Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information to

Sterically demanding binaphthol-based chiral diboranes for metal-free and isotactic poly(propylene oxide)

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Experimental

Materials and Synthesis

Propylene oxide (PO, *TCI Chemicals*, > 99,0 %) was stirred over CaH_2 overnight. After distillation under nitrogen, the monomer was degassed twice the by freeze-pump-thaw method and then stored inside the glove box (LabMaster, *MBraun*, Germany, freezer at -36 °C). Toluene, THF and DCM used in polymerizations were taken from a solvent purification system (*MBraun*, Germany) and kept over molecular sieves (3 Å) inside the glove box. Allyl bromide (*Sigma-Aldrich*, > 99,0 %),(*R*)-[2,3':1,1":3,2"-quaternaphthalene]-2,2'diol (*abcr*, > 95.0 %), (*R*)-3,3'-bis([1,1'-biphenyl]-4-yl)-[1,1'-binaphthalene]-2,2'-diol (*abcr*, > 98,0 %), (*S*)-3,3'bis[3,5-bis(methylphenyl]-1,1'-bi-2-naphthol (*abcr*, > 98,0%), (S)-3,3'-bis(2,4,6-triisopropylphenyl)-1,1'-bi-2-naphthol (*abcr*, > 95,0 %),(S)-3,3'-bis(3,5-bis(trifluoromethyl)phenyl)-[1,1'-binaphthalene]-2,2'diol (abcr, > 98,0%),(R)-3,3'-bis(3,5 -bis(trifluoromethyl)phenyl)-[1,1'-binaphthalene]-2,2'diol (abcr, > 98,0%) and (R)-3,3'-bis ([1,1':3',1"-terphenyl)-[1,1'-binaphthalene]-2,2'-diol (abcr, >98,0%) were used as received. 9-Borabicyclo[3.3.1]nonane (*Sigma Aldrich*, 0.5 M solution in THF) and the phosphazene base (P_2-*t*Bu, *Sigma-Aldrich*, 2.0 M solution in THF) were used as received and stored in the glove box. For the diborane (**2-7**) synthesis, see below.

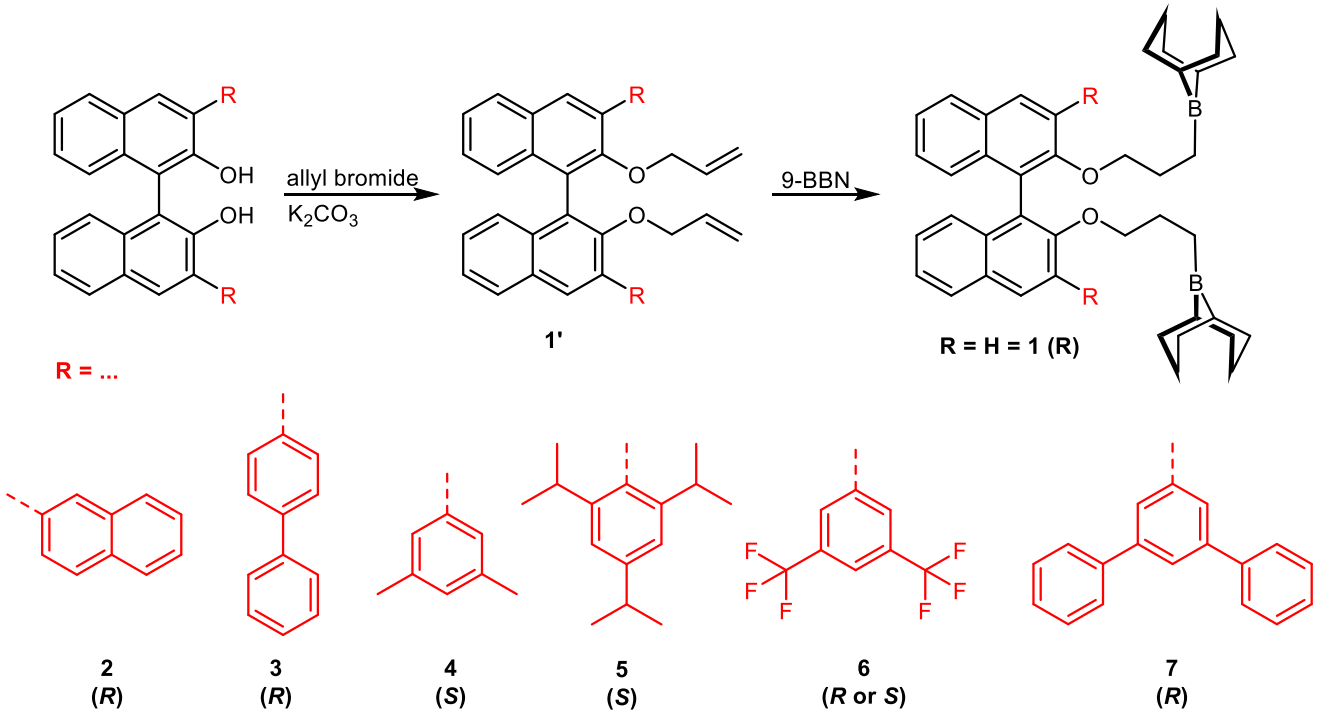


Figure S1. General procedure for the preparation of diboranes **2-7** used in this work.

Procedural Information

Synthesis of Diallyl Species 2'-7'

General Procedure: In an oven-dried Schlenk flask, BINOL-derivative and allyl bromide were dissolved in acetonitrile. Then, K_2CO_3 was added and the reaction mixture was stirred at room temperature for 72 h. The reaction was monitored by GC-MS where possible. After filtration and salt removal, the solvent and excess amount of allyl bromide were removed in vacuo to yield the colorless product.

Diallyl 2'

First, (*R*)-[2,3′:1,1":3",2"-quaternaphthalene]-2,2′diol (1.00 g, 1.8 mmol) and allyl bromide (0.8 mL, 8.9 mmol, 5 equiv.) were dissolved in 10 mL acetonitrile, then K_2CO_3 (1.65 g, 11.9 mmol) was added and the reaction mixture was stirred at room temperature for 72 h. Via filtration the potassium salts were removed. The solvent and excess amount of allyl bromide were removed in vacuo. Yield: 0.929 g (1.50 mmol, 81 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.27 (*d*, 2H), 8.11 (*s*, 2H), 7.91-7.99 (*m*, 10H), 7.53-7.56 (*m*, 4H), 7.44-7.48 (*m*, 2H), 7.32 (*d*, 2H), 5.21-5.31 (*m*,2H), 4.65-4.68 (*tt*, 2H), 4.55-4.60 (*tt*, 2H), 4.01-4.05 (*tt*, 2H), 3.77-3.81 (*tt*, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.6, 136.8, 135.4, 133.9, 133.7, 132.8, 131.0, 130.8, 128.4, 128.2, 128.1, 127.8, 126.5, 126.2, 125.2, 73.9, 68.1, 35.0, 31.1, 29.6, 25.8 ppm.

Diallyl 3'

First, (*R*)-3,3′-bis[(1,1′-biphenyl]-4-yl)-1,1′-binaphthalene]-2,2′-diol (1.00 g, 1.69 mmol) and allyl bromide (0.4 mL, 4.05 mmol, 2.4 equiv.) were dissolved in 10 mL acetonitrile, then K_2CO_3 (1.65 g, 12.67 mmol) was added and the reaction mixture was stirred at room temperature for 72 h. Via filtration the potassium salts were removed. The solvent and excess amount of allyl bromide were removed in vacuo. Yield: 0.857 g (1.27 mmol, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (s, 2H), 7.96 (d, 2H), 7.89 (d, 4H), 7.72 (t, 8H), 7.37-7.53 (m, 8H), 7.29-7.31 (m, 4H), 5.26-5.36 (m, 2H), 4.60-4.72 (m, 4H), 4.03-4.08 (td, 2H), 3.80-3.84 (td, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.4, 140.9, 140.1, 138.1, 135.0, 133.9, 130.9, 130.3, 130.0, 128.9, 128.1, 127.5, 127.2, 127.0, 126.5, 126.4, 126.1, 125.1, 73.8, 68.1, 25.7 ppm.

Diallyl 4'

First, (*S*)-3,3′-bi[3,5-bis(methylphenyl)]-1,1′-bis-2-naphthol (1.00 g, 2.0 mmol) and allyl bromide (0.8 mL, 9.7 mmol, 5 equiv.) were dissolved in 10 mL acetonitrile, then K_2CO_3 (1.79 g, 12.9 mmol) was added and the reaction mixture was stirred at room temperature for 72 h. Via filtration, the potassium salts were removed. The solvent and excess amount of allyl bromide were removed under reduced pressure. Yield: 0.942 g (1.63 mmol, 81 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (s, 2H), 7.89 (d, 2H), 7.36-7.41 (m, 6H), 7.22-7.24 (dd, 4H), 7.01 (s, 2H), 5.23-5.33 (m, 2H), 4.58-4.71 (qq, 4H), 3.97-4.02 (tt, 2H), 3.72-3.77 (tt, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 137.6, 134.0, 130.2, 128.9, 127.9, 127.2, 126.1, 116.0, 73.6, 31.0, 21.4 ppm.

Diallyl 5'

First, (*S*)-3,3′-bi(2,4,6-triisopropylphenyl)-1,1′-bi-2-naphthol (0.500 g, 0.72 mmol) and allyl bromide (0.3 mL, 1.73 mmol, 2.4 equiv.) were dissolved in 10 mL acetonitrile, then K_2CO_3 (0.60 g, 4.61 mmol) was added and the reaction mixture was stirred at room temperature for 72 h. Via filtration the potassium salts were removed. The solvent and excess amount of allyl bromide were removed in vacuo. Yield: 0.423 g (0.55 mmol, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (*d,* 2H), 7.79 (*s*, 2H), 7.30-7.45 (*m*, 6H), 7.08-7.10 (*dd*, 4H), 4.93-5.04 (*m*, 2H), 4.49-4.53 (*qq*, 2H), 4.24-4.29 (*qq*, 2H), 3.71-3.73 (*tt*, 2H), 3.68-3.70 (*tt,* 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.3, 148.3, 147.4, 146.7, 134.4, 133.8, 133.7, 133.1, 130.6, 130.3, 127.9, 125.9, 125.3, 124.6, 120.6, 115.1, 34.4, 31.0, 25.7, 24.2, 23.2 ppm.

Diallyl 6'

First, (*S*)-3,3′-bis(3,5-bis(trifluoromethyl)phenyl)-[1,1′-binaphthalene]-2,2′-diol or (*R*)-3,3′-bis(3,5-bis(trifluoromethyl)phenyl)-[1,1′-binaphthalene]-2,2′-diol (1.00 g, 1.4 mmol) and allyl bromide (0.6 mL, 6.7 mmol, 5 equiv.) were dissolved in 10 mL acetonitrile, then K_2CO_3 (1.25 g, 9.1 mmol) was added and the reaction mixture was stirred at room temperature for 72 h. Via filtration, the potassium salts were removed. The solvent and excess amount of allyl bromide were removed under reduced pressure. Yield: 0.940 g (1.18 mmol, 84 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (*s,* 4H), 8.02 (*s*, 2H), 7.98 (*d*, 2H), 7.90 (*s*, 2H), 7.47-7.51 (*td*, 2H), 7.32-7.37 (*td*, 2H), 7.22 (*d*, 2H), 5.22-5.32 (*m*,

2H), 4.73-4.76 (*qq*, 2H), 4.62-4.68 (*qq*, 2H), 3.90-3.96 (*tt*, 2H), 3.69-3.74 (*tt*, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.5, 140.7, 134.2, 132.8, 132.4, 131.9, 131.4, 130.9, 130.7, 129.6, 128.4, 127.4, 126.3, 125.9, 124.2, 122.7, 121.1, 116.7, 74.1, 25.6 ppm.

Diallyl 7'

(*R*)-3,3′-bis([1,1′:3′,1"-terphenyl]-5′-yl)-[1,1′-binaphthalene]-2,2′diol (1.00 g, 1.34 mmol) and allyl bromide (0.7 mL, 6.50 mmol, 5 equiv.) were dissolved in 10 mL acetonitrile, then K_2CO_3 (1.23 g, 8.64 mmol) was added and the reaction mixture was stirred at room temperature for 72 h. Via filtration, the potassium salts were removed. Solvent and excess amount of allyl bromide were removed under reduced pressure. Yield: 0.978 g (1.18 mmol, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 (*s*, 2H), 7.96-8.02 (*dd*, 6H), 7.86 (*t*, 2H), 7.74-7.77 (*d*, 8H), 7.46-7.51 (*m*, 10H), 7.38-7.42 (*m*, 4H), 7.31-7.32 (*m*, 4H), 5.32-5.41 (*m*, 2H), 4.62-4.70 (*m*, 4H), 4.12-4.17 (*dd*, 2H), 3.86-3.91 (*dd*, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.1, 134.2, 133.9, 133.8, 129.4, 129.3, 129.2, 128.0, 126.4, 126.3, 125.6, 123.7, 116.5, 115.8. 70.1 ppm.

Synthesis of Diborane Catalysts

Diboranes

General Procedure: In the glove box, 9-borabicyclo[3.3.1]nonane in THF (0.5 M) was added to the diallyl-species. The reaction mixture was stirred at room temperature in the glove box overnight. The mixture was concentrated in vacuo to afford the crude product. After recrystallization from diethyl ether/pentane (-36°C), the diboranes were obtained as white solids. Full removal of all solvent molecules, in particular those able to coordinate the Lewis acidic borane functionalities (THF/diethyl ether), is challenging and may require extended periods under vacuum.

Diborane (*R*)-2

The general procedure was employed, using diallyl-species **2'** (0.929 g, 1.50 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane in THF (0.5 M) (8.7 mL, 3.00 mmol, 2 equiv.). The reaction mixture was stirred at room temperature overnight. After purification, diborane **(*R*)-2** was obtained as a white solid. Yield: 1.13 g (1.31 mmol, 88 %). ^{1}H NMR (400

MHz, $CDCl_3$) δ = 8.23 (*s*, 2H), 8.06 (*s*, 2H), 7.88-7.96 (*m*, 10H), 7.49-7.52 (*m*, 4H), 7.39-7.42 (*td*, 2H), 7.28-7.31 (*td*, 2H), 3.45-3.53 (*q*, 2H), 3.16-3.21 (*q*, 2H), 1.77-1.87 (*m*, 12H), 1.55-1.65 (*m*, 14H), 1.21-1.31 (*m*, 8H), 0.69-0.77 (*m*, 2H), 0.47-0.55 (*m*, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.2, 137.2, 135.6, 134.1, 133.7, 132.8, 131.0, 130.6, 128.2, 127.8, 127.6, 126.3, 126.1, 124.9, 34.3, 33.6, 33.0, 24.9, 23.3, 23.2, 22.5, 14.2 ppm. ^{11}B NMR (100 MHz, $CDCl_3$) δ = 59.3 ppm. HRMS (ESI): m/z calc. for $C_{62}H_{62}B_2O_2$ = 860.51, found $C_{62}H_{62}B_2O_2^+$: 861.51.

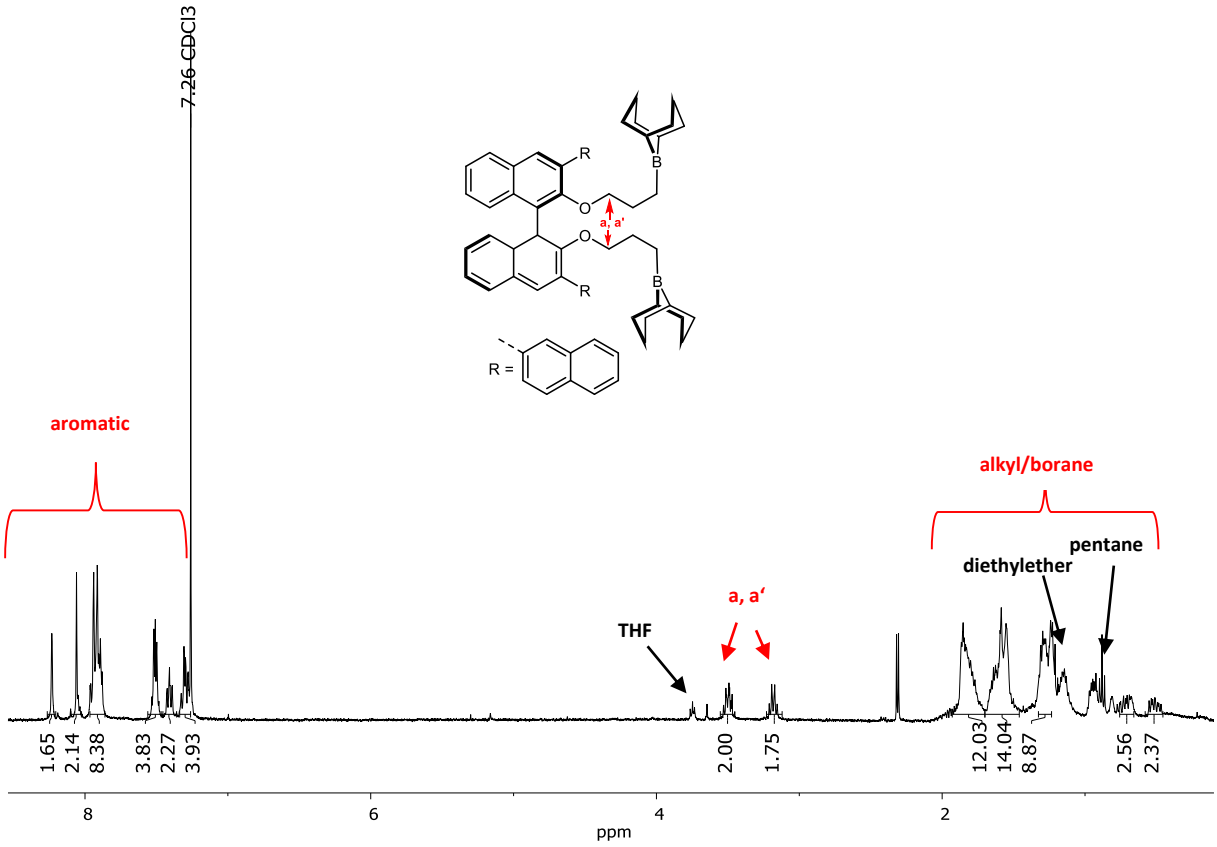


Figure S2. ^1H NMR analysis ($CDCl_3$, 400 MHz) of compound (***R***)-**2**.

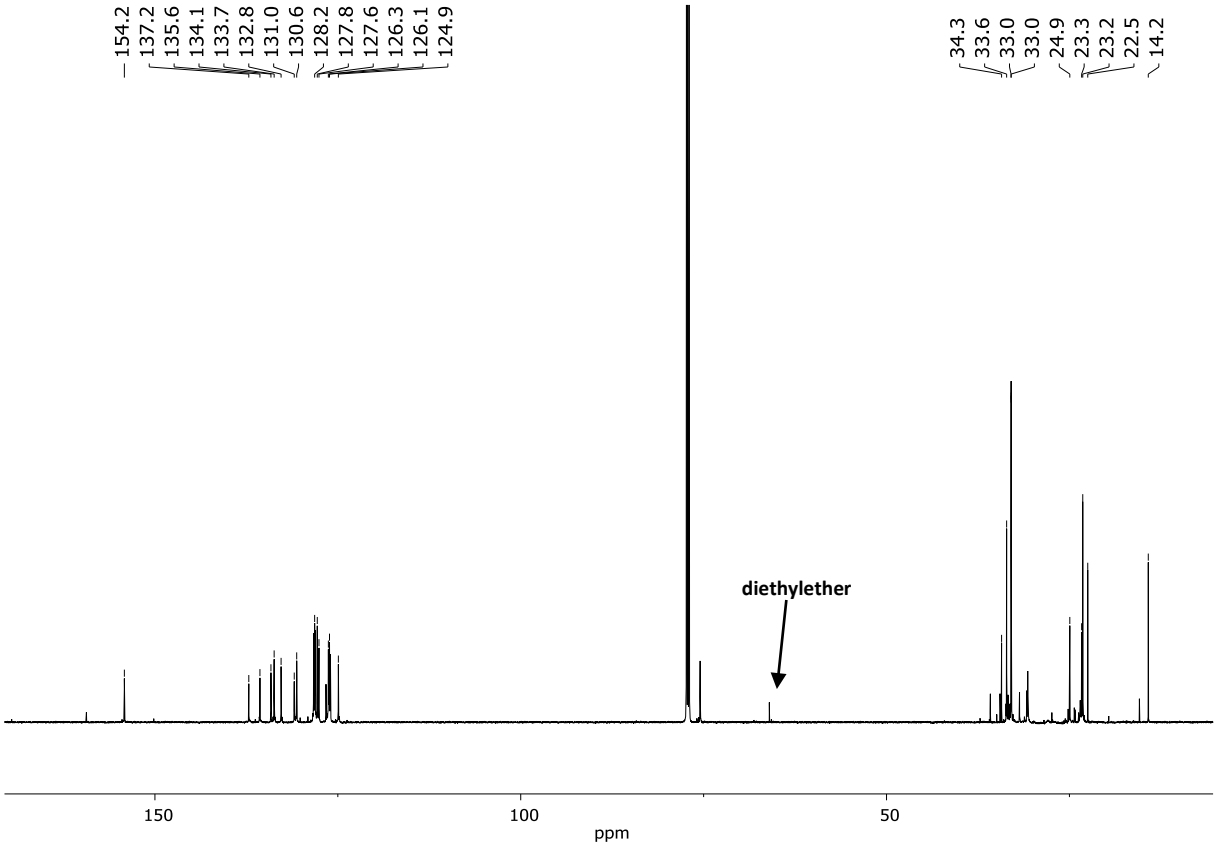


Figure S3. ^{13}C NMR analysis ($CDCl_3$, 101 MHz) of compound (***R***)-**2**.

Diborane (*R*)-3

The general procedure was employed, using diallyl-species **3'** (0.700 g, 1.04 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane in THF (0.5 M) (4.2 mL, 2.08 mmol, 2 equiv.). The reaction mixture was stirred at room temperature overnight. After purification, diborane **(*R*)-3** was obtained as a white solid. Yield: 0.827 g (0.91 mmol, 87 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (*s*, 2H), 7.88-7.95 (*q*, 6H), 7.69-7.74 (*m*, 8H), 7.48-7.52 (*t*, 4H), 7.37-7.45 (*m*, 4H), 7.27-7.33 (*m*, 6H), 3.53-3.59 (*q*, 2H), 3.20-3.26 (*q*, 2H), 1.60-1.70 (*m*, 14H), 1.24-1.38 (*m*, 14H), 0.96-1.02 (*m*, 4H), 0.74-0.83 (*m*, 2H), 0.51-0.60 (*m*, 2H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$) δ = 154.1, 141.1, 140.0, 135.3, 134.1, 130.9, 130.2, 130.0, 128.9, 128.1, 127.4, 127.2, 126.9, 126.6, 126.2, 124.9, 33.0, 30.8, 25.0, 23.2 ppm. ^{11}B NMR (MHz, $CDCl_3$) δ = 58.6 ppm. HRMS (ESI): m/z calc. for $C_{66}H_{68}B_2O_2$ = 914.54, found $C_{66}H_{69}B_2O_2^+$: 915.55.

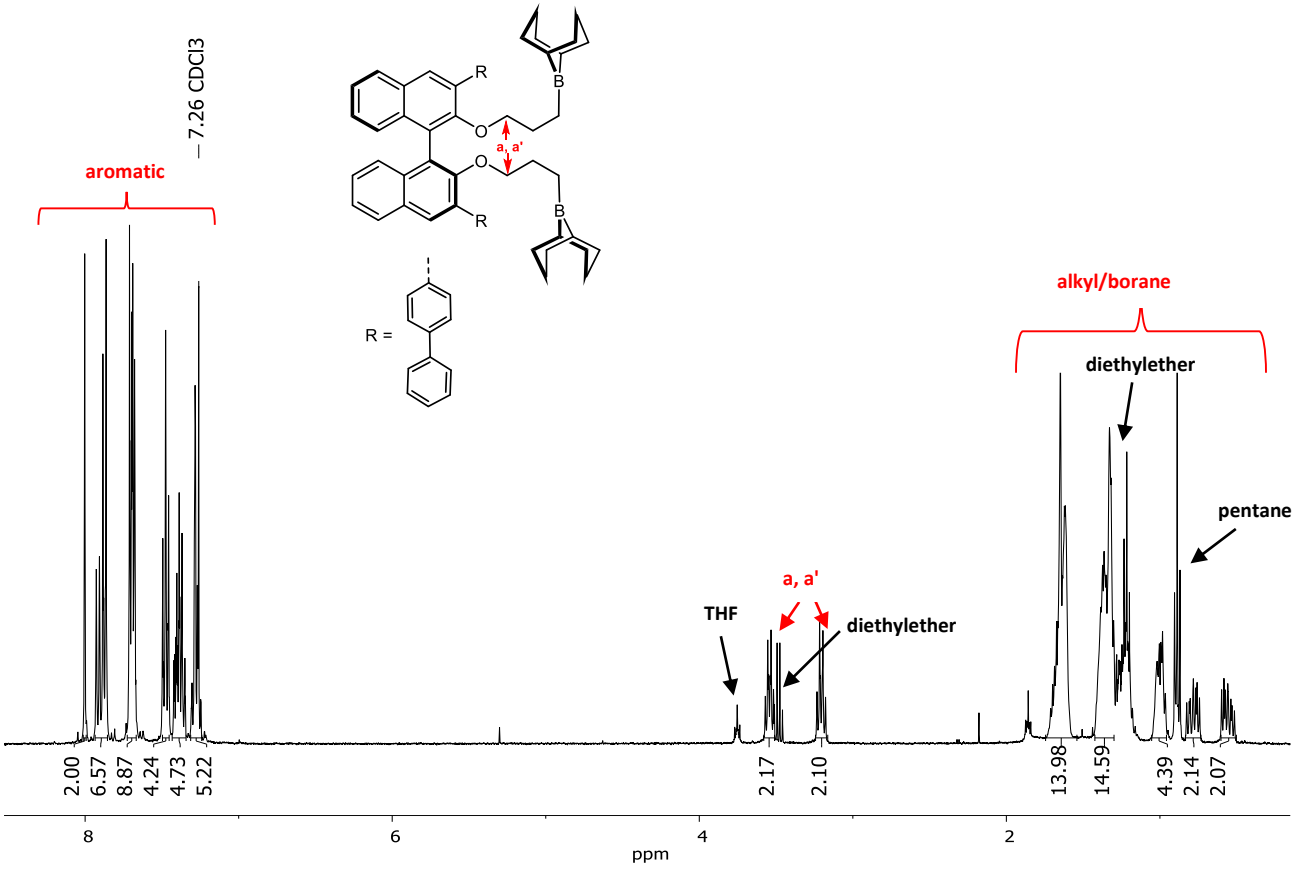


Figure S4. ^{1}H NMR analysis ($CDCl_3$, 400 MHz) of compound (***R***)-**3**.

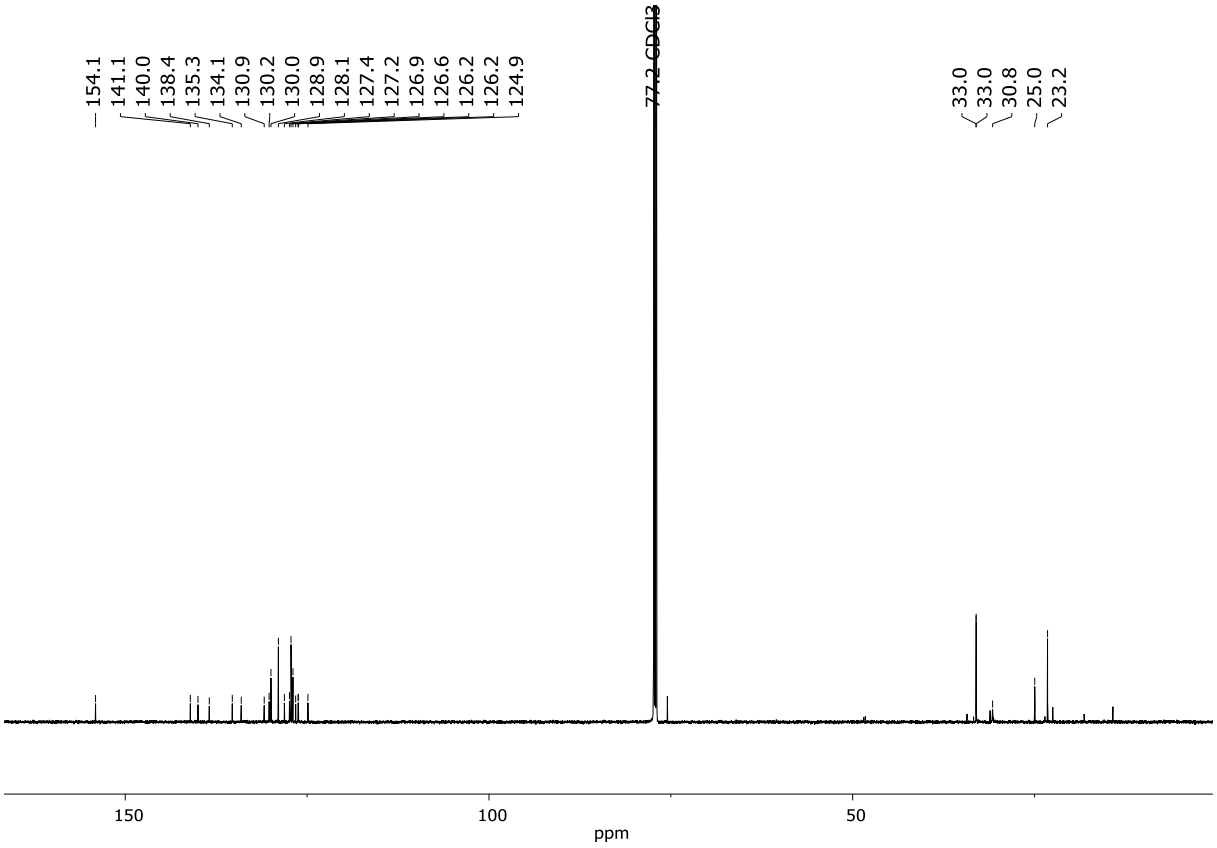


Figure S5. ^{13}C NMR analysis ($CDCl_3$, 101 MHz) of compound (***R***)-**3**.

Diborane (*S*)-4

The general procedure was employed, using diallyl-species **4'** (0.942 g, 1.64 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane in THF (0.5 M) (6.5 mL, 3.27 mmol, 2 equiv.). The reaction mixture was stirred at room temperature overnight. After purification, enantiopure diborane **(*S*)-4** was obtained as a white solid. Yield: 1.23 g (1.50 mmol, 92 %). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.91 (*s*, 2H), 7.87 (*d*, 2H), 7.37 (*d*, 6H), 7.23-7.26 (*m*, 4H), 7.00 (*s*, 2H), 3.48-3.53 (*q*, 2H), 3.14-3.20 (*q*, 2H), 2.38 (*s*, 12H), 1.65-1.83 (*m*, 14H), 1.17-1.40 (*m*, 14H), 1.01-1.05 (*m*, 4H), 0.73-0.82 (*m*, 2H), 0.56-0.64 (*m*, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.0, 139.3, 137.6, 135.9, 133.9, 130.8, 130.1, 128.9, 128.0, 127.4, 126.5, 126.2, 126.0, 124.7, 42.1, 33.1, 30.8, 27.3, 25.8, 24.9, 23.3, 21.5 ppm. ^{11}B NMR (100 MHz, $CDCl_3$) δ = 58.4 ppm. HRMS (ESI): m/z calc. for $C_{58}H_{68}B_2O_2$ = 818.54, found $C_{58}H_{68}B_2O_2$: 818.54.

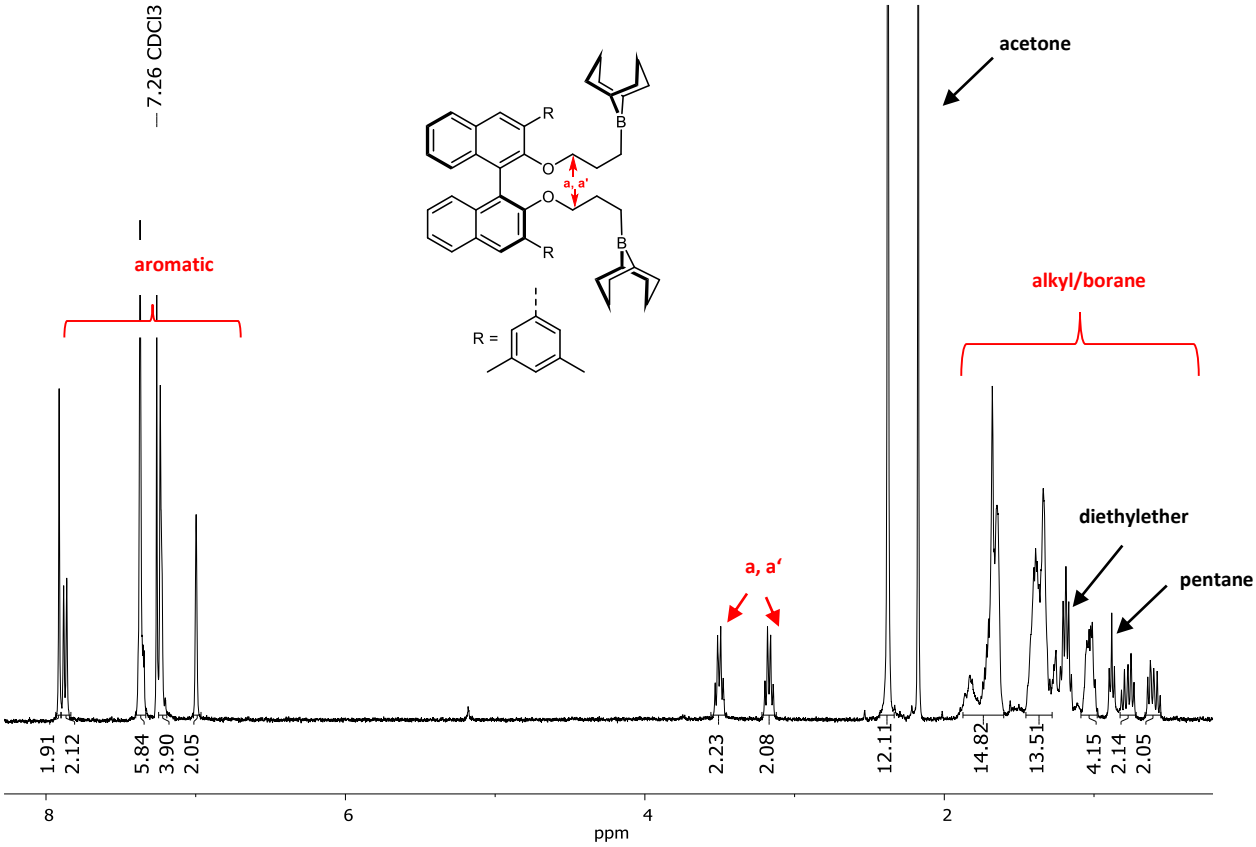


Figure S6. ^{1}H NMR analysis ($CDCl_3$, 400 MHz) of compound (***S***)-**4**.

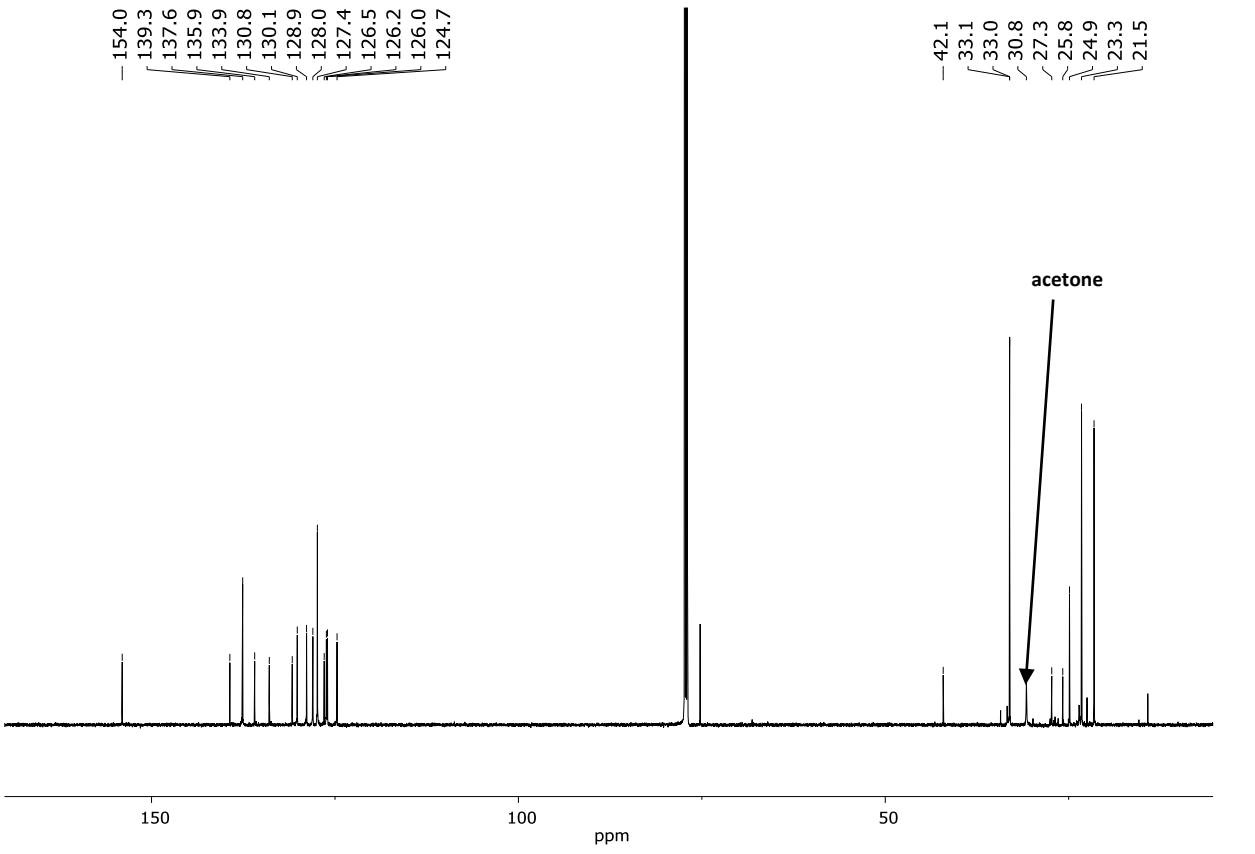


Figure S7. ^{13}C NMR analysis ($CDCl_3$, 101 MHz) of compound (***S***)-**4**.

Diborane (*S*)-5

The general procedure was employed, using diallyl-species **5'** (0.400 g, 0.52 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane in THF (0.5 M) (3.0 mL, 1.04 mmol, 2 equiv.). The reaction mixture was stirred at room temperature overnight. After purification, enantiopure diborane **(*S*)-5** was obtained as a white solid. Yield: 0.452 g (0.44 mmol, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79-7.81 (*d*, 2H), 7.73 (*s*, 2H), 7.32-7.36 (*m*, 4H), 7.22-7.26 (*m*, 2H), 7.03-7.06 (*dd*, 4H), 3.12-3.17 (*q*, 2H), 3.01-3.06 (*q*, 2H), 2.81-2.93 (*m*, 6H), 1.60-1.70 (*m*, 14H), 1.21-1.36 (*m*, 28H), 1.13-1.15 (*d*, 12H), 0.97-0.99 (*d*, 2H), 0.74-0.83 (*m*, 2H), 0.54-0.62 (*m*, 2H), 0.43-0.52 (*m*, 2H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$) δ = 154.8, 148.1, 147.5, 146.8, 134.7, 134.1, 133.5, 130.7, 130.3, 127.9, 126.1, 125.7, 124.4, 120.7, 42.1, 34.4, 34.3, 32.9, 31.1, 30.9, 27.3, 27.2, 26.8, 24.8, 24.3, 24.2, 23.5, 23.4, 23.2, 22.1 ppm. ^{11}B NMR (100 MHz, $CDCl_3$) δ = 59.1 ppm. HRMS (ESI): m/z calc. for $C_{72}H_{96}B_2O_2$ = 1014.70, found $C_{72}H_{97}B_2O_2^+$: 1015.68.

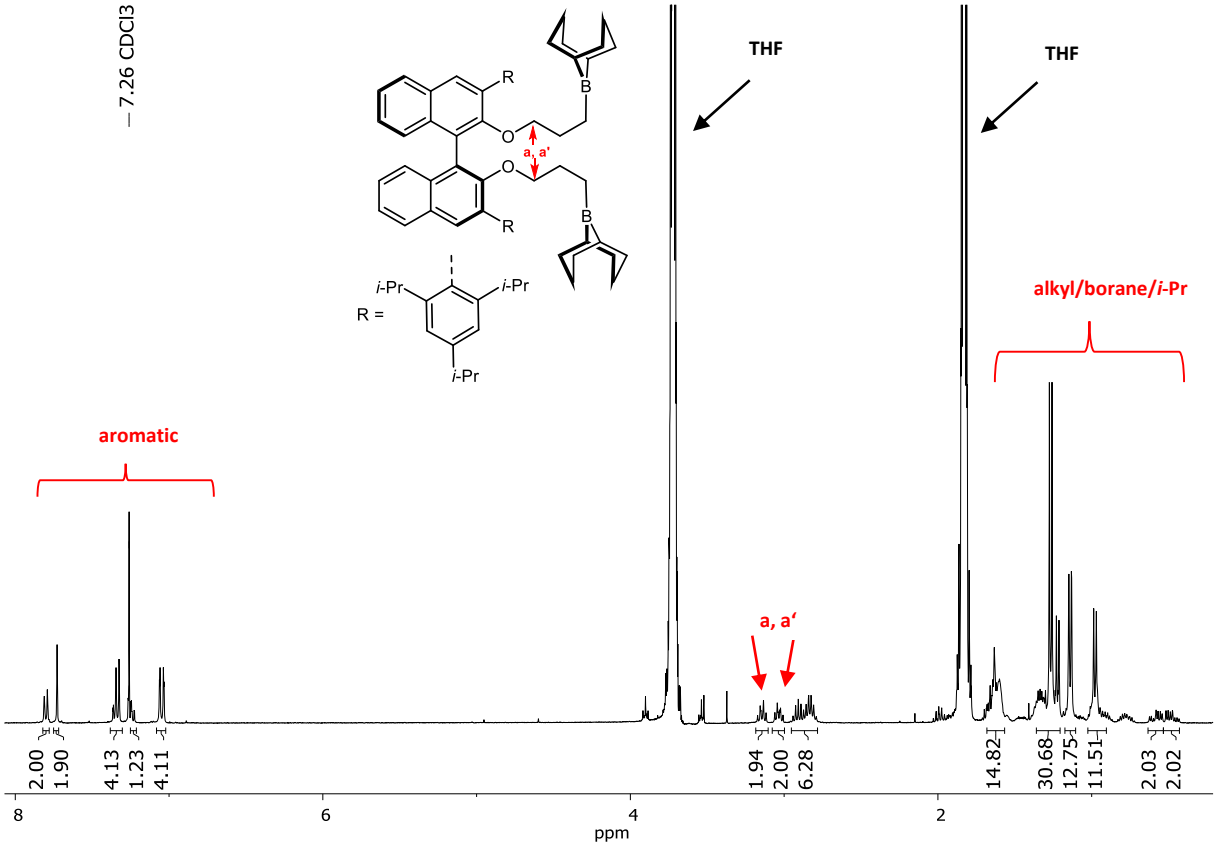


Figure S8. ^{1}H NMR analysis ($CDCl_3$, 400 MHz) of compound **(*S*)-5**.

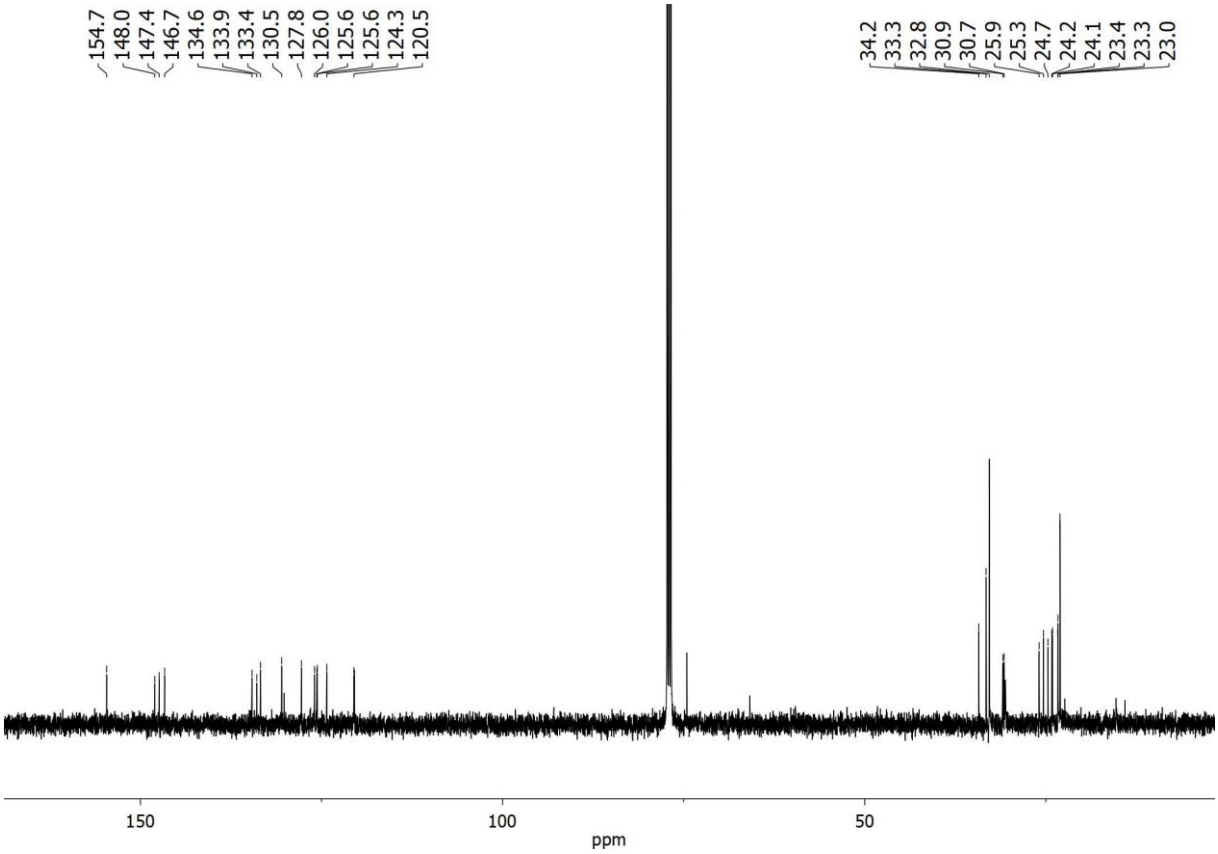


Figure S9. ^{13}C NMR analysis ($CDCl_3$, 101 MHz) of compound (***S***)-**5**.

Diborane (*R*)- or (*S*)-6

The general procedure was employed, using diallyl-species **6'** ((*R*) or (*S*)-enantiomer, 0.940 g, 1.18 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane in THF (0.5 M) (4.7 mL, 2.37 mmol, 2 equiv.). The reaction mixture was stirred at room temperature overnight. After purification, diborane **(*R*)-6/(*S*)-6** was obtained as a white solid. Yield: 1.10 g (1.06 mmol, 90 %). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.26 (*s*, 4H), 8.01 (*s*, 2H), 7.96 (*d*, 2H,), 7.90 (*s*, 2H), 7.44-7.48 (*td*, 2H), 7.31-7.35 (*td*, 2H), 7.24 (*s*, 2H), 3.41-3.47 (*q*, 2H), 3.12-3.17 (*q*, 2H), 1.63-1.87 (*m*, 14H), 1.15-1.34 (*m*, 14H), 0.96-1.03 (*m*, 4H), 0.71-0.80 (*m*, 2H), 0.54-0.62 (*m*, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.2, 141.2, 134.6, 132.6, 130.8, 129.7, 128.5, 127.4, 126.1, 125.7, 124.4, 122.8, 33.0, 30.8, 24.8, 23.1 ppm. ^{11}B NMR (100 MHz, $CDCl_3$) δ = 58.9 ppm. HRMS (ESI): m/z calc. for $C_{58}H_{56}B_2F_{12}O_2$ = 1034.43, found $C_{58}H_{56}B_2F_{12}O_2$: 1034.42.

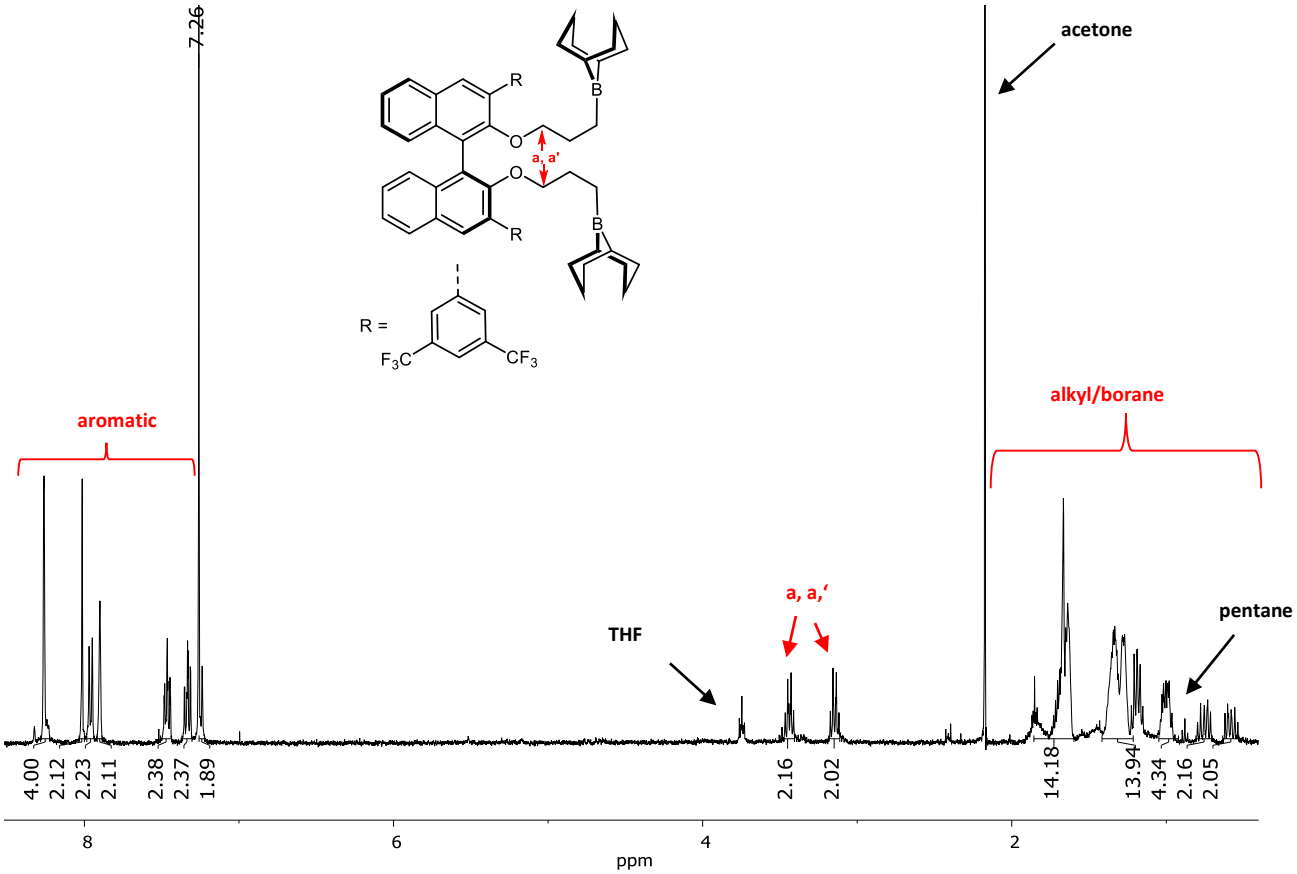


Figure S10. ^{1}H NMR analysis ($CDCl_3$, 400 MHz) of compound (***S***)-**6**.

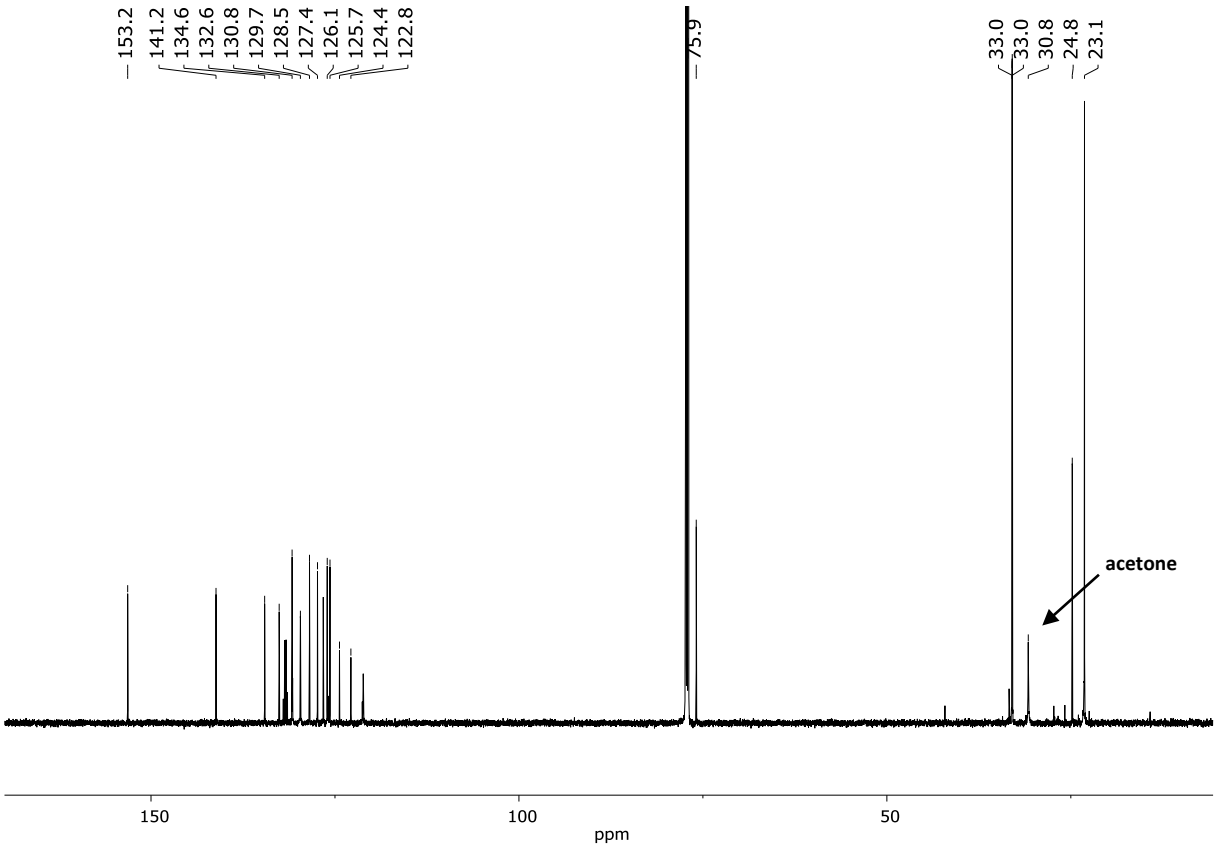


Figure S11. ^{13}C NMR analysis ($CDCl_3$, 101 MHz) of compound (***S***)-**6**.

Diborane (*R*)-7

The general procedure was employed, using diallyl-species **7'** (0.978 g, 1.19 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane in THF (0.5 M) (4.7 mL, 2.38 mmol, 2 equiv.). The reaction mixture was stirred at room temperature overnight. After purification, diborane **(*R*)-7** was obtained as a white solid. Yield: 1.02 g (0.95 mmol, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (s, 2H), 7.81 (d, 4H), 7.73-7.75 (d, 2H), 7.64 (t, 2H), 7.52-7.55 (d, 8H), 7.05-7.28 (m, 18H), 3.45-3.57 (*q*, 2H), 3.09-3.15 (*q*, 2H), 1.33-1.46 (*m*, 14H), 1.02-1.12 (*m*, 16H), 0.67-0.75 (*m*, 4H), 0.56-0.65 (*m*, 2H), 0.40-0.48 (*m*, 2H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$) δ = 153.9, 141.8, 141.3, 140.3, 135.6, 134.1, 130.9, 130.4, 128.9, 128.2, 127.6, 127.4, 126.7, 126.4, 125.0, 33.6, 33.4, 33.0, 30.7, 25.1, 23.2, 14.2 ppm. ^{11}B NMR (100 MHz, $CDCl_3$) δ = 58.5 ppm. HRMS (ESI): m/z calc. for $C_{78}H_{76}B_2O_2$ = 1067.08, found $C_{78}H_{77}B_2O_2^+$: 1068.50.

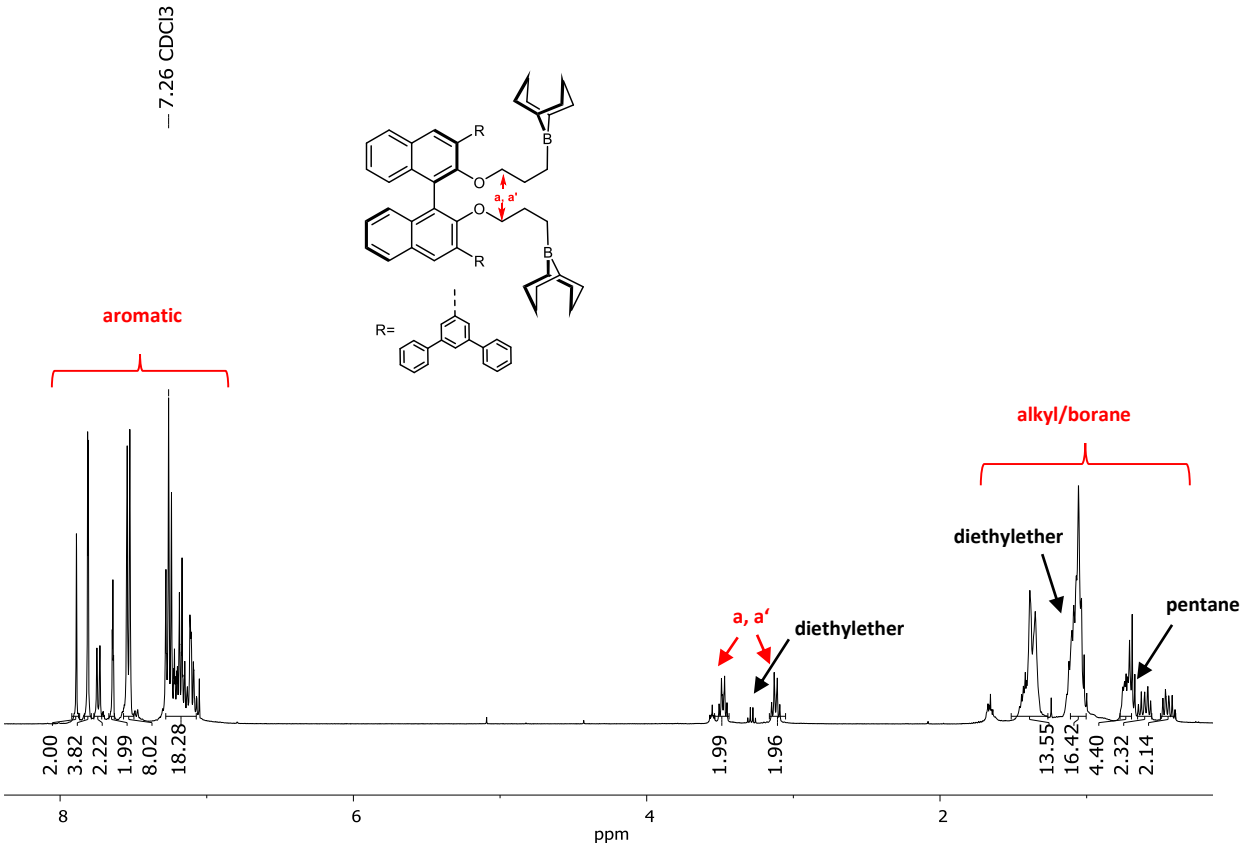


Figure S12. ^{1}H NMR analysis ($CDCl_3$, 400 MHz) of compound **(*R*)-7**.

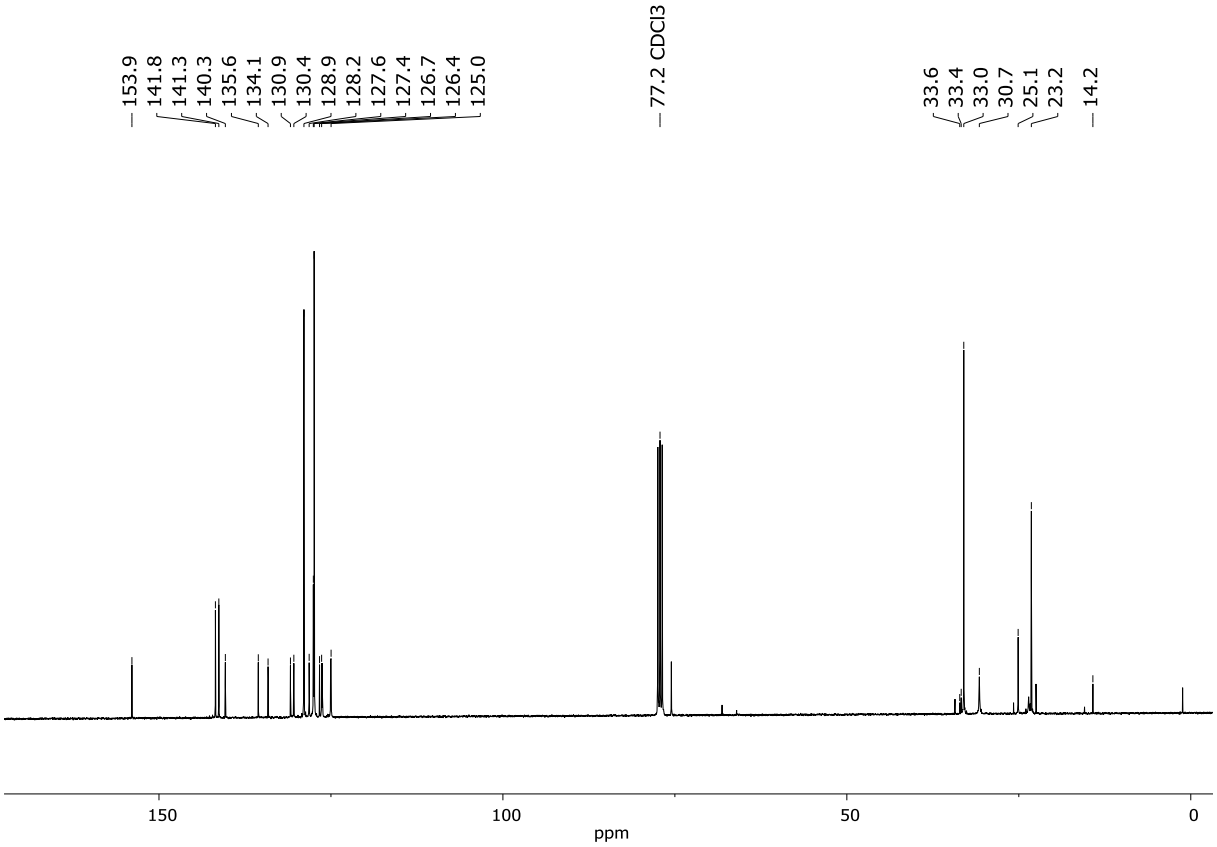


Figure S13. ^{13}C NMR analysis ($CDCl_3$, 101 MHz) of compound (***R***)-**7**.

General Polymerization Procedures

All polymerizations were assembled inside the glove box. First the diborane (0.017 mmol, 2 equiv.) was dissolved in PO (0.494 g, 8.52 mmol, 1000 equiv.). Subsequently, the initiator (BnOH, 0.0213 mmol, 2.5 equiv.) and the organobase P_2-^{t}Bu (0.0085 mmol, 1 equiv.) was added to result in a total molar ratio of P_2-^{t}Bu/diborane/initiator/PO = 1:2:2.5:1000. The reaction was quenched by evaporation of the monomer. The molecular weight of the polyether was determined *via* GPC analysis ($CHCl_3$) and ^{1}H NMR; the number of average PO-repeating units (x) was likewise calculated from ^{1}H-NMR ($CDCl_3$) using the PO(-$\underline{CH_2}$)- (δ = 3.38-3.42 ppm) and Ph-$\underline{CH_2}$-OR signal (δ = 4.55 ppm). Conversion of PO is determined from the initial [PO]/[-OH] ratio and the thus calculated number of incorporated PO units.

General Procedure for Kinetic Analyses

The reactions were assembled inside the glove box. First the diborane (0.017 mmol, 2 equiv.) was dissolved in (*R*)- or (*S*)-PO (0.493 g, 8.52 mmol, 1000 equiv.) and THF (4.28 mL). Subsequently, the initiator (BnOH, 0.0213 mmol, 2.5 equiv.) and the organobase P_2-^{t}Bu (0.0085 mmol, 1 equiv.) was added to result in a total molar ratio of P_2-^{t}Bu/diborane/initiator/PO = 1:2:2.5:1000. After the polymerization was started, aliquots of 20 µL were collected via pipette (*Eppendorf*) in specific

time intervals and quenched with wet $CDCl_3$. The molecular weight of the polyether was determined *via* GPC analysis ($CHCl_3$) and ^{1}H NMR; the number of average PO-repeating units (x) was likewise calculated from ^{1}H-NMR ($CDCl_3$) using the PO(-$\underline{CH_2}$)- (δ = 3.38-3.42 ppm) and Ph-$\underline{CH_2}$-OR signal (δ = 4.55 ppm). Conversion of PO is determined from the initial [PO]/[-OH] ratio and the thus calculated number of incorporated PO units.

Chain Equilibration Experiment

The polymerizations were assembled inside the glove box. First the diborane **(*R*)-6** (0.017 mmol, 2 equiv.) was dissolved in (*S*)-PO (0.493 g, 8.52 mmol, 1000 equiv.) and THF (4.28 mL, 2M concentration). Subsequently, the initiator (BnOH, 0.0213 mmol, 2.5 equiv.) and P_2-^{t}Bu (0.0085 mmol, 1 equiv.) was added to result in a total molar ratio of P_2-^{t}Bu/diborane/initiator/PO = 1:2:2.5:1000. After the polymerization was started, aliquots of 20 µL were collected via pipette (*Eppendorf*) in specific time intervals and quenched with wet $CDCl_3$. After 0.5 h further diborane **(*S*)-6** (0.034 mmol, 4 equiv.) was added to the polymerization, and samples were withdrawn as described above. The molecular weight of the polyether was determined *via* GPC analysis ($CHCl_3$) and ^{1}H NMR; the number of average PO-repeating units (x) was likewise calculated from ^{1}H-NMR ($CDCl_3$) using the PO(-$\underline{CH_2}$)- (δ = 3.38-3.42 ppm) and Ph-$\underline{CH_2}$-OR signal (δ = 4.55 ppm). Conversion of PO is determined from the initial [PO]/[-OH] ratio and the thus calculated number of incorporated PO units.

Characterization and Analysis

NMR Spectroscopy

The ^{1}H, ^{13}C and ^{11}B NMR spectra were recorded at room temperature on a *Bruker Avance III* 400 spectrometer (^{1}H at 400 MHz, ^{13}C at 101 MHz and ^{11}B at 128 MHz). The chemical shifts are being reported relative to reference peaks of the applied deuterated solvent ($CDCl_3$: δ = 7.26 ppm for ^{1}H and δ = 77.16 ppm for ^{13}C).

Gel Permeation Chromatography

Gel permeation chomatography (GPC) was used to determine relative molar masses and molar mass distribution ($Đ_M$) of the polymer samples. GPC was measured at 30 °C in chloroform on an *Agilent Technologies* 1200 Infinity Series instrument. The instrument was calibrated against polystyrene standards (800 g/mol – $2{\cdot}10^6$ g/mol). The setup consists of three consecutive SDS PSS (8 mm x 300 mm) columns and a RI detector *Agilent* 1200 Series G1362. A flow rate of 1.0 mL min^{-1} and a sample concentration of 2 mg/ml was applied. The injection volume was 100 µL.

Differential Scanning Calorimetry

A DSC 4000 instrument (*Perkin Elmer*) was employed. For the measurements, approximately 2 mg of the sample was placed in a 50 µL sample container and heated from -60°C to 90°C using scan rates of 10 K/min with a nitrogen flow of 20 mL/min, followed by a sequence from 90°C to 0°C and 0°C to 90 °C with 5 K/min or 20 K/min. All thermograms were analyzed using the second heating branch.

Calculation of Polymer Tacticity via NMR Spectroscopy

^{13}C NMR analysis can be used to conveniently determine tacticity of various aliphatic polyethers. For PPO, the well separated *m*- (δ=73.5 ppm/72.4 ppm) and *r*-diad (δ=73.0 ppm/71.5 ppm) signals can be directly used for evaluation. Further details can be found in the cited literature[1] and Figure S15-S16.

Polymerizations

Representative GPC Examples of Stereocontrolled PPO

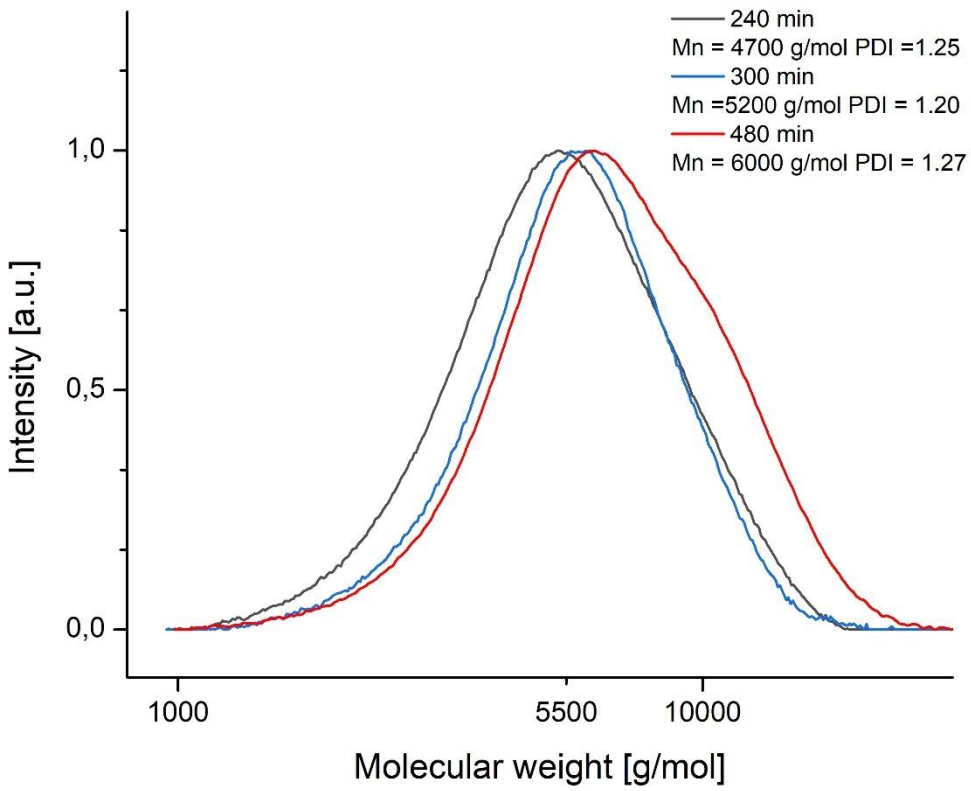


Figure S14. GPC traces received from polymerization of (S)-PO using ***(R)*-6**/P_2-^{t}Bu. Conditions: tBu-P_2/***(R)*-6**/BnOH/(S)-PO = 1:2:2.5:1000. $[M]_0$ = 2.0 mol/L, THF, room temperature.

Representative Examples for Stereoanalysis via ^{13}C NMR

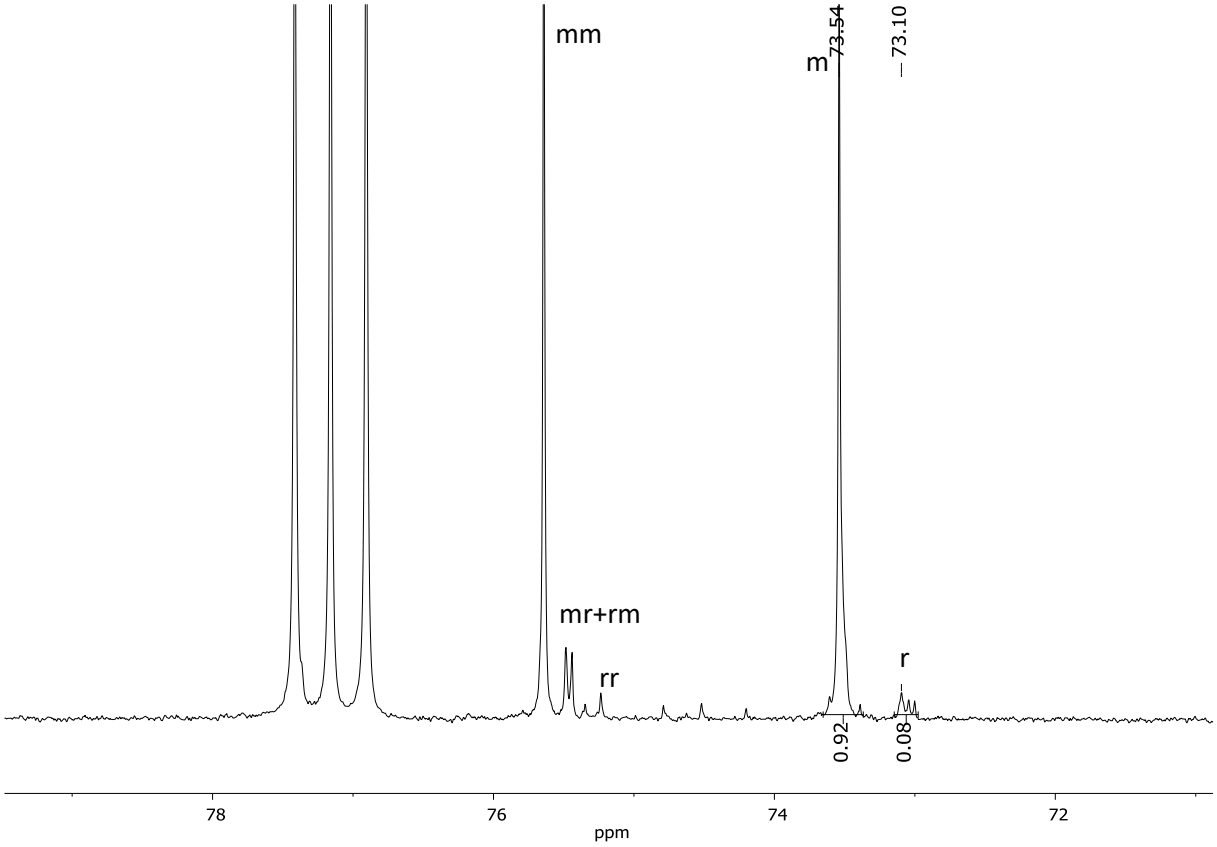


Figure S15. ^{13}C NMR analysis ($CDCl_3$, 300 K) with diad/triad assignment and diad analysis of PPO. Polymer resulting from application of tBu-P_2/***(R)*-6** after 48 h at -36 °C.

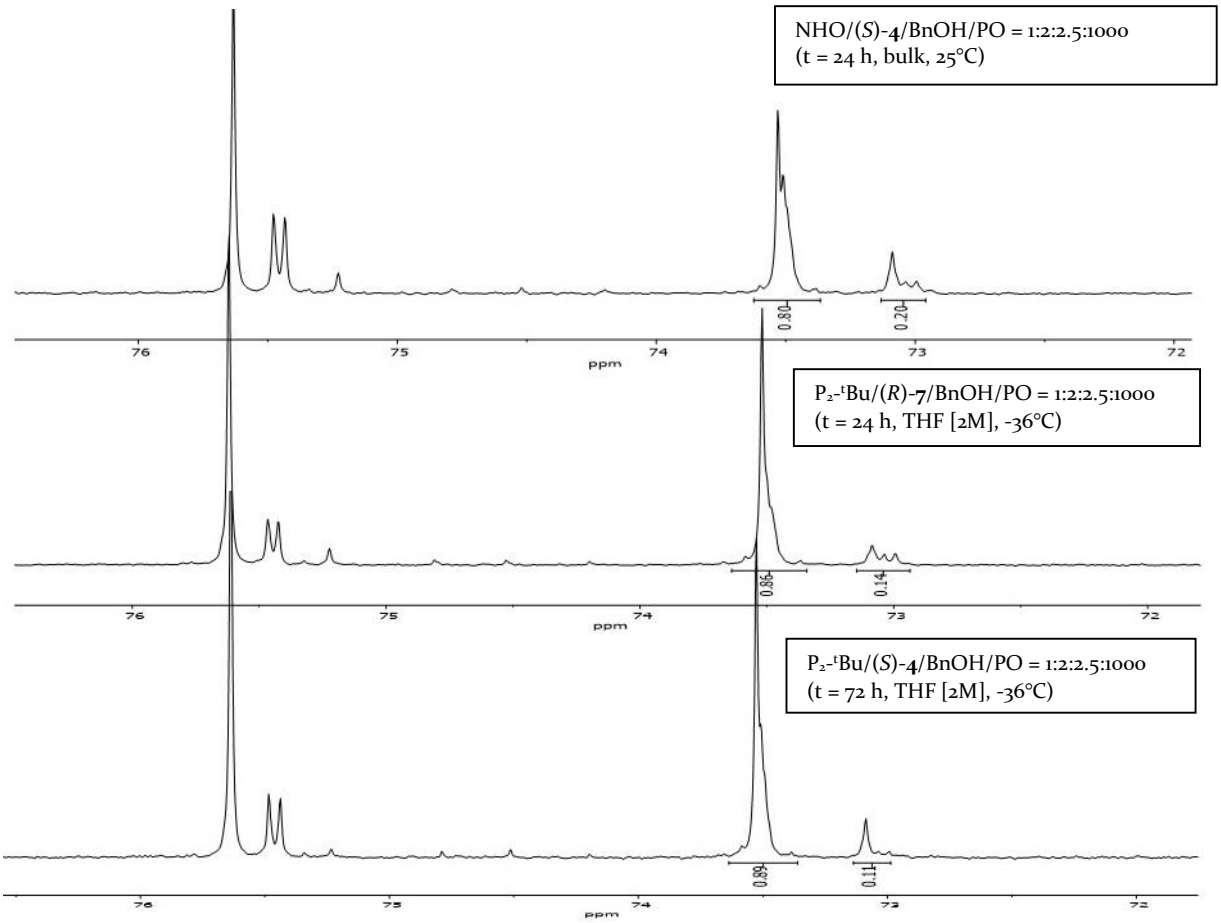


Figure S16. Examples of ^{13}C NMR analysis ($CDCl_3$, 300 K) with diad sequence analysis of PPO prepared under different conditions.

Polymerization Kinetics

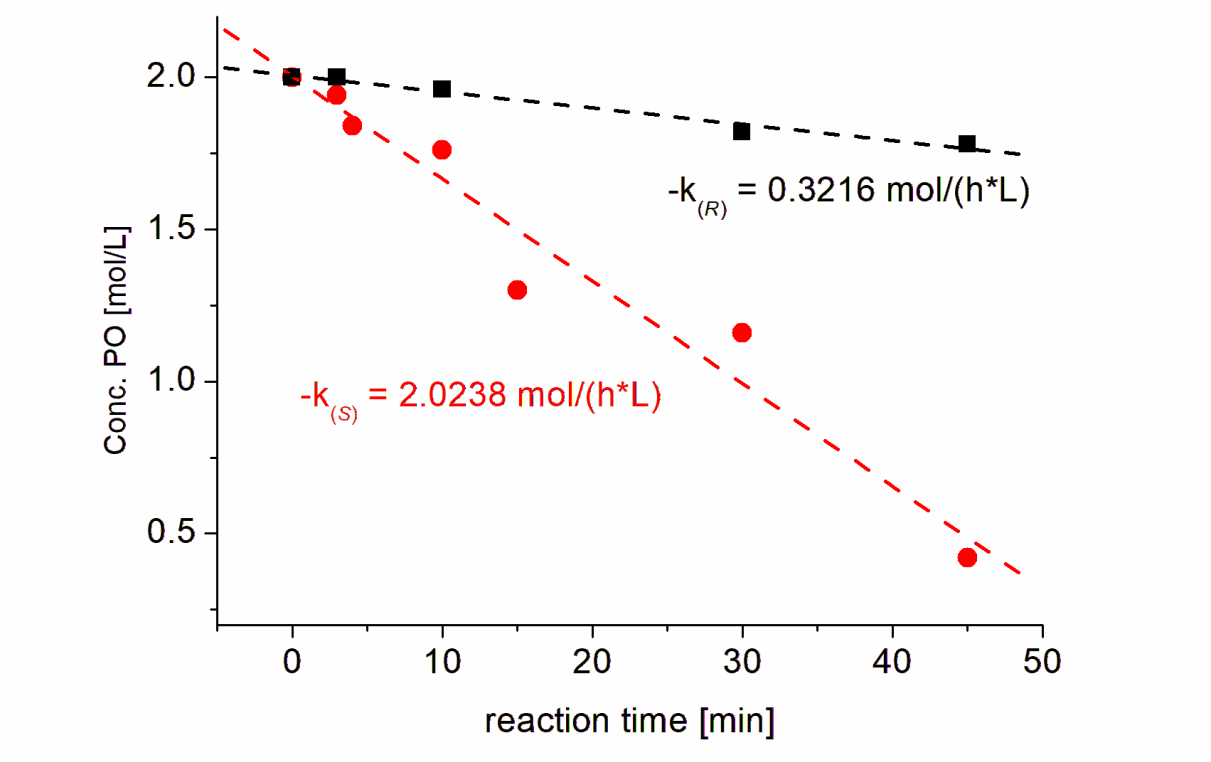


Figure S17. Correlation of [PO] vs. reaction time using tBu-P_2/(***R***)-**6**/BnOH/enantiopure PO = 1:2:2.5:1000 (molar ratio, RT, 2M in THF).

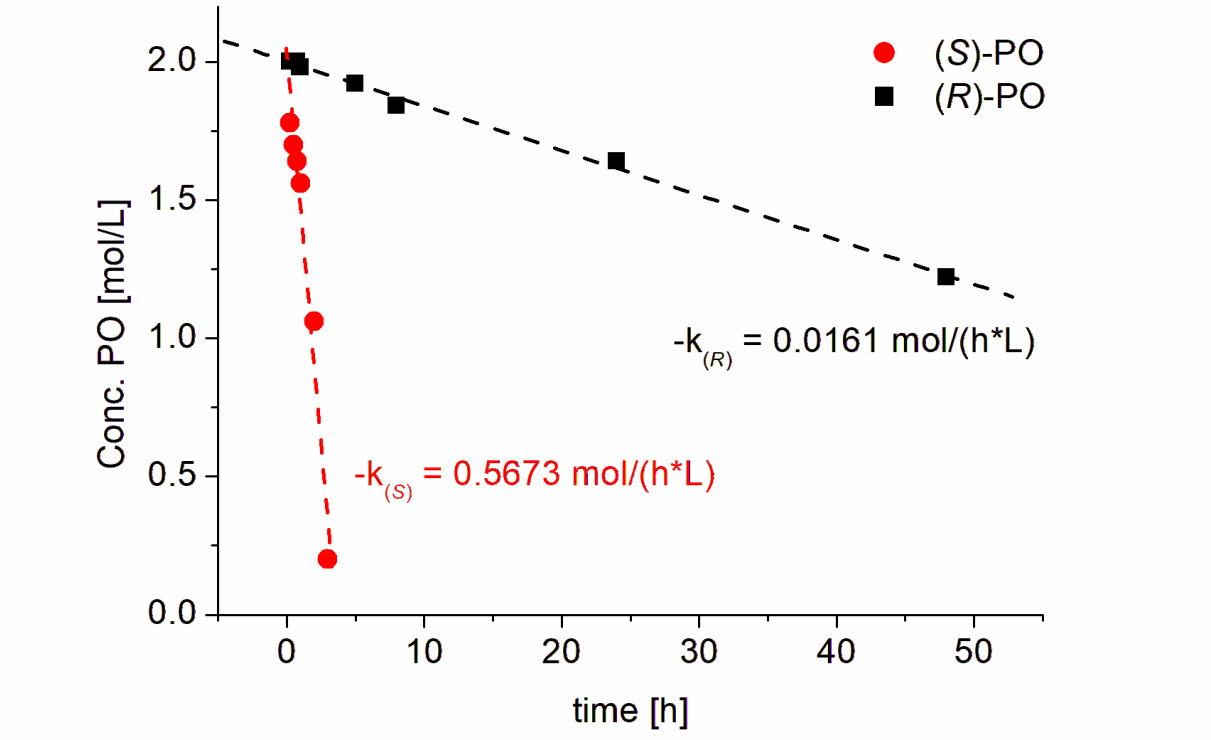
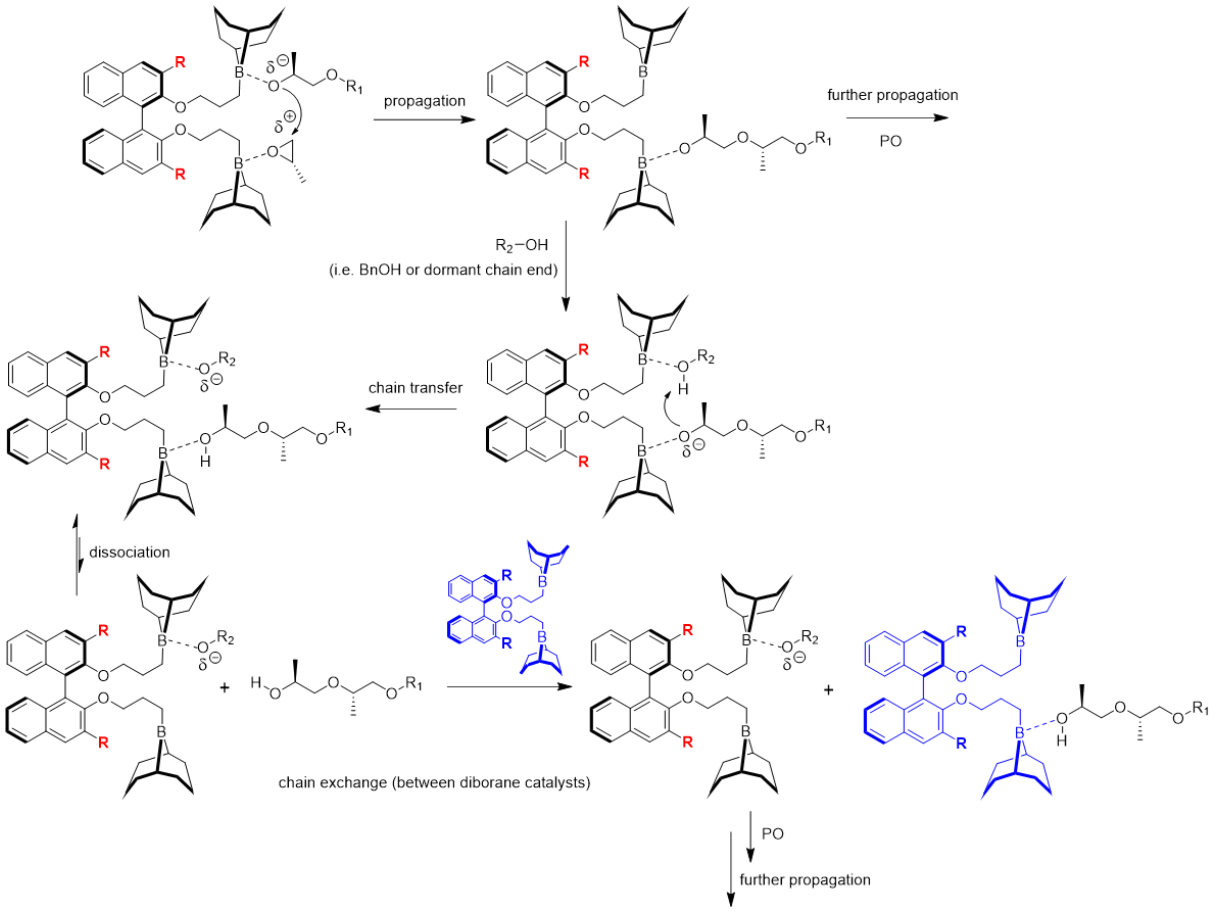


Figure S18. Correlation of [PO] vs. reaction time using tBu-P_2/(***R***)-**6**/BnOH/enantiopure PO = 1:2:2.5:1000 (molar ratio, -36°C, 2M in THF).

Polyether Chain Exchange between Catalysts



Scheme 2. Mechanistic details, including propagation step, chain transfer events and polyether chain exchange between diborane catalysts (black/blue).

Polymerization of PO

Table S1. Dataset of PO polymerizations using P_2-tBu (B) in combination with various diboranes (C) and BnOH as initiator (I).

#	Cat (C)	Organo-base (B)	B/C/I/PO	solvent [PO]	T [°C]	t [h]	x[a] ($Đ_M$)[b]	$M_{n(calc)}$[c] [g/mol]	$M_{n(GPC)}$[b] [g/mol]	*m*[d] [%]	*mm*[d] [%]	Conv.[c] [%]
1	(*R*)-2	P_2-tBu	1:2:2.5:1000	bulk	25	2.0	139 (1.27)	8100	7000	73	51	35
2	(*R*)-2	P_2-tBu	1:2:2.5:1000	THF [4M]	25	24	84 (1.23)	4900	5000	76	55	21
3	(*R*)-2	P_2-tBu	1:2:2.5:1000	THF [2M]	-36	48	228 (1.24)	13000	11000	79	60	57
4	(*R*)-2	P_2-tBu	1:2:2.5:1000	THF [4M]	-36	48	152 (1.20)	9000	7000	81	63	38
5	(*R*)-3	P_2-tBu	1:2:2.5:1000	THF[4M]	25	24	382 (1.18)	22000	14000	74	54	95
6	(*S*)-4	P_2-tBu	1:2:2.5:1000	bulk	25	1.5	149 (1.37)	8700	5000	77	66	37
7	(*S*)-4	P_2-tBu	1:2:2.5:1000	THF [4M]	25	24	150 (1.16)	8800	9000	81	63	38
8	(*S*)-4	P_2-tBu	1:2:2.5:1000	bulk	-36	24	312 (1.17)	18200	18000	66	68	78
9	(*S*)-4	P_2-tBu	1:2:2.5:1000	THF [2M]	-36	72	235 (1.22)	13700	10000	89	75	59
10	(*S*)-4	P_2-tBu	1:2:2.5:1000	THF [4M]	-36	48	280 (1.22)	10000	9000	88	75	42
11	(*S*)-5	P_2-tBu	1:2:2.5:1000	bulk	25	24	117 (1.27)	6900	7000	75	59	29
12	(*S*)-5	P_2-tBu	1:2:2.5:1000	THF [4M]	25	24	83 (1.13)	4900	3000	81	64	21
13	(*S*)-5	P_2-tBu	1:2:2.5:1000	THF [2M]	25	24	102 (1.23)	6000	6000	80	62	26
14	(*S*)-5	P_2-tBu	1:2:2.5:1000	bulk	-36	24	83 (1.18)	4900	4000	80	64	21
15	(*S*)-6	P_2-tBu	1:2:2.5:1000	bulk	25	1.0	133 (1.31)	7800	7000	85	68	33
16	(*S*)-6	P_2-tBu	1:2:2.5:1000	THF [2M]	25	24	246 (1.29)	14000	11000	86	73	75
17	(*S*)-6	P_2-tBu	1:2:2.5:1000	bulk	-36	5.0	393 (1.34)	23000	19000	86	77	98
18	(*S*)-6	P_2-tBu	1:2:2.5:1000	THF [2M]	-36	48	145 (1.22)	8500	8000	92	83	36
19	(*S*)-6	P_2-tBu	1:2:2.5:1000	THF [4M]	-36	48	115 (1.22)	6700	7000	91	80	29
20	*rac*-6	P_2-tBu	1:2:2.5:1000	THF [2M]	-36	48	396 (1.11)	23000	19000	90	79	99
21	(*S*)-6	P_2-tBu	1:2:2.5:1000	THF [2M]	-36	24	135 (1.21)	7900	7000	90	80	34
22	(*S*)-6	P_2-tBu	1:2:2.5:1000	toluene [2M]	-36	48	29 (1.39)	1700	1200	91	77	7
23	(*R*)-7	P_2-tBu	1:2:2.5:1000	bulk	25	1.0	268 (1.23)	15600	9000	84	70	67
24	(*R*)-7	P_2-tBu	1:2:2.5:1000	THF [2M]	25	24	204 (1.27)	12000	11000	86	73	51
25	(*R*)-7	P_2-tBu	1:2:2.5:1000	THF [2M]	-36	48	165 (1.19)	9600	7000	92	81	41
26	(*R*)-7	P_2-tBu	1:2:2.5:1000	THF [4M]	-36	24	180 (1.22)	10500	8000	90	79	45
27	(*R*)-7	P_2-tBu	1:2:2.5:1000	Toluene [2M]	-36	48	63 (1.18)	3700	3000	86	74	16
28	(*R*)-7	P_2-tBu	1:2:2.5:1000	Pentane [2M]	-36	48	107 (1.56)	6300	9000	87	76	27
29	(*S*)-4	P_2-tBu	1:2:2.5:500	bulk	-78	7.0	130 (1.19)	7700	6000	86	73	33
30	(*R*)-6	P_2-tBu	1:2:2.5:500	bulk	-78	7.0	136 (1.41)	8000	7000	86	72	34
31	(*R*)-6	P_2-tBu	1:2:2.5:500	THF [4M]	-78	7.0	18 (1.30)	1200	1000	90	80	5
32	(*R*)-6	P_2-tBu	1:2:2.5:1000	THF [4M]	-78	7.0	42 (1.10)	2500	3000	91	81	11
33	(*R*)-6	P_2-tBu	1:2:2.5:1000	THF [2M]	-78	7.0	25 (1.35)	1600	1000	92	83	6

a) Average number of PO repeat units determined via ^{1}H NMR spectroscopy ($CDCl_3$). b) determined *via* GPC analysis ($CHCl_3$). c) determined via ^{1}H NMR ($CDCl_3$). d) diad placement determined *via* ^{13}C NMR spectroscopy.

DSC Analysis

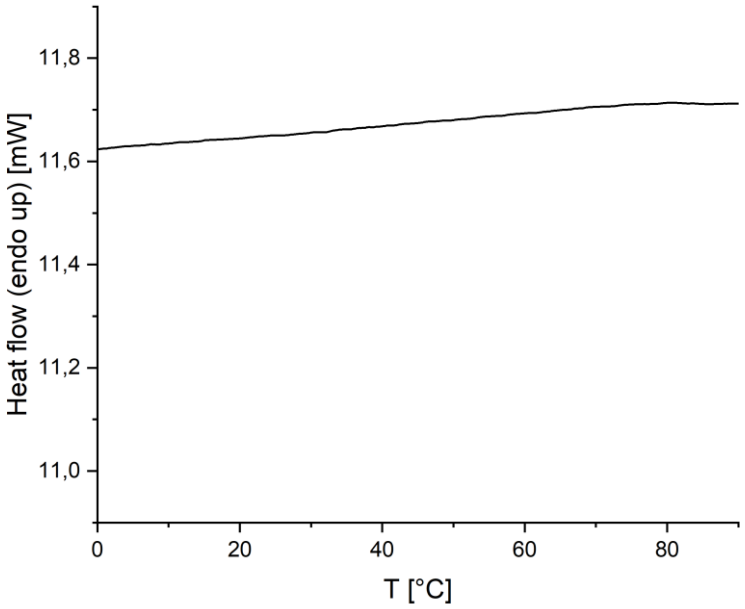


Figure S19. DSC investigation (5K/min, second cycle) of PPO with *m* = 80%, received by the action of tBu-P_2/(**S**)-**4**/BnOH/PO = 1:2:2.5:1000 (molar ratio, rt, 4M in THF).

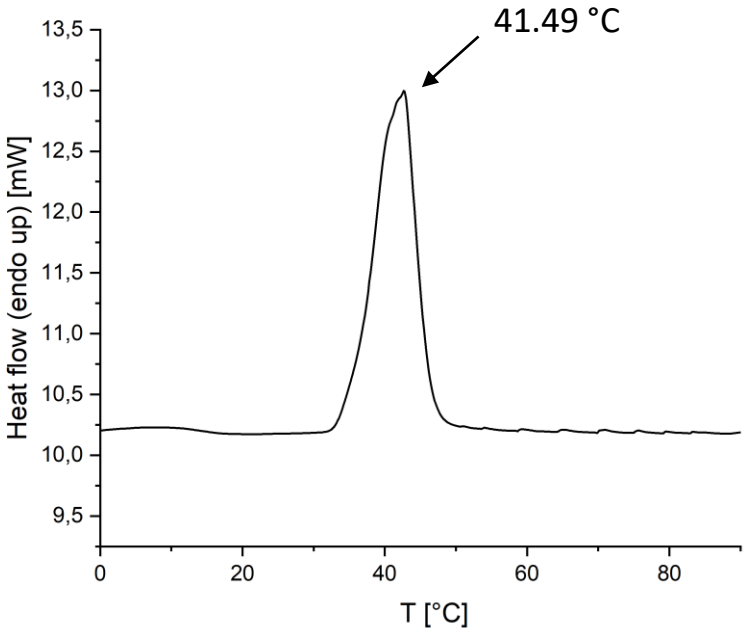


Figure S20. DSC investigation (5K/min, second cycle) of PPO with *m* = 86%, received by the action of tBu-P_2/(**S**)-**6**/BnOH/PO = 1:2:2.5:1000 (molar ratio, rt, 2M in THF).

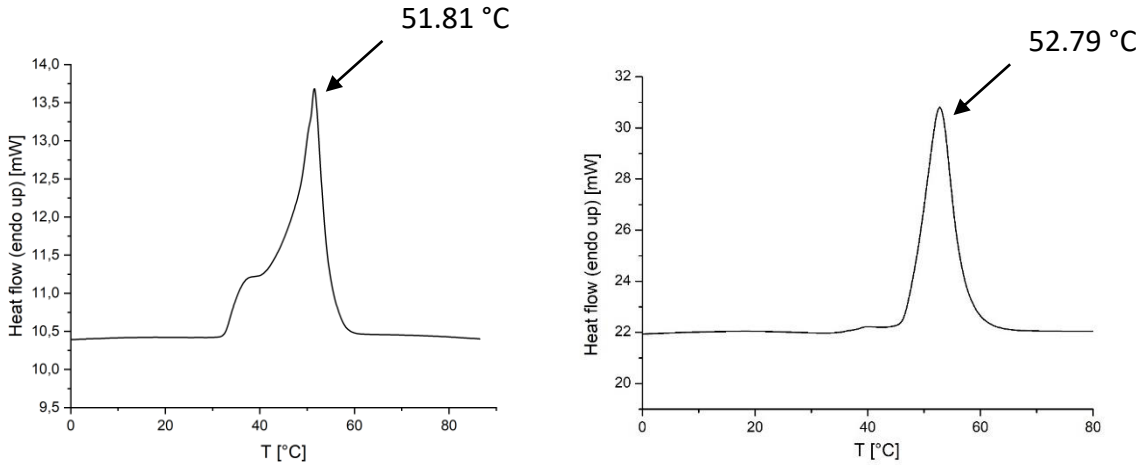


Figure S21. DSC investigation (left: 5K/min, right: 20K/min, second cycle) of PPO with *m* = 90%, received by the action of tBu-P_2/(***rac***)-**6**/BnOH/PO = 1:2:2.5:1000 (molar ratio, -36 °C, 2M in THF).

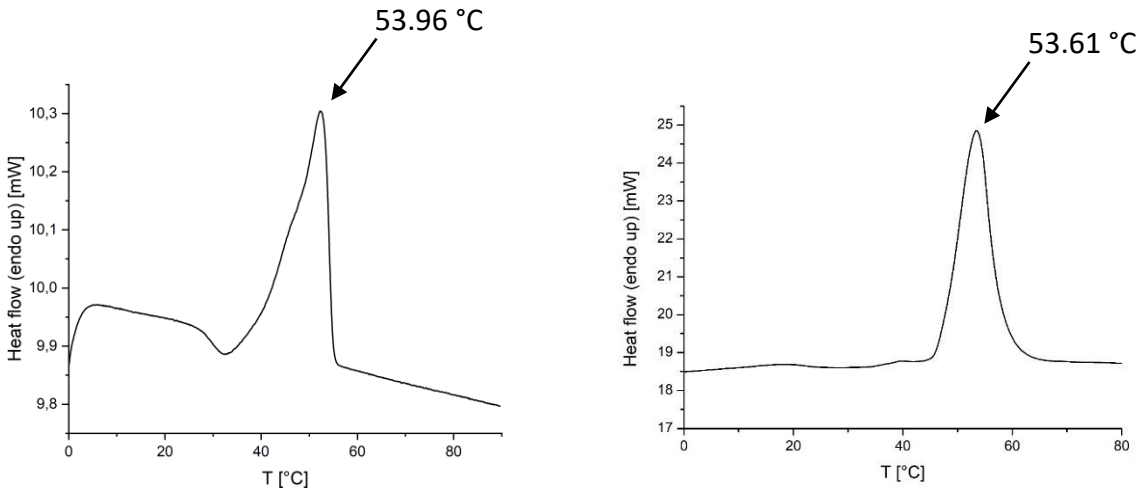


Figure S22. DSC investigation (left: 5K/min, right: 20K/min, second cycle) of PPO with *m* = 91% , received by the action of tBu-P_2/(***S***)-**6**/BnOH/PO = 1:2:2.5:1000 (molar ratio, -36°C, 2M in THF).

References

[1] Renee M. Thomas, Peter C.B. Widger, Syud M. Ahmed, Ryan C. Jeske, Wataru Hirahata, Emil B. Lobovsky, Geoffrey W. Coates, *J. Am. Chem. Soc.*, 2010, **132**, 16520-16525.