

Supporting Information

for

Ring-Opening Polymerization of β -Thiobutyrolactone Catalyzed by Phosphazenes

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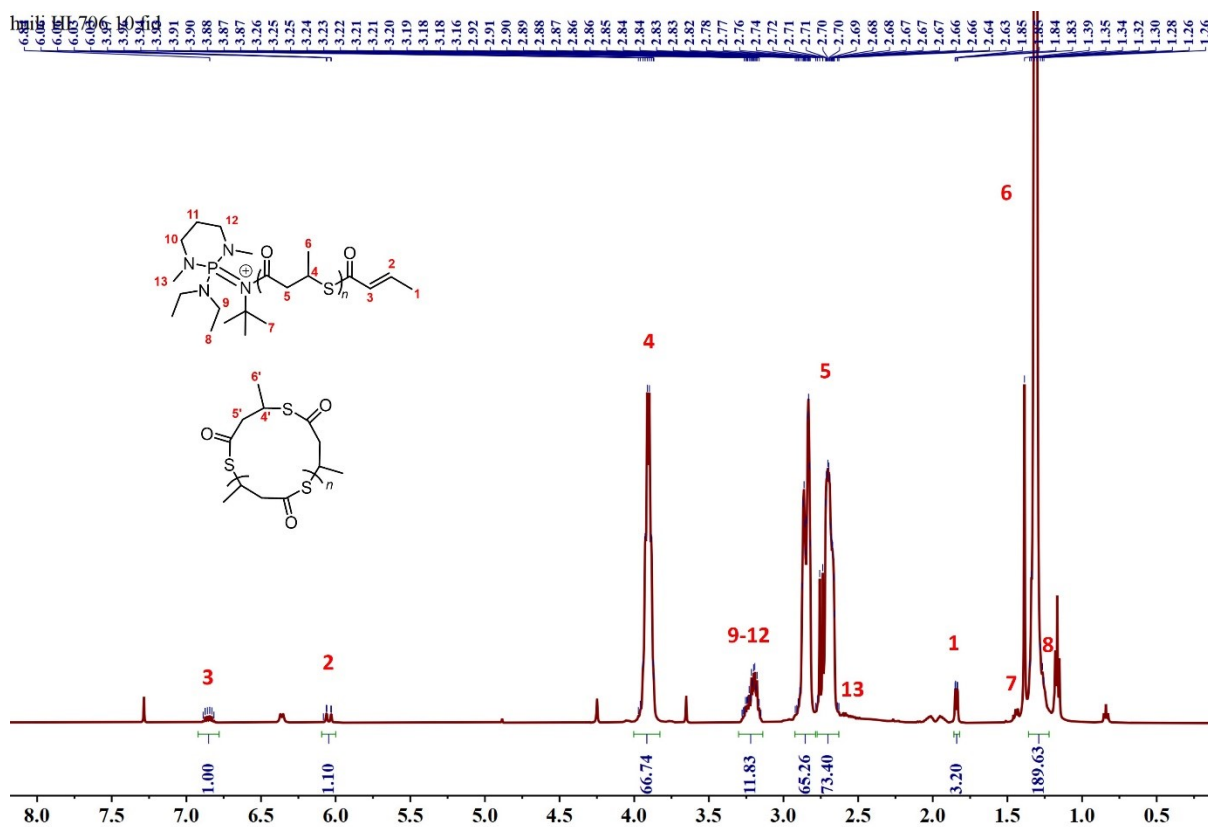


Figure S1. ^1H NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of a P3TB prepared with BEMP in bulk conditions (Table 1, entry 1) and proposed possible topologies of P3TB macromolecules formed.

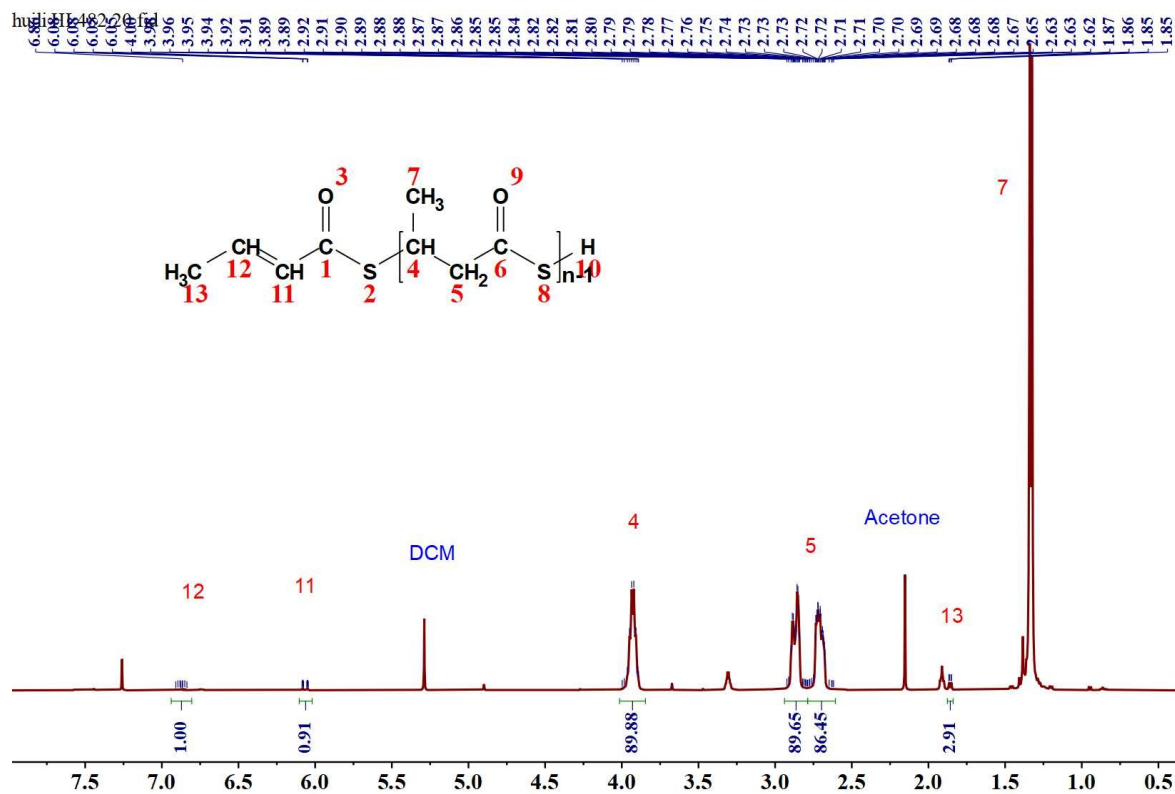


Figure S2. ^1H NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of a P3TB prepared with *t*Bu- P_1 in toluene (Table 1, entry 3).

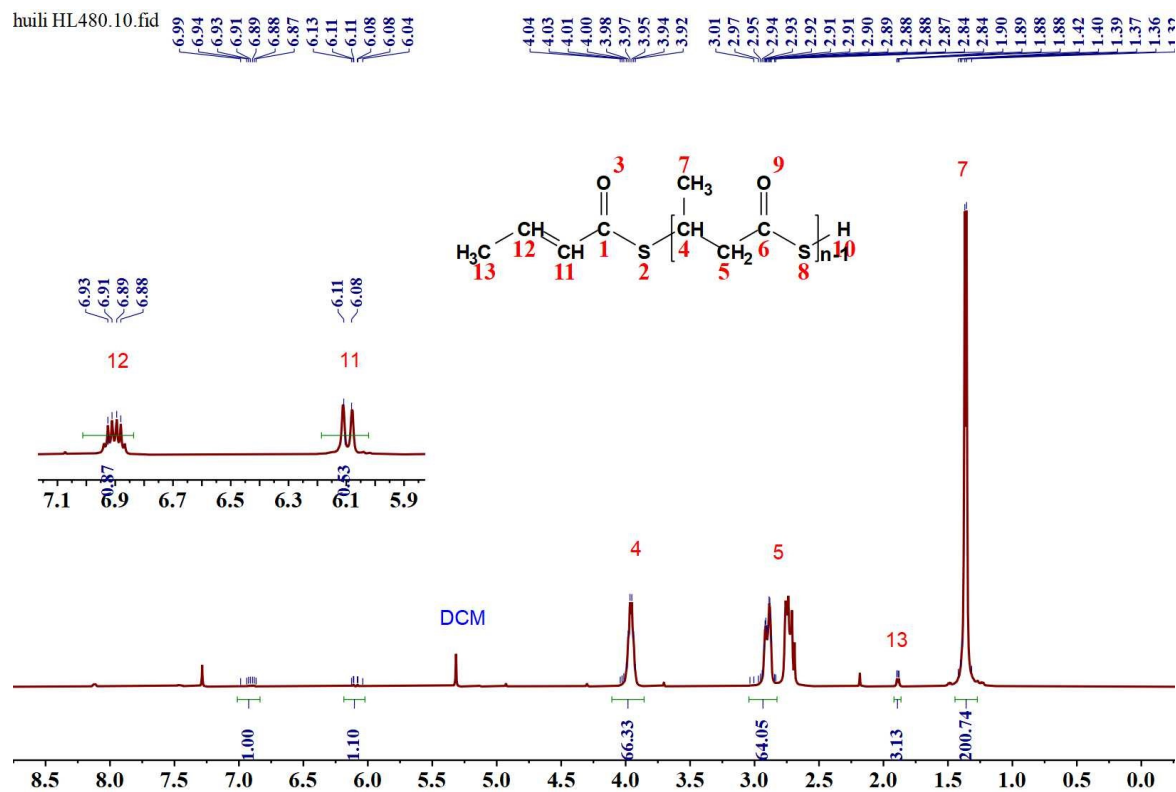


Figure S3. ^1H NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of a P3TB prepared with *t*Bu- P_2 in toluene (Table 1, entry 4).

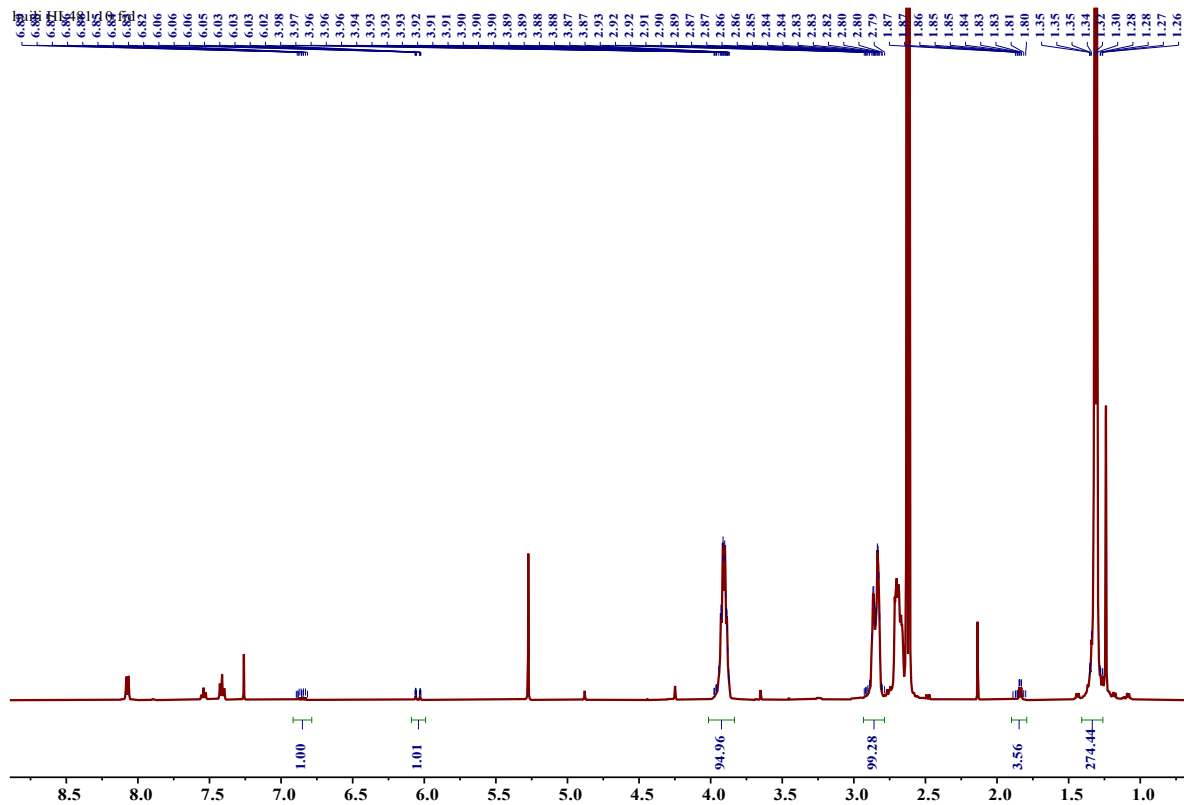


Figure S4. ^1H NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of a P3TB prepared with *t*Bu- P_4 in toluene (Table 1, entry 5).

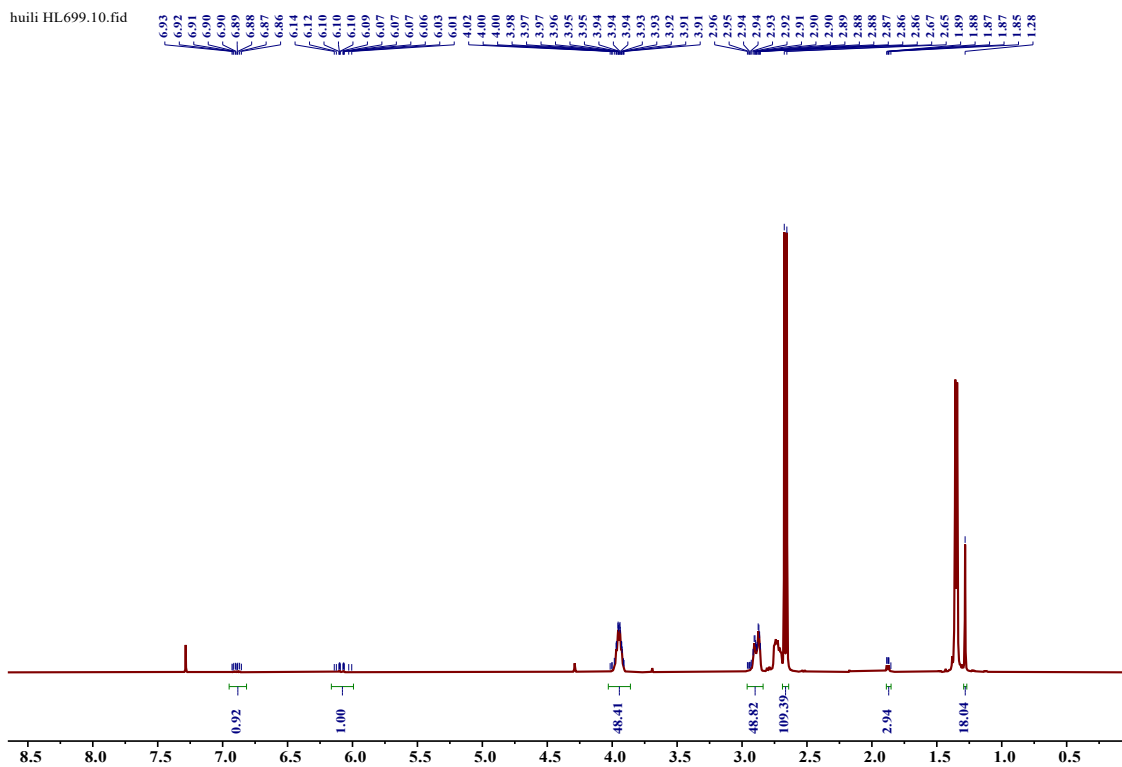


Figure S5. ^1H NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of a P3TB prepared with *t*Bu- P_4 in THF (Table 1, entry 7).

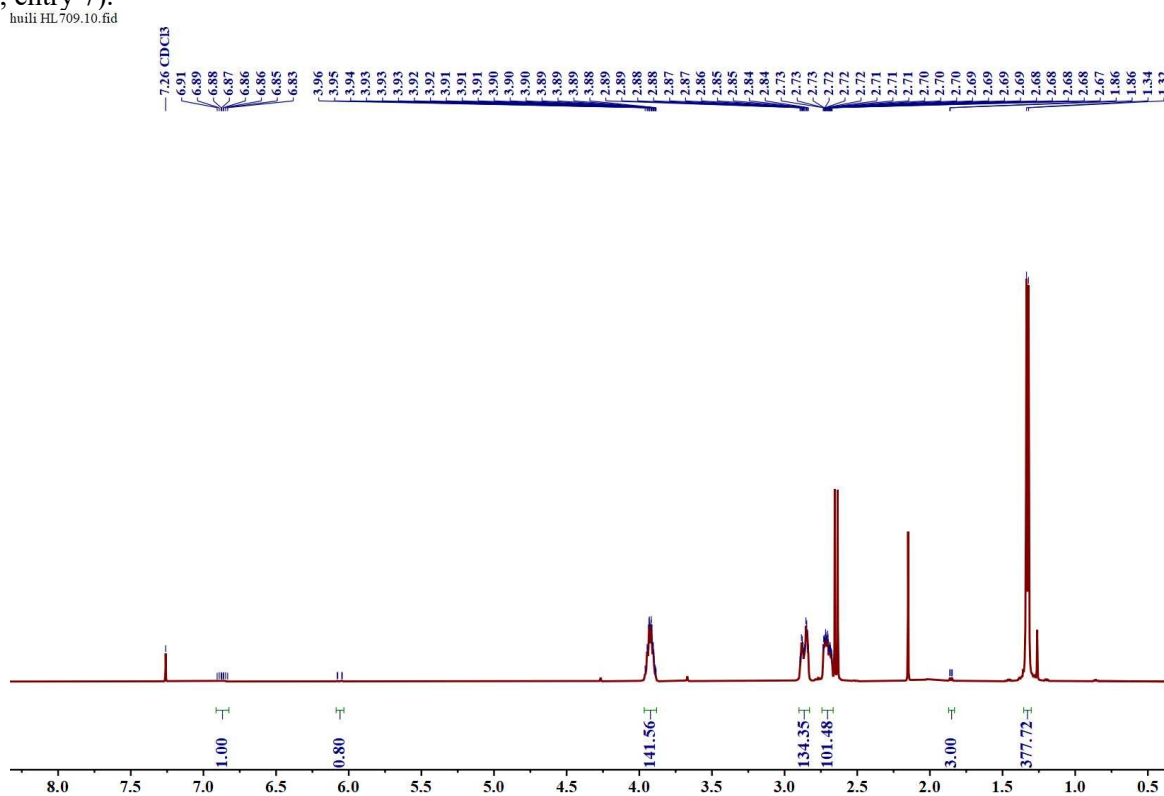


Figure S6. ^1H NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of a P3TB prepared with *t*Bu- P_4 in THF in the presence of BnOH (Table 1, entry 11).

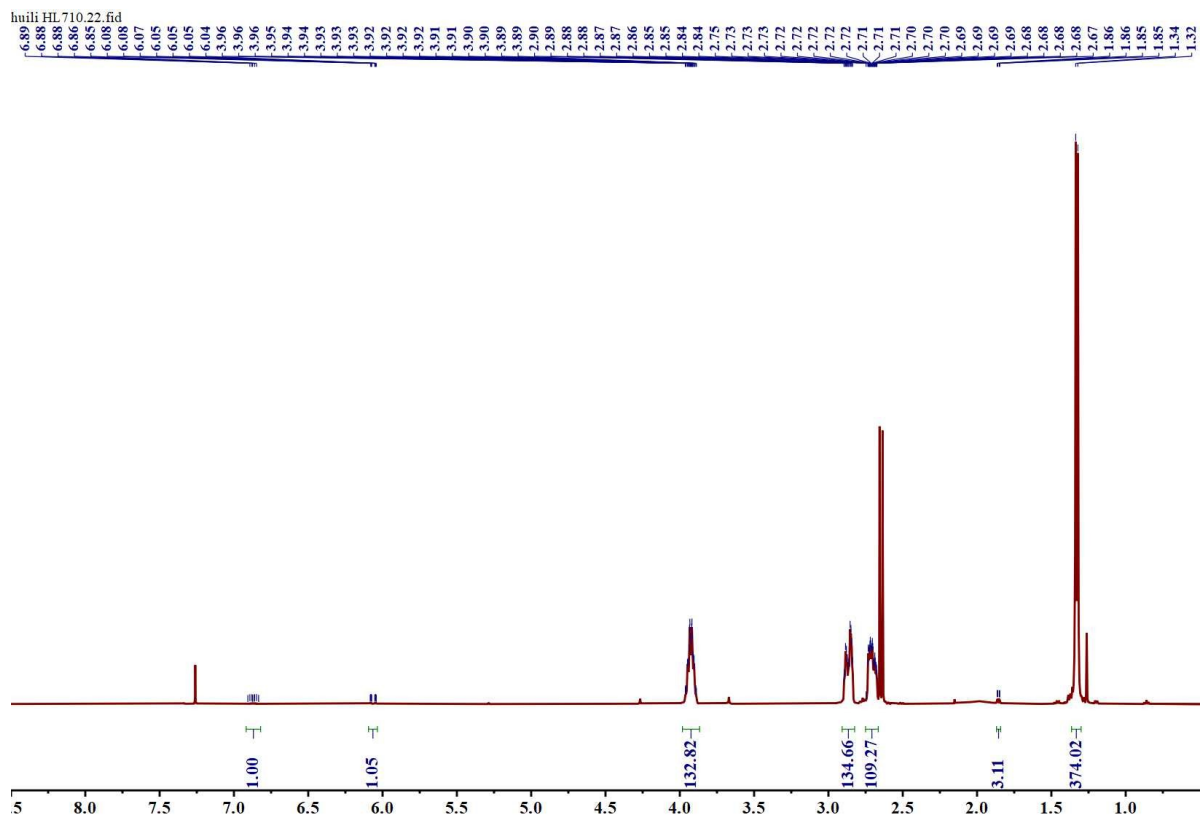


Figure S7. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of a P3TB prepared with *t*Bu-P₄ in THF in the presence of BnOH (Table 1, entry 12).

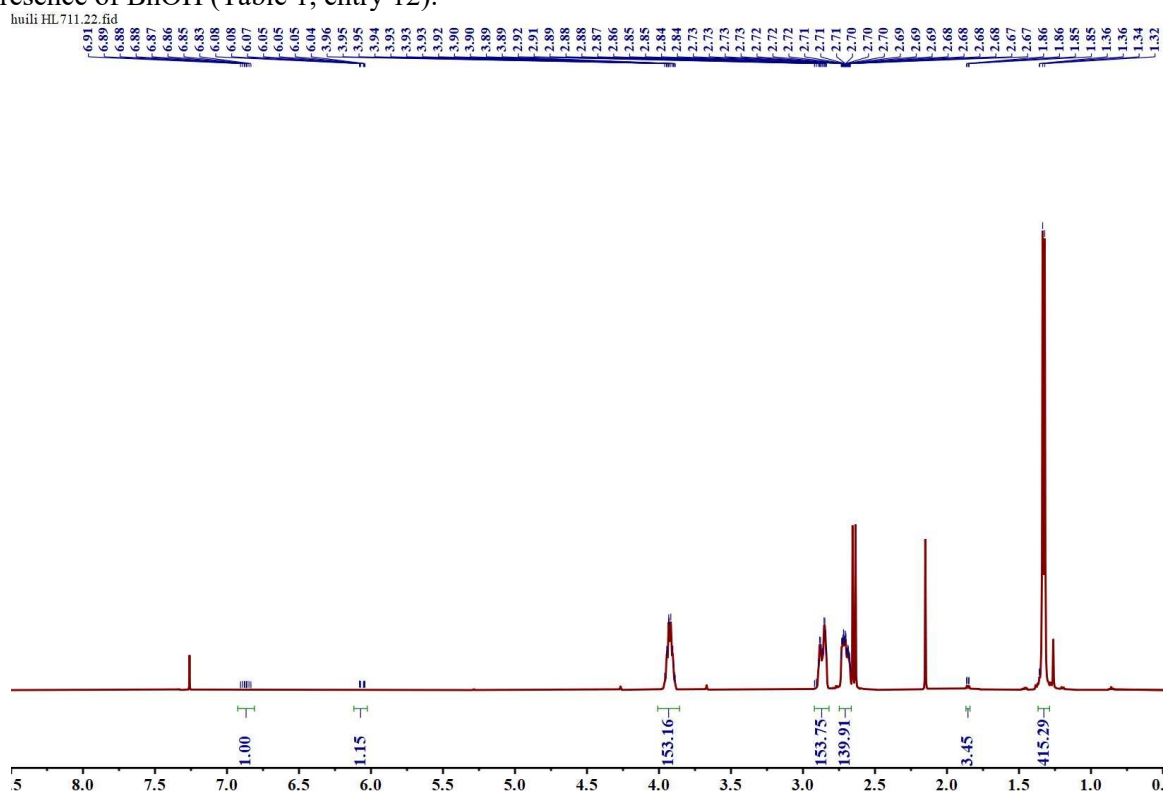
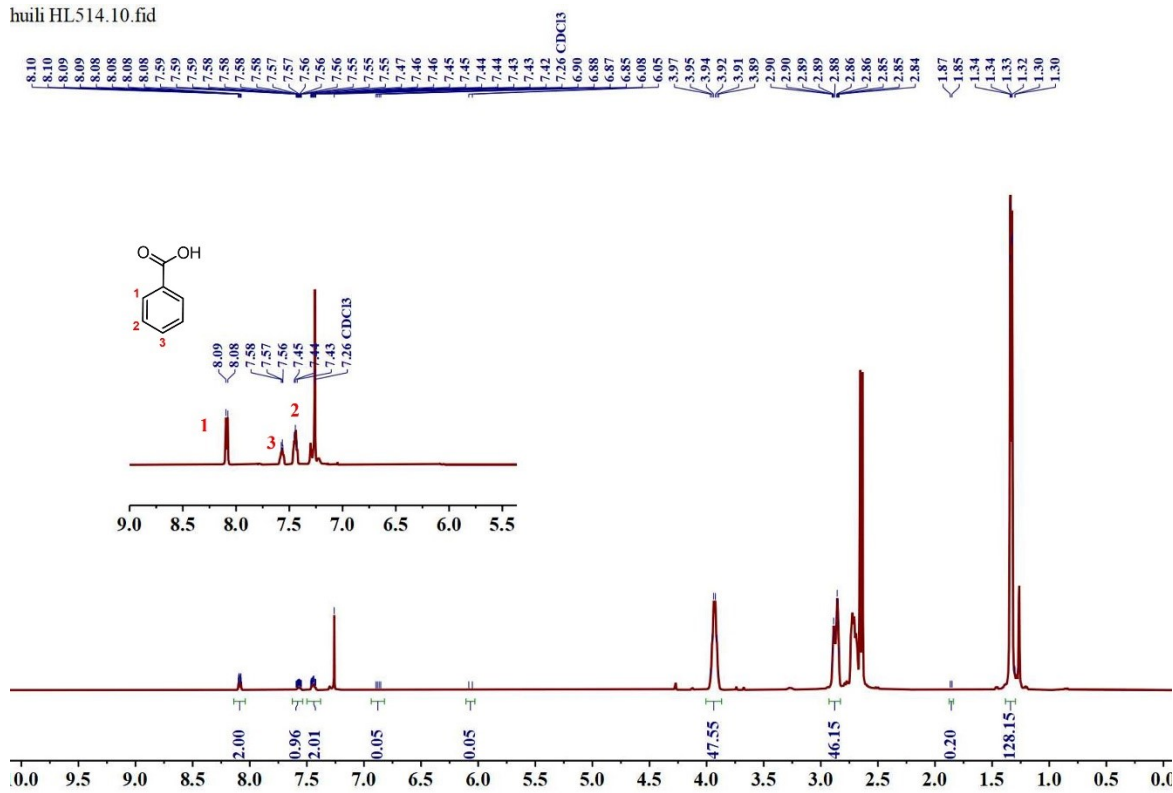


Figure S8. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of a P3TB prepared with *t*Bu-P₄ in THF in the presence of BnOH (Table 1, entry 13).

huili HL514.10.fid



Fig

ure S9. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of a P3TB prepared with *t*Bu-P₄ in toluene in the presence of BnSH (Table 1, entry 14). The low-field signals at δ ca. 7.45, 7.65 and 8.15 ppm arise from residual benzoic acid used for quenching (as a 5wt% CHCl₃ solution).

huili HL450.10.fid

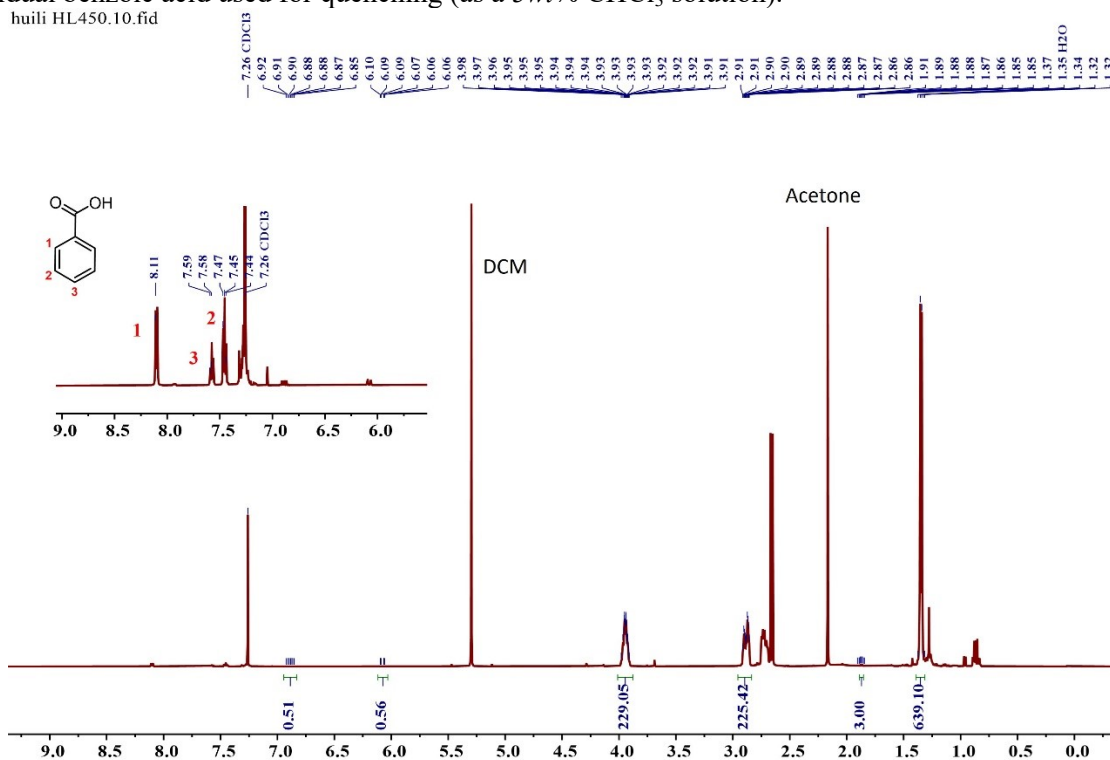


Figure S10. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of a P3TB prepared with *t*Bu-P₄ in toluene in the presence of BnSH (Table 1, entry 15). The low-intensity, low-field signals at δ ca. 7.45, 7.65 and 8.15 ppm arise from residual benzoic acid used for quenching (as a 5wt% CHCl₃ solution).

huili HL719.10.fid

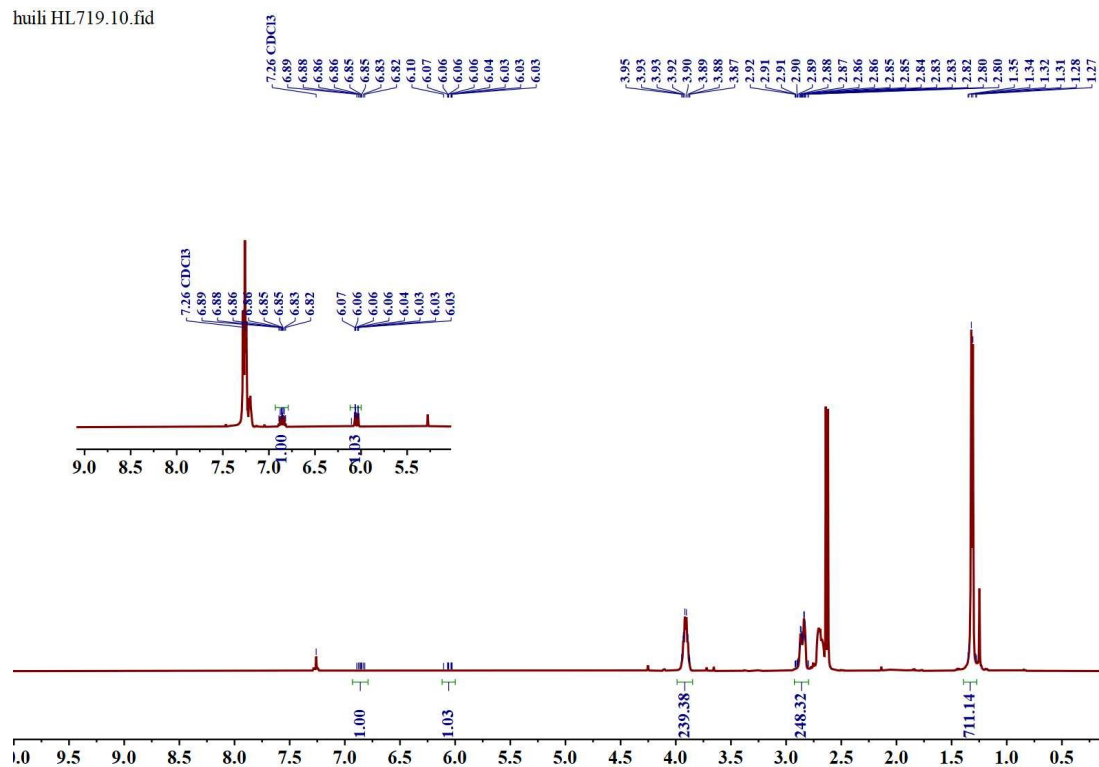


Figure S11. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of a P3TB prepared with *t*Bu-P₄ in THF in the presence of BnSH (Table 1, entry 16); the reaction was quenched with “wet” commercial-grade *n*-hexane.

huili HL702.10.fid

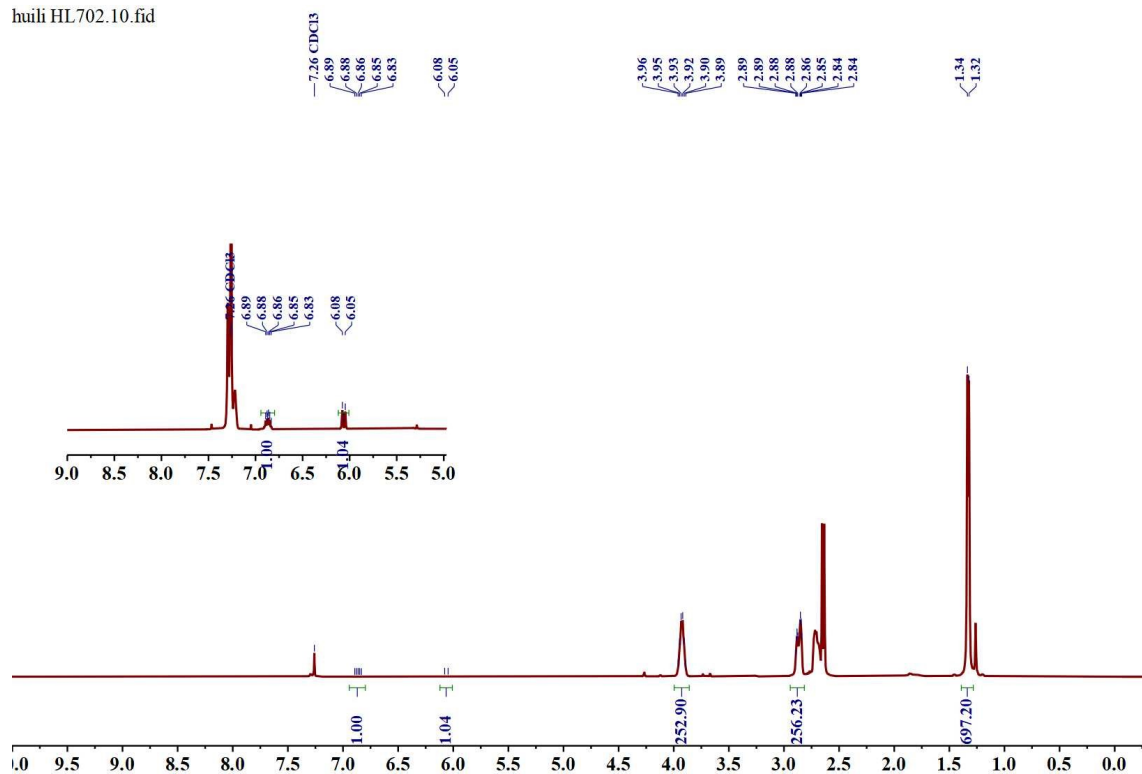


Figure S12. ^1H NMR spectrum (500 MHz, CDCl_3 , 25 °C) of a P3TB prepared with $t\text{Bu-P}_4$ in THF in the presence of BnSH (Table 1, entry 16 duplicated); the reaction was quenched with “wet” commercial-grade n -hexane.

Representative SEC traces of P3TBs

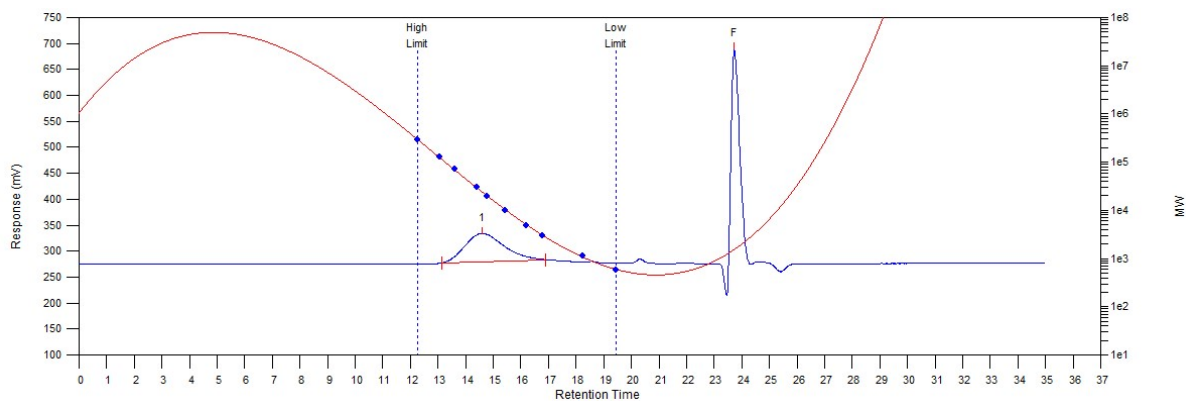


Figure S13. SEC trace of an isolated P3TB (Table 1, entry 1).

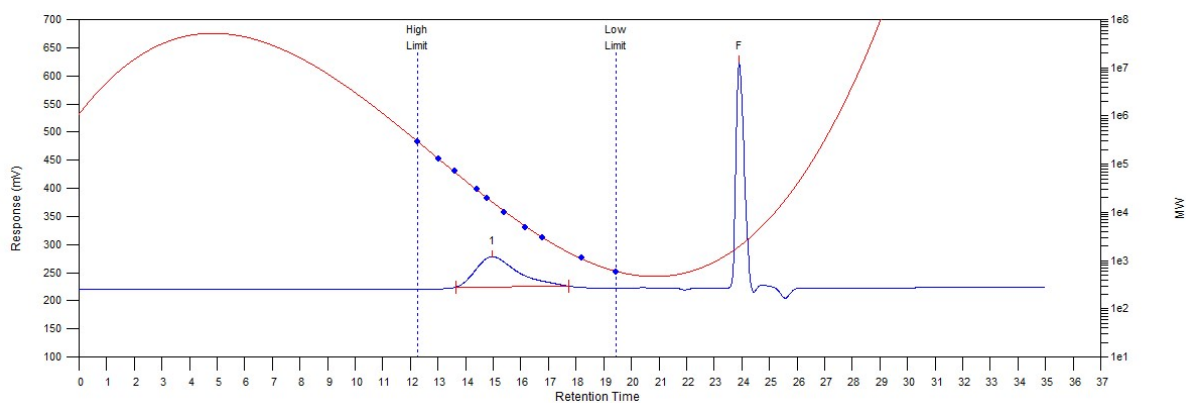


Figure S14. SEC trace of an isolated P3TB (Table 1, entry 3).

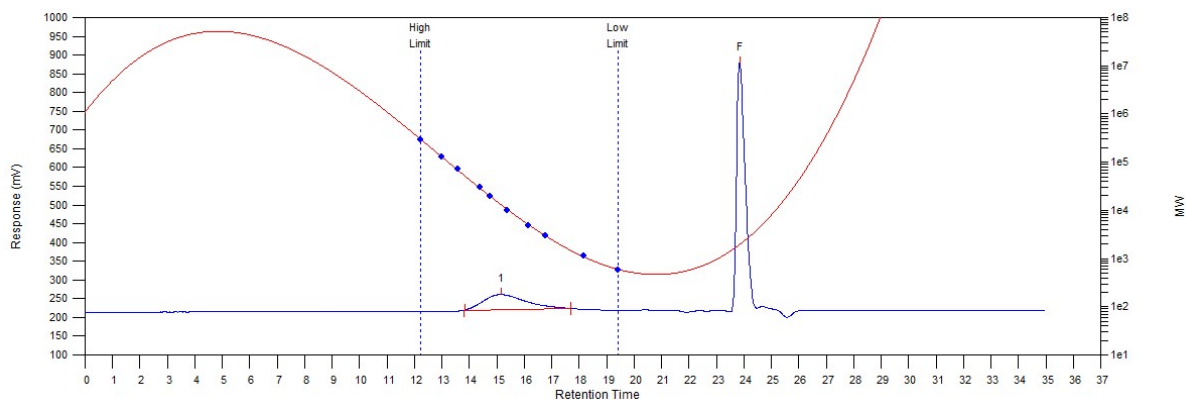


Figure S15. SEC trace of an isolated P3TB (Table 1, entry 5).

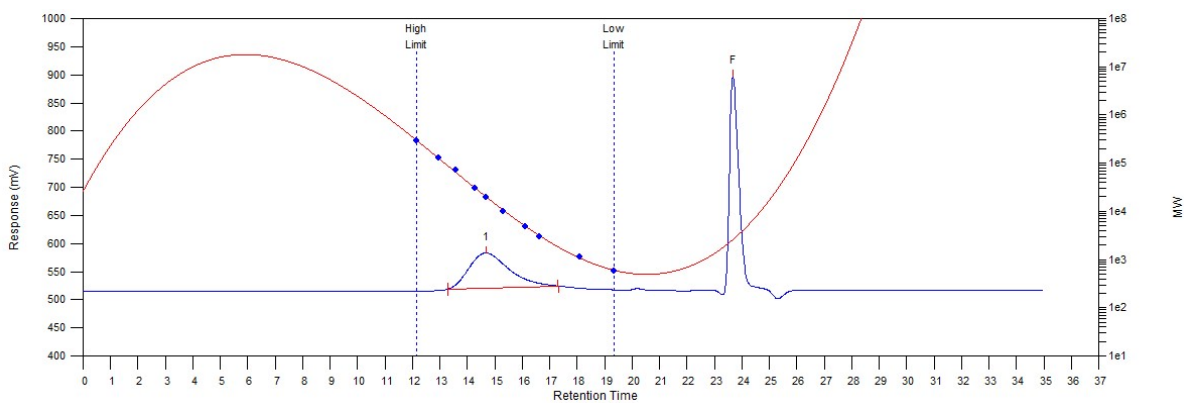


Figure S16. SEC trace of an isolated P3TB (Table 1, entry 6).

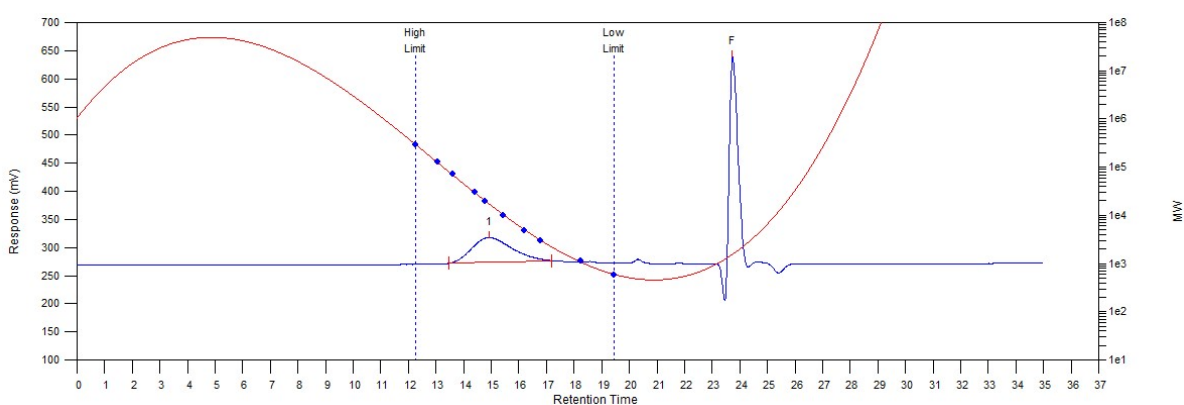


Figure S17. SEC trace of an isolated P3TB (Table 1, entry 7).

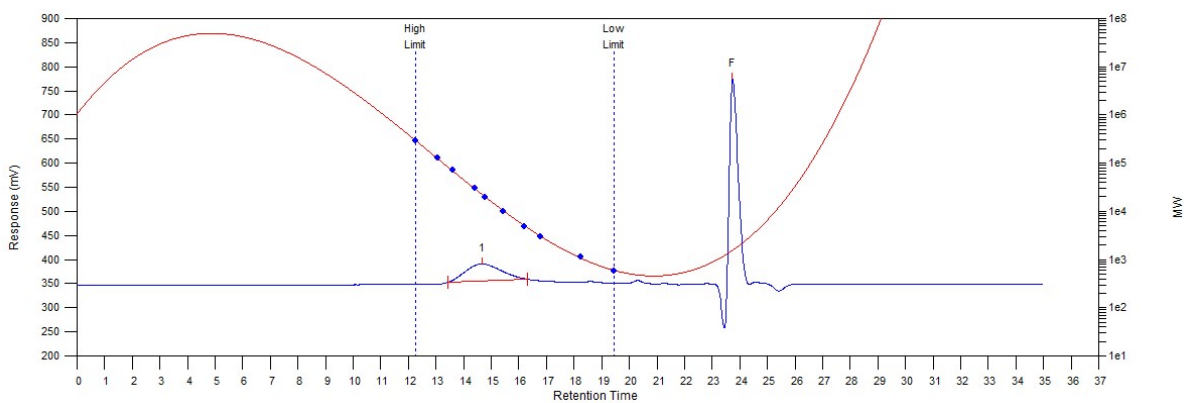


Figure S18. SEC trace of an isolated P3TB (Table 1, entry 8).

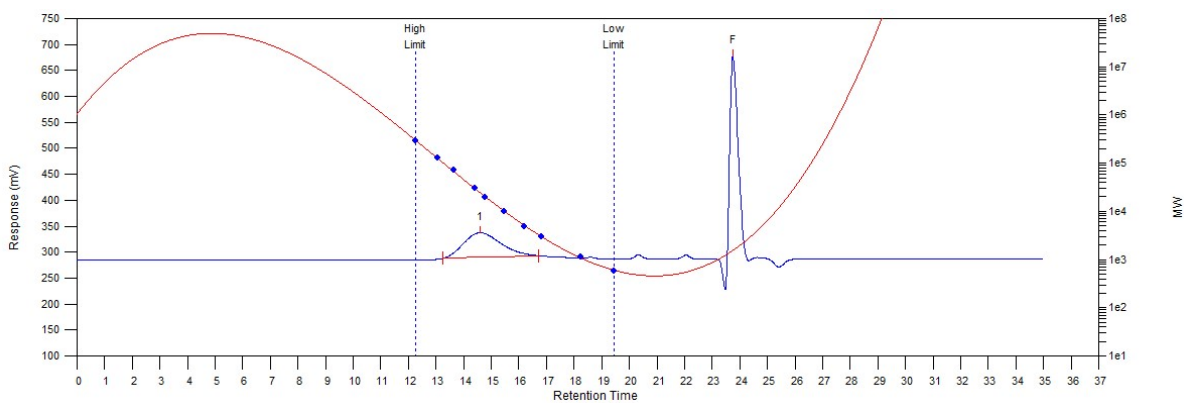


Figure S19. SEC trace of an isolated P3TB (Table 1, entry 9).

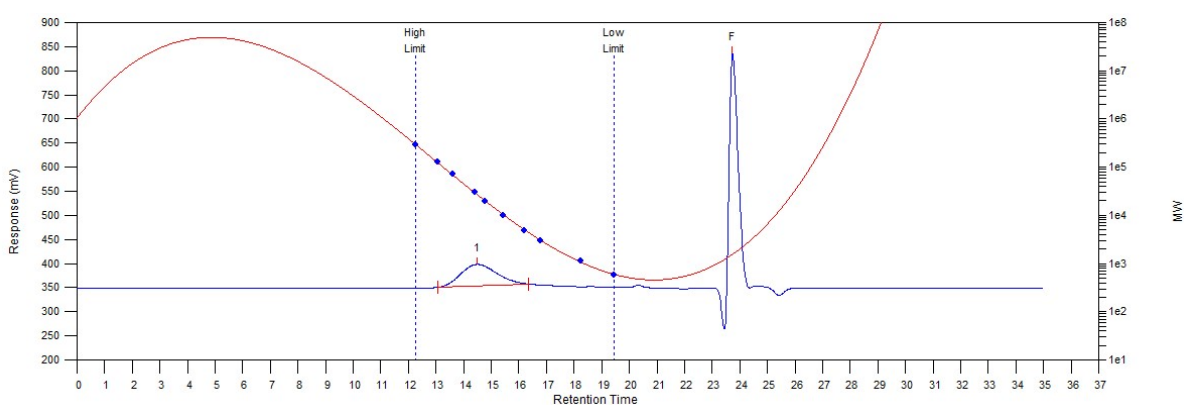


Figure S20. SEC trace of an isolated P3TB (Table 1, entry 10).

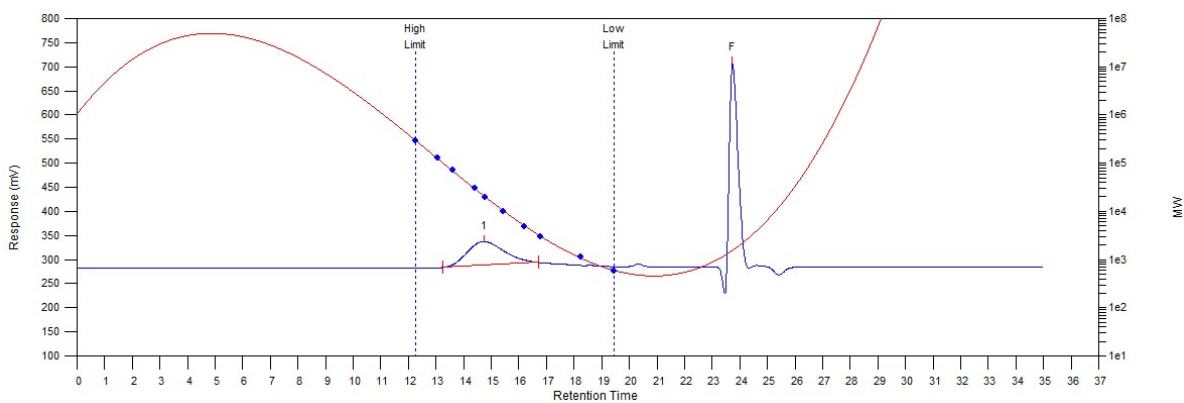


Figure S21. SEC trace of an isolated P3TB (Table 1, entry 11).

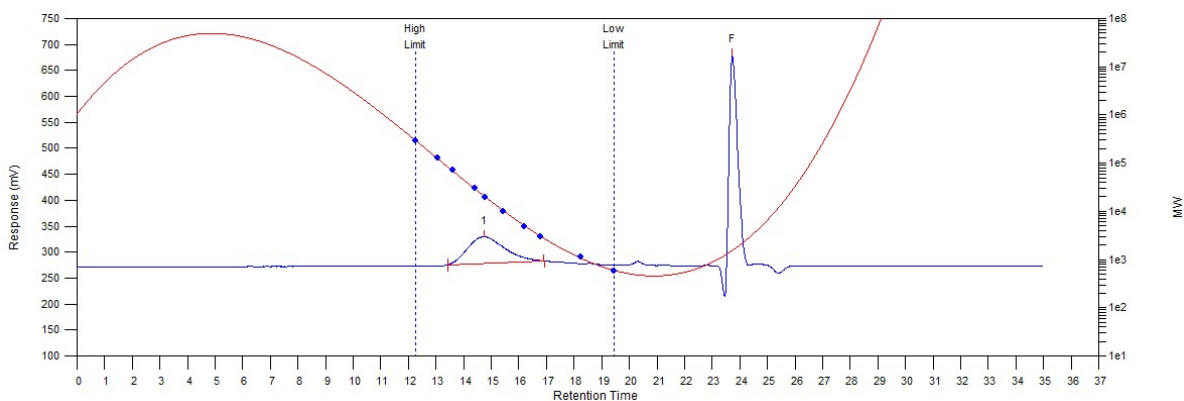


Figure S22. SEC trace of an isolated P3TB (Table 1, entry 12).

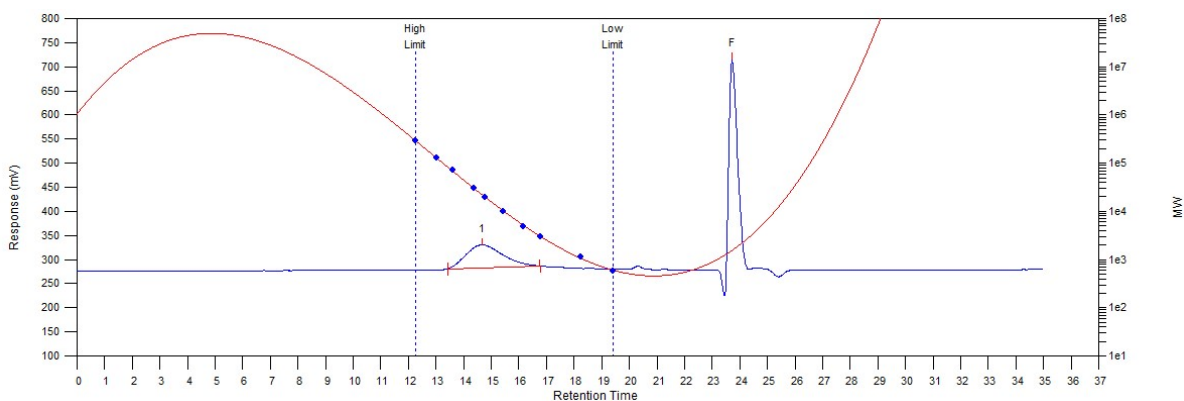


Figure S23. SEC trace of an isolated P3TB (Table 1, entry 13).

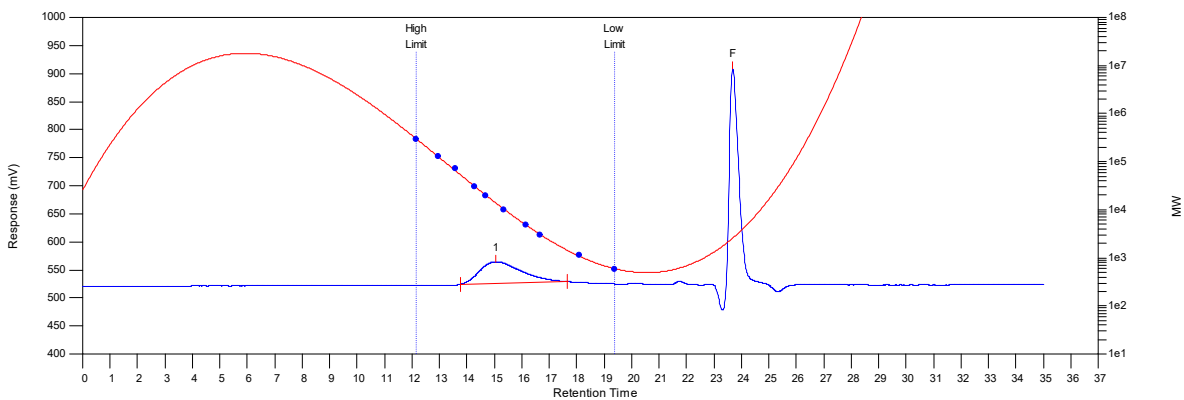


Figure S24. SEC trace of an isolated P3TB (Table 1, entry 14).

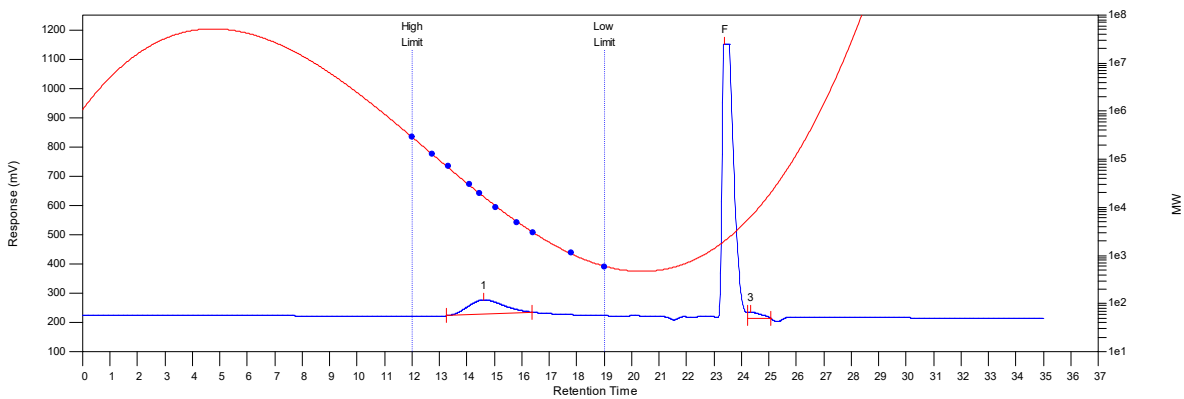


Figure S25. SEC trace of an isolated P3TB (Table 1, entry 15).

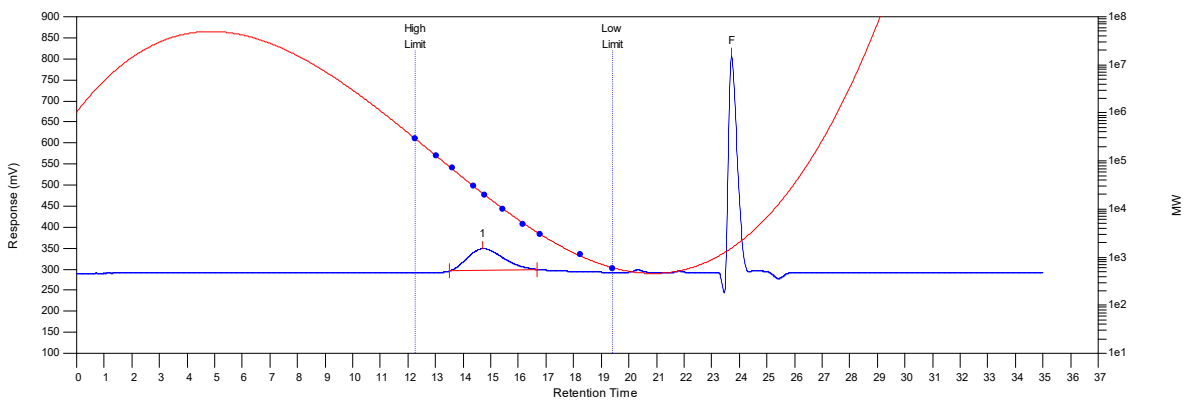


Figure S26. SEC trace of an isolated P3TB (Table 1, entry HL16).

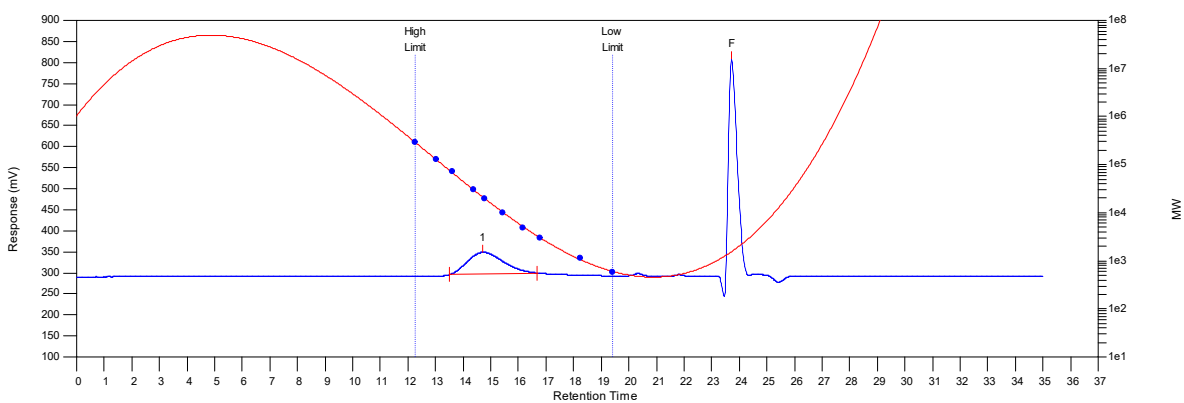
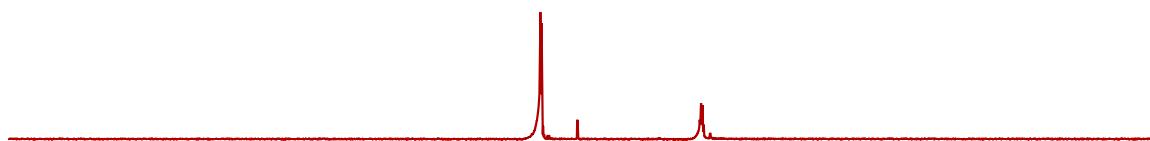


Figure S27. SEC trace of an isolated P3TB (repetition of Table 1, entry 16).

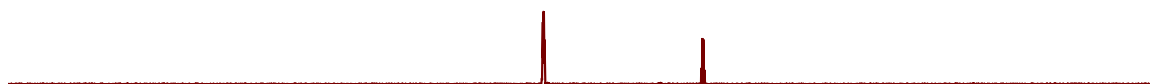
huili HL-(P4+TBL).15.fid

(a)



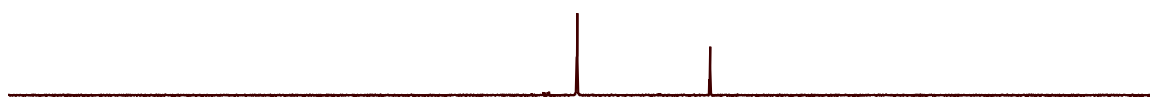
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(b)



huili HL-P4.12.fid

(c)



130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120

Figure S28. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (202 MHz, C_6D_6 , 25 °C) of: (a) 1:1 (*mol/mol*) mixture of *t*Bu- P_4 and *rac*-TBL; (b) 1:1 (*mol/mol*) mixture of *t*Bu- P_4 and benzoic acid; (c) native *t*Bu- P_4 .

huili HL-(P4+TBL).10.fid

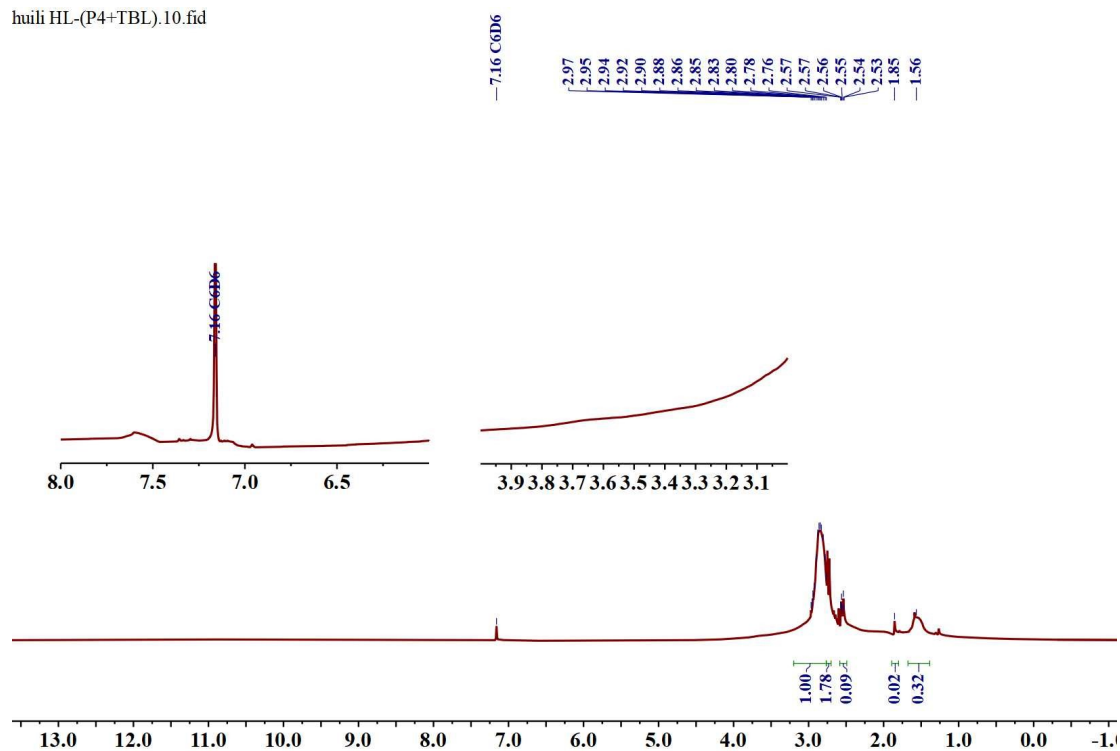


Figure S29. ^1H NMR spectrum (500 MHz, C_6D_6 , 25 °C) of 1:1 (*mol/mol*) mixture of *t*Bu- P_4 and *rac*-TBL.

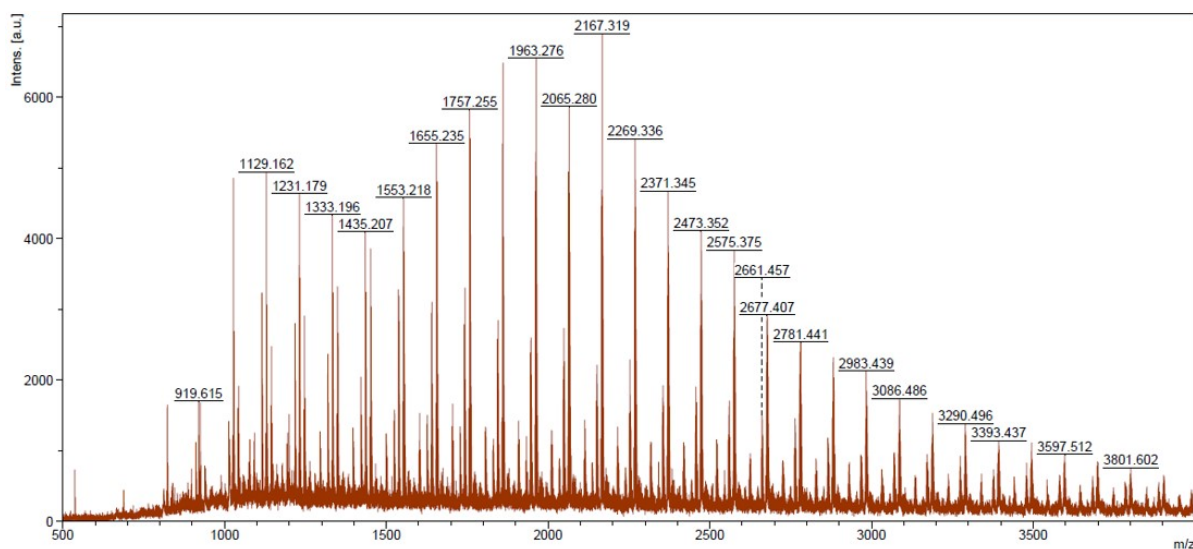


Figure S30. MALDI-ToF mass spectrum of a P3TB prepared with *t*Bu-P₁ in toluene (Table 1, entry 3) recorded at very high laser power.

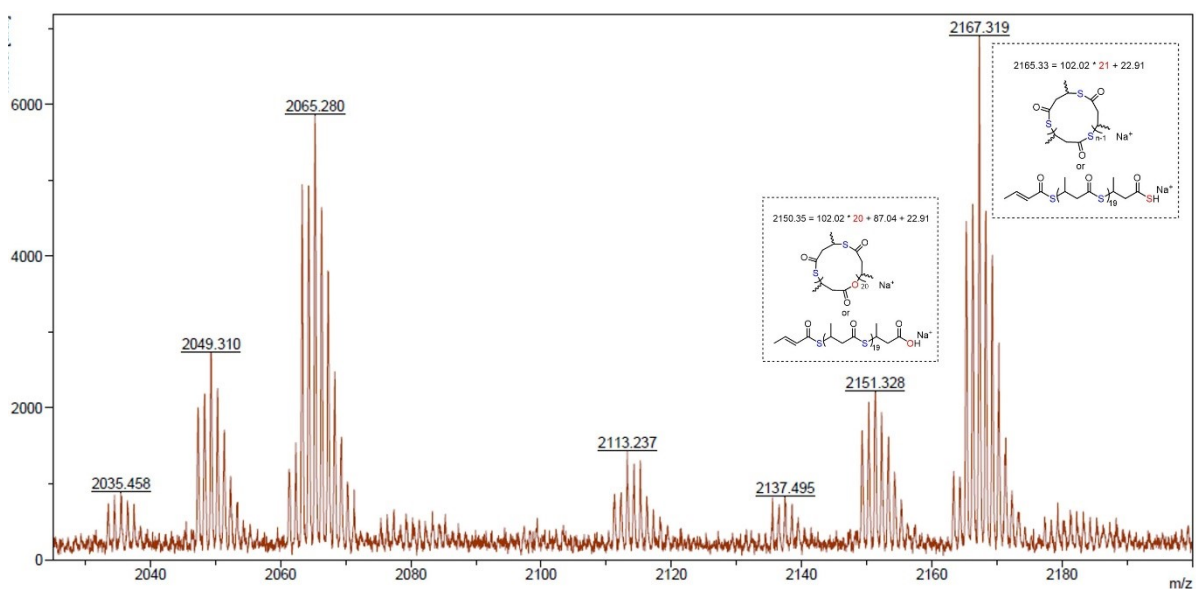


Figure S31. Details of the MALDI-ToF mass spectrum (Figure S30) of a P3TB prepared with *t*Bu-P₁ in toluene (Table 1, entry 3), including a major population of cyclic P3TB. The two less intense populations have not been identified yet.

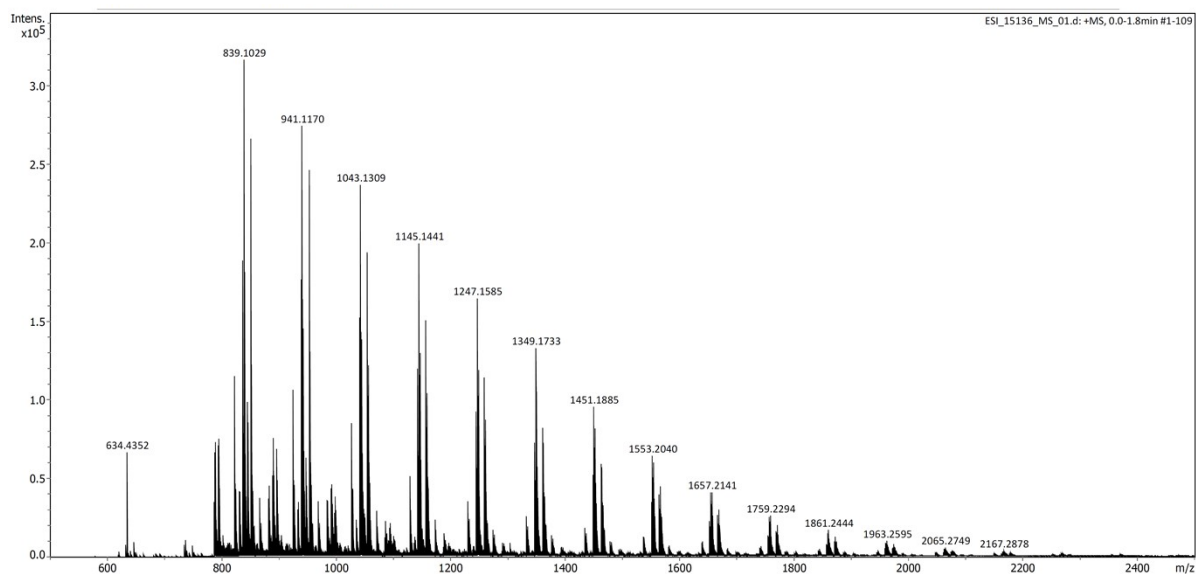


Figure S32. ESI mass spectrum (positive mode, MeOH) of a P3TB prepared with *t*Bu-P₄ in THF (Table 1, entry 7) (intensity of the signals above *m/z* = 880 has been enhanced). The most intense series (with peak picking values) corresponds to $\{\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{S}[\text{C}_4\text{H}_6\text{OS}]_{n-1}\text{H}+\text{Na}\}^+$ or $\{[\text{C}_4\text{H}_6\text{OS}]_n+\text{Na}\}^+$ with, for *n* = 8, *m/z* exp = 839.1029 vs. *m/z* theo = 839.1012; for *n* = 9, *m/z* exp = 941.1170 vs. *m/z* theo = 941.1152; for *n* = 10, *m/z* exp = 1043.1309 vs. *m/z* theo = 1043.1291; for *n* = 11, *m/z* exp = 1145.1441 vs. *m/z* theo = 1145.1431; for *n* = 12, *m/z* exp = 1247.1585 vs. *m/z* theo = 1247.1570.

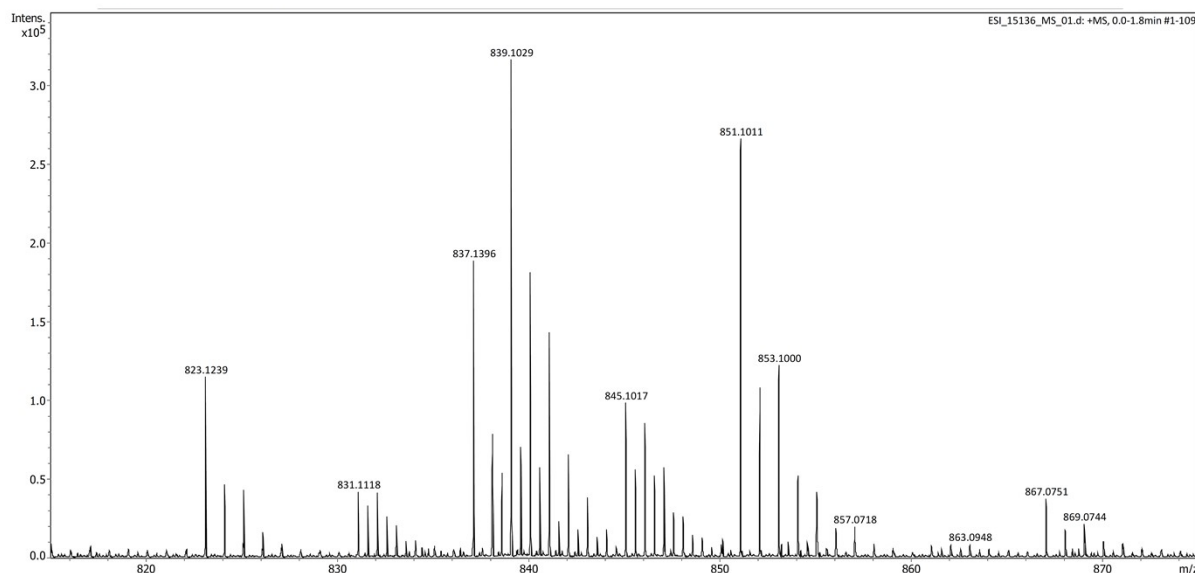


Figure S33. Details of the ESI mass spectrum (positive mode, MeOH; Figure S32) of a P3TB prepared with *t*Bu-P₄ in THF (Table 1, entry 7), showing the major populations of macromolecular ions for a polymerization degree, *n*, of 8. For $\{\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{S}[\text{C}_4\text{H}_6\text{OS}]_7\text{H}+\text{Na}\}^+$ or $\{[\text{C}_4\text{H}_6\text{OS}]_8+\text{Na}\}^+$ *m/z* exp = 839.1029 vs. *m/z* theo = 839.1012; for $\{[\text{CH}_3\text{CH}=\text{CHCOS}][\text{C}_4\text{H}_6\text{OS}]_6[\text{CH}(\text{CH}_3)\text{CH}_2\text{COOH}]+\text{Na}\}^+$ *m/z* exp = 823.1239 vs. *m/z* theo = 823.1235; for $\{[\text{CH}_3\text{CH}=\text{CHCOS}][\text{C}_4\text{H}_6\text{OS}]_6[\text{CH}(\text{CH}_3)\text{CH}_2\text{CO}_2\text{CH}_3]+\text{Na}\}^+$ *m/z* exp = 837.1396 vs. *m/z* theo = 837.1397; the macromolecular ion at *m/z* = 851.1011 could not be identified.

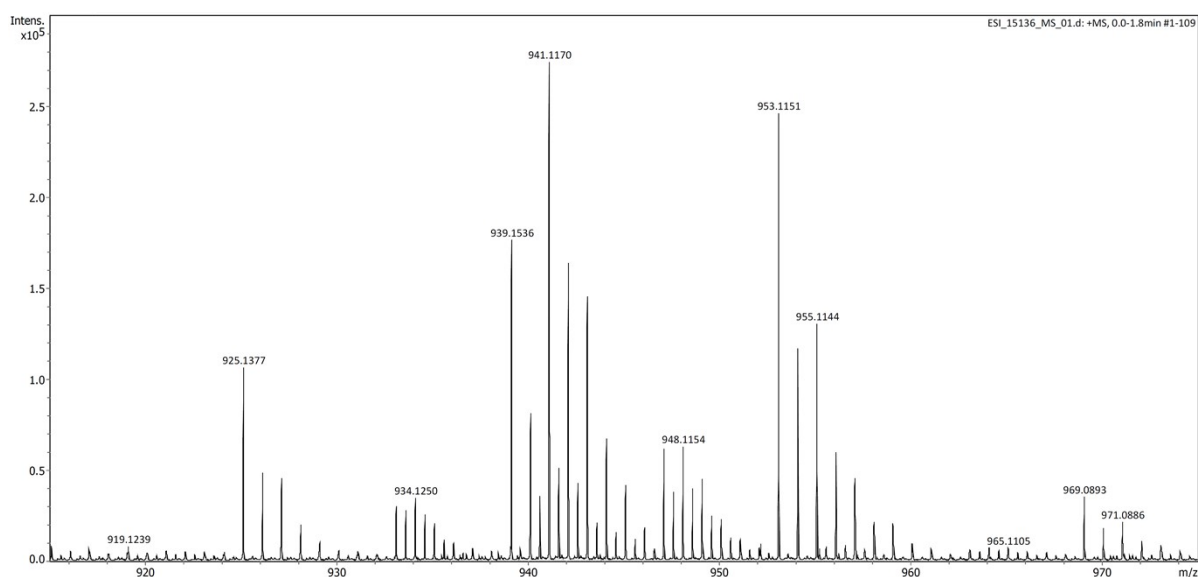


Figure S34. Details of the ESI mass spectrum (positive mode, MeOH; Figure S32) of a P3TB prepared with *t*Bu-P₄ in THF (Table 1, entry 7), showing the major populations of macromolecular ions for a polymerization degree, *n*, of 9. For $\{\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{S}[\text{C}_4\text{H}_6\text{OS}]_8\text{H}+\text{Na}\}^+$ or $\{[\text{C}_4\text{H}_6\text{OS}]_9+\text{Na}\}^+$ m/z exp = 941.1170 vs. m/z theo = 941.1152; for $\{[\text{CH}_3\text{CH}=\text{CHCOS}][\text{C}_4\text{H}_6\text{OS}]_7[\text{CH}(\text{CH}_3)\text{CH}_2\text{COOH}]+\text{Na}\}^+$ m/z exp = 925.1377 vs. m/z theo = 925.1375; for $\{[\text{CH}_3\text{CH}=\text{CHCOS}][\text{C}_4\text{H}_6\text{OS}]_7[\text{CH}(\text{CH}_3)\text{CH}_2\text{CO}_2\text{CH}_3]+\text{Na}\}^+$ m/z exp = 939.1536 vs. m/z theo = 939.1537; the macromolecular ion at $m/z = 953.1151$ could not be identified.

Thermal studies

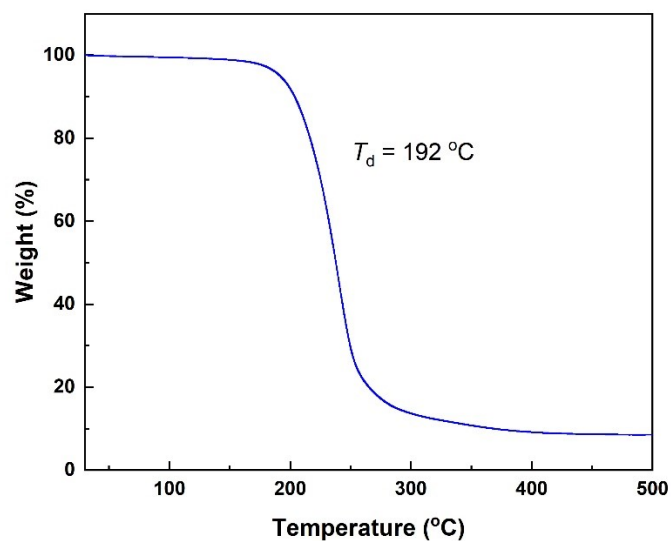


Figure S35. TGA thermogram of a P3TB sample prepared by BEMP in toluene (Table 1, entry 2; T_d defined as the temperature for 5% weight loss; polymer sample was heated from ambient temperature to 500 °C at a rate of 10 °C min⁻¹).

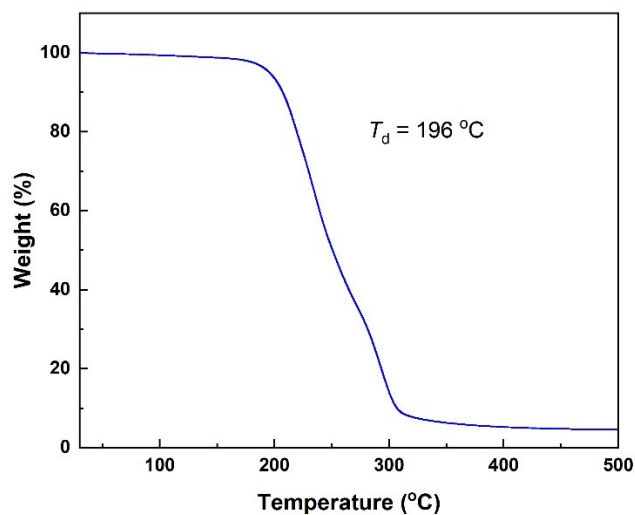


Figure S36. TGA thermogram of a P3TB sample prepared by *t*Bu-P₁ in toluene (Table 1, entry 3; T_d defined as the temperature for 5% weight loss; polymer sample was heated from ambient temperature to 500 °C at a rate of 10 °C min⁻¹).

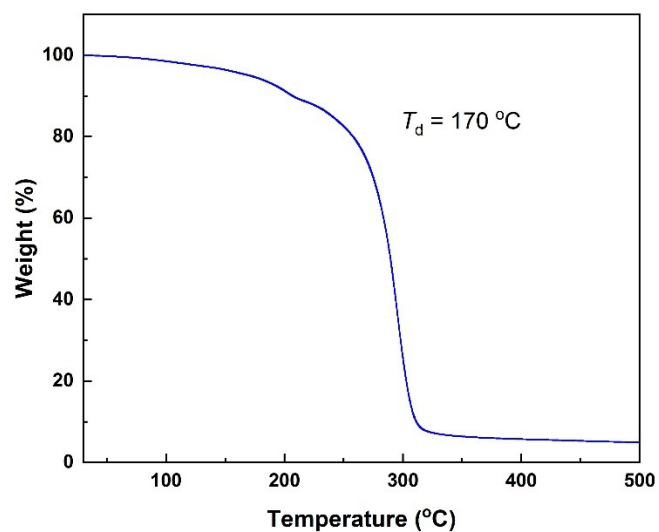


Figure S37. TGA thermogram of a P3TB sample prepared by *t*Bu-P₄ in THF (Table 1, entry 9; T_d defined as the temperature for 5% weight loss; polymer sample was heated from ambient temperature to 500 °C at a rate of 10 °C min⁻¹).

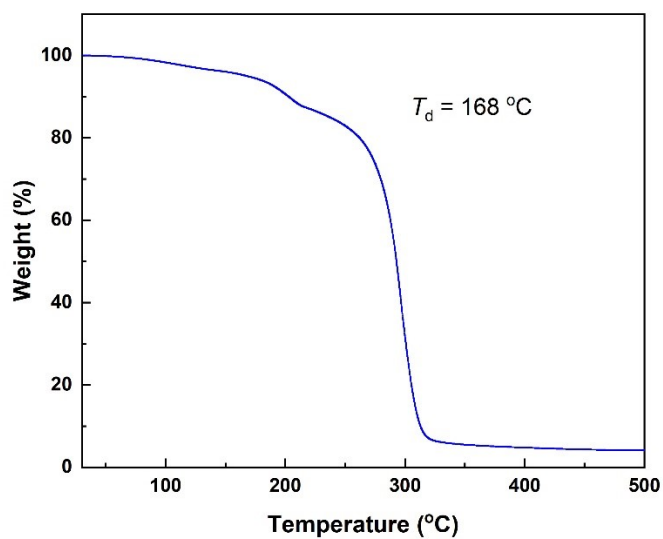


Figure S38. TGA thermogram of a P3TB sample prepared by *t*Bu-P₄ in THF (Table 1, entry 10; T_d defined as the temperature for 5% weight loss; polymer sample was heated from ambient temperature to 500 °C at a rate of 10 °C min⁻¹).