Supporting Information

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Tacticity Control of Cyclic Poly(3-Thiobutyrate) Prepared by Ring-Opening Polymerization of Racemic β-Thiobutyrolactone

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Abstract: We report here on the ring-opening polymerization (ROP) of racemic β-thiobutyrolactone (*rac*-TBL), as the first chemical synthesis of poly(3-thiobutyrolactone) (P3TB), the thioester analogue of the ubiquitous poly(3-hydroxybutyrate) (P3HB). The ROP reactions proceed very fast (TOF > 12,000 h^{-1} at r.t.) in the presence of various metal-based catalysts. Remarkably, catalyst systems based on non-chiral yttrium complexes stabilized by tetradentate amino alkoxy- or diamino-bis(phenolate) ligands $\{ONXO^{R1,R2}\}^{2-}$ (X = O, N) provide access to cyclic P3TB with either high isoselectivity (P_m up to 0.90) or high syndiotactic bias (P_r up to 0.70). The stereoselectivity can be controlled by manipulation of the substituents on the ligand platform and adequate choice of the reaction solvent and temperature as well. The cyclic polymer topology is evidenced by MALDI-ToF MS, NMR and TGA. Highly isotactic P3TB is a semi-crystalline material as revealed by DSC.

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SUPPORTING INFORMATION

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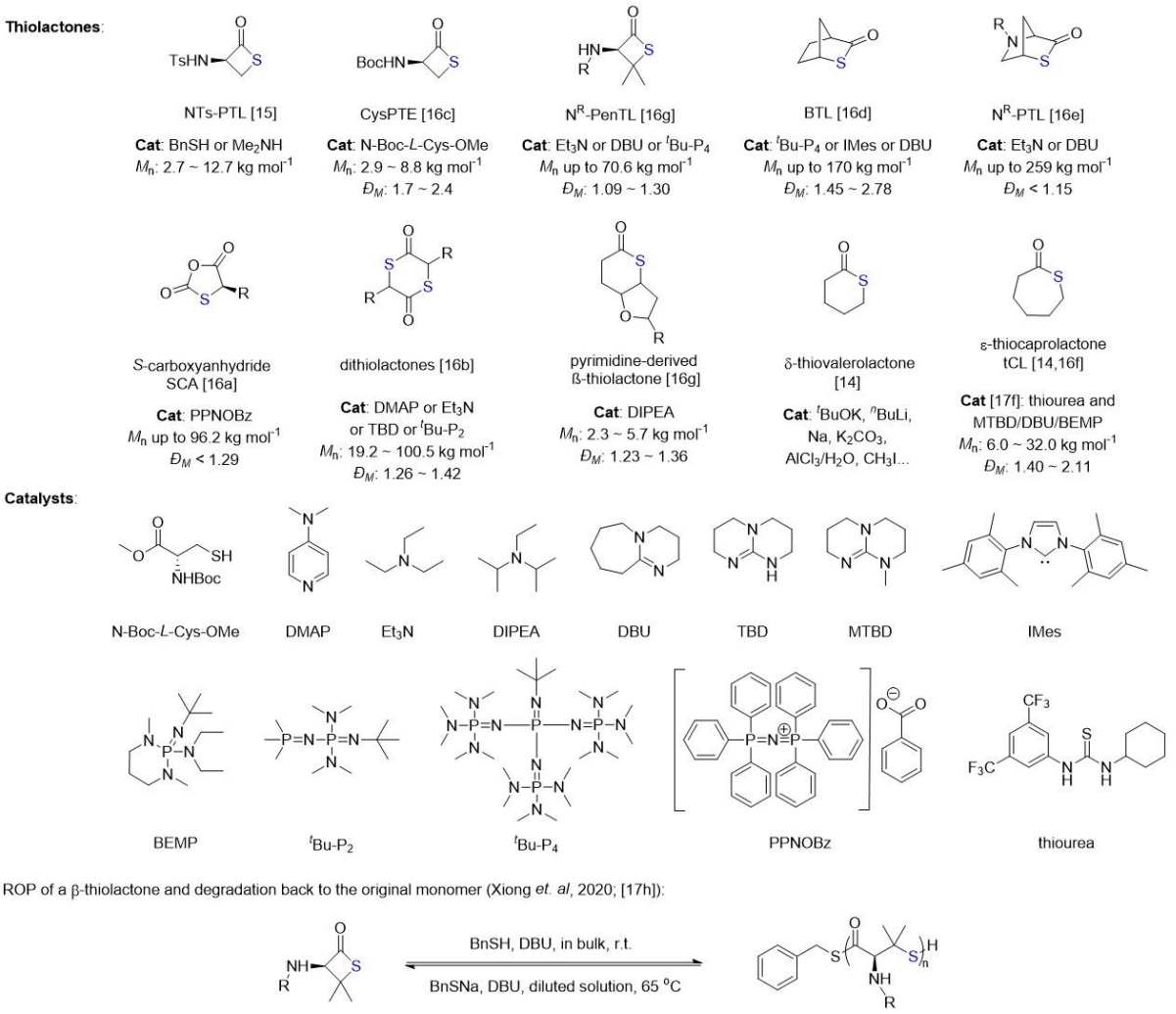


Scheme S1. Thiolactones and organocatalysts reported for the ROP chemical synthesis of various polythioesters (PTEs) (see references mentioned).

Experimental Section

General Considerations. All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flame-dried Schlenk-type glassware on a vacuum dual-manifold Schlenk line or in an argon-filled glovebox. HPLC-grade organic solvents were first purged extensively with nitrogen during filling 20-L solvent reservoirs, and then dried by passage through activated alumina [for dichloromethane] and through Q-5 supported copper catalyst [for toluene] stainless steel columns. *n*-Hexane, 1,4-dioxane, 2-methyl-tetrahydrofuran (2-MeTHF), tetrahydrofuran (THF), acetonitrile and toluene were degassed and dried over sodium/benzophenone followed by distillation under argon. *iso*-Propanol (^{i}PrOH), benzyl alcohol (BnOH), isopropyl mercaptan (^{i}PrSH), benzyl mercaptan (BnSH) were purified by distillation from CaH_2. (SalBinam)AlO^{i}Pr {SalBinam = *N*,*N*′-bis(salicylidene)-1,1′-binaphthyl-2,2′-diamine} (**1**), (BDI)ZnN$(SiMe_3)_2$ (**2a**), {Zn{N$(SiMe_3)_2$}$_2$}$_2$ (**2b**), the amido yttrium-salan complex **4**, bisphenol {ONXO^{R2}}H_2 proligands ***a-l*** and yttrium amide precursors were synthesized according to the methods reported in the literature.[1,2]

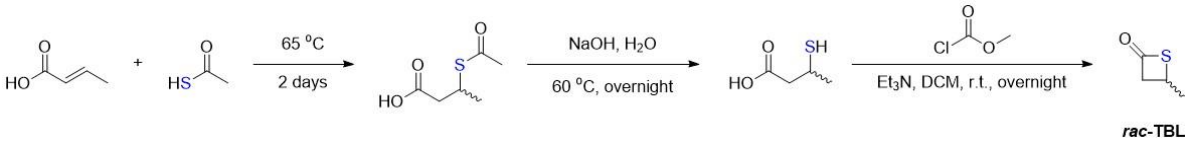
^{1}H (500, 400 and 300 MHz), ^{13}C{^{1}H} (125 and 100 MHz) and two-dimensional (2D) NMR spectra were recorded on Bruker Avance III HD 500, Av III 400 or Av III 300 spectrometers at 25 °C, fitted with direct broadband 5 mm probe heads (BBO/BBFO) carefully tuned on both ^{1}H and ^{13}C channels. 1D ^{13}C NMR spectra were acquired using Bruker standard zgpg30 sequence, acquisition time was 1.05 s and relaxation delay D1 5.00 s. Two-dimensional NMR experiments were acquired using standard pulse sequences (hsqcedetgpsisp2.3 with a selective ^{13}C refocussing pulse for band-selective HSQC experiments; shmbcctetgpl2nd for band-selective HMBC experiments), 2D spectra were processed using Topspin software (Bruker Biospin, Billerica, MA, USA) and analyzed in MestReNova 14.2.1 (Mestrelab Research S.L). The ^{13}C projections were prepared in Topspin software by summing F1 traces from the 2D HMBC and HSQC spectra across the region of interest.

Number and weight average molar mass ($M_{n,SEC}$ and $M_{w,SEC}$) and dispersity ($Đ_M = M_w/M_n$) values of the polymers were determined by size-exclusion chromatography (SEC) in THF at 30 °C (flow rate = 1.0 mL min^{-1}) on a Polymer Laboratories PL50 apparatus equipped with a refractive index detector and a set of two ResiPore PLgel 3 µm MIXED-D 300 × 7.5 mm columns. The polymer samples were dissolved in THF (2 mg mL^{-1}). All elution curves were calibrated with polystyrene standards (M_n range = 580−126,000 g mol^{-1}); the $M_{n,\ SEC}$ values of the P3TB reported in all Tables are uncorrected for the possible difference in hydrodynamic radius *versus* that of polystyrene.

High resolution Matrix Assisted Laser Desorption Ionization – Time of Flight (MALDI-ToF) mass spectra were recorded using an ULTRAFLEX III TOF/TOF spectrometer (Bruker Daltonik Gmbh, Bremen, Germany) in positive ionization mode at Centre Régional de Mesures Physiques de l'Ouest (CRMPO, ScanMAT UAR 2025 CNRS, Université de Rennes 1). Spectra were recorded using reflectron mode and an accelerating voltage of 25 kV. A mixture of a freshly prepared solution of the polymer in CH_2Cl_2 (HPLC grade) and DCTB (*trans*-2-(3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene) malononitrile in CH_2Cl_2 (HPLC grade, 10 mg mL^{-1}) , and a MeOH or CH_2Cl_2/CH_3CN (50:50, *v*/*v*) solution of the cationizing agent (NaI, 10 mg mL^{-1}) were prepared. The solutions were combined in a 1:1:1 (*v*/*v*/*v*) ratio of matrix-to-sample-to-cationizing agent. The resulting solution (0.25–0.5 µL) was deposited onto the sample target (Prespotted AnchorChip PAC II 384/96 HCCA) and air or vacuum dried. High resolution mass spectrum of *rac*-TBL (Figure S5) was performed using a time-of-flight Maxis 4G (Bruker Daltonik Gmbh, Bremen, Germany) in ASAP (direct introduction, desorption temperature: 45 °C) positive mode at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO, ScanMAT, Université de Rennes1).

Melting-transition (T_m) and glass-transition (T_g) temperatures were measured by differential scanning calorimetry (DSC) on a DSC2500, TA Instrument. All T_m and T_g values were obtained from the second heating run. The first heating rate was 10 °C min^{-1}, while the cooling rate was 10 °C min^{-1} and the second heating rate was 10 °C min^{-1}. The onset decomposition temperatures (T_d, defined as the temperature for 5% weight loss) of the polymers were measured by thermal gravimetric analysis (TGA) on a Mettler-Toledo TGA-DSC-1 apparatus under dry nitrogen flow. Polymer samples were heated from ambient temperatures to 500 °C at a rate of 10 °C min^{-1}.

Synthesis of *rac*-β-thiobutyrolactone (*rac*-TBL). The synthesis of *rac*-TBL relies on the cyclization of β-thiobutyric acid, initially prepared by the addition reaction of crotonic acid with thioacetic acid (Scheme S2), following optimization of literature procedures (see below).



Scheme S2. Synthesis of *rac*-β-TBL.

Synthesis of 3-thiobutyric acid.[3] Crotonic acid (Thermo Fisher Scientific, 84 g, 1.0 mol) and thioacetic acid (TCI, 83.6 g, 1.1 mol) were placed in a round-bottom flask (1 L). The resulting mixture was heated up to 65 °C for 2 days. The crude product containing 3-acetylthiobutyric acid was treated with NaOH (500 mL of a 3 M aqueous solution, 1.5 mol) overnight. The resulting solution was acidified with HCl (ca. 300 mL of a 2.5 M aqueous solution, 0.75 mol) until pH = 3 and extracted with diethyl ether (2 × 500 mL). The organic phase was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure, and the residue was purified by distillation under vacuum (*ca.* 400 mTorr) at 95 °C, to give 3-thiobutyric acid, as a yellowish liquid (96.9 g, 81% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, Figure S1): δ (ppm) 11.35 (s, 1H, COO*H*), 3.30–3.44 (dq, *J* = 14 and 7 Hz, 1H, C*H*), 2.58–2.73 (m, 2H, CH_2), 1.86 (d, *J* = 7 Hz, 1H, S*H*), 1.41 (d, *J* = 7 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C, Figure S2): δ (ppm) 177.83 (*C*O), 45.72 (*C*H_2), 30.97 (*C*H), 24.92 (*C*H_3).

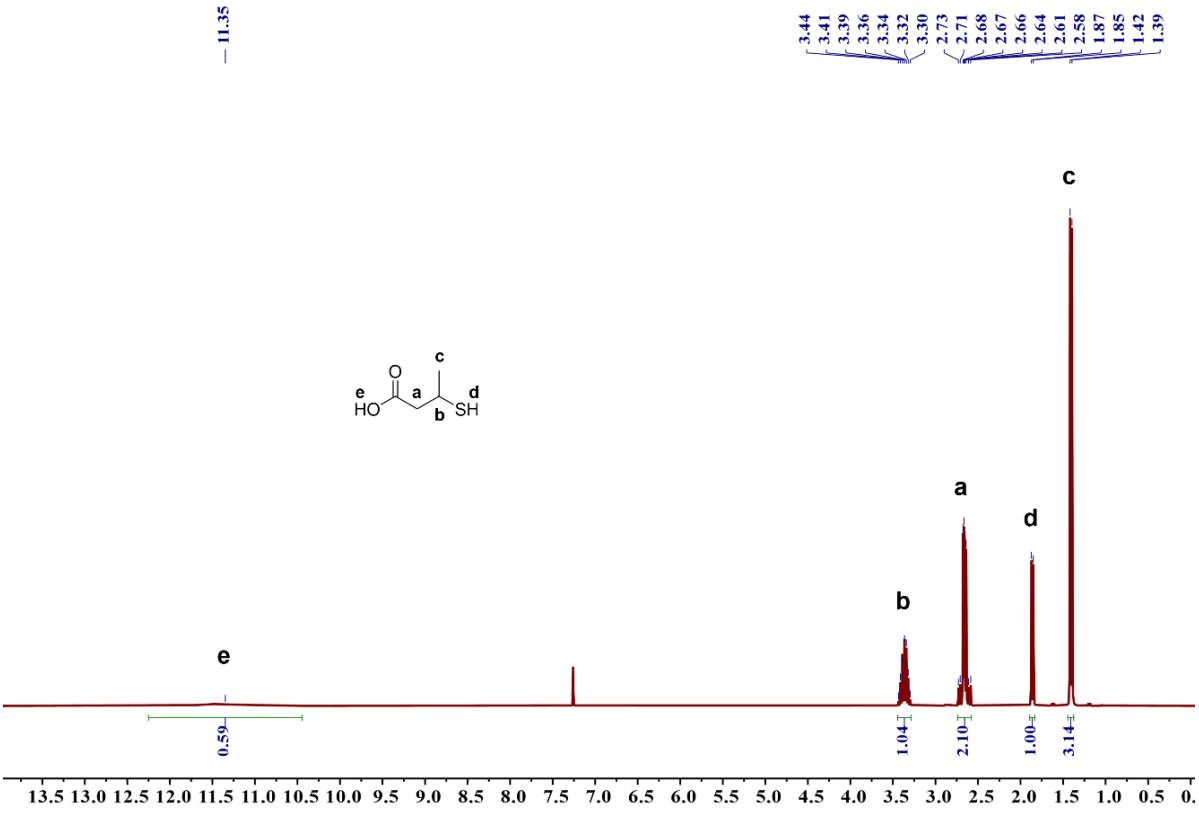


Figure S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of 3-thiobutyric acid.

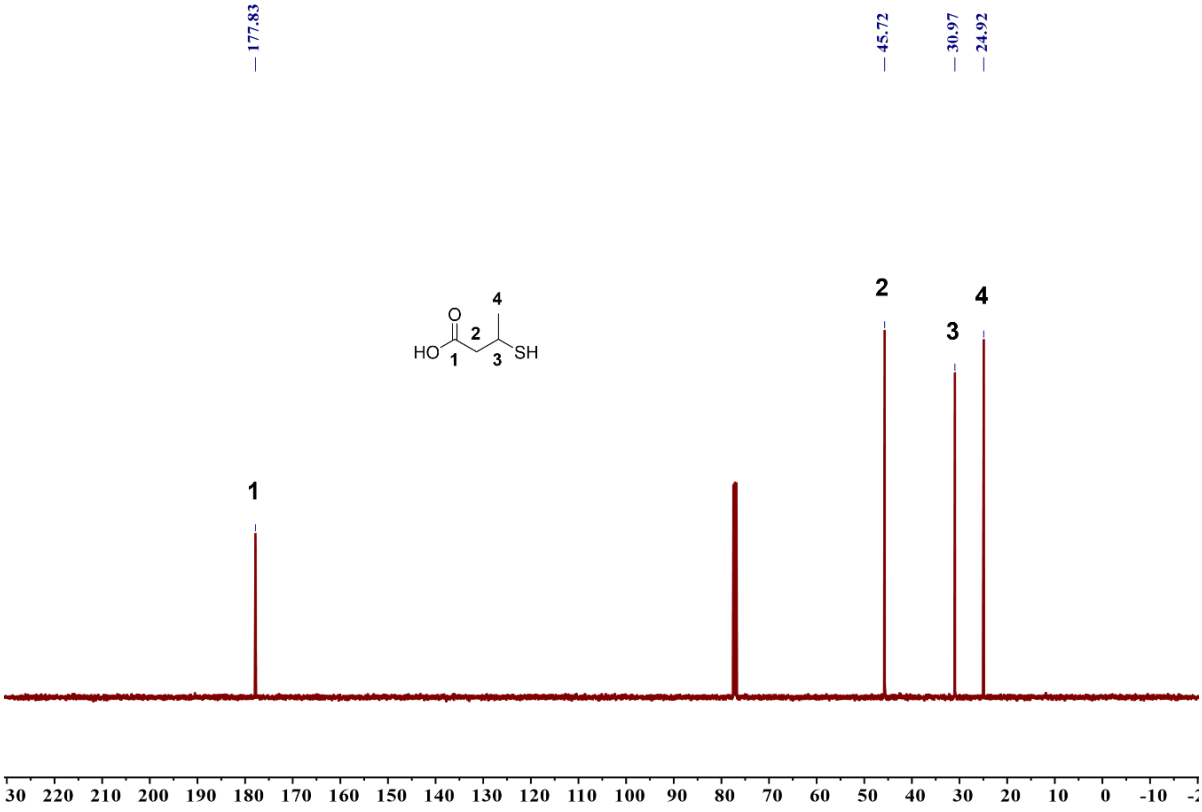


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of 3-thiobutyric acid.

Synthesis of rac-β-thiobutyrolactone (rac-TBL). Racemic β-thiobutyrolactone (*rac*-TBL) was then synthesized using a modified (optimization of the purification procedure) literature procedure.[4] Methyl chloroformate (21.5 mL, 0.275 mmol) was added dropwise at 0 °C to a solution of 3-thiobutyric acid (26.4 mL, 0.25 mol) and triethylamine (38.4 mL, 0.275 mol) in dry dichloromethane (350 mL). Once the addition was completed, the reaction mixture was warmed to room temperature and stirred until evolution of CO_2 ceased. The resulting mixture was washed with water (2 × 100 mL), saturated $NaHCO_3$ (250 mL), brine (250 mL) and the separated organic layer was dried over $MgSO_4$ and rotavapored under reduced pressure. The residue was purified by distillation using the Glass Oven B-585 under vacuum twice (35 °C, 500 mTorr) to give pure *rac*-TBL as a colorless liquid (6.5 g, 26% yield, Caution: *rac*-TBL will degrade or polymerize spontaneously if purified by column chromatography on silica or neutral alumina). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, Figure S3): δ (ppm) 4.10 (dd, *J* = 17 and 7 Hz, 1H, C*H*H), 3.72 (pd, *J* = 7 and 4 Hz, 1H, C*H*), 3.52 (dd, *J* = 17 and 4 Hz, 1H, CH*H*), 1.67 (d, *J* = 7 Hz, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C, Figure S4): δ (ppm) 190.43 (*C*O), 62.88 (*C*H_2), 28.10 (*C*H), 23.78 (*C*H_3). HRMS (ESI, Figure S5): calculated for C_4H_6SO $[M]^+$ *m/z* = 103.0212; found: 103.0212.

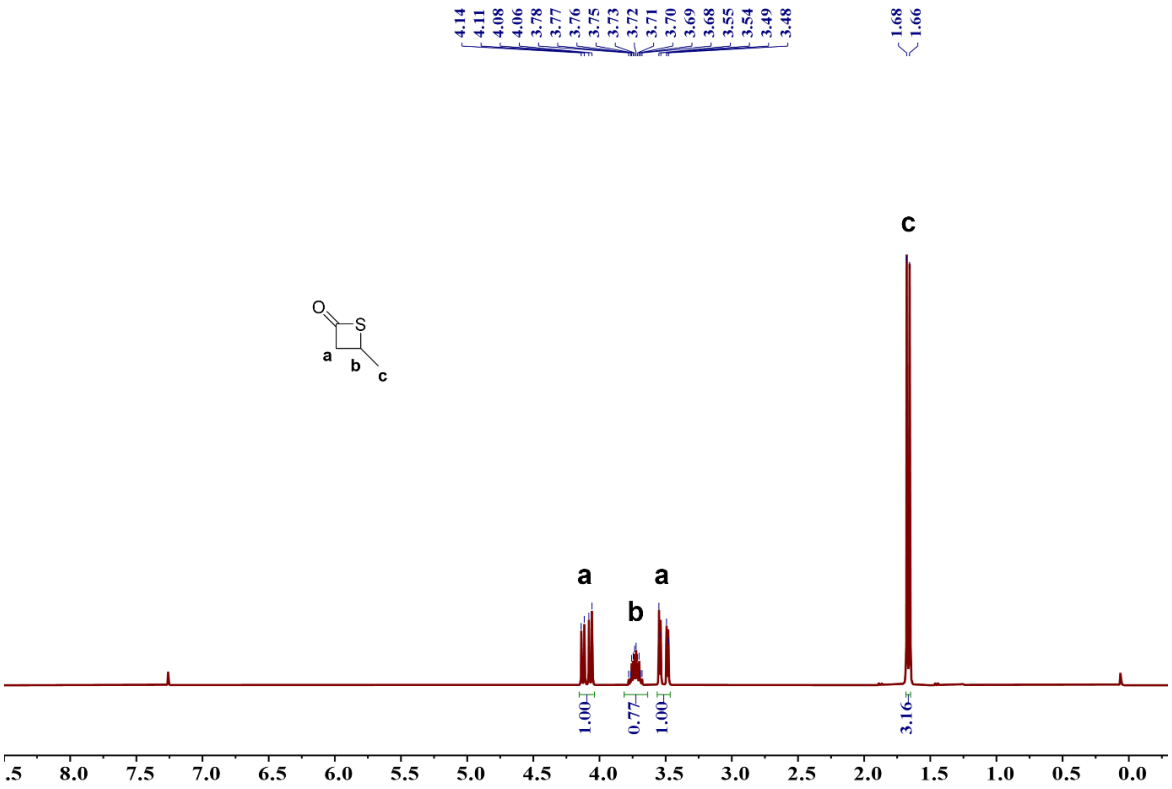


Figure S3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of *rac*-β-thiobutyrolactone (*rac*-TBL); the weak signal at 0.06 ppm is silicone grease.

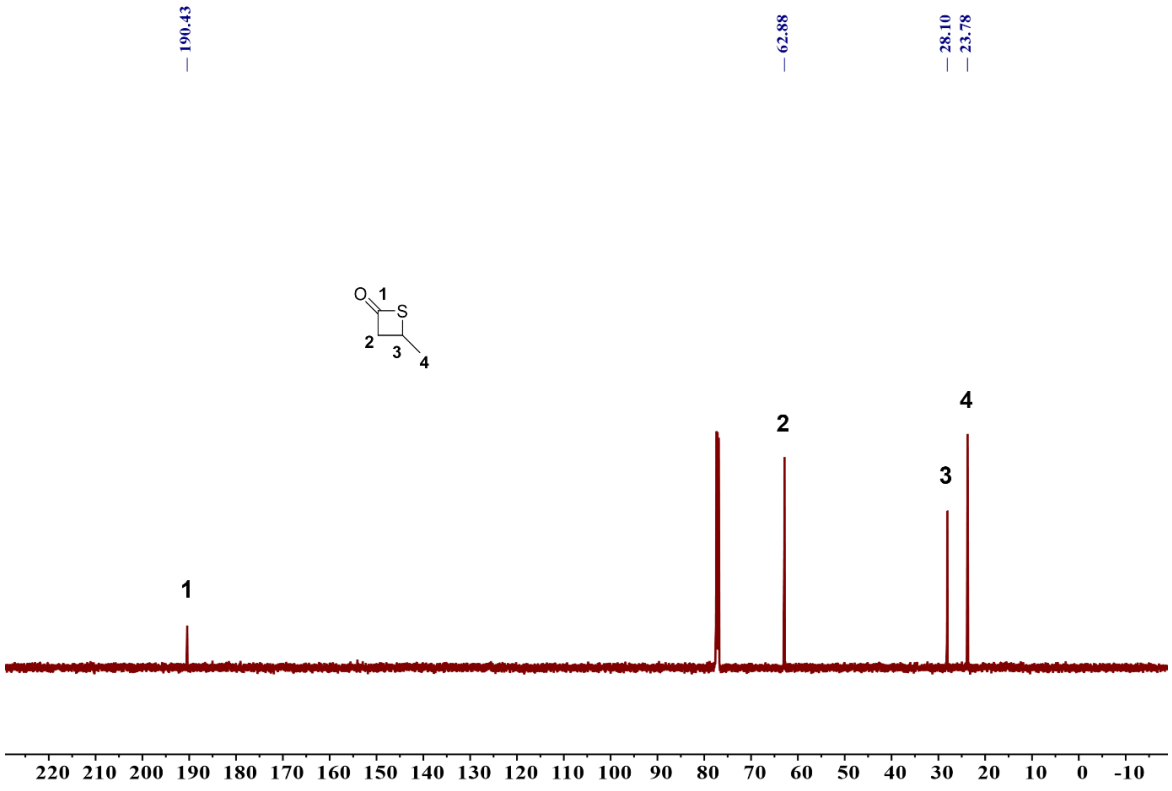


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of *rac*-β-thiobutyrolactone (*rac*-TBL).

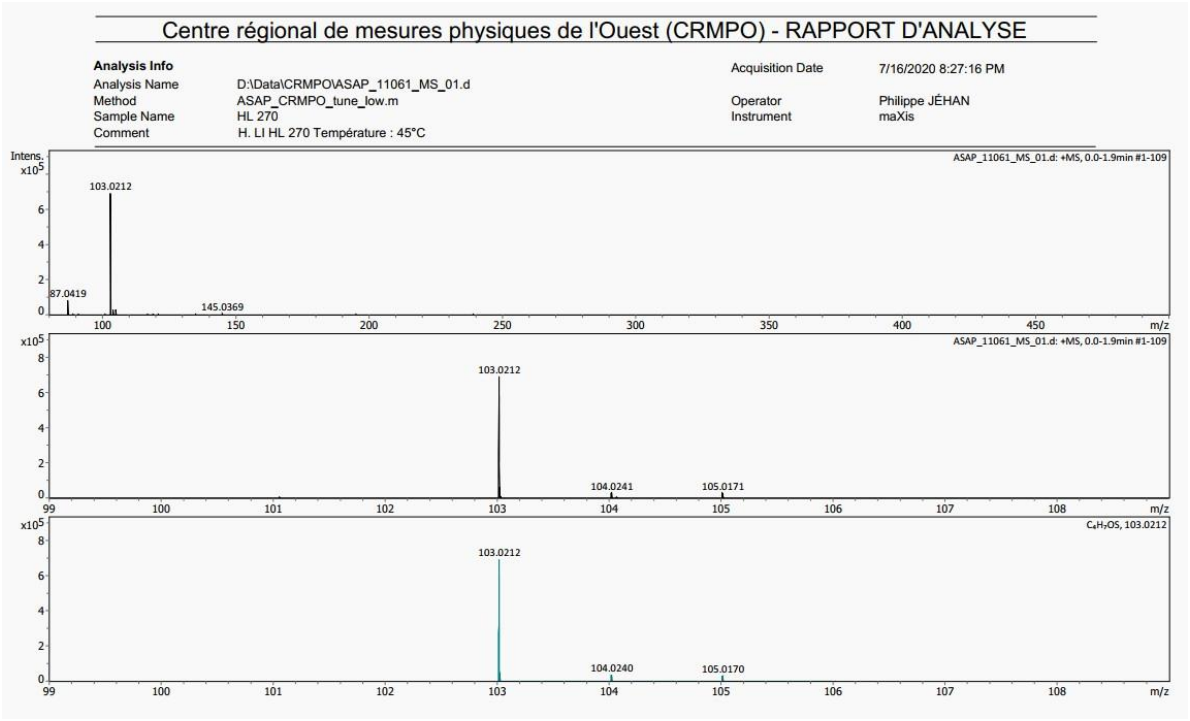
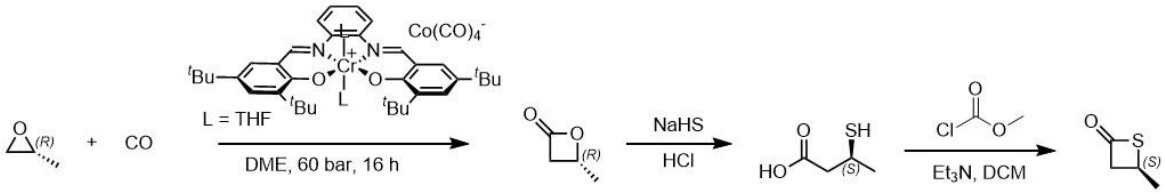


Figure S5. HRMS spectra of *rac*-TBL. Top: ESI mass spectrum of *rac*-TBL; middle: zoomed spectrum of top spectrum (*ca.* 104 *m/z*); bottom: simulated spectrum of *rac*-TBL.

Synthesis of (*S*)-β-thiobutyrolactone ((*S*)-TBL). The fundamental steps involved in the synthesis of monomer (*S*)-TBL are depicted in Scheme S3. It relies on the cyclization of enantiomerically pure β-thiobutyric acid, initially prepared from (*R*)-β-butyrolactone.



Scheme S3. Synthesis of enantiomerically pure (*S*)-TBL.

***Synthesis of (R)-β-butyrolactone ((R)-BL)*:** (*R*)-β-Butyrolactone was synthesized using a modified literature procedure (reaction conducted at higher pressure, i.e. 60 bars instead of 1 bar).[5] In the glovebox, a Schlenk flask was charged with $[salph(Cr(THF)_2)]^+[Co(CO)_4]^-$ (520 mg, 0.57 mmol). On a Schlenk line, dry DME (10 mL) was syringed into the reaction flask and the resulting solution was cannulated into a degassed high-pressure reactor which was then pressurized with carbon monoxide to 30 bars, followed by stirring for 15 min before depressurization. A solution of (*R*)-propylene oxide (Acros Organics, 98% *ee*, 15 mL, 0.22 mol) in dry DME (5 mL) was then transferred into the reactor which was then pressurized with CO to 60 bars. The reaction mixture was stirred overnight at 23 °C. The reactor was vented to atmospheric pressure, volatiles were removed under vacuum and the crude product was purified by distillation at 40 °C to afford (*R*)-BL as a colorless viscous liquid (4.6 g, 26 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, Figure S6**)**: *δ* (ppm) 4.74–4.67 (m, 1H, C*H*), 3.60–3.54 (m, 1H, C*H*H), 3.06 (dd, *J* = 16 and 4 Hz, 1H, CH*H*), 1.57 (d, *J* = 6 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, Figure S7**)**: *δ* (ppm) 168.17 (*C*O), 68.02 (CH_2), 44.43 (*C*H), 20.71 (CH_3).

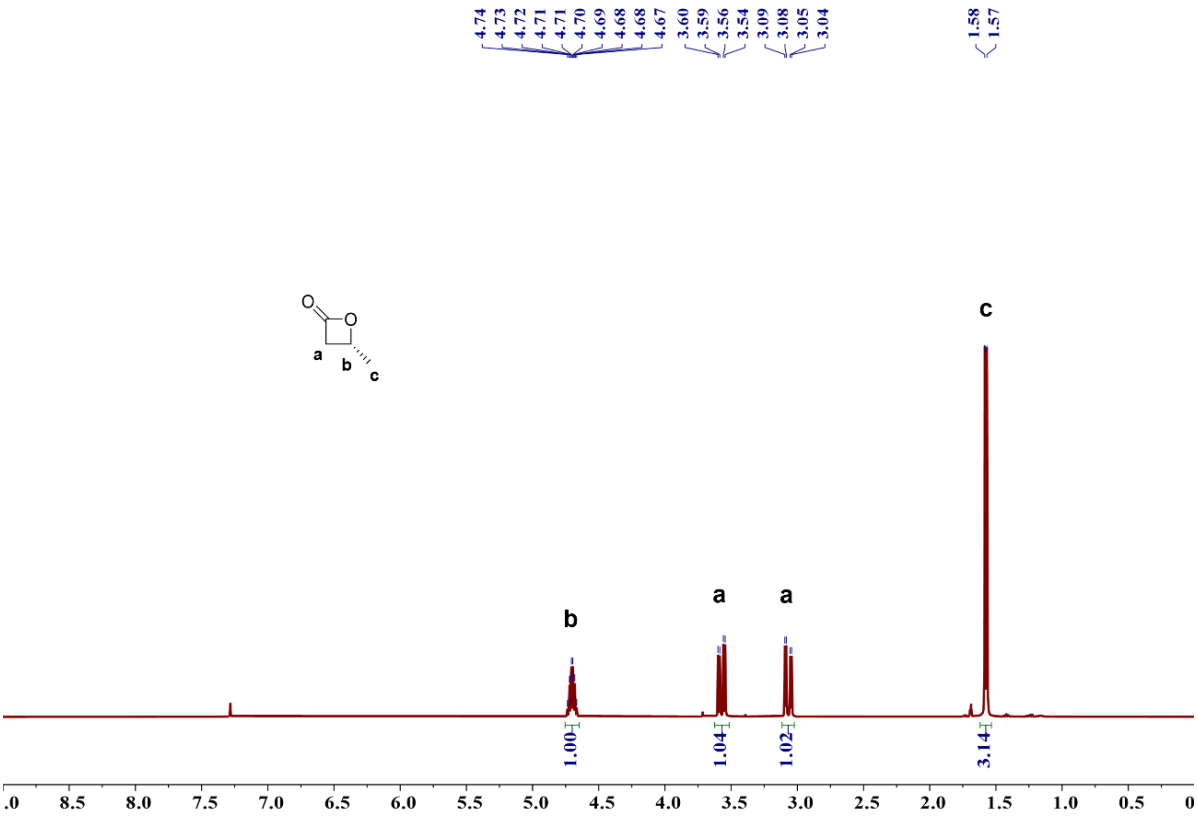


Figure S6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of (*R*)-β-butyrolactone.

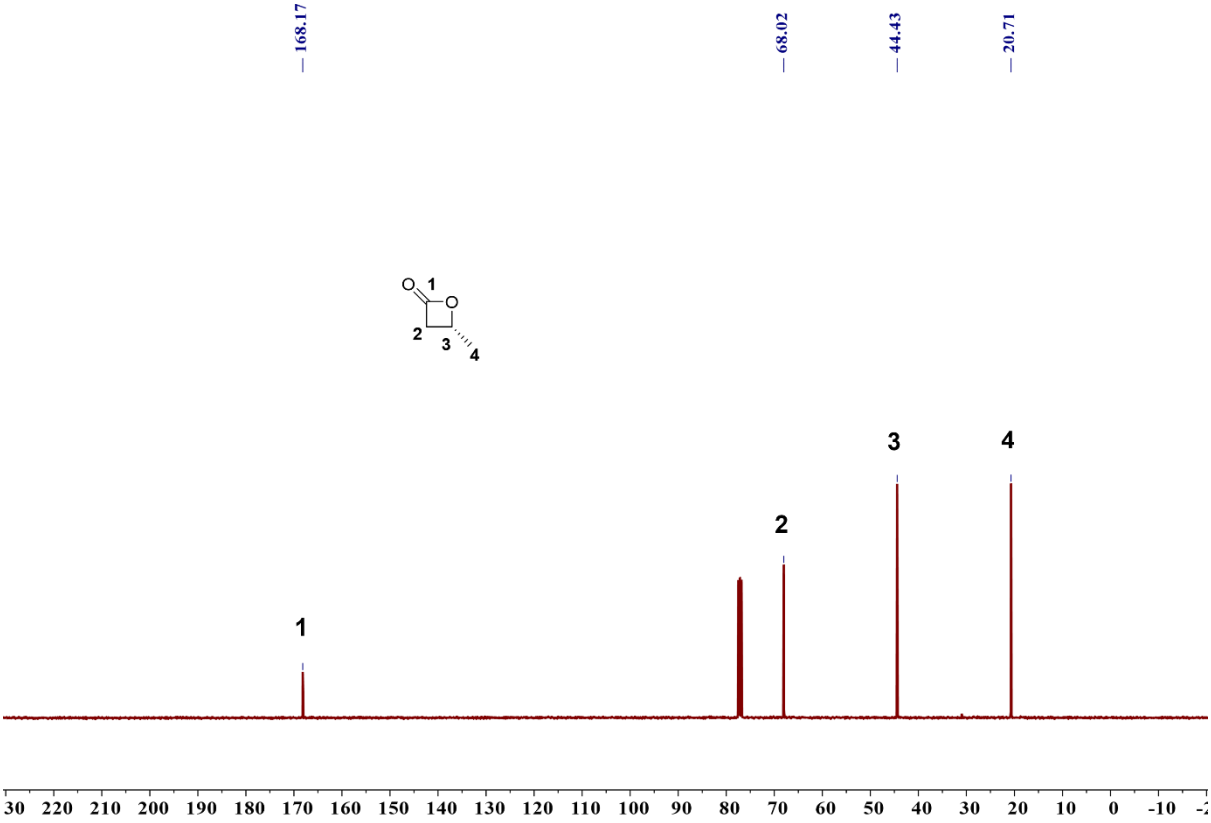


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of (*R*)-β-butyrolactone.

Synthesis of (S)-β-thiobutyrolactone ((S)-TBL). (*S*)-3-Thiobutyric acid was synthesized using a literature procedure.[6] (*R*)-BL (7.54 g, 87.6 mmol) was added dropwise at 0 °C to a solution of $NaSH{\cdot}H_2O$ (5.06 g, 90.2 mmol) in water (90 mL). The mixture was then stirred for 1 h at 0 °C and for 24 h at 23 °C. Then, HCl (2.4 N aqueous solution) was added to adjust the pH ≈ 2 and the mixture was extracted with Et_2O (3 × 150 mL). The resulting organic phase was dried over $MgSO_4$, the solvent was removed under reduced pressure and the residue was distilled to give a ca. 2:1 mixture of (*S*)-3TBA and (*R*)-3HBA isolated as a colorless liquid (3.90 g, *ca.* 38% yield). This mixture of the two compounds was dissolved in a solution of triethylamine (3.6 mL, 0.036 mol) in dry dichloromethane (50 mL), and methyl chloroformate (2.8 mL, 0.036 mol) was then added dropwise at 0 °C. Once the addition was completed, the reaction mixture was warmed to room temperature and stirred until evolution of CO_2 ceased. The resulting mixture was washed with water (2 × 30 mL), saturated $NaHCO_3$ (50 mL), brine (50 mL); the separated organic layer was dried over $MgSO_4$ and rotavapored under reduced pressure. Ultimately, (*S*)-TBL was isolated as described above for *rac*-TBL and recovered as a colorless liquid (335 mg, 3.3 mmol, 10% yield); NMR characteristics are identical to those of *rac*-TBL. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, Figure S8): δ (ppm) 4.10 (dd, *J* = 17 and 7 Hz, 1H, C*H*H), 3.72 (pd, *J* = 7 and 4 Hz, 1H, C*H*), 3.52 (dd, *J* = 17 and 4 Hz, 1H, CH*H*), 1.67 (d, *J* = 7 Hz, 3H, CH_3).

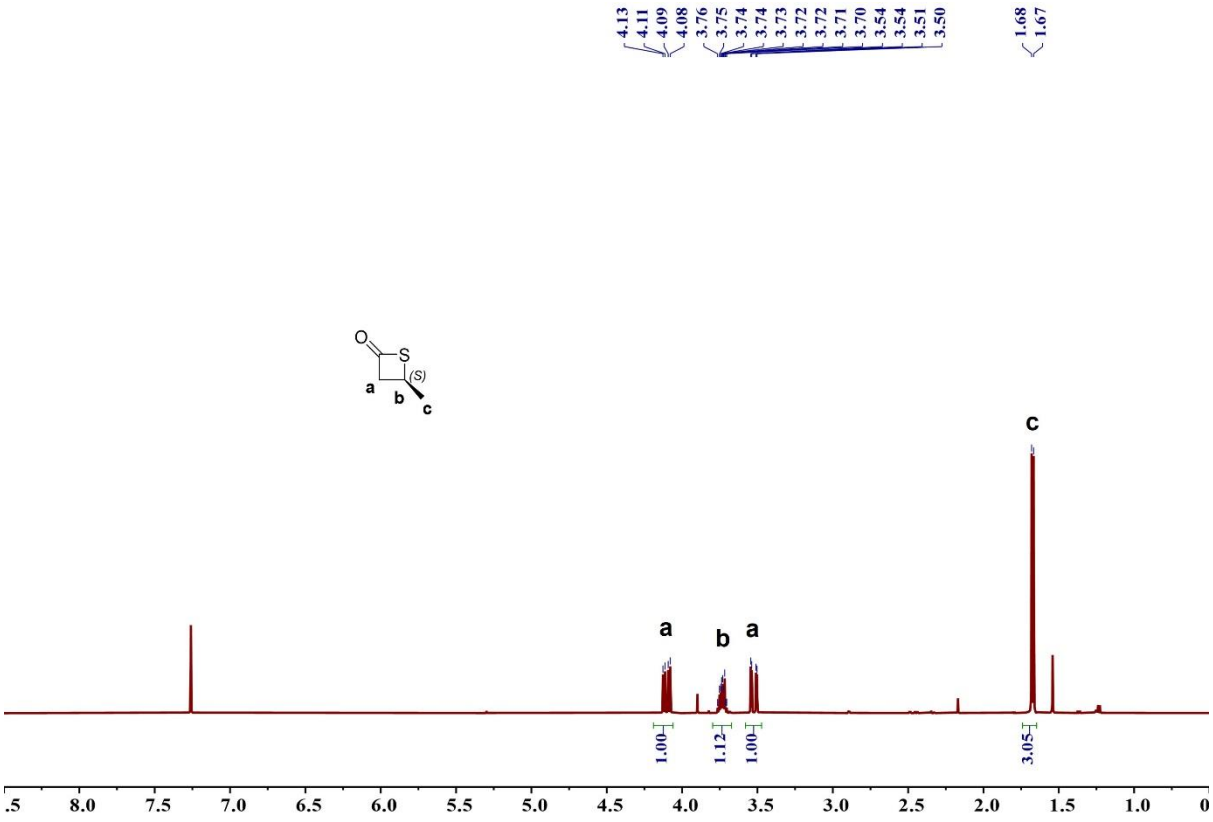


Figure S8. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of (*S*)-TBL; the weak signals at *δ* 2.18 and 1.56 ppm correspond to residual acetone and water, respectively.

General Polymerization Procedure. In the glovebox, a Schlenk flask was charged with $[Y(N(SiHMe_2)_2)_3](THF)_2$ (6.3 mg, 10 µmol) and the desired $\{ONXO^{R2}\}H_2$ proligand (10 µmol), and toluene (0.88 mL) was added. To this solution, in the glove box, ^{i}PrOH (10 µmol, 38 µL of a 2% (*v/v*) solution in toluene) was added under stirring at 14 °C. After 5 min, *rac*-TBL (102 mg, 1.0 mmol, 100 *equiv.* vs. Y) was added rapidly. After the desired period, the polymerization was quenched by addition of benzoic acid (0.5 mL of 10 mg mL^{-1} solution in $CHCl_3$). An aliquot (0.1 mL) of the reaction mixture was used to determine the monomer conversion by ^{1}H NMR analysis. The resulting mixture was then concentrated to dryness under vacuum, and the resulting crude polymer was subsequently dissolved in CH_2Cl_2 (*ca*. 2 mL) and precipitated in pentane (*ca*. 50 mL, not cooled), filtered, and dried in a vacuum oven at room temperature till constant weight. The P3TB polymer was recovered as a white powder, and analyzed by NMR spectroscopy and SEC. Pure isotactic P3TB was prepared from ROP of (*S*)-TBL (50 equiv.) with the **5a**/^{i}PrOH (1:1) system in toluene at room temperature (P_m > 0.95, M_n = 3.2 kg mol^{-1}, $Đ_M$ = 1.52).

^{1}H and ^{13}C NMR spectra of isolated P3TBs

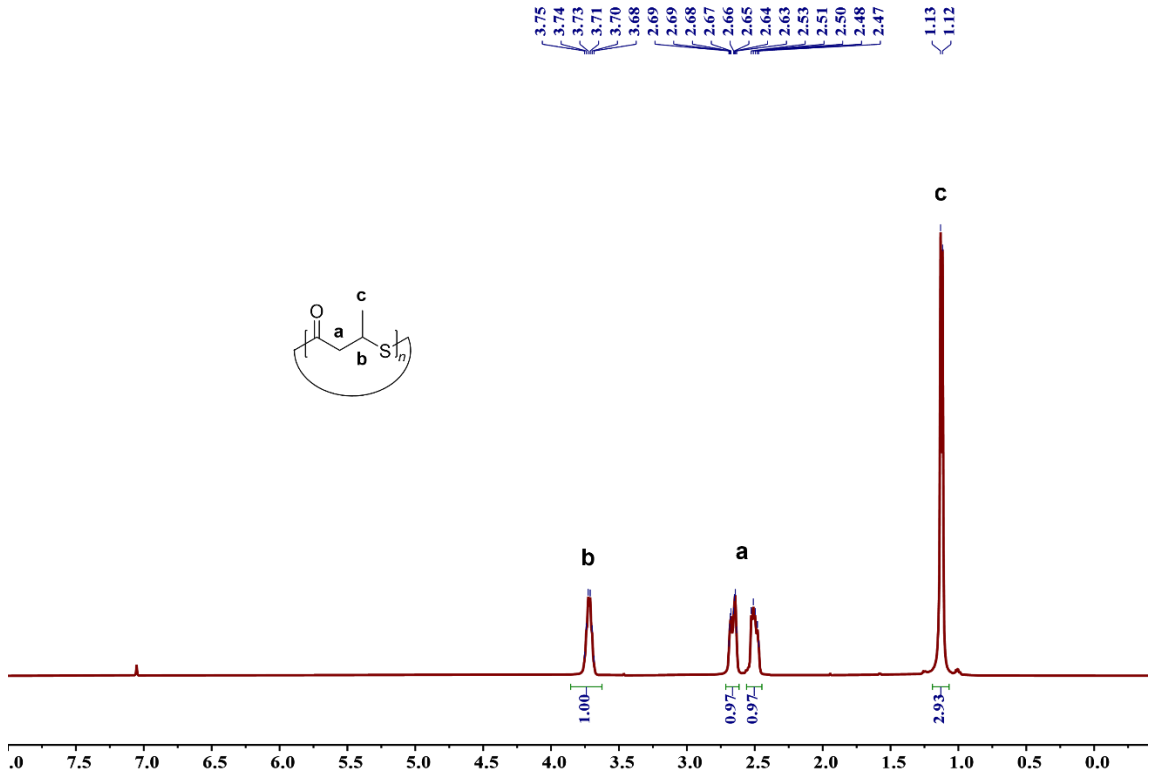


Figure S9. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of an isolated cyclic P3TB produced by the system **5a**/^{i}PrOH (100:1:1, r.t., toluene, entry 17).

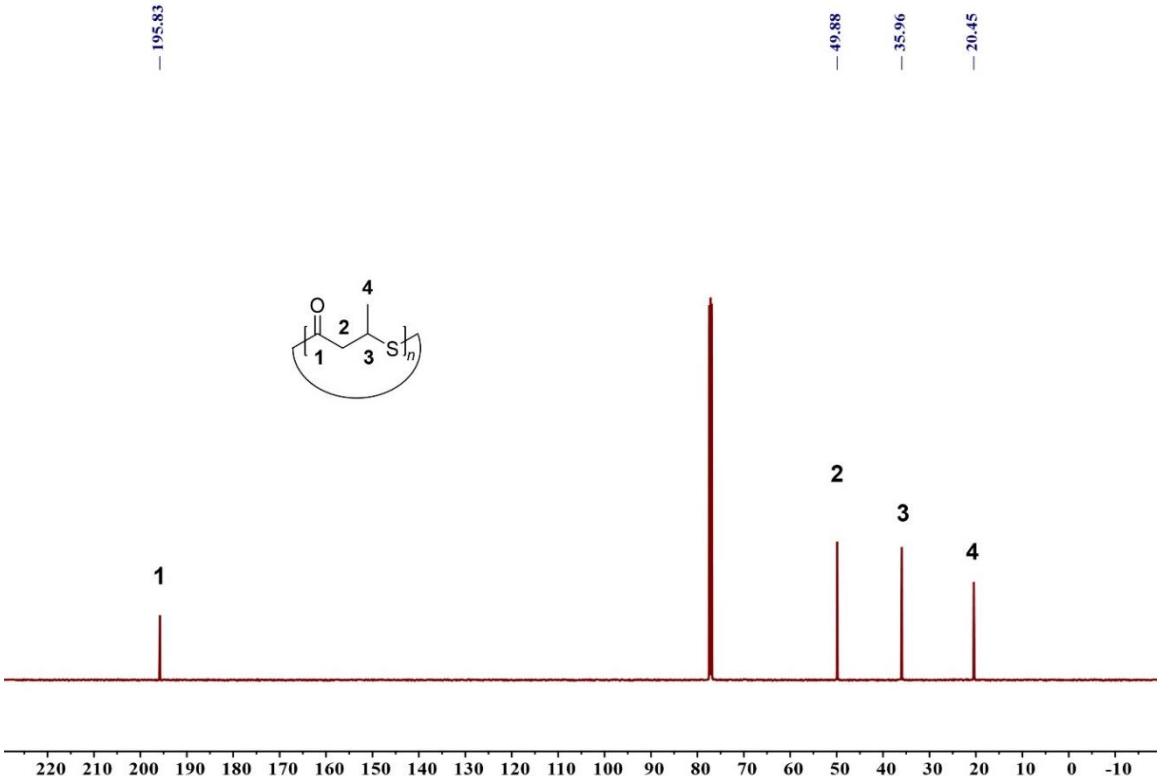


Figure S10. ^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an isolated cyclic P3TB produced by the system **5a**/^{i}PrOH (100:1:1, r.t., toluene, entry 17).

MALDI-ToF mass spectra of isolated P3TBs

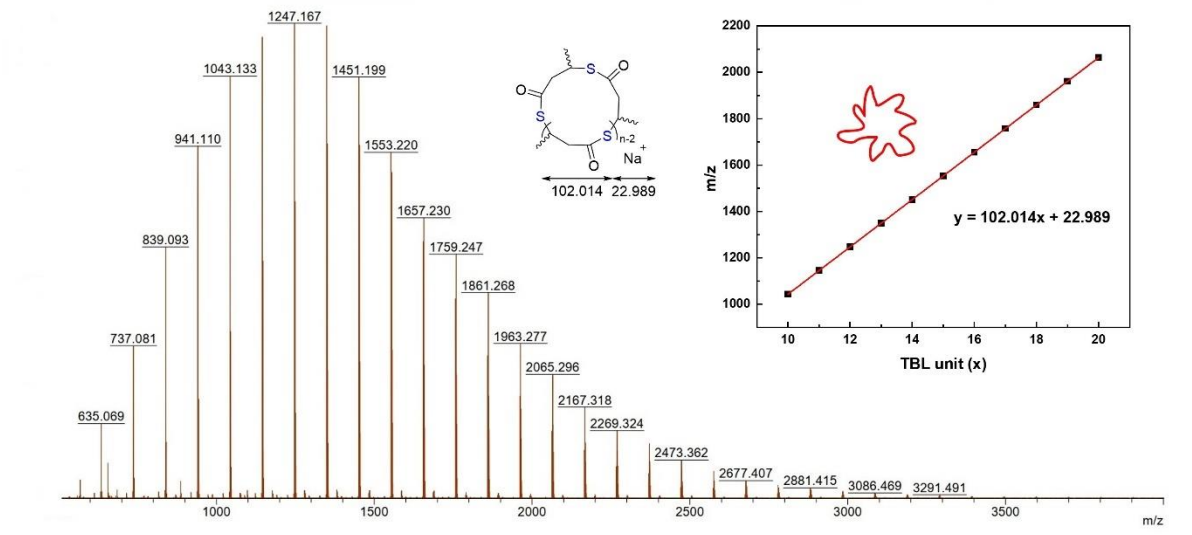


Figure S11. MALDI-ToF mass spectrum of a cyclic P3TB produced by the system Y{ONNO$^{t\text{Bu2}}$}{N(SiHMe$_2$)$_2$}(THF) (**5a**) / ^{i}PrOH (1:1) in toluene (Table 1, entry 12), with a plot of experimental *m*/*z* values vs. theoretical number of TBL repeat units. For *n* = 12, *m*/*z* exp = 1247.167 vs. *m*/*z* theo = 1247.156 for {[$C_4H_6OS]_{12}$+Na}$^+$.

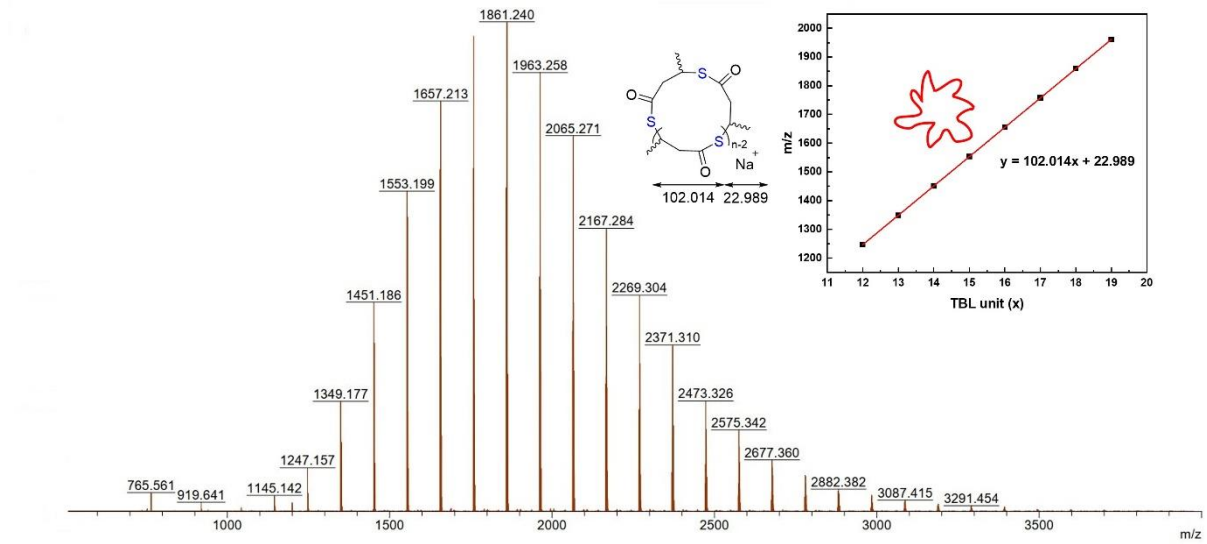


Figure S12. MALDI-ToF mass spectrum of a cyclic P3TB produced by the system Y{ONNO$^{t\text{Bu2}}$}{N(SiHMe$_2$)$_2$}(THF) (**5a**) / ^{i}PrSH (1:1) in toluene (Table 1, entry 13), with a plot of experimental *m*/*z* values vs. theoretical number of TBL repeat units. For *n* = 18, *m*/*z* exp = 1859.246 vs. *m*/*z* theo = 1859.240 for {[$C_4H_6OS]_{18}$+Na}$^+$.

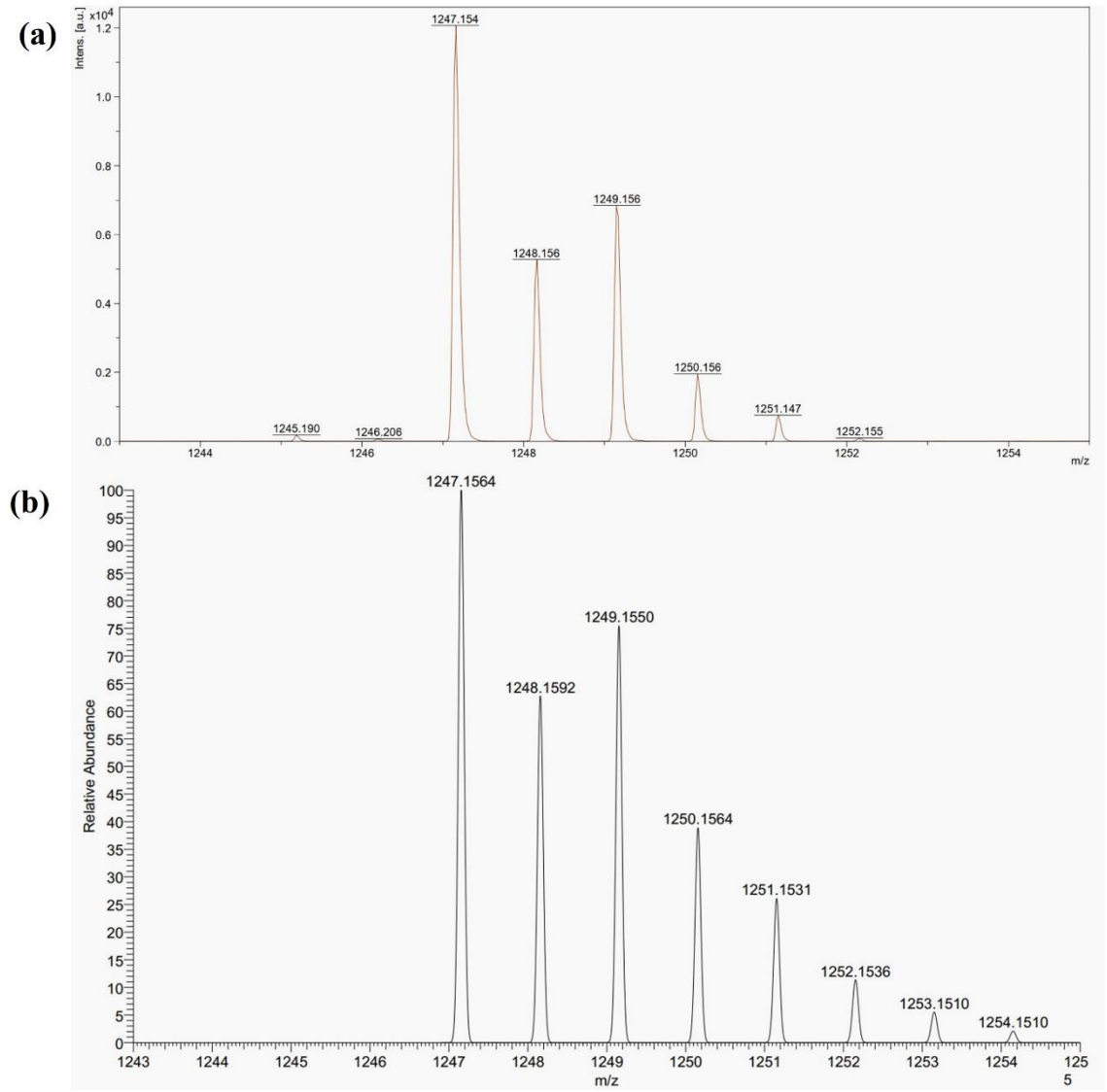


Figure S13. Details (isotopic distribution) of the MALDI-ToF mass spectrum of a cyclic P3TB produced by Y{ONNO^{tBu2}}{N(SiHMe$_2$)$_2$}(THF) (**5a**) in toluene in the absence of co-initiator, showing the isotopic distribution for macromolecules {[$C_4H_6SO]_{12}$+Na}$^+$: a) experimental spectrum (Table 1, entry 10); b) calculated spectrum.

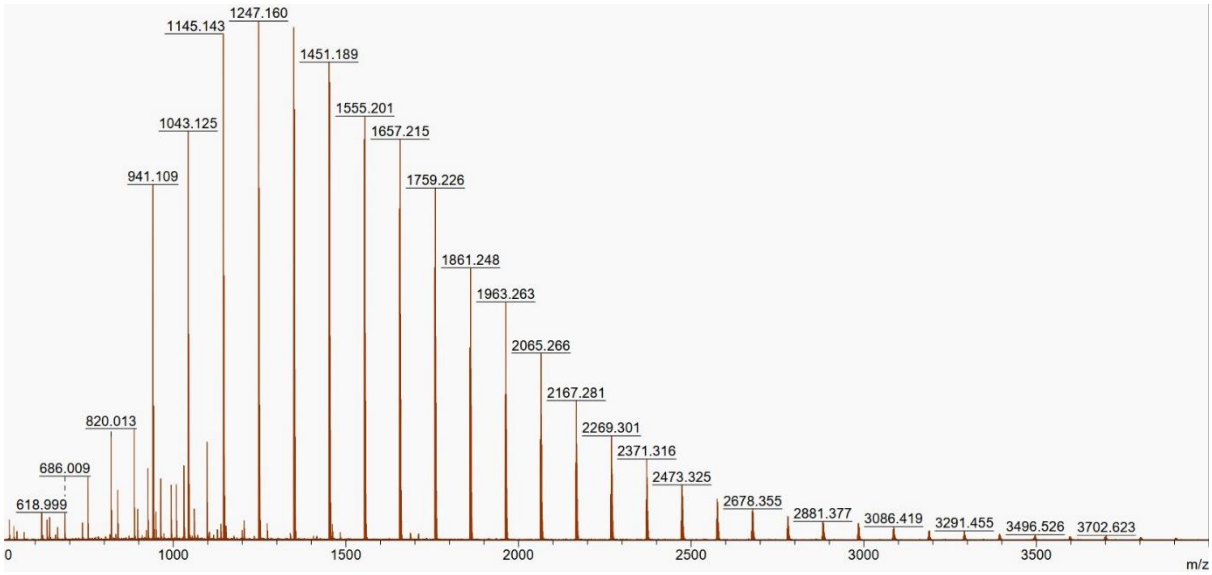


Figure S14. MALDI-ToF mass spectrum of a cyclic P3TB produced by Y{ONNO^{tBu2}}{N(SiHMe$_2$)$_2$}(THF) (**5a**) in THF in the absence of co-initiator (25:1:0, at r.t., in THF, 1 min, conv = 99%). For *n* = 12, *m*/*z* exp = 1247.160 vs. *m*/*z* theo = 1247.156 for {[C_4H_6OS]$_{12}$+Na}$^+$.

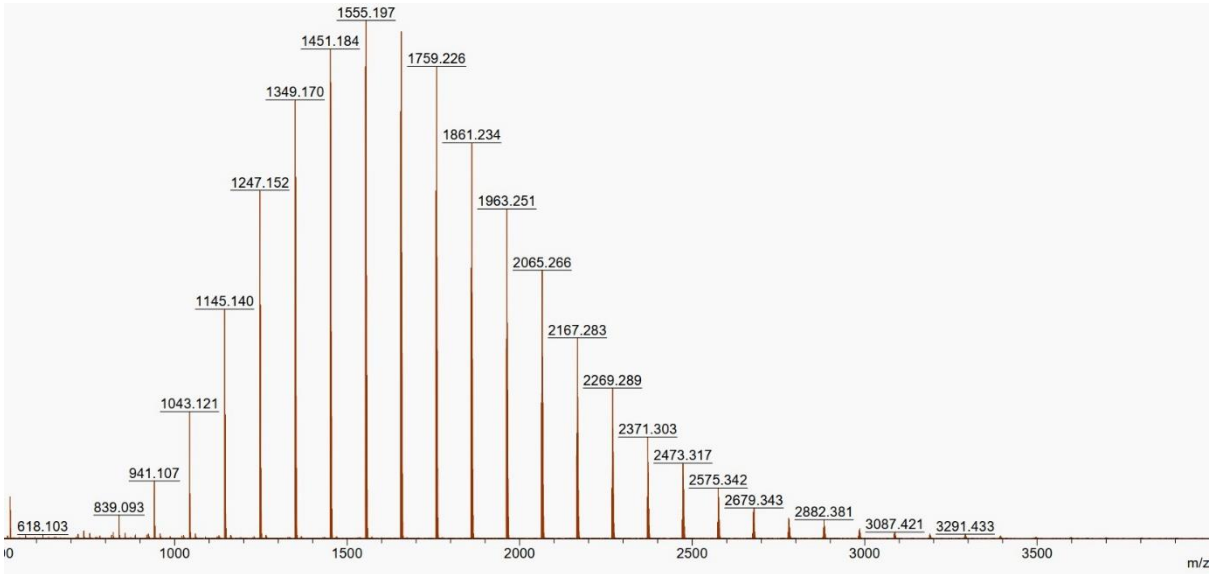


Figure S15. MALDI-ToF mass spectrum of a cyclic P3TB produced by Y{ONNO^{Cl2}}{N(SiHMe$_2$)$_2$}(THF) (**5k**) in THF in the absence of co-initiator (25:1:0, at r.t., 1 min, conv = 99%, $M_{n,SEC}$ = 4100 g mol^{-1}, $Đ_M$ = 1.72). For *n* = 15, *m*/*z* exp = 1553.194 vs. *m*/*z* theo = 1553.198 for {[C_4H_6OS]$_{15}$+Na}$^+$.

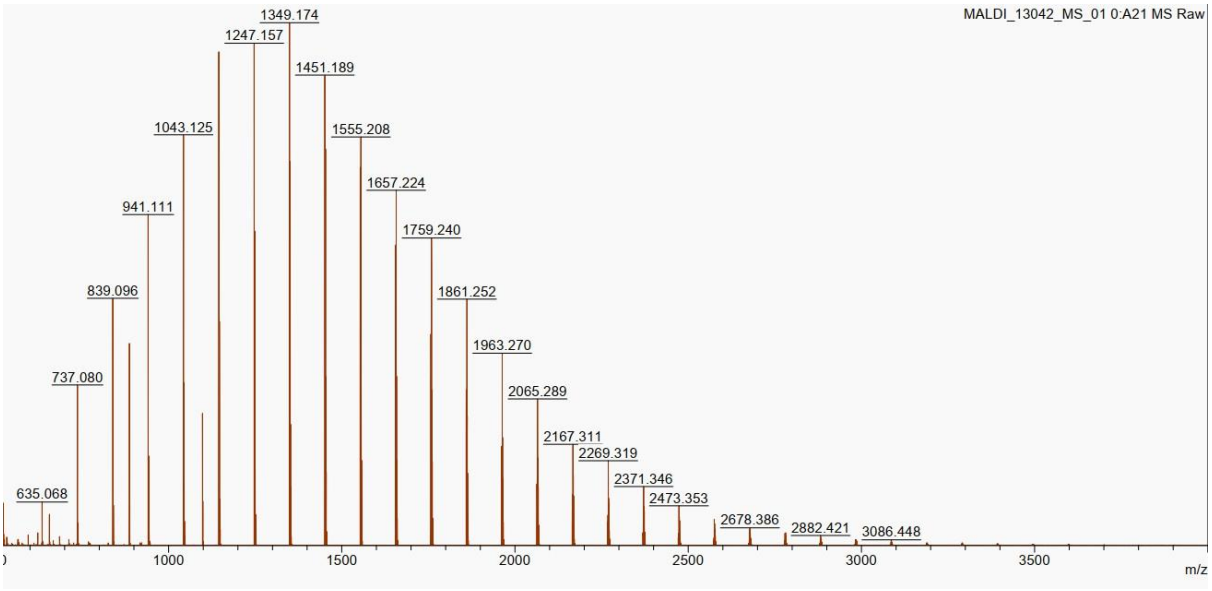


Figure S16. MALDI-ToF mass spectrum of a cyclic P3TB produced by Y{ONNO^{Cl2}}{N(SiHMe$_2$)$_2$}(THF) (**5k**) in THF in the absence of co-initiator (25:1:0, at r.t., 1 min, conv = 99%). For *n* = 13, *m*/*z* exp = 1349.174 vs. *m*/*z* theo = 1349.170 for {[C_4H_6OS}$_{13}$+Na]$^+$.

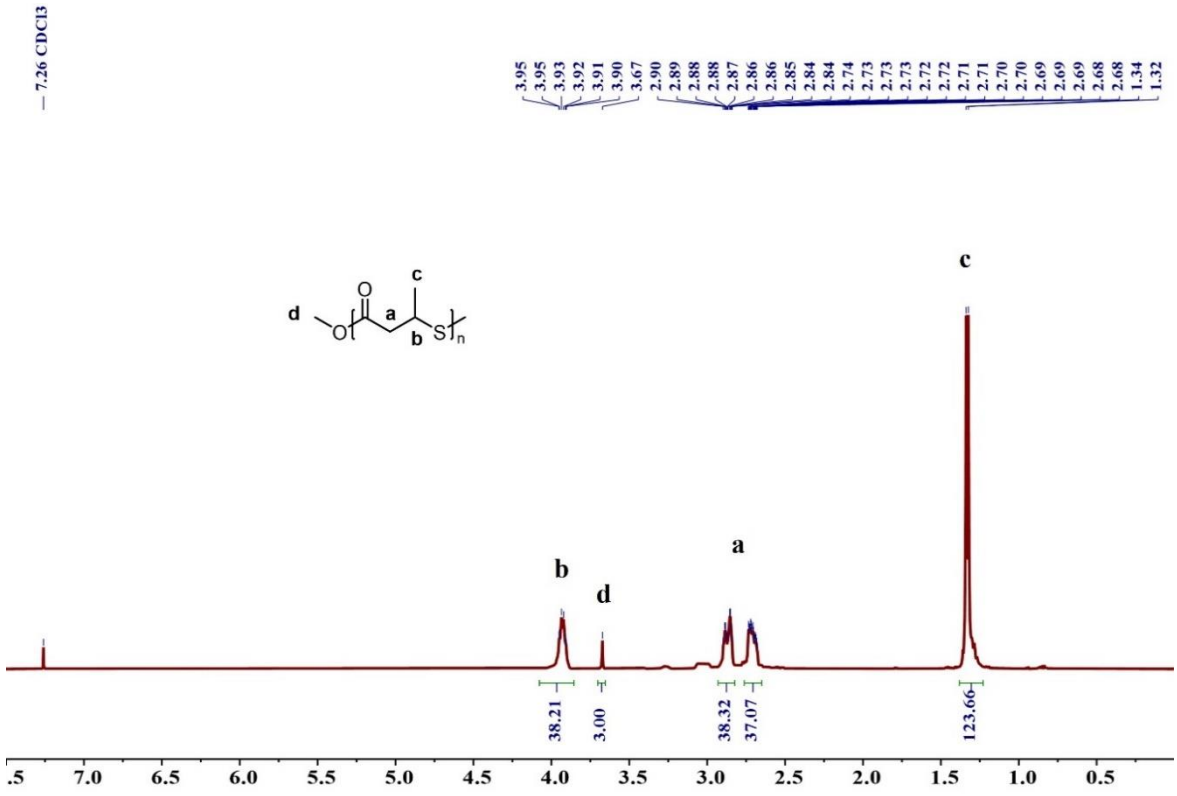


Figure S17. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of an isolated P3TB (at least in part linear) produced by the NaOMe system (23:1, r.t., C_6D_6; Table 1, entry 1; $DP_{n,NMR}$ = ca. 38; $M_{n,NMR}$ = ca. 3900 g mol^{-1}).

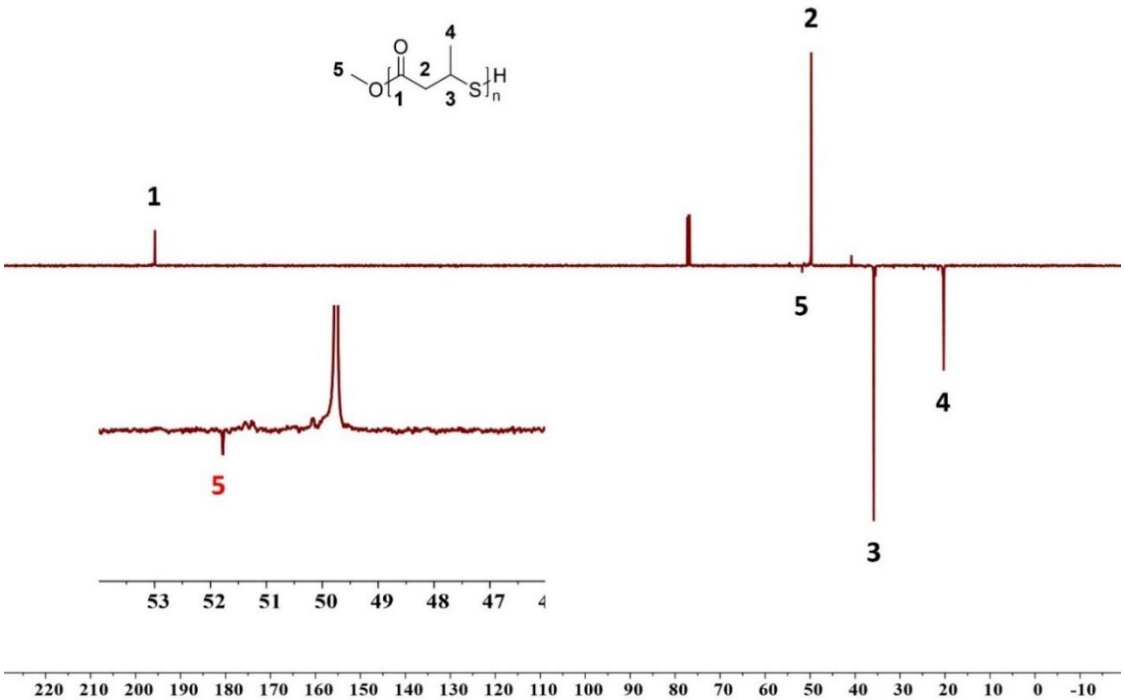


Figure S18. J-MOD spectrum (125 MHz, $CDCl_3$, 25 °C) of an isolated P3TB (at least in part linear) produced by the NaOMe system (23:1, r.t., C_6D_6; Table 1, entry 1).

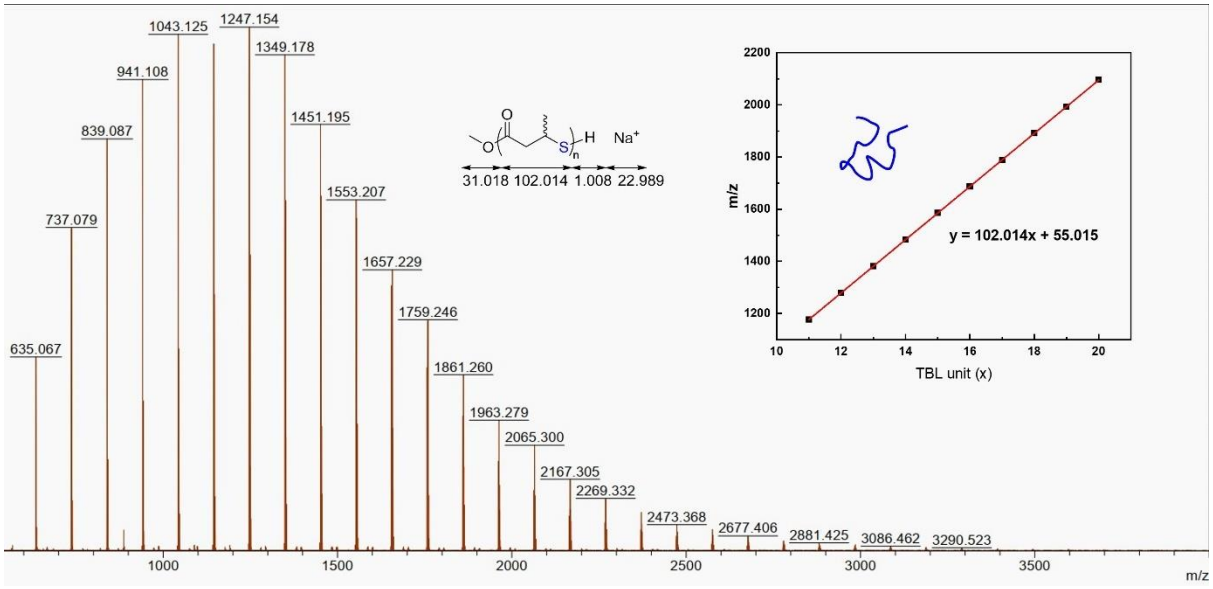


Figure S19. MALDI-ToF mass spectrum of an essentially linear P3TB produced by the system NaOMe in C_6D_6, (Table 1, entry 1), with a plot of experimental m/z values vs. theoretical number of TBL repeat units; the minor population corresponds to cyclic P3TB. For *n* = 20, *m*/*z* exp = 2095.306 vs. *m*/*z* theo = 2095.294 for $\{MeO\text{-}[C_4H_6OS]_{20}\text{-}H+Na\}^+$ (see details in Figure S20).

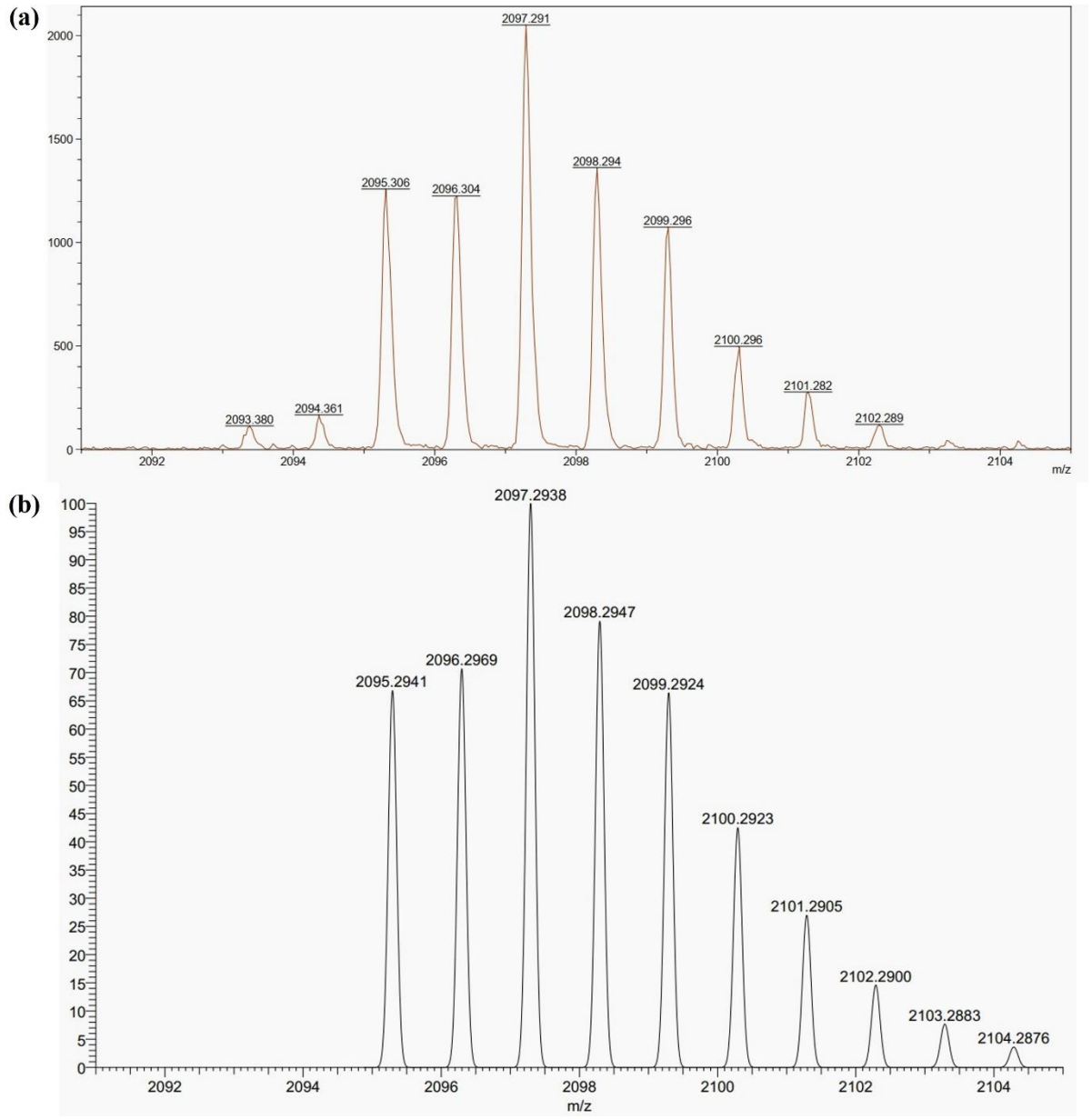


Figure S20. Details (isotopic distribution) of the MALDI-ToF mass spectrum of a linear P3TB produced by NaOMe in C_6D_6, showing the isotopic distribution for macromolecules $\{MeO\text{-}[C_4H_6SO]_{20}\text{-}H+Na\}^+$: a) experimental spectrum (Table 1, entry 1); b) calculated spectrum.

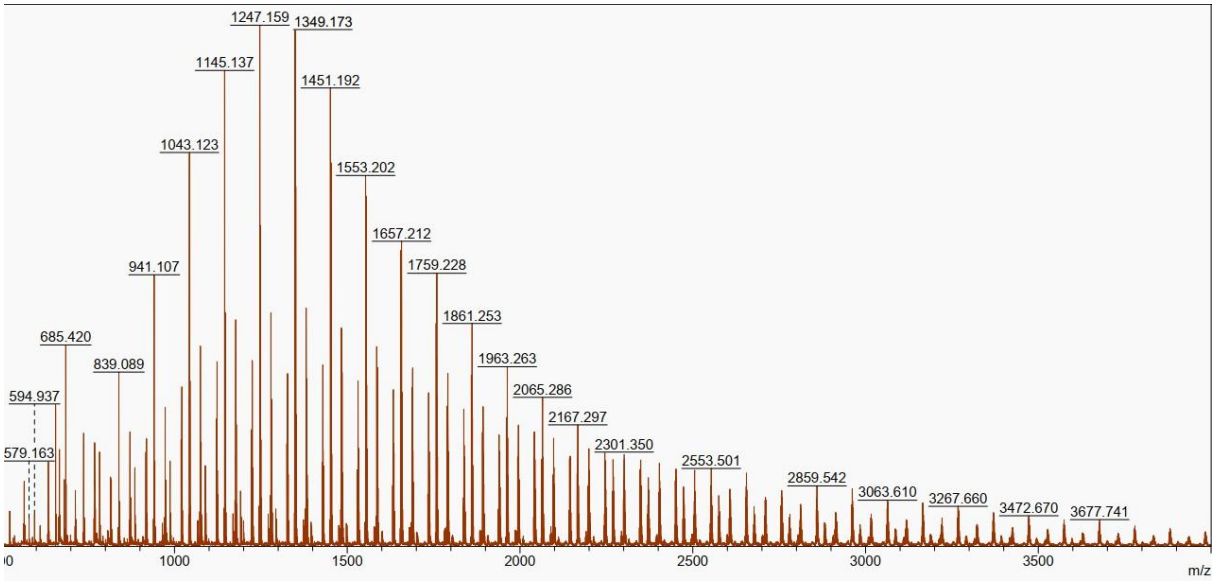


Figure S21a. MALDI-ToF mass spectrum of a mixture of several populations of P3TB, including cyclic (major) and linear (less intense) P3TB, produced by the ROP of *rac*-TBL with NaOMe in toluene (40:1, toluene, 35 °C, 1 h, conv = 52 %). One of the two less intense populations corresponds to linear {MeO-[TBL$_n$]-H+Na}$^+$ macromolecules; for instance, for n = 12, *m/z* exp = 1279.185 vs. *m/z* theo = 1279.183 for {MeO-[$C_4H_6SO]_n$-H+Na}$^+$; the second less intense population (*m/z* obs. = 1225.265) and other minor ones could not be unambiguously identified (see details in Fig. S21b).

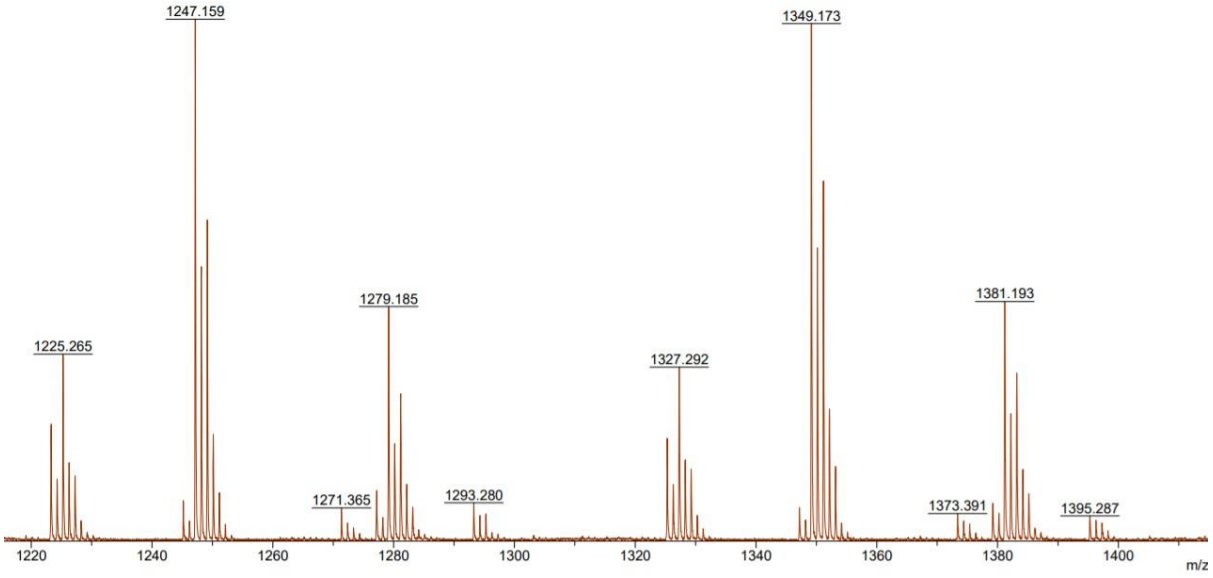


Figure S21b. Details of the MALDI-ToF mass spectrum of a mixture of several populations of P3TB, including a cyclic (major) and a linear (less intense) P3TB, produced by the ROP of *rac*-TBL with NaOMe in toluene (40:1, toluene, 35 °C, 1 h, conv = 52 %). One of the two less intense populations corresponds to linear {MeO-[TBL$_n$]-H+Na}$^+$ macromolecules; for instance, for n = 12, *m/z* exp = 1279.185 vs. *m/z* theo = 1279.183 for {MeO-[$C_4H_6SO]_n$-H+Na}$^+$; the second less intense population and other minor ones could not be unambiguously identified.

Representative SEC traces of P3TBs

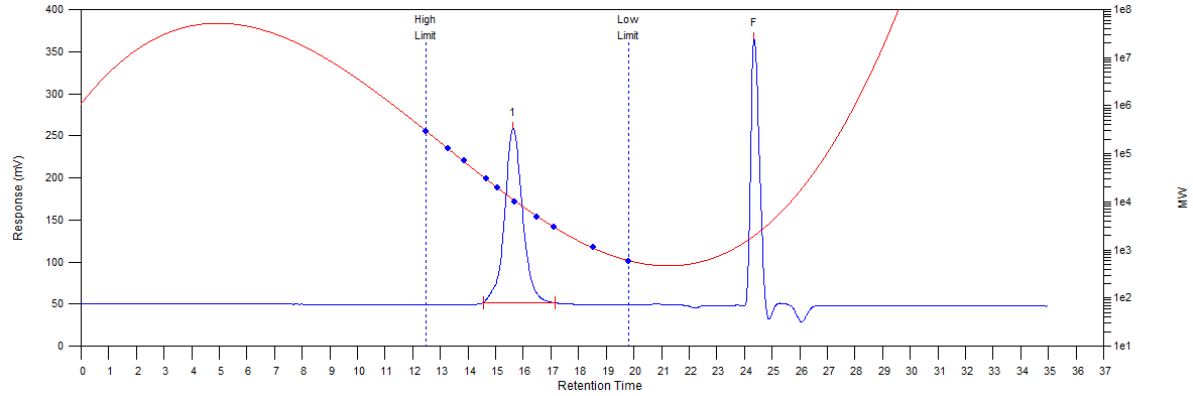


Figure S22. SEC trace of an isolated P3TB (Table S2, entry 11)

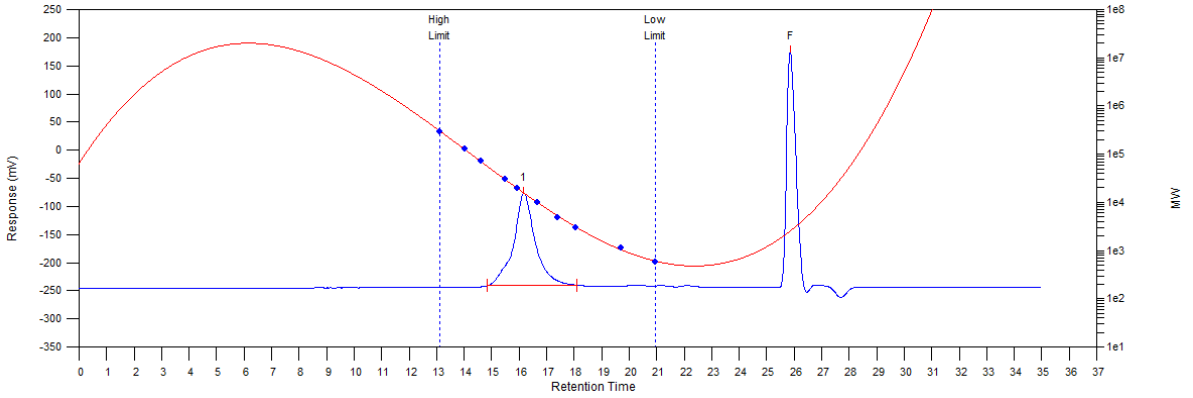


Figure S23. SEC trace of an isolated P3TB (Table S2, entry 10)

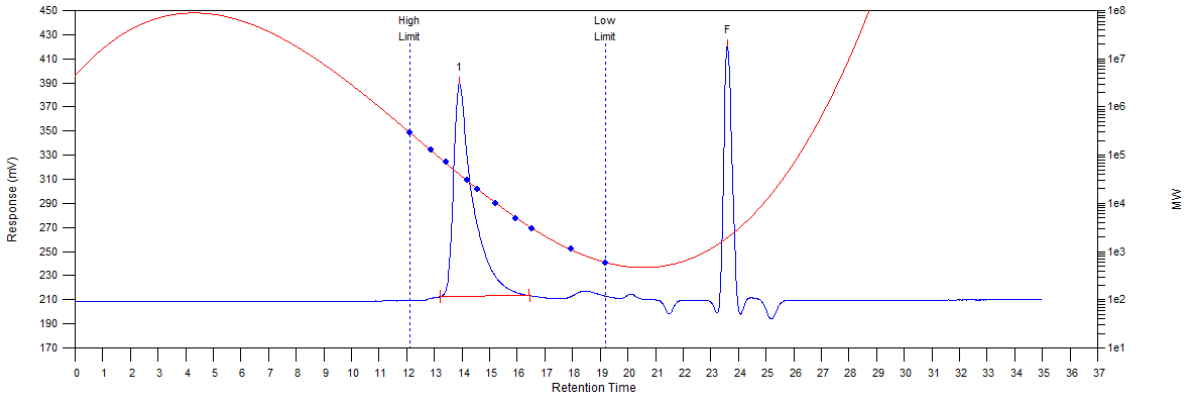


Figure S24. SEC trace of an isolated P3TB (Table 2, entry 48)

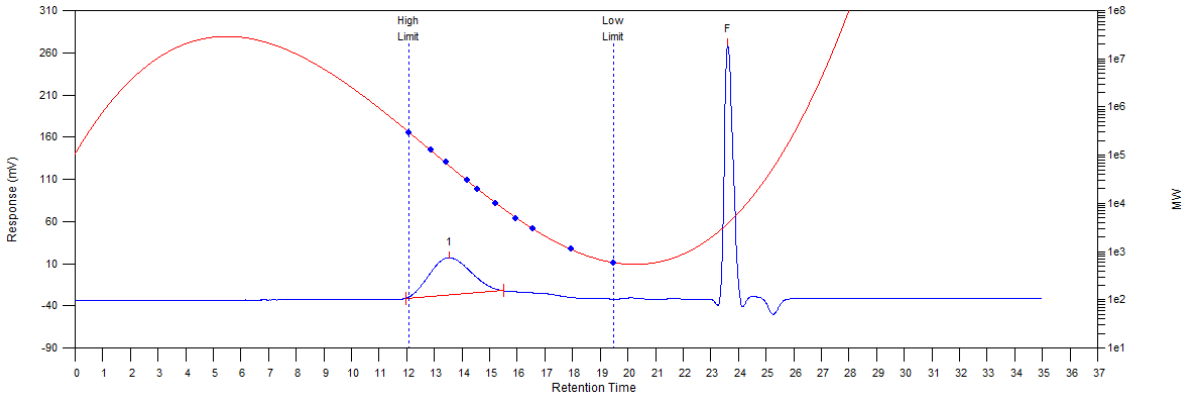


Figure S25. SEC trace of an isolated P3TB (Table 2, entry 32)

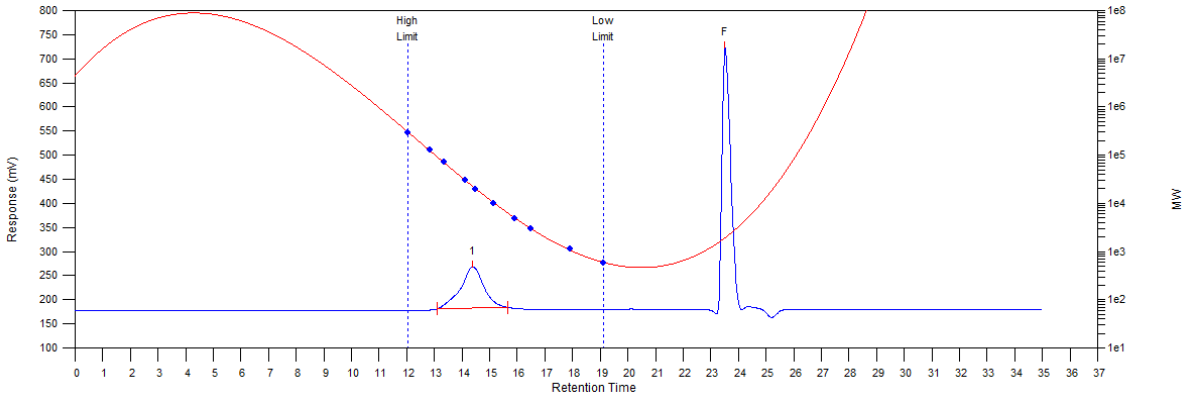


Figure S26. SEC trace of an isolated P3TB (Table 2, entry 34)

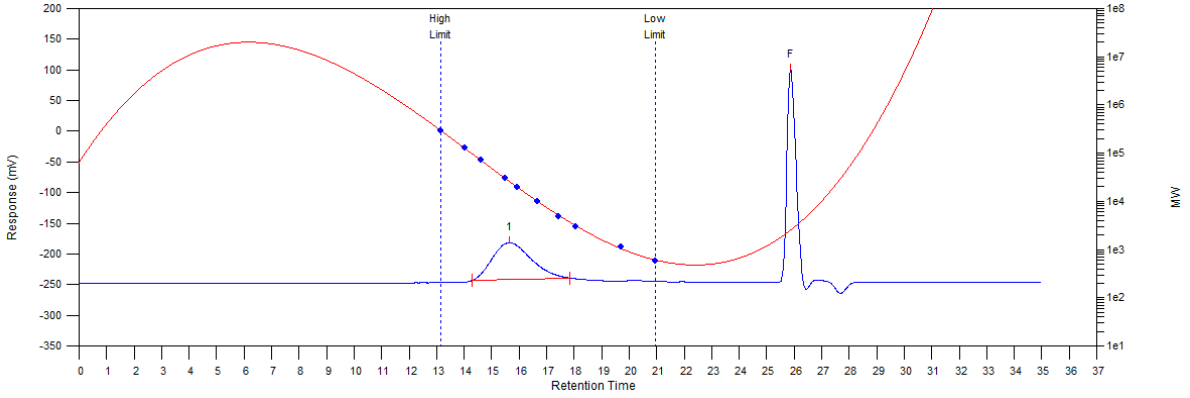


Figure S27. SEC trace of an isolated P3TB (Table 2, entry 17)

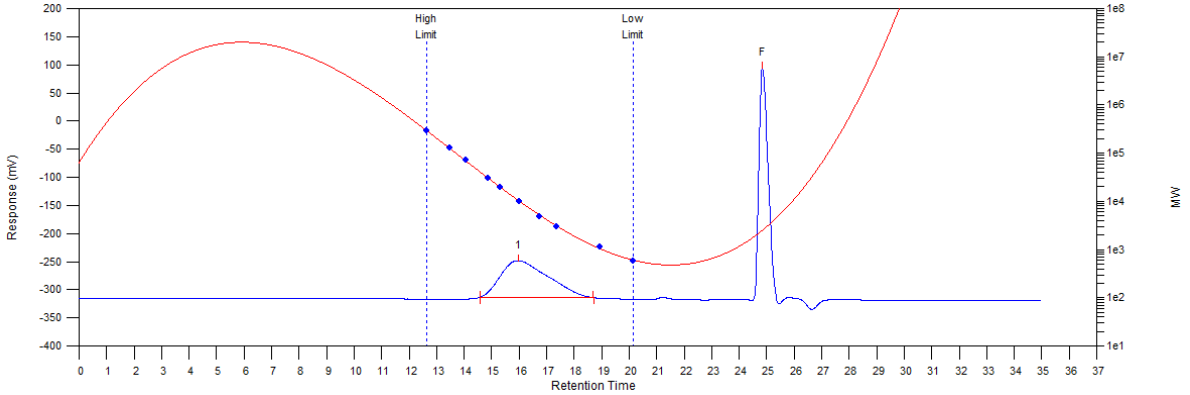


Figure S28. SEC trace of an isolated P3TB (Table 1, entry 15)

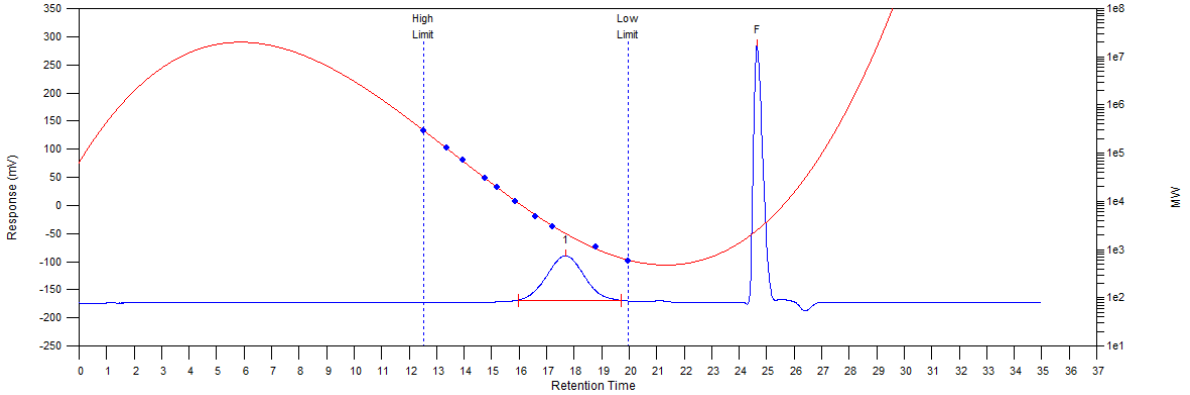


Figure S29. SEC trace of an isolated P3TB (Table 2, entry 35)

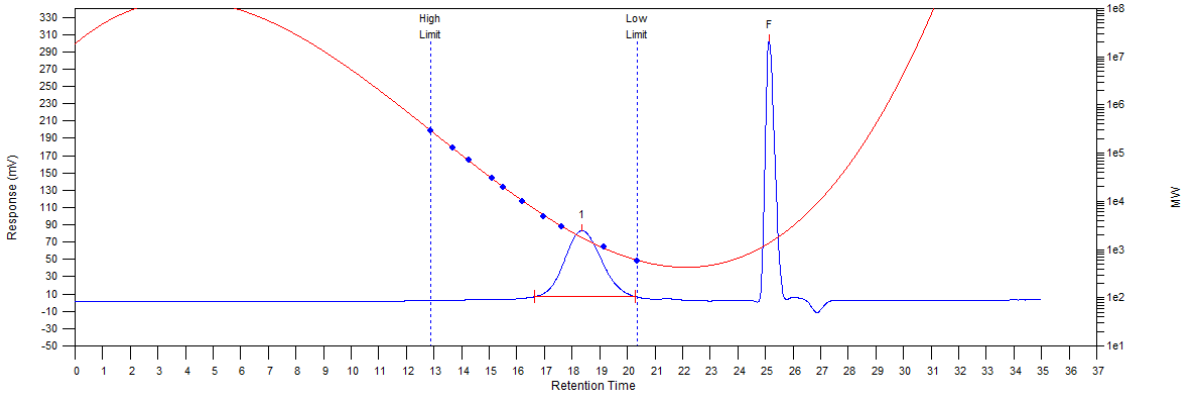


Figure S30. SEC trace of an isolated P3TB (Table 1, entry 7)

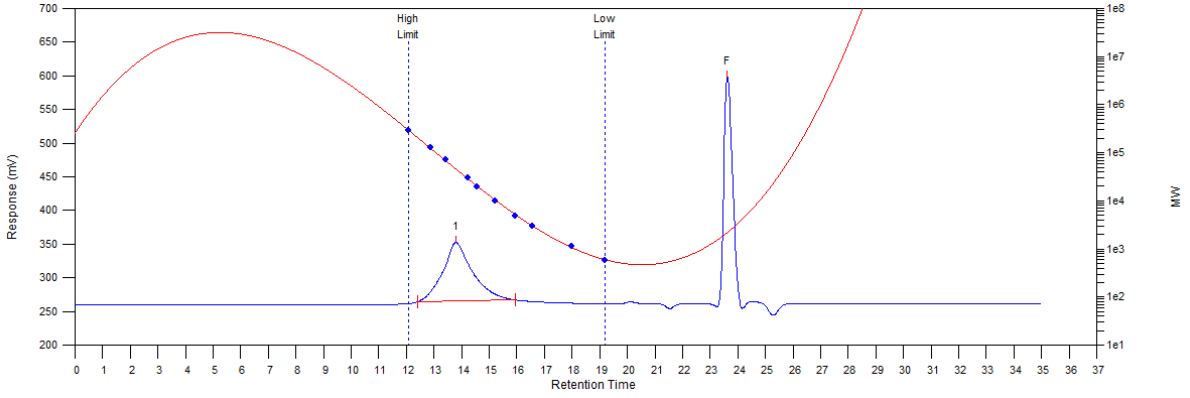


Figure S31. SEC trace of an isolated P3TB (Table 2, entry 21)

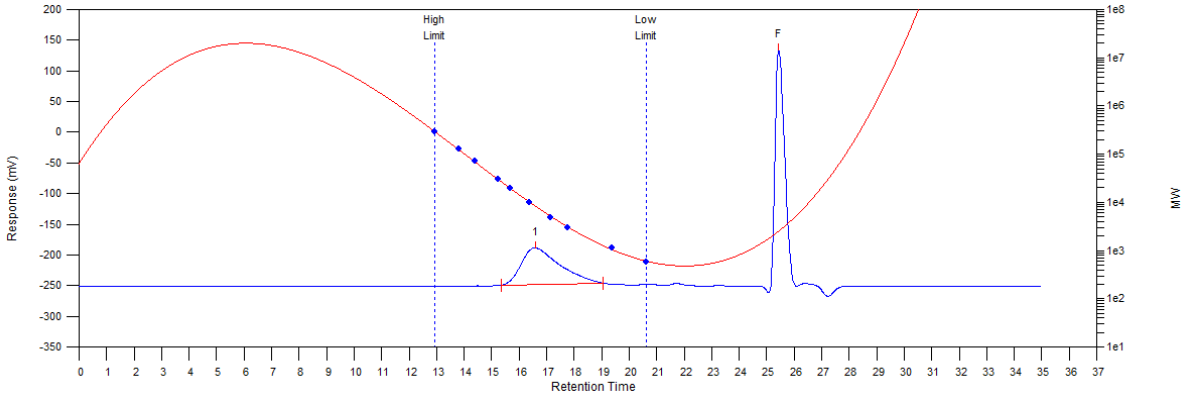


Figure S32. SEC trace of an isolated P3TB (Table 2, entry 26)

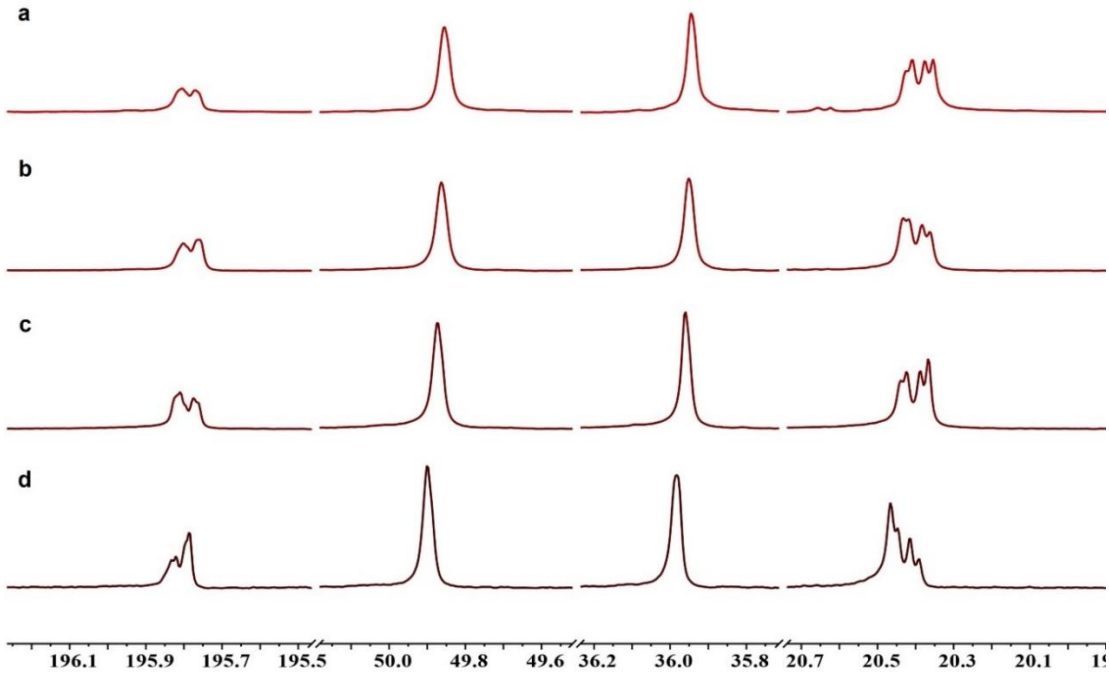


Figure S33. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^{1}H\}$ NMR spectra (125 MHz, $CDCl_3$, 20 °C) of isolated P3TBs. a) atactic, essentially linear P3TB produced by NaOMe in C_6D_6 at room temperature (Table 1, entry 1, P_m = 0.51). b) atactic cyclic P3TB produced by complex **1** in toluene at room temperature (Table 1, entry 2, P_m = 0.48). c) atactic cyclic P3TB produced by the system **4**/^{i}PrOH (1:1) in toluene at room temperature (Table 1, entry 9, P_m = 0.52). d) syndiotactic-biased cyclic P3TB produced by complex **5a** in the absence of co-initiator in toluene at room temperature (Table 1, entry 11, P_m = 0.32).

Table S1. Influence of the solvent on the stereoselective ROP of *rac*-TBL promoted by complex **5k** without a co-initiator.[a]

Entry	$[TBL]_0/[Cat.]$	Solvent	Dielectric constant	$[TBL]_0$ (mol/L)	Reaction time (min)[b]	TBL Conv. (%)[c]	$M_{n,theo}$ (kg/mol)[d]	$M_{n,SEC}$ (kg/mol)[d]	$Đ_M$ [e]	P_m [f]
1	100:1	*n*-Hexane	1.89	0.2	1	67	10.2	5.5	1.46	0.53
2	100:1	1.4-Dioxane	2.21	0.5	1	>99	10.2	5.3	1.61	0.50
3	100:1	Toluene	2.38	0.5	1	93	9.4	4.3	1.41	0.55
4	100:1	2-MeTHF	6.75	0.5	1	>99	10.2	4.9	1.55	0.53
5	100:1	THF	7.52	0.5	1	68	7.0	4.4	1.42	0.57
6	100:1	DCM	9.0	0.5	1	>99	10.2	4.4	1.34	0.53
7	100:1	Acetonitrile	36.64	0.5	1	21	2.1	n.d.	n.d.	n.d.

[a] Polymerizations performed at ambient temperature (15–20 °C). [b] The reaction times were not necessarily optimized. [c] Conversion of *rac*-TBL as determined by ^{1}H NMR analysis of the crude polymerization mixture. [d] Molar mass calculated according to $M_{n,theo} = [TBL]_0/[Cat.] \times Conv._{TBL} \times M_{TBL}$. [e] Number-average molar mass ($M_{n,SEC}$) and dispersity ($Đ_M$) of isolated P3TBs as determined by SEC analysis in THF at 30 °C vs. polystyrene standards (uncorrected values). [f] P_m is the probability of *meso* enchainment between TBL units as determined by $^{13}C\{^1H\}$ NMR analysis of isolated P3TBs.

Table S2. Influence of the solvent on the stereoselective ROP of *rac*-TBL promoted by the system **5c**/^{i}PrOH (1:1).[a]

Ref.	$[M]_0/[Cat.]/[Init.]$	Solvent	Dielectric constant	$[M]_0$ (mol/L)	Reaction time (min)[b]	TBL Conv. (%)[c]	$M_{n,theo}$ [d] (kg/mol)	$M_{n,SEC}$ [e] (kg/mol)	$Đ_M$ [e]	P_m [f]
8	100:1:1	*n*-Hexane	1.89	0.2	1	>99	10.2	21.9	1.37	0.37
9	100:1:1	1.4-Dioxane	2.21	1.0	1	>99	10.2	19.0	1.16	0.39
10	100:1:1	Toluene	2.38	1.0	1	>99	10.2	13.8	1.19	0.38
11	100:1:1	2-MeTHF	6.75	1.0	1	>99	10.2	10.3	1.10	0.35
12	100:1:1	THF	7.52	1.0	2	>99	10.2	6.7	1.26	0.58
13	100:1:1	DCM	9.0	1.0	1	>99	10.2	35.0	1.48	0.35
14	100:1:1	Acetonitrile	36.64	1.0	2	>99	10.2	28.9	1.52	0.34

[a] Polymerizations performed at ambient temperature (15-20 °C), co-initiator ([Init.]) is ^{i}PrOH. [b] The reaction times were not necessarily optimized. [c] Conversion of *rac*-TBL as determined by ^{1}H NMR analysis of the crude polymerization mixture. [d] Molar mass calculated according to $M_{n,theo} = [TBL]_0/[Cat.] \times Conv._{TBL} \times M_{w,\,TBL}$. [e] Number-average molar mass ($M_{n,SEC}$) and dispersity ($Đ_M$) of isolated P3TBs as determined by SEC analysis in THF at 30 °C vs. polystyrene standards (uncorrected values). [f] P_m is the probability of *meso* enchainment between TBL units as determined by $^{13}C\{^{1}H\}$ NMR analysis of isolated P3TBs.

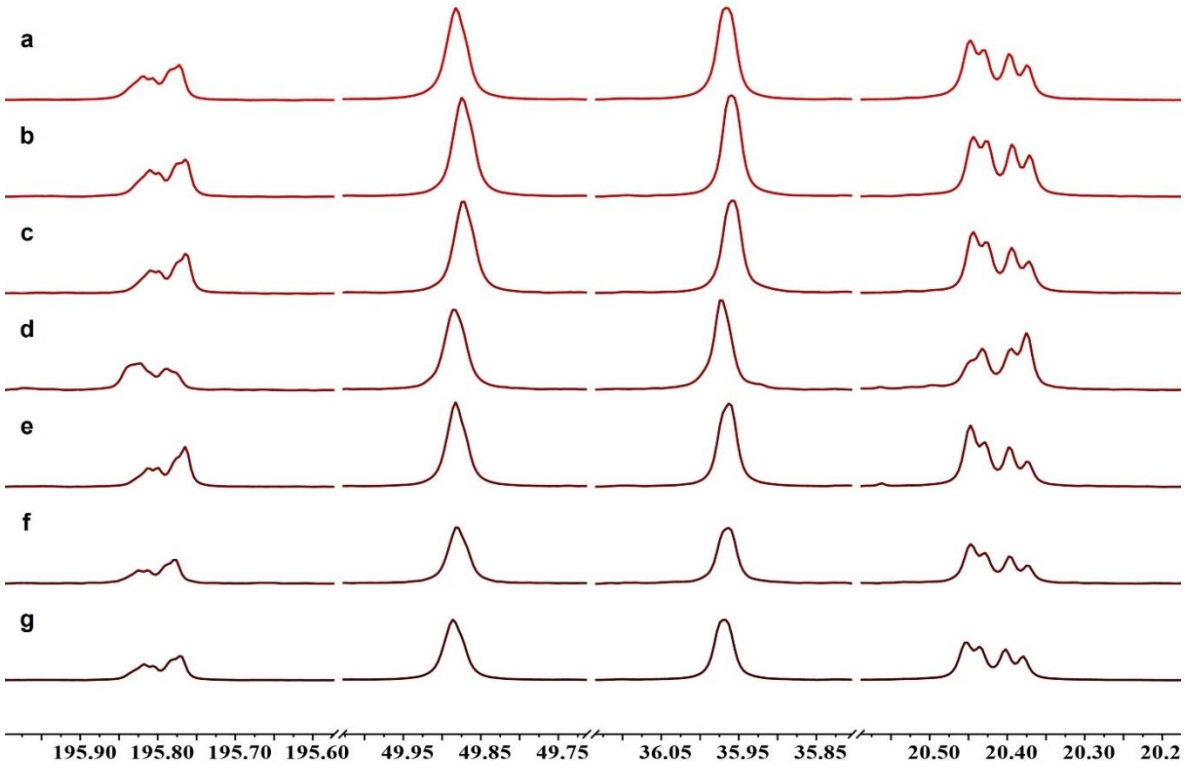


Figure S34. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^{1}H\}$ NMR spectra (125 MHz, $CDCl_3$, 20 °C) of isolated cyclic P3TBs produced in different solvents by the system **5c**/^{i}PrOH (1:1) (Table S2): a) acetonitrile, P_m = 0.34; b) 1,4-dioxane, P_m = 0.39; c) Me-THF, P_m = 0.35; d) THF, P_m = 0.58; e) dichloromethane, P_m = 0.35; f) toluene, P_m = 0.38; g) *n*-hexane, P_m = 0.37.

Determination of tacticity of P3TB by ^{13}C NMR spectroscopy

Deconvolutions-calculations performed on the two series of methyl and carbonyl ^{13}C NMR resonances returned consistent P_m/P_r values. For instance, for entry 48 (Table 2; see spectra below), the normalized intensity of the *m* dyad accounts for 0.897, i.e. P_m = ca. 0.90. From this experimental value, one can calculate the theoretical value of the triad distribution, and then compare it to the experimental ones (Table S3). The P_m values reported in Tables 1, 2, S1 and S2 correspond to the square root of the relative normalized intensity of the *mm* triad.

Table S3. Statistical analysis of the carbonyl and methyl resonances of isotactic cyclic P3TB (entry 48) made from integration determined by regular ^{13}C{^{1}H} NMR.

Theoretical values	Experimental values
(*mm*) = (*m*) × (*m*) = 0.805	(*mm*) = (*m*) × (*m*) = 0.828
(*rr*) = (*r*) × (*r*) = 0.011	(*rr*) = (*r*) × (*r*) = 0.003
(*rm*) = (*mr*) = (*m*) × (*r*) = 0.092	(*rm*) = (*mr*) = (*m*) × (*r*) = 0.084*

* average experimental value = [0.085 + 0.082]/2; the Bernoulli model triad test was not calculated due to large error on the *rr* value.

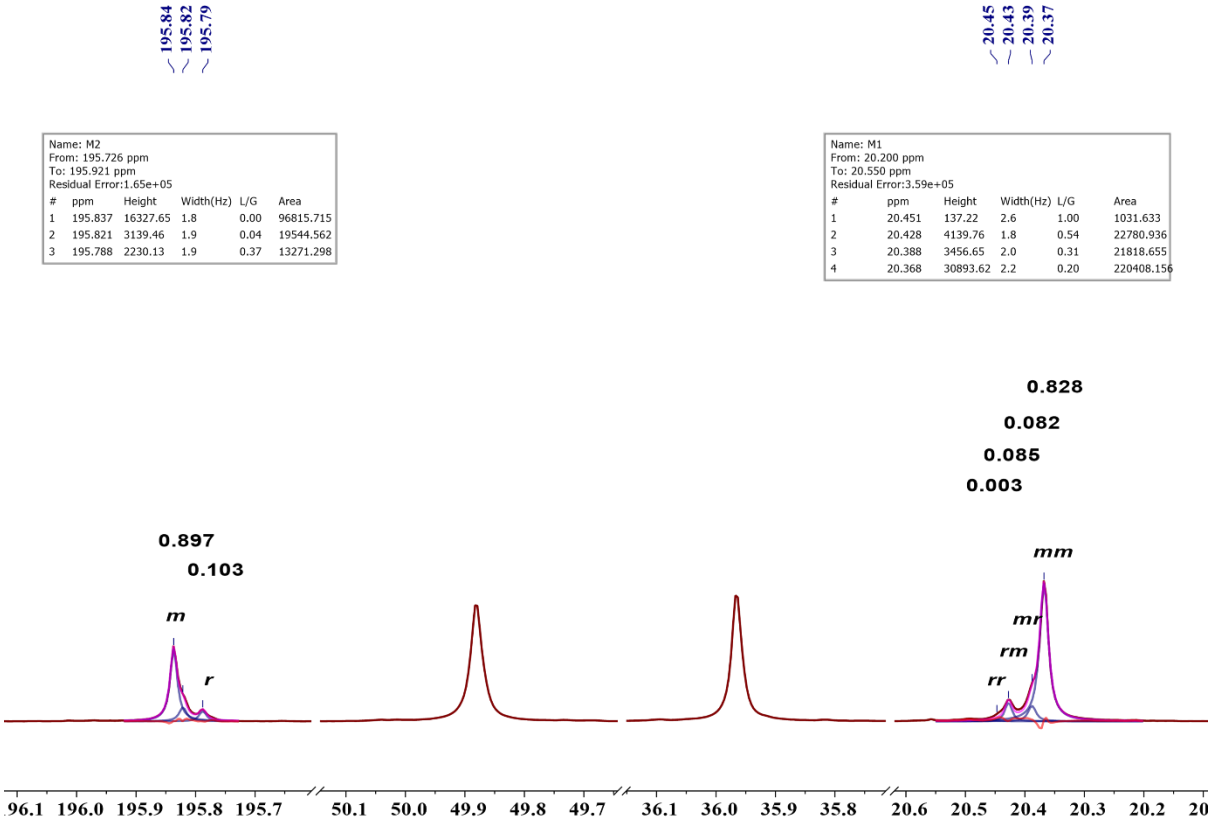
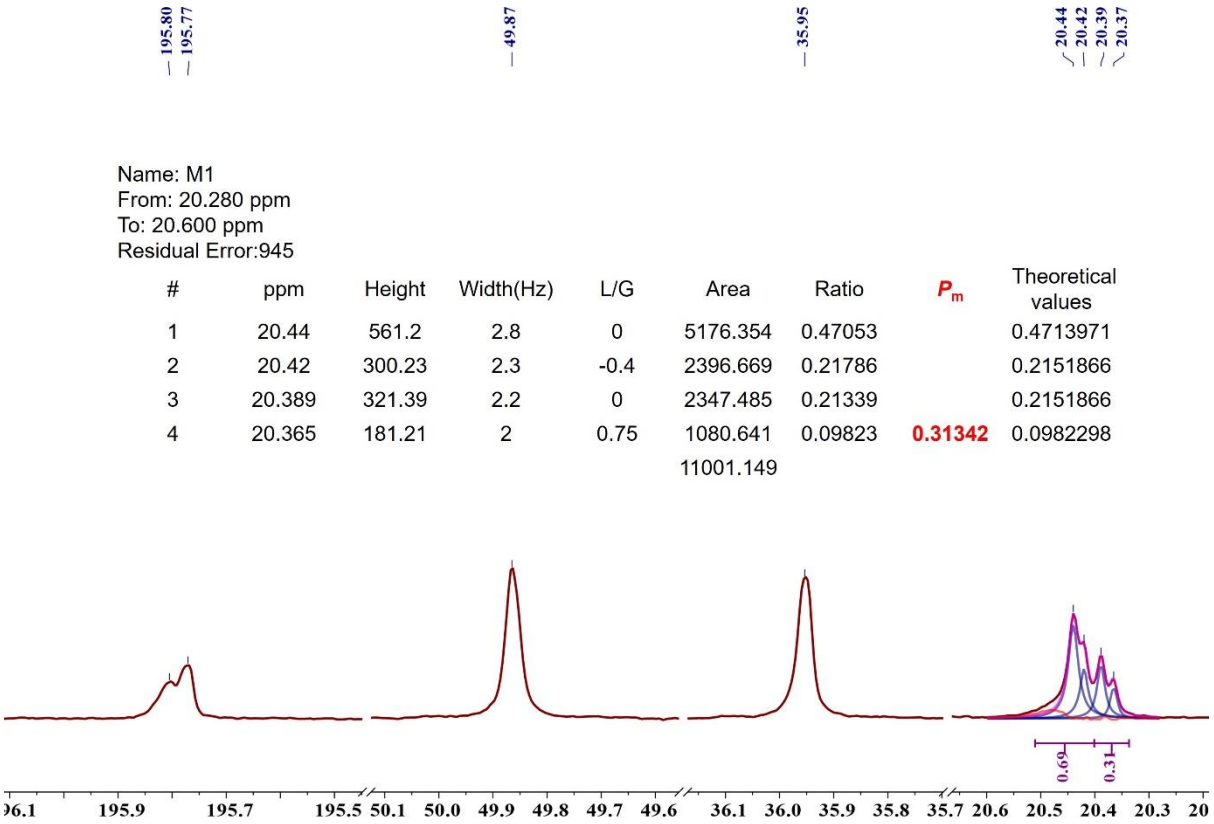


Figure S35. Carbonyl, methine, methylene and methyl regions of the ^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an isotactic-enriched cyclic P3TB (Table 2, entry 48).



Name: M1
From: 20.280 ppm
To: 20.600 ppm
Residual Error:945

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical values
1	20.44	561.2	2.8	0	5176.354	0.47053		0.4713971
2	20.42	300.23	2.3	-0.4	2396.669	0.21786		0.2151866
3	20.389	321.39	2.2	0	2347.485	0.21339		0.2151866
4	20.365	181.21	2	0.75	1080.641	0.09823	**0.31342**	0.0982298
					11001.149			

Figure S36. Carbonyl, methine, methylene and methyl regions of the "regular" $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of a syndiotactic cyclic P3TB (Table 1, entry 14).

Some deconvolutions-calculations were also performed on the carbonyl ^{13}C projection extracted from the band-selective HMBC spectrum. For instance, for entry 14 (Table 1; see spectra below), the normalized intensity of the *rr* triad accounts for 0.463, i.e., P_r = ca. 0.68 ($P_m = 1 - P_r = 0.32$). From this experimental value, one can calculate the theoretical value of the triad distribution, and then compare it to the experimental ones (Table S4).

Table S4. Statistical analysis of the carbonyl resonances of a syndiotactic P3TB (Table 1, entry 14) made from integration determined by ^{13}C projection extracted from band-selective HMBC spectrum.

Theoretical values	Experimental values
(*mm*) = (*m*) × (*m*) = 0.102	(*mm*) = (*m*) × (*m*) = 0.104
(*rr*) = (*r*) × (*r*) = 0.463	(*rr*) = (*r*) × (*r*) = 0.463
(*rm*) = (*mr*) = (*m*) × (*r*) = 0.217	(*rm*) = (*mr*) = (*m*) × (*r*) = 0.216*

* average experimental value = [0.247 + 0.185]/2. Bernoulli model triad test, B = ([(*mm*) × (*rr*)]/[(*rm*) × (*mr*)]= 1.03

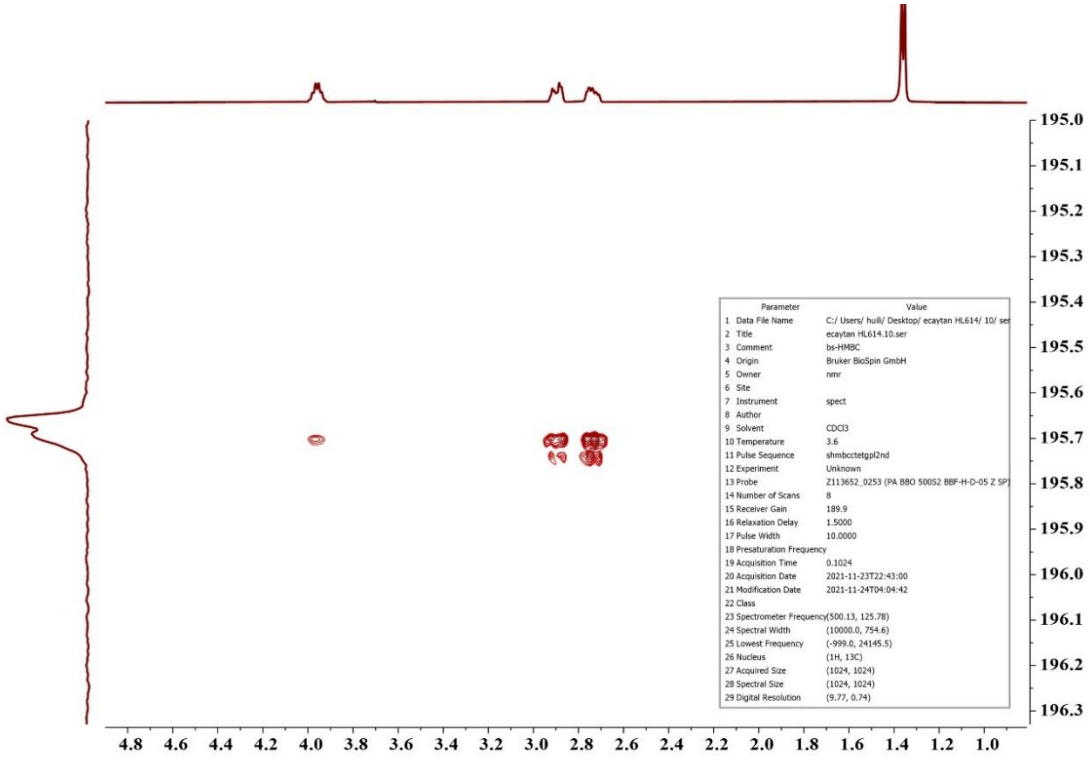
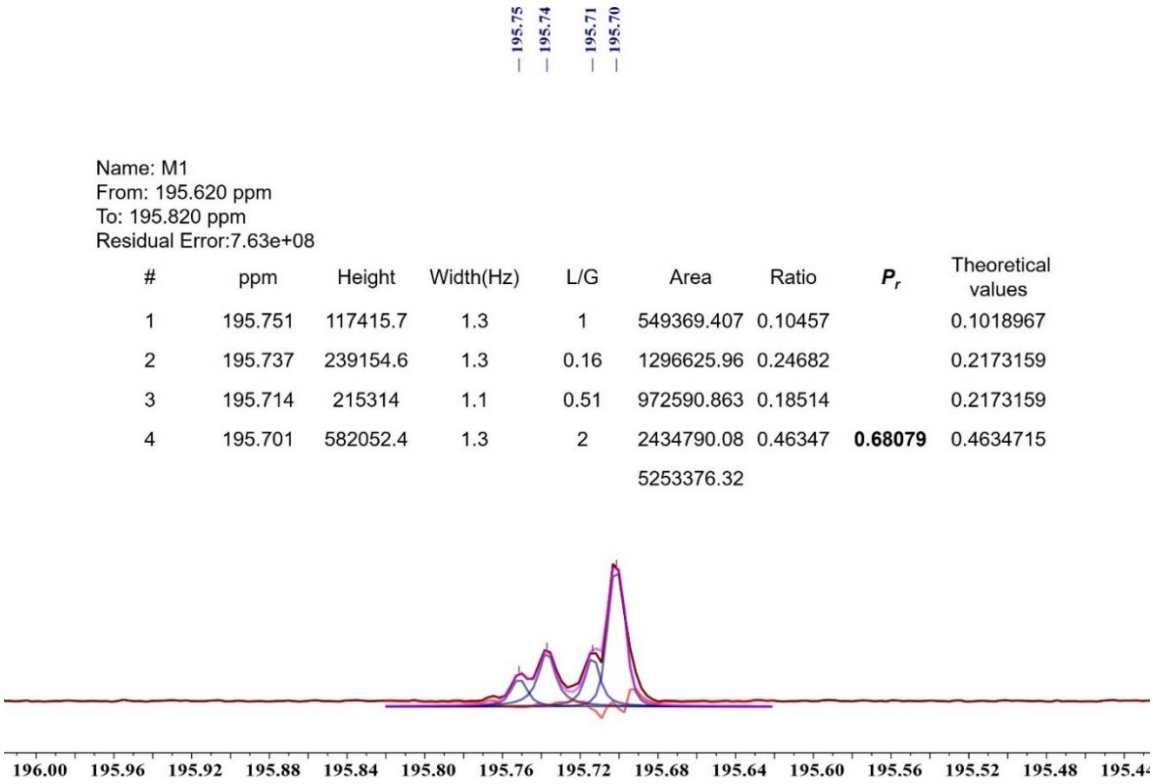


Figure S37. Band-selective HMBC spectrum of a syndiotactic cyclic P3TB (Table 1, entry 14). The ^{1}H NMR (500 MHz) spectrum is plotted on the F2 axis and the ^{13}C NMR (125 MHz) spectrum is plotted on the F1 axis.



#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_r	Theoretical values
1	195.751	117415.7	1.3	1	549369.407	0.10457		0.1018967
2	195.737	239154.6	1.3	0.16	1296625.96	0.24682		0.2173159
3	195.714	215314	1.1	0.51	972590.863	0.18514		0.2173159
4	195.701	582052.4	1.3	2	2434790.08	0.46347	**0.68079**	0.4634715
					5253376.32			

Figure S38. ^{13}C projection extracted from the band-selective HMBC of a syndiotactic cyclic P3TB (Table 1, entry 14) by summing columns between δ ^{1}H 2.60 and 3.00 ppm.

The same deconvolutions-calculations can be performed on the methyl ^{13}C projection extracted from the band-selective HSQC spectrum. For instance, for entry 14 (Table 1, see spectra below), the normalized intensity of the *mm* triad accounts for 0.100, i.e., P_m = ca. 0.32 ($P_r = 1 - P_m = 0.68$). From this experimental value, one can calculate the theoretical value of the triad distribution, and then compare it to the experimental ones (Table S5).

Table S5. Statistical analysis of the methyl resonances of a syndiotactic-enriched P3TB (Table 1, entry 14) made from integration determined by ^{13}C projection extracted from band-selective HSQC spectrum.

Theoretical values	Experimental values
(*mm*) = (*m*) × (*m*) = 0.100	(*mm*) = (*m*) × (*m*) = 0.100
(*rr*) = (*r*) × (*r*) = 0.467	(*rr*) = (*r*) × (*r*) = 0.454
(*rm*) = (*mr*) = (*m*) × (*r*) = 0.216	(*rm*) = (*mr*) = (*m*) × (*r*) = 0.216

Bernoulli model triad test, B = [(*mm*) × (*rr*)]/[(*rm*) × (*mr*)] = 0.97.

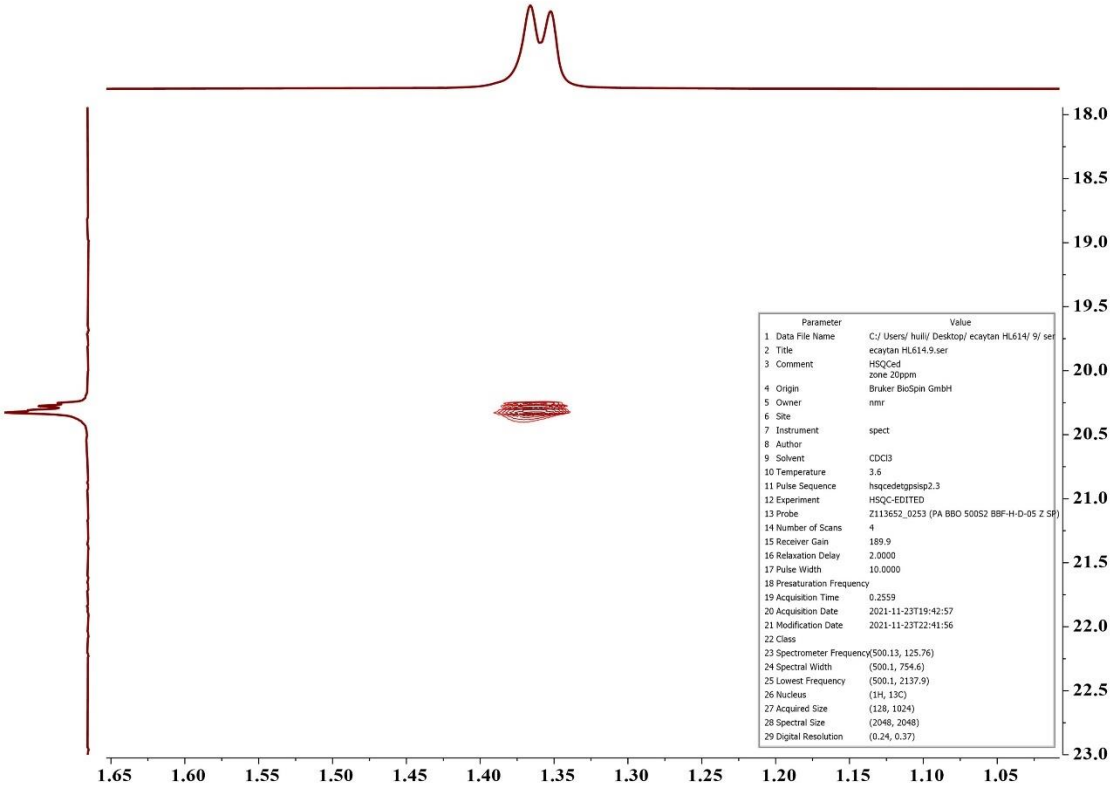


Figure S39. Band-selective HSQC spectrum of a syndiotactic-enriched cyclic P3TB (Table 1, entry 14). The ^{1}H NMR (500 MHz) spectrum is plotted on the F2 axis and the ^{13}C NMR (125 MHz) spectrum is plotted on the F1 axis.

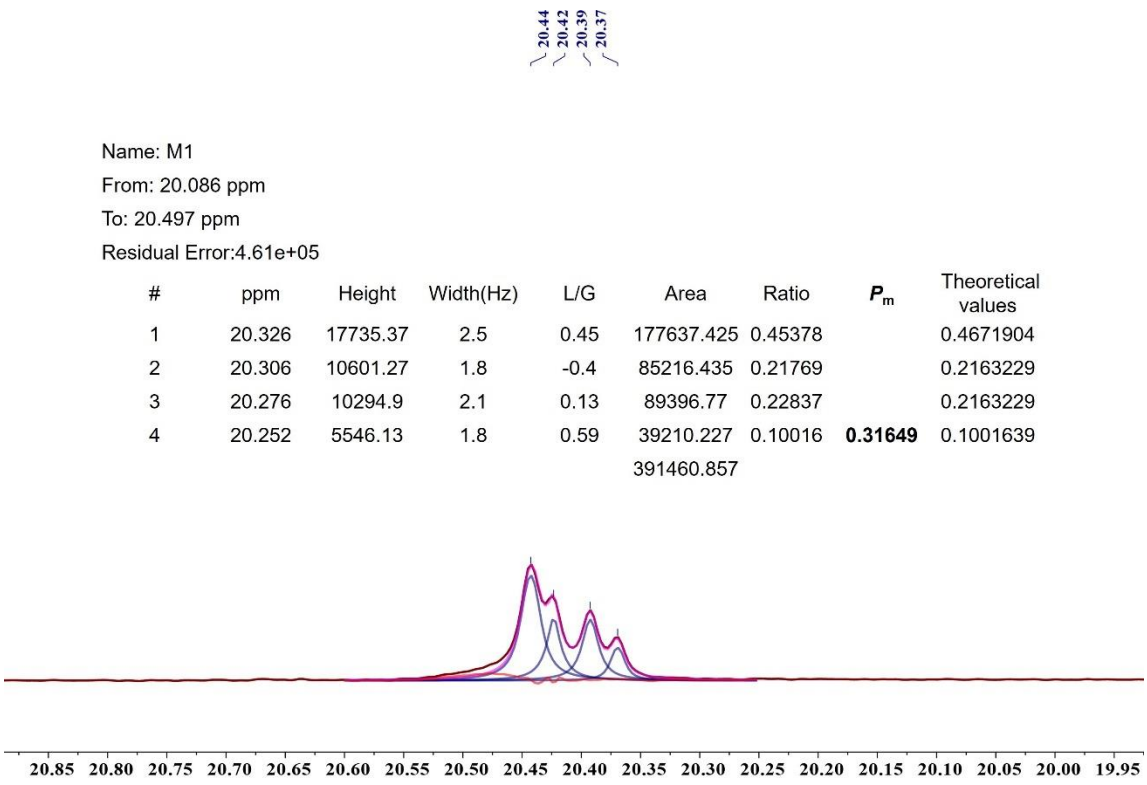


Figure S40. ^{13}C projection extracted from the band-selective HSQC of a syndiotactic-enriched cyclic P3TB (Table 1, entry 14) by summing columns between δ ^{1}H 1.30 and 1.45 ppm.

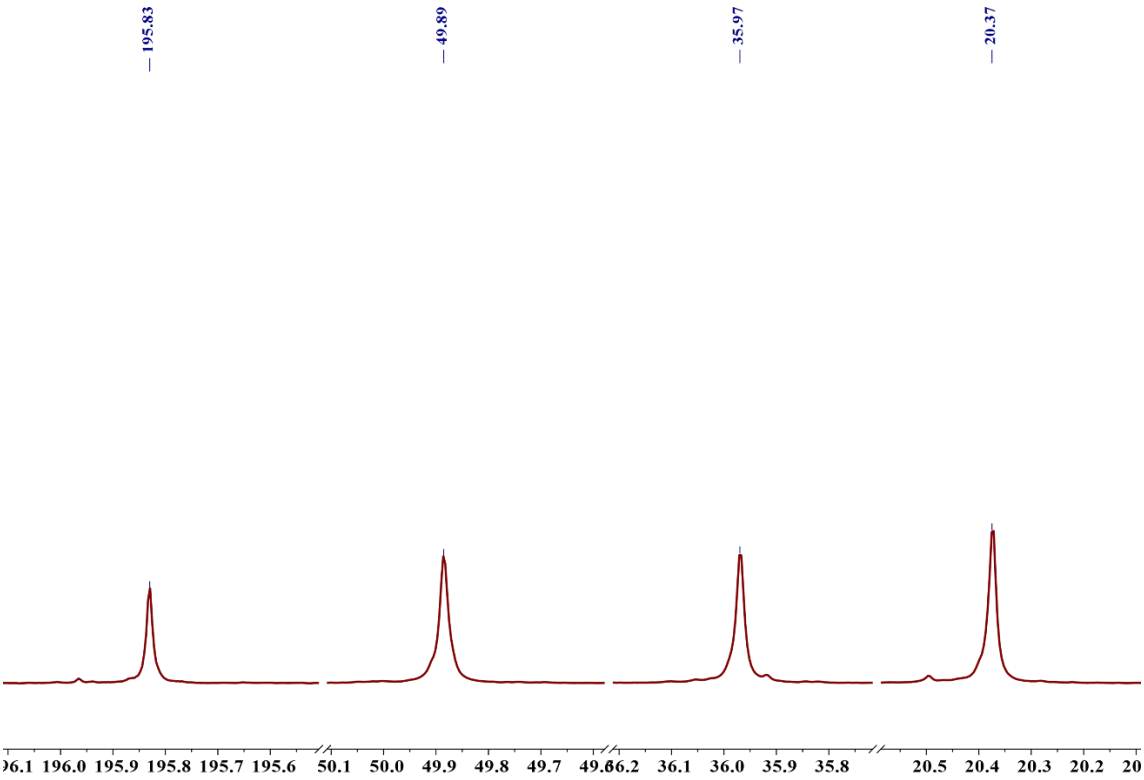
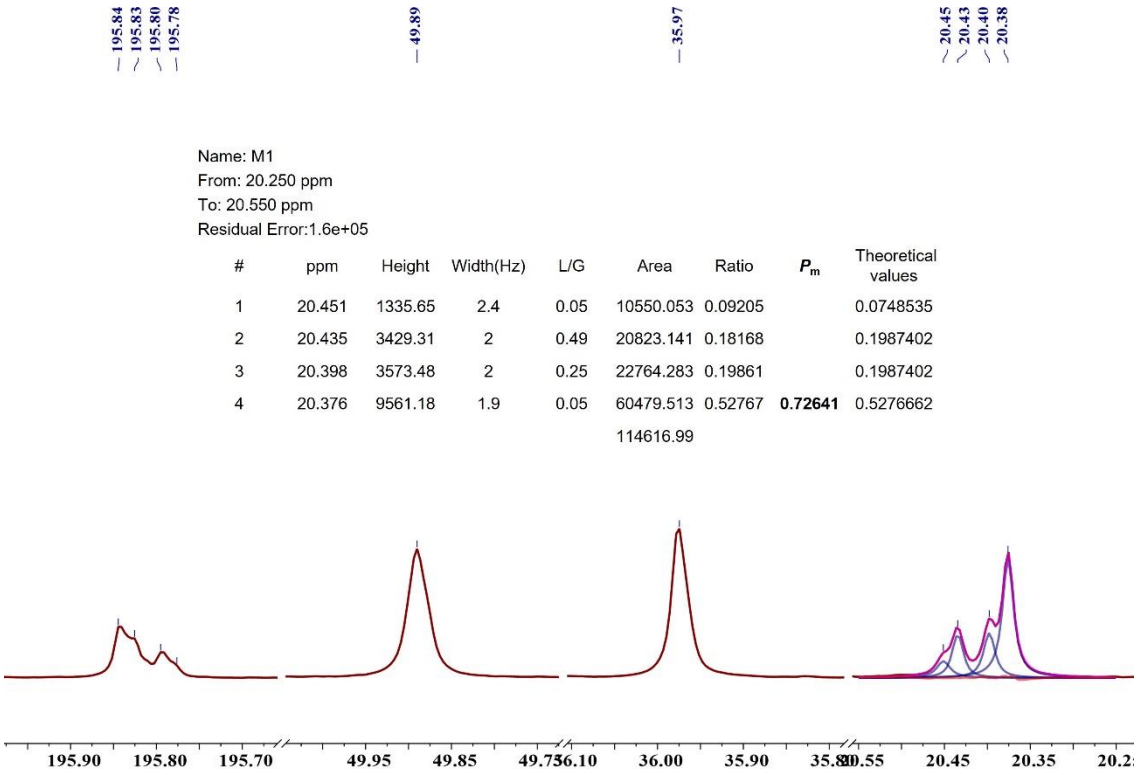


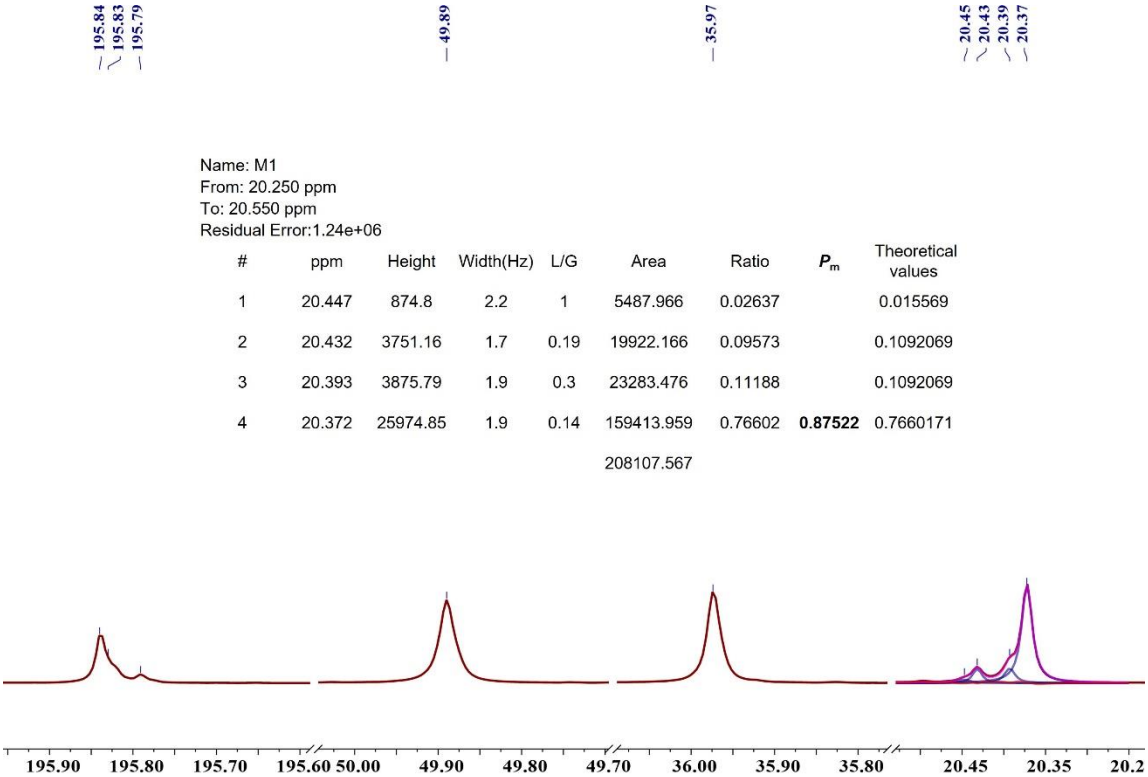
Figure S41. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of a highly isotactic cyclic P3TB (P_m > 0.95) prepared from the ROP of (*S*)-TBL.



Name: M1
From: 20.250 ppm
To: 20.550 ppm
Residual Error:1.6e+05

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical values
1	20.451	1335.65	2.4	0.05	10550.053	0.09205		0.0748535
2	20.435	3429.31	2	0.49	20823.141	0.18168		0.1987402
3	20.398	3573.48	2	0.25	22764.283	0.19861		0.1987402
4	20.376	9561.18	1.9	0.05	60479.513	0.52767	**0.72641**	0.5276662
					114616.99			

Figure S42. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an isotactic-enriched cyclic P3TB (Table 2, entry 30).



Name: M1
From: 20.250 ppm
To: 20.550 ppm
Residual Error:1.24e+06

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical values
1	20.447	874.8	2.2	1	5487.966	0.02637		0.015569
2	20.432	3751.16	1.7	0.19	19922.166	0.09573		0.1092069
3	20.393	3875.79	1.9	0.3	23283.476	0.11188		0.1092069
4	20.372	25974.85	1.9	0.14	159413.959	0.76602	**0.87522**	0.7660171
					208107.567			

Figure S43. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an isotactic-enriched cyclic P3TB (Table 2, entry 33).

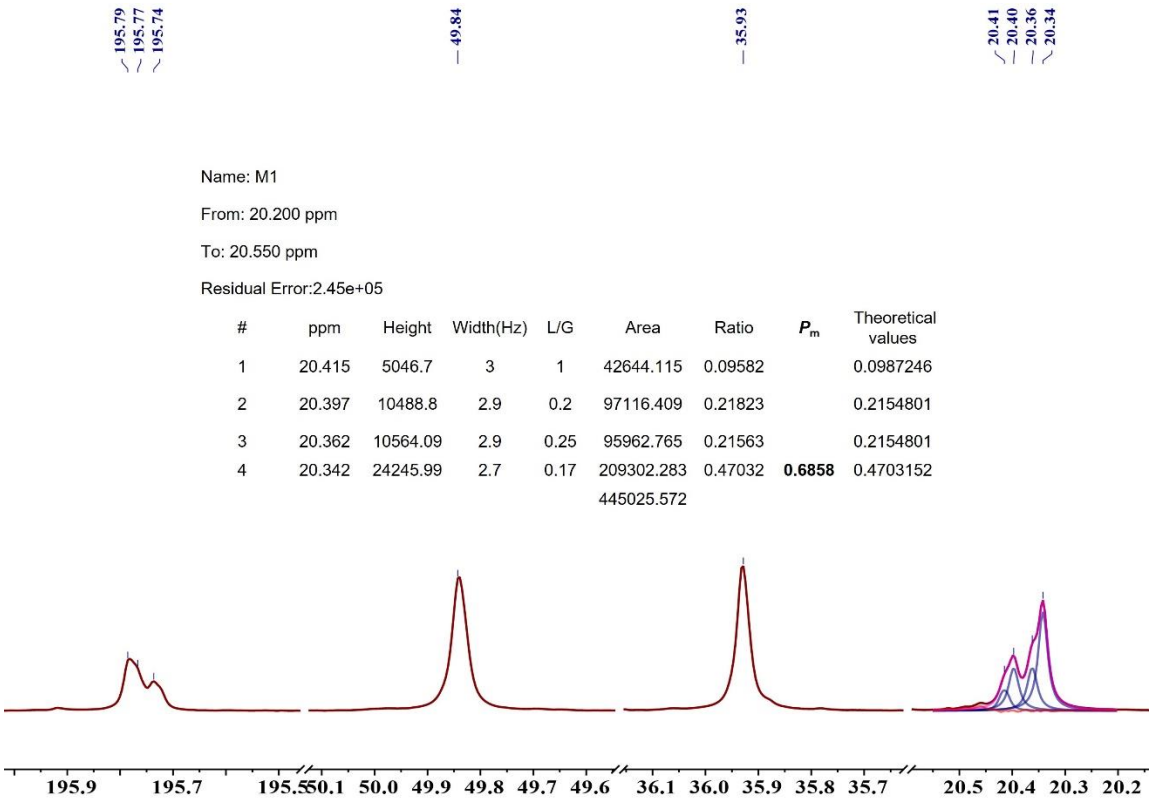


Figure S44. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an isotactic-enriched cyclic P3TB (Table 2, entry 42).

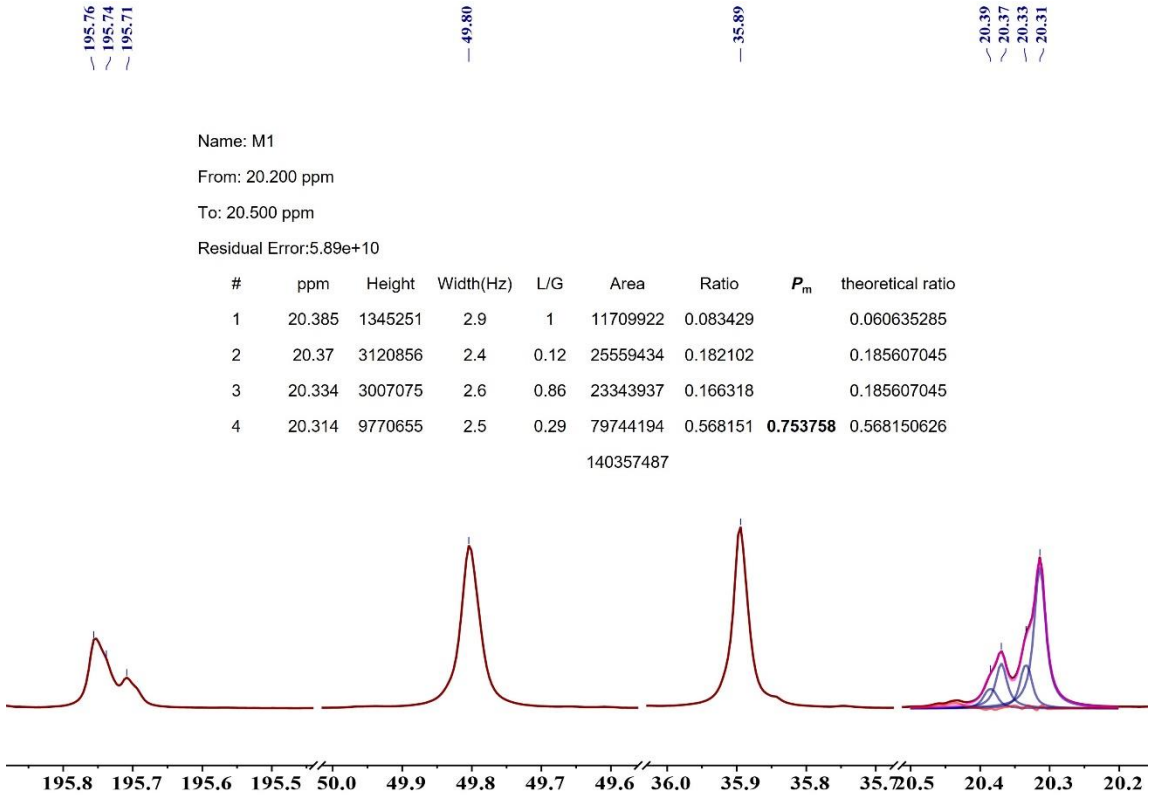


Figure S45. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an isotactic-enriched cyclic P3TB (Table 2, entry 44).

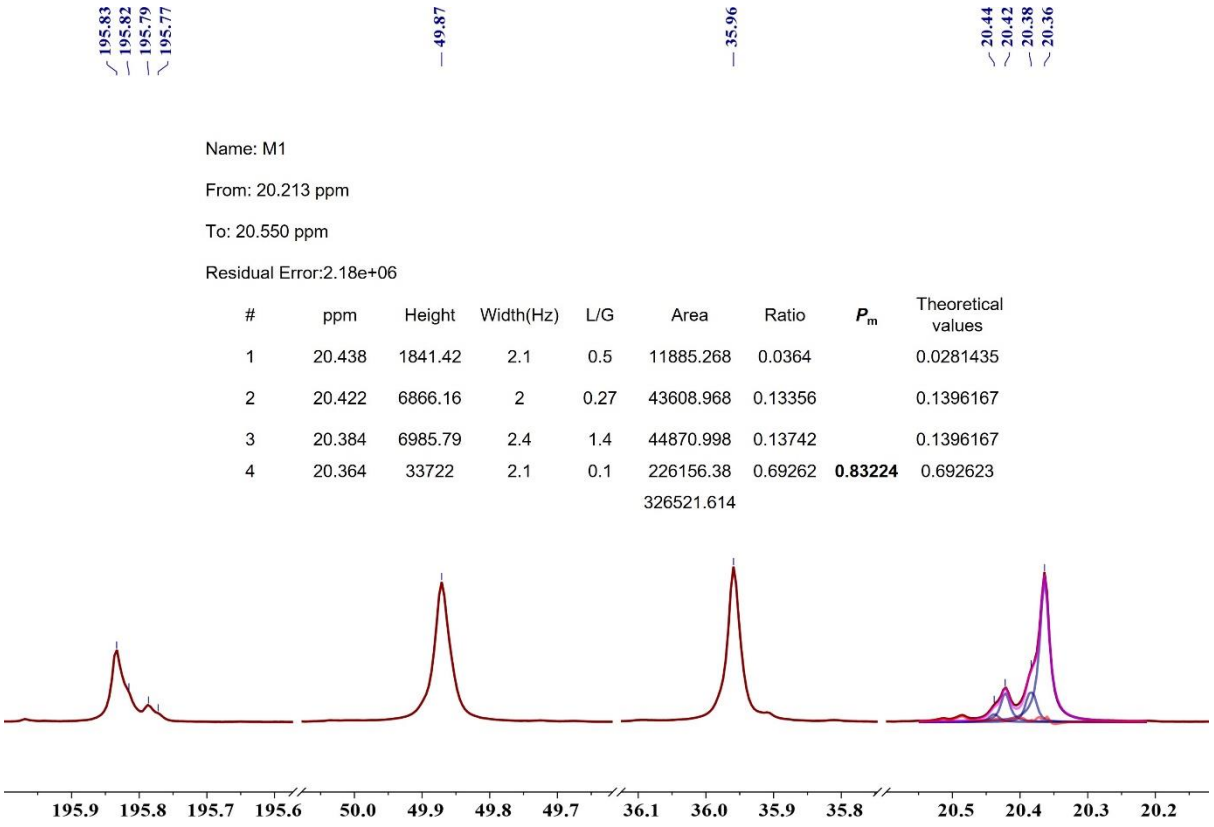


Figure S46. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an isotactic-enriched cyclic P3TB (Table 2, entry 50).

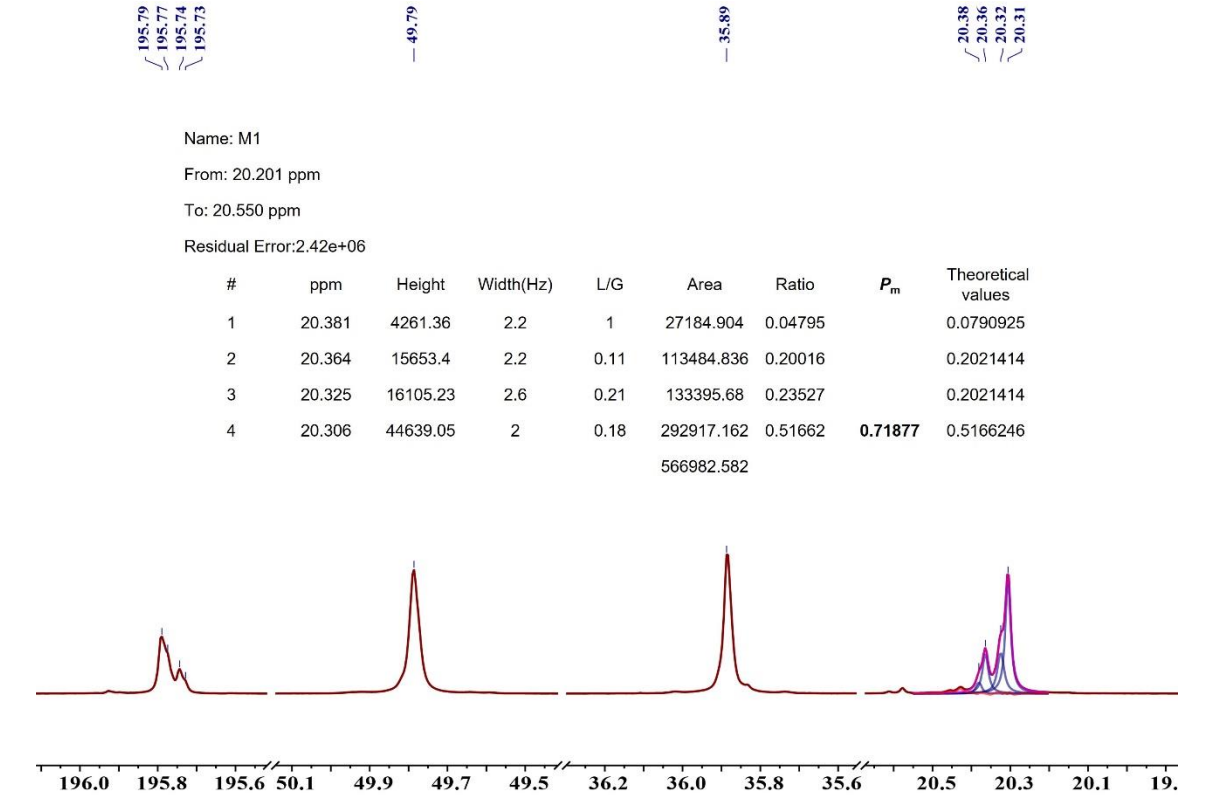
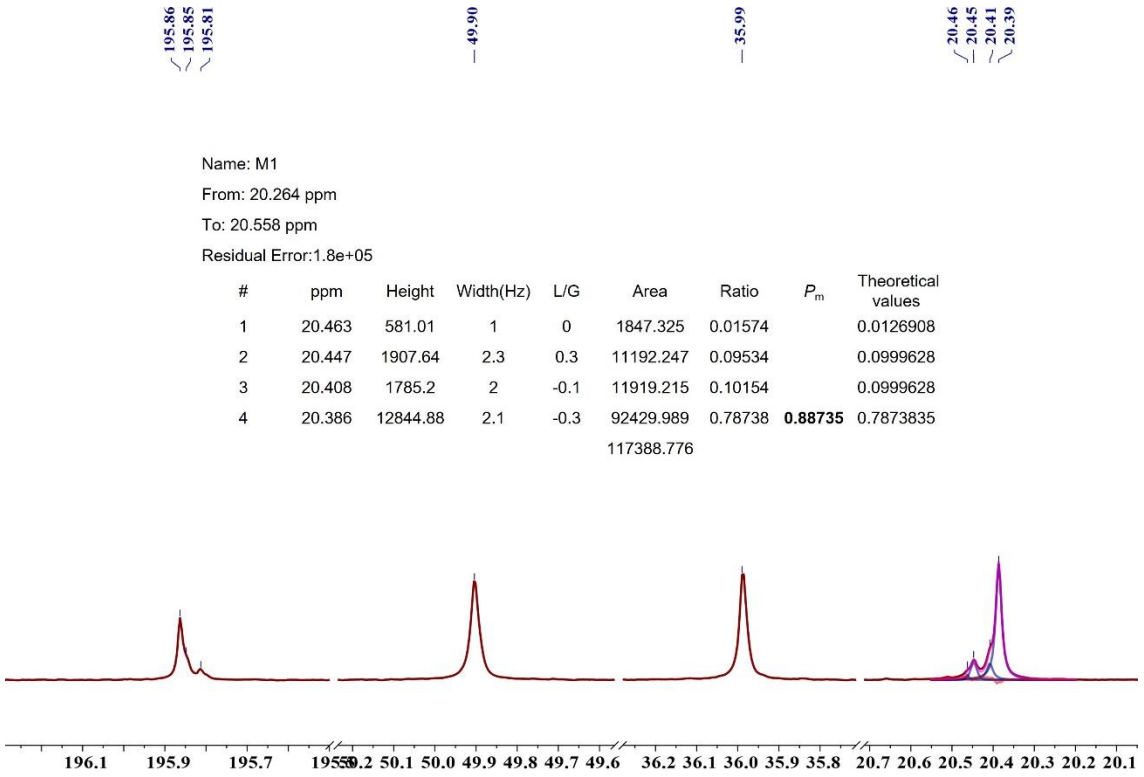


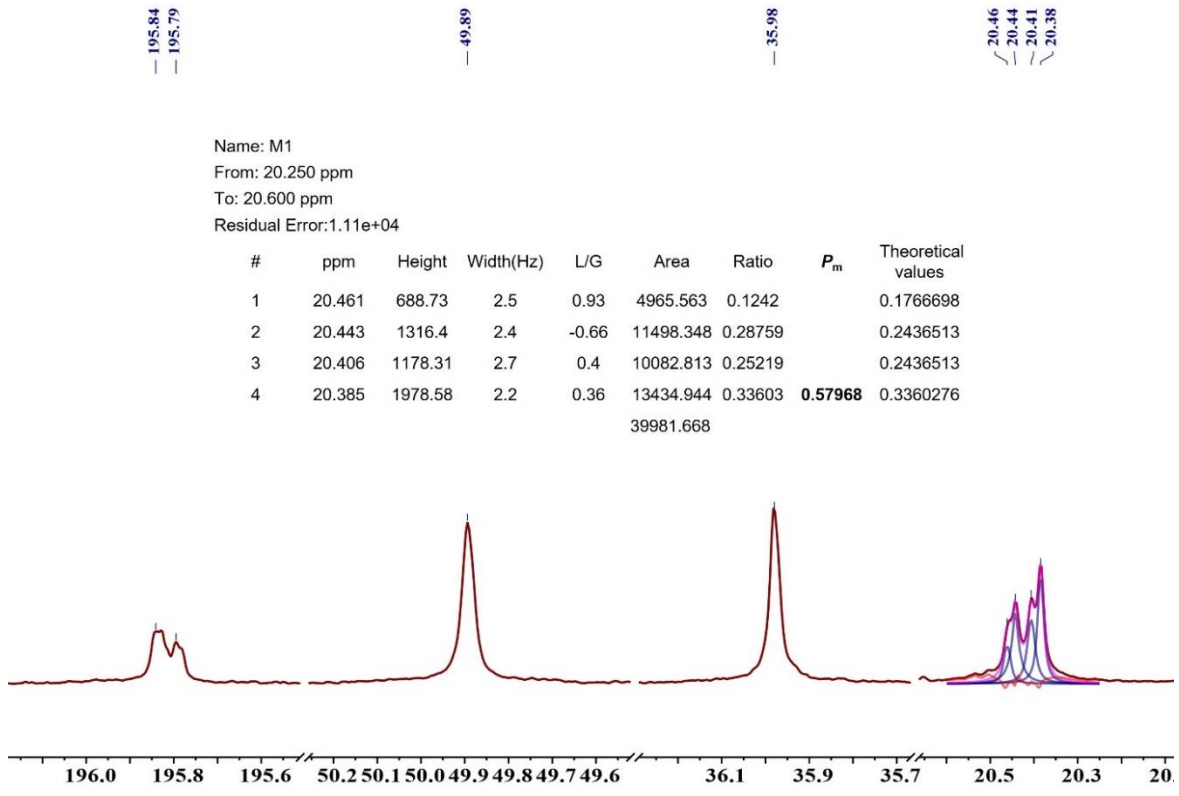
Figure S47. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an isotactic-enriched cyclic P3TB (Table 2, entry 47).



Name: M1
From: 20.264 ppm
To: 20.558 ppm
Residual Error:1.8e+05

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical values
1	20.463	581.01	1	0	1847.325	0.01574		0.0126908
2	20.447	1907.64	2.3	0.3	11192.247	0.09534		0.0999628
3	20.408	1785.2	2	-0.1	11919.215	0.10154		0.0999628
4	20.386	12844.88	2.1	-0.3	92429.989	0.78738	**0.88735**	0.7873835
					117388.776			

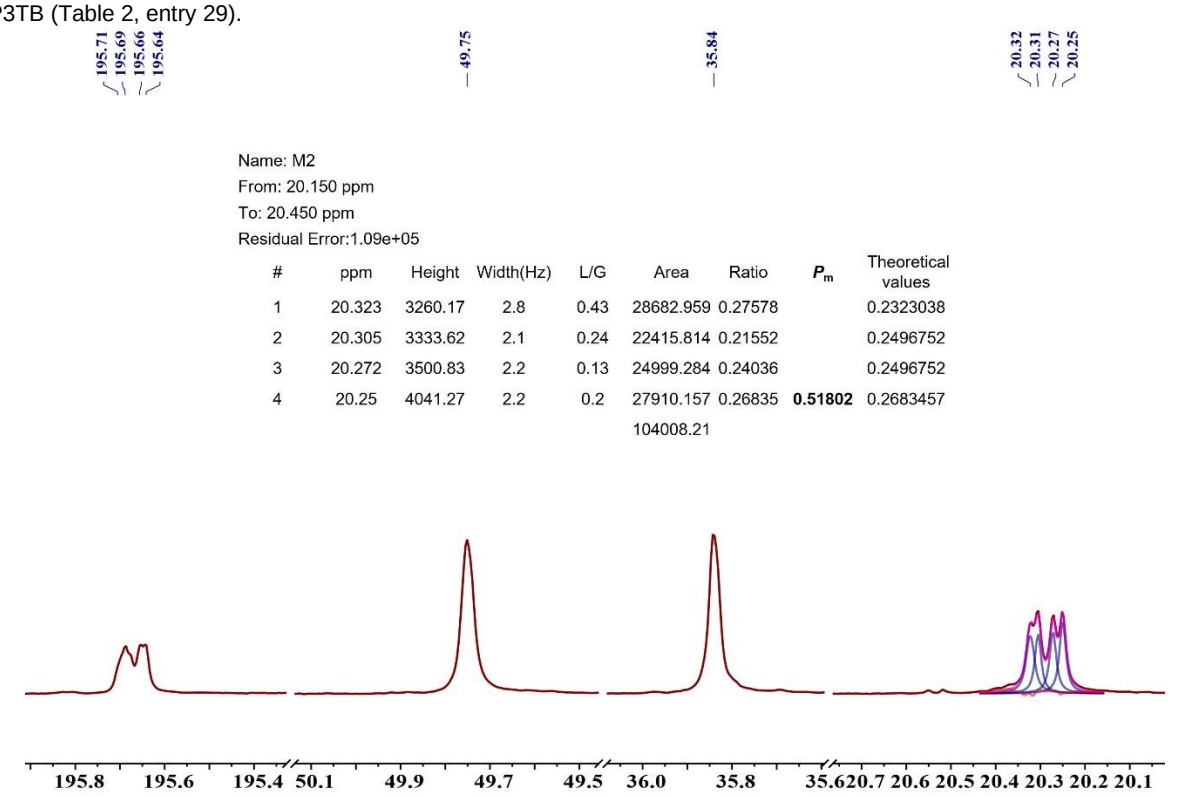
Figure S48. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an isotactic-enriched cyclic P3TB (Table 2, entry 34).



Name: M1
From: 20.250 ppm
To: 20.600 ppm
Residual Error:1.11e+04

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical values
1	20.461	688.73	2.5	0.93	4965.563	0.1242		0.1766698
2	20.443	1316.4	2.4	-0.66	11498.348	0.28759		0.2436513
3	20.406	1178.31	2.7	0.4	10082.813	0.25219		0.2436513
4	20.385	1978.58	2.2	0.36	13434.944	0.33603	**0.57968**	0.3360276
					39981.668			

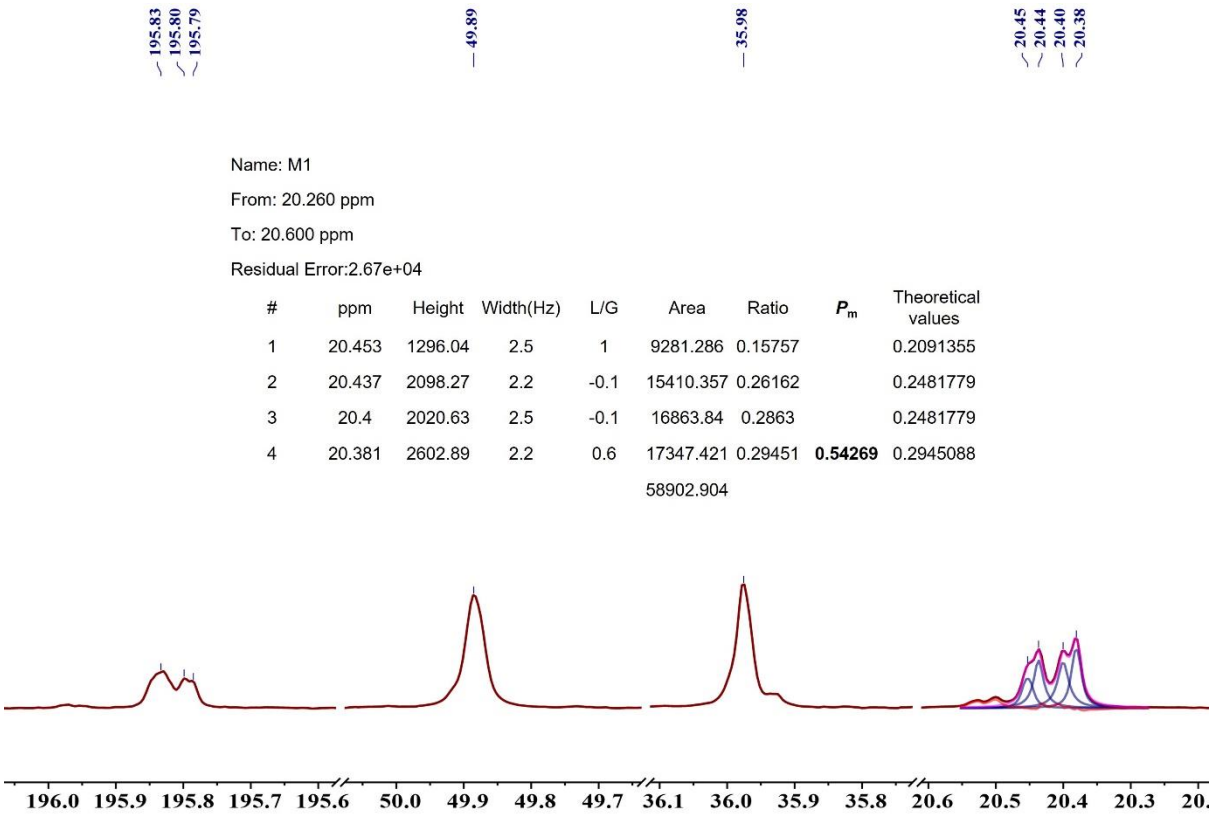
Figure S49. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an atactic cyclic P3TB (Table 2, entry 29).



Name: M2
From: 20.150 ppm
To: 20.450 ppm
Residual Error:1.09e+05

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical values
1	20.323	3260.17	2.8	0.43	28682.959	0.27578		0.2323038
2	20.305	3333.62	2.1	0.24	22415.814	0.21552		0.2496752
3	20.272	3500.83	2.2	0.13	24999.284	0.24036		0.2496752
4	20.25	4041.27	2.2	0.2	27910.157	0.26835	**0.51802**	0.2683457
					104008.21			

Figure S50. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an atactic cyclic P3TB (Table 2, entry 26).



Name: M1

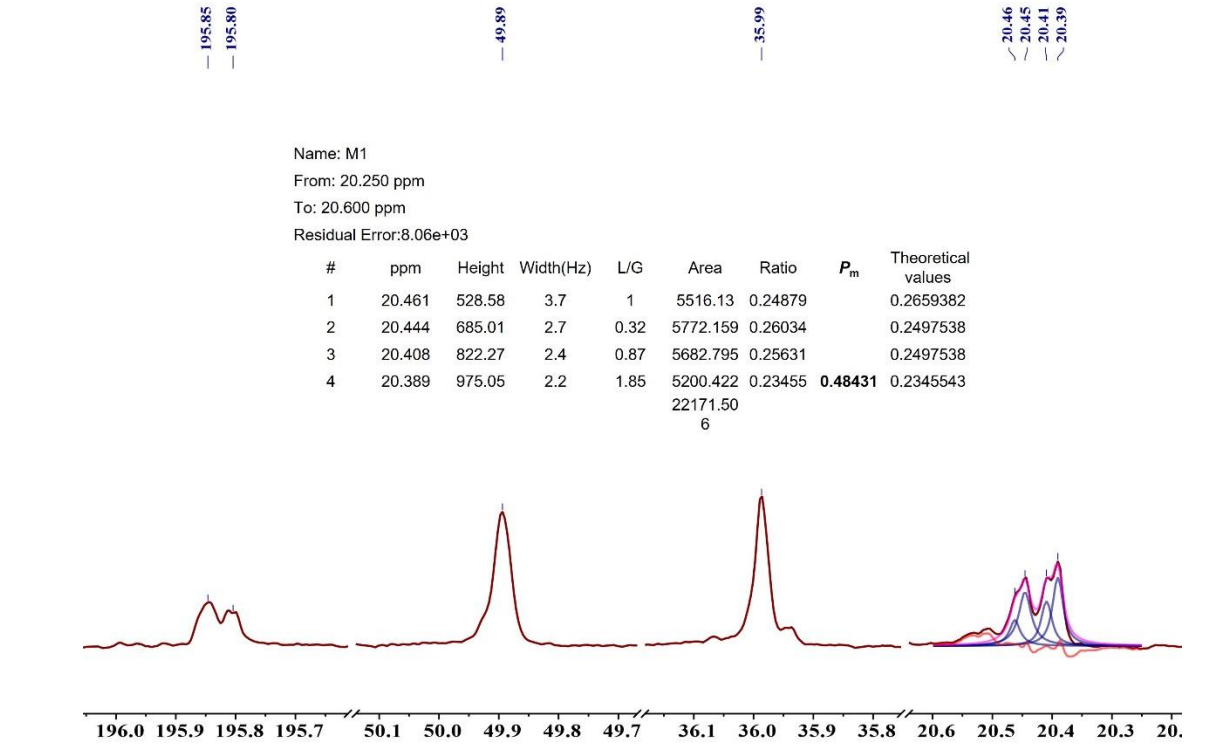
From: 20.260 ppm

To: 20.600 ppm

Residual Error:2.67e+04

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical values
1	20.453	1296.04	2.5	1	9281.286	0.15757		0.2091355
2	20.437	2098.27	2.2	-0.1	15410.357	0.26162		0.2481779
3	20.4	2020.63	2.5	-0.1	16863.84	0.2863		0.2481779
4	20.381	2602.89	2.2	0.6	17347.421	0.29451	**0.54269**	0.2945088
					58902.904			

Figure S51. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an atactic cyclic P3TB (Table 2, entry 35).



Name: M1

From: 20.250 ppm

To: 20.600 ppm

Residual Error:8.06e+03

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical values
1	20.461	528.58	3.7	1	5516.13	0.24879		0.2659382
2	20.444	685.01	2.7	0.32	5772.159	0.26034		0.2497538
3	20.408	822.27	2.4	0.87	5682.795	0.25631		0.2497538
4	20.389	975.05	2.2	1.85	5200.422	0.23455	**0.48431**	0.2345543
					22171.506			

Figure S52. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an atactic cyclic P3TB (Table 1, entry 7).

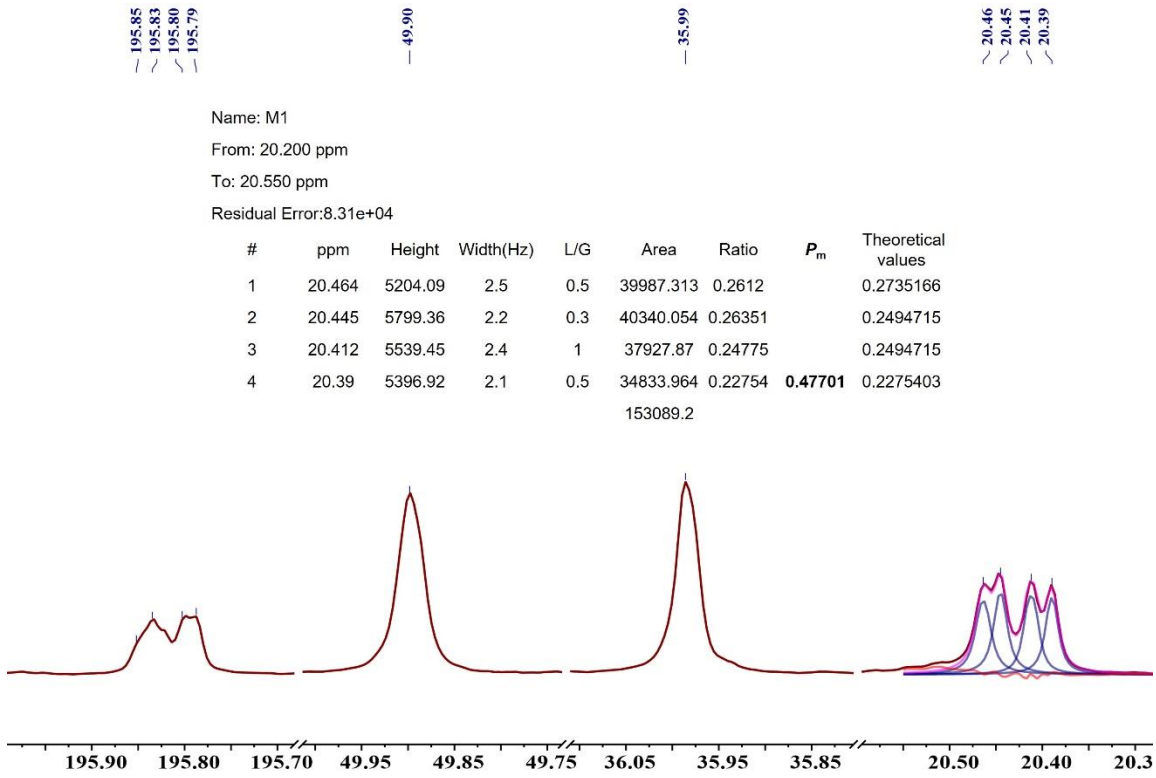


Figure S53. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an atactic cyclic P3TB (Table 2, entry 19).

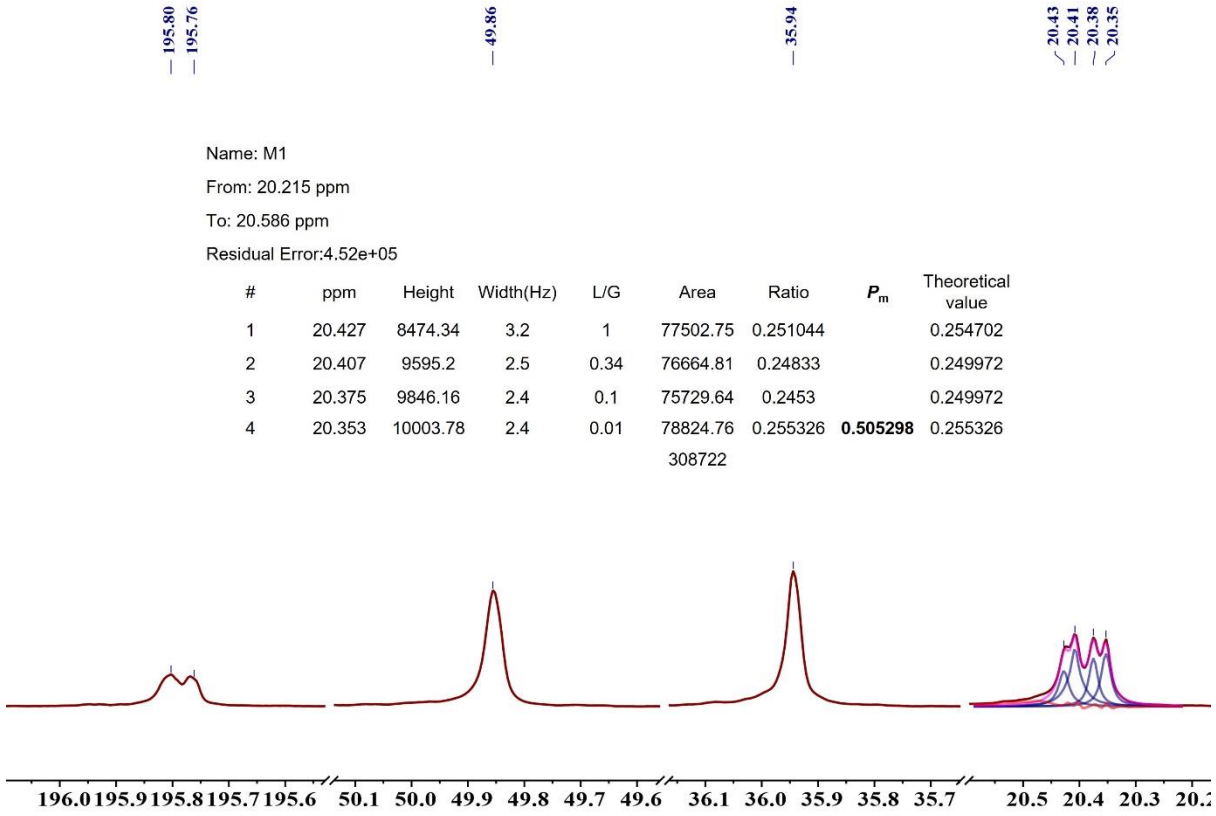
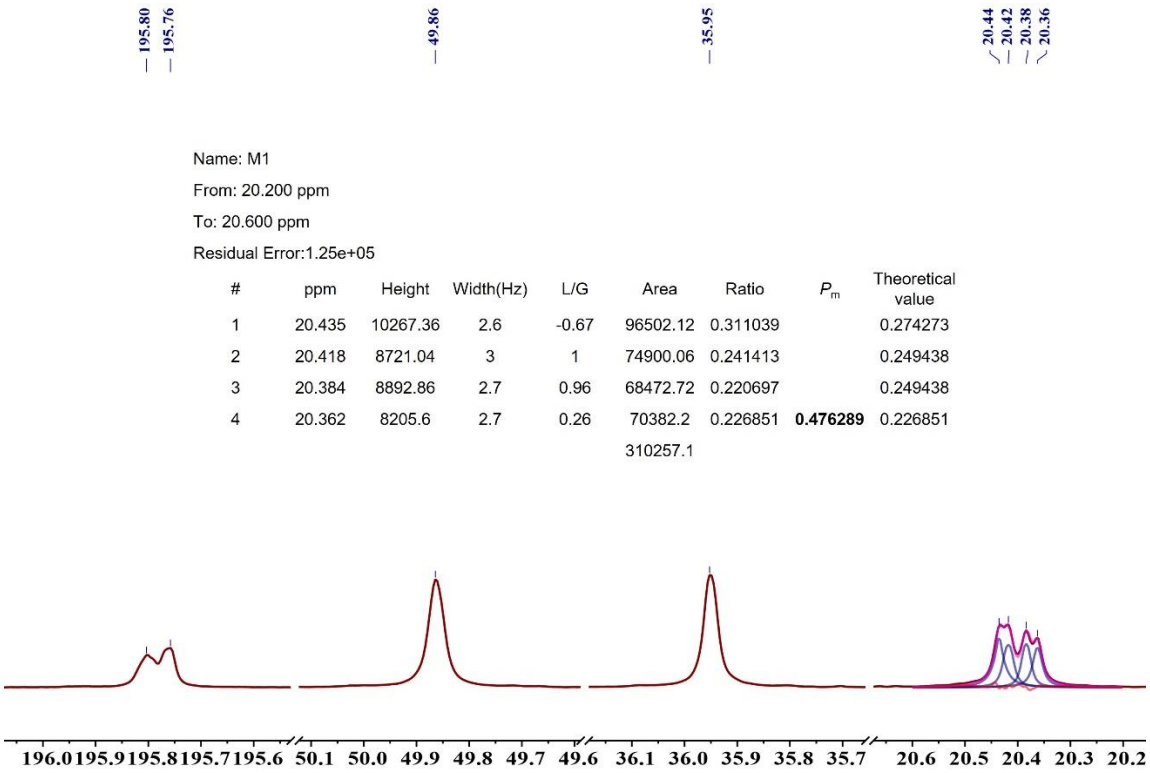


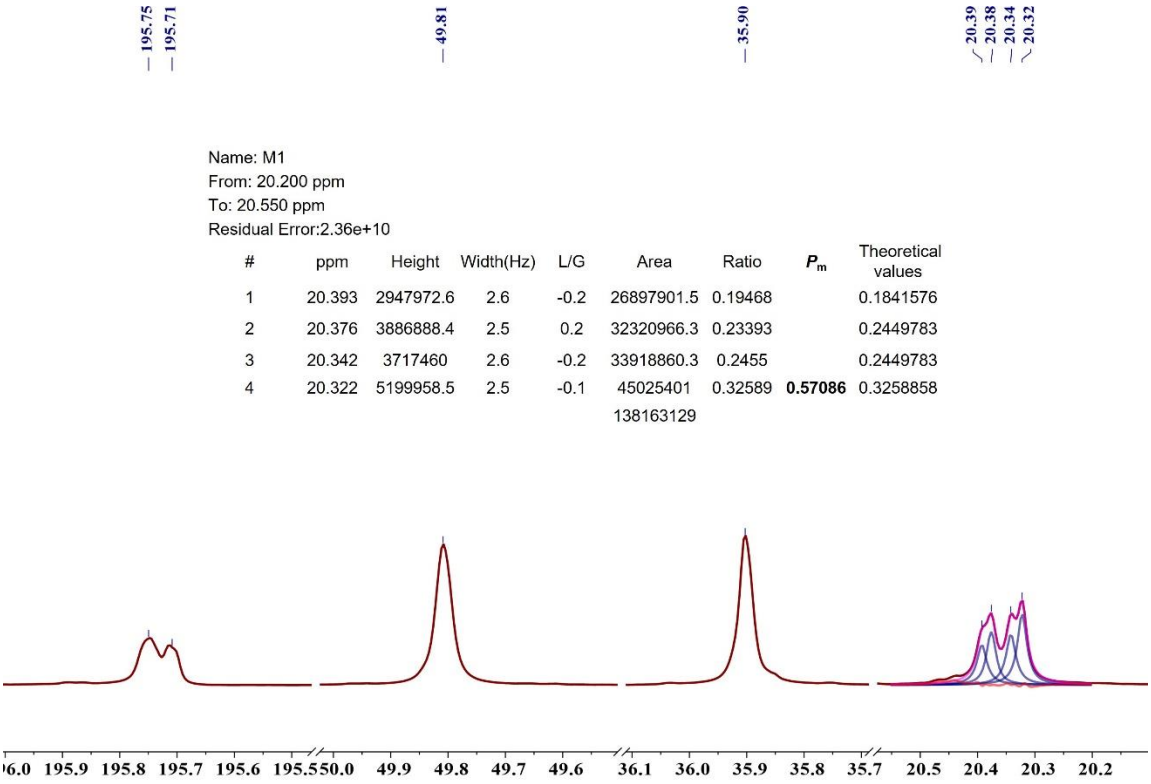
Figure S54. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an atactic cyclic P3TB (Table 1, entry 1).



Name: M1
From: 20.200 ppm
To: 20.600 ppm
Residual Error:1.25e+05

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical value
1	20.435	10267.36	2.6	-0.67	96502.12	0.311039		0.274273
2	20.418	8721.04	3	1	74900.06	0.241413		0.249438
3	20.384	8892.86	2.7	0.96	68472.72	0.220697		0.249438
4	20.362	8205.6	2.7	0.26	70382.2	0.226851	**0.476289**	0.226851
					310257.1			

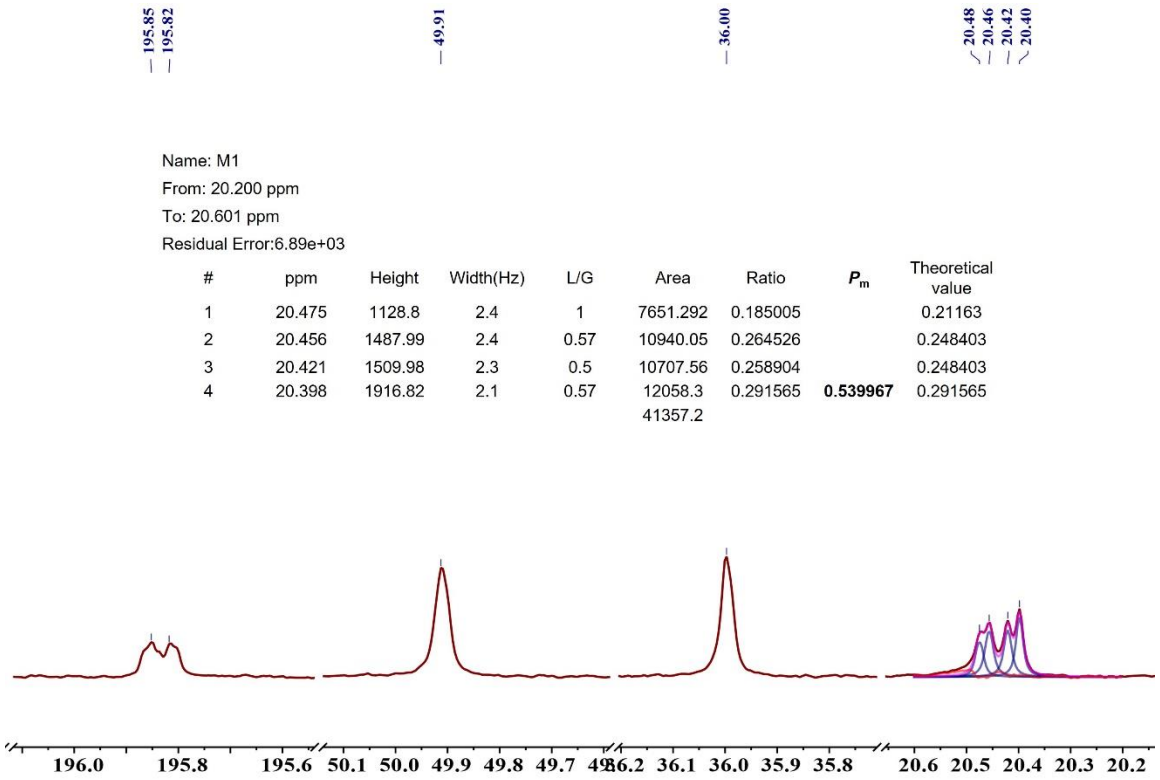
Figure S55. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an atactic cyclic P3TB (Table 1, entry 2).



Name: M1
From: 20.200 ppm
To: 20.550 ppm
Residual Error:2.36e+10

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical values
1	20.393	2947972.6	2.6	-0.2	26897901.5	0.19468		0.1841576
2	20.376	3886888.4	2.5	0.2	32320966.3	0.23393		0.2449783
3	20.342	3717460	2.6	-0.2	33918860.3	0.2455		0.2449783
4	20.322	5199958.5	2.5	-0.1	45025401	0.32589	**0.57086**	0.3258858
					138163129			

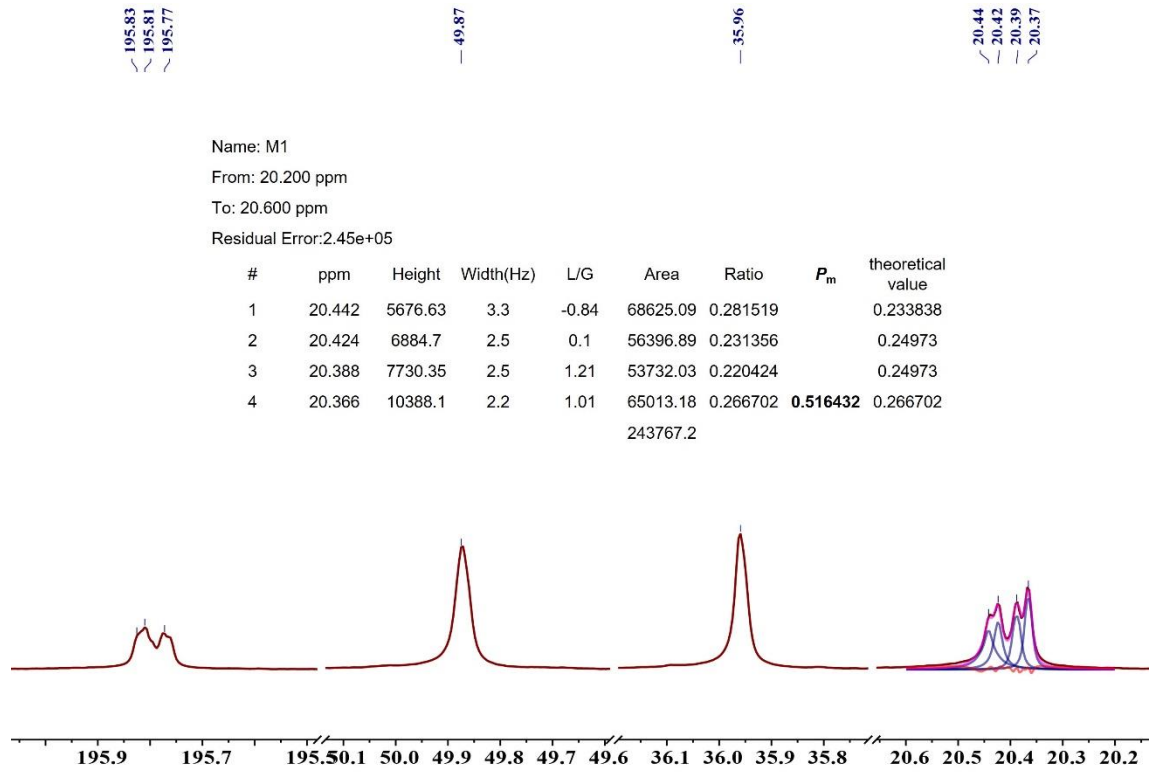
Figure S56. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an atactic cyclic P3TB (Table 2, entry 46).



Name: M1
From: 20.200 ppm
To: 20.601 ppm
Residual Error:6.89e+03

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical value
1	20.475	1128.8	2.4	1	7651.292	0.185005		0.21163
2	20.456	1487.99	2.4	0.57	10940.05	0.264526		0.248403
3	20.421	1509.98	2.3	0.5	10707.56	0.258904		0.248403
4	20.398	1916.82	2.1	0.57	12058.3	0.291565	**0.539967**	0.291565
					41357.2			

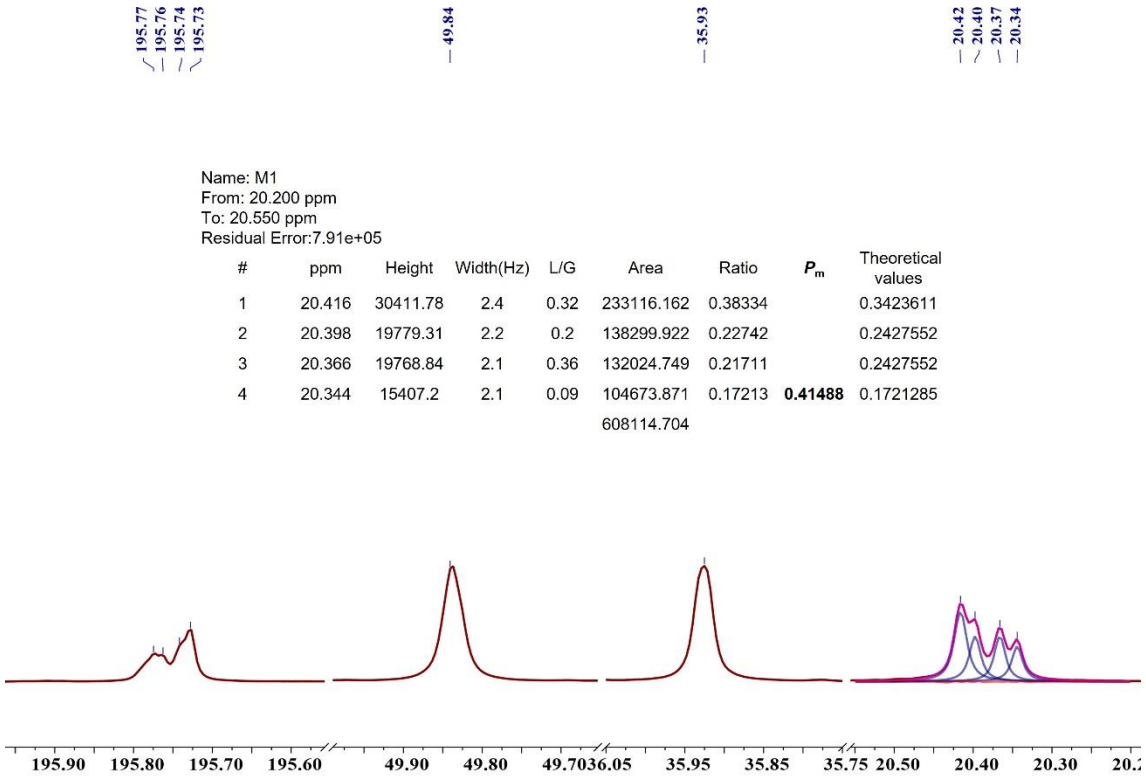
Figure S57. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an atactic cyclic P3TB (Table 1, entry 8).



Name: M1
From: 20.200 ppm
To: 20.600 ppm
Residual Error:2.45e+05

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	theoretical value
1	20.442	5676.63	3.3	-0.84	68625.09	0.281519		0.233838
2	20.424	6884.7	2.5	0.1	56396.89	0.231356		0.24973
3	20.388	7730.35	2.5	1.21	53732.03	0.220424		0.24973
4	20.366	10388.1	2.2	1.01	65013.18	0.266702	**0.516432**	0.266702
					243767.2			

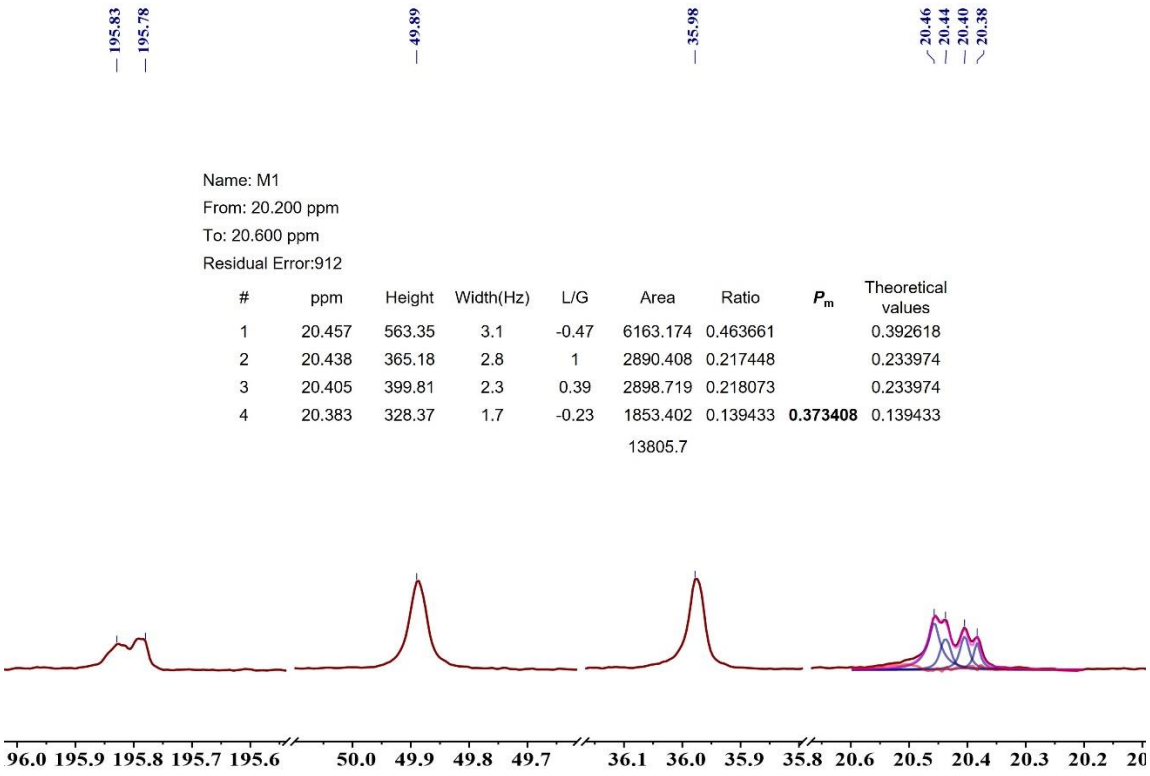
Figure S58. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an atactic cyclic P3TB (Table 1, entry 9).



Name: M1
From: 20.200 ppm
To: 20.550 ppm
Residual Error:7.91e+05

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical values
1	20.416	30411.78	2.4	0.32	233116.162	0.38334		0.3423611
2	20.398	19779.31	2.2	0.2	138299.922	0.22742		0.2427552
3	20.366	19768.84	2.1	0.36	132024.749	0.21711		0.2427552
4	20.344	15407.2	2.1	0.09	104673.871	0.17213	**0.41488**	0.1721285
					608114.704			

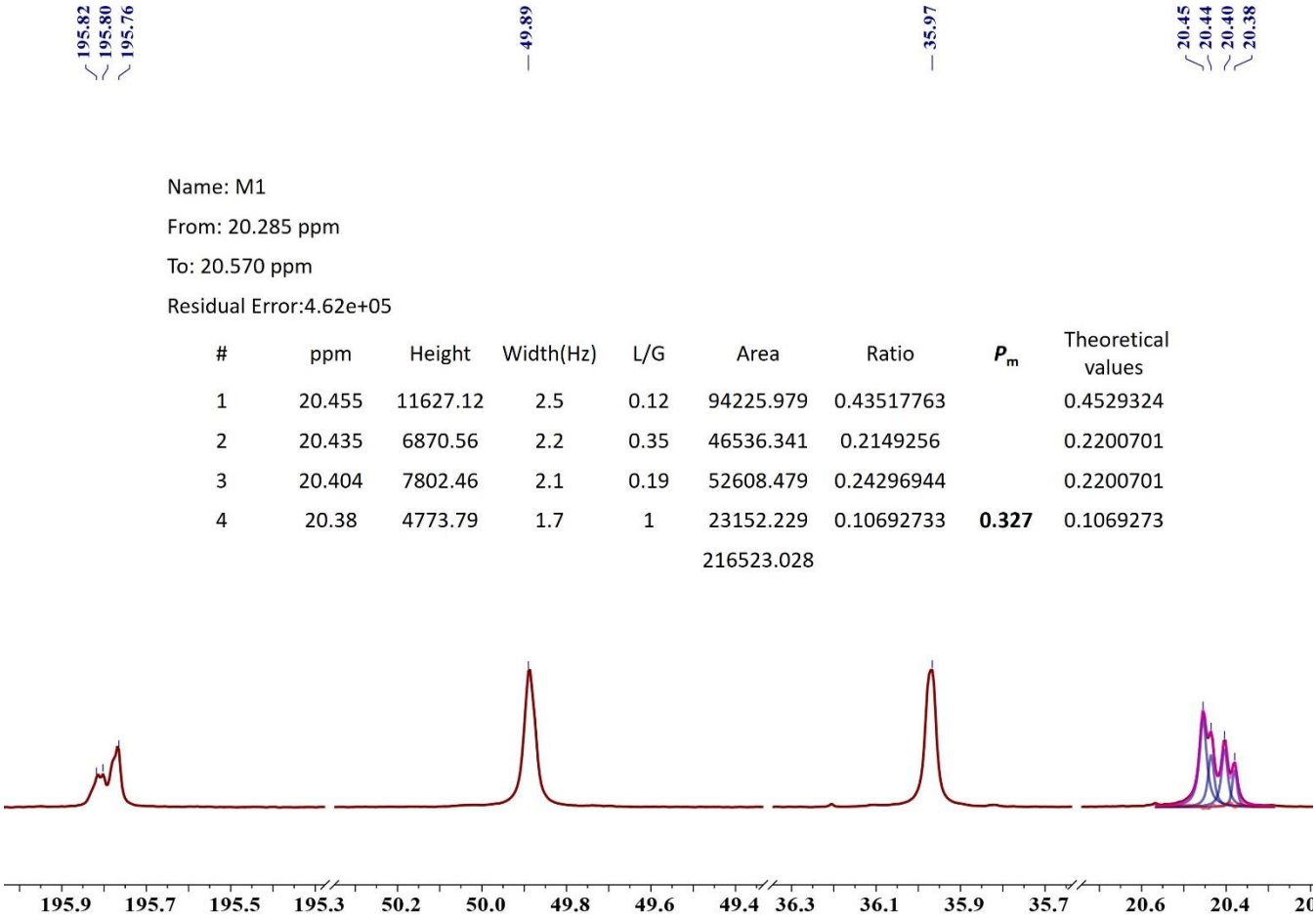
Figure S59. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of an atactic cyclic P3TB (Table 2, entry 27).



Name: M1
From: 20.200 ppm
To: 20.600 ppm
Residual Error:912

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical values
1	20.457	563.35	3.1	-0.47	6163.174	0.463661		0.392618
2	20.438	365.18	2.8	1	2890.408	0.217448		0.233974
3	20.405	399.81	2.3	0.39	2898.719	0.218073		0.233974
4	20.383	328.37	1.7	-0.23	1853.402	0.139433	**0.373408**	0.139433
					13805.7			

Figure S60. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of a syndiotactic-biased cyclic P3TB (Table 1, entry 10).



Name: M1
From: 20.285 ppm
To: 20.570 ppm
Residual Error:4.62e+05

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical values
1	20.455	11627.12	2.5	0.12	94225.979	0.43517763		0.4529324
2	20.435	6870.56	2.2	0.35	46536.341	0.2149256		0.2200701
3	20.404	7802.46	2.1	0.19	52608.479	0.24296944		0.2200701
4	20.38	4773.79	1.7	1	23152.229	0.10692733	**0.327**	0.1069273
					216523.028			

Figure S61. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of a syndiotactic-biased cyclic P3TB (Table 2, entry 20).

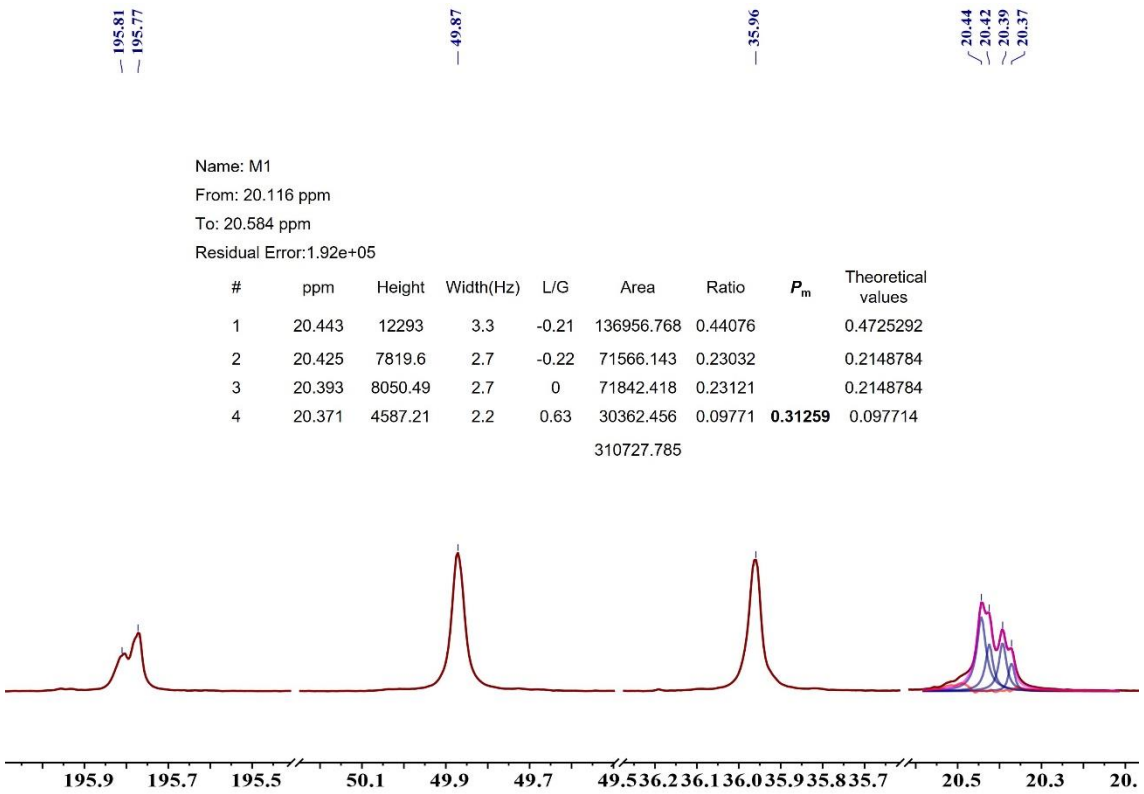


Figure S62. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of a syndiotactic-enriched cyclic P3TB (Table 1, entry 11).

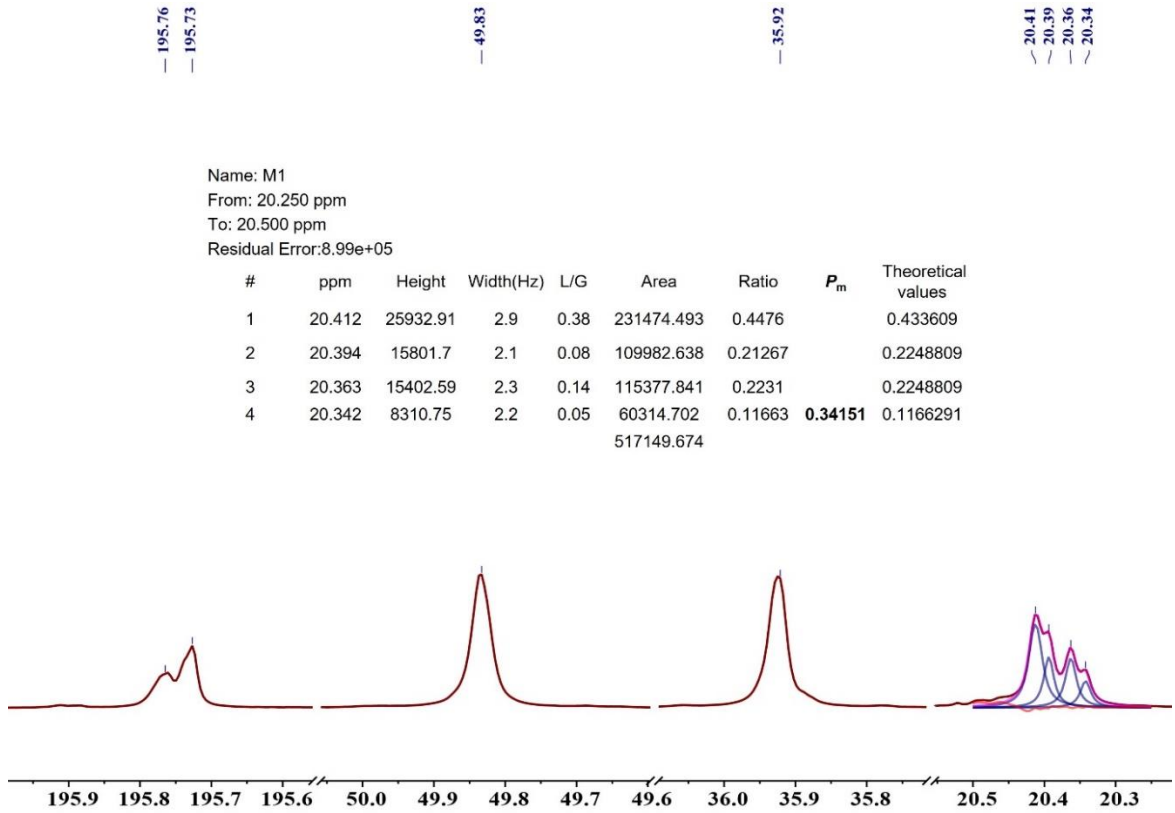
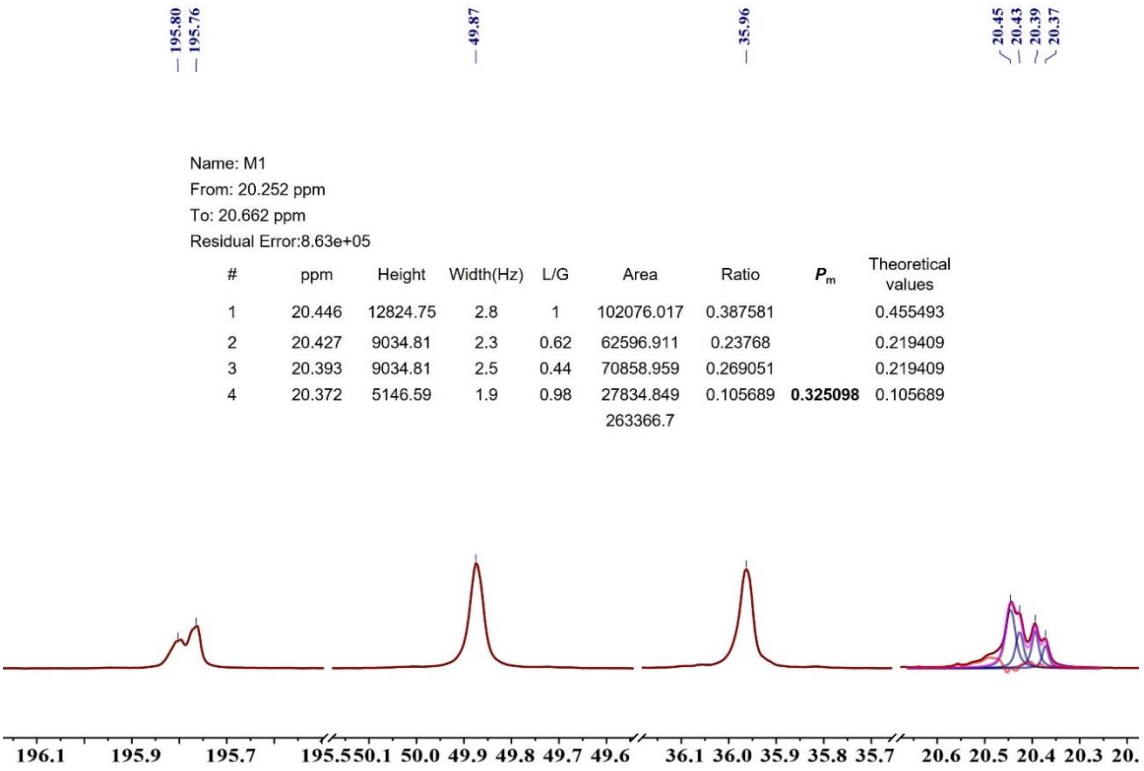


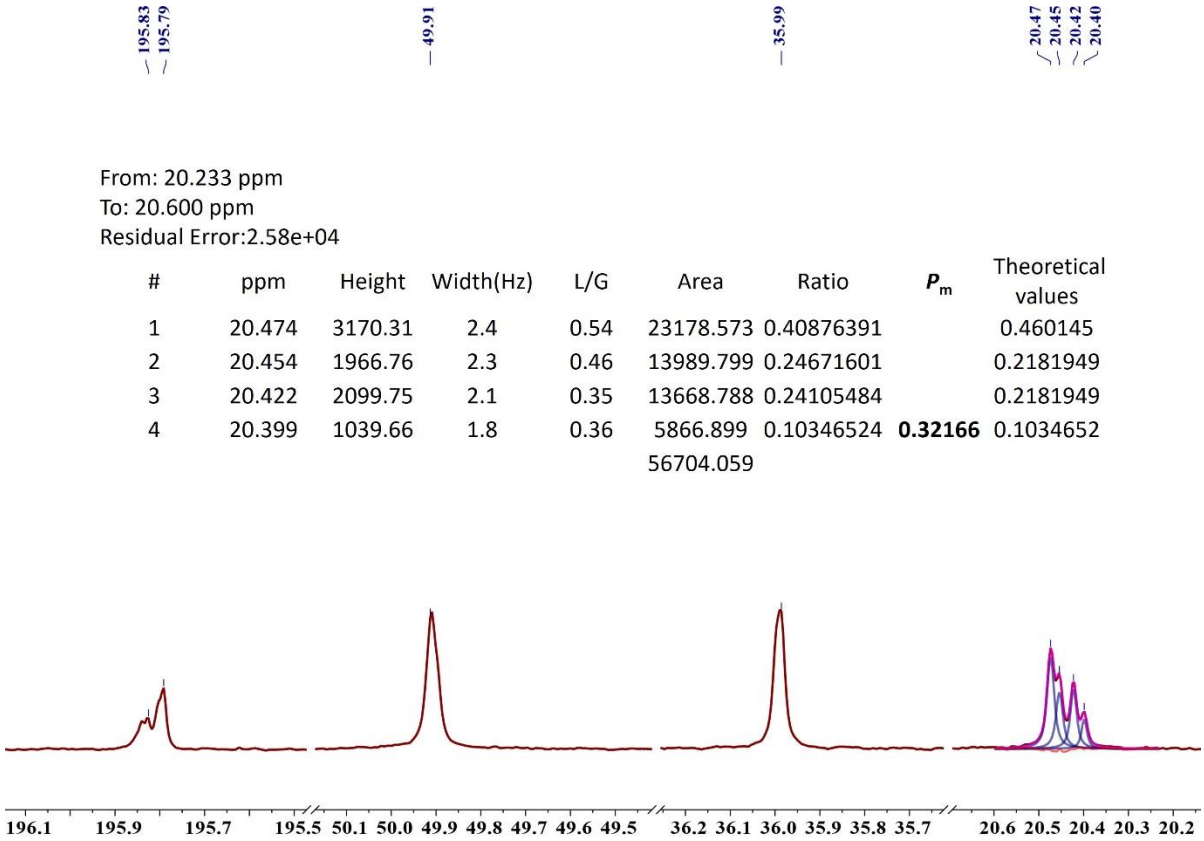
Figure S63. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of a syndiotactic-enriched cyclic P3TB (Table 1, entry 12).



Name: M1
From: 20.252 ppm
To: 20.662 ppm
Residual Error:8.63e+05

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical values
1	20.446	12824.75	2.8	1	102076.017	0.387581		0.455493
2	20.427	9034.81	2.3	0.62	62596.911	0.23768		0.219409
3	20.393	9034.81	2.5	0.44	70858.959	0.269051		0.219409
4	20.372	5146.59	1.9	0.98	27834.849	0.105689	**0.325098**	0.105689
					263366.7			

Figure S64. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of a syndiotactic-enriched cyclic P3TB (Table 1, entry 13).



From: 20.233 ppm
To: 20.600 ppm
Residual Error:2.58e+04

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical values
1	20.474	3170.31	2.4	0.54	23178.573	0.40876391		0.460145
2	20.454	1966.76	2.3	0.46	13989.799	0.24671601		0.2181949
3	20.422	2099.75	2.1	0.35	13668.788	0.24105484		0.2181949
4	20.399	1039.66	1.8	0.36	5866.899	0.10346524	**0.32166**	0.1034652
					56704.059			

Figure S65. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of a syndiotactic-enriched cyclic P3TB (Table 2, entry 25).

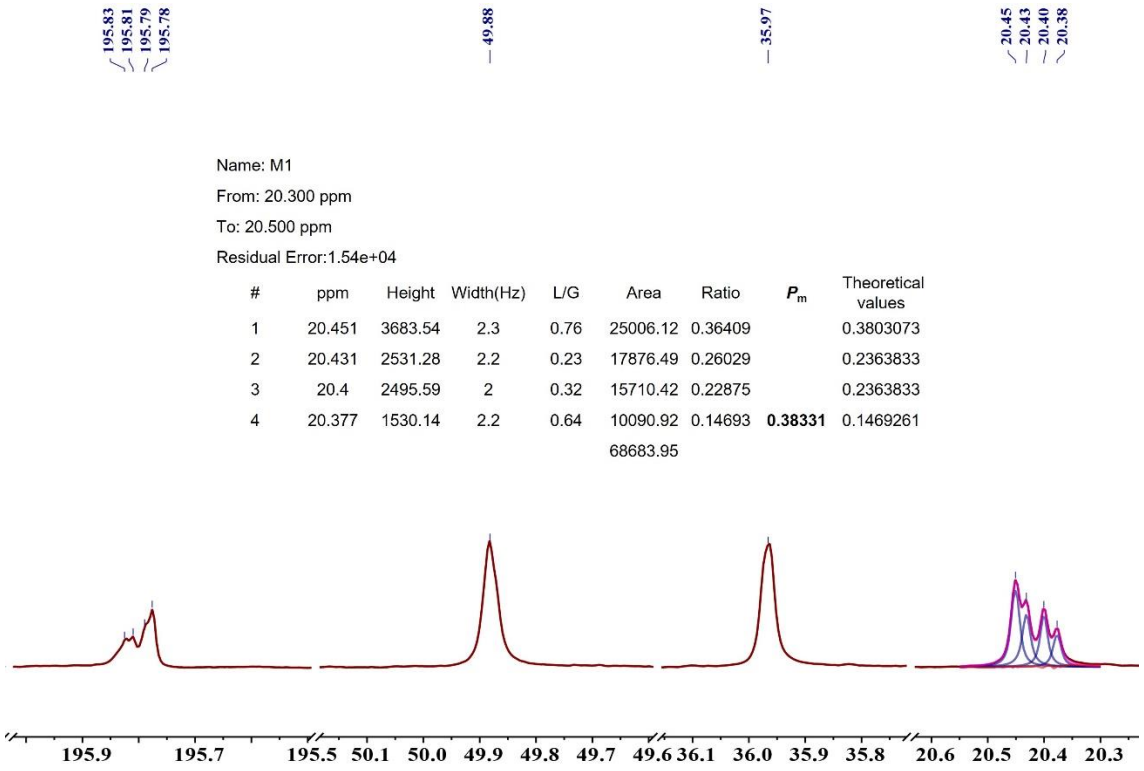


Figure S66. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of a syndiotactic-enriched cyclic P3TB (Table 2, entry 17).

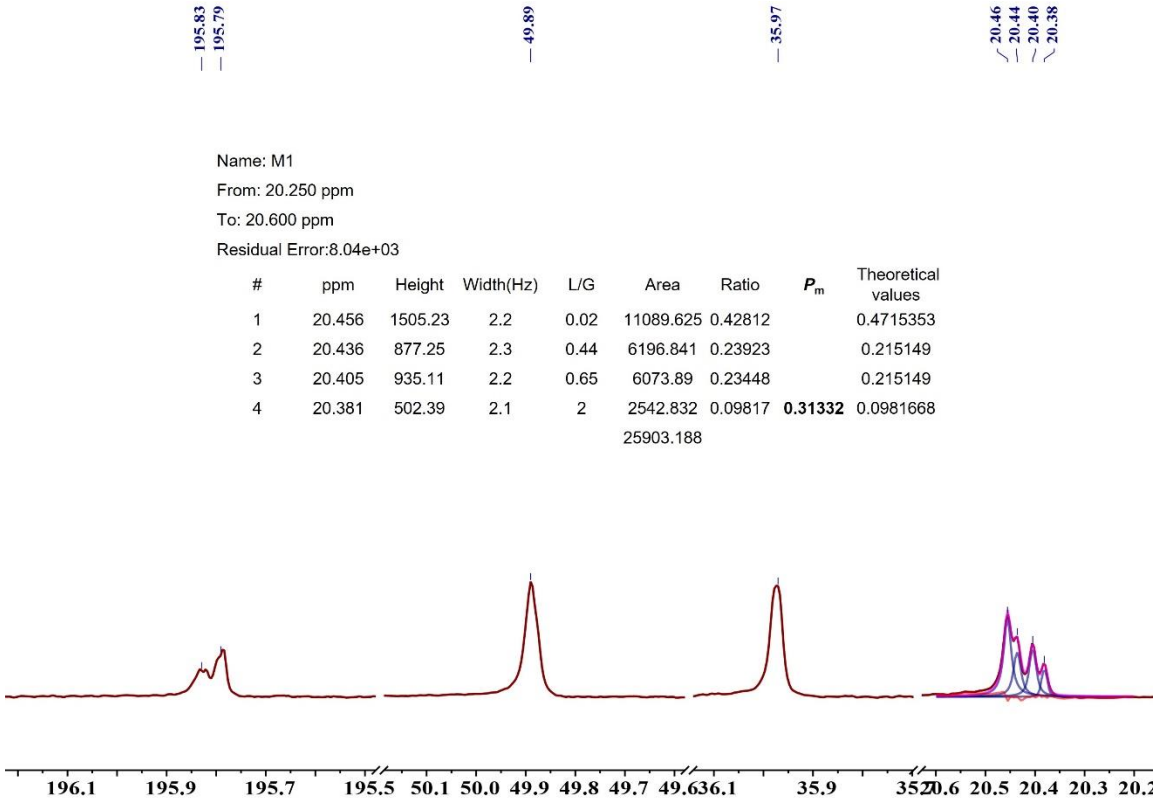
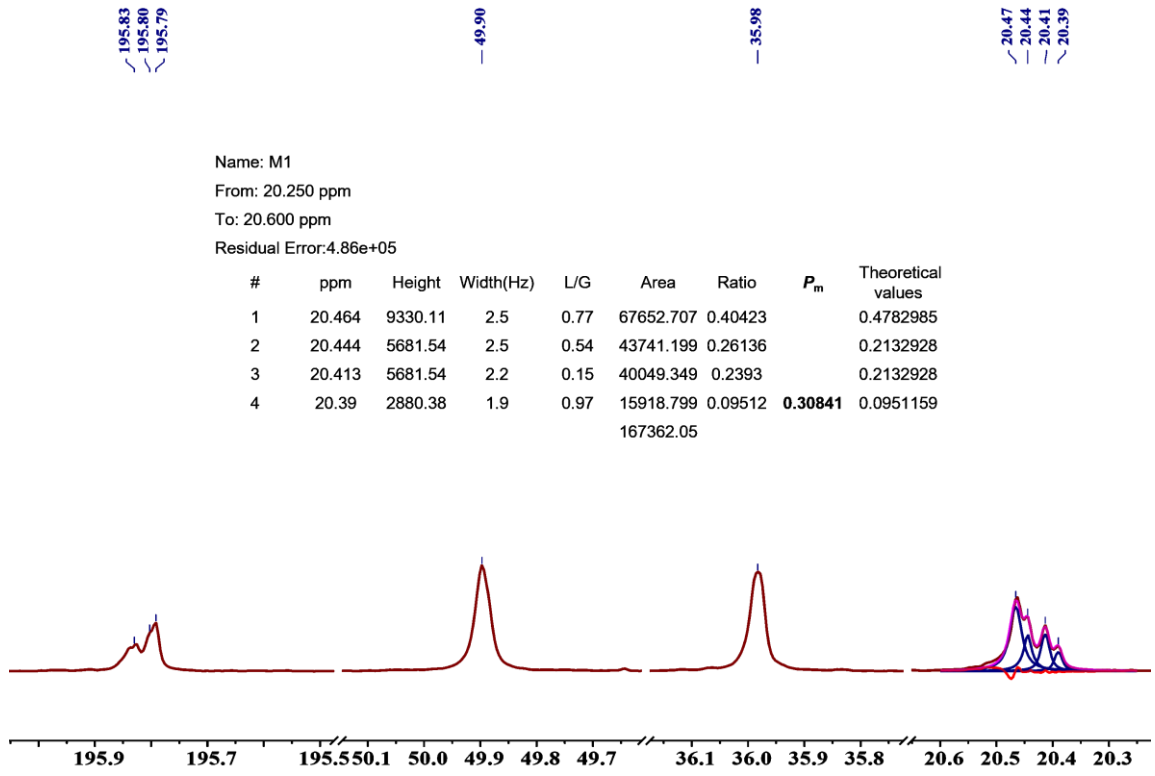


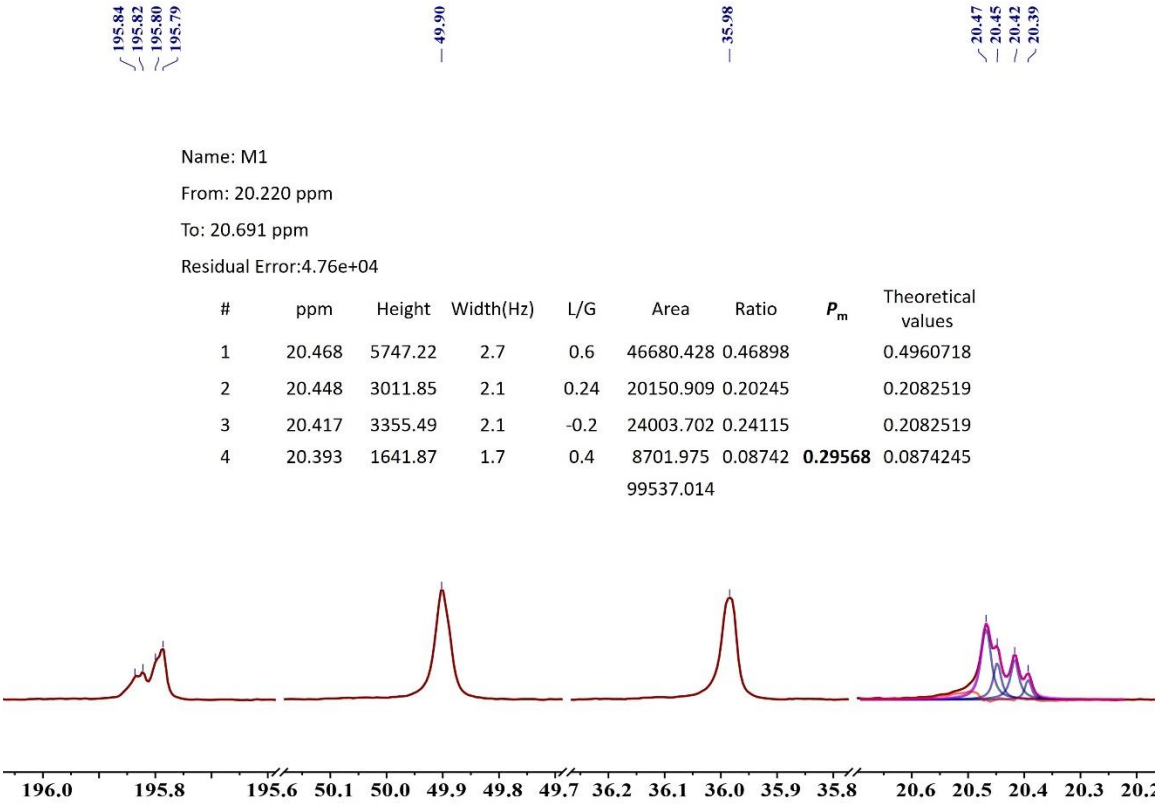
Figure S67. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of a syndiotactic-enriched cyclic P3TB (Table S2, entry 10).



Name: M1
From: 20.250 ppm
To: 20.600 ppm
Residual Error:4.86e+05

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical values
1	20.464	9330.11	2.5	0.77	67652.707	0.40423		0.4782985
2	20.444	5681.54	2.5	0.54	43741.199	0.26136		0.2132928
3	20.413	5681.54	2.2	0.15	40049.349	0.2393		0.2132928
4	20.39	2880.38	1.9	0.97	15918.799	0.09512	**0.30841**	0.0951159
					167362.05			

Figure S68. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of a syndiotactic-enriched cyclic P3TB (Table 1, entry 15).



Name: M1
From: 20.220 ppm
To: 20.691 ppm
Residual Error:4.76e+04

#	ppm	Height	Width(Hz)	L/G	Area	Ratio	P_m	Theoretical values
1	20.468	5747.22	2.7	0.6	46680.428	0.46898		0.4960718
2	20.448	3011.85	2.1	0.24	20150.909	0.20245		0.2082519
3	20.417	3355.49	2.1	-0.2	24003.702	0.24115		0.2082519
4	20.393	1641.87	1.7	0.4	8701.975	0.08742	**0.29568**	0.0874245
					99537.014			

Figure S69. Carbonyl, methine, methylene and methyl regions of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 25 °C) of a syndiotactic-enriched cyclic P3TB (Table 2, entry 24).

Propagation Statistics

Table S6. Bernoulli model triad test B = [(*mm*) × (*rr*)]/[(*rm*) × (*mr*)]

Entry	B
Table 2, entry 34 (P_m = 0.89), **cat.5g**	1.28
Table 2, entry 33 (P_m = 0.87), **cat. 5g**	1.77
Table 2, entry 50 (P_m = 0.83), **cat. 5l**	1.37
Table 2, entry 30 (P_m = 0.73), **cat. 5g**	1.35
Table 2, entry 47 (P_m = 0.72), **cat. 5k**	0.53
Table 1, entry 14 (P_m = 0.32), **cat.5a**	1.03
Table 1, entry 11 (P_m = 0.32), **cat.5a**	0.81
Table 2, entry 24 (P_m = 0.30), **cat. 5c**	0.84

Thermal studies

TGA thermograms

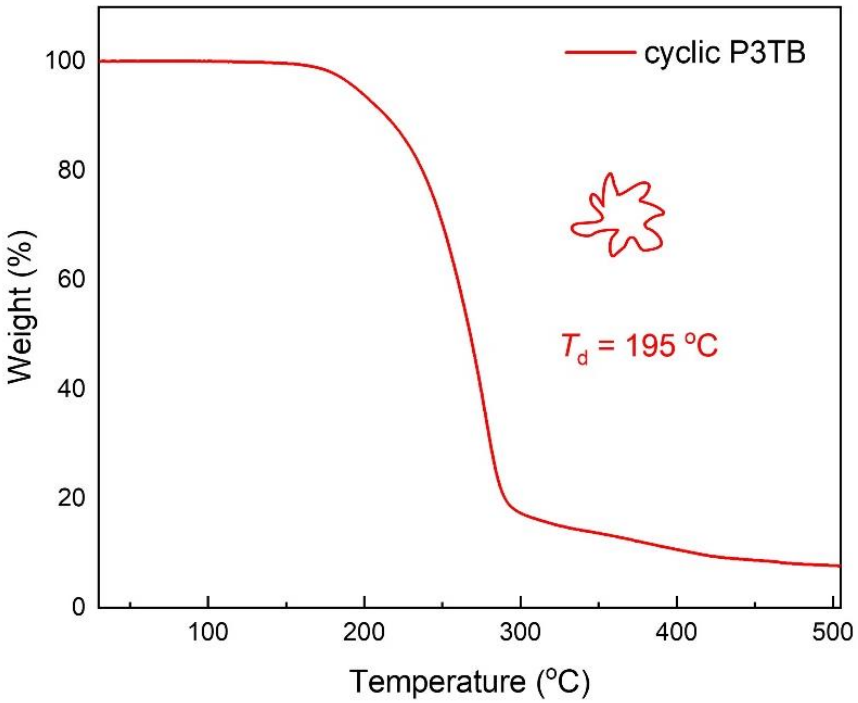


Figure S70. TGA thermogram of a cyclic P3TB sample prepared from complex **5a** in the presence of ^{i}PrOH in toluene at r.t. (50:1:1, $M_{n,SEC}$ = 6.1 kg mol^{-1}, P_m = 0.32; entry 12).

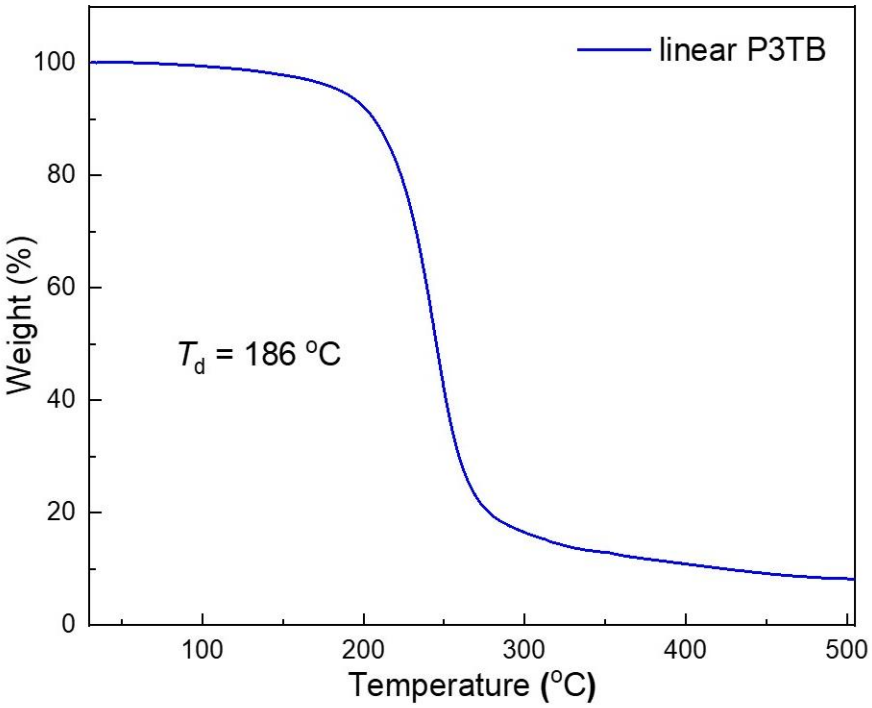


Figure S71. TGA thermogram of a linear P3TB sample prepared from NaOMe in the C6D6 at r.t. (23:1, $M_{n,SEC}$ = 4.0 kg mol^{-1}, P_m = 0.50; entry 1).

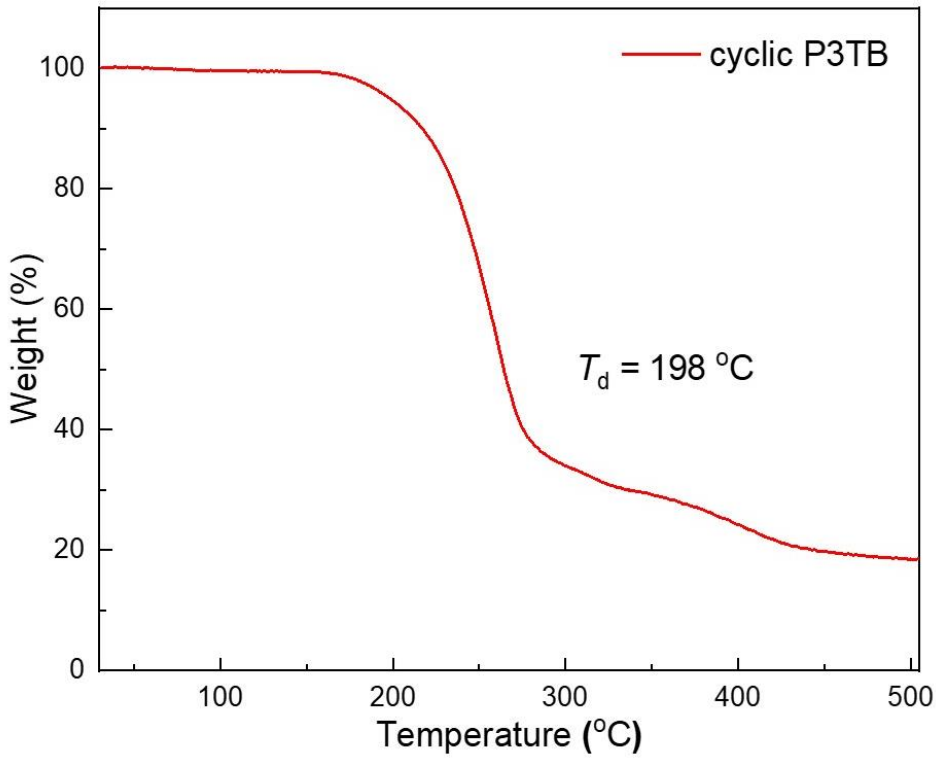


Figure 72. TGA thermogram of a cyclic P3TB sample prepared from complex **5a** in the absence of ^{i}PrOH in toluene at r.t. (25:1:0, $M_{n,SEC}$ = 4.9 kg mol^{-1}, P_m = 0.37; entry 10).

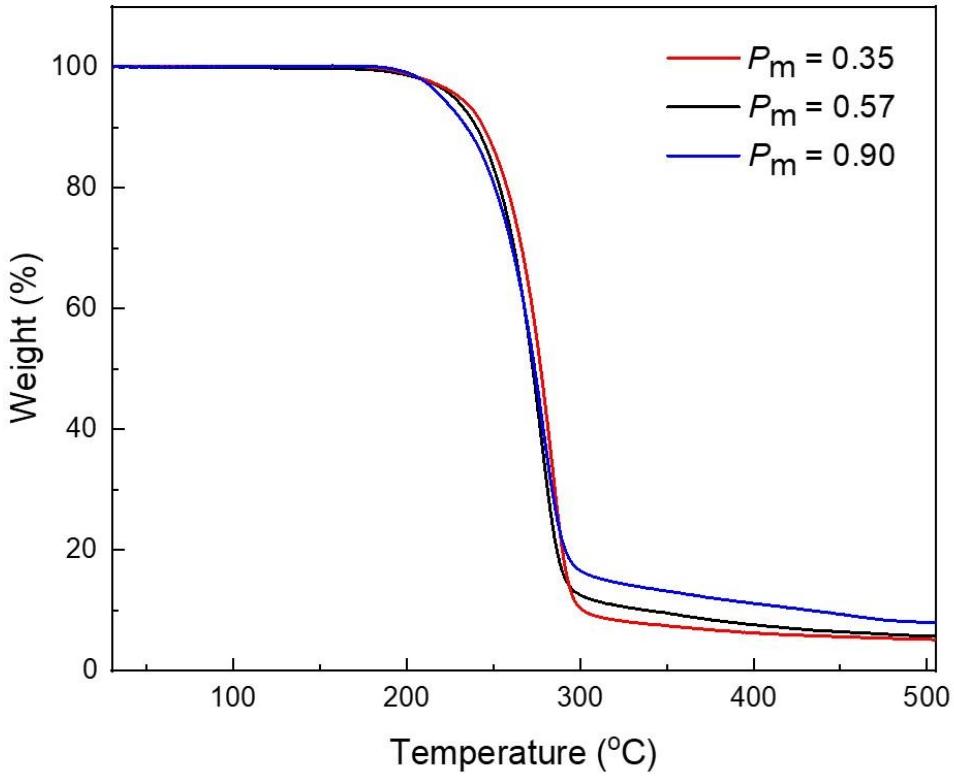


Figure 73. TGA thermogram of syndiotactic, atactic, isotactic cyclic P3TB samples with different stereoregularity but comparable molar mass (Table 2, entries 21, 36 and 48).

DSC curves

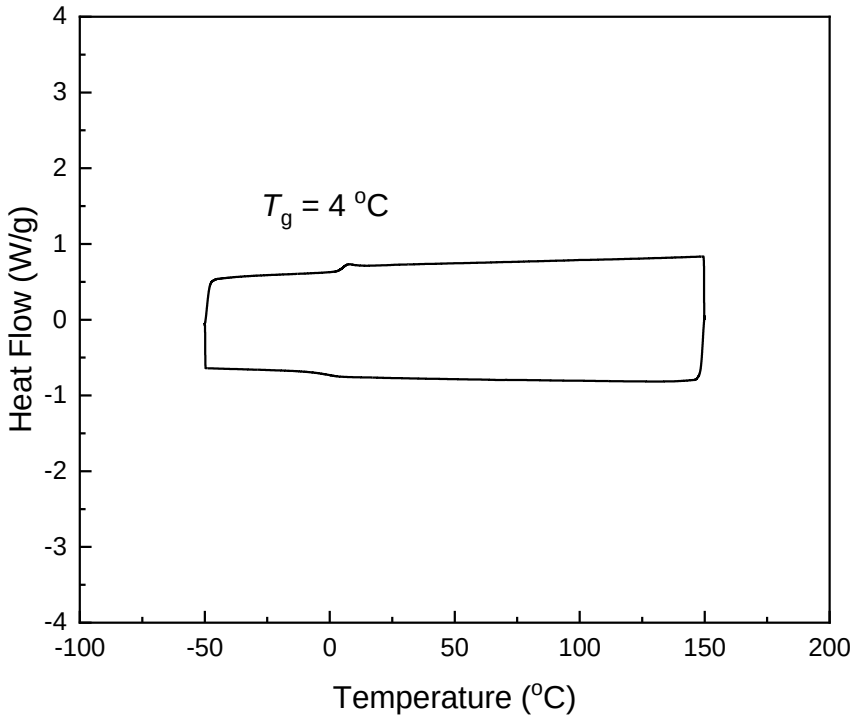


Figure 74. DSC curve of an isolated syndiotactic-enriched cyclic P3TB (Table 2, entry 24, P_m = 0.30) (heating rate = 10 °C min^{-1}, cooling rate = 10 °C min^{-1}).

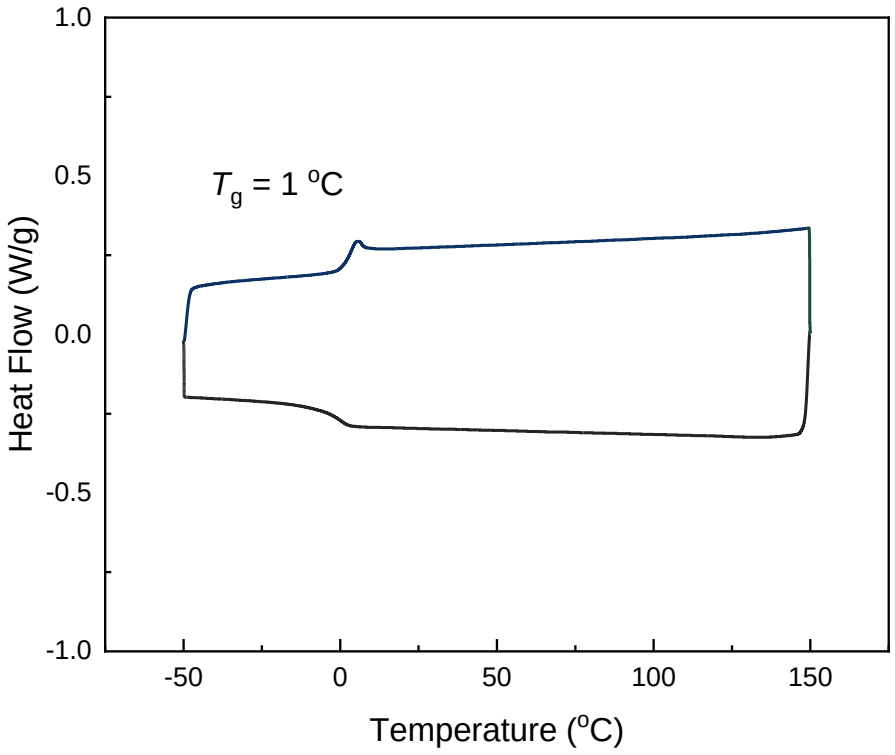


Figure 75. DSC curve of an isolated isotactic-enriched cyclic P3TB (Table 2, entry 30, P_m = 0.73) (heating rate = 10 °C min^{-1}, cooling rate = 10 °C min^{-1}).

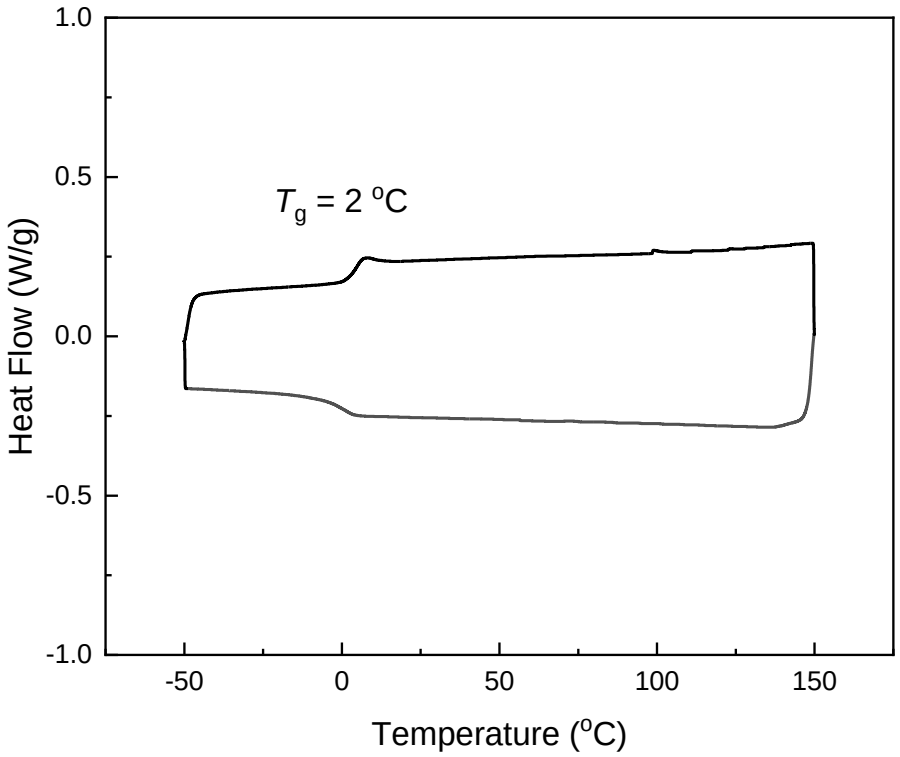


Figure 76. DSC curve of an isolated atactic cyclic P3TB (Table 2 entry 28, P_m = 0.52) (heating rate = 10 °C min^{-1}, cooling rate = 10 °C min^{-1}).

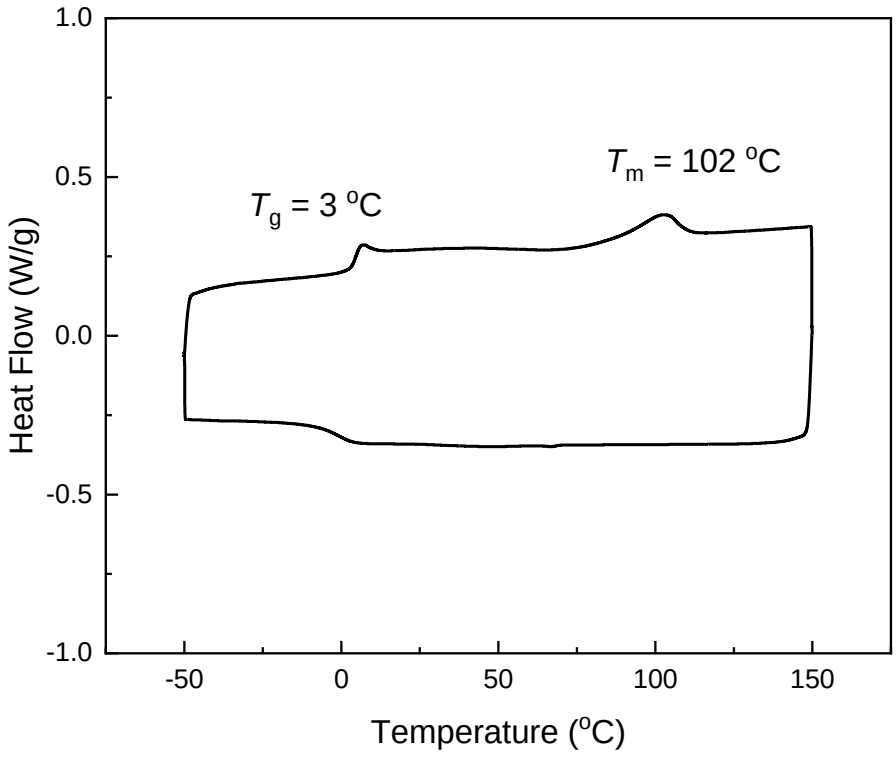


Figure 77. DSC curve of an isolated isotactic-enriched cyclic P3TB (Table 2, entry 33, P_m = 0.87) (heating rate = 10 °C min^{-1}, cooling rate = 10 °C min^{-1}).

Structural parameters of β-thiobutyrolactone vs. β-butyrolactone

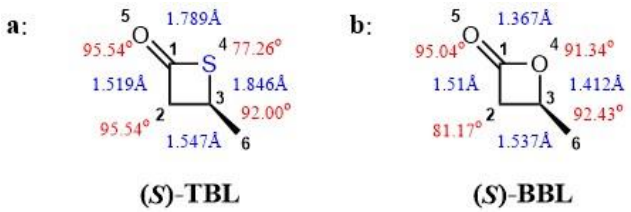


Figure 78. Structural parameters of (a) (*S*)-TBL (see: Yu. A. Borisov, A. F. Kolomiets, A. V. Fokin, The Structure and CH-Acidity of CF_3-Substituted β-Thiolactones. A Theoretical Study, *Russ. Chem. Bull.* **1998**, *47*, 1670-1676) and (b) (*S*)-BBL (calculated from Chem3D).

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Author Contributions

J.-F. C and S. M. G. are co-leading this project. H. L. designed and conducted experiments related to monomer, catalysts, polymer synthesis, as well as polymer characterizations, and J. O. performed experiments related to mass spectrometry and thermal analysis. H. L. and J.-F. C. wrote the initial manuscript draft, S. M. G. revised subsequent versions of the manuscript, and all authors contributed to the revised manuscript.