Supporting Information for Manuscript Entitled with

Synthesis of glycerol-based (co)polyethers *via* ring-opening polymerization of glycidyl butyrate catalyzed by one-component phosphonium tetraborane Lewis pair

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Chemicals

All moisture/oxygen-sensitive reactions/compounds were performed using standard Schlenk techniques or glovebox techniques in an atmosphere of high-purity nitrogen. Propylene oxide (PO) and methanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (R)-glycidyl butyrate (*R*GB), (S)-glycidyl butyrate (*S*GB), 1,2-butylene oxide (BO), allyl glycidyl ether (AGE), *tert*-butyl glycidyl ether (*t*-BGE) styrene oxide (SO), phosphorus trichloride (PCl_3), pent-4-en-1-ylmagnesium bromide, 5-bromopent-1-ene and 9-borabicyclo[3.3.1]nonane (9-BBN) were purchased from Energy Chemical. Calcium hydride (CaH_2), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and deuterated solvents were Aladdin. Tetrahydrofuran (THF), acetonitrile dichloromethane ethyl acetate and n-hexane were purchased as Super-dry solvent from *J&K* chemical company. $CDCl_3$, *R*GB, *S*GB, PO, BO, AGE, *t*-BGE and SO were dried over CaH_2 for 48 h, distilled and stored under nitrogen atmosphere. All other chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted.

Characterization and Analysis

NMR Spectroscopy

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE NEO 400 MHz NMR spectrometer (^{1}H NMR 400 MHz, $^{13}C\{^1H\}$ NMR 100 MHz, 128 MHz $^{11}B\{^1H\}$ NMR, 162 MHz ^{31}P NMR) at 298 K. ^{1}H and $^{13}C\{^1H\}$ NMR Chemical shifts were reported in δ (ppm) with the residual deuterated solvent peak as reference [^{1}H: TMS in $CDCl_3$ = 0 ppm; $^{13}C\{^1H\}$: $CDCl_3$ = 77.16 ppm; $^{11}B\{^1H\}$:

BF_3*Et_2O (external standard) = 0 ppm, $^{31}P\{^1H\}$: 85% H_3PO_4 (external standards) = 0 ppm]. Data are reported as follows: Chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad signals, etc.), coupling constant *J* in Hz, integration, and (where applicable) interpretation.

MALDI-TOF-MS

Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDITOF-MS) analyses were conducted on a Bruker Microflex LRF MS spectrometer equipped with a 337 nm nitrogen laser operating at a positive ion, linear mode (modified according to experiments). The polymer samples (10 mg mL^{-1}), trans-2[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, 25 mg mL-1) and CF_3COONa (5 mg mL^{-1}) were dissolved in THF and mixed in a volume ratio of 20:5:5 (Sample concentration, matrix type, ionic salt and volume ratio are modified according to experimental conditions).

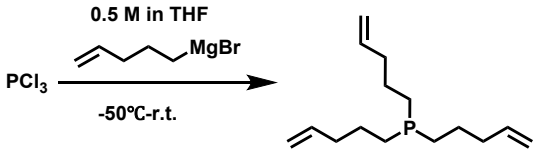
GPC

Gel permeation chromatography (GPC) experiments were performed on an Agilent HPLC system equipped with a model 1260 Hip degasser, a model 1260 Iso pump and a model 1260 differential refractometer detector with using THF as mobile phase at a flow rate of 1.0 mL min^{-1} at 40 °C. One PLgel 5 μm guard column and three Mz-Gel SDplus columns (103Å, 104Å and 105Å, linear range of M_W = 1000 – 2*10^6 Da) were connected in series. The molecular weight and dispersity were calculated using polystyrene as standard. The sample concentration used for GPC

analyses was 5-10 mg mL^{-1}.

Compounds Syntheses

Synthesis of tri(pent-4-en-1-yl)phosphane

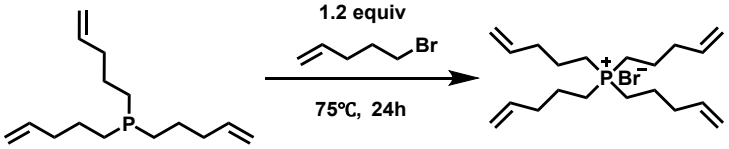


General procedure: PCl_3 (5.1 mL, 8.0 g, 58.3 mmol) was dissolved in THF (20 mL) and cooled down to -50 °C. A solution of the respective pent-4-en-1-ylmagnesium bromide solution (3.1 equiv.) in THF was added at -50 °C. The suspension was stirred for 16 hours at room temperature. THF was removed under vacuum and the crude mixture was stirred in hexane (100 ml). All solids were removed by filtration on celite and were washed by n-hexane. The solvent was removed and the product was isolated using vacuum distillation.

PCl_3 (5.1 mL, 58.3 mmol) and 0.5 M pent-4-en-1-ylmagnesium bromide /THF solution (361.5 mL, 180.7 mmol) yielded 8.6 g (36.08 mmol, 62%) of a light yellow oil.

^1H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 5.80 (ddt, 3H), 5.00 (dd, 6H), 2.13 (q, 6H), 1.52 (q, 6H), 1.48-1.35 (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm) = 138.3, 114.8, 35.4 (d, J = 11.0 Hz), 26.8 (d, J = 12.2 Hz), 25.3 (d, J = 13.4 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) = 31.1.

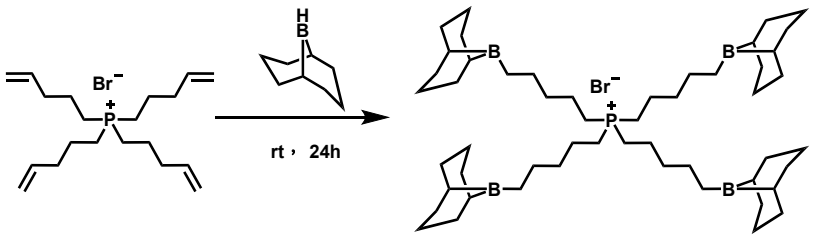
Synthesis of tetra(pent-4-en-1-yl)phosphonium bromide



In a flame-dried Schlenk vessel, tri(pent-4-en-1-yl)phosphane (3.0 g, 12.59 mmol, 1 equiv.) was dissolved in 10 mL acetonitrile, to which 5-bromopent-1-ene (1.79 mL, 15.1 mmol, 1.2 equiv.) was slowly added. The reaction mixture was allowed to stir at 75°C for 24 h. The white precipitates were filtered and washed with n-hexane (10 mL) for 3 times. The white powder was dried at ambient temperature over high vacuum pump to yield quantitative product.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 5.70 (ddt, 4H), 5.11-5.06 (m, 8H), 2.50-2.28 (m, 8H), 2.24 (q, 8H), 1.70-1.60 (m, 8H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm) = 138.8, 117.5, 34.3 (d, J = 15.5 Hz), 21.2 (d, J = 4.2 Hz), 18.8 (d, J = 47.7 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) = 33.8.

Synthesis of P4B-Br



In a flame-dried Schlenk vessel, tetra(pent-4-en-1-yl)phosphonium bromide (500mg, 1.29 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane (9-BBN) (708.7 mg, 5.81 mmol, 4.5 equiv.) were dissolved in 10 mL CH_2Cl_2. The reaction mixture was allowed to stir at r.t. for 24 h. Removal of all the volatiles and the resultant white solid was washed with n-hexane for 3 times (5 mL) to give the desired product in quantitative yield.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 2.51 (tt, 8H), 1.83 (dp, 24H), 1.67-1.53 (m, 48H), 1.37 (t, 8H), 1.20 (m, 8H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298

K) δ (ppm) = 33.9, 31.0, 27.7, 24.0, 23.2, 22.0 (d, *J* = 4.9 Hz), 19.7 (d, *J* = 46.8 Hz). $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$, 298 K) δ (ppm) = 88.0. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) = 32.7.

Representative procedure for the ring-opening polymerization (ROP) of epoxides and methanolysis treatment

Take *R*GB/**P4B-Br** = 50:1 as an example (the catalyst dosage is calculated based on the tetranuclear boron phosphonium salt, that is, 1-fold molar amount of catalyst is equivalent to 4-fold molar amount of boron active centers). Polymerization is carried out in a 15.0 mL pre-dried pressure-resistant tube (containing a magnetic stirrer bar). In a glove box, **P4B-Br** (62.7 mg, 71.6 μmol), RGB (500 μL, 3.58 mmol) and anhydrous THF (500 μL) are respectively added, and then the mixture is placed in a water bath set at 25 °C to react for a predetermined time. After the reaction, 50 μL of the reaction solution is taken, and 0.4 mL of $CDCl_3$ containing 1% acetic acid is added for ^{1}H NMR testing to determine the conversion rate of *R*GB, as well as GPC testing for the molecular weight and molecular weight distribution of the sample. The remaining reaction mixture is dissolved in methanol containing a few drops of acetic acid, and left standing overnight at -20 °C, and the product will slowly precipitate again. After pouring out the supernatant, a colorless viscous liquid product is obtained at room temperature, and vacuum drying is carried out.

The obtained poly(glycidyl butyrate) (P*R*GB, 0.3 g, containing 2.1 mmol of ester groups) and TBD (14.1 mg, 0.10 mmol) were dissolved in methanol (2.5 mL) at

room temperature. The mixture was stirred at room temperature for 12 h, and then 50 μL was taken for ^{1}H NMR analysis to determine the degree of alcoholysis.

NMR Spectra of the Synthesized Compounds

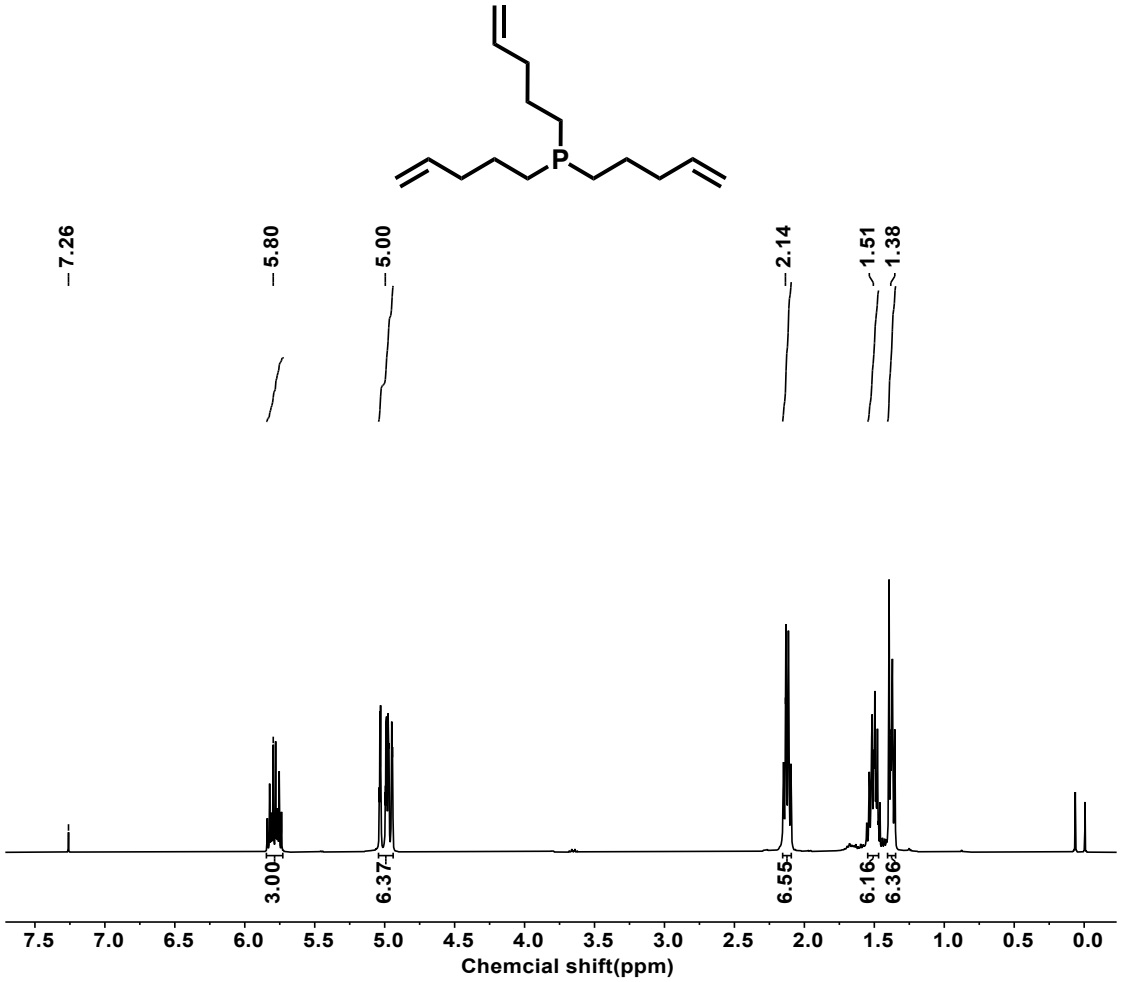


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of tri(pent-4-en-1-yl)phosphane

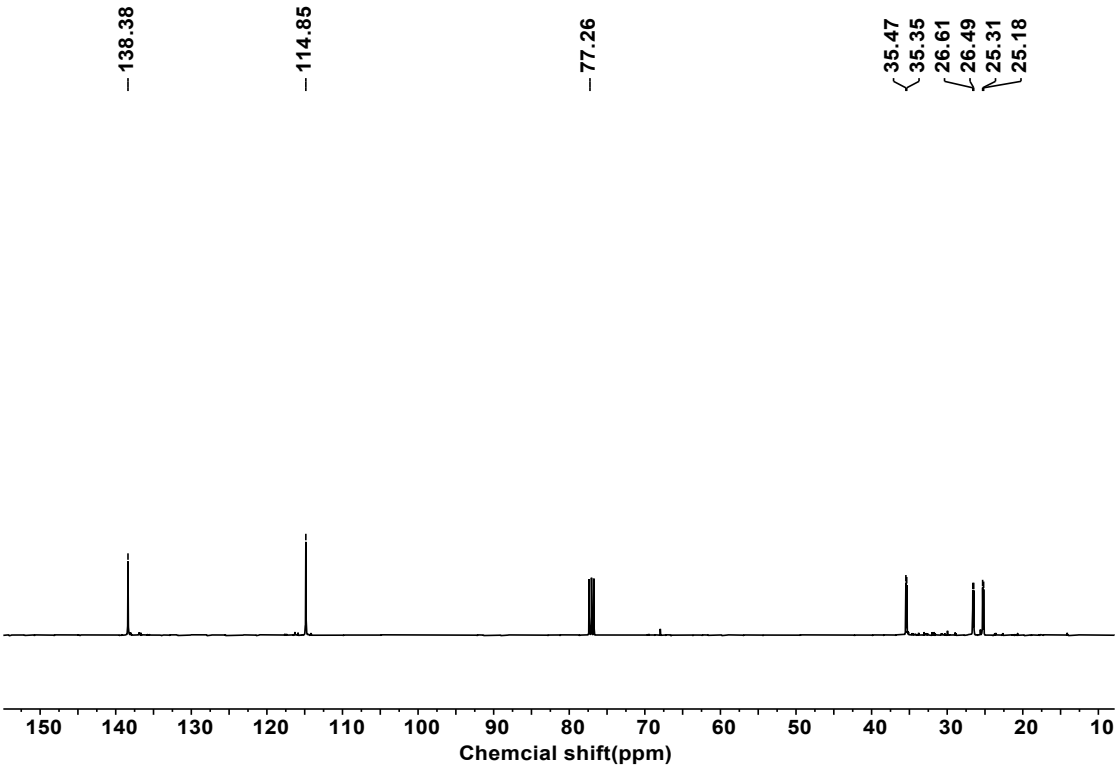
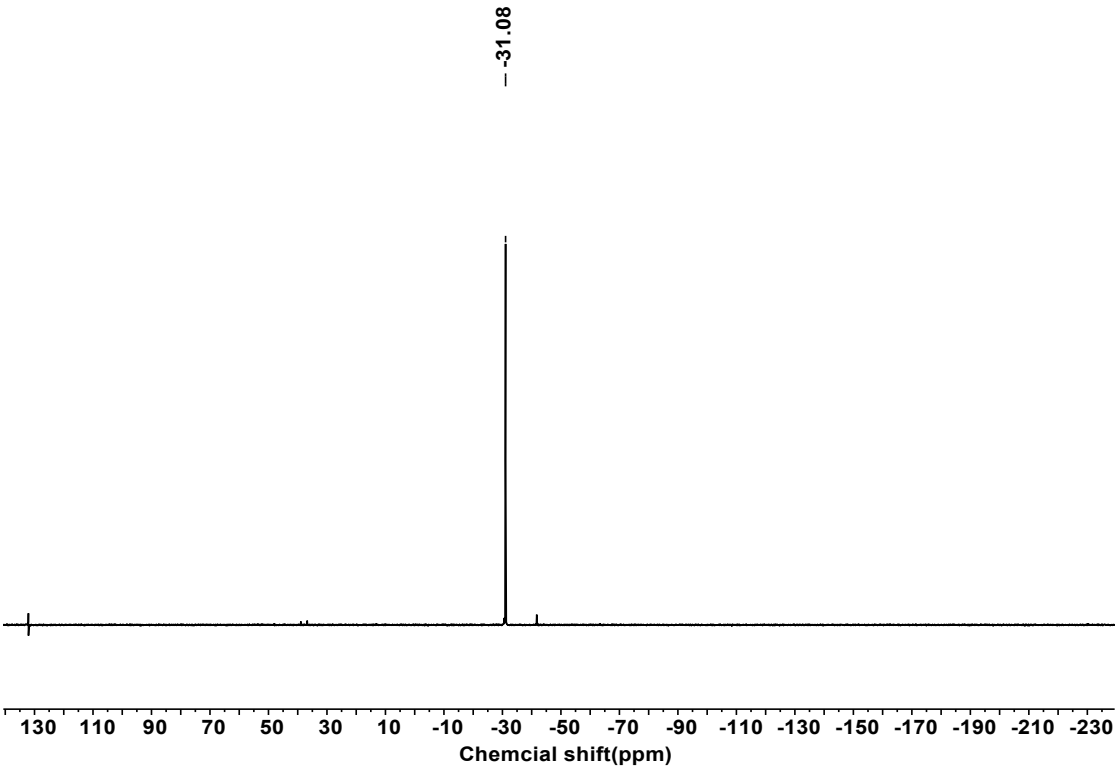
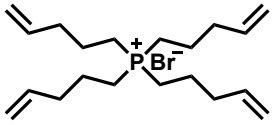


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of tri(pent-4-en-1-yl)phosphane



F**igure S3.** $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298 K) of tri(pent-4-en-1-yl)phosphane



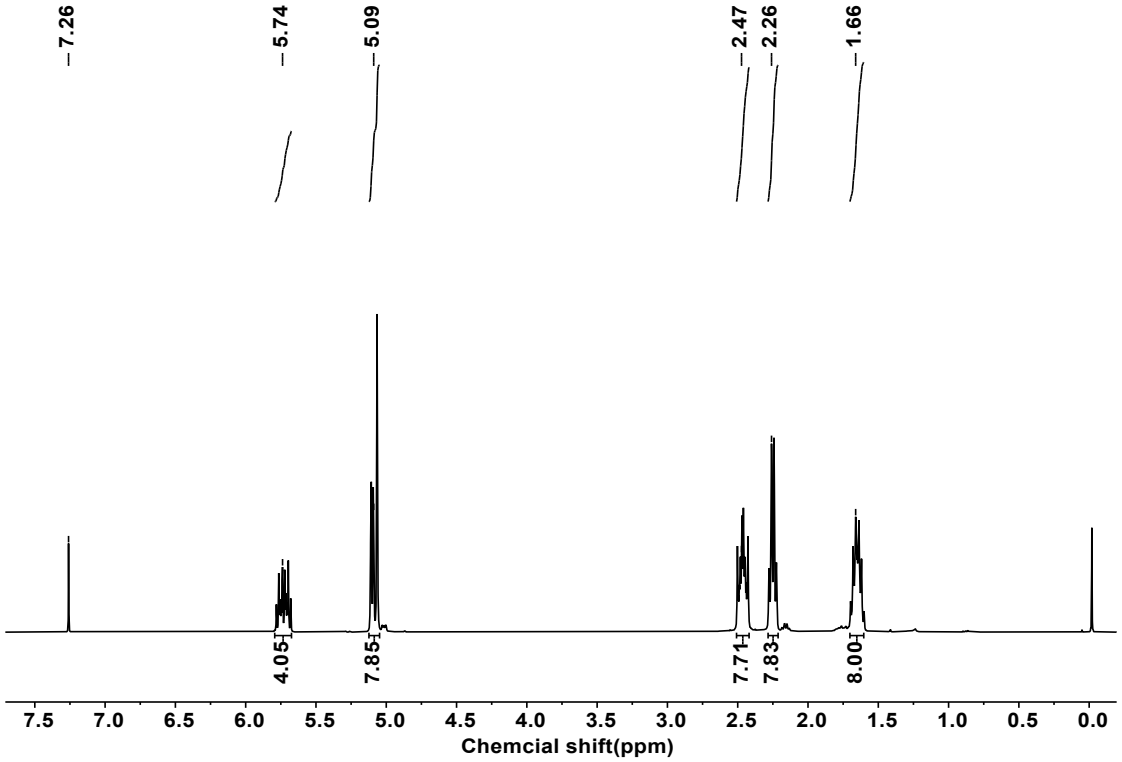


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of tetra(pent-4-en-1-yl)phosphonium bromide

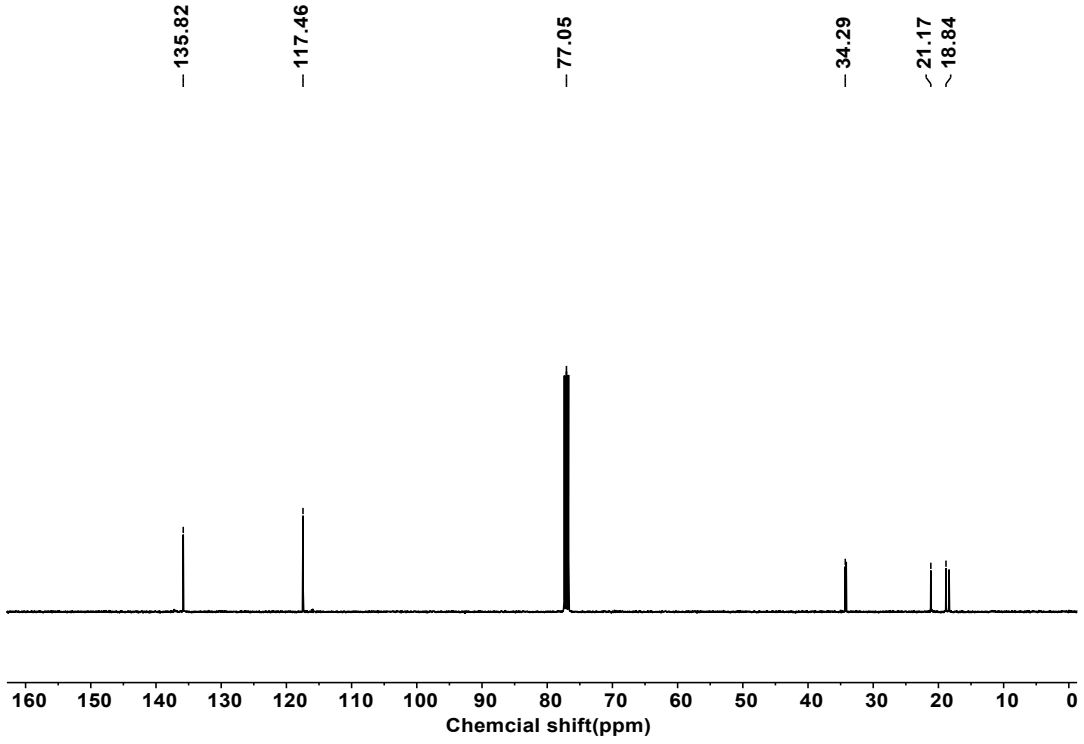


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of tetra(pent-4-en-1-yl)phosphonium bromide

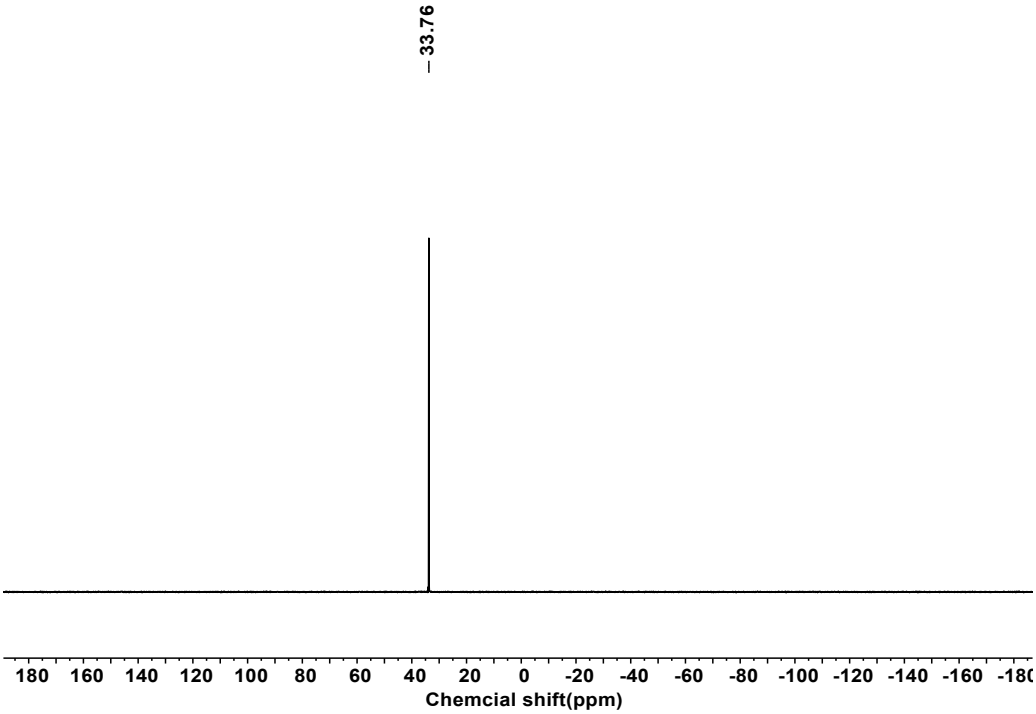


Figure S6. $^{31}P\{^{1}H\}$ spectrum (162 MHz, $CDCl_3$, 298 K) of tetra(pent-4-en-1-yl)phosphonium bromide

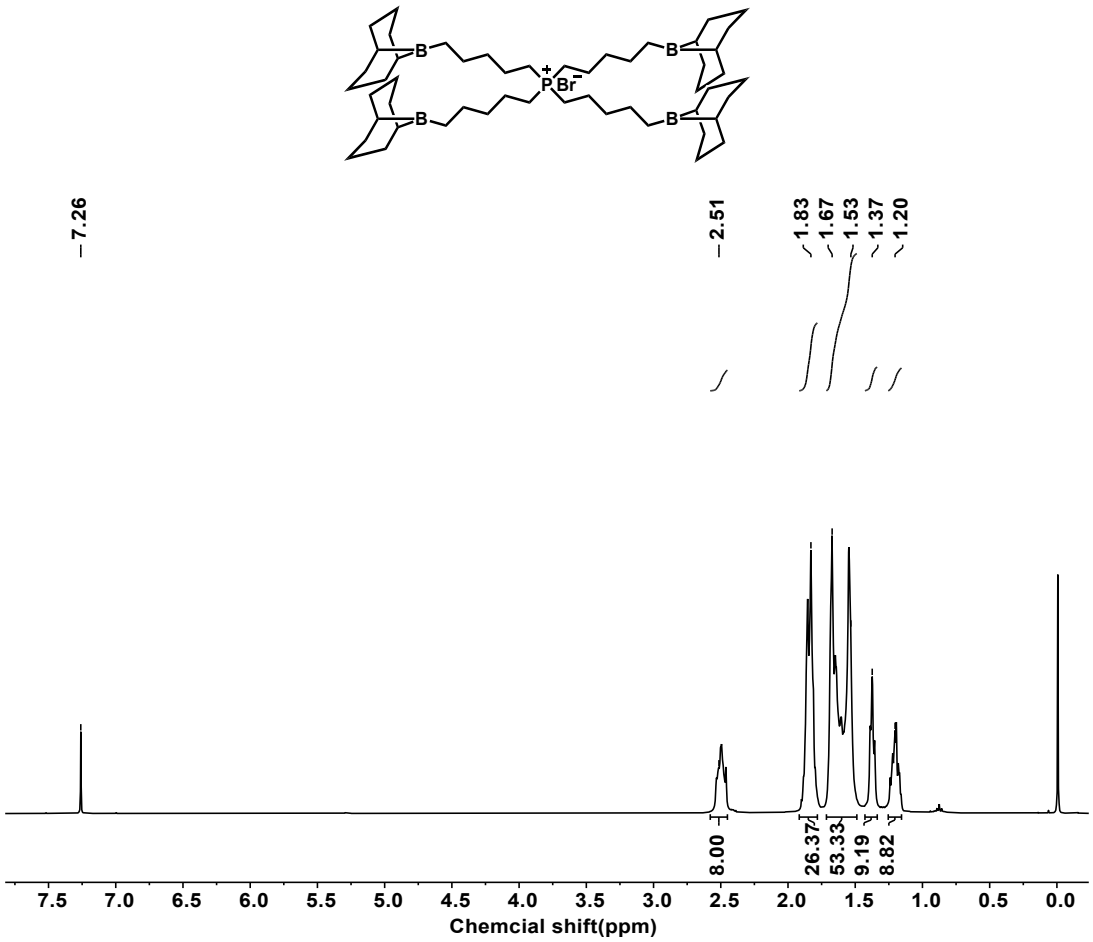


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **P4B-Br**

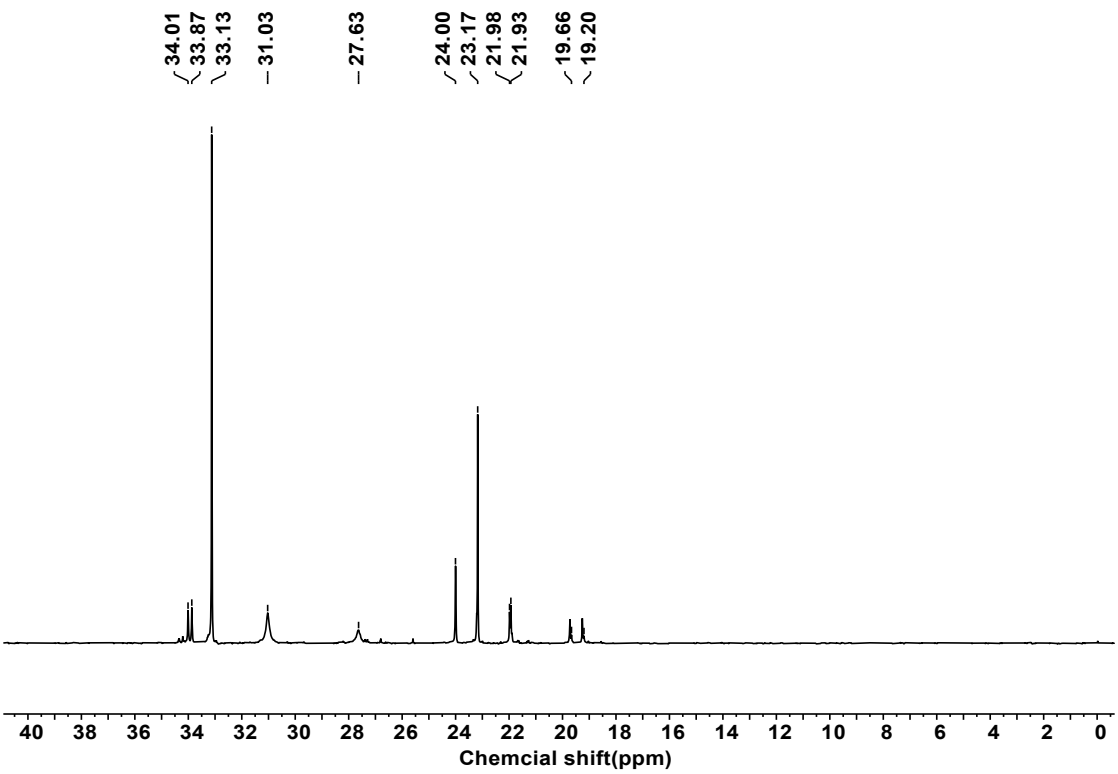


Figure S8. $^{13}C\{^{1}H\}$ spectrum (100 MHz, $CDCl_3$, 298 K) of **P4B-Br**

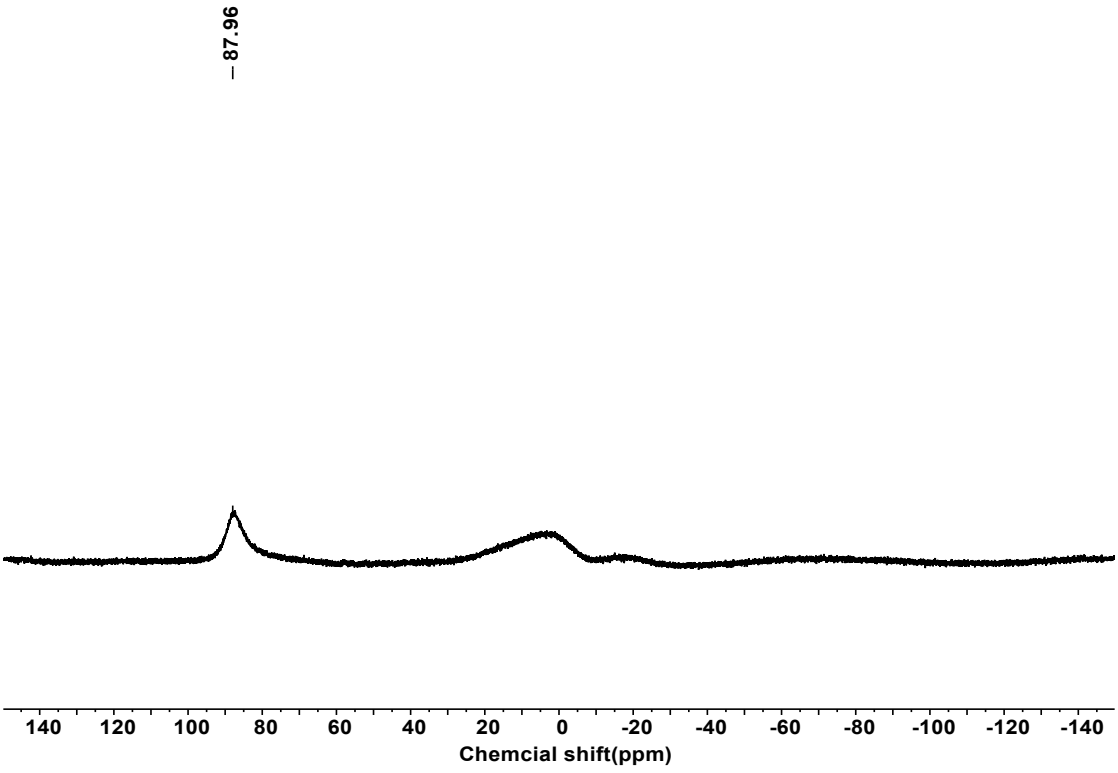


Figure S9. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz, $CDCl_3$, 298 K) of **P4B-Br**

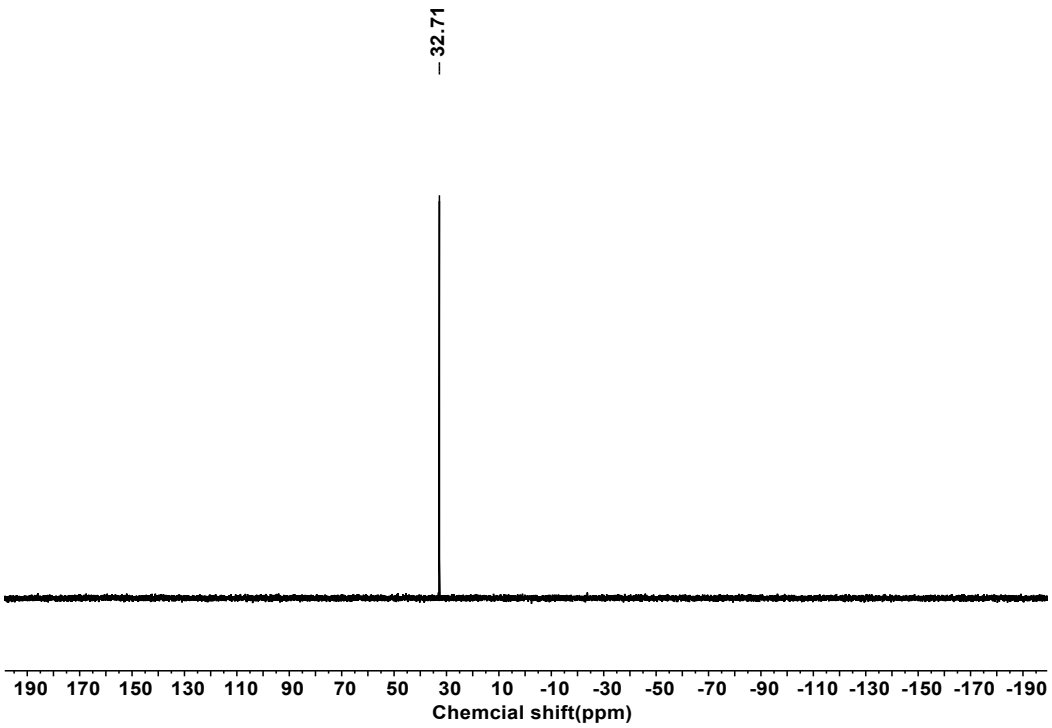


Figure S10. $^{31}P\{^{1}H\}$ spectrum (162 MHz, $CDCl_3$, 298 K) of **P4B-Br**

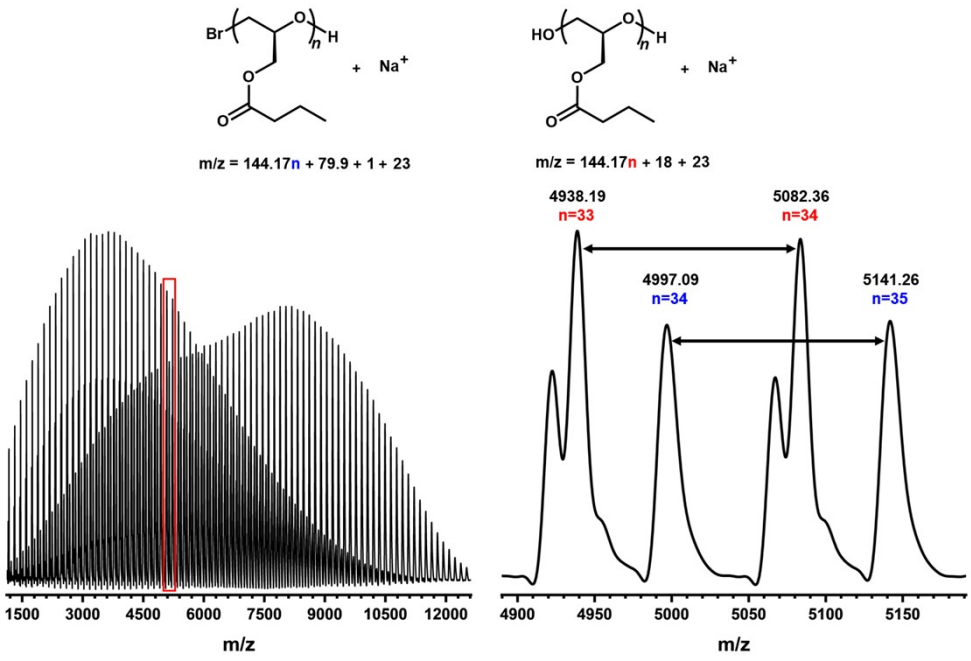


Figure S11. MALDI-TOF mass spectrum of a high molecular weight *R*GB obtained (Table 1, run 8).

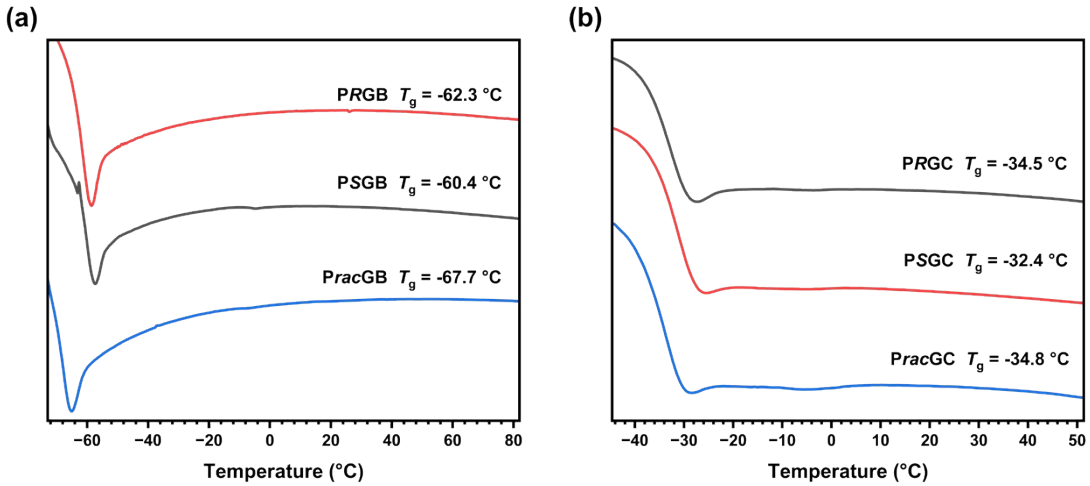


Figure S12. (a) DSC traces of P*R*GB (run 3 in Table 1), P*S*GB (run 11 in Table 1) and P*rac*GB (run 12 in Table 1); (b) Corresponding DSC traces of P*R*GC, P*S*GC and P*rac*GC.

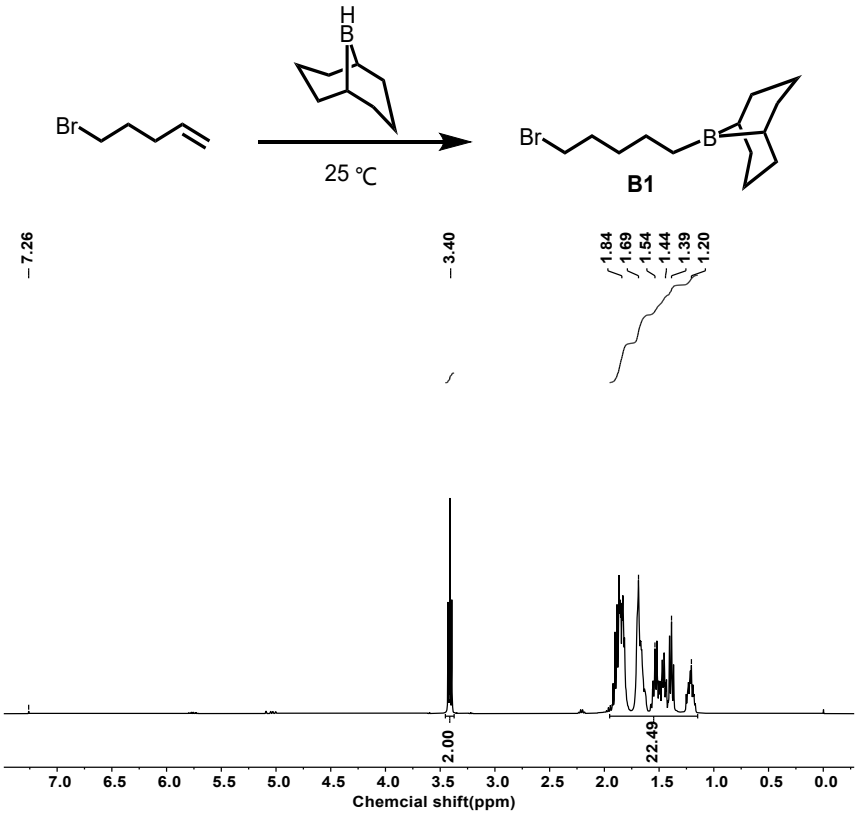


Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **B1**

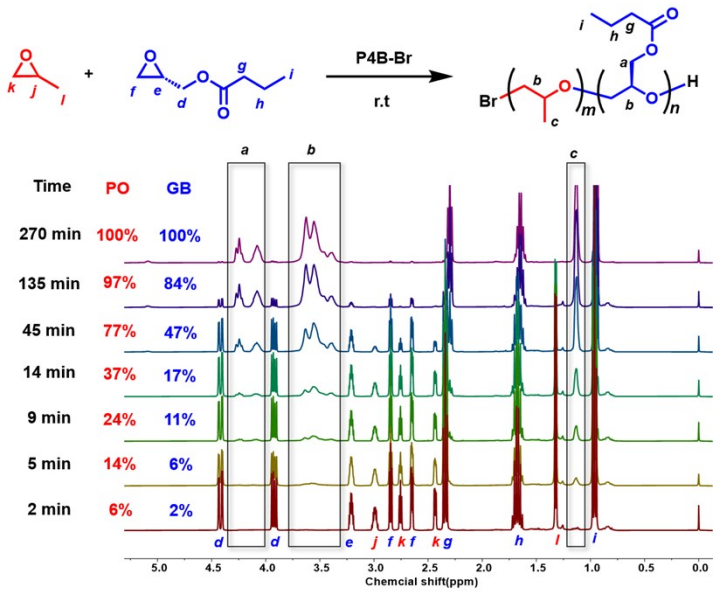


Figure. S14. *In situ* ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of aliquots withdrawn at different reaction times (Table 2, run1).

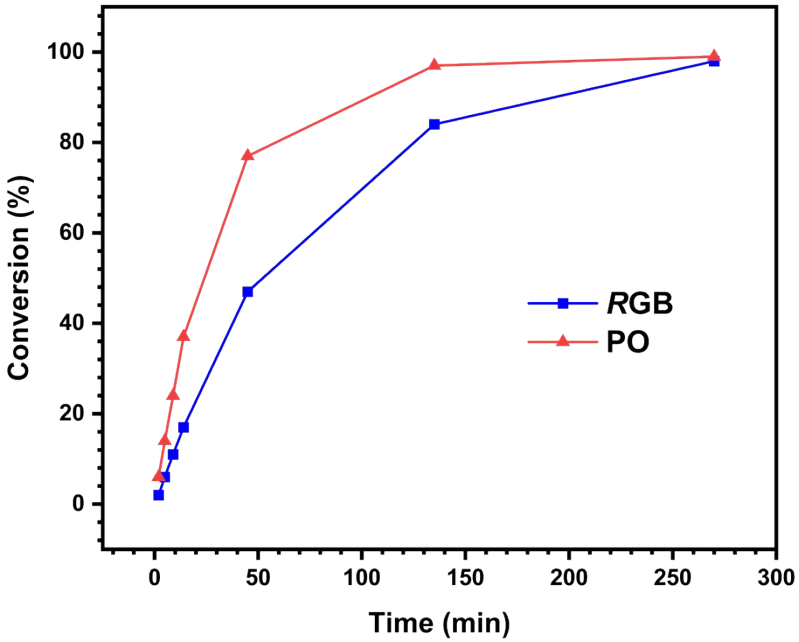


Figure S15. Variations in monomer conversion rates of PO and RGB with reaction time (Table 2, run1).

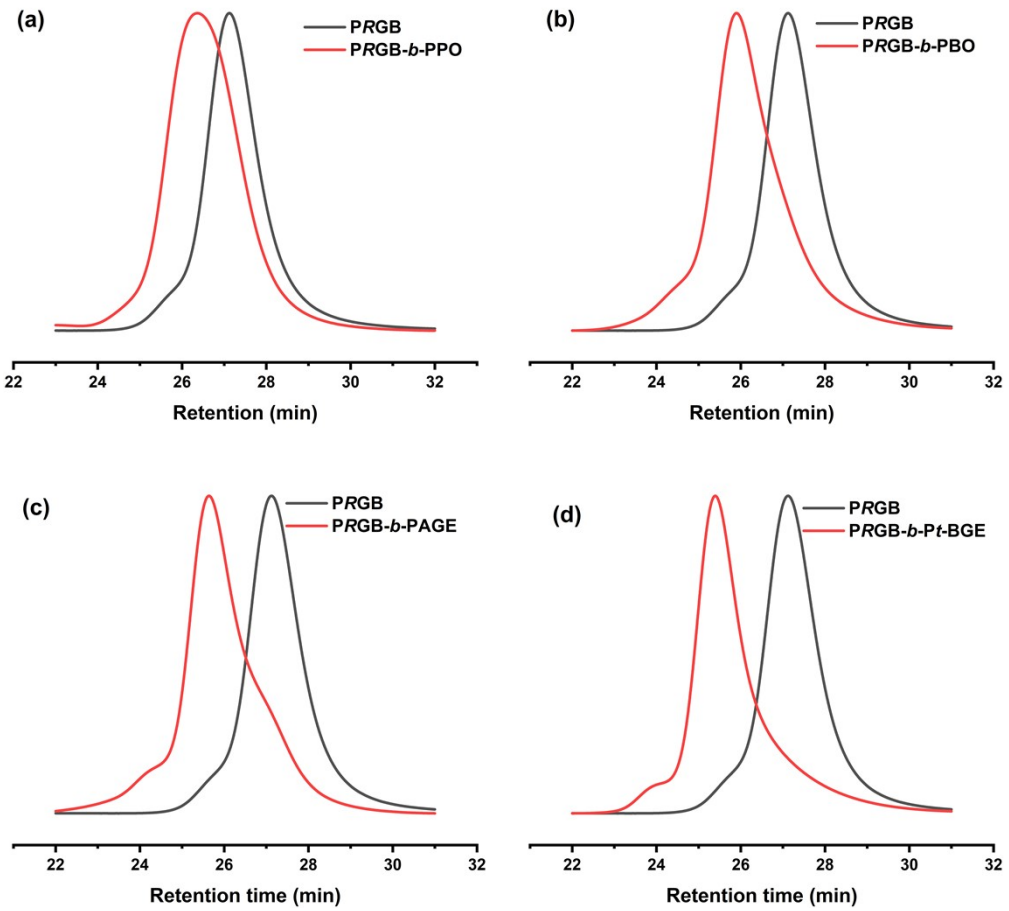


Figure S16. (a) GPC traces of the P*R*GB precursor and the P*R*GB-*b*-PPO diblock copolymer; (b) GPC traces of the P*R*GB precursor and the P*R*GB-*b*-PBO diblock copolymer; (c) GPC traces of the P*R*GB precursor and the P*R*GB-*b*-PAGE diblock copolymer; (d) GPC traces of the P*R*GB precursor and the P*R*GB-*b*-P*t*-BGE diblock copolymer.

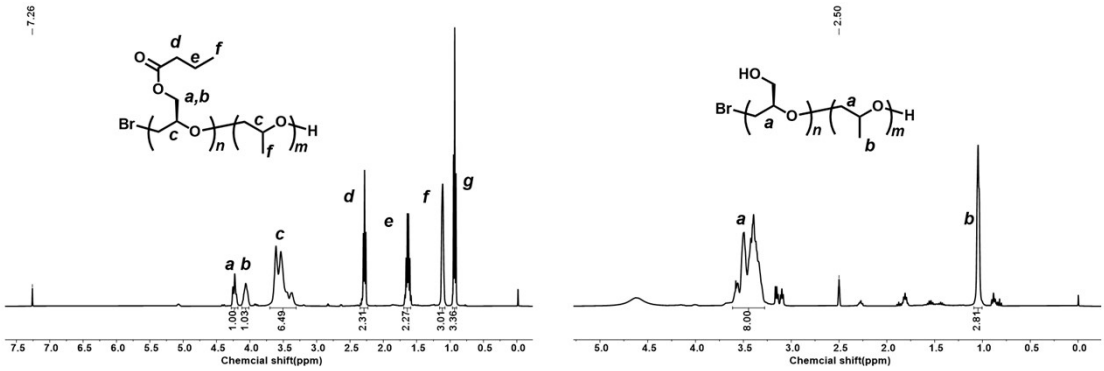


Figure S17. ^{1}H NMR spectrum of PPO-*b*-P*R*GB (400 MHz, $CDCl_3$, 298 K) and ^{1}H NMR spectrum of PPO-*b*-PGC (400 MHz, DMSO-d_6, 298 K)

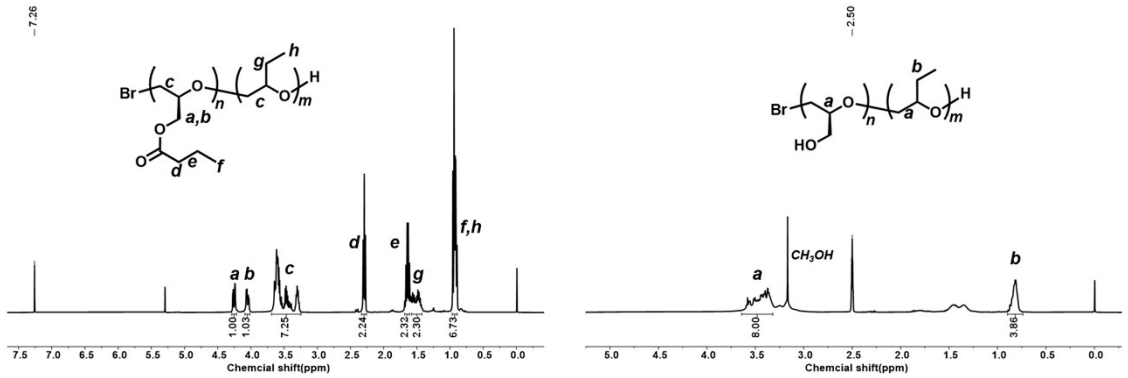


Figure S18. ^{1}H NMR spectrum of PBO-*b*-P*R*GB (400 MHz, $CDCl_3$, 298 K) and ^{1}H NMR spectrum of PBO-*b*-PGC (400 MHz, DMSO-d_6, 298 K)

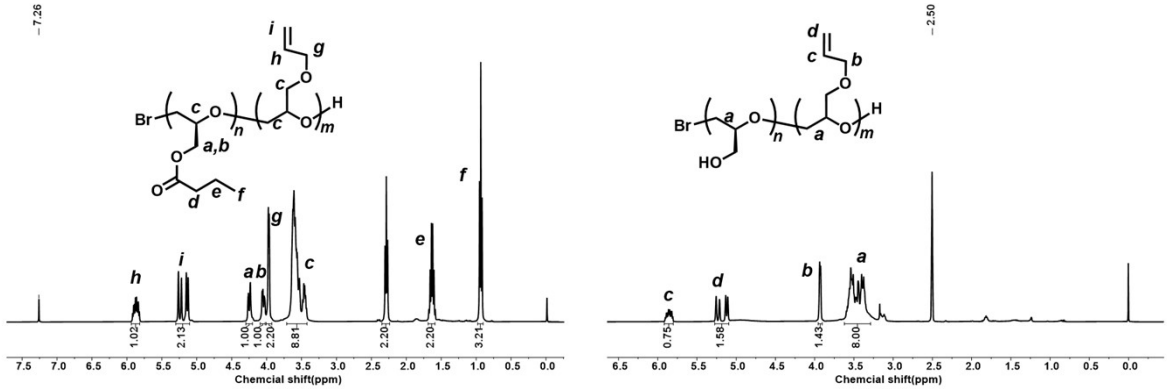


Figure S19. ^{1}H NMR spectrum of PAGE-*b*-P*R*GB (400 MHz, $CDCl_3$, 298 K) and ^{1}H NMR spectrum of PAGE-*b*-PGC (400 MHz, DMSO-d_6, 298 K)

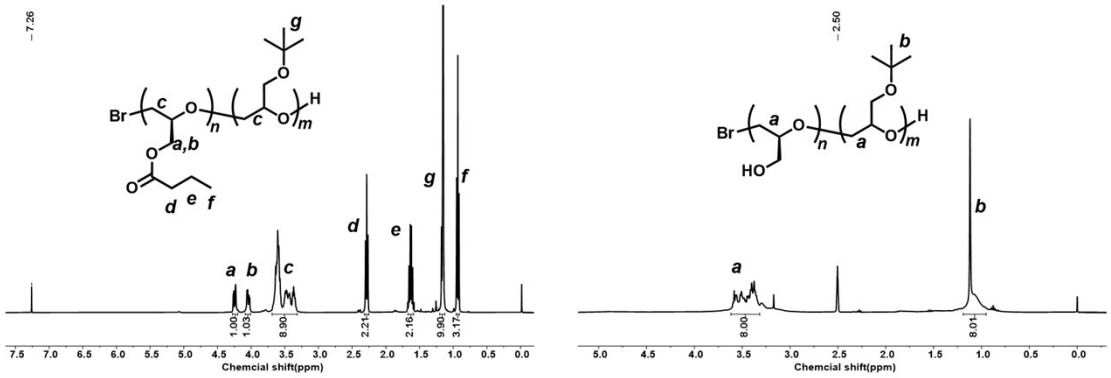


Figure S20. ^{1}H NMR spectrum of P*t*-BGE-*b*-P*R*GB (400 MHz, $CDCl_3$, 298 K) and ^{1}H NMR spectrum of P*t*-BGE-*b*-PGC (400 MHz, DMSO-d_6, 298 K)

GPC traces of PGB

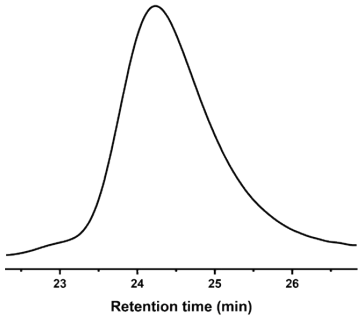


Figure S21. GPC curve of obtained P*R*GB from Table 1, run 2

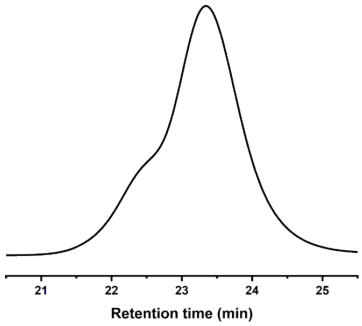


Figure S22. GPC curve of obtained P*R*GB from Table 1, run 3

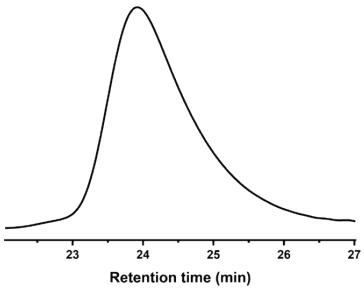


Figure S23. GPC curve of obtained P*R*GB from Table 1, run 4

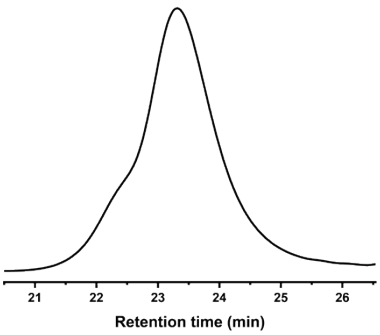


Figure S24. GPC curve of obtained P*R*GB from Table 1, run 5

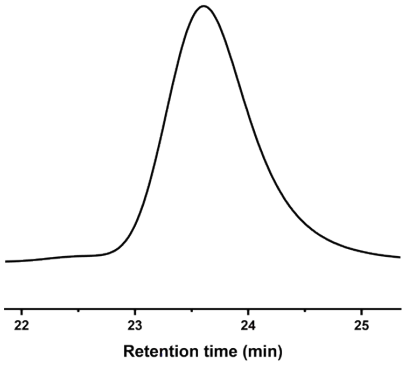


Figure S25. GPC curve of obtained P*R*GB from Table 1, run 6

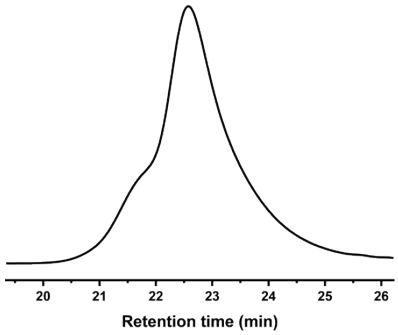


Figure S26. GPC curve of obtained P*R*GB from Table 1, run 7

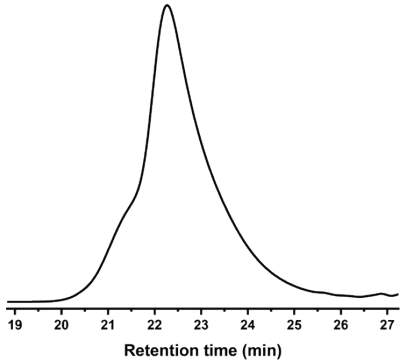


Figure S27. GPC curve of obtained P*R*GB from Table 1, run 8

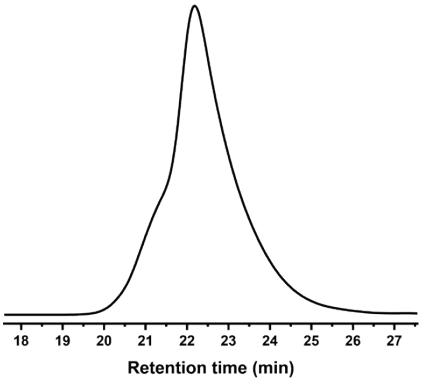


Figure S28. GPC curve of obtained P*R*GB from Table 1, run 9

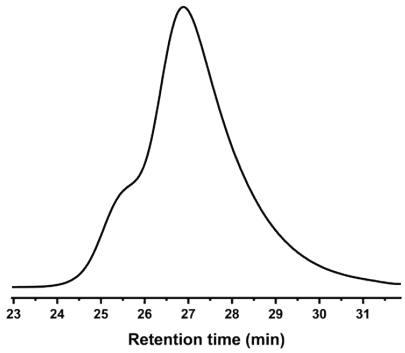


Figure S29. GPC curve of obtained P*R*GB from Table 1, run 10

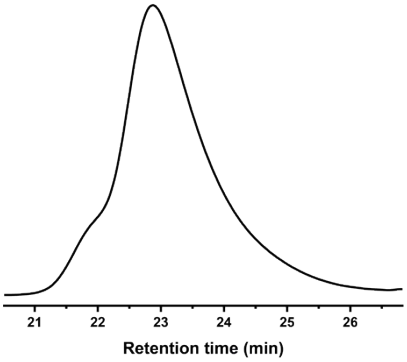


Figure S30. GPC curve of obtained P*S*GB from Table 1, run 11

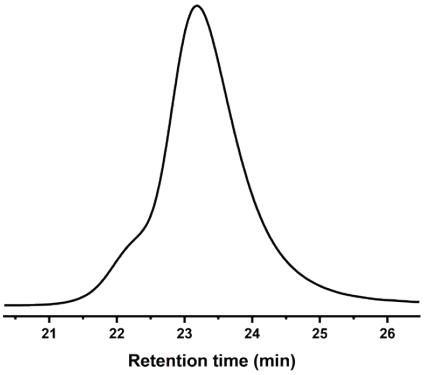


Figure S31. GPC curve of obtained P*rac*GB from Table 1, run 12