Supporting Information to

Chiral Diboranes as Catalysts for the Stereoselective Organopolymerization of Epoxides

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Contents

Experimental

Materials and Synthesis

Propylene oxide (PO, *TCI Chemicals*, > 99,0 %), butylene oxide (BO, *TCI Chemicals*, > 99,0 %), styrene oxide (SO, *TCI Chemicals*, >98%) and allyl glycidyl ether (AGE, *Sigma-Aldrich*, > 99,0 %) were stirred over CaH_2 overnight. After distillation under nitrogen, the monomers PO, BO, SO and AGE were degassed twice by the 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)-(+)-1,1′-bi(2-naphtol) (*Sigma-Aldrich*, > 99.0 %), 1,4-benzenedimethanol (*TCI Chemicals*, > 99,0 %) and 1,1′-bi-2-naphtol (*TCI Chemicals*, > 99,0 %) were used as received. 9-Borabicyclo[3.3.1]nonane (*Sigma Aldrich*, 0.5 M solution in THF), 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU, *Sigma-Aldrich*) 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. The NHO was synthesized as described earlier and stored inside the glove box at -36 °C.[1,2] The commercial macroinitiator samples PCL10K (polycaprolactone with M_n = 10 000 g/mol, *Sigma Aldrich*), PEG8K (polyethylene glycol with M_n = 8 000 g/mol, *abcr*) and PLA20K (polylactide with M_n = 20 000 g/mol, *Sigma Aldrich*) were used as received. PCL7K[1] and PCL2K[3] were prepared according to published procedures. PCL11K-diol was prepared in the same manner as PCL2K but BDM (1,4-benzol-dimethanol) was used as an initiator. For the diborane (**1-4**) synthesis, see below.

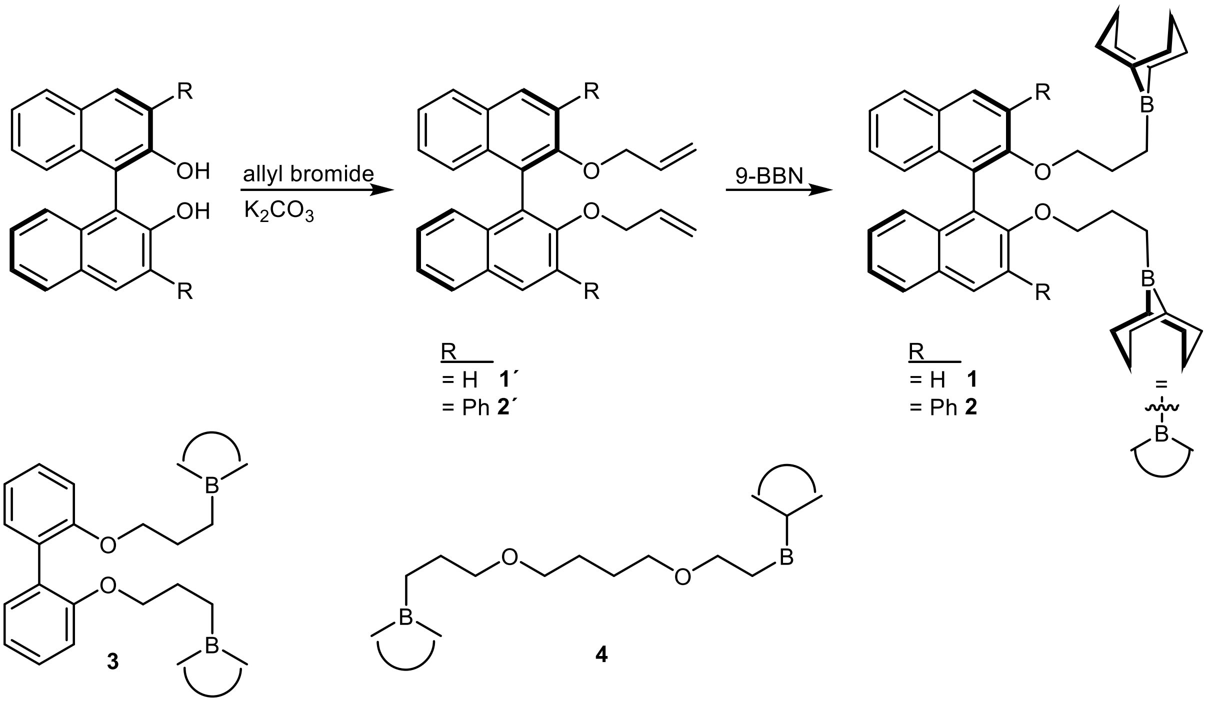

Figure S1. General procedure for the preparation of diboranes **1-4** used in this work.

Procedural Information

Synthesis of diallyl species

General Procedure: In an oven-dried Schlenk flask, (*R*)-BINOL ((*R*)-(+)-1,1′-bi-2-naphthol) 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. After filtration and salt removal, the solvent and excess amount of allyl bromide were removed in vacuo to yield the colorless product.

Diallyl 1'

First, (*R*)-BINOL ((*R*)-(+)-1,1′-bi-2-naphtol) (5.00 g, 17.5 mmol) and allyl bromide (3.63 mL, 42.0 mmol, 2.4 equiv.) were dissolved in 30 mL acetonitrile, then K_2CO_3 (16.08 g, 0.116 mol) was added and the reaction mixture was stirred at room temperature for 72 h. The reaction was monitored by GC-MS. Via filtration, the potassium salts were removed. The solvent and excess amount of allyl bromide were removed under reduced pressure. Yield: 2.91 g (7.94 mmol, 45 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85-7.95 (*dd*, 4H), 7.14-7.41 (*m*, 8H), 5.70-5.80 (*m*, 2H), 4.97-5.04 (*m*, 4H), 4.51-4.53 (*m*, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.0, 134.1, 133.8, 129.3, 129.2, 127.9, 126.2, 125.5, 123.6, 120.4, 116.4, 115.7, 69.9 ppm.

Diallyl (*S*)-1'

First, (*S*)-BINOL ((*S*)-(-)-1,1′-bi-2-naphtol) (5.00 g, 17.5 mmol) and allyl bromide (3.63 mL, 42.0 mmol, 2.4 equiv.) were dissolved in 30 mL acetonitrile, then K_2CO_3 (16.08 g, 0.116 mol) was added and the reaction mixture was stirred at room temperature for 72 h. The reaction was monitored by GC-MS. Via filtration, the potassium salts were removed. The solvent and excess amount of allyl bromide were removed under reduced pressure. Yield: 2.81 g (7.67 mmol, 43 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84-7.95 (*dd*, 4H), 7.13-7.41 (*m*, 8H), 5.68-5.81 (*m*, 2H), 4.96-5.04 (*m*, 4H), 4.50-4.53 (*m*, 4H) ppm.

Diallyl *rac*-1'

First, BINOL 1,1′-bi-2-naphtol (5.00 g, 17.5 mmol) and allyl bromide (3.63 mL, 42.0 mmol, 2.4 equiv.) were dissolved in 30 mL acetonitrile, then K_2CO_3 (16.08 g, 0.116 mol) was added and the reaction mixture was stirred at room temperature for 72 h. The reaction was monitored by GC-MS. Via filtration, the potassium salts were removed. The solvent and excess amount of allyl bromide were removed under reduced pressure. Yield: 2.78 g (7.58 mmol, 43 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69-7.79 (*dd*, 4H), 7.25 (*d*, 2H), 7.13-7.18 (*dt*, 2H), 7.01-7.06 (*dt*, 2H), 6.94 (*d*, 2H), 5.54-5.63 (*m*, 2H), 4.81-4.87 (*m*, 4H), 4.35-4.37 (*m*, 4H) ppm.

Diallyl *2'*

First, (*R*)-3,3′-diphenyl-[1,1′-binaphthalene]-2,2′-diol (1.00 g, 2.28 mmol) and allyl bromide (0.51 mL, 5.50 mmol, 2.4 equiv.) were dissolved in 4 mL acetonitrile, then K_2CO_3 (2.09 g, 0.015 mol) was added and the reaction mixture was stirred at room temperature for 72 h. The reaction was monitored by GC-MS. Via filtration the potassium salts were removed. The solvent and excess amount of allyl bromide were removed in vacuo. Yield: 0.500 g (0.964 mmol, 42 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (*s*, 2H), 7.91 (*d*, 2H), 7.75 (*dd*, 4H), 7.37-7.47 (*m*, 8H), 7.25 (*dd*, 4H), 5.23-5.33 (*m*, 2H), 4.53-4.67 (*m*, 4H), 3.93-3.98 (*m*, 2H), 3.69-3.74 (*m*, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 128.5, 128.4, 127.1, 32.2, 31.8 22.1 ppm.

Diallyl 3'

First, 2,2′-biphenol (5.00 g, 26.85 mmol) and allyl bromide (6.10 mL, 64.44 mmol, 2.4 equiv.) were dissolved in 40 mL acetonitrile, then K_2CO_3 (24.00 g, 0.173 mol) was added and the reaction mixture was stirred at room temperature for 72 h. The reaction was monitored by GC-MS. Via filtration the potassium salts were removed. The solvent and excess amount of allyl bromide were removed in vacuo. Yield: 4.01 g (15.10 mmol, 56 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26 (*dd*, 4H), 6.98 (*dt*, 2H), 6.91 (*d*, 2H), 5.84-5.93 (*m*, 2H), 5.08- 5.21 (*m*, 4H), 4.67 (*q*, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.1, 133.6, 133.6, 131.5, 128.4, 128.4, 120.5, 116.4, 112.3, 68.9 ppm.

Diallyl 4'

1,4-Butanediol (1.00 g, 11.09 mmol) and allyl bromide (2.30 mL, 26.61 mmol, 2.4 equiv.) were dissolved in 25 mL acetonitrile, then K_2CO_3 (8.10 g, 0.05 mol) was added and the reaction mixture was stirred at room temperature for 72 h. The reaction was monitored by GC-MS. Via filtration, the potassium salts were removed. Solvent and excess amount of allyl bromide were removed under reduced pressure. Yield: 0.400 g (2.35 mmol, 21 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.86-5.95 (*m*, 2H), 5.23-5.29 (*m*, 2H), 5.14-5.18 (*m*, 2H), 3.96 (*dt*, 4H), 3.43-3.46 (*m*, 4H), 1.64-1.67 (*m*, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 135.0, 134.9, 116.7, 71.8, 70.1, 26.5 ppm.

Synthesis of Diborane Catalysts

Diboranes

General Procedure: To an oven-dried Schlenk flask the corresponding diallyl-species was added under nitrogen flow. The suitable amount of 9-borabicyclo[3.3.1]nonane in THF (0.5 M) was added via cannula/septum. The reaction mixture was stirred at 60 °C overnight (condenser). After cooling to room temperature, the mixture was concentrated in vacuo to afford the crude product which was transferred into the glove box. After recrystallization from pentane (-36°C), the diboranes were obtained as white solids.

Diborane **1**

The general procedure was employed, using diallyl-species **1’** (0.400 g, 1.09 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane in THF (0.5 M) (4.4 mL, 3.16 mmol, 2.9 equiv.). The reaction mixture was stirred at 60 °C overnight. After purification, enantiopure diborane **1** was obtained as a white solid. Crystals suitable for structure analysis were received from recrystallization in pentane at -36°C in the glove box. Yield: 0.612 g (1.00 mmol, 92 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82-7.92 (*dd*, 4H), 7.41-7.43 (*d*, 2H), 7.18-7.31 (*m*, 6H), 3.87-4.0 (*m*, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.8, 134.4, 129.4, 129.2, 127.9, 126.2, 123.5, 120.9, 116.3, 116.3, 72.3, 33.1, 30.9, 24.6, 23.2 ppm. ^{11}B NMR (100 MHz, $CDCl_3$) δ = 90.64 ppm. HRMS (ESI): m/z calc. for $C_{42}H_{52}B_2O_2$ = 610.42, found $C_{42}H_{52}B_2O_2Na^+$: 633.36.

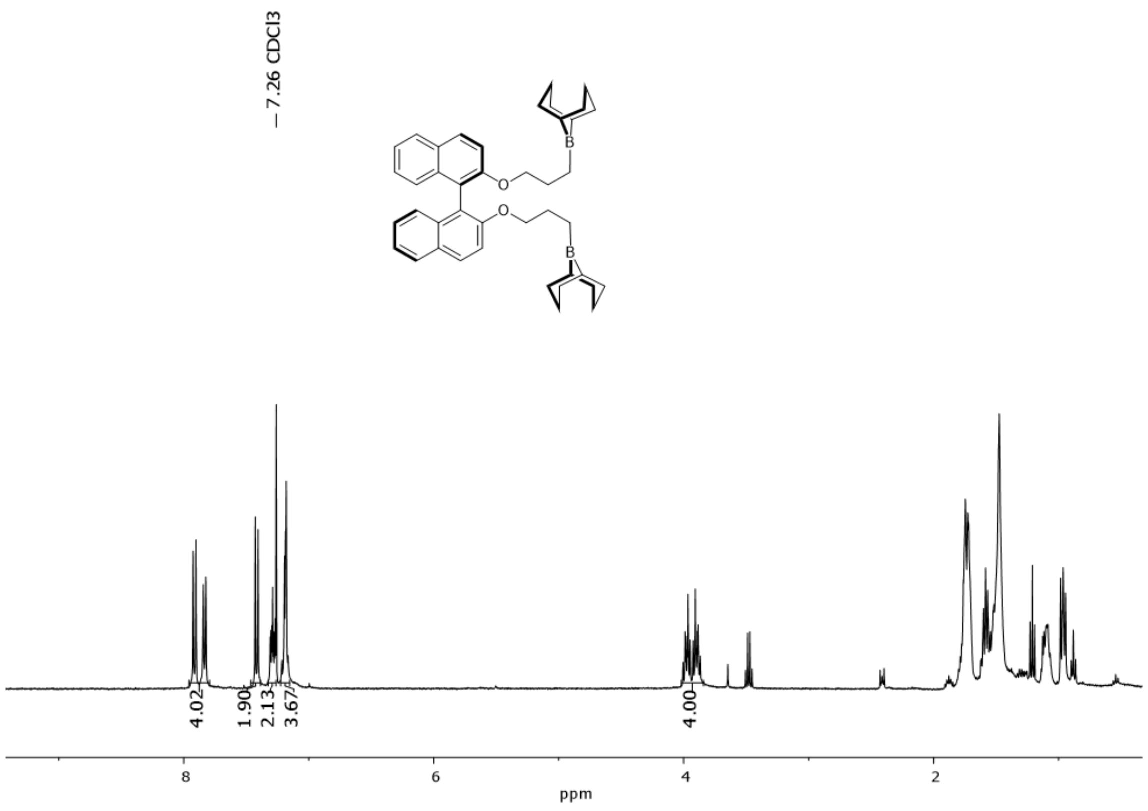

Figure S2. ^{1}H NMR analysis ($CDCl_3$, 400 MHz) of compound **1**.

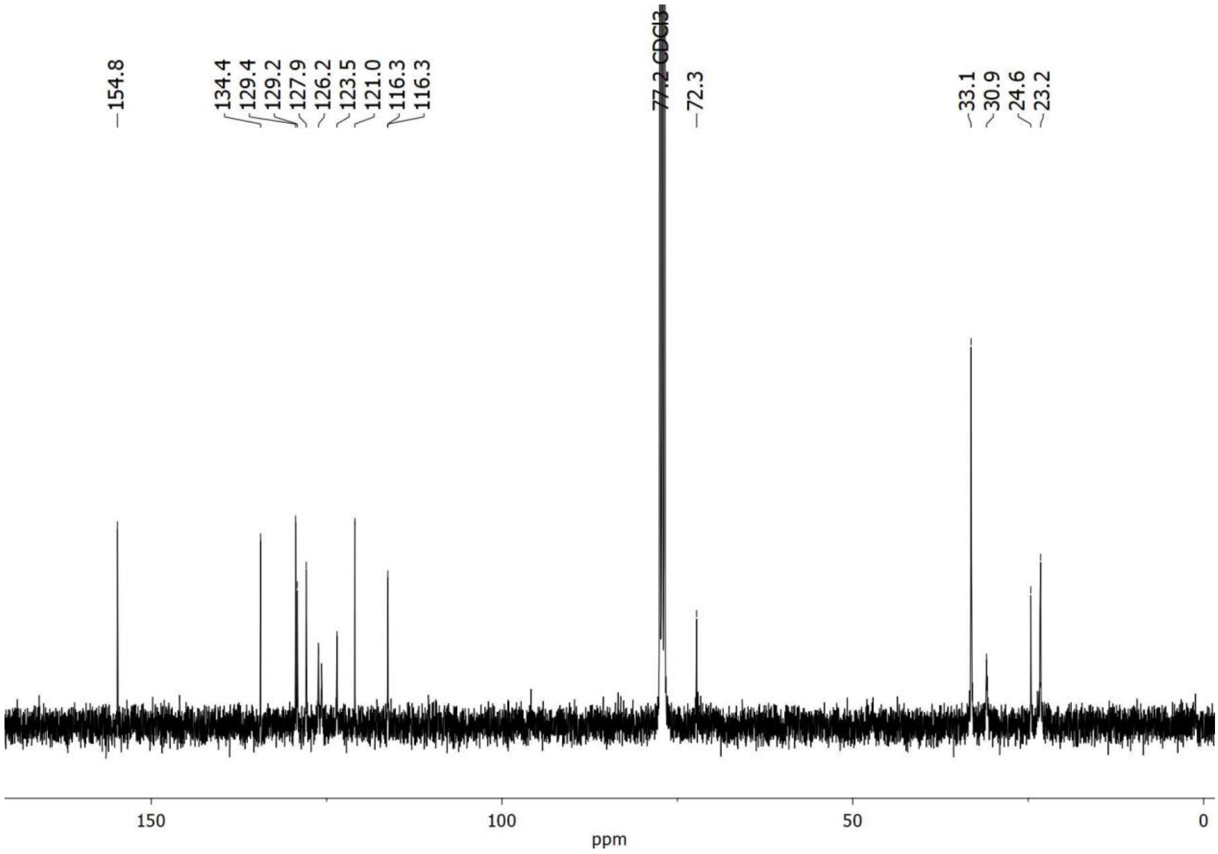

Figure S3. ^{13}C NMR analysis (CDCl$_3$, 101 MHz) of compound **1**.

Diborane *(S)*-**1**

The general procedure was employed, using diallyl-species *(S)*-**1'** (0.600 g, 1.63 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane in THF (0.5 M) (7.5 mL, 5.38 mmol, 2.9 equiv.). The reaction mixture was stirred at 60 °C overnight. After purification, diborane *rac*-**1** was obtained as a white solid. Yield: 0.890 g (1.45 mmol, 89 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.90-8.00 (*dd*, 4H), 7.48-7.50 (*d*, 2H), 7.26-7.39 (*m*, 2H), 7.26-7.27 (*m*, 4H), 3.94-4.08 (*m*, 4H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 154.7, 154.3, 134.3, 129.1, 127.8, 126.2, 125.5, 123.4, 120.8, 115.9, 72.1, 33.0, 26.7, 25.7, 24.5, 23.1 ppm.

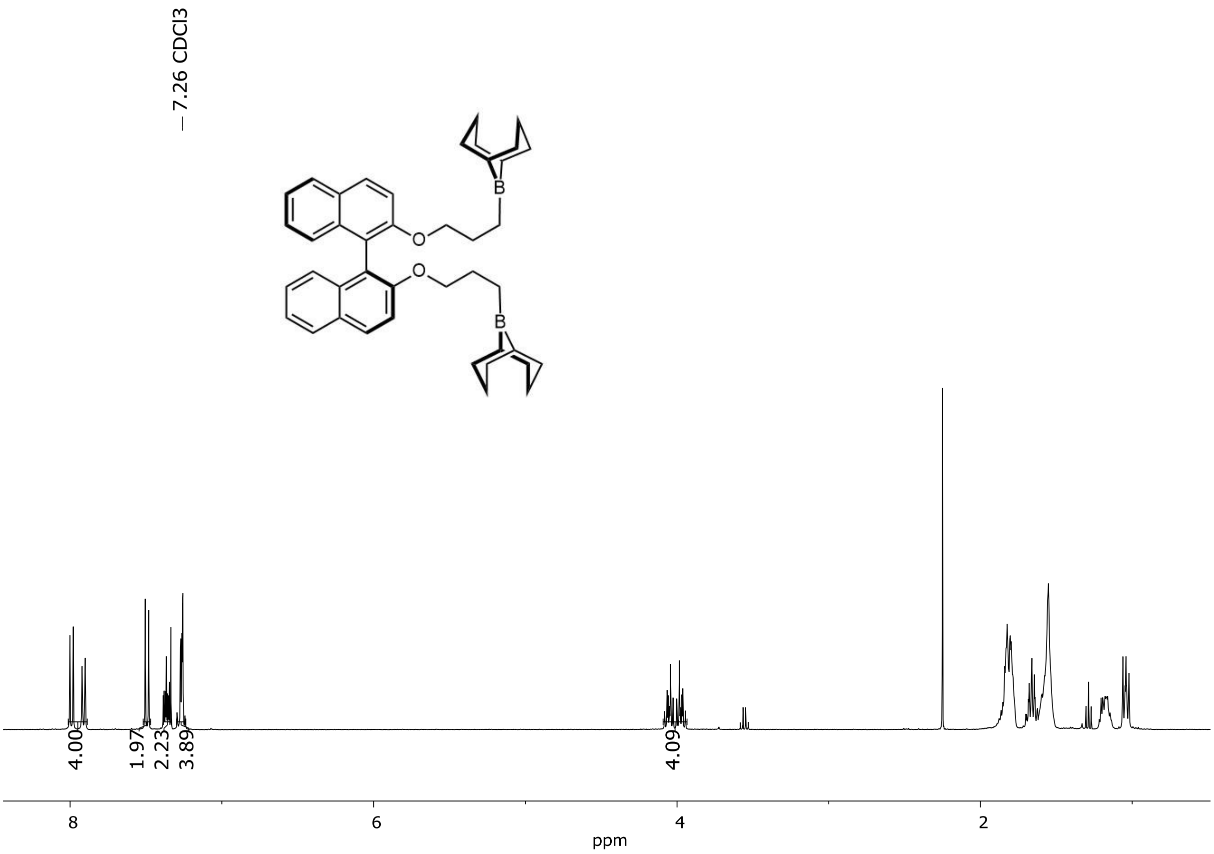

Figure S4. ^{1}H NMR analysis ($CDCl_3$, 400 MHz) of compound ***(S)*-1**.

Diborane *rac*-1

The general procedure was employed, using diallyl-species *rac*-**1**' (0.400 g, 1.09 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane in THF (0.5 M) (4.4 mL, 3.16 mmol, 2.9 equiv.). The reaction mixture was stirred at 60 °C overnight. After purification, diborane *rac*-**1** was obtained as a white solid. Yield: 0.572 g (0.93 mmol, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82-7.93 (*dd*, 4H), 7.41-7.43 (*d*, 2H), 7.18-7.30 (*m*, 6H), 3.87-4.01 (*m*, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.7, 134.3, 129.3, 129.0, 127.8, 126.0, 125.6, 123.4, 120.8, 116.1, 72.1, 33.0, 30.8, 24.5, 23.1 ppm. HRMS (ESI): m/z calc. for $C_{42}H_{52}B_2O_2$ = 610.42, found $C_{42}H_{52}B_2O_2Na^+$: 633.35.

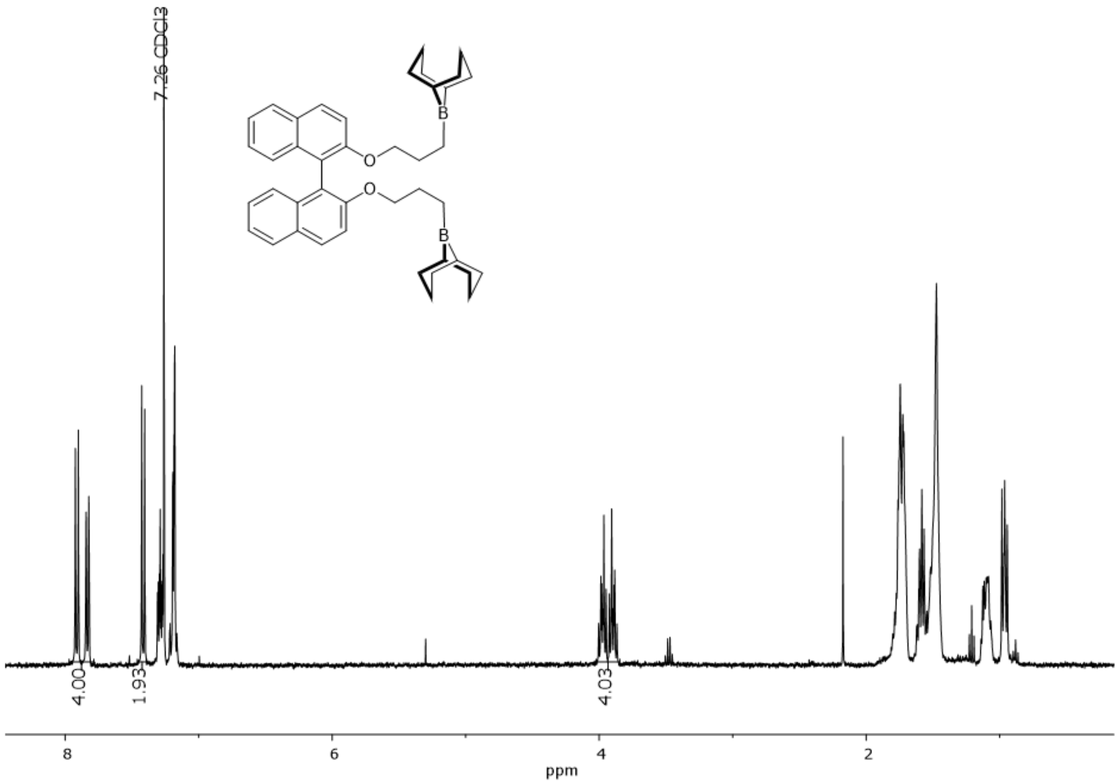

Figure S5. ¹H NMR analysis ($CDCl_3$, 400 MHz) of compound **rac-1**.

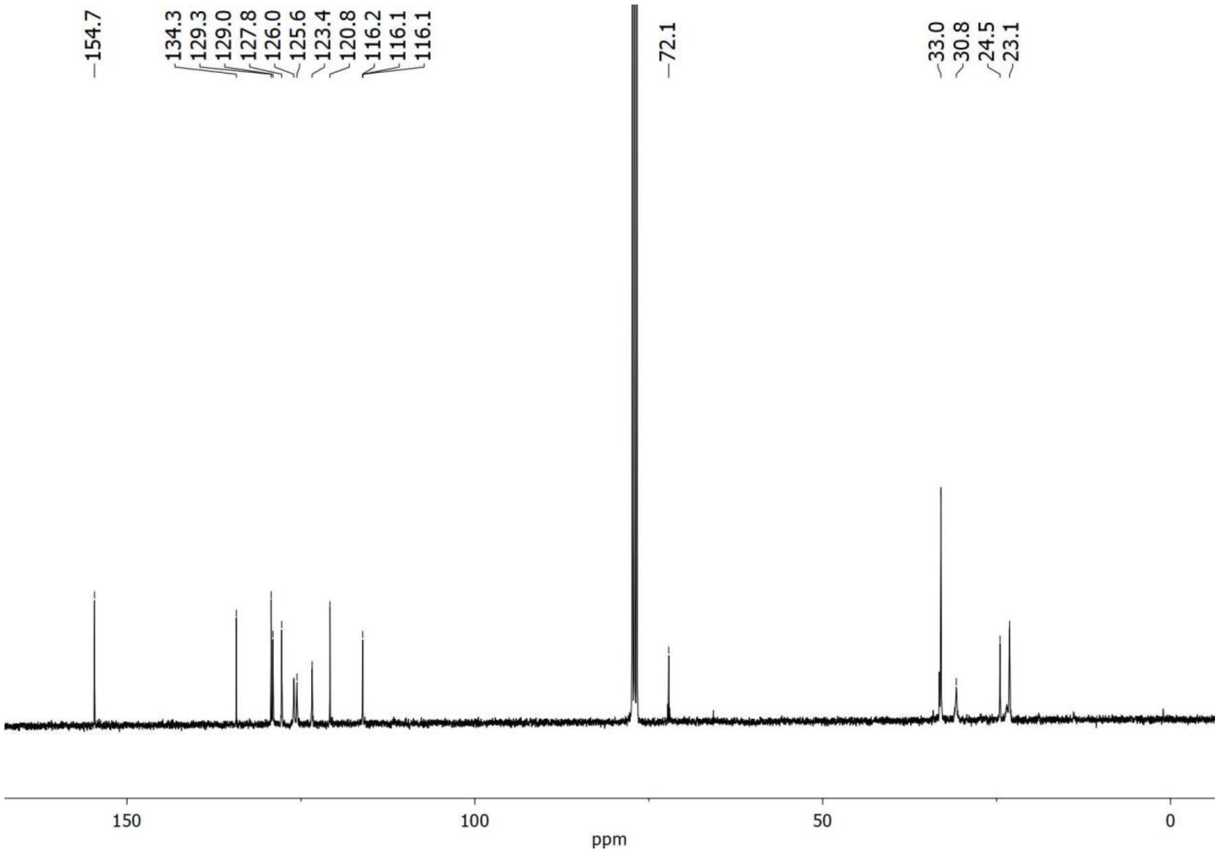

Figure S6. ¹³C NMR analysis ($CDCl_3$, 101 MHz) of compound **rac-1**.

Diborane 2

The general procedure was employed, using diallyl-species **2'** (0.400 g, 0.771 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane in THF (0.5 M) (3 mL, 2.18 mmol, 2.9 equiv.). The reaction mixture was stirred at 60 °C overnight. After purification, enantiopure diborane **2** was obtained as a white solid. Yield: 0.490 g (6.42 mmol, 90 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.96 (*s*, 2H), 7.91 (*d*, 2H), 7.79 (*dd*, 4H), 7.38-7.48 (*m*, 8H), 7.27 (*dd*, 4H), 3.48 (*q*, 2H), 3.17 (*q*, 2H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 152.8, 138.2, 134.6, 132.8, 129.6, 129.0, 128.4, 127.0, 126.9, 126.0, 125.3, 124.9, 123.6, 31.8, 29.5, 24.6, 23.7, 22.0 ppm. ^{11}B NMR (100 MHz, CDCl$_3$) δ = 58.53 ppm. HRMS (ESI): m/z calc. for $C_{52}H_{60}B_2O_2$ = 762.48, found $C_{52}H_{60}B_2O_2Na^+$: 785.46.

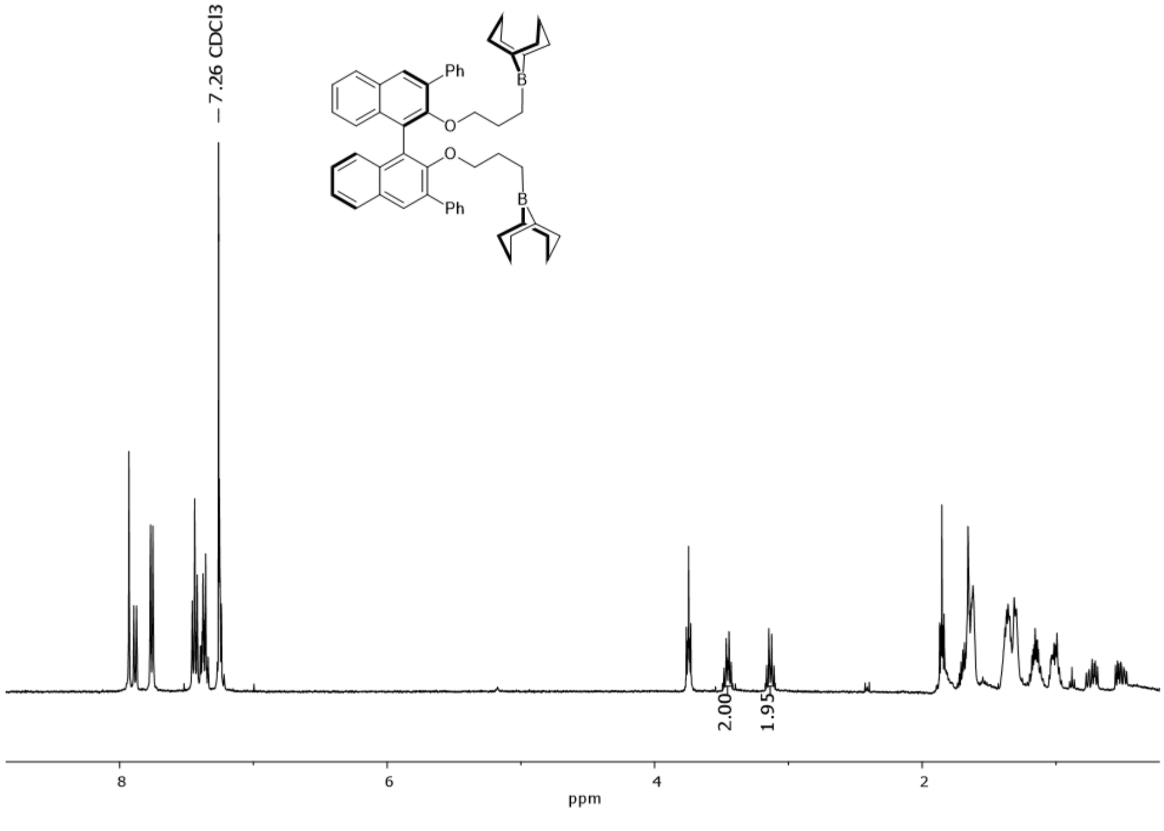

Figure S7. ^{1}H NMR analysis (CDCl$_3$, 400 MHz) of compound **2**.

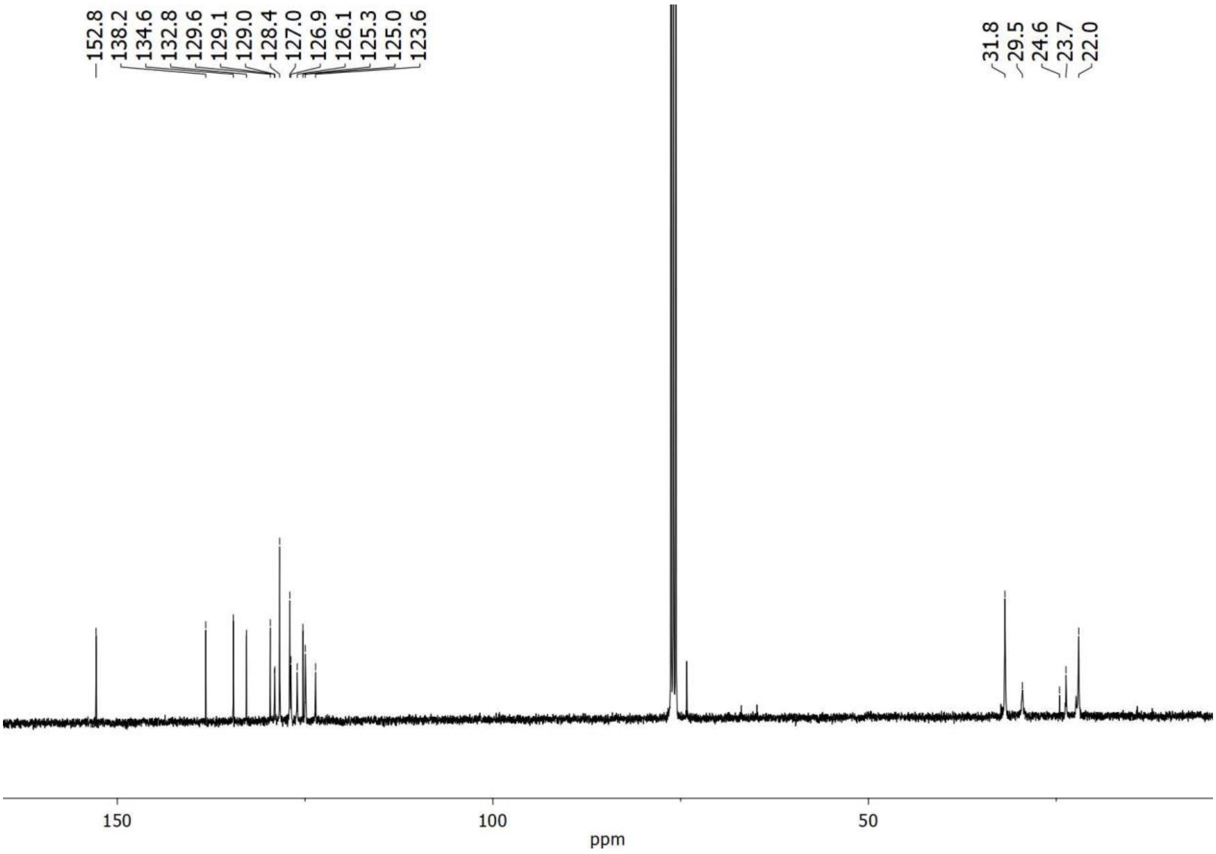

Figure S8. ^{13}C NMR analysis ($CDCl_3$, 101 MHz) of compound **2**.

Diborane 3

The general procedure was employed, using diallyl-species **3'** (1.00 g, 3.75 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane in THF (0.5 M) (15 mL, 10.88 mmol, 2.9 equiv.). The reaction mixture was stirred at 60 °C overnight. After purification, diborane **3** was obtained as a white solid. Yield: 1.53 g (2.99 mmol, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25-7.29 (*m*, 4H), 6.94-6.98 (*m*, 4H), 3.88 (*t*, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.8, 131.8, 128.5, 128.4, 120.1, 112.5, 33.2, 24.5, 23.3 ppm. ^{11}B NMR (100 MHz, $CDCl_3$) δ = 58.59 ppm. HRMS (ESI): m/z calc. for $C_{32}H_{48}B_2O_2$ = 510.38, found $C_{32}H_{49}B_2O_2^+$: 511.39.

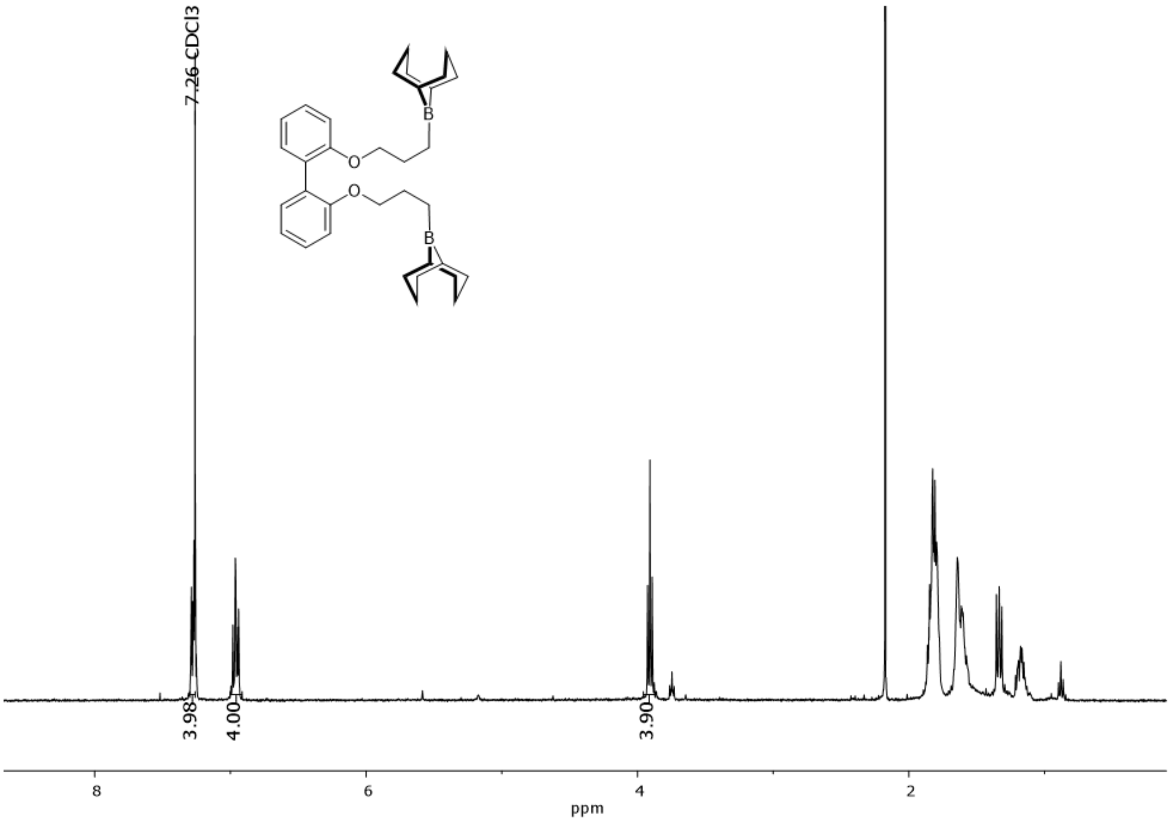

Figure S9. ^{1}H NMR analysis (CDCl$_3$, 400 MHz) of compound **3**.

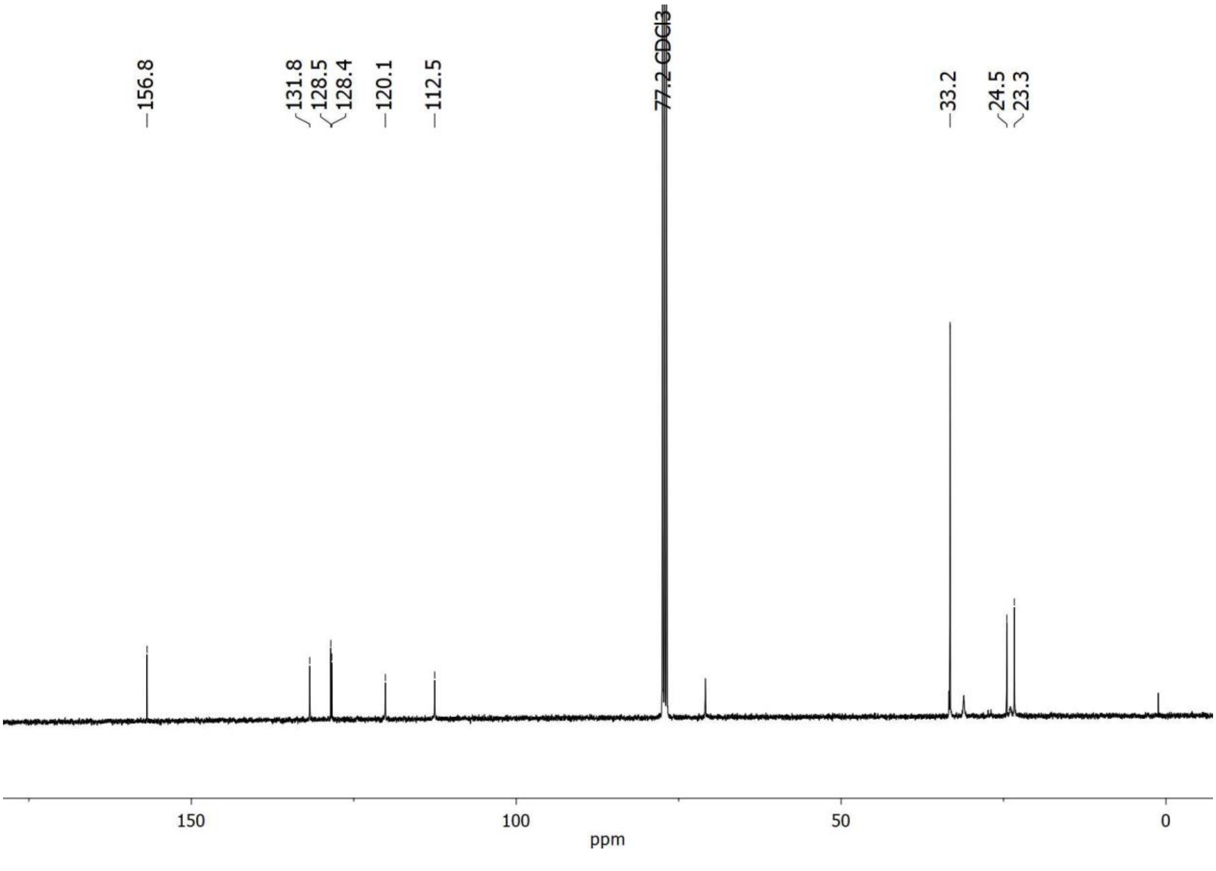

Figure S10. ^{13}C NMR analysis (CDCl$_3$, 101 MHz) of compound **3**.

Diborane *4*

The general procedure was employed, using diallyl-species **4**’ (0.180 g, 1.05 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane in THF (0.5 M) (4.3 mL, 3.06 mmol, 2.9 equiv.). The reaction mixture was stirred at 60 °C overnight. After aliphatic diborane **4** was obtained as a white solid. Yield: 0.387 g (0.933 mmol, 89 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.48-3.51 (*m*, 4H), 3.42 (*t*, 4H), 1.76-1.87 (*m*, 18H), 1.62-1.72 (*m*, 14H), 1.22-1.30 (*m*, 8H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 73.2, 71.0, 33.6, 33.4, 26.3, 25.1, 23.5, 23.3 ppm. HRMS (ESI): m/z calc. for $C_{26}H_{48}B_2O_2$ = 414.38, found $C_{26}H_{49}B_2O_2^+$: 415.26.

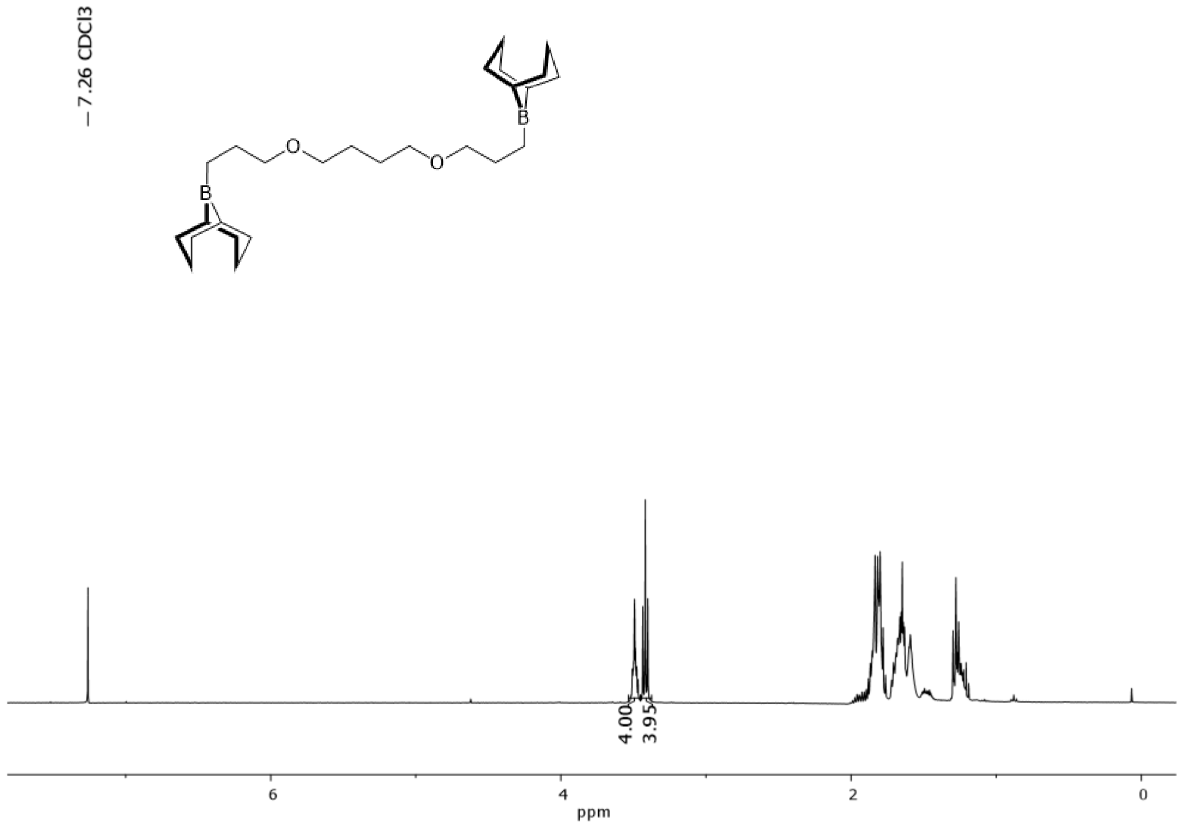

Figure S11. ^{1}H NMR analysis ($CDCl_3$, 400 MHz) of compound **4**.

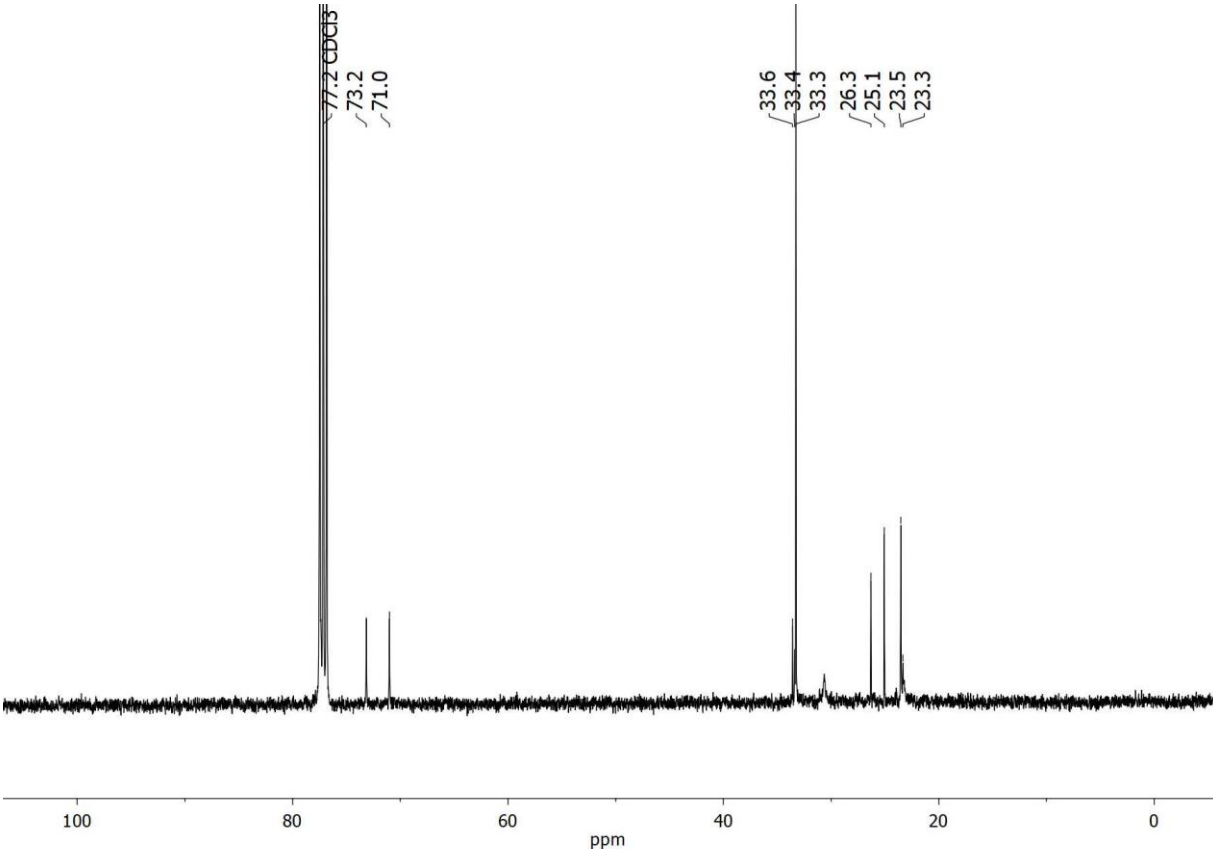

Figure S12. ^{13}C NMR analysis (CDCl$_3$, 101 MHz) of compound **4**.

General Polymerization Procedures

All polymerizations were assembled inside the glove box. First the diborane (0.017 mmol, 2 equiv.) was dissolved in PO (0.987 g, 17.04 mmol, 2000 equiv.). Subsequently, the initiator (BnOH, 0.0425 mmol, 5 equiv.) and the corresponding organobase (0.0085 mmol, 1 equiv.) was added to result in a total molar ratio of organobase/diborane/initiator/PO = 1:2:5:2000. 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).

General Procedure for Kinetic Analyses

The polymerizations 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, 0.0425 mmol, 5 equiv.) and the corresponding organobase (0.0085 mmol, 1 equiv.) was added to result in a total molar ratio of organobase/diborane/initiator/PO = 1:2:5:1000. 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 ^1H NMR; the number of average PO-repeating units (x) was likewise calculated from ^1H-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).

General Procedure for Block Copolymer Preparation

Polymerizations were assembled inside the glovebox. First the diborane **1** (0.017 mmol, 2 equiv.) was dissolved in PO (0.493 g, 8.52 mmol, 1000 equiv.) and THF (4.28 mL). Subsequently, the macroinitiator (PCL2-11K/PEO8K/PLA20K, 0.021 mmol, 2.5 equiv.) and the NHO (0.0085 mmol, 1 equiv.) was added to result in a total molar ratio of NHO/**1**/initiator/PO = 1:2:2.5:1000. The reaction was quenched by evaporation of the monomer. The molecular weight and copolymer formation of the polyether was investigated *via* GPC analysis ($CHCl_3$), ^1H NMR and ^1H DOSY NMR analysis; the number of average PO repeat units (x) was calculated from ^1H-NMR ($CDCl_3$) using the PO(-$\underline{CH_2}$)- (δ = 3.38-3.42 ppm) signal and a characteristic signal of the macroinitiator repeat units (PCL: δ = 4.17 ppm, PEO 8K: δ = 3.64 ppm, PLA: δ = 5.16 ppm).

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 and ^{13}C at 101 MHz). The chemical shifts are being reported relative to reference peaks of the applied deuterated solvent ($CDCl_3$: $\delta = 7.26$ ppm for ^{1}H and $\delta = 77.16$ 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 0°C to 120°C at scan rates of 5-20 K/min^{-1} with a nitrogen flow of 20 mL/min^{-1}. All thermograms were analyzed using the second heating/cooling cycle.

MALDI-ToF

MALDI-ToF (matrix-assisted laser desorption ionization-time of flight) mass spectrometry measurements were conducted on a *Bruker* Autoflex III (337 nm, reflector mode). The samples were prepared by mixing a matrix solution (2,5-dihydroxybenzoic acid, 5 mg/mL in THF), PPO solution (7 mg/mL in THF) and sodium trifluoromethanesulfonate solution as cationization agent (0.1 M in 90% acetone/water = 9:1) with ratio of 2:1:2. For calibration, a polystyrene standard was employed.

Calculation of Polymer Tacticity via NMR Spectroscopy

^{13}C NMR analysis can be used to conveniently determine tacticity of various aliphatic polyethers. For PPO and PBO, 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. For AGE, the deconvolution of the signal at δ=78.9 ppm and analysis of the triad structure can be used to calculate the *m*-value, accordingly. Details for all three polyethers can be found in the cited literature.[4]

Polymerizations

Polymerization Kinetics

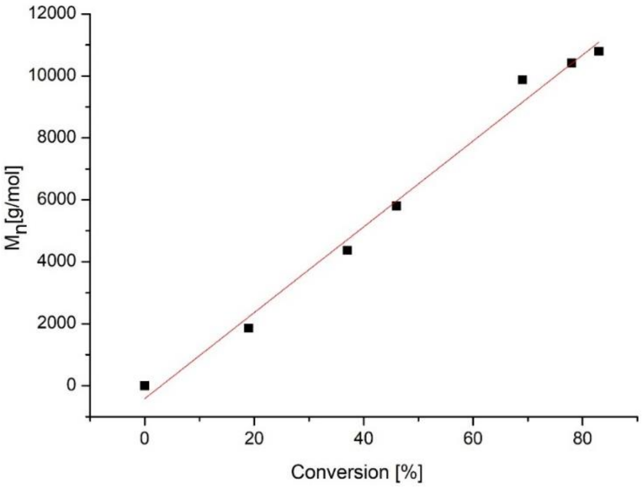

Figure S13. Correlation of molar mass (determined by GPC/$CHCl_3$) vs. conversion for PO polymerization (molar ratio of NHO/**1**/BnOH/PO = 1:2:2,5:500 $[M]_0$ = 2.0 mol/L, THF, T = 25 °C).

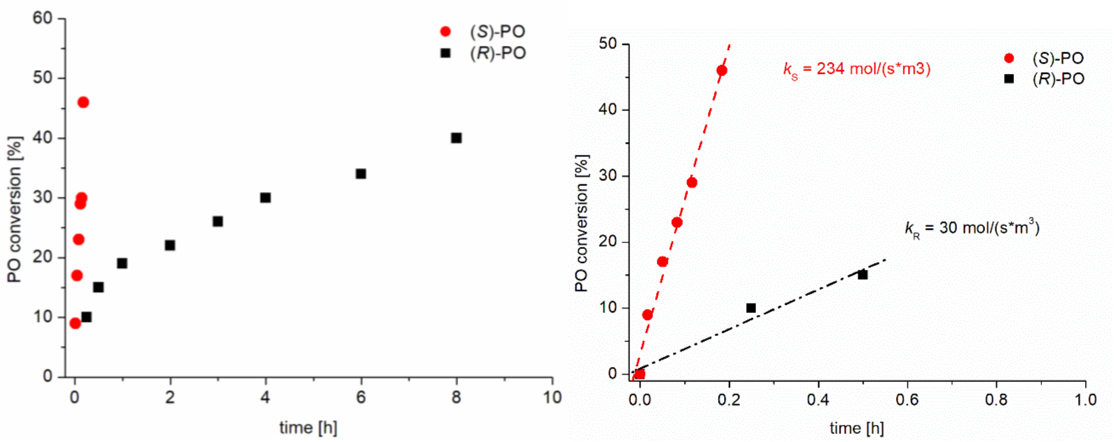

Figure S14. Conversion vs. time using **1** and (*R*)- and (*S*)-PO, respectively, under identical conditions (molar ratio of NHO/**1**/BnOH/PO = 1:2:5:2000, bulk, T = 25 °C).

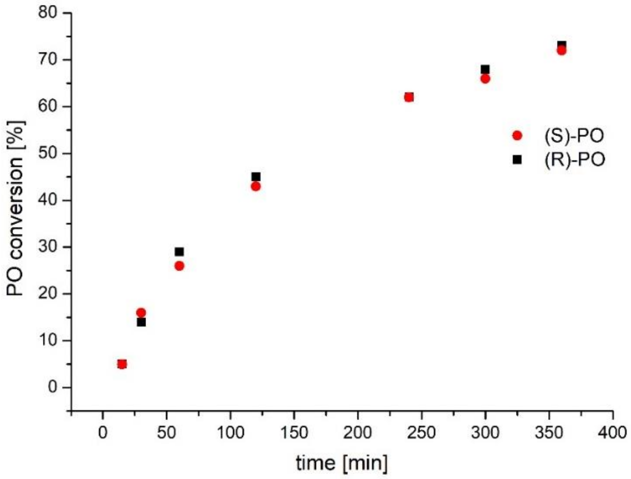

Figure S15. Conversion vs. time using **rac-1** and (*R*)- and (*S*)-PO, respectively, under identical conditions (molar ratio of NHO/**rac-1**/BnOH/PO= 1:2:5:2000, $[M]_0$ = 2.0 mol/L, THF, T = 25 °C).

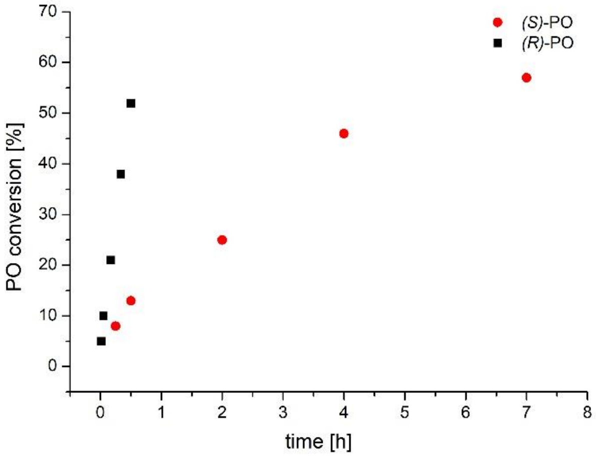

Figure S16. Conversion vs. time using ***(S)*-1** and (*R*)- and (*S*)-PO, respectively, under identical conditions (molar ratio of NHO/*(S)*-**1**/BnOH/PO = 1:2:5:2000, bulk, T = 25 °C).

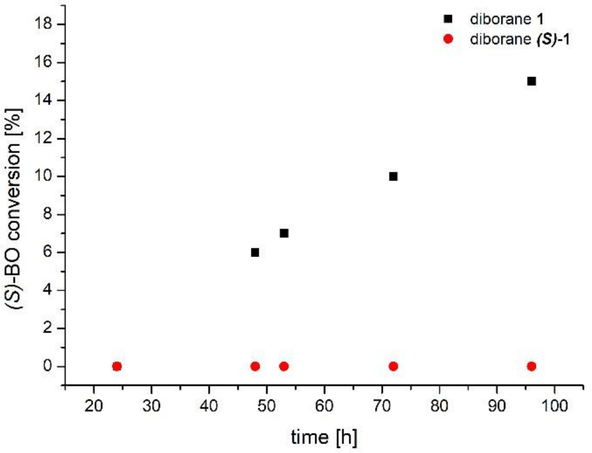

Figure S17. Conversion vs. time using diboranes **1** ((*R*)-configuration)) or ***(S)*-1** and *(S)*-BO, respectively, under identical conditions (molar ratio of NHO/*(S)*-**1**/BnOH/(*S*)-BO = 1:2:2.5:1000, $[M]_0$ = 2.0 mol/L, THF, T = 25 °C).

Polymerization of PO

Table S1. Data set of PO polymerizations using NHO, P_2-tBu and DBU in combination with various diboranes and BnOH (I) as initiator.

#	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} [%]	Conv.^{c} [%]
1	1	NHO	1:2:5:2000	bulk	25	1.5	213 (1.18)	13000	16000	62	53
2	1	NHO	1:2:5:2000	bulk	-36	2.0	279 (1.18)	16000	20000	65	70
3	1	NHO	1:2:5:2000	bulk	-78	3.0	235 (1.17)	15000	18000	66	59
4	1	NHO	1:2:2.5:5000	toluene [2M]	-36	24	743 (1.12)	50000	67000	78	37
5	1	NHO	1:2:2.5:1000	toluene [2M]	-36	24	321 (1.14)	25000	26000	82	80
6	1	NHO	1:2:2.5:5000	Toluene [2M]	25	24	643 (1.05)	44000	54000	75	32
7	1	P_2-tBu	1:2:5:2000	bulk	25	2.0	197 (1.24)	12000	15000	69	49
8	1	P_2-tBu	1:2:5:2000	bulk	-36	3 d	301 (1.16)	24000	24000	68	75
9	1	DBU	1:2:5:2000	bulk	25	24	106 (1.18)	6000	8000	62	27
10	1	NHO	1:2:2.5:1000	toluene [2M]	25	3.0	247 (1.13)	21000	24000	75	62
11	1	NHO	1:2:2.5:1000	toluene [2M]	-36	24	321 (1.14)	25000	26000	82	80
12	1	NHO	1:2:2.5:10000	toluene [2M]	-36	24	2130 (1.18)	123000	111000	79	63
13	1	NHO	1:1:1:1000	bulk	25	32	48 (1.10)	3000	5000	77	5
14	1	NHO	1:1:1:1000	THF [2M]	25	4 d	266 (1.11)	16000	19000	72	27
15	rac-1	NHO	1:2:2.5:1000	bulk	25	20	256 (1.32)	19000	21000	59	64
16	rac-1	NHO	1:2:2.5:1000	THF [2M]	-36	48	138 (1.20)	28000	23000	75	35
17	rac-1	NHO	1:2:2.5:1000	bulk	-36	48	279 (1.22)	20000	21000	63	70
18	rac-1	NHO	1:2:2.5:1000	DCM [2M]	-36	72	44 (1.12)	3000	3000	70	11
19	rac-1	NHO	1:2:2.5:1000	pentane [2M]	-36	72	315 (1.10)	19000	23000	63	79
20	rac-1	NHO	1:2:2.5:1000	toluene [2M]	-36	72	235 (1.13)	14000	18000	80	59
21	2	NHO	1:4:5:1000	bulk	-36	24	88 (1.17)	5000	6000	74	22
22	2	NHO	1:4:5:10000	bulk	-36	24	134 (1.11)	8000	10000	80	7
23	2	NHO	1:2:2.5:1000	THF [4M]	25	24	280 (1.25)	16000	13000	78	70
24	2	NHO	1:2:2.5:1000	THF [2M]	25	8 d	65 (1.14)	4000	5000	88	16
25	2	NHO	1:2:2.5:1000	THF [2M]	50	24	67 (1.15)	4000	4000	73	17
26	2	NHO	1:2:2.5:1000	DCM [4M]	25	6 d	65 (1.17)	4000	4000	65	16
27	2	NHO	1:2:2.5:1000	DCM [2M]	25	12 d	50 (1.16)	3000	4000	75	13
28	2	P_2-tBu	1:4:5:2000	bulk	25	2	253 (1.3)	15000	14000	70	63
29	2	P_2-tBu	1:4:5:2000	bulk	-36	4	67 (1.16)	4000	5000	75	17
30	2	DBU	1:4:5:2000	bulk	25	72	98 (1.23)	6000	5000	68	24
31	3	NHO	1:4:5:2000	bulk	25	5 min	266 (1.21)	15000	14000	58	66
32	3	P_2-tBu	1:4:5:2000	bulk	-36	1 min	303 (1.18)	18000	18000	57	75
33	3	DBU	1:4:5:2000	bulk	25	30 min	260 (1.06)	15000	15000	56	65
34	3	DBU	1:4:5:2000	bulk	-36	24	281 (1.26)	16000	19000	57	70
35	4	DBU	1:4:5:2000	bulk	25	24	207 (1.18)	12000	12000	57	52
36	4	DBU	1:4:5:5000	bulk	-36	72	853 (1.22)	49000	43000	56	85

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 (CDCl3). d) diad placement determined *via* ^{13}C NMR spectroscopy.

Polymerization of 1-Butylene oxide (BO)

Table S2. Data set of BO polymerization using diborane (C)/NHO in combination with BnOH (I) as initiator.

#	Cat (C)	NHO/C/I/BO (molar)	solvent [BO]	T [°C]	t [h]	x^a ($Đ_M$)^b	$M_{n(calc)}$^{c} [g/mol]	$M_{n(GPC)}$^{b} [g/mol]	*m*^{d} [%]	Conv.^{c} [%]
1	1	1:2:2.5:10000	toluene [2M]	-36	19 d	142 (1.36)	10300	10300	85	4
2	1	1:2:2.5:1000	toluene [2M]	-36	10 d	59 (1.13)	4300	4200	84	15
3	1	1:2:2.5:1000	toluene [2M]	25	3 d	109 (1.16)	8000	7900	75	27
4	2	1:2:2.5:1000	bulk	25	24	42 (1.17)	3100	3000	75	14
5	2	1:2:2.5:1000	THF [2M]	25	3 d	44 (1.07)	3300	3100	72	15
6	2	1:2:2.5:1000	bulk	-36	48	86 (1.16)	6300	6400	85	20

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 spectroscopy ($CDCl_3$). d) diad placement determined *via* ^{13}C NMR spectroscopy.

Polymerization of Allyl Glycidyl Ether (AGE)

Table S3. Data set of AGE polymerization using diborane (C)/NHO in combination with BnOH (I) as initiator.

#	Cat (C)	NHO/C/I/AGE (molar)	solvent [AGE]	T [°C]	t [h]	x^a ($Đ_M$)^b	$M_{n(calc)}$^{c} [g/mol]	$M_{n(GPC)}$^{b} [g/mol]	*m*^{d} [%]	Conv.^{c} [%]
1	1	1:2:2.5:10000	toluene [2M]	-36	14 d	114 (1.33)	13100	12700	62	53
2	1	1:2:2.5:1000	bulk	-36	24	272 (1.15)	31100	31300	78	70

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 spectroscopy ($CDCl_3$). d) diad placement determined *via* ^{13}C NMR spectroscopy.

Preparation of Block Copolymers

Table S4. Preparation of block copolymers using different macroinitiators (I) and *rac*-PO as monomer in the presence of **1**/NHO.

#	Initiator	NHO/**1**/I/PO (molar)	solvent [PO]	T [°C]	t [h]	x^a ($Đ_M$)^b	$M_{n(GPC)}$^{b} [g/mol]	m^c [%]	Conv.^{d} [%]
1	PCL10K	1:2:2.5:1000	toluene [2M]	25	48	211 (1.24)	38000	80	53
2	PCL7K	1:2:2.5:1000	toluene [2M]	25	20	150(1.20)	12000	76	38
3	PCL2K	1:2:2.5:1000	toluene [2M]	25	4 d	53(1.20)	6000	77	13
4	PCL11K-diol	1:2:2.5:1000	toluene [2M]	25	24	124 (1.16)	13000	76	31
5	PEO8K	1:2:2.5:2000	bulk	25	2.5	780 (1.11)	84000	67	97
6	PLA20K	1:2:2.5:1000	THF [2M]	25	7 d	106 (1.23)	47000	68	27

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

Representative Examples for Stereoanalysis via ^{13}C NMR

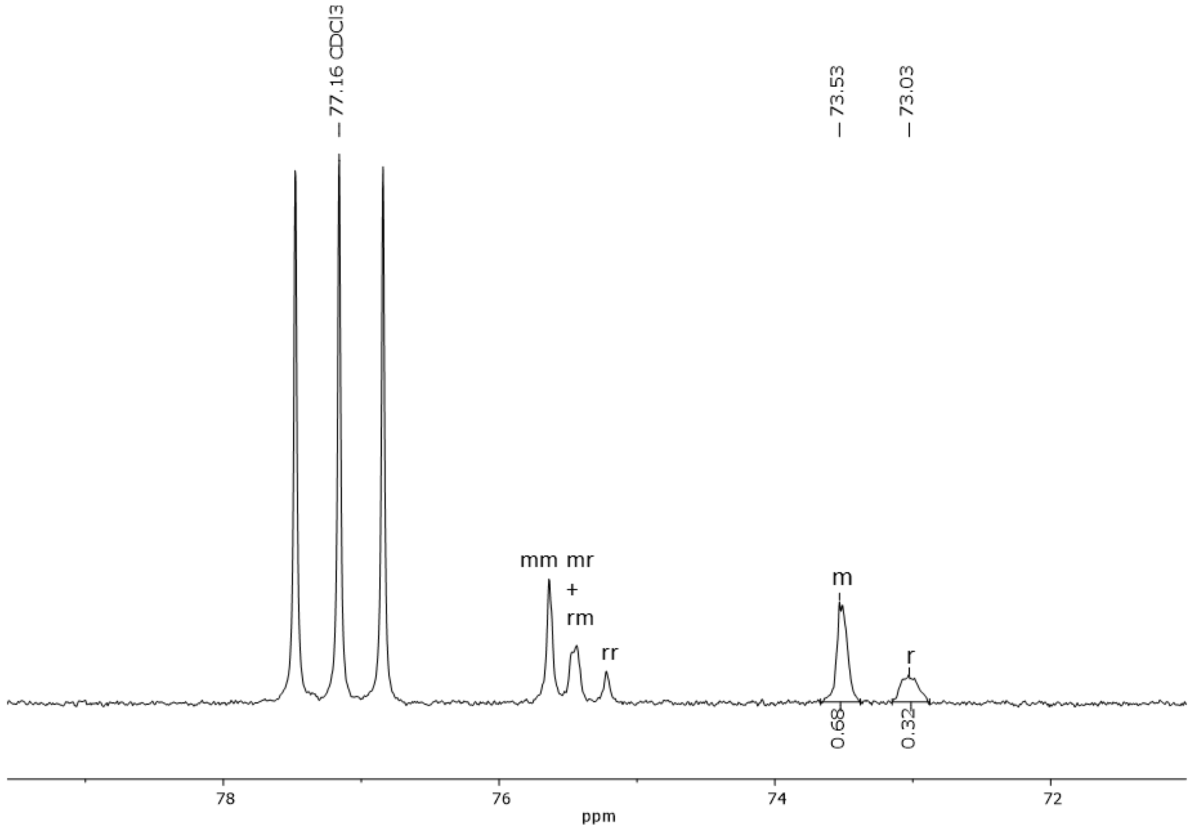

Figure S18. ^{13}C NMR analysis (CDCl$_3$, 300 K) with diad/triad sequence assignment of PPO. Polymer resulting from application of NHO/**1** after 3 h at -85 °C.

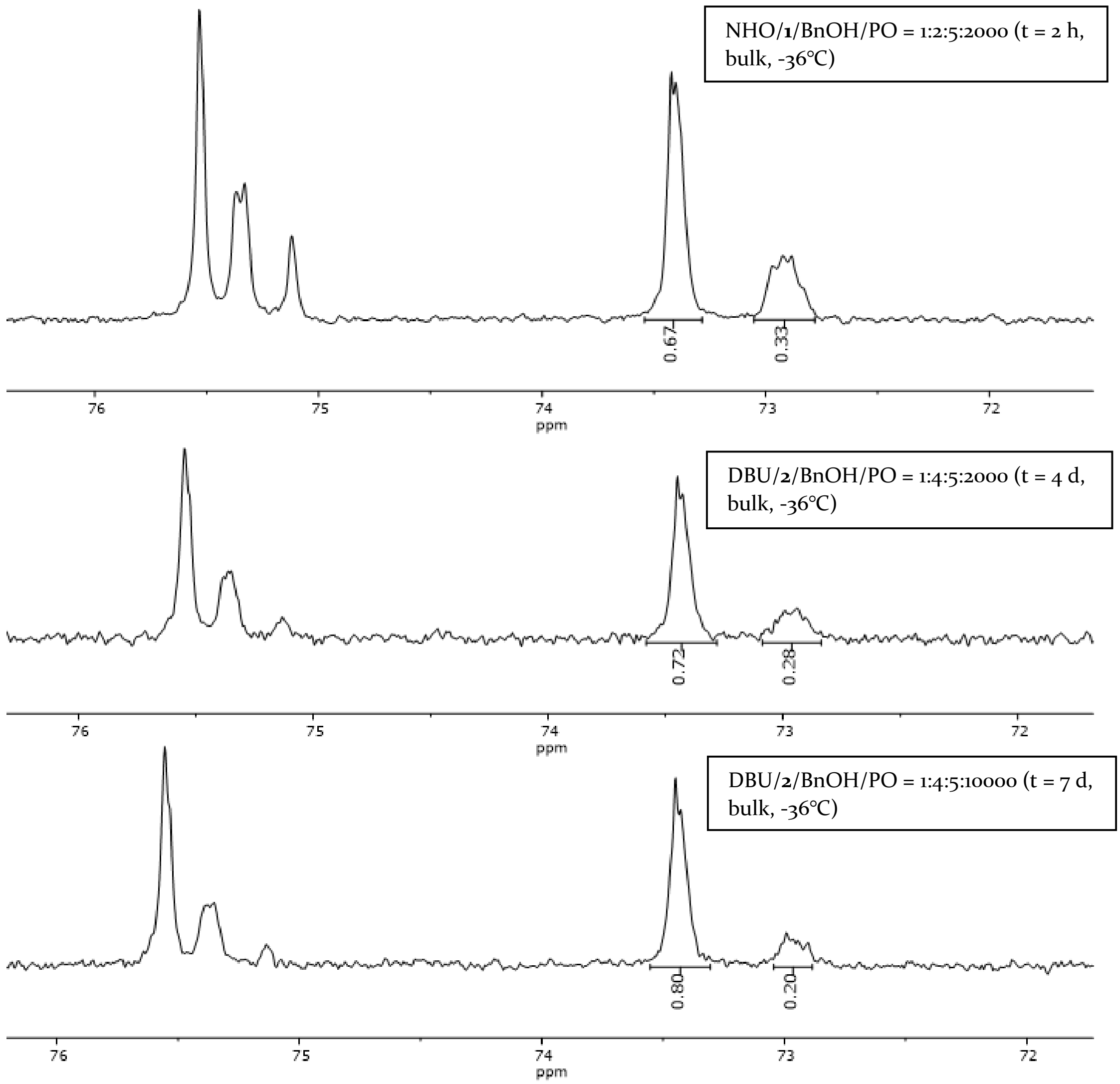

Figure S19. Examples of ^{13}C NMR analysis (CDCl$_3$, 300 K) with diad sequence analysis of PPO prepared under different conditions.

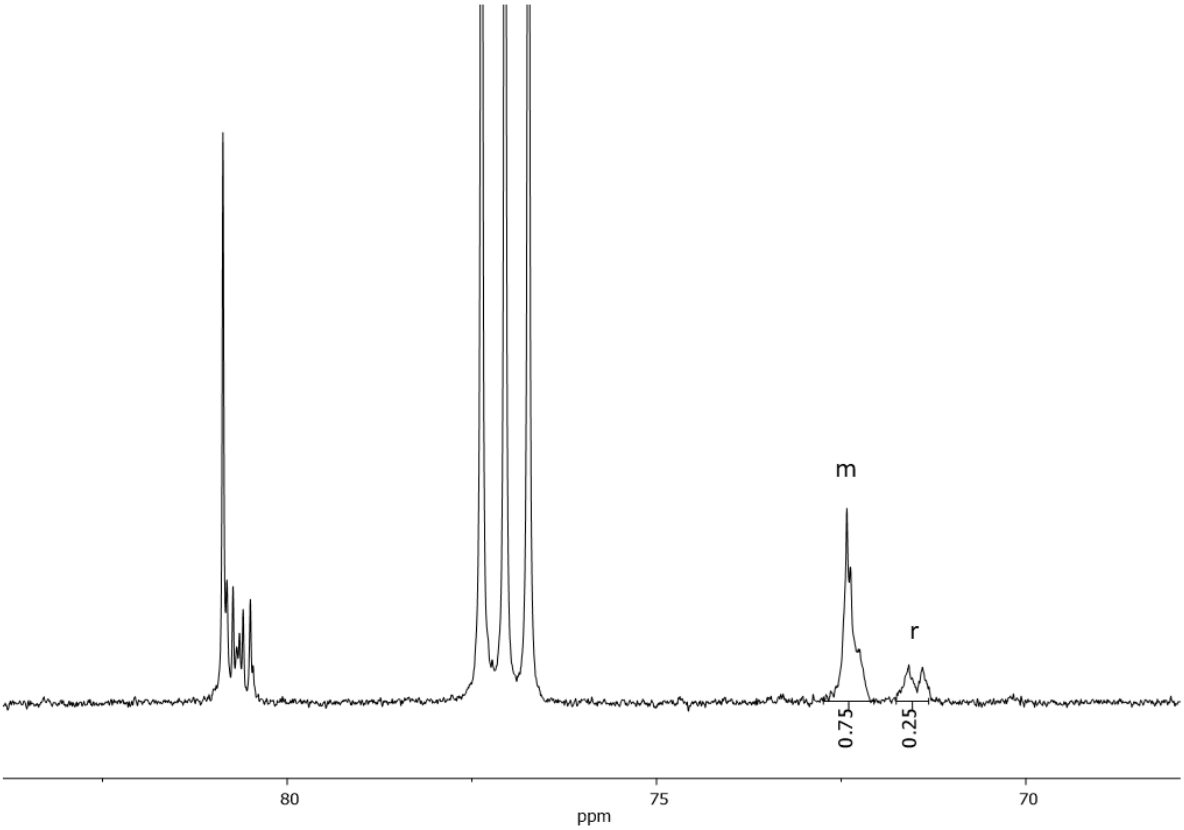

Figure S20. Example for ^{13}C NMR analysis ($CDCl_3$, 300 K) with diad sequence analysis of PBO resulting from application NHO/**1** after 72 h at room temperature.

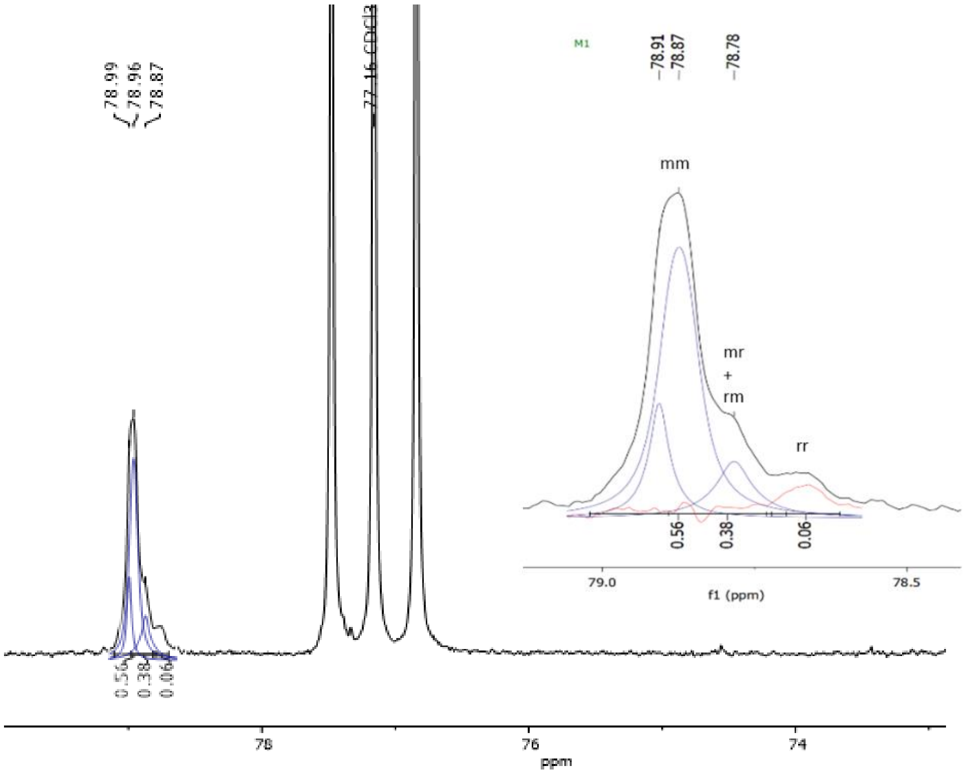

Figure S21. Example for ^{13}C NMR spectroscopy ($CDCl_3$, 300 K) with triad sequence analysis of PAGE resulting from application NHO/**1** after 14 d at -36 °C.

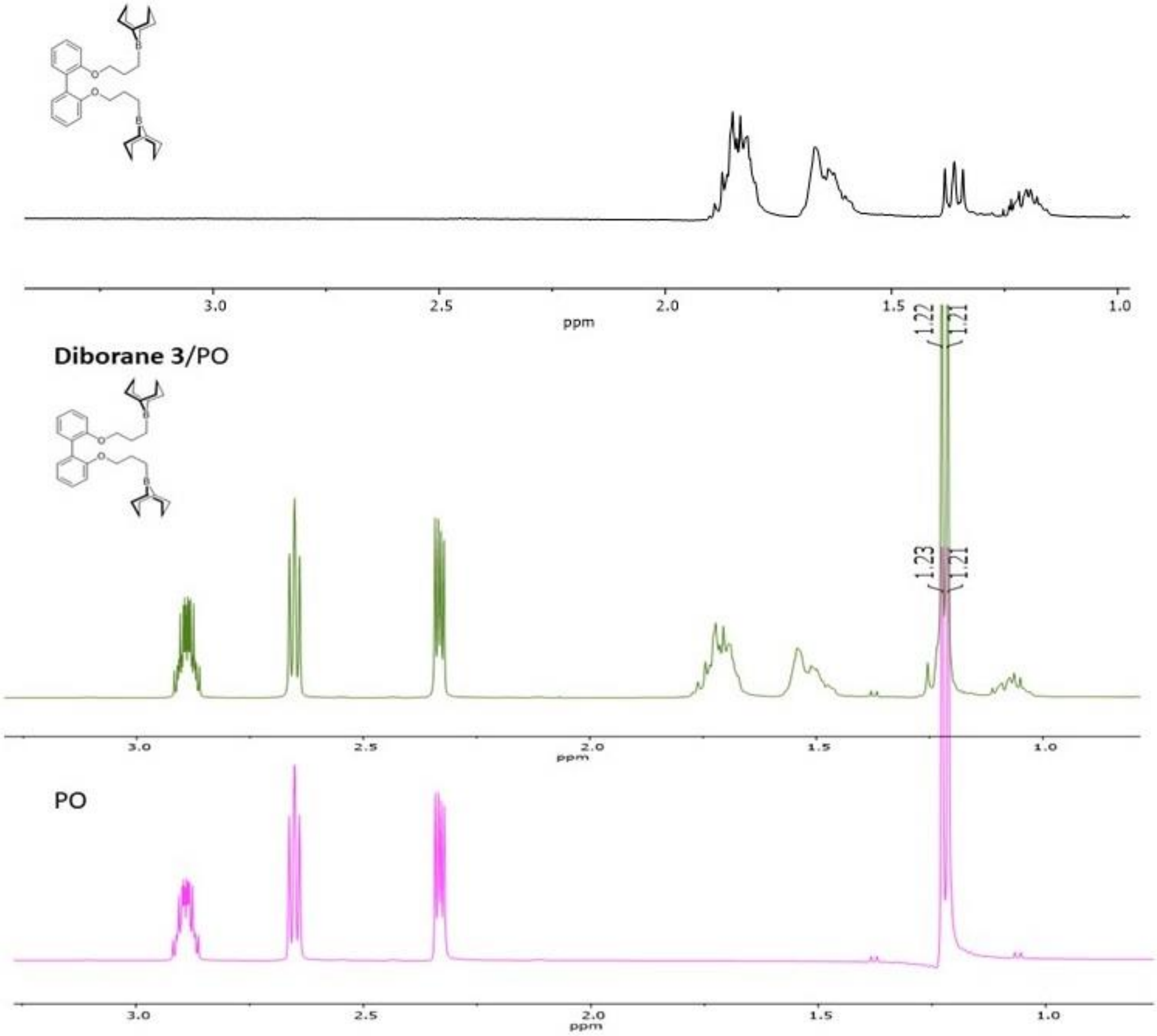

Figure S22. ^{1}H NMR analysis ($CDCl_3$, 400 MHz) of PO in the presence of diborane **3** (middle); the separate compounds are shown top and bottom.

DSC Analysis

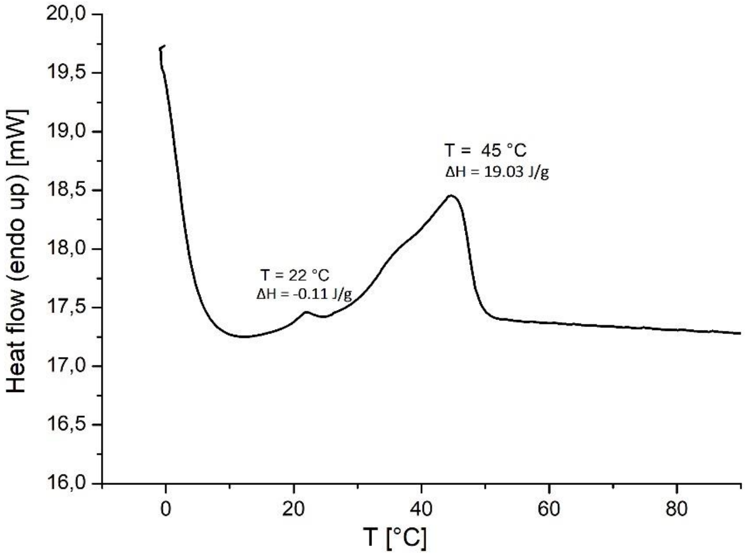

Figure S23. DSC investigation (5K/min, second cycle) of PPO with *m* = 88 % (semicrystalline).

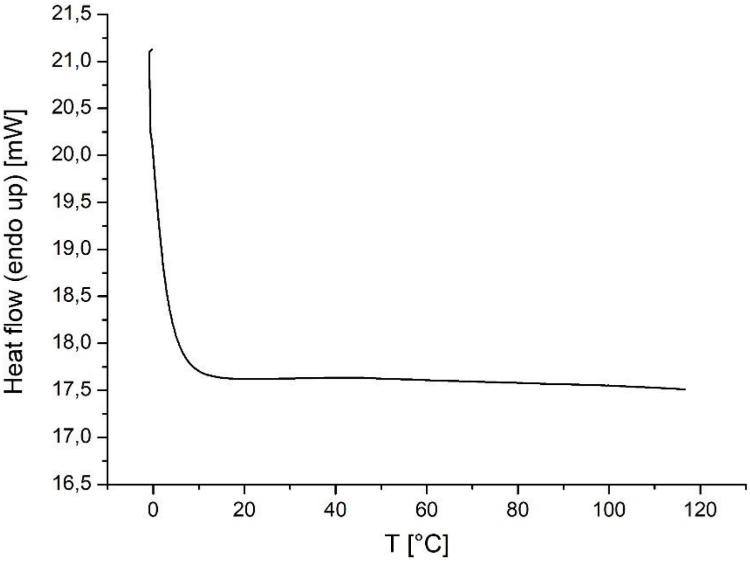

Figure S24. DSC investigation (5K/min, second cycle) of PPO with *m* = 65 % (amorphous).

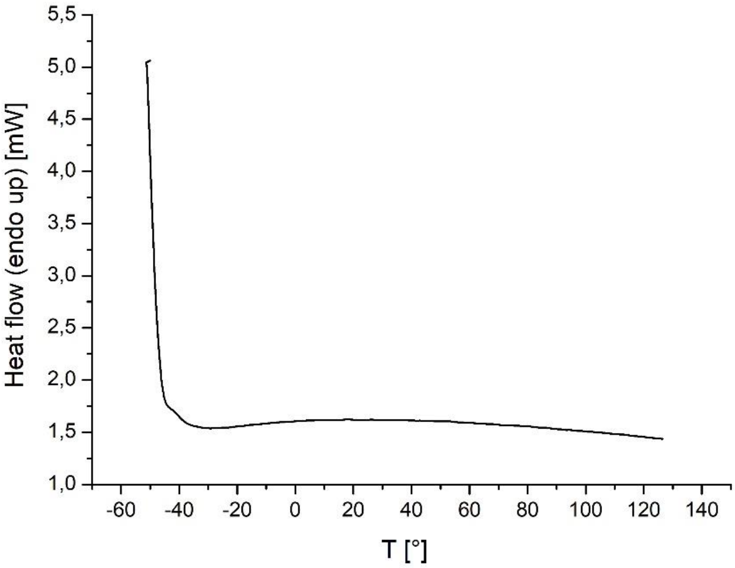

Figure S25. DSC investigation (5K/min, second cycle) of PBO with m = 75 % (amorphous).

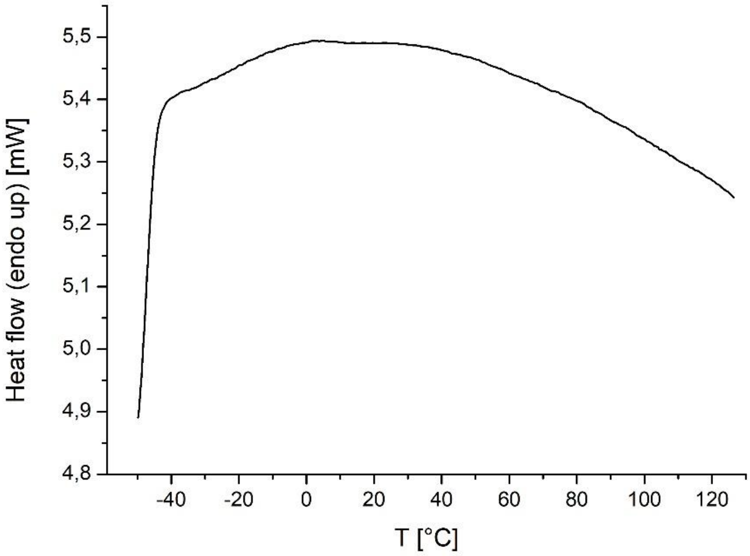

Figure S26. DSC investigation (5K/min, second cycle) of PAGE with m = 62 % (amorphous).

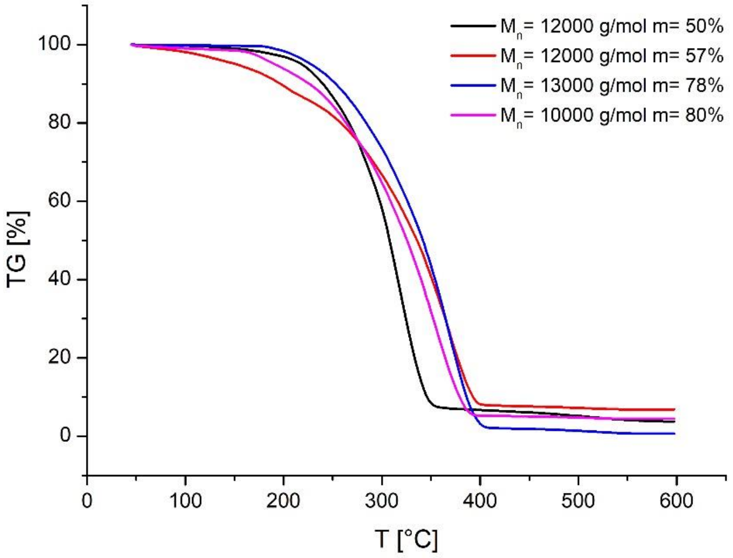

Figure S27. TGA curves of PPO recorded between 45 °C and 600 °C applying a heating rate of 10 K/min.

^{1}H-DOSY NMR Analysis

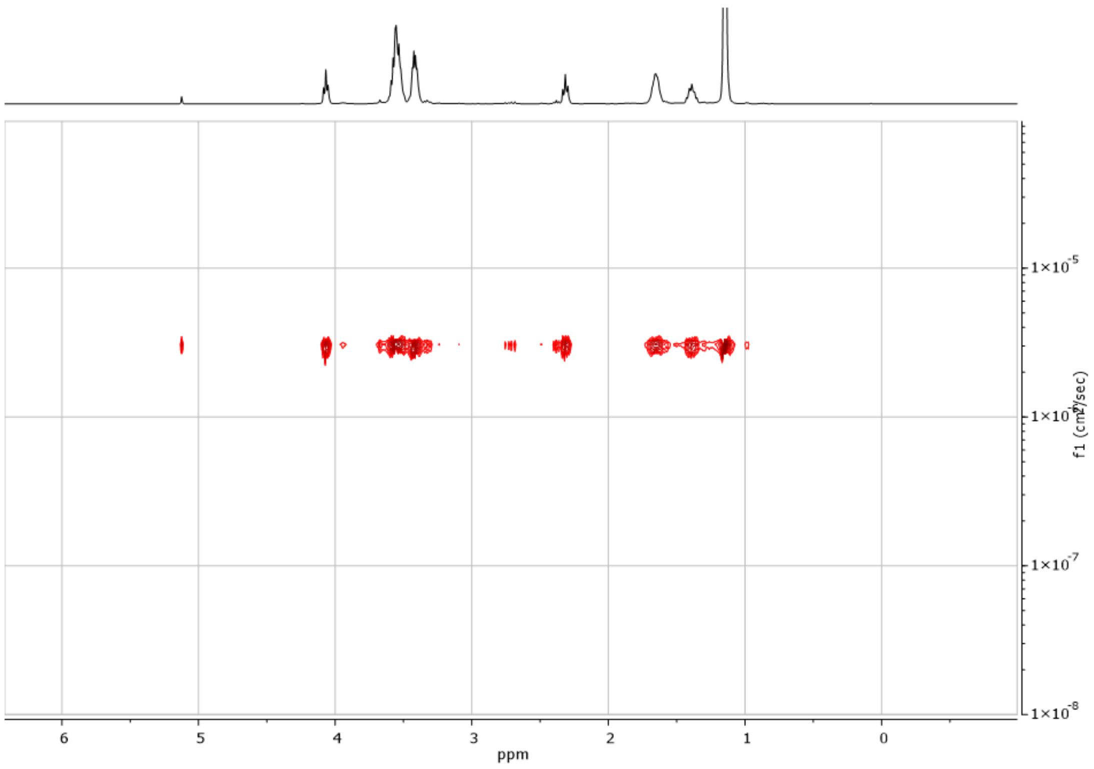

Figure S28. ^{1}H-DOSY NMR analysis of PCL-*b*-(*it*)-PPO. Conditions: NHO/**1**/PCL2K/PO = 1:2:2.5:1000, $[PO]_0$ = 2.0 mol/L, toluene, T = 25 °C, see Table S4, entry 3).

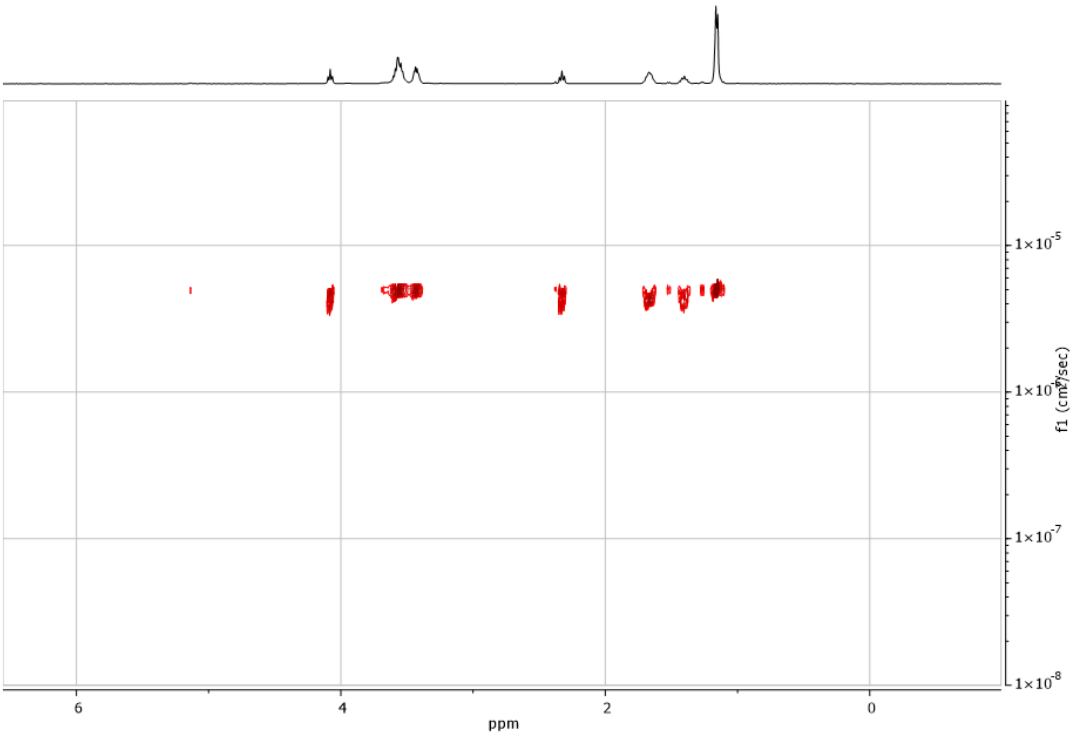

Figure S29. ^{1}H-DOSY NMR analysis of PCL-*b*-(*it*)-PPO. Conditions: NHO/**1**/PCL7K/PO = 1:2:2.5:1000, [PO]$_0$ = 2.0 mol/L, toluene, T = 25 °C, see Table S4, entry 2).

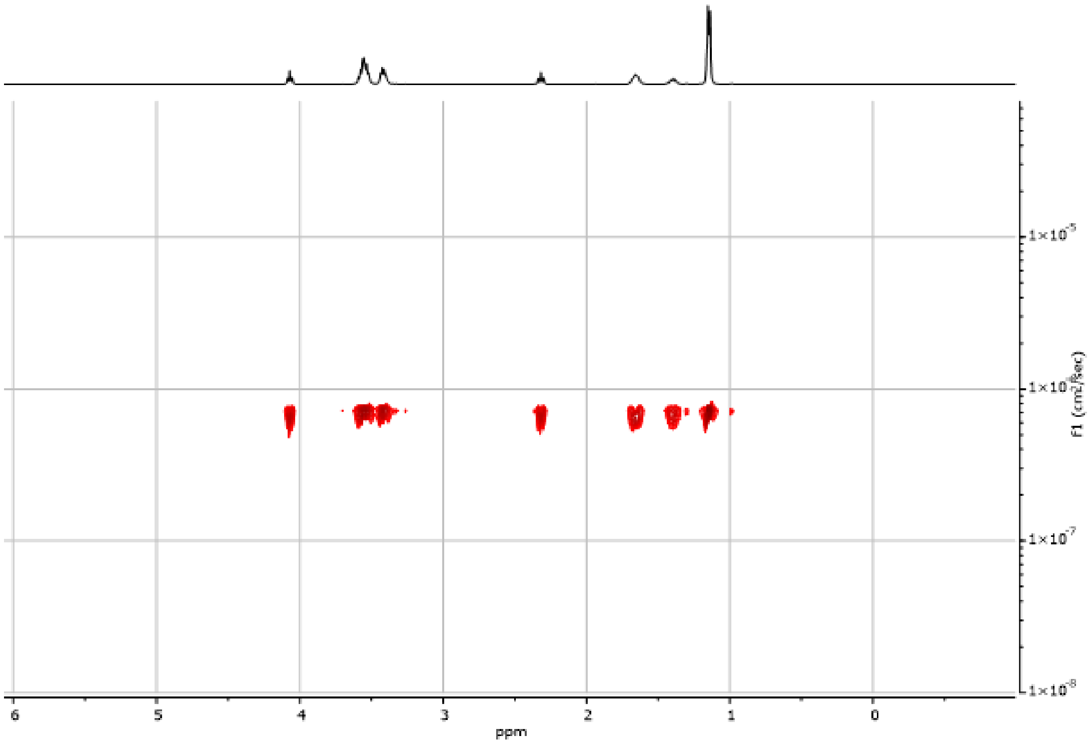

Figure S30. ^{1}H-DOSY NMR analysis of PCL-*b*-(*it*)-PPO. Conditions: NHO/**1**/PCL10K/PO = 1:2:2.5:1000, [PO]$_0$ = 2.0 mol/L, Toluene, T = 25 °C, see Table S4, entry 1.

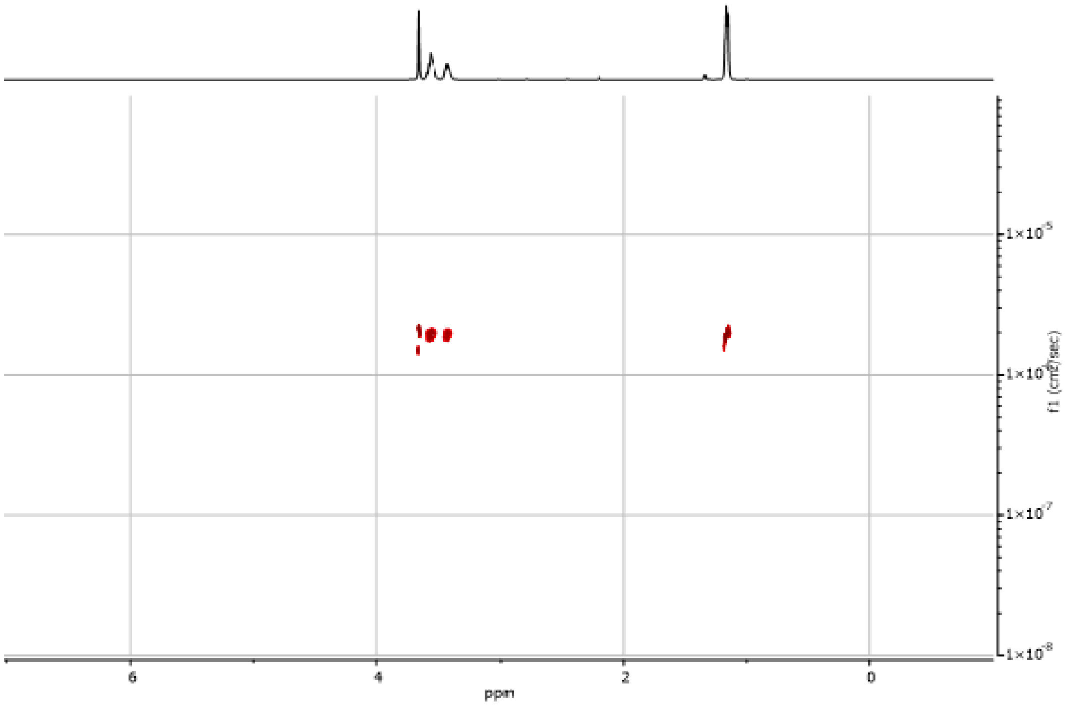

Figure S31. ^{1}H-DOSY NMR analysis of (*it*)-PPO-*b*-PEO-*b*-(*it*)-PPO. Conditions: NHO/**1**/PEO8K/PO = 1:2:2.5:2000, bulk, T = 25 °C, see Table S4, entry 4.

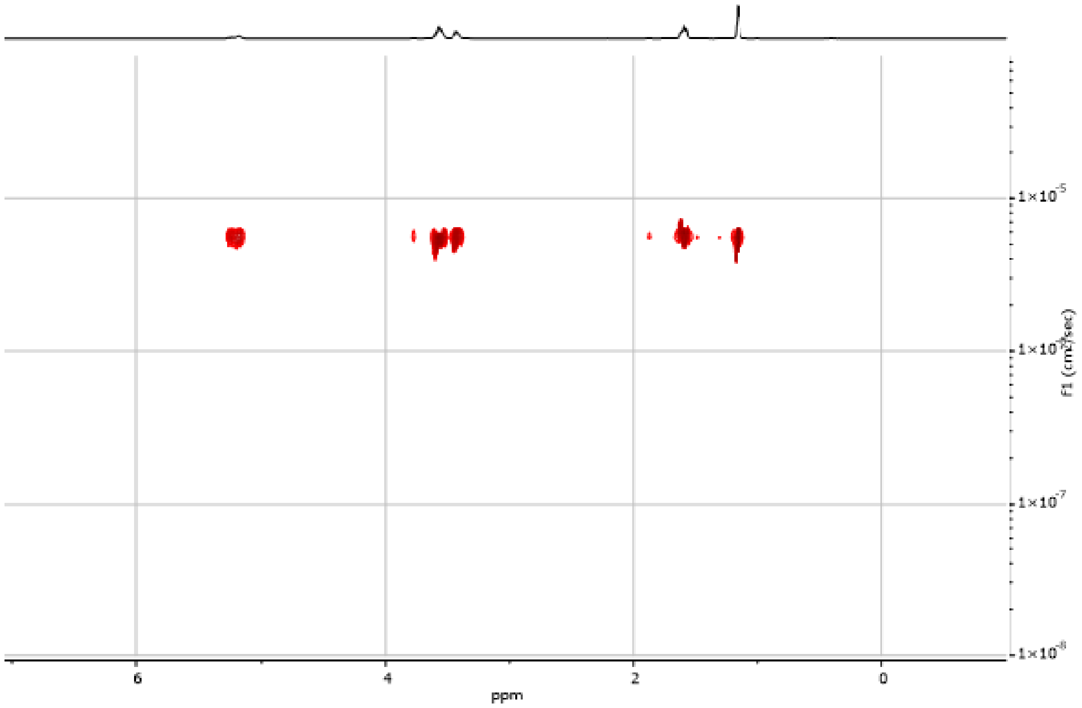

Figure S32. ^{1}H-DOSY NMR spectroscopy of PLA-*b*-(*it*)-PPO. Conditions: NHO/**1**/PLA/PO = 1:2:2.5:1000, $[PO]_0$ = 2.0 mol/L, THF, T = 25 °C, see Table S4, entry 5.

GPC traces, PPO and Copolymers

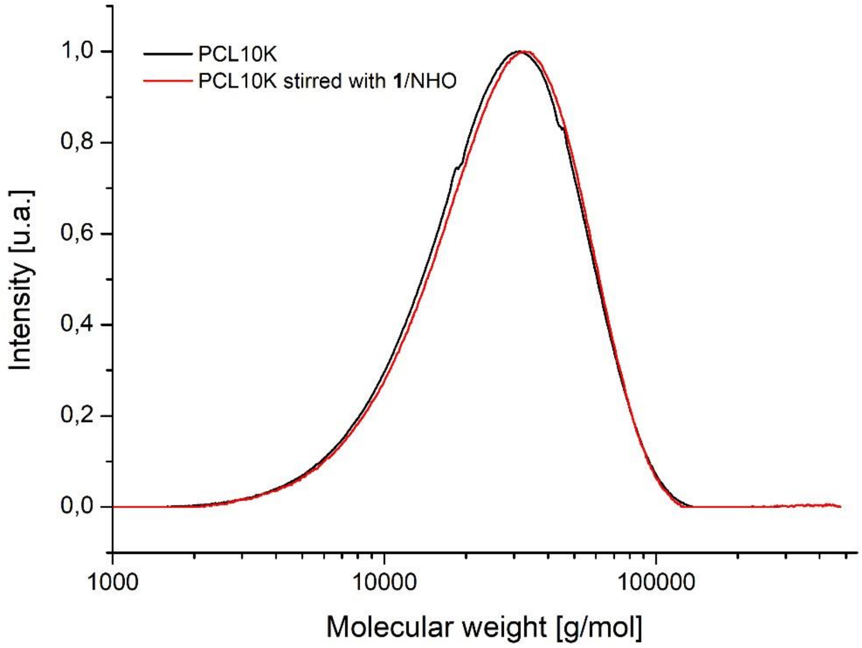

Figure S33. GPC trace received from PCL10K (starting material) and PCL10K stirred in the presence of diborane **1**/NHO (THF, no PO) for 24 h at RT.

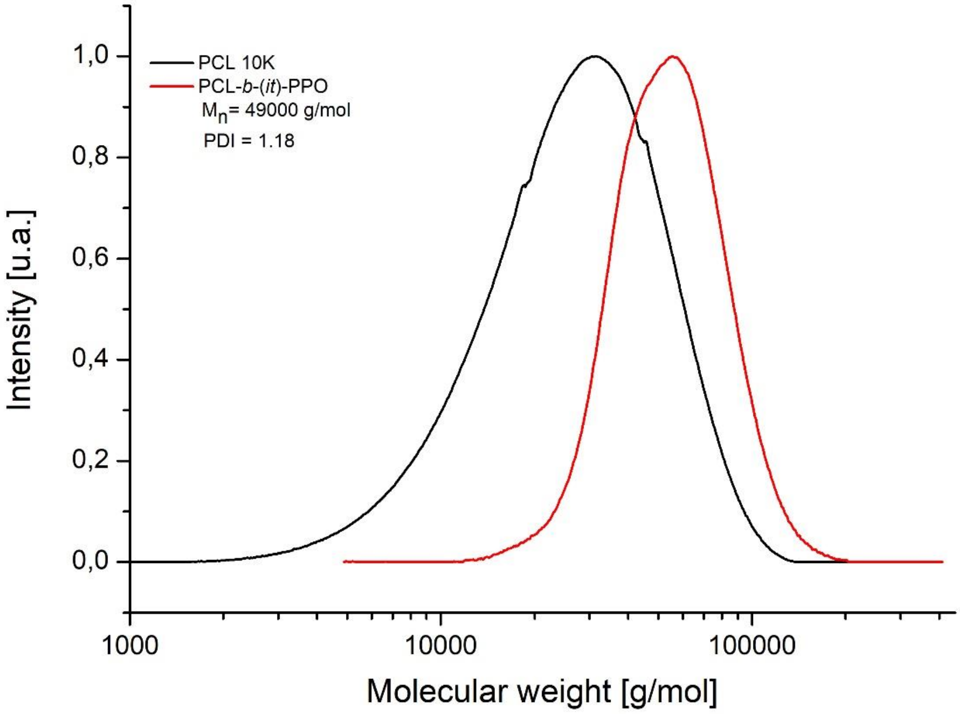

Figure S34. GPC trace received from PCL10K (macroinitiator) and after polymerization of PO (PCL-*b*-(*it*)-PPO).

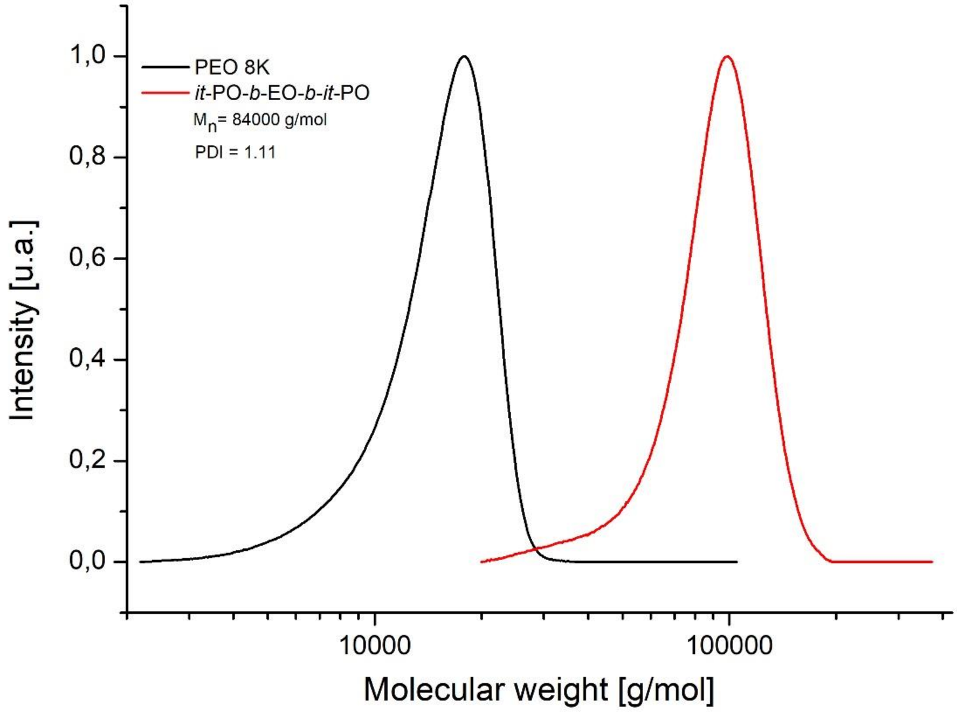

Figure S35. GPC trace received from PEO8K (macroinitiator) and after polymerization of PO ((*it*)-PPO-*b*-PEO-*b*-(*it*)-PPO).

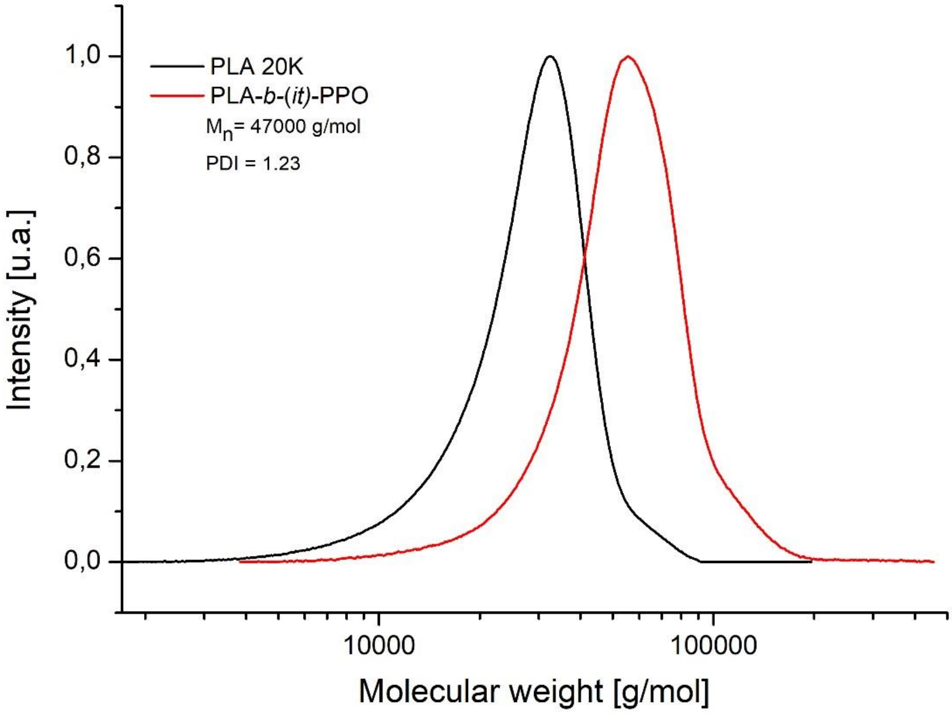

Figure S36. GPC trace received from PLA20K (macroinitiator) and after polymerization of PO (PLA-*b*-(*it*)-PPO)

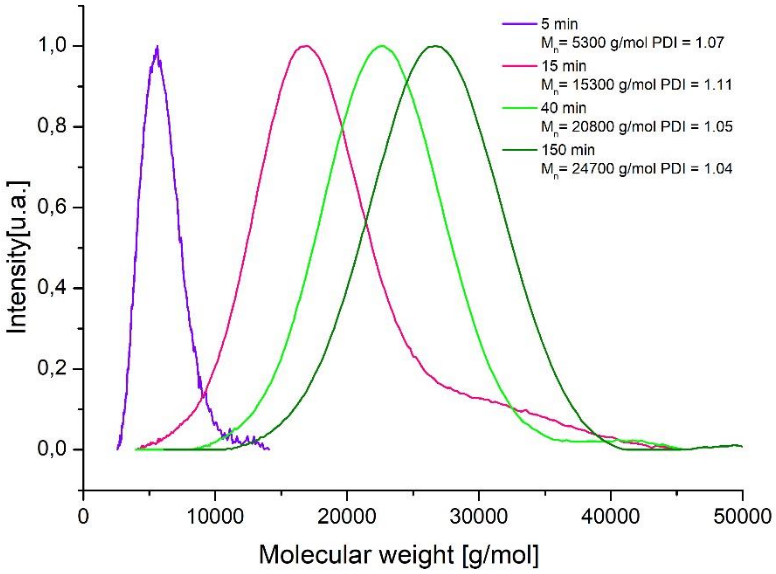

Figure S37. GPC traces received from polymerization of (*S*)-PO using **1**/NHO. Conditions: NHO/**1**/BnOH/(S)-PO = 1:2:5:2000 $[M]_0$ = 2.0 mol/L, THF, room temperature.

Crystal Structure Analysis, Tabular Data for Diborane 1

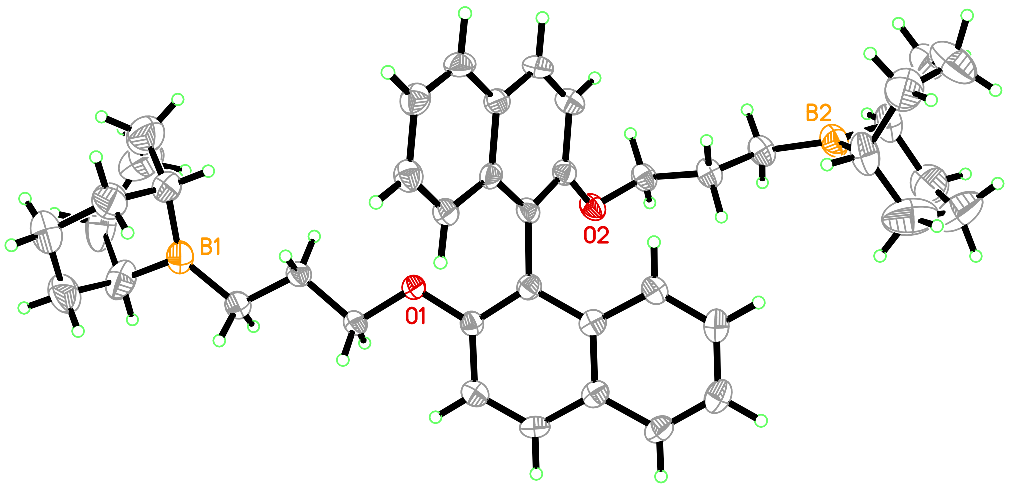

Figure S38. Single crystal X-ray structure of diborane **1**.

Empirical formula	C42 H52 B2 O2
Formula weight	610.45
Temperature	140(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 11.4900(7) Å α = 90°
	b = 7.2911(6) Å β = 93.200(4)°
	c = 20.7910(16) Å γ = 90°
Volume	1739.0(2) Å^3
Z	2
Calculated density	1.166 Mg/m^3
Absorption coefficient	0.518 mm^{-1}
F(000)	660
Crystal size	0.223 x 0.100 x 0.025 mm
Theta range for data collection	2.128 to 65.995 deg.
Limiting indices	-13<=h<=10, -8<=k<=8, -23<=l<=24
Reflections collected / unique	21005 / 5877 [R(int) = 0.0605]
Completeness to theta = 65.995	98.3 %

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.6606
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5877 / 13 / 415
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0484, wR2 = 0.1187
R indices (all data)	R1 = 0.0680, wR2 = 0.1278
Absolute structure parameter	0.04(21)
Extinction coefficient	n/a
Largest diff. peak and hole	0.364 and -0.222 e.A^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for buch350. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	3621(2)	7575(4)	5252(1)	27(1)
C(1)	3796(3)	7488(5)	4138(2)	24(1)
B(1)	2773(4)	7285(7)	7587(2)	39(1)
C(2)	4332(3)	7674(5)	4748(2)	23(1)
O(2)	2992(2)	4186(3)	3677(1)	30(1)
B(2)	2520(4)	1897(7)	1350(2)	42(1)
C(3)	5544(3)	7918(5)	4837(2)	28(1)
C(4)	6217(3)	7938(5)	4320(2)	29(1)
C(5)	5730(3)	7771(5)	3688(2)	27(1)
C(6)	6423(3)	7821(5)	3142(2)	31(1)
C(7)	5930(3)	7708(5)	2536(2)	35(1)

C(8)	4715(3)	7582(5)	2434(2)	33(1)
C(9)	4020(3)	7539(5)	2948(2)	28(1)
C(10)	4498(3)	7597(5)	3591(2)	24(1)
C(11)	4151(3)	7731(5)	5892(2)	26(1)
C(12)	3202(3)	7649(6)	6358(2)	27(1)
C(13)	3680(3)	7592(6)	7058(2)	31(1)
C(14)	3142(4)	6967(7)	8316(2)	54(1)
C(15)	2277(6)	5525(8)	8627(2)	75(2)
C(16)	1282(5)	4890(9)	8137(3)	82(2)
C(17)	646(5)	6272(9)	7801(3)	73(2)
C(18)	1435(3)	7644(8)	7489(2)	52(1)
C(19)	1330(4)	9561(7)	7787(2)	55(1)
C(20)	1761(4)	9655(7)	8492(2)	54(1)
C(21)	2995(4)	8909(8)	8602(2)	56(1)
C(22)	2516(3)	7125(5)	4033(2)	24(1)
C(23)	2142(3)	5473(5)	3766(2)	25(1)
C(24)	951(3)	5135(5)	3606(2)	32(1)
C(25)	144(3)	6462(5)	3722(2)	31(1)
C(26)	467(3)	8147(5)	4008(2)	26(1)
C(27)	-362(3)	9518(6)	4137(2)	31(1)
C(28)	-48(3)	11113(6)	4432(2)	34(1)
C(29)	1131(3)	11435(6)	4607(2)	32(1)
C(30)	1965(3)	10170(5)	4483(2)	28(1)
C(31)	1663(3)	8483(5)	4175(2)	24(1)
C(32)	2756(3)	2691(5)	3235(2)	30(1)
C(33)	2700(3)	3271(5)	2537(2)	32(1)
C(34)	2620(3)	1604(6)	2093(2)	36(1)
C(35)	2546(4)	3767(6)	988(2)	52(1)
C(36)	1477(5)	3897(8)	514(3)	68(2)
C(37)	1288(5)	2275(10)	77(3)	85(2)
C(38)	1446(5)	419(8)	386(3)	66(2)

C(39)	2517(4)	242(7)	871(2)	50(1)
C(40)	3698(5)	322(9)	566(3)	68(2)
C(41)	3969(5)	2139(11)	265(3)	90(2)
C(42)	3724(5)	3796(9)	665(4)	88(2)

Table 3. Bond lengths [A] and angles [deg] for buch350.

O(1)-C(2)	1.368(4)
O(1)-C(11)	1.436(4)
C(1)-C(2)	1.384(4)
C(1)-C(10)	1.434(4)
C(1)-C(22)	1.499(4)
B(1)-C(18)	1.561(6)
B(1)-C(14)	1.569(6)
B(1)-C(13)	1.574(5)
C(2)-C(3)	1.405(4)
O(2)-C(23)	1.374(4)
O(2)-C(32)	1.442(4)
B(2)-C(35)	1.558(7)
B(2)-C(34)	1.557(6)
B(2)-C(39)	1.564(7)
C(3)-C(4)	1.358(5)
C(3)-H(3)	0.9500
C(4)-C(5)	1.404(5)
C(4)-H(4)	0.9500
C(5)-C(10)	1.424(4)
C(5)-C(6)	1.425(5)
C(6)-C(7)	1.355(5)
C(6)-H(6)	0.9500

C(7)-C(8)	1.403(5)
C(7)-H(7)	0.9500
C(8)-C(9)	1.370(5)
C(8)-H(8)	0.9500
C(9)-C(10)	1.415(4)
C(9)-H(9)	0.9500
C(11)-C(12)	1.499(4)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.527(4)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(21)	1.549(7)
C(14)-C(15)	1.607(8)
C(14)-H(14)	1.0000
C(15)-C(16)	1.558(8)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(17)	1.409(8)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.519(7)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.535(7)
C(18)-H(18)	1.0000
C(19)-C(20)	1.524(6)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900

C(20)-C(21)	1.524(7)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-C(23)	1.385(5)
C(22)-C(31)	1.434(5)
C(23)-C(24)	1.412(5)
C(24)-C(25)	1.371(5)
C(24)-H(24)	0.9500
C(25)-C(26)	1.406(5)
C(25)-H(25)	0.9500
C(26)-C(27)	1.417(5)
C(26)-C(31)	1.421(5)
C(27)-C(28)	1.354(5)
C(27)-H(27)	0.9500
C(28)-C(29)	1.403(5)
C(28)-H(28)	0.9500
C(29)-C(30)	1.365(5)
C(29)-H(29)	0.9500
C(30)-C(31)	1.421(5)
C(30)-H(30)	0.9500
C(32)-C(33)	1.509(5)
C(32)-H(32A)	0.9900
C(32)-H(32B)	0.9900
C(33)-C(34)	1.526(5)
C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900
C(34)-H(34A)	0.9900
C(34)-H(34B)	0.9900
C(35)-C(36)	1.533(7)

C(35)-C(42)	1.544(8)
C(35)-H(35)	1.0000
C(36)-C(37)	1.501(8)
C(36)-H(36A)	0.9900
C(36)-H(36B)	0.9900
C(37)-C(38)	1.504(9)
C(37)-H(37A)	0.9900
C(37)-H(37B)	0.9900
C(38)-C(39)	1.553(7)
C(38)-H(38A)	0.9900
C(38)-H(38B)	0.9900
C(39)-C(40)	1.531(7)
C(39)-H(39)	1.0000
C(40)-C(41)	1.505(9)
C(40)-H(40A)	0.9900
C(40)-H(40B)	0.9900
C(41)-C(42)	1.503(10)
C(41)-H(41A)	0.9900
C(41)-H(41B)	0.9900
C(42)-H(42A)	0.9900
C(42)-H(42B)	0.9900

C(2)-O(1)-C(11)	117.7(2)
C(2)-C(1)-C(10)	118.7(3)
C(2)-C(1)-C(22)	122.3(3)
C(10)-C(1)-C(22)	119.0(3)
C(18)-B(1)-C(14)	111.2(4)
C(18)-B(1)-C(13)	124.8(4)
C(14)-B(1)-C(13)	122.9(4)
O(1)-C(2)-C(1)	116.3(3)
O(1)-C(2)-C(3)	122.4(3)

C(1)-C(2)-C(3)	121.4(3)
C(23)-O(2)-C(32)	119.5(3)
C(35)-B(2)-C(34)	126.6(4)
C(35)-B(2)-C(39)	111.5(4)
C(34)-B(2)-C(39)	121.5(4)
C(4)-C(3)-C(2)	120.0(3)
C(4)-C(3)-H(3)	120.0
C(2)-C(3)-H(3)	120.0
C(3)-C(4)-C(5)	121.6(3)
C(3)-C(4)-H(4)	119.2
C(5)-C(4)-H(4)	119.2
C(4)-C(5)-C(10)	118.8(3)
C(4)-C(5)-C(6)	122.2(3)
C(10)-C(5)-C(6)	118.9(3)
C(7)-C(6)-C(5)	121.1(3)
C(7)-C(6)-H(6)	119.4
C(5)-C(6)-H(6)	119.4
C(6)-C(7)-C(8)	120.3(3)
C(6)-C(7)-H(7)	119.8
C(8)-C(7)-H(7)	119.8
C(9)-C(8)-C(7)	120.1(3)
C(9)-C(8)-H(8)	119.9
C(7)-C(8)-H(8)	119.9
C(8)-C(9)-C(10)	121.6(3)
C(8)-C(9)-H(9)	119.2
C(10)-C(9)-H(9)	119.2
C(9)-C(10)-C(5)	117.9(3)
C(9)-C(10)-C(1)	122.8(3)
C(5)-C(10)-C(1)	119.4(3)
O(1)-C(11)-C(12)	108.0(2)
O(1)-C(11)-H(11A)	110.1

C(12)-C(11)-H(11A)	110.1
O(1)-C(11)-H(11B)	110.1
C(12)-C(11)-H(11B)	110.1
H(11A)-C(11)-H(11B)	108.4
C(11)-C(12)-C(13)	112.4(3)
C(11)-C(12)-H(12A)	109.1
C(13)-C(12)-H(12A)	109.1
C(11)-C(12)-H(12B)	109.1
C(13)-C(12)-H(12B)	109.1
H(12A)-C(12)-H(12B)	107.9
C(12)-C(13)-B(1)	117.0(3)
C(12)-C(13)-H(13A)	108.1
B(1)-C(13)-H(13A)	108.1
C(12)-C(13)-H(13B)	108.1
B(1)-C(13)-H(13B)	108.1
H(13A)-C(13)-H(13B)	107.3
C(21)-C(14)-B(1)	101.9(4)
C(21)-C(14)-C(15)	111.1(4)
B(1)-C(14)-C(15)	110.2(4)
C(21)-C(14)-H(14)	111.1
B(1)-C(14)-H(14)	111.1
C(15)-C(14)-H(14)	111.1
C(16)-C(15)-C(14)	112.3(4)
C(16)-C(15)-H(15A)	109.1
C(14)-C(15)-H(15A)	109.1
C(16)-C(15)-H(15B)	109.1
C(14)-C(15)-H(15B)	109.1
H(15A)-C(15)-H(15B)	107.9
C(17)-C(16)-C(15)	117.0(6)
C(17)-C(16)-H(16A)	108.1
C(15)-C(16)-H(16A)	108.1

C(17)-C(16)-H(16B)	108.1
C(15)-C(16)-H(16B)	108.1
H(16A)-C(16)-H(16B)	107.3
C(16)-C(17)-C(18)	112.1(5)
C(16)-C(17)-H(17A)	109.2
C(18)-C(17)-H(17A)	109.2
C(16)-C(17)-H(17B)	109.2
C(18)-C(17)-H(17B)	109.2
H(17A)-C(17)-H(17B)	107.9
C(17)-C(18)-C(19)	111.5(4)
C(17)-C(18)-B(1)	116.2(5)
C(19)-C(18)-B(1)	101.5(3)
C(17)-C(18)-H(18)	109.1
C(19)-C(18)-H(18)	109.1
B(1)-C(18)-H(18)	109.1
C(20)-C(19)-C(18)	113.6(4)
C(20)-C(19)-H(19A)	108.9
C(18)-C(19)-H(19A)	108.9
C(20)-C(19)-H(19B)	108.9
C(18)-C(19)-H(19B)	108.9
H(19A)-C(19)-H(19B)	107.7
C(19)-C(20)-C(21)	112.2(4)
C(19)-C(20)-H(20A)	109.2
C(21)-C(20)-H(20A)	109.2
C(19)-C(20)-H(20B)	109.2
C(21)-C(20)-H(20B)	109.2
H(20A)-C(20)-H(20B)	107.9
C(20)-C(21)-C(14)	112.9(4)
C(20)-C(21)-H(21A)	109.0
C(14)-C(21)-H(21A)	109.0
C(20)-C(21)-H(21B)	109.0

C(14)-C(21)-H(21B)	109.0
H(21A)-C(21)-H(21B)	107.8
C(23)-C(22)-C(31)	118.9(3)
C(23)-C(22)-C(1)	119.5(3)
C(31)-C(22)-C(1)	121.6(3)
O(2)-C(23)-C(22)	116.2(3)
O(2)-C(23)-C(24)	122.4(3)
C(22)-C(23)-C(24)	121.4(3)
C(25)-C(24)-C(23)	119.5(3)
C(25)-C(24)-H(24)	120.3
C(23)-C(24)-H(24)	120.3
C(24)-C(25)-C(26)	121.7(3)
C(24)-C(25)-H(25)	119.1
C(26)-C(25)-H(25)	119.1
C(25)-C(26)-C(27)	122.2(3)
C(25)-C(26)-C(31)	118.9(3)
C(27)-C(26)-C(31)	118.9(3)
C(28)-C(27)-C(26)	121.8(3)
C(28)-C(27)-H(27)	119.1
C(26)-C(27)-H(27)	119.1
C(27)-C(28)-C(29)	119.4(4)
C(27)-C(28)-H(28)	120.3
C(29)-C(28)-H(28)	120.3
C(30)-C(29)-C(28)	121.1(4)
C(30)-C(29)-H(29)	119.5
C(28)-C(29)-H(29)	119.5
C(29)-C(30)-C(31)	120.9(3)
C(29)-C(30)-H(30)	119.6
C(31)-C(30)-H(30)	119.6
C(30)-C(31)-C(26)	117.9(3)
C(30)-C(31)-C(22)	122.5(3)

C(26)-C(31)-C(22)	119.6(3)
O(2)-C(32)-C(33)	113.4(3)
O(2)-C(32)-H(32A)	108.9
C(33)-C(32)-H(32A)	108.9
O(2)-C(32)-H(32B)	108.9
C(33)-C(32)-H(32B)	108.9
H(32A)-C(32)-H(32B)	107.7
C(32)-C(33)-C(34)	110.9(3)
C(32)-C(33)-H(33A)	109.5
C(34)-C(33)-H(33A)	109.5
C(32)-C(33)-H(33B)	109.5
C(34)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	108.1
C(33)-C(34)-B(2)	119.3(4)
C(33)-C(34)-H(34A)	107.5
B(2)-C(34)-H(34A)	107.5
C(33)-C(34)-H(34B)	107.5
B(2)-C(34)-H(34B)	107.5
H(34A)-C(34)-H(34B)	107.0
C(36)-C(35)-C(42)	114.2(4)
C(36)-C(35)-B(2)	109.2(4)
C(42)-C(35)-B(2)	105.3(4)
C(36)-C(35)-H(35)	109.4
C(42)-C(35)-H(35)	109.4
B(2)-C(35)-H(35)	109.4
C(37)-C(36)-C(35)	115.1(5)
C(37)-C(36)-H(36A)	108.5
C(35)-C(36)-H(36A)	108.5
C(37)-C(36)-H(36B)	108.5
C(35)-C(36)-H(36B)	108.5
H(36A)-C(36)-H(36B)	107.5

C(36)-C(37)-C(38)	116.1(5)
C(36)-C(37)-H(37A)	108.3
C(38)-C(37)-H(37A)	108.3
C(36)-C(37)-H(37B)	108.3
C(38)-C(37)-H(37B)	108.3
H(37A)-C(37)-H(37B)	107.4
C(37)-C(38)-C(39)	115.1(4)
C(37)-C(38)-H(38A)	108.5
C(39)-C(38)-H(38A)	108.5
C(37)-C(38)-H(38B)	108.5
C(39)-C(38)-H(38B)	108.5
H(38A)-C(38)-H(38B)	107.5
C(40)-C(39)-C(38)	114.6(4)
C(40)-C(39)-B(2)	105.3(4)
C(38)-C(39)-B(2)	108.9(4)
C(40)-C(39)-H(39)	109.3
C(38)-C(39)-H(39)	109.3
B(2)-C(39)-H(39)	109.3
C(41)-C(40)-C(39)	114.5(5)
C(41)-C(40)-H(40A)	108.6
C(39)-C(40)-H(40A)	108.6
C(41)-C(40)-H(40B)	108.6
C(39)-C(40)-H(40B)	108.6
H(40A)-C(40)-H(40B)	107.6
C(42)-C(41)-C(40)	115.3(5)
C(42)-C(41)-H(41A)	108.4
C(40)-C(41)-H(41A)	108.4
C(42)-C(41)-H(41B)	108.4
C(40)-C(41)-H(41B)	108.4
H(41A)-C(41)-H(41B)	107.5
C(41)-C(42)-C(35)	115.2(5)

C(41)-C(42)-H(42A)	108.5
C(35)-C(42)-H(42A)	108.5
C(41)-C(42)-H(42B)	108.5
C(35)-C(42)-H(42B)	108.5
H(42A)-C(42)-H(42B)	107.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for buch350.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	23(1)	36(1)	21(1)	-1(1)	1(1)	0(1)
C(1)	25(2)	23(2)	25(2)	-1(2)	3(1)	2(2)
B(1)	48(2)	36(3)	33(2)	-3(2)	7(2)	-2(2)
C(2)	26(2)	22(2)	22(2)	0(2)	1(1)	-1(2)
O(2)	30(1)	28(1)	30(1)	-6(1)	-4(1)	4(1)
B(2)	45(3)	46(3)	35(3)	-8(2)	-2(2)	4(2)
C(3)	28(2)	25(2)	30(2)	0(2)	-2(1)	1(2)
C(4)	19(2)	30(2)	37(2)	1(2)	0(1)	-2(2)
C(5)	28(2)	21(2)	33(2)	-1(2)	6(1)	2(2)
C(6)	28(2)	31(2)	36(2)	-1(2)	9(2)	0(2)
C(7)	42(2)	30(2)	34(2)	1(2)	14(2)	4(2)
C(8)	44(2)	31(2)	24(2)	0(2)	5(2)	2(2)
C(9)	31(2)	26(2)	26(2)	-1(2)	-1(1)	0(2)

C(10)	27(2)	18(2)	30(2)	1(2)	2(1)	3(2)
C(11)	26(2)	29(2)	22(2)	-1(2)	-2(1)	-1(2)
C(12)	27(2)	31(2)	24(2)	1(2)	0(1)	-3(2)
C(13)	33(2)	31(2)	29(2)	-2(2)	1(2)	-1(2)
C(14)	57(3)	63(3)	40(2)	7(2)	11(2)	19(2)
C(15)	138(5)	47(3)	43(3)	13(2)	30(3)	23(3)
C(16)	63(3)	74(4)	112(5)	0(4)	30(3)	-3(3)
C(17)	69(3)	71(4)	81(4)	-15(3)	23(3)	-16(3)
C(18)	44(2)	72(3)	40(2)	-11(2)	11(2)	-15(3)
C(19)	49(3)	69(3)	46(3)	-1(2)	-5(2)	7(2)
C(20)	74(3)	47(3)	41(3)	-5(2)	-4(2)	9(2)
C(21)	64(3)	67(3)	37(3)	-3(2)	-9(2)	3(3)
C(22)	26(2)	27(2)	19(2)	1(1)	-2(1)	0(1)
C(23)	25(2)	28(2)	22(2)	0(2)	-1(1)	4(2)
C(24)	30(2)	30(2)	34(2)	-3(2)	-5(2)	-3(2)
C(25)	21(2)	35(2)	36(2)	-1(2)	-5(2)	-2(2)
C(26)	24(2)	32(2)	23(2)	4(2)	0(1)	0(2)
C(27)	20(2)	40(2)	34(2)	3(2)	-2(2)	2(2)
C(28)	32(2)	37(2)	33(2)	1(2)	3(2)	9(2)
C(29)	35(2)	31(2)	30(2)	-2(2)	0(2)	4(2)
C(30)	27(2)	33(2)	23(2)	0(2)	0(1)	1(2)
C(31)	24(2)	31(2)	18(2)	2(1)	3(1)	3(2)
C(32)	35(2)	26(2)	28(2)	-4(2)	-3(1)	4(2)
C(33)	38(2)	29(2)	28(2)	-2(2)	-2(2)	1(2)
C(34)	44(2)	32(2)	32(2)	-4(2)	-3(2)	1(2)
C(35)	79(3)	44(3)	32(2)	1(2)	-4(2)	2(2)
C(36)	65(3)	78(4)	59(3)	8(3)	6(3)	19(3)
C(37)	77(4)	95(5)	77(4)	-9(4)	-36(3)	8(4)
C(38)	63(3)	80(4)	53(3)	-14(3)	-5(3)	-18(3)
C(39)	68(3)	48(3)	34(2)	-3(2)	1(2)	-2(2)
C(40)	59(3)	76(4)	69(4)	-18(3)	2(3)	16(3)

C(41)	60(3)	101(5)	112(5)	0(4)	41(3)	0(3)
C(42)	61(3)	72(4)	130(6)	15(4)	5(4)	-16(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for buch350.

	x	y	z	U(eq)
H(3)	5892	8068	5259	33
H(4)	7037	8069	4388	34
H(6)	7246	7937	3203	37
H(7)	6408	7713	2178	42
H(8)	4373	7526	2008	39
H(9)	3199	7469	2873	34
H(11A)	4578	8906	5940	31
H(11B)	4711	6715	5977	31
H(12A)	2721	6543	6267	33
H(12B)	2692	8736	6294	33
H(13A)	4091	8763	7153	37
H(13B)	4267	6600	7099	37
H(14)	3971	6547	8371	64
H(15A)	2729	4441	8782	90
H(15B)	1929	6097	9003	90
H(16A)	1628	4079	7817	98
H(16B)	728	4139	8373	98
H(17A)	155	6927	8103	88
H(17B)	122	5701	7464	88

H(18)	1216	7713	7018	62
H(19A)	1784	10439	7537	66
H(19B)	503	9947	7748	66
H(20A)	1228	8939	8754	65
H(20B)	1743	10946	8639	65
H(21A)	3199	8868	9071	68
H(21B)	3545	9757	8404	68
H(24)	711	3997	3420	38
H(25)	-655	6237	3606	37
H(27)	-1160	9314	4013	38
H(28)	-621	12005	4519	41
H(29)	1352	12552	4815	38
H(30)	2759	10421	4605	33
H(32A)	2005	2118	3332	36
H(32B)	3373	1752	3303	36
H(33A)	3404	3991	2450	38
H(33B)	2010	4065	2449	38
H(34A)	1936	875	2209	44
H(34B)	3319	840	2193	44
H(35)	2525	4791	1307	62
H(36A)	775	4060	764	81
H(36B)	1556	5007	246	81
H(37A)	1833	2373	-274	102
H(37B)	487	2346	-123	102
H(38A)	1519	-506	42	79
H(38B)	735	122	612	79
H(39)	2459	-929	1118	60
H(40A)	4317	38	901	82
H(40B)	3717	-642	231	82
H(41A)	4803	2152	170	108
H(41B)	3509	2241	-151	108

H(42A)	3747	4898	388	105
H(42B)	4357	3920	1006	105

Table 6. Torsion angles [deg] for buch350.

C(11)-O(1)-C(2)-C(1)	179.0(3)
C(11)-O(1)-C(2)-C(3)	0.0(5)
C(10)-C(1)-C(2)-O(1)	179.4(3)
C(22)-C(1)-C(2)-O(1)	-2.3(5)
C(10)-C(1)-C(2)-C(3)	-1.6(5)
C(22)-C(1)-C(2)-C(3)	176.6(3)
O(1)-C(2)-C(3)-C(4)	177.5(3)
C(1)-C(2)-C(3)-C(4)	-1.3(5)
C(2)-C(3)-C(4)-C(5)	1.8(6)
C(3)-C(4)-C(5)-C(10)	0.7(5)
C(3)-C(4)-C(5)-C(6)	178.9(3)
C(4)-C(5)-C(6)-C(7)	-178.2(4)
C(10)-C(5)-C(6)-C(7)	0.0(6)
C(5)-C(6)-C(7)-C(8)	1.6(6)
C(6)-C(7)-C(8)-C(9)	-1.2(6)
C(7)-C(8)-C(9)-C(10)	-0.8(6)
C(8)-C(9)-C(10)-C(5)	2.3(5)
C(8)-C(9)-C(10)-C(1)	-177.7(4)
C(4)-C(5)-C(10)-C(9)	176.4(4)
C(6)-C(5)-C(10)-C(9)	-1.9(5)
C(4)-C(5)-C(10)-C(1)	-3.7(5)
C(6)-C(5)-C(10)-C(1)	178.1(3)
C(2)-C(1)-C(10)-C(9)	-175.9(3)
C(22)-C(1)-C(10)-C(9)	5.8(5)

C(2)-C(1)-C(10)-C(5)	4.1(5)
C(22)-C(1)-C(10)-C(5)	-174.2(3)
C(2)-O(1)-C(11)-C(12)	178.1(3)
O(1)-C(11)-C(12)-C(13)	173.8(3)
C(11)-C(12)-C(13)-B(1)	-173.4(4)
C(18)-B(1)-C(13)-C(12)	-20.3(6)
C(14)-B(1)-C(13)-C(12)	172.7(4)
C(18)-B(1)-C(14)-C(21)	-70.4(5)
C(13)-B(1)-C(14)-C(21)	98.2(5)
C(18)-B(1)-C(14)-C(15)	47.6(5)
C(13)-B(1)-C(14)-C(15)	-143.8(4)
C(21)-C(14)-C(15)-C(16)	109.9(5)
B(1)-C(14)-C(15)-C(16)	-2.2(6)
C(14)-C(15)-C(16)-C(17)	-50.6(7)
C(15)-C(16)-C(17)-C(18)	50.8(7)
C(16)-C(17)-C(18)-C(19)	-115.0(5)
C(16)-C(17)-C(18)-B(1)	0.6(7)
C(14)-B(1)-C(18)-C(17)	-50.4(6)
C(13)-B(1)-C(18)-C(17)	141.3(5)
C(14)-B(1)-C(18)-C(19)	70.6(5)
C(13)-B(1)-C(18)-C(19)	-97.7(5)
C(17)-C(18)-C(19)-C(20)	65.2(6)
B(1)-C(18)-C(19)-C(20)	-59.1(5)
C(18)-C(19)-C(20)-C(21)	53.2(6)
C(19)-C(20)-C(21)-C(14)	-52.3(6)
B(1)-C(14)-C(21)-C(20)	58.0(5)
C(15)-C(14)-C(21)-C(20)	-59.4(5)
C(2)-C(1)-C(22)-C(23)	-114.2(4)
C(10)-C(1)-C(22)-C(23)	64.1(4)
C(2)-C(1)-C(22)-C(31)	68.7(4)
C(10)-C(1)-C(22)-C(31)	-113.0(4)

C(32)-O(2)-C(23)-C(22)	-161.1(3)
C(32)-O(2)-C(23)-C(24)	19.9(5)
C(31)-C(22)-C(23)-O(2)	-176.2(3)
C(1)-C(22)-C(23)-O(2)	6.6(4)
C(31)-C(22)-C(23)-C(24)	2.8(5)
C(1)-C(22)-C(23)-C(24)	-174.3(3)
O(2)-C(23)-C(24)-C(25)	178.3(3)
C(22)-C(23)-C(24)-C(25)	-0.6(5)
C(23)-C(24)-C(25)-C(26)	-1.2(5)
C(24)-C(25)-C(26)-C(27)	-179.3(3)
C(24)-C(25)-C(26)-C(31)	0.6(5)
C(25)-C(26)-C(27)-C(28)	177.8(3)
C(31)-C(26)-C(27)-C(28)	-2.1(5)
C(26)-C(27)-C(28)-C(29)	1.0(6)
C(27)-C(28)-C(29)-C(30)	0.2(6)
C(28)-C(29)-C(30)-C(31)	-0.3(6)
C(29)-C(30)-C(31)-C(26)	-0.8(5)
C(29)-C(30)-C(31)-C(22)	179.6(3)
C(25)-C(26)-C(31)-C(30)	-177.9(3)
C(27)-C(26)-C(31)-C(30)	1.9(5)
C(25)-C(26)-C(31)-C(22)	1.7(5)
C(27)-C(26)-C(31)-C(22)	-178.5(3)
C(23)-C(22)-C(31)-C(30)	176.2(3)
C(1)-C(22)-C(31)-C(30)	-6.7(5)
C(23)-C(22)-C(31)-C(26)	-3.3(5)
C(1)-C(22)-C(31)-C(26)	173.8(3)
C(23)-O(2)-C(32)-C(33)	71.7(4)
O(2)-C(32)-C(33)-C(34)	172.0(3)
C(32)-C(33)-C(34)-B(2)	178.4(3)
C(35)-B(2)-C(34)-C(33)	3.0(6)
C(39)-B(2)-C(34)-C(33)	176.0(4)

C(34)-B(2)-C(35)-C(36)	-127.6(5)
C(39)-B(2)-C(35)-C(36)	58.9(5)
C(34)-B(2)-C(35)-C(42)	109.4(5)
C(39)-B(2)-C(35)-C(42)	-64.2(5)
C(42)-C(35)-C(36)-C(37)	66.8(7)
B(2)-C(35)-C(36)-C(37)	-50.7(6)
C(35)-C(36)-C(37)-C(38)	43.5(7)
C(36)-C(37)-C(38)-C(39)	-42.6(7)
C(37)-C(38)-C(39)-C(40)	-68.7(7)
C(37)-C(38)-C(39)-B(2)	48.9(6)
C(35)-B(2)-C(39)-C(40)	65.5(5)
C(34)-B(2)-C(39)-C(40)	-108.4(5)
C(35)-B(2)-C(39)-C(38)	-57.8(5)
C(34)-B(2)-C(39)-C(38)	128.3(4)
C(38)-C(39)-C(40)-C(41)	65.7(6)
B(2)-C(39)-C(40)-C(41)	-53.9(6)
C(39)-C(40)-C(41)-C(42)	45.8(7)
C(40)-C(41)-C(42)-C(35)	-44.7(8)
C(36)-C(35)-C(42)-C(41)	-67.8(7)
B(2)-C(35)-C(42)-C(41)	52.0(7)

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