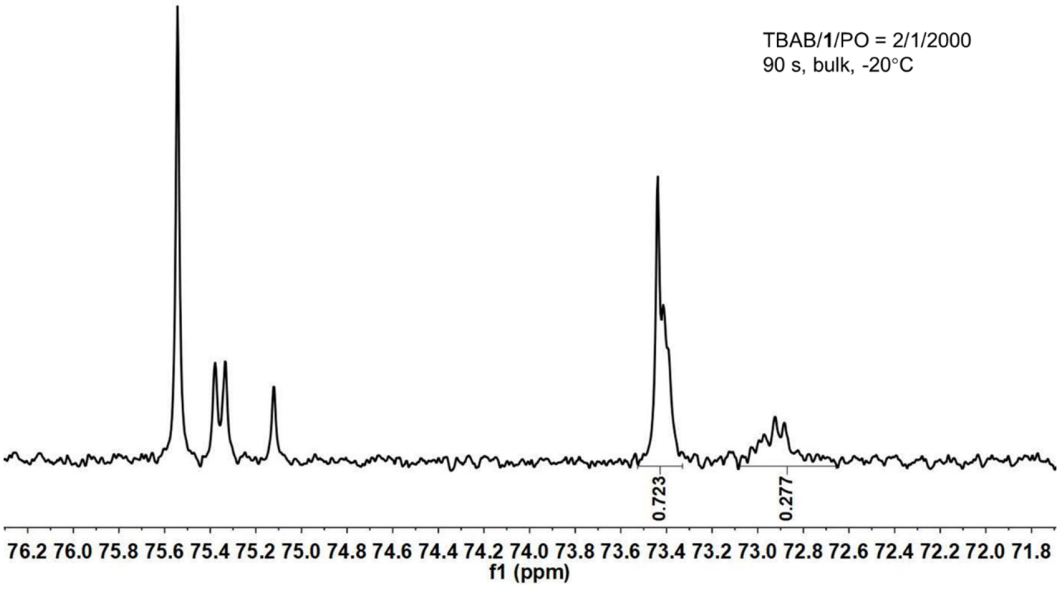


Figure S6. ^{13}C NMR spectrum of the PPO with *m* = 72.3%

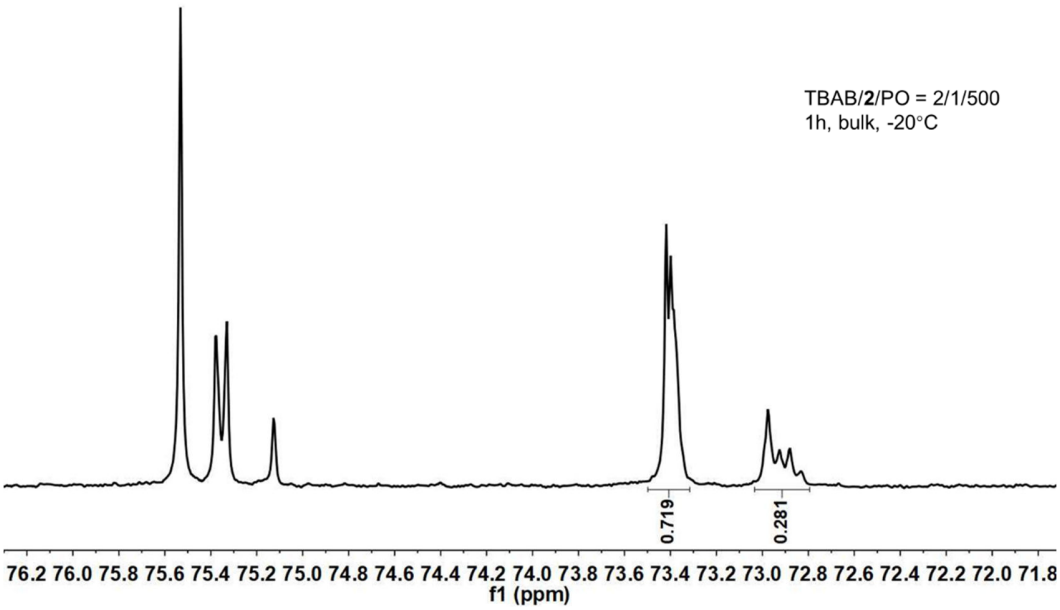


Figure S7. ^{13}C NMR spectrum of the PPO with *m* = 71.9%

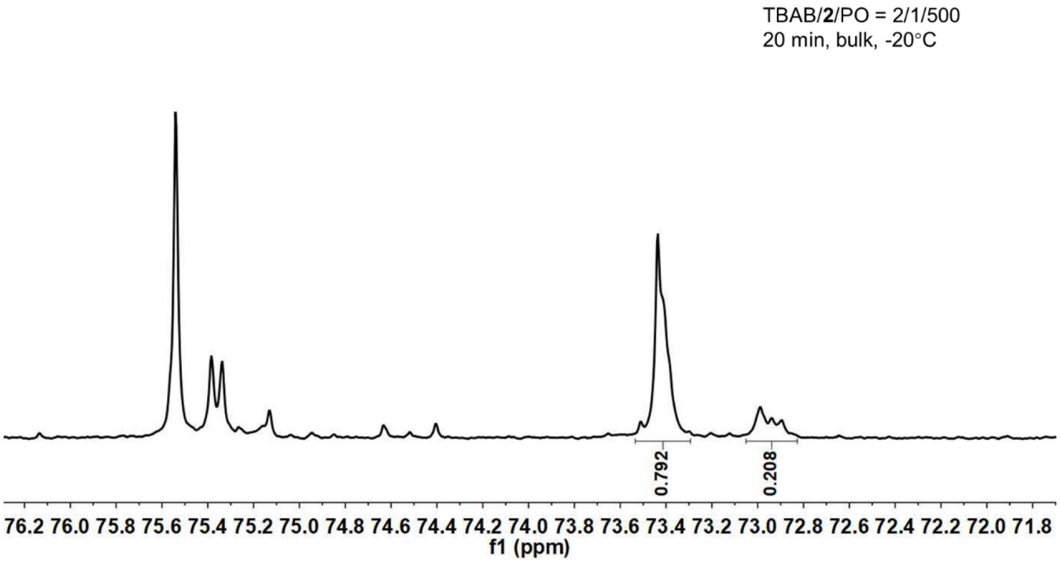


Figure S8. ^{13}C NMR spectrum of the PPO with *m* = 79.2%

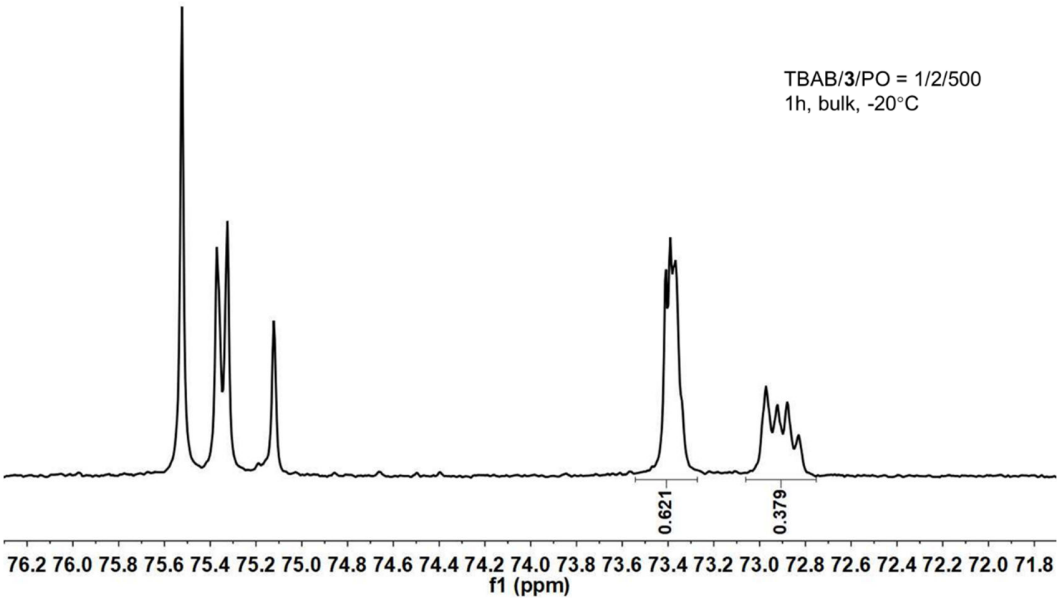


Figure S9. ^{13}C NMR spectrum of the PPO with *m* = 62.1%

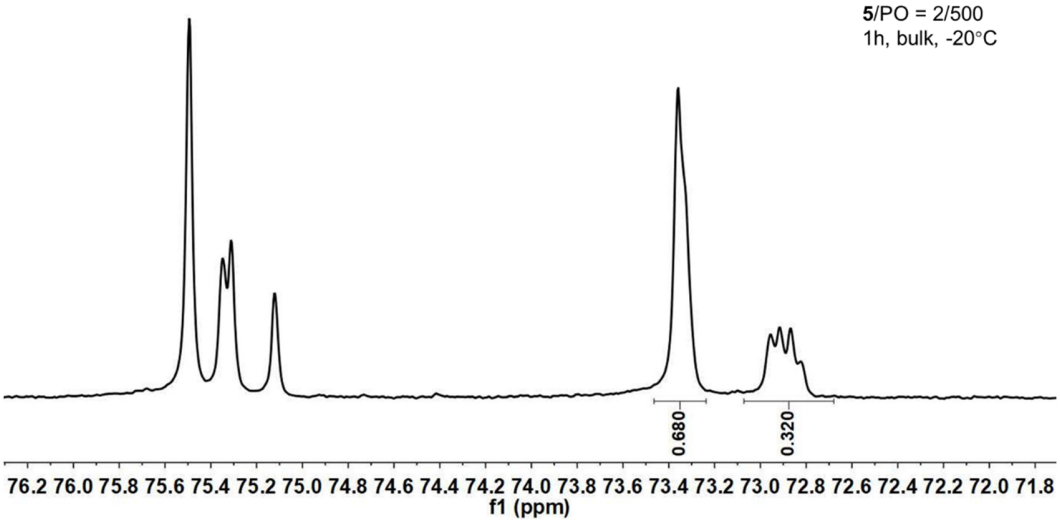


Figure S10. ^{13}C NMR spectrum of the PPO with *m* = 68.0%

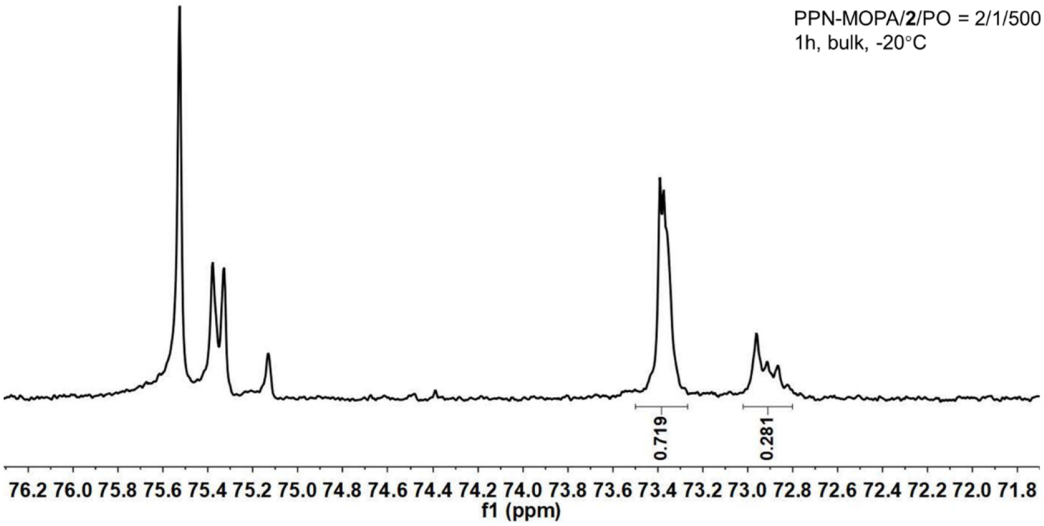


Figure S11. ^{13}C NMR spectrum of the PPO with m = 71.9%

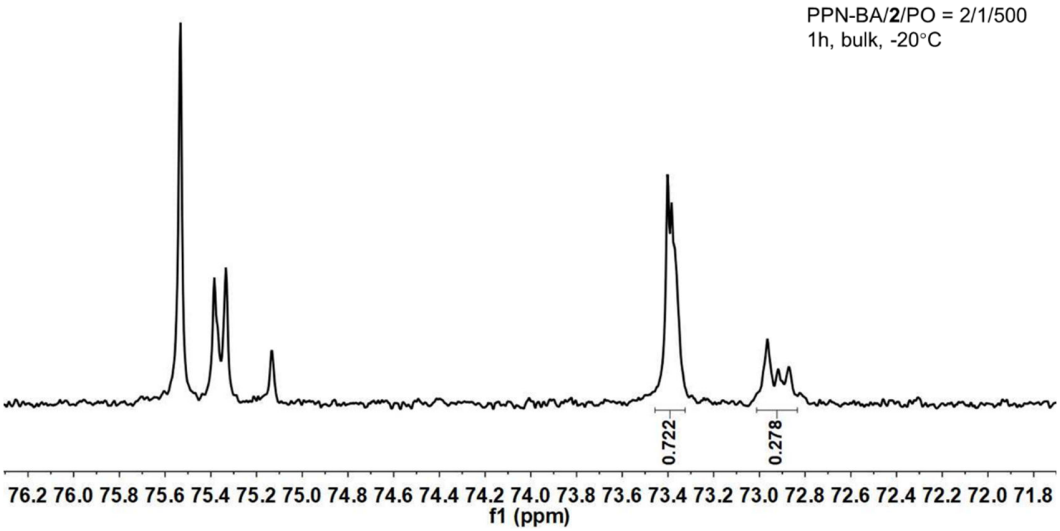


Figure S12. ^{13}C NMR spectrum of the PPO with m = 72.2%

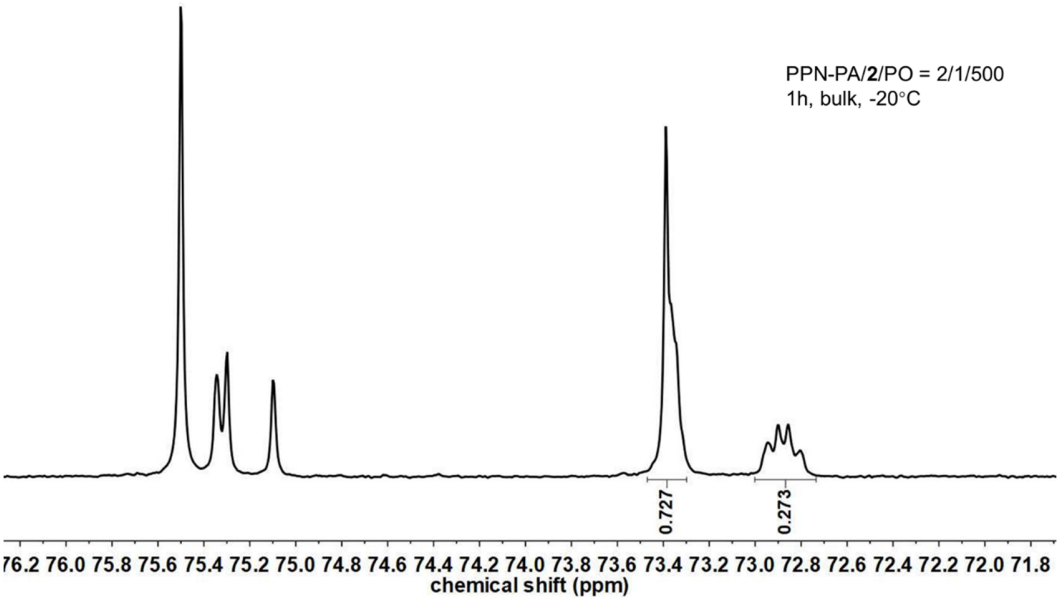


Figure S13. ^{13}C NMR spectrum of the PPO with *m* = 72.7%

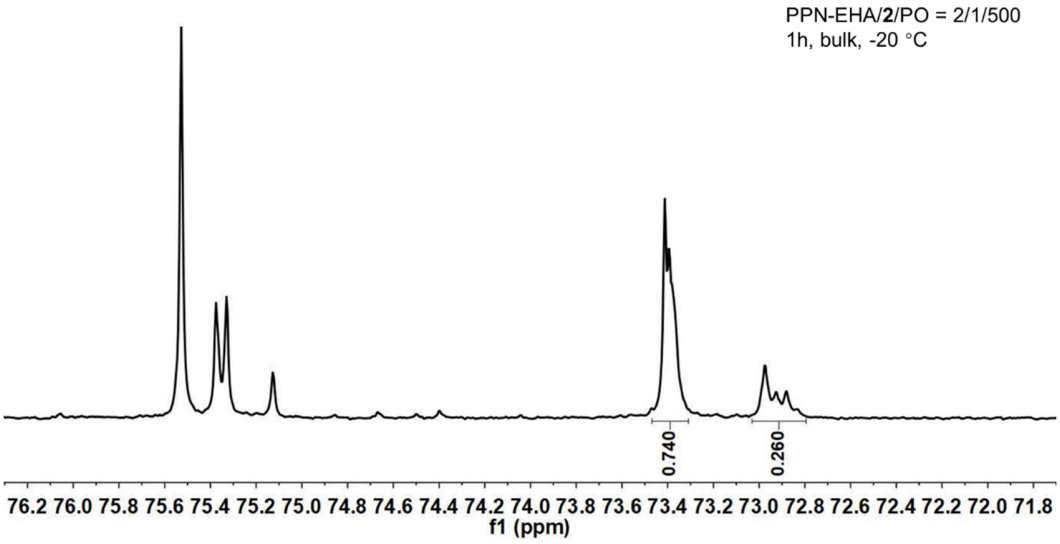


Figure S14. ^{13}C NMR spectrum of the PPO with *m* = 74.0%

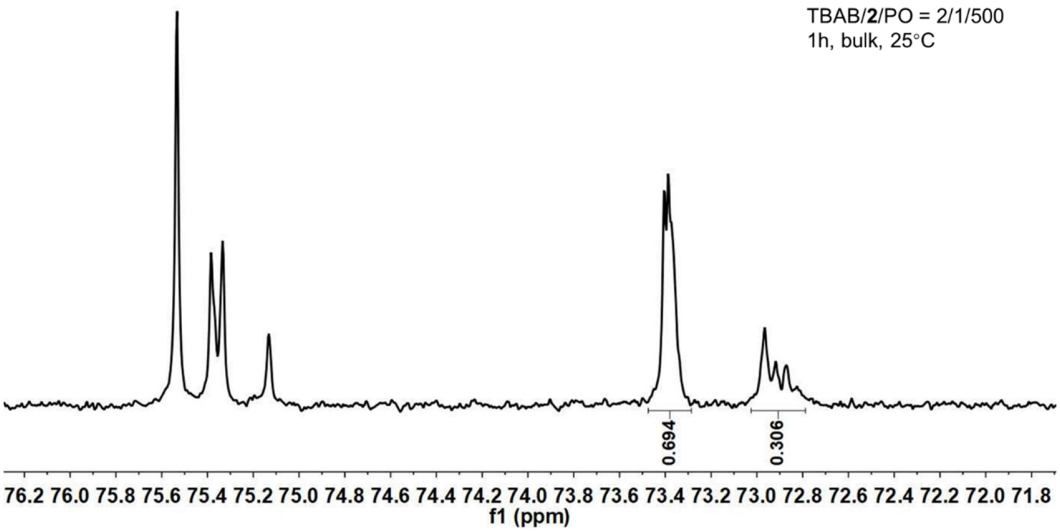


Figure S15. ^{13}C NMR spectrum of the PPO with *m* = 69.4%

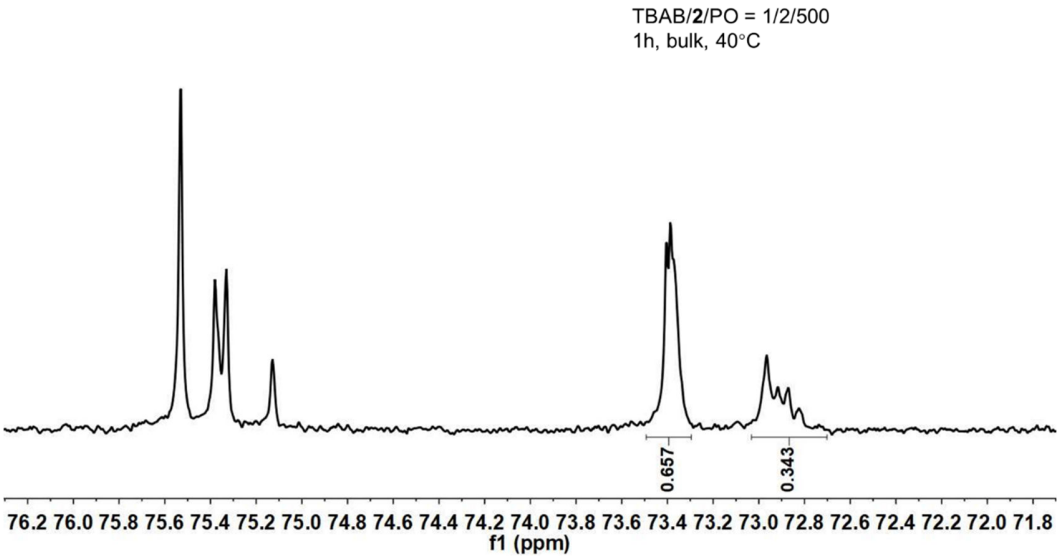


Figure S16. ^{13}C NMR spectrum of the PPO with *m* = 65.7%

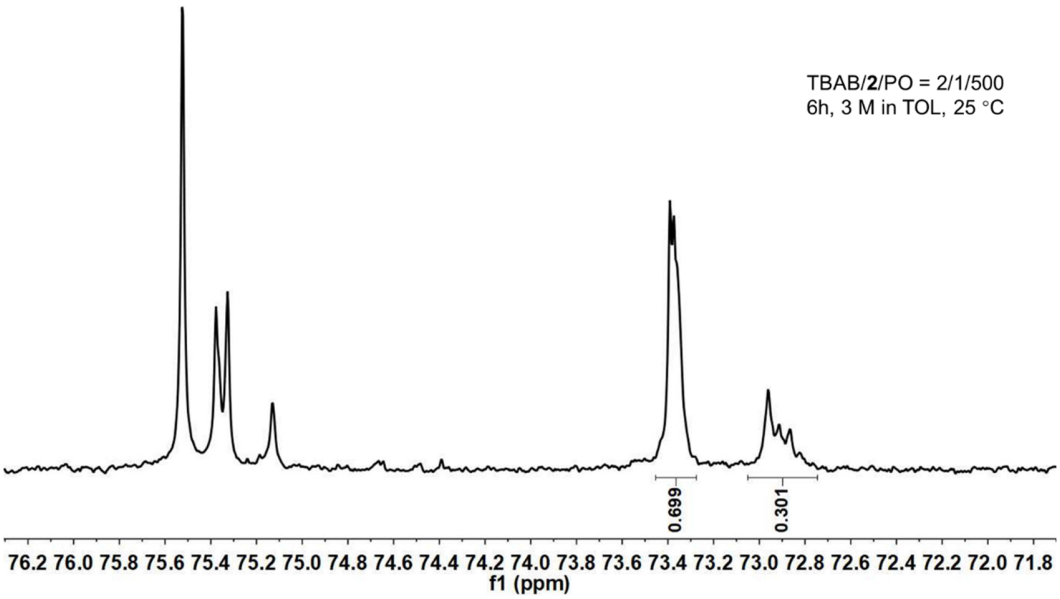


Figure S17. ^{13}C NMR spectrum of the PPO with m = 69.9%

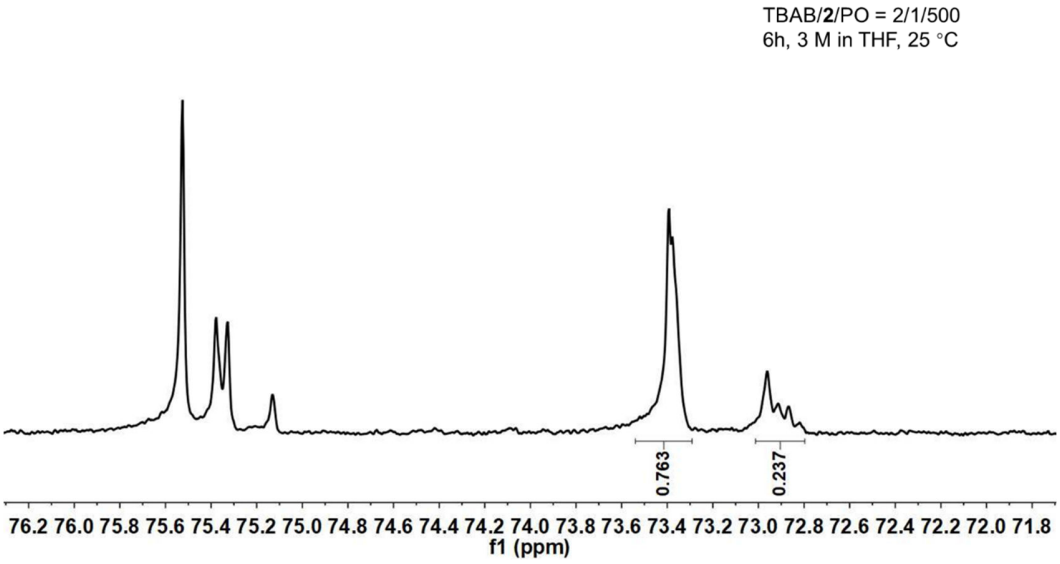


Figure S18. ^{13}C NMR spectrum of the PPO with m = 76.3%

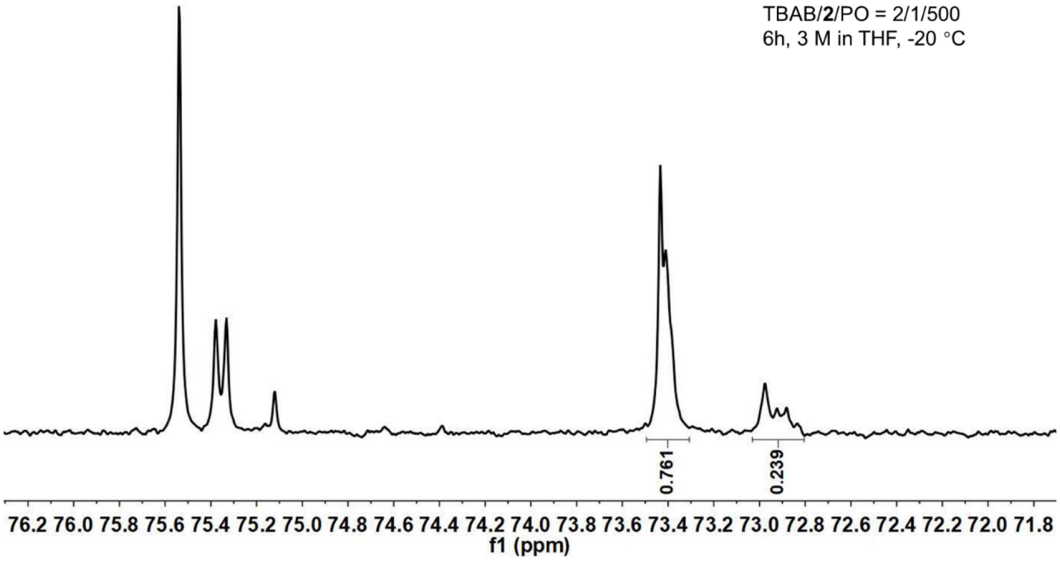


Figure S19. ^{13}C NMR spectrum of the PPO with *m* = 76.1%

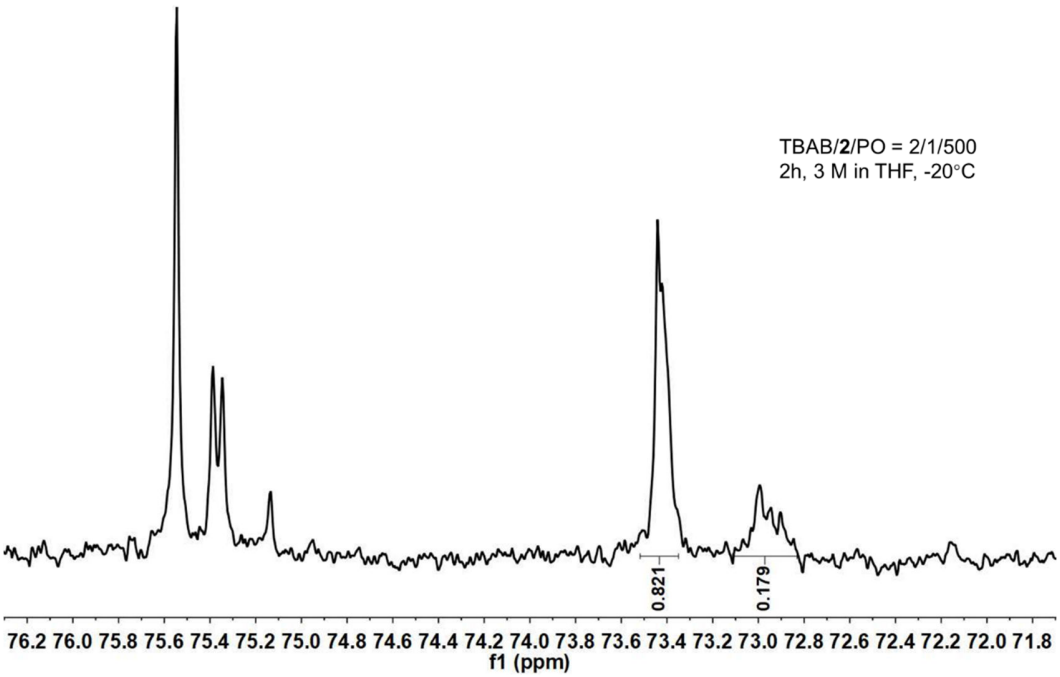


Figure S20. ^{13}C NMR spectrum of the PPO with *m* = 82.1%

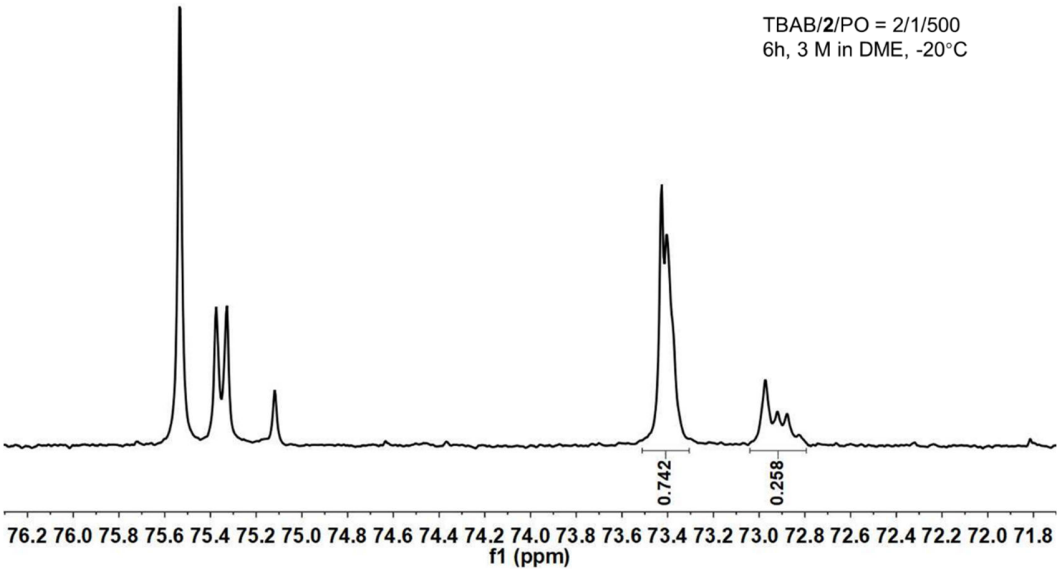


Figure S21. ^{13}C NMR spectrum of the PPO with m = 74.2%

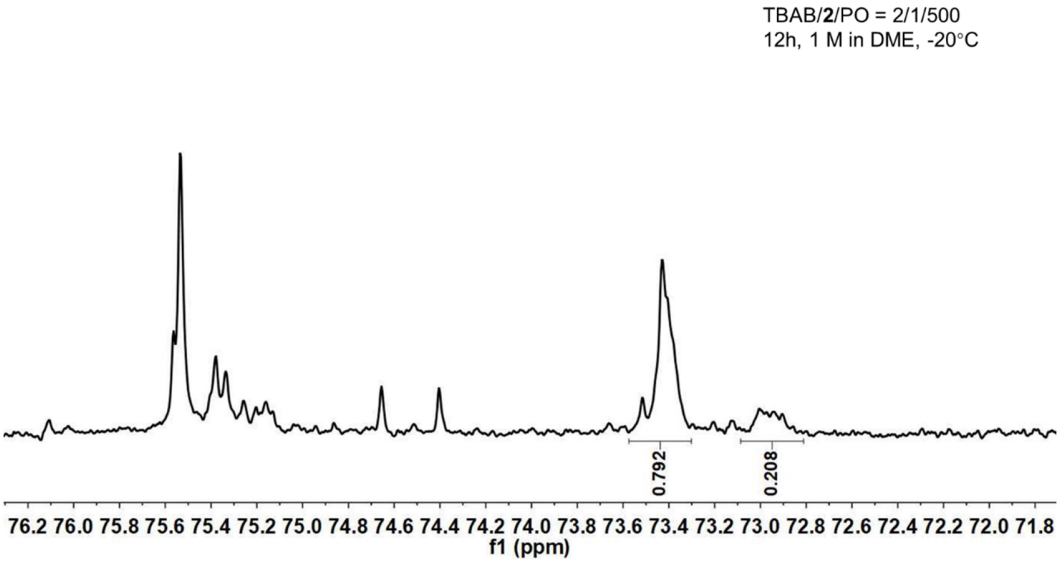


Figure S22. ^{13}C NMR spectrum of the PPO with m = 79.2%

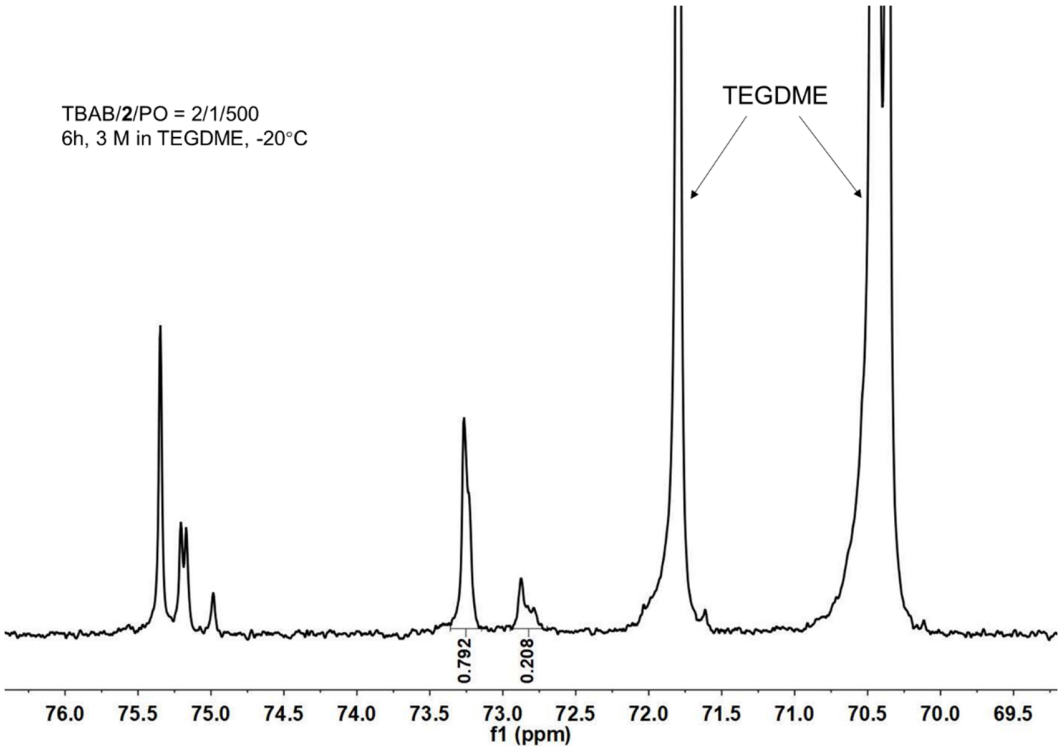


Figure S23. ^{13}C NMR spectrum of the PPO with *m* = 79.2%

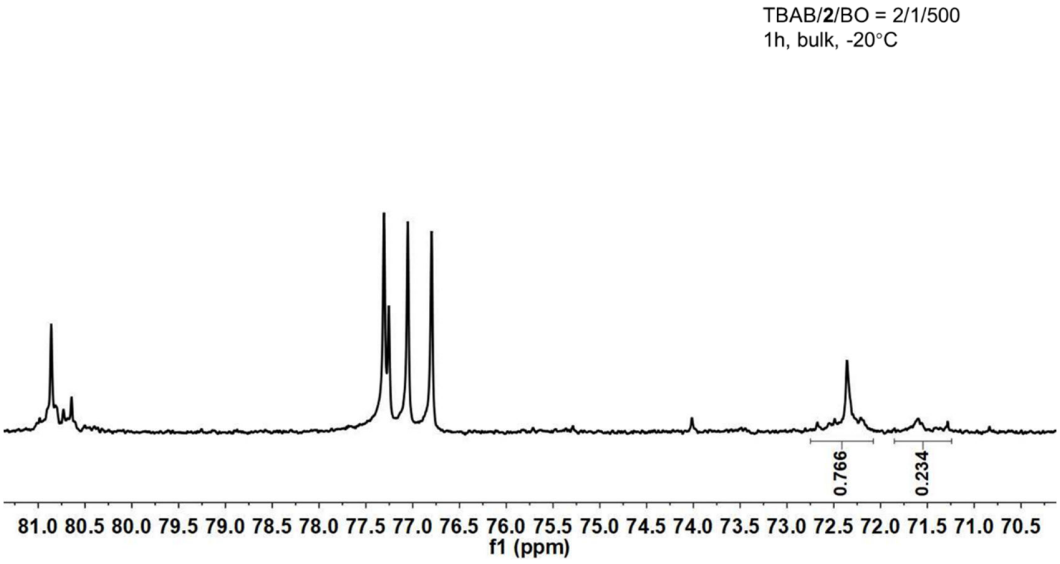


Figure S24. ^{13}C NMR spectrum of the PBO with *m* = 76.6%

Proofs of the high end-group fidelity of the polyether produced using (*R*)-2/PPN-MOPA

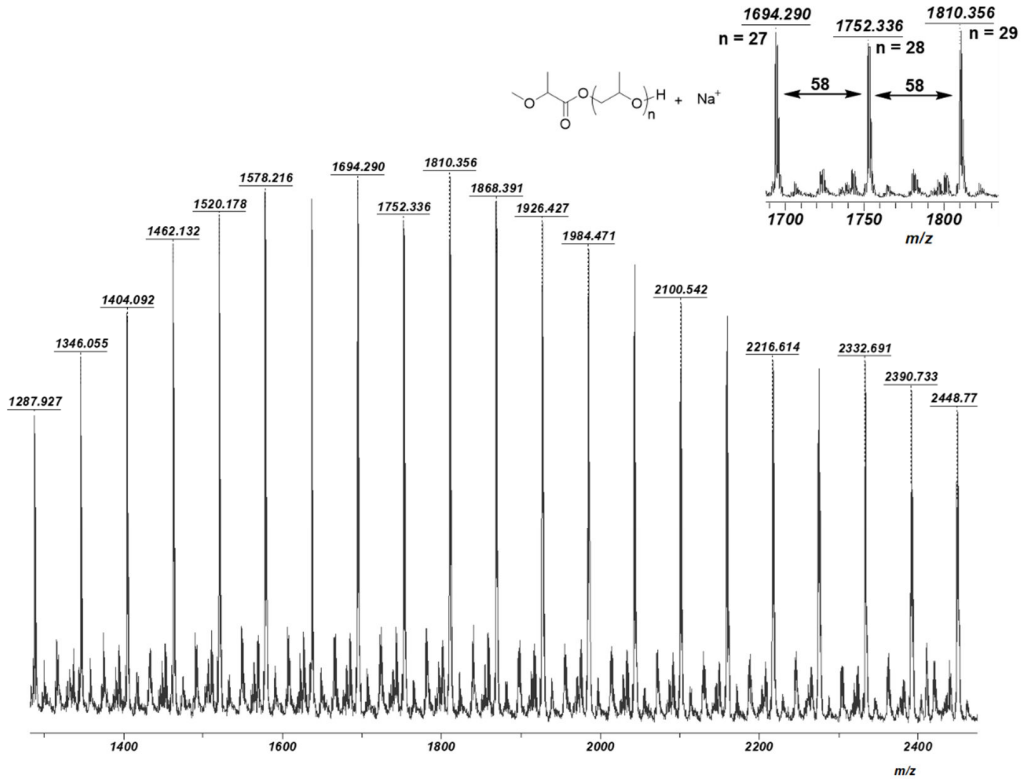


Figure S25. MALDI-TOF MS of PPO sample synthesized by **(*R*)-2**/PPN-MOPA with a feed ratio of PPN-MOPA/**(*R*)-2**/PO = 2/1/250, the polymerization was conducted at -20 °C in neat racemic PO for 30 min

^{1}H and ^{13}C NMR spectra of synthesized compounds

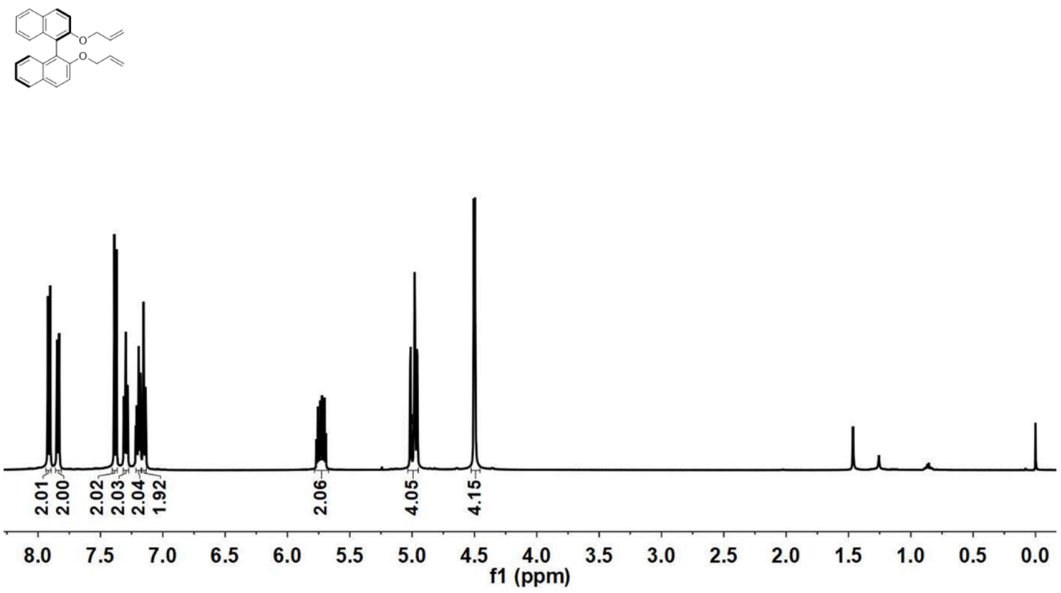


Figure S26. ^{1}H NMR spectrum of **1a** in $CDCl_3$(400M).

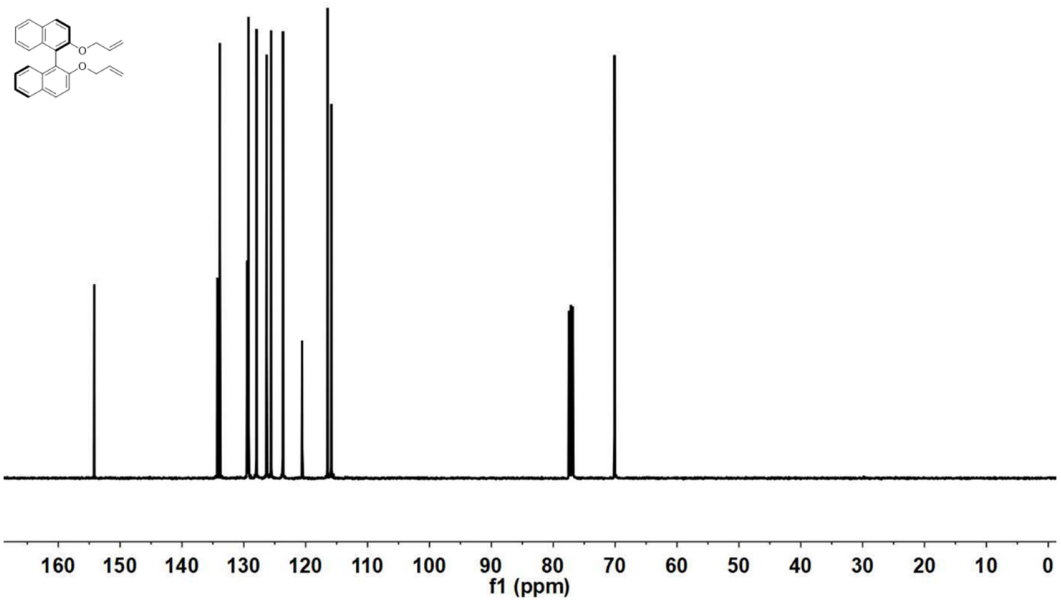


Figure S27. ^{13}C NMR spectrum of **1a** in $CDCl_3$(400M).

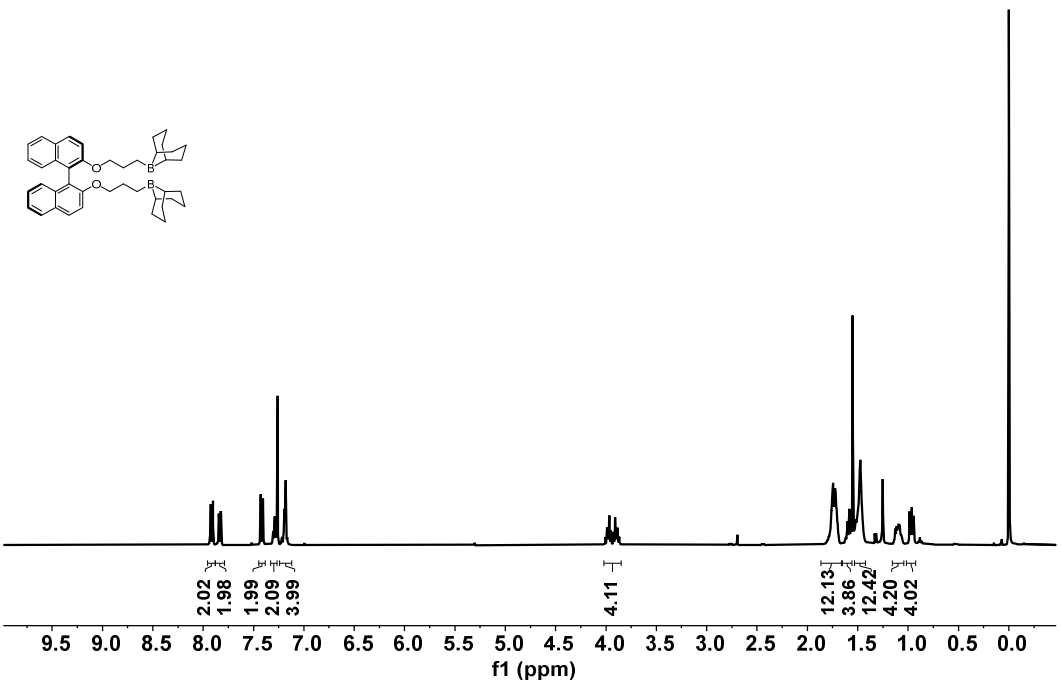


Figure S28. ^{1}H NMR spectrum of chiral organoboron catalyst **1** in $CDCl_3$(400M).

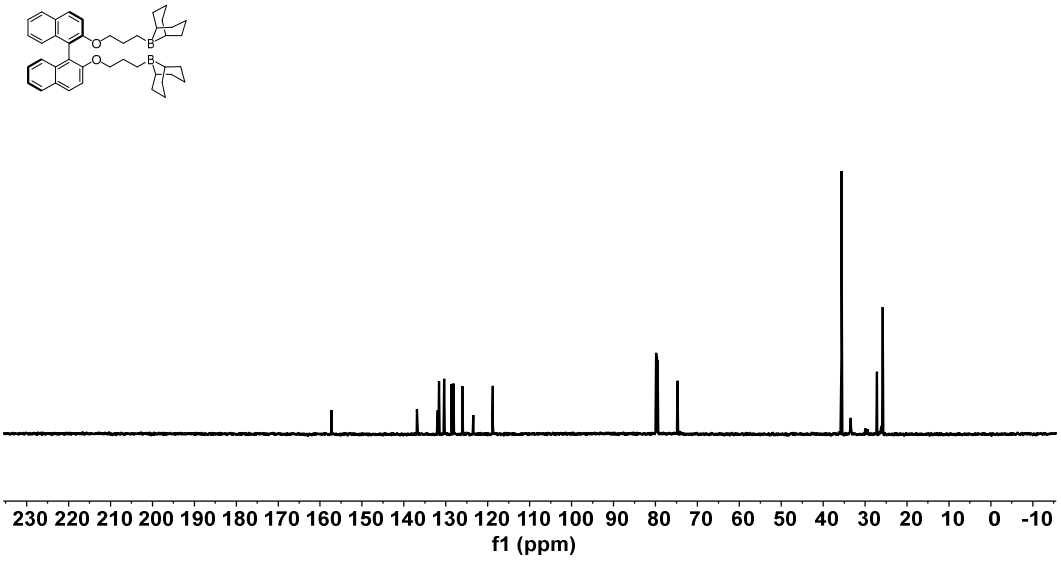


Figure S29. ^{13}C NMR spectrum of chiral organoboron catalyst **1** in $CDCl_3$(400M).

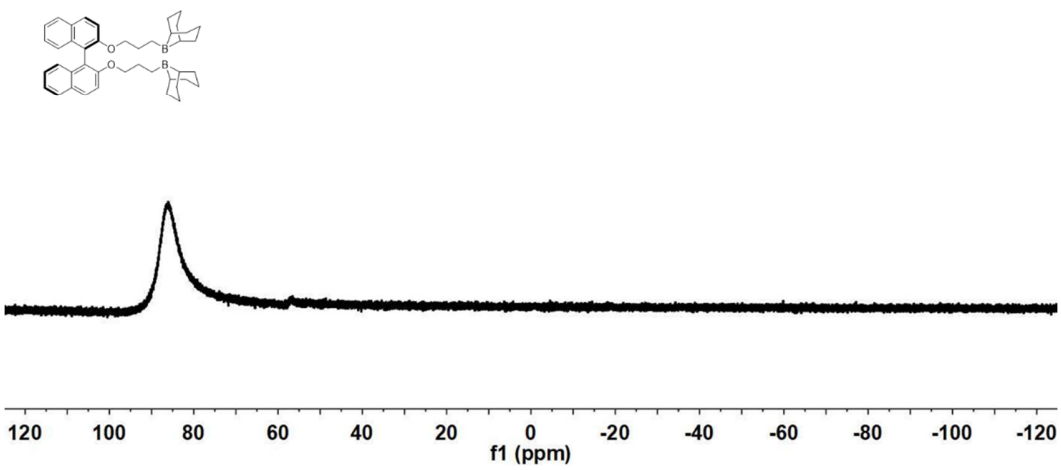


Figure S30. ^{11}B NMR spectrum of chiral organoboron catalyst **1** in $CDCl_3$(400M).

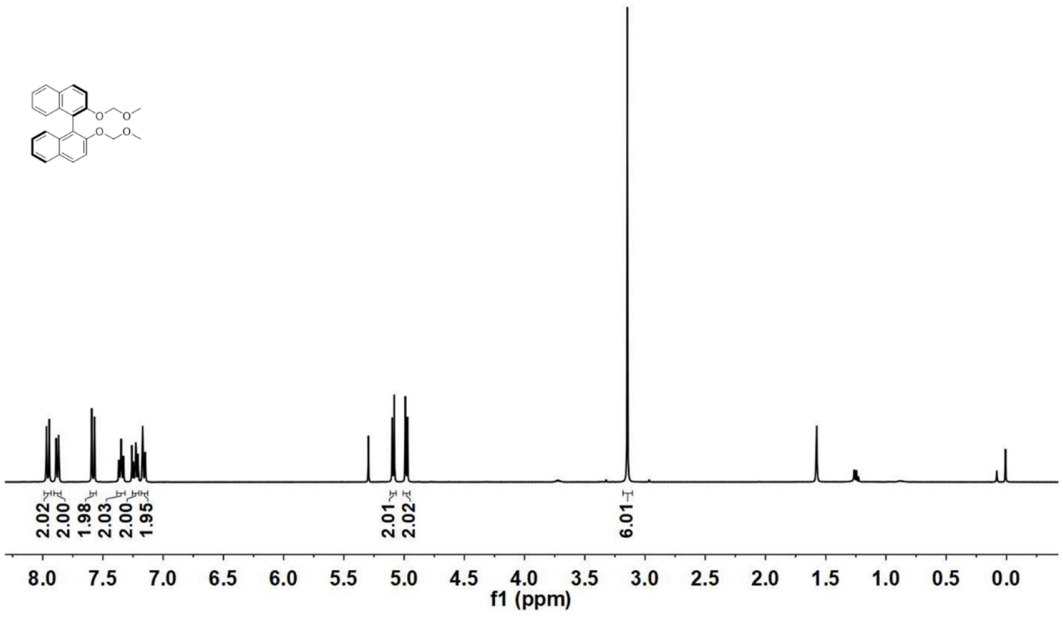


Figure S31. ^{1}H NMR spectrum of **2a** in $CDCl_3$(400M).

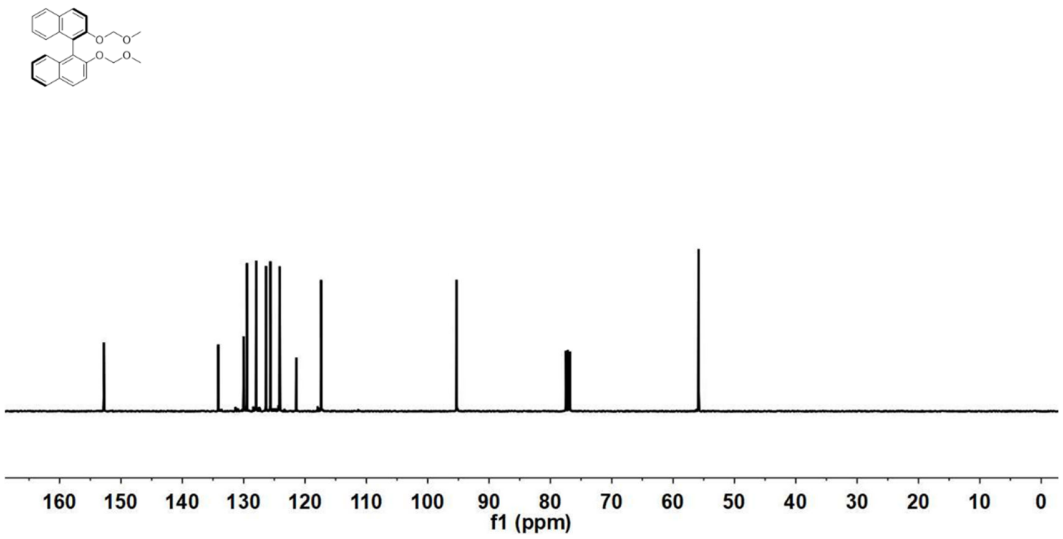


Figure S32. ^{13}C NMR spectrum of **2a** in $CDCl_3$(400M).

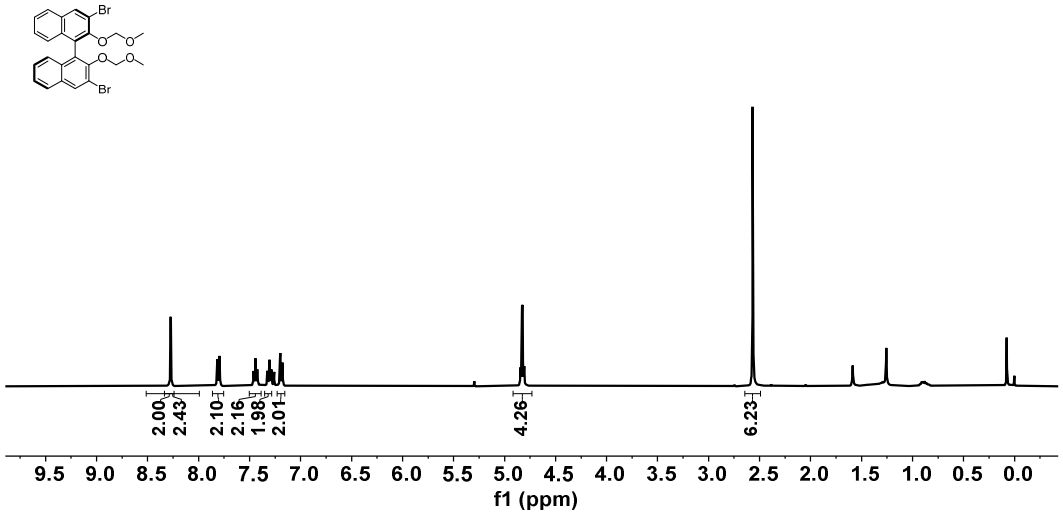


Figure S33. ^{1}H NMR spectrum of **2b** in $CDCl_3$(400M).

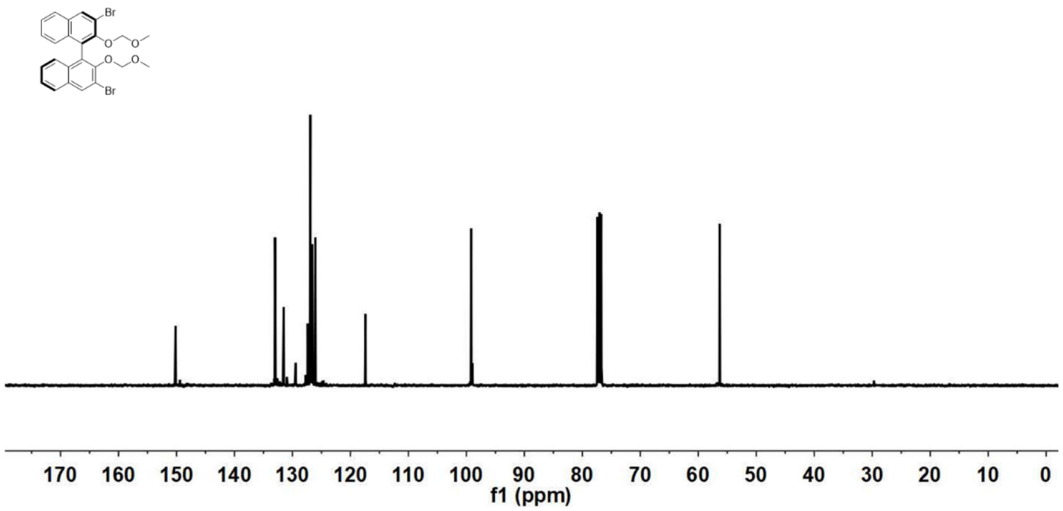


Figure S34. ^{13}C NMR spectrum of **2b** in $CDCl_3$(400M).

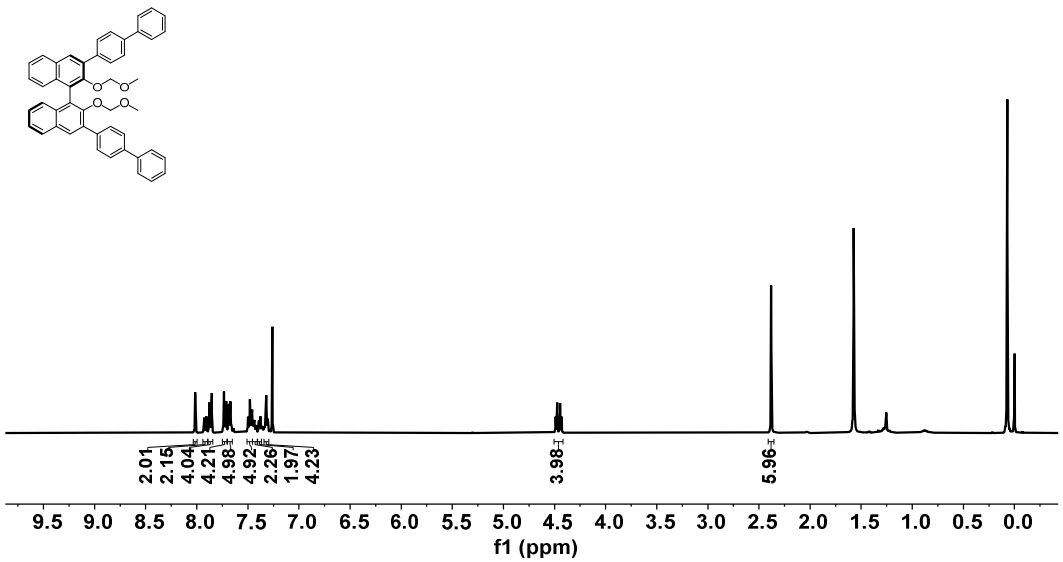


Figure S35. ^{1}H NMR spectrum of **2c** in $CDCl_3$(400M).

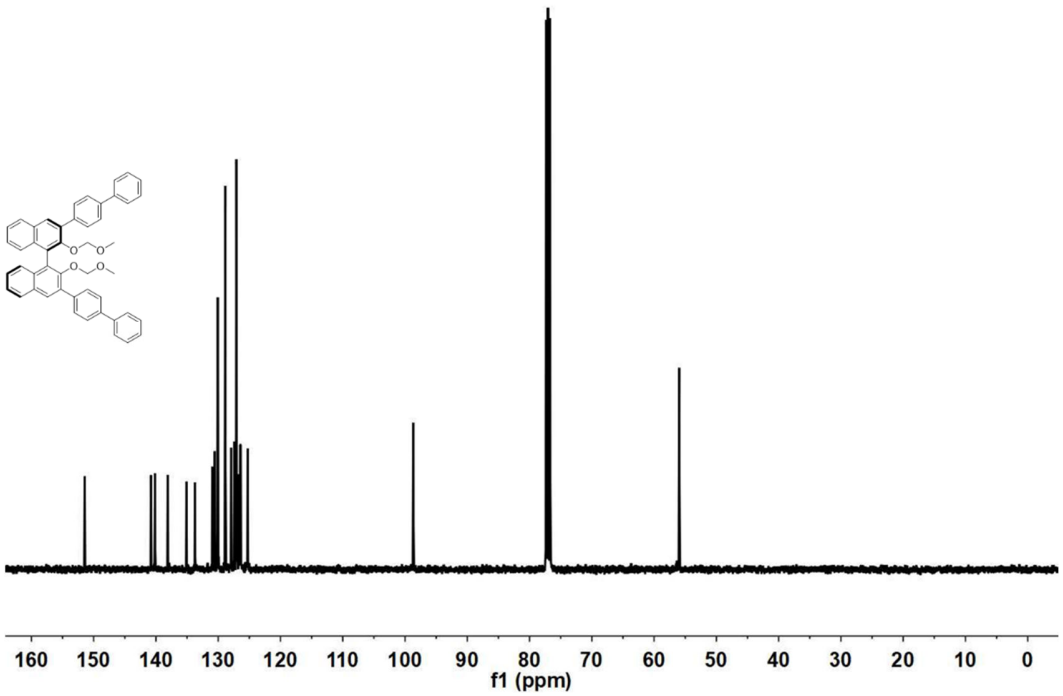


Figure S36. ^{13}C NMR spectrum of **2c** in $CDCl_3$(400M).

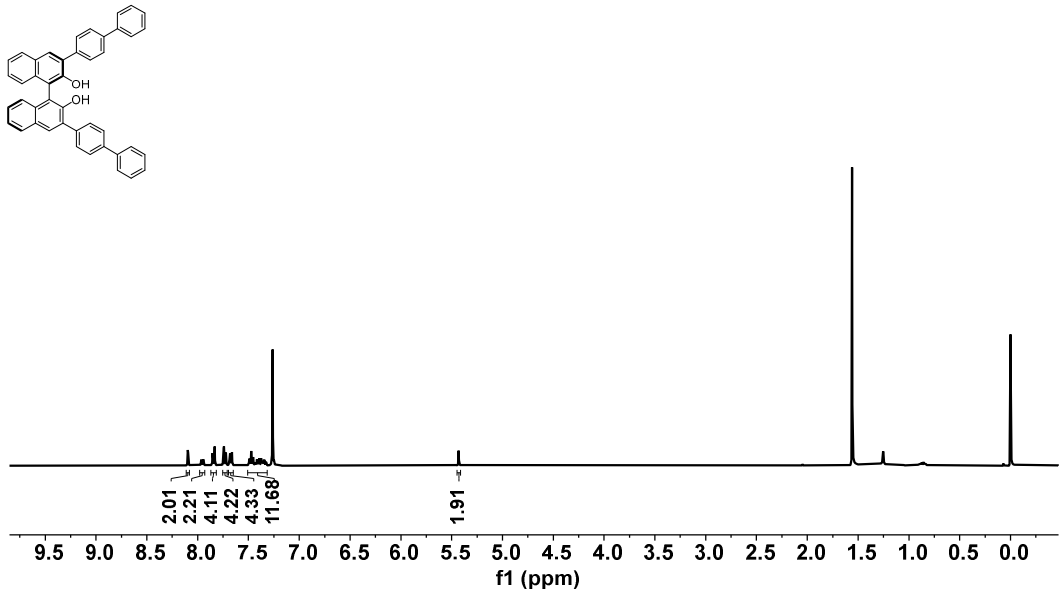


Figure S37. ^{1}H NMR spectrum of **2d** in $CDCl_3$(400M).

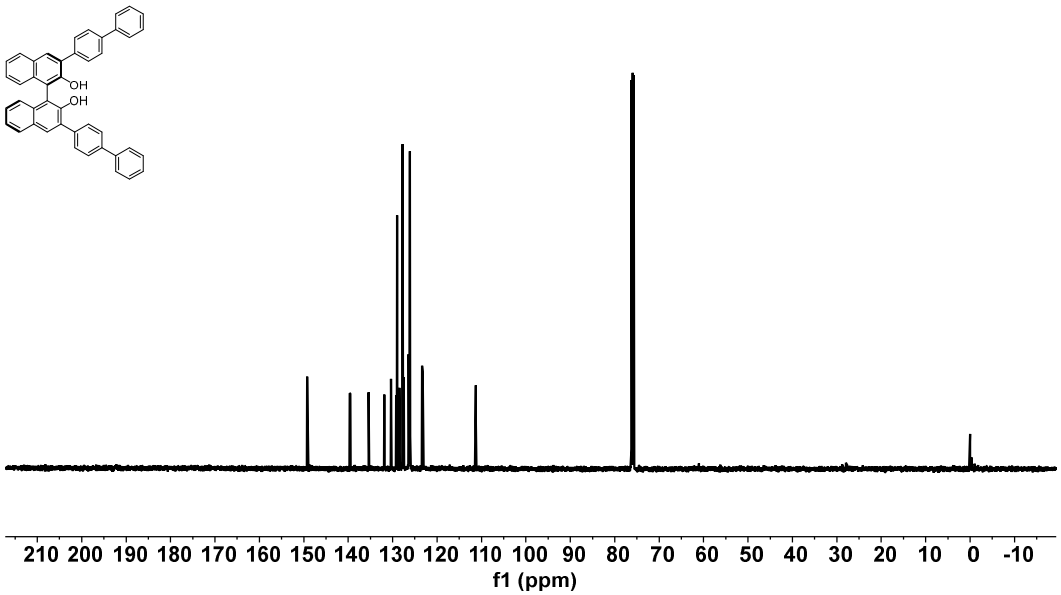


Figure S38. ^{13}C NMR spectrum of **2d** in $CDCl_3$(400M).

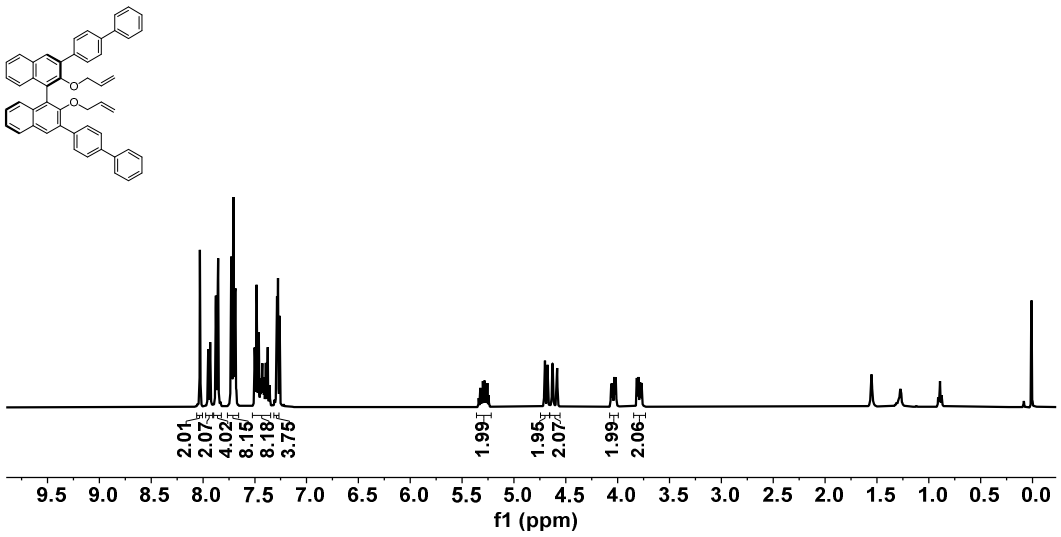


Figure S39. ^{1}H NMR spectrum of **2e** in $CDCl_3$(400M).

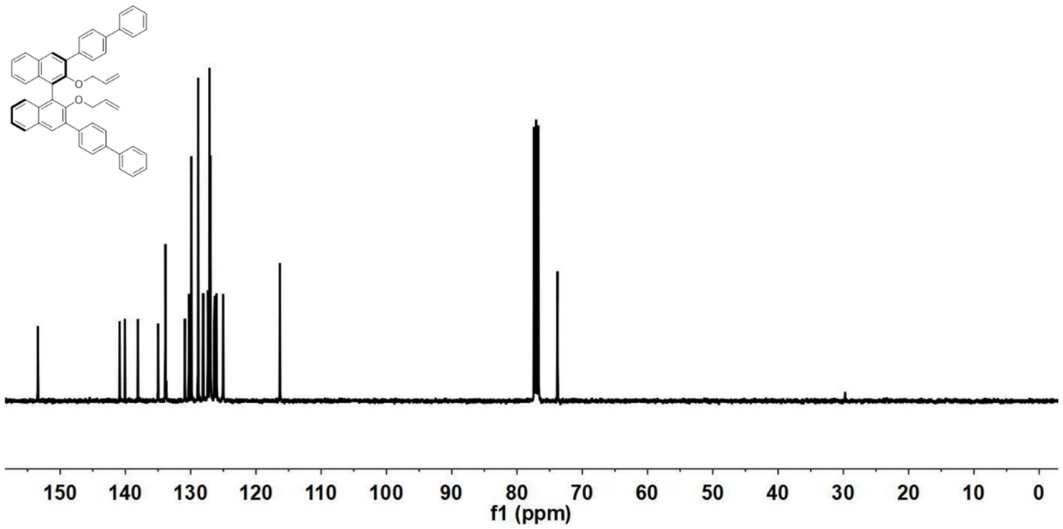


Figure S40. ^{13}C NMR spectrum of **2e** in $CDCl_3$(400M).

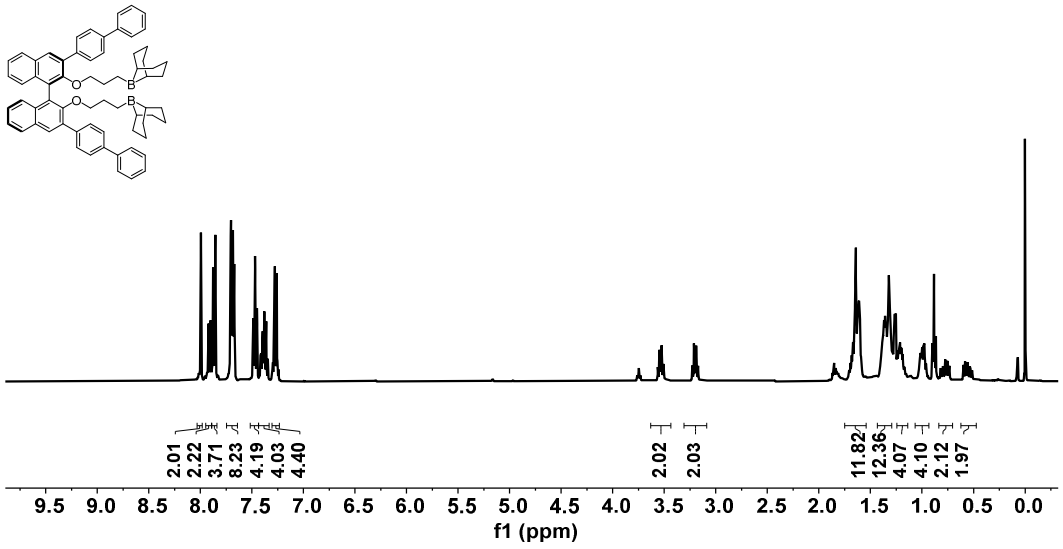


Figure S41. ^{1}H NMR spectrum of chiral organoboron catalyst **2** in $CDCl_3$(400M).

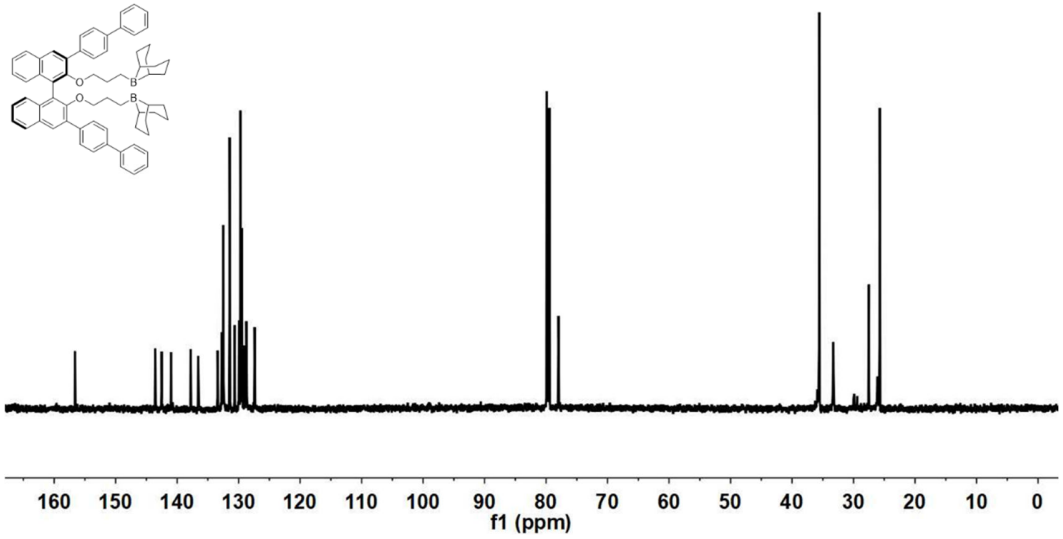


Figure S42. ^{13}C NMR spectrum of chiral organoboron catalyst **2** in $CDCl_3$(400M).

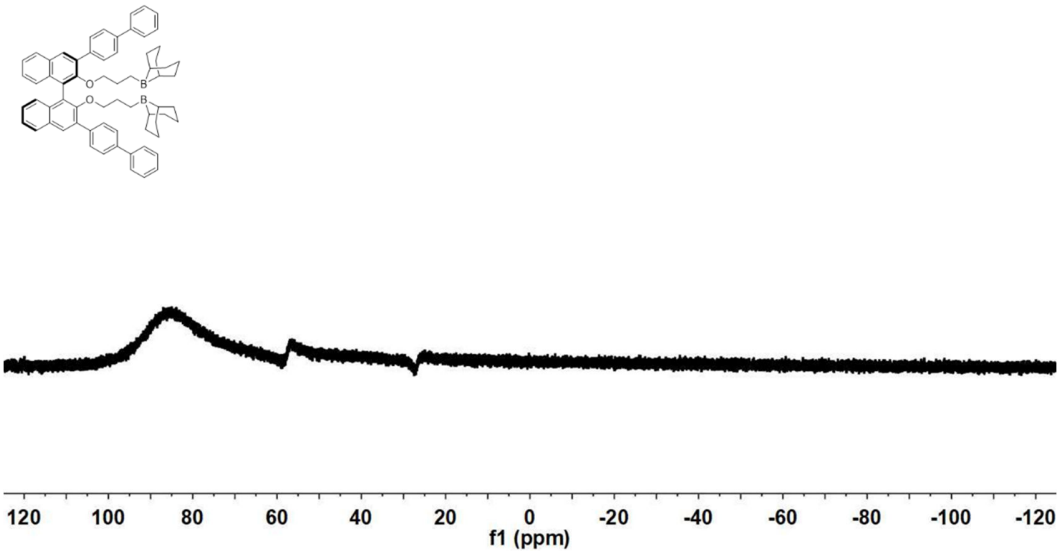


Figure S43. ^{11}B NMR spectrum of chiral organoboron catalyst **2** in $CDCl_3$(400M).

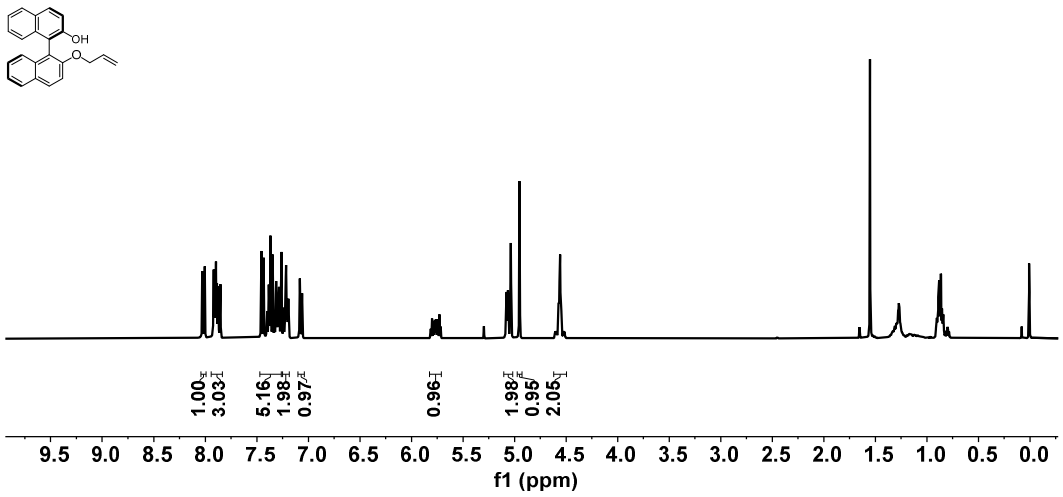


Figure S44. ^{1}H NMR spectrum of **3a** in $CDCl_3$(400M).

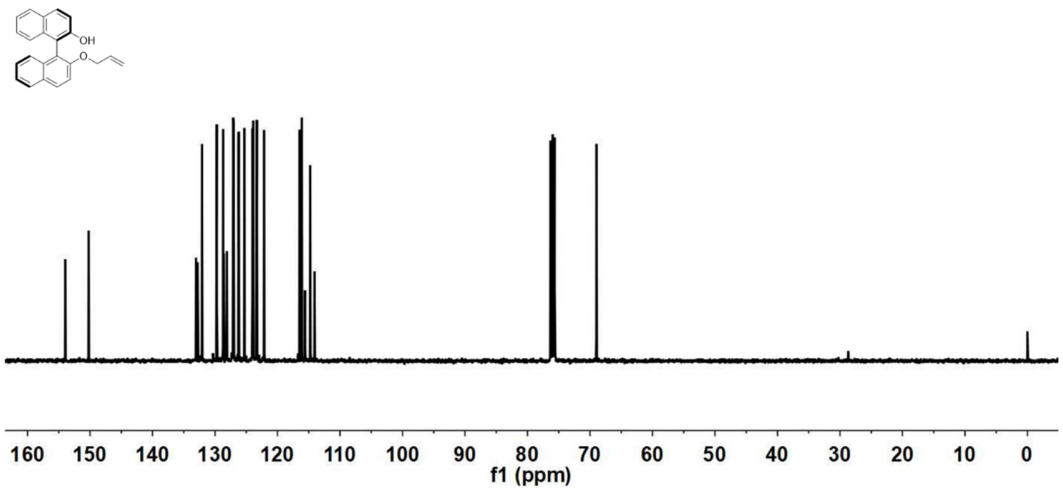


Figure S45. ^{13}C NMR spectrum of **3a** in $CDCl_3$(400M).

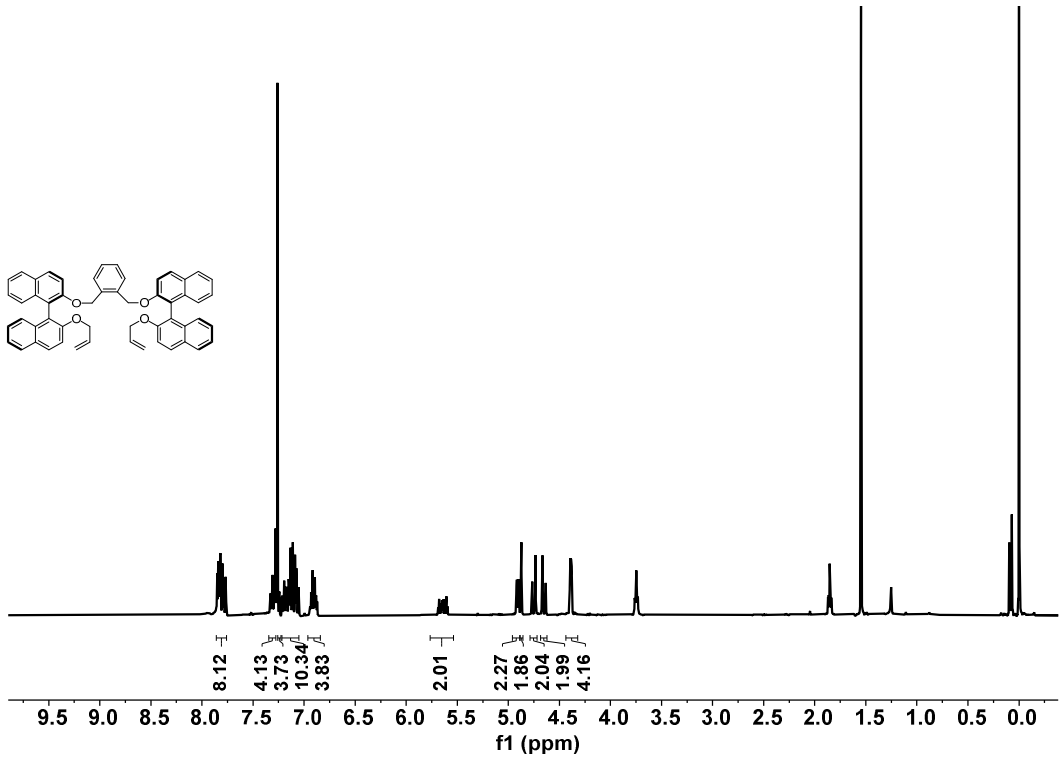


Figure S46. ^{1}H NMR spectrum of **3b** in $CDCl_3$(400M).

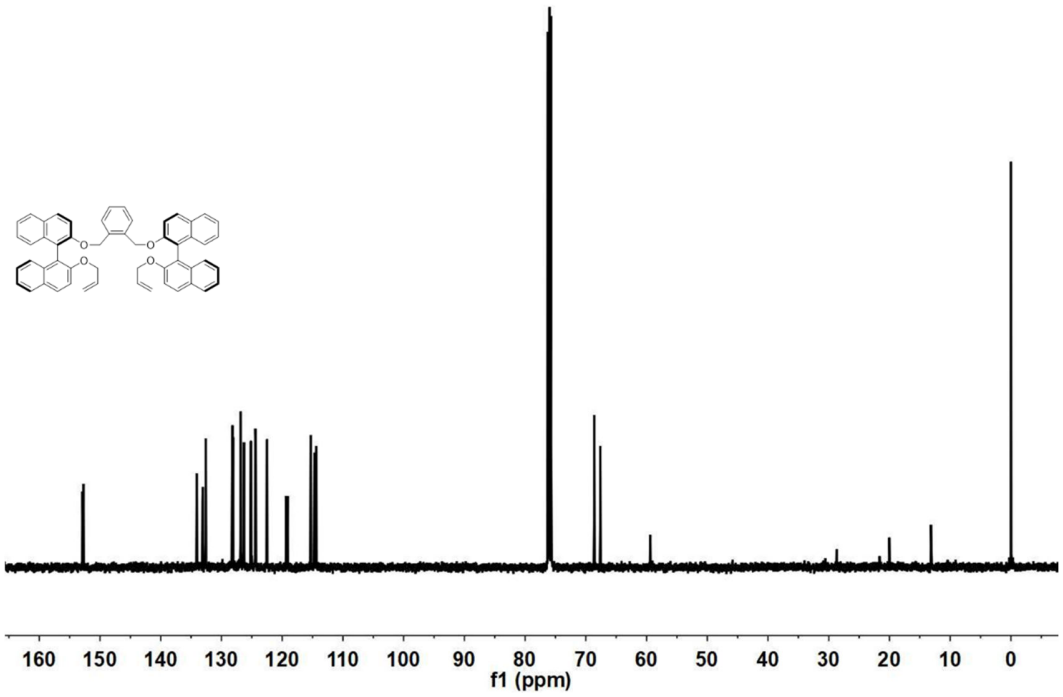


Figure S47. ^{13}C NMR spectrum of **3b** in $CDCl_3$(400M).

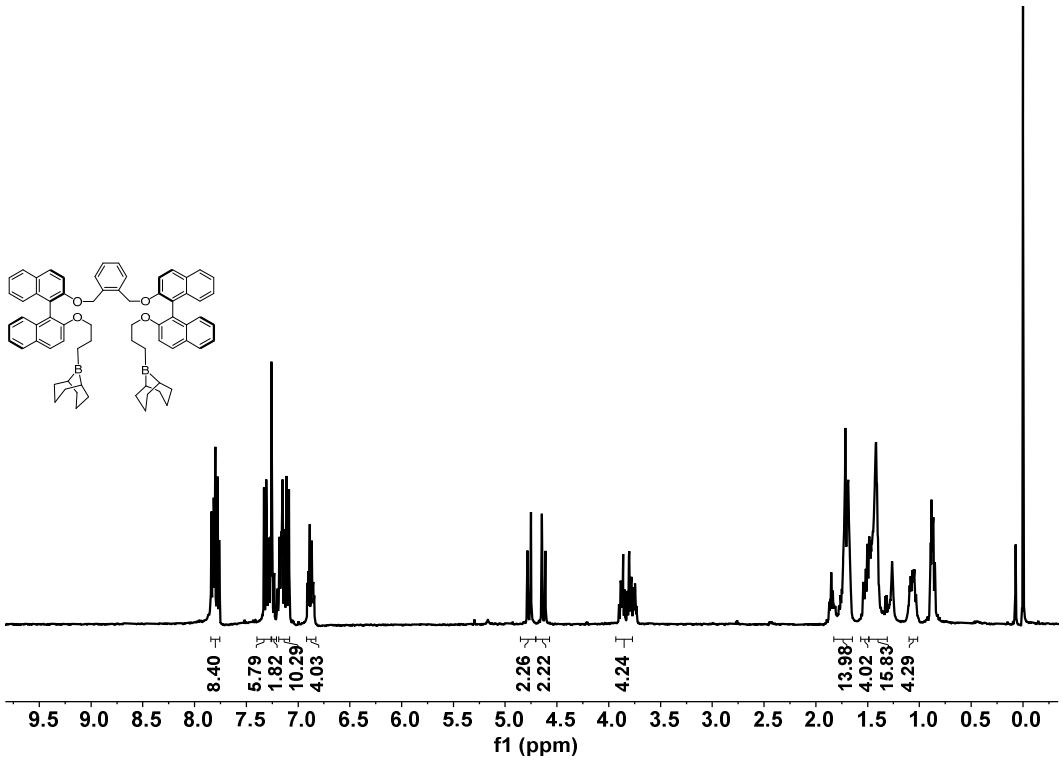


Figure S48. ^{1}H NMR spectrum of chiral organoboron catalyst **3** in $CDCl_3$(400M).

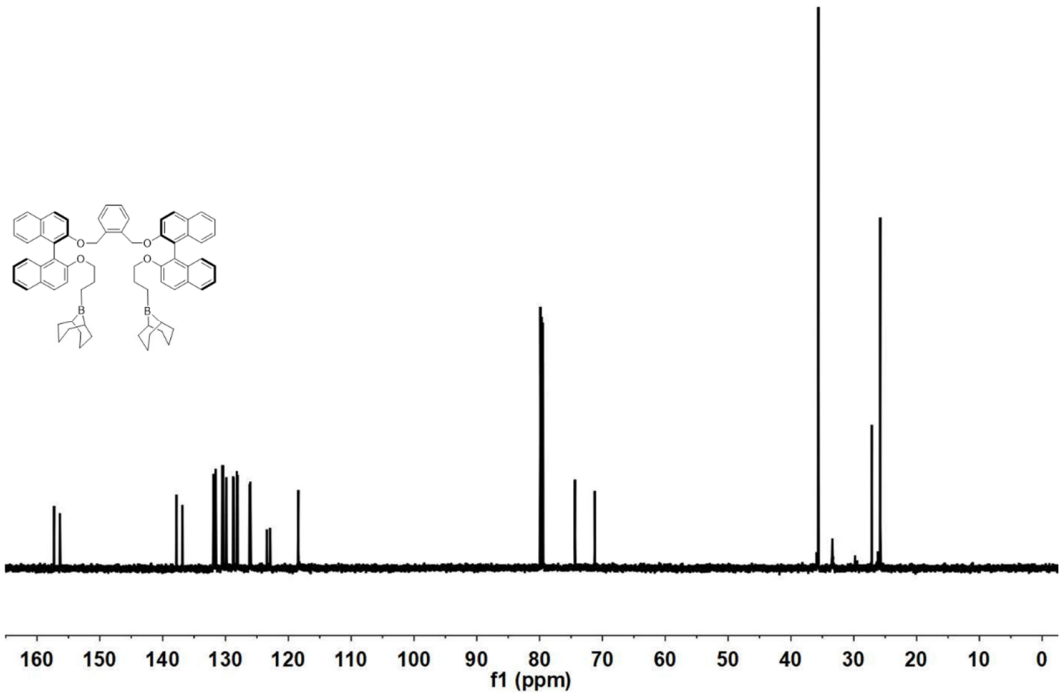


Figure S49. ^{13}C NMR spectrum of chiral organoboron catalyst **3** in $CDCl_3$(400M).

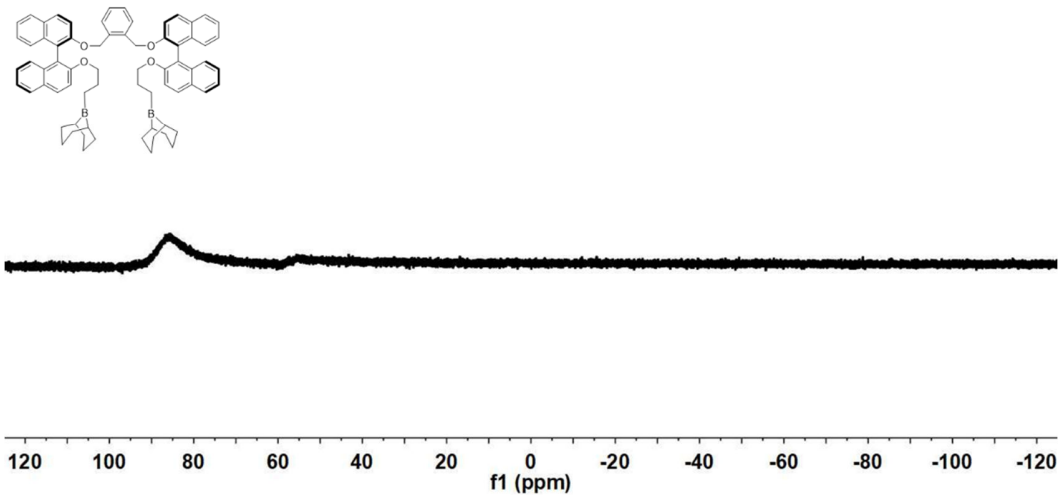


Figure S50. ^{11}B NMR spectrum of chiral organoboron catalyst **3** in $CDCl_3$(400M).

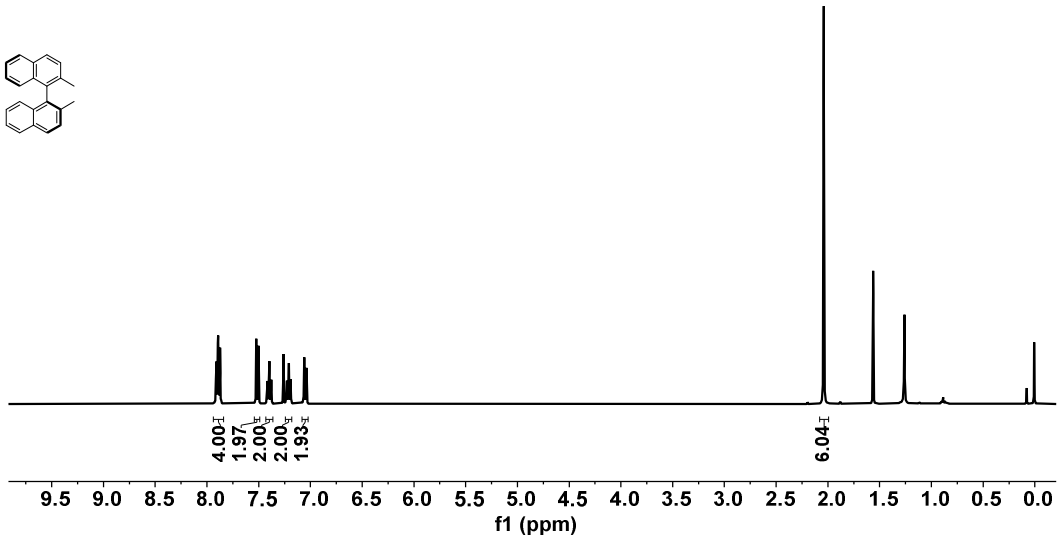


Figure S51. ^{1}H NMR spectrum of **5a** in $CDCl_3$(400M).

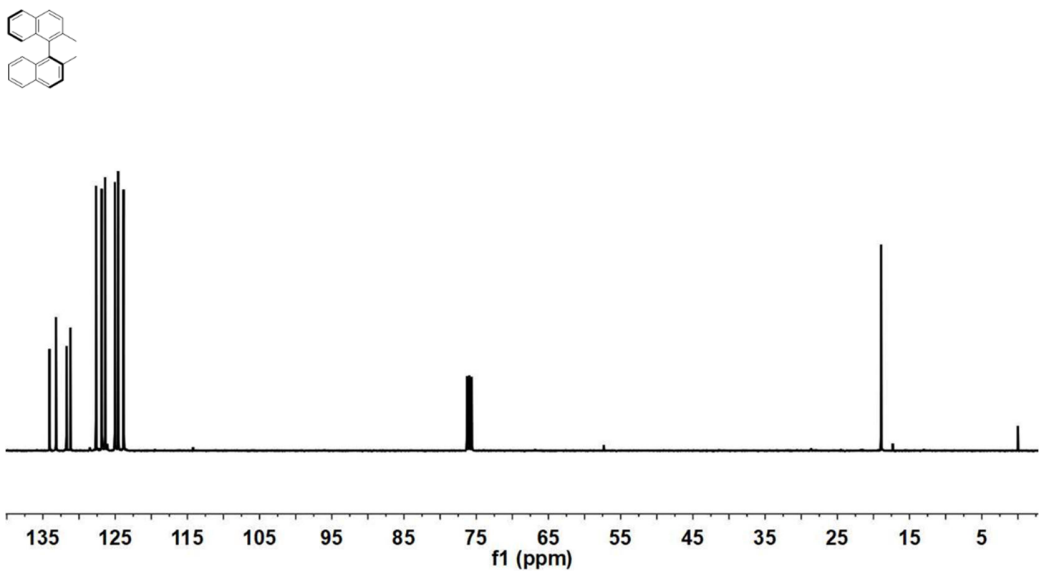


Figure S52. ^{13}C NMR spectrum of **5a** in $CDCl_3$(400M).

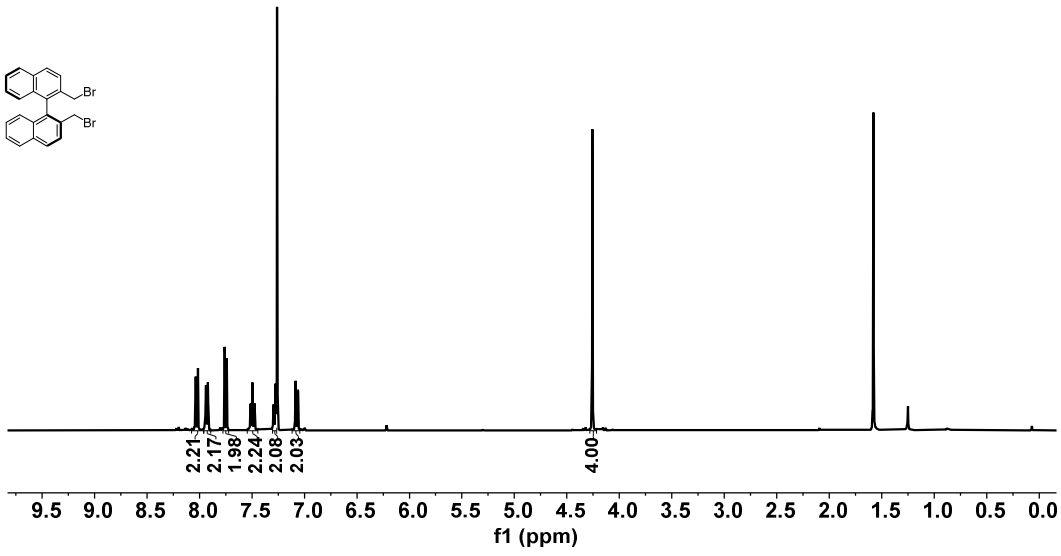


Figure S53. ^{1}H NMR spectrum of **5b** in $CDCl_3$(400M).

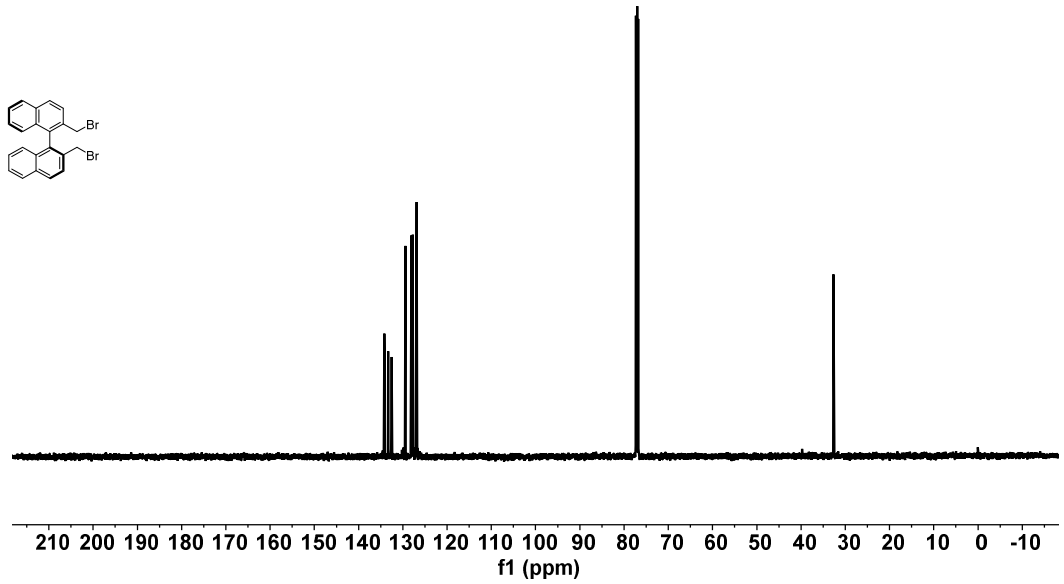


Figure S54. ^{13}C NMR spectrum of **5b** in $CDCl_3$(400M).

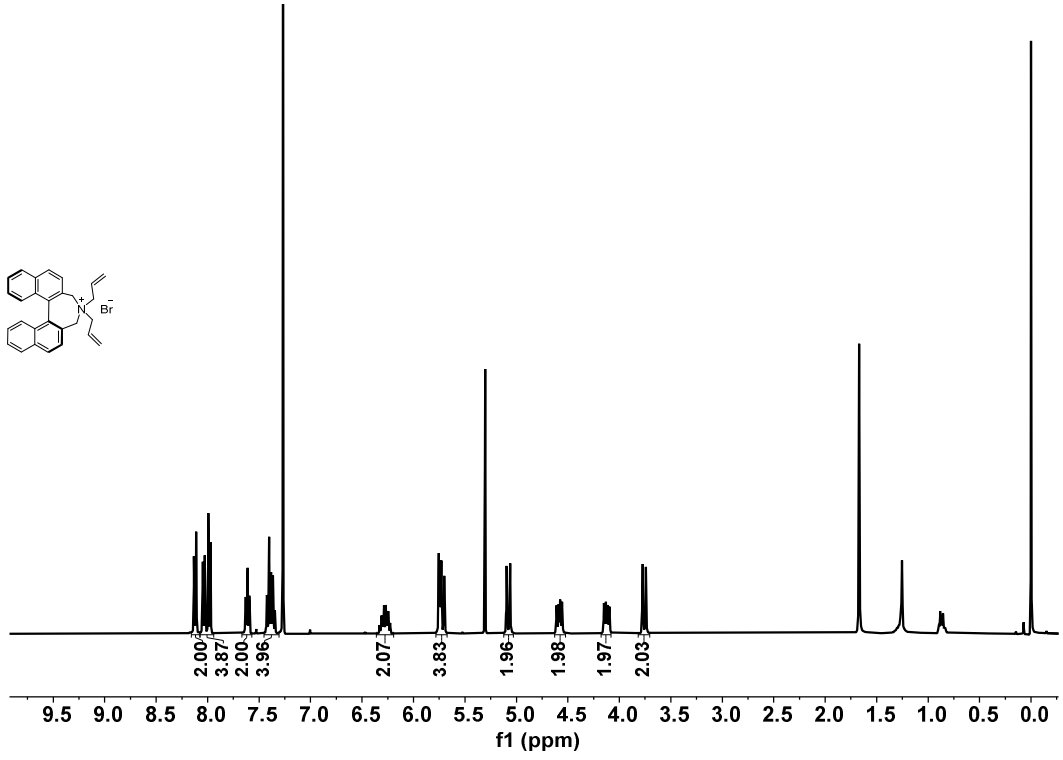


Figure S55. ^{1}H NMR spectrum of **5c** in $CDCl_3$(400M).

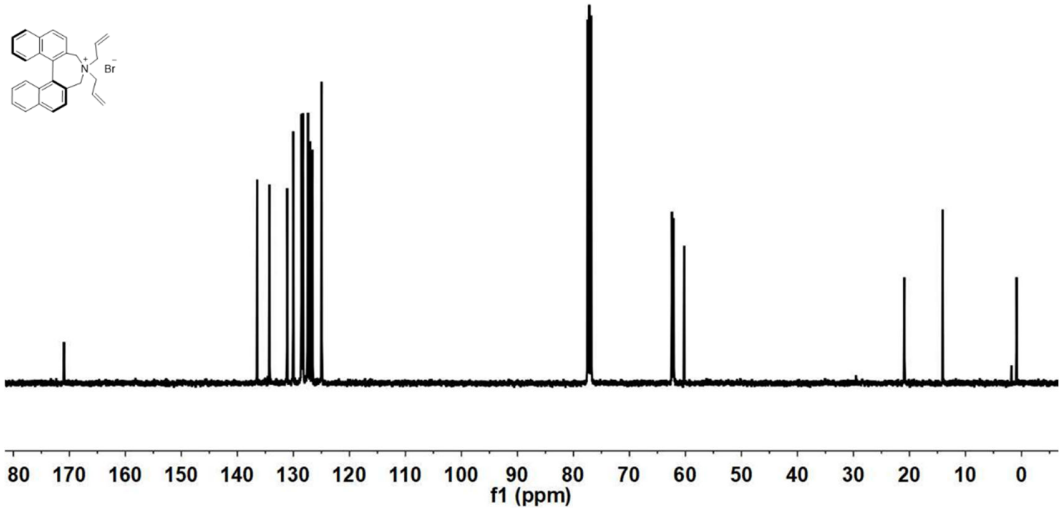


Figure S56. ^{13}C NMR spectrum of **5c** in $CDCl_3$(400M).

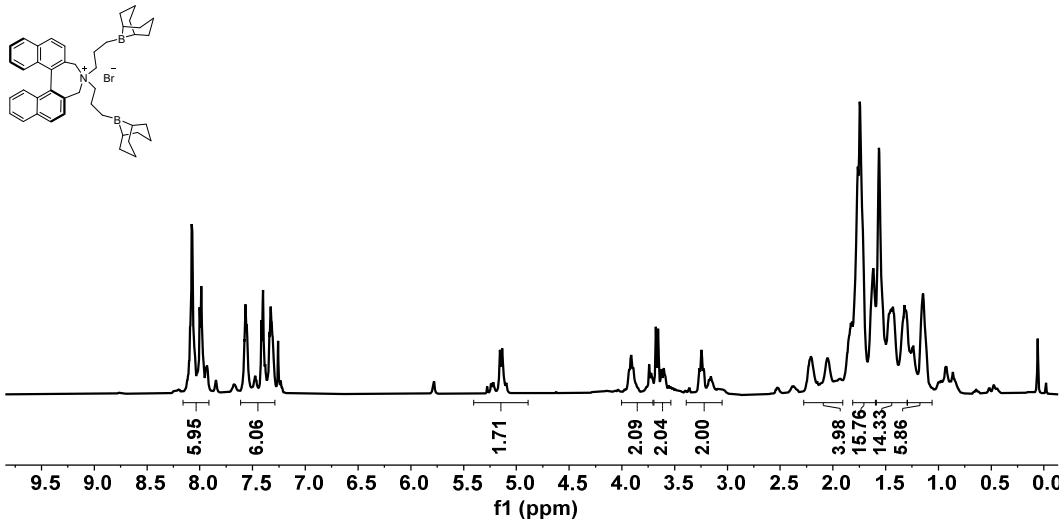


Figure S57. ^{1}H NMR spectrum of chiral organoboron catalyst **5** in DMSO-d_6(400M).

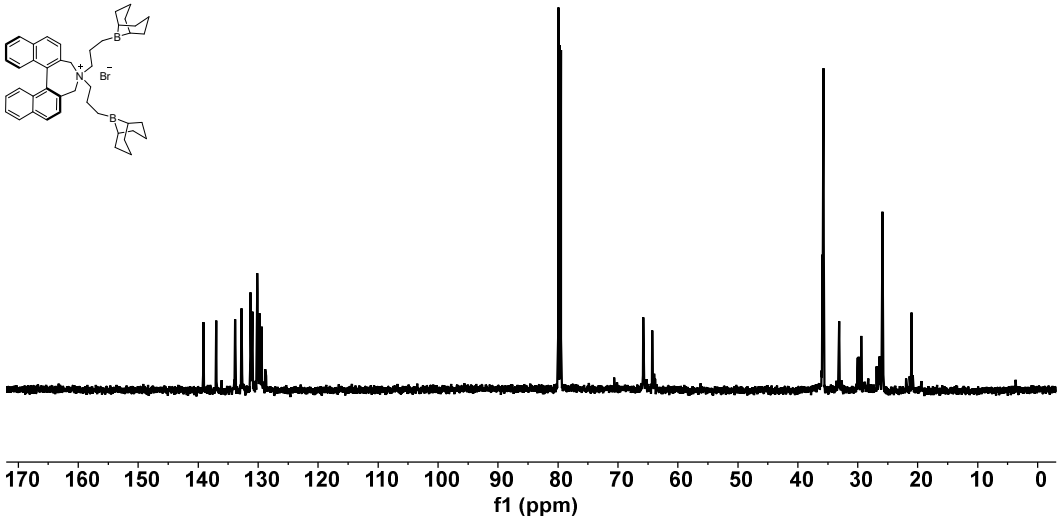


Figure S58. ^{13}C NMR spectrum of chiral organoboron catalyst **5** in $CDCl_3$(400M).

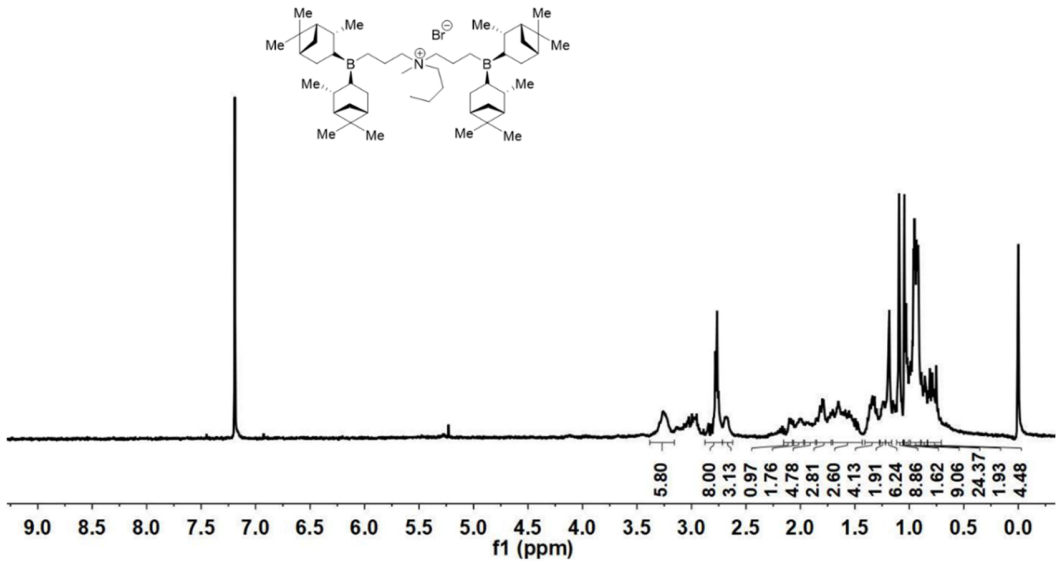


Figure S59. ^{1}H NMR spectrum of chiral organoboron catalyst **6** in $CDCl_3$(400M).

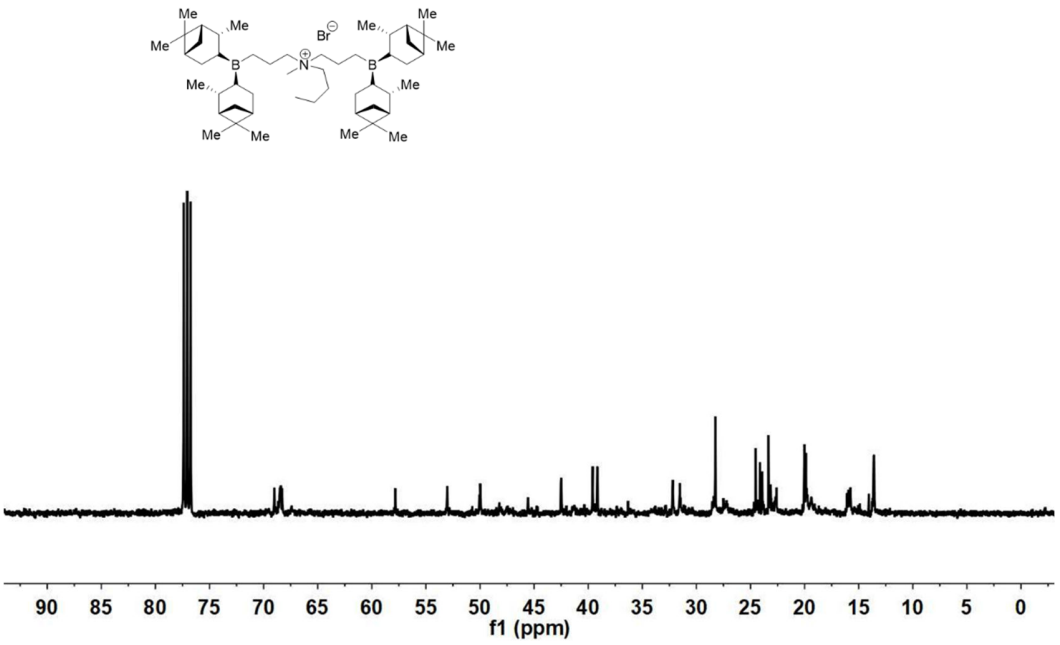


Figure S60. ^{13}C NMR spectrum of chiral organoboron catalyst **6** in $CDCl_3$(400M).

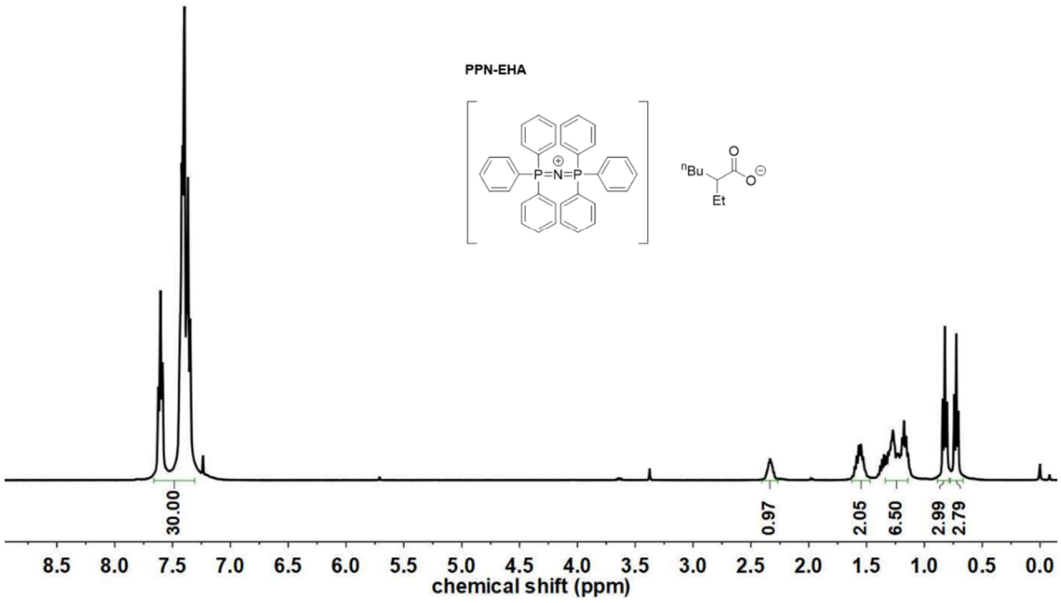


Figure S61. ^{1}H NMR spectrum of PPN-EHA in $CDCl_3$(400M).

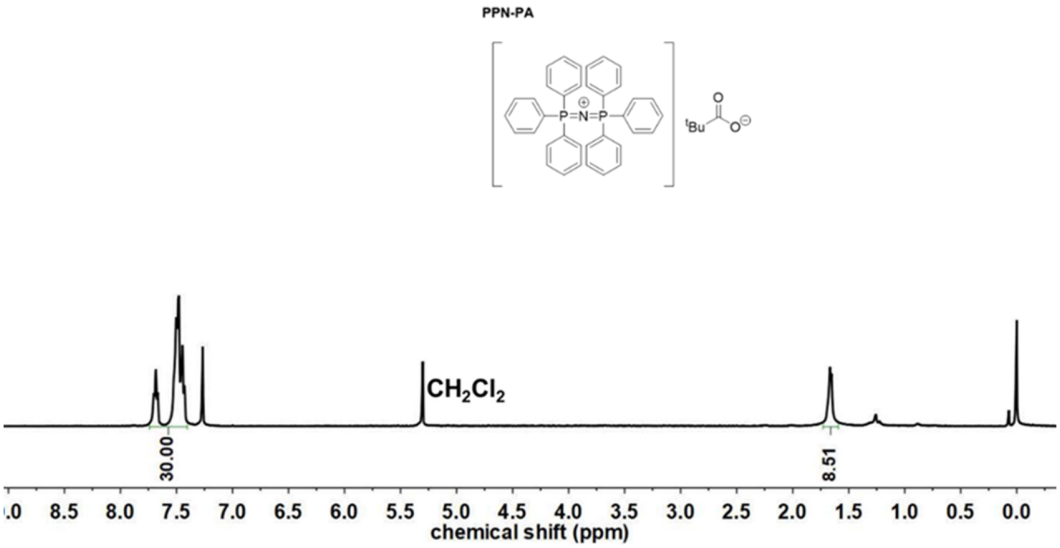


Figure S62. ^{1}H NMR spectrum of PPN-PA in $CDCl_3$(400M).

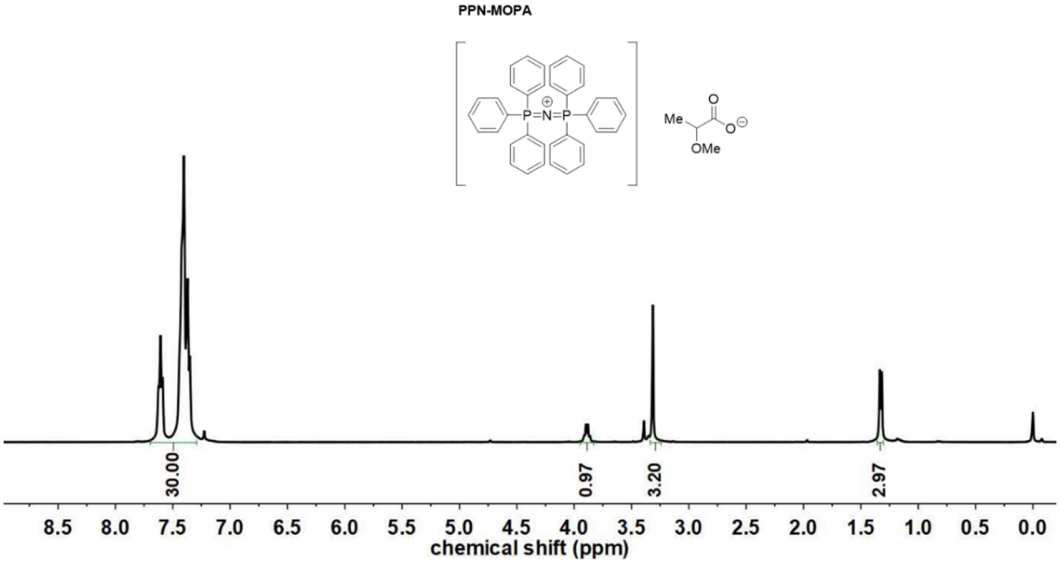


Figure S63. ^{1}H NMR spectrum of PPN-MOPA in $CDCl_3$(400M).

GPC of Stereocontrolled PPO

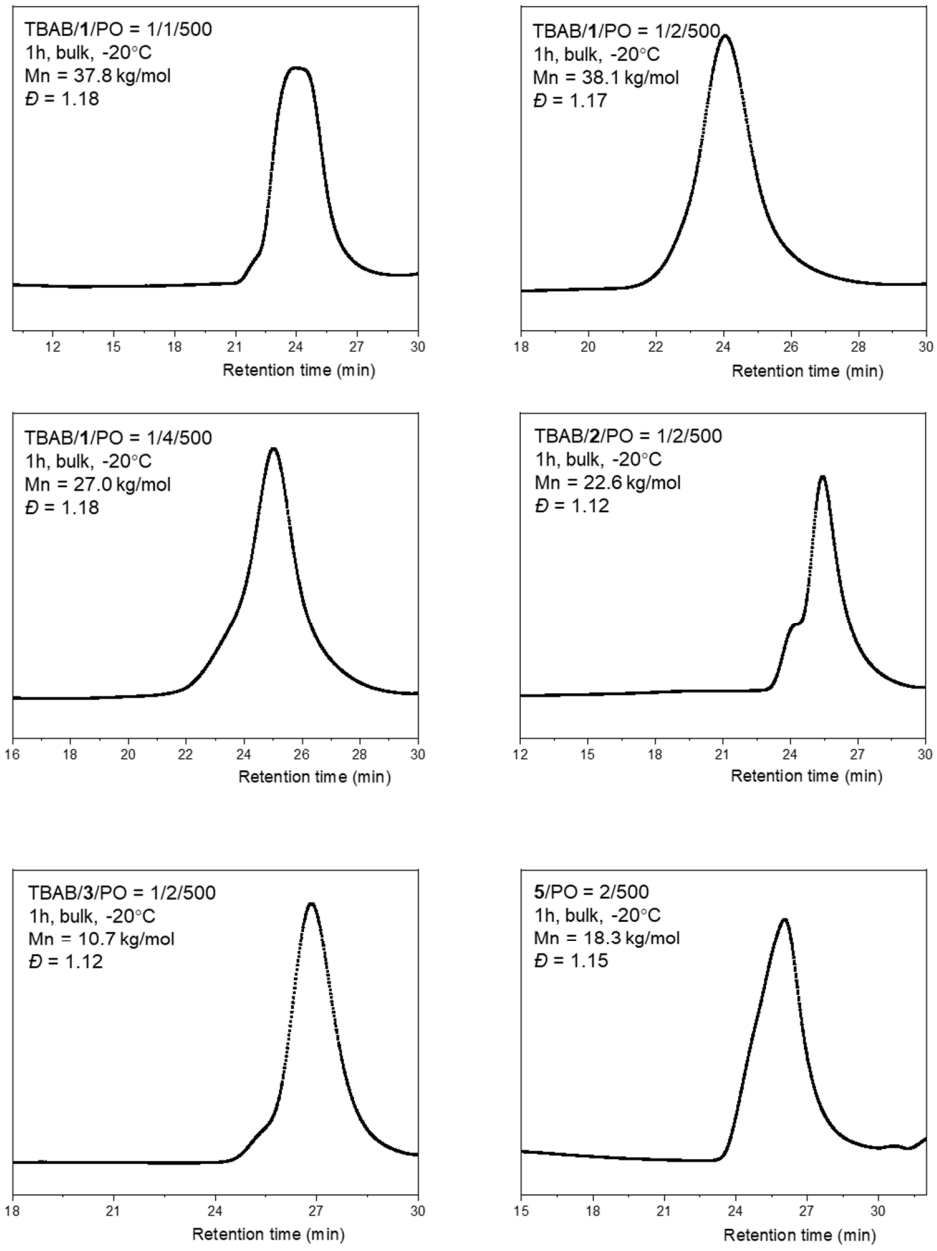


Figure S64-1. GPC traces of stereocontrolled PPO

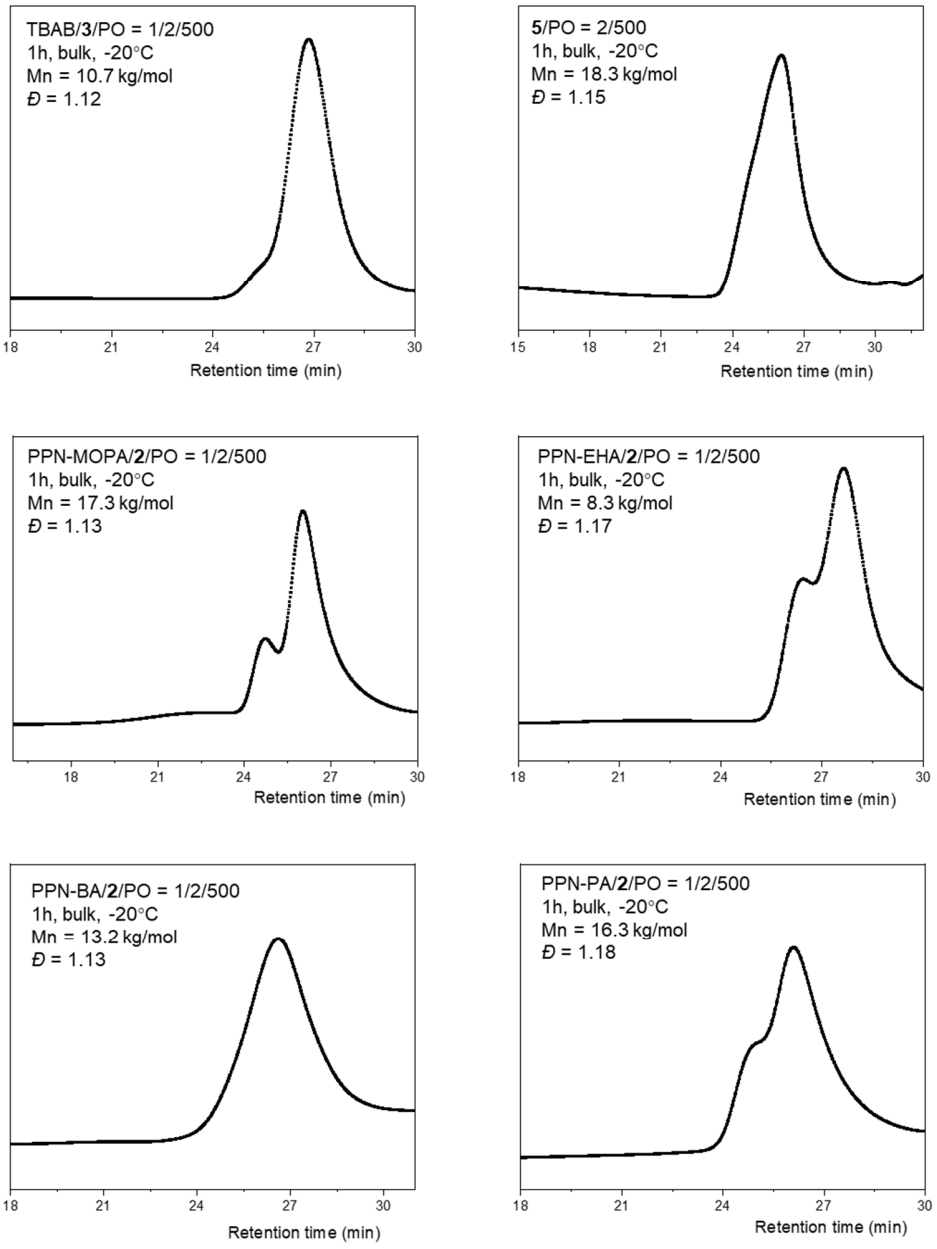


Figure S64-2. GPC traces of stereocontrolled PPO

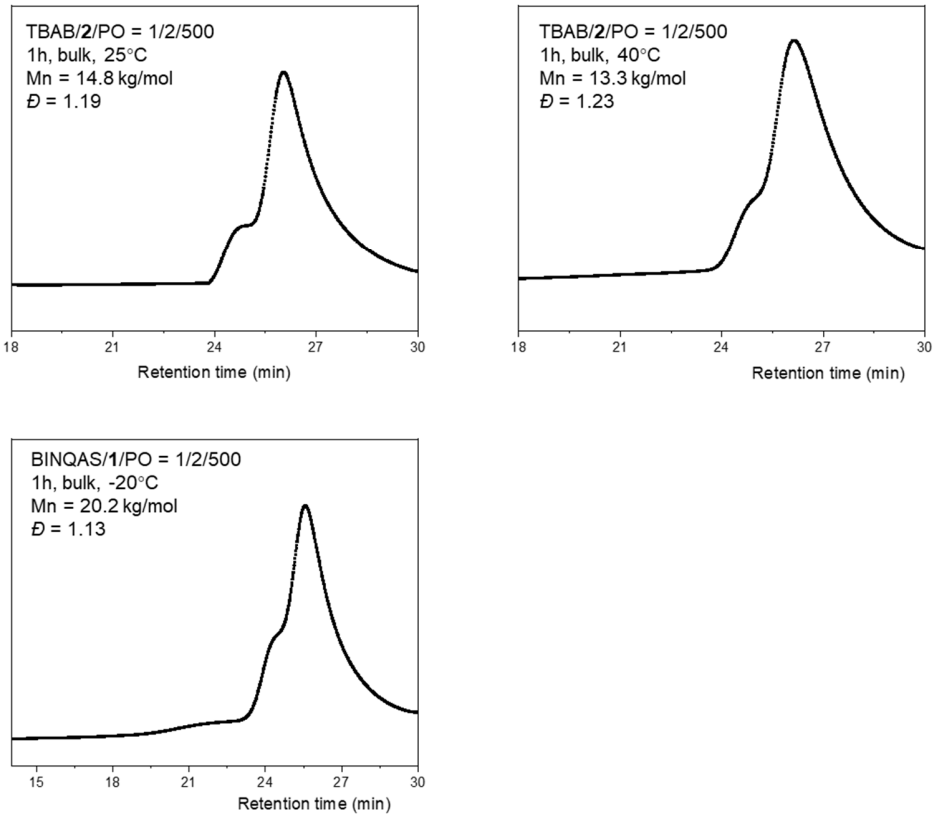


Figure S64-3. GPC traces of stereocontrolled PPO

Polymerization Kinetics

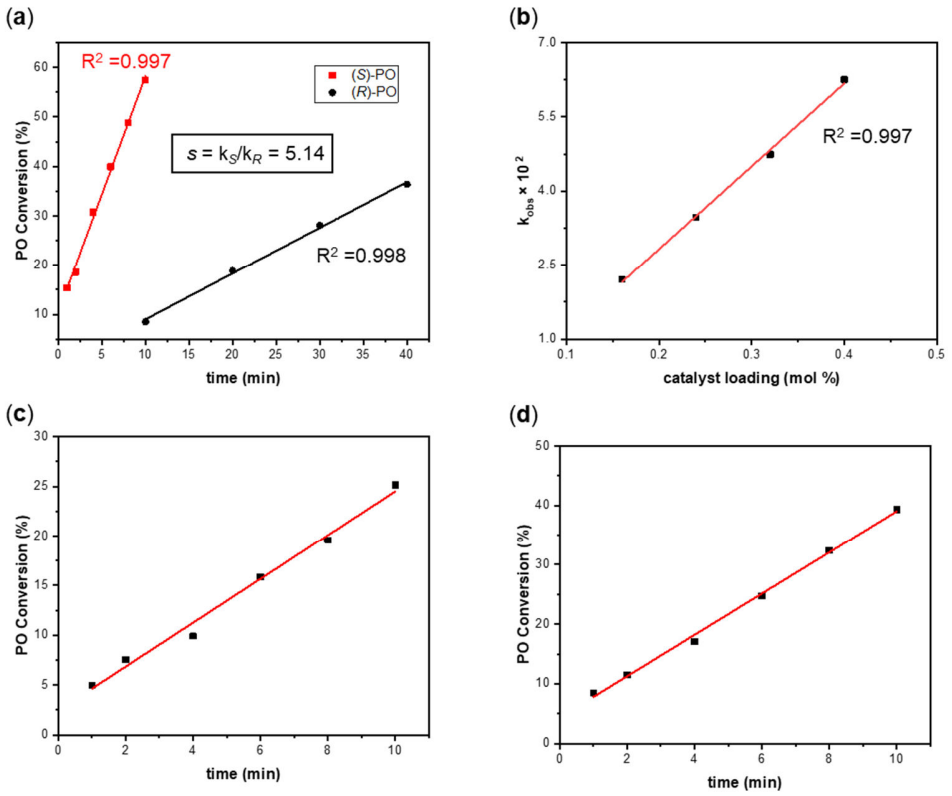


Figure S64. (a) Conversion vs. reaction time using **(*R*)-2**/TBAB/enantiopure PO = 2/1/500 (-20 °C, bulk) and calculated selectivity factor *s*. (b) Reaction kinetic analysis to determine order in **(*R*)-2** (first order) (c) Conversion vs. reaction time using **(*R*)-2**/TBAB/PO = 2/1/1250 (-20 °C, bulk) (d) Conversion vs. reaction time using **(*R*)-2**/TBAB/PO = 2/1/800 (-20 °C, bulk)

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