

Electronic Supplementary Information

Synthesis of Functional and Boronic Acid-Containing Aliphatic Polyesters via Suzuki Coupling

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Experimental Section:

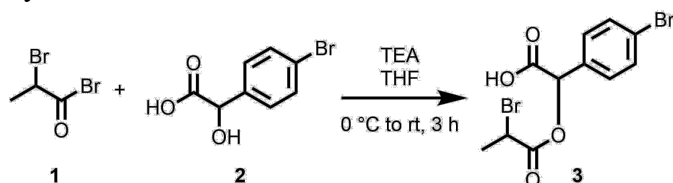
Instrumentation

^1H and ^{13}C NMR spectra were recorded on an Inova 500 spectrometer. ^1H NMR chemical shifts in CDCl_3 or $\text{DMSO}-d_6$ are referenced to TMS (δ 0.00 ppm) or $\text{CHD}_2\text{SOCD}_3$ (2.50 ppm), respectively. ^{13}C NMR chemical shifts in CDCl_3 are referenced to deuterated chloroform (77.16 ppm).

Size-exclusion chromatography was performed in *N,N*-dimethylacetamide with 50 mM LiCl at 50 °C and a flow rate of 1.0 mL/min (Agilent isocratic pump, degasser, and autosampler; columns: ViscoGel I-series 5 μm guard + two ViscoGel I-series G3078 mixed bed columns, molecular weight range 0–20 $\times 10^3$ and 0–100 $\times 10^4$ g/mol). Detection consisted of a Wyatt Optilab T-rEX refractive index detector operating at 658 nm. Apparent molecular weights were calculated using 9 polystyrene standards from 327,300 g/mol to 1,370 g/mol.

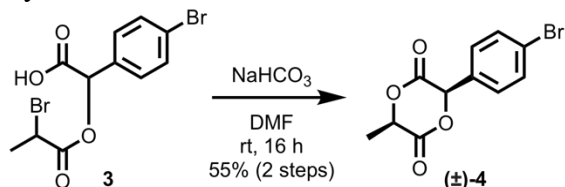
HRMS was conducted with an Agilent 6220 time-of-flight (TOF) mass spectrometer using the electrospray ionization (ESI) ion source.

Synthesis of 3



2-Bromopropionyl bromide (2.30 mL, 21.6 mmol) was added to a stirred solution of 4-bromomandelic acid (5.00 g, 21.6 mmol) and TEA (3.17 mL, 22.7 mmol) in anhydrous THF (200 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 3 h. The solution was filtered and concentrated. The resulting material was dissolved in diethyl ether (150 mL). The organic layer was washed with brine (50 mL \times 3), dried (MgSO_4), filtered, and concentrated to give a colorless oil, which was used in the next step without further purification.

Synthesis of 4

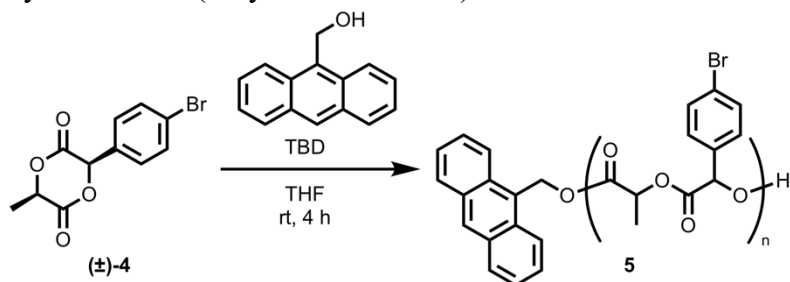


A solution of 3 in DMF (15 mL) was added to a stirred solution of sodium bicarbonate (2.73 g, 32.5 mmol) in DMF (200 mL) dropwise via a syringe pump. The solution was diluted with water (150 mL), and the resulting solution was extracted with DCM (100 mL \times 3). The combined organic layers were washed with satd. aq. NaHCO_3 (200 mL \times 2) and brine (200 mL \times 3), dried (MgSO_4), filtered, and concentrated. The resulting material was washed with diethyl ether to give (\pm)-4 as a white solid [3.41 g, 12.0 mmol, 55% (2 steps)].

^1H NMR (500 MHz, CDCl_3): δ 7.60 (d, J = 8.5 Hz, 2H, Ar-*H*), 7.31 (d, J = 8.5 Hz, 2H, Ar-*H*), 5.89 (s, 1H, CHAr), 5.19 (q, J = 6.8 Hz, 1H, CHCH₃), and 1.69 (d, J = 6.8 Hz, 3H CHCH₃).

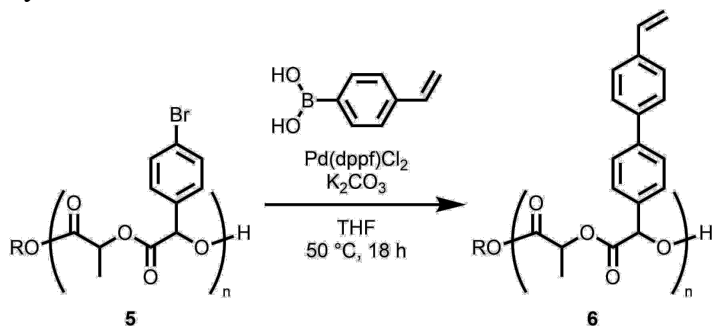
^{13}C NMR (125 MHz, CDCl_3): δ 116.7, 165.3, 132.3, 130.4, 129.3, 124.5, 77.2, 72.9, and 16.5.
HRMS (ESI-TOF): Calculated for $\text{C}_{11}\text{H}_{13}\text{BrNO}_4^+$ [$\text{M} + \text{NH}_4$] $^+$ requires 302.0022; found 302.0032.

Synthesis of **5** (Polymerization of **4**)



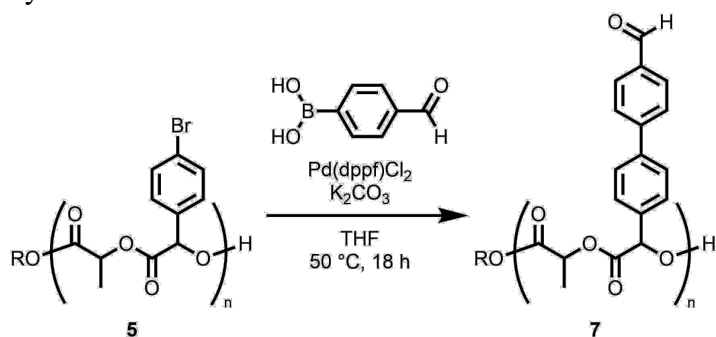
(\pm)-**4** (400 mg, 1.40 mmol) and 9-anthracenemethanol (2.9 mg, 1.4×10^{-2} mmol) were charged in a vial, and the vial was purged with argon. The mixture was dissolved in THF (1.4 mL). Gentle heating of the reaction mixture was necessary to dissolve the sample. TBD (3.9 mg, 2.8×10^{-2} mmol) was added to the mixture, and the solution was stirred at rt for 4 h. The reaction was quenched by an addition of acetic acid. The resulting solution was precipitated into cold methanol, filtered, and dried to yield **5** as a white solid.

Synthesis of **6**



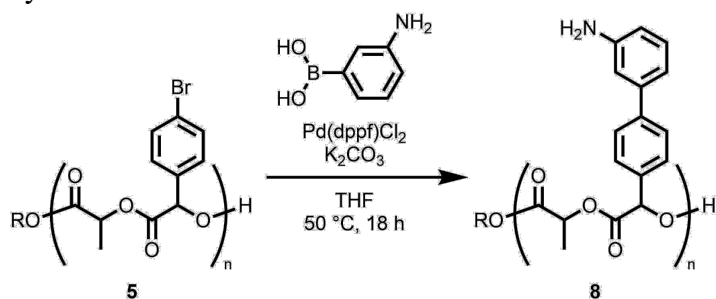
5 (50 mg, 0.18 mmol), 4-vinylphenylboronic acid (78 mg, 0.53 mmol), K_2CO_3 (97 mg, 0.70 mmol) were charged in a vial and purged with argon. $\text{Pd}(\text{dppf})\text{Cl}_2$ (64 mg, 0.085 mmol) was added to the mixture, and the vial was purged with argon again. THF (0.9 mL) was added to the mixture, and the solution was stirred at 50 °C for 18 h. The resulting solution was filtered, precipitated into cold methanol, filtered, and dried to yield **6** as a brown solid.

Synthesis of 7



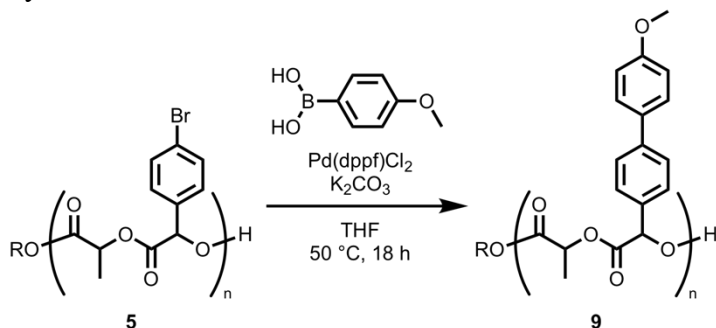
5 (50 mg, 0.18 mmol), 4-formylphenylboronic acid (79 mg, 0.53 mmol), K₂CO₃ (97 mg, 0.70 mmol) were charged in a vial and purged with argon. Pd(dppf)Cl₂ (64 mg, 0.085 mmol) was added to the mixture, and the vial was purged with argon again. THF (0.9 mL) was added to the mixture, and the solution was stirred at 50 °C for 18 h. The resulting solution was filtered, precipitated into cold methanol, filtered, and dried to yield **7** as a brown solid.

Synthesis of 8



5 (50 mg, 0.18 mmol), 3-aminophenylboronic acid (72 mg, 0.53 mmol), K₂CO₃ (97 mg, 0.70 mmol) were charged in a vial and purged with argon. Pd(dppf)Cl₂ (64 mg, 0.085 mmol) was added to the mixture, and the vial was purged with argon again. THF (0.9 mL) was added to the mixture, and the solution was stirred at 50 °C for 18 h. The resulting solution was filtered, precipitated into cold methanol, filtered, and dried to yield **8** as a brown solid.

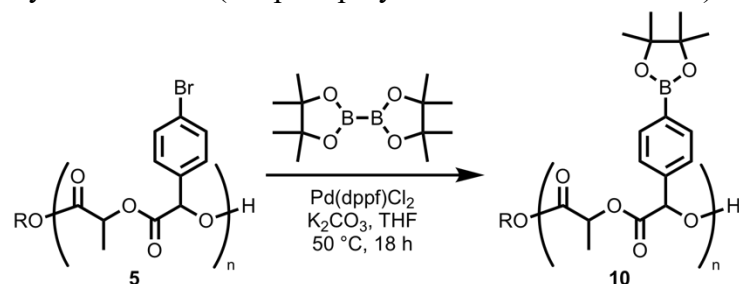
Synthesis of 9



5 (50 mg, 0.18 mmol), 4-methoxyphenylboronic acid (81 mg, 0.53 mmol), K₂CO₃ (97 mg, 0.70 mmol) were charged in a vial and purged with argon. Pd(dppf)Cl₂ (64 mg, 0.085 mmol) was added to the mixture, and the vial was purged with argon again. THF (0.9 mL) was added to the mixture,

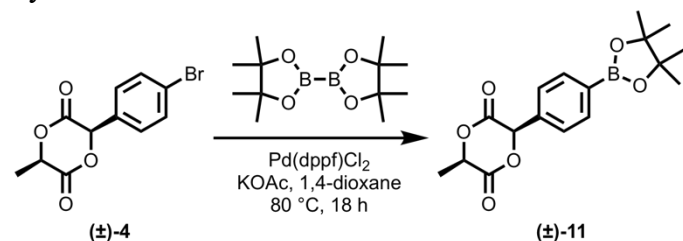
and the solution was stirred at 50 °C for 18 h. The resulting solution was filtered, precipitated into cold methanol, filtered, and dried to yield **9** as a brown solid.

Synthesis of **10** (via post-polymerization modification)



5 (50 mg, 0.18 mmol), bis(pinacolato)diboron (135 mg, 0.532 mmol), K_2CO_3 (97 mg, 0.70 mmol) were charged in a vial and purged with argon. $Pd(dppf)Cl_2$ (64 mg, 0.085 mmol) was added to the mixture, and the vial was purged with argon again. THF (0.9 mL) was added to the mixture, and the solution was stirred at 50 °C for 18 h. The resulting solution was filtered, precipitated into cold methanol, filtered, and dried to yield the resulting material as a brown solid.

Synthesis of **11**



(±)-**4** (250 mg, 0.877 mmol), bis(pinacolato)diboron (267 mg, 1.05 mmol), KOAc (129 mg, 1.32 mmol) were charged in a vial and purged with argon. $Pd(dppf)Cl_2$ (128 mg, 0.175 mmol) was added to the mixture, and the vial was purged with argon again. 1,4-Dioxane (5.0 mL) was added to the mixture, and the solution was stirred at 80 °C for 18 h. The resulting solution was concentrated, and the crude material was purified by flash column chromatography (3:1 hexanes/EtOAc). The resulting material was washed with diethyl ether to yield (±)-**11** (121 mg, 0.364 mmol, 42%) as a white solid.

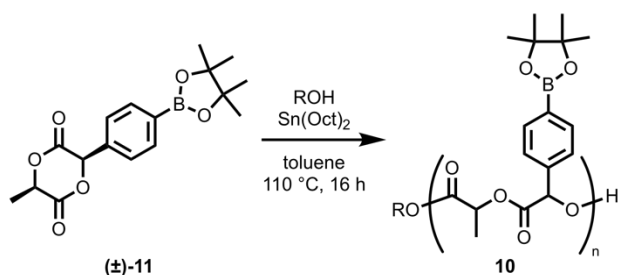
1H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, $J = 8.1$ Hz, 2H, Ar-*H*), 7.43 (d, $J = 8.0$ Hz, 2H, Ar-*H*), 5.96 (s, 1H, CHAr), 5.17 (q, $J = 6.9$ Hz, 1H, CHCH₃), 1.63 (d, $J = 6.9$ Hz, 3H, CHCH₃), and 1.35 [s, 12H, (C(CH₃)₂)₂].

^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9, 165.3, 135.4, 134.2, 126.5, 84.2, 77.8, 73.0, 25.0, and 16.8. The boron-bound carbon was not observed due to quadrupolar relaxation.

HRMS (ESI-TOF): Calculated for $C_{17}H_{25}BNO_6^+$ [$M + NH_4$]⁺ requires 350.1773; found 350.1788.

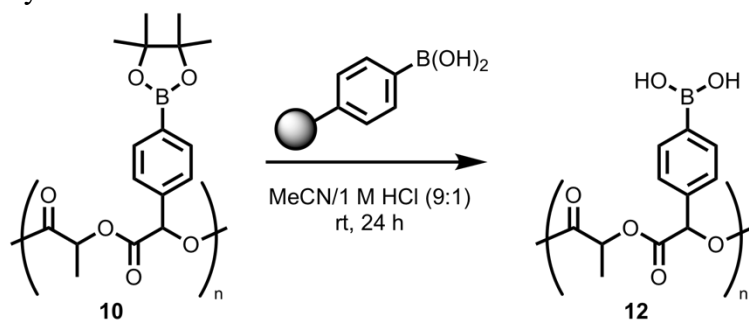
TLC: R_f (3:1 hexanes:EtOAc) = 0.2.

Synthesis of **10** (via polymerization of **11**)



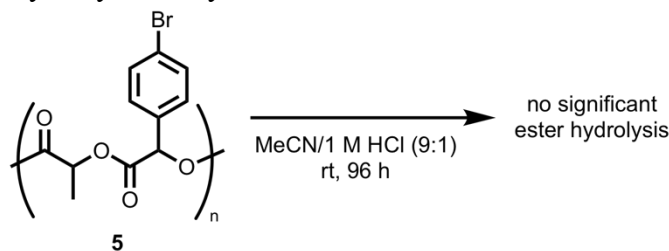
$(\pm)\text{-11}$ (100 mg, 0.30 mmol) and 9-anthracenemethanol (1.3 mg, 0.60×10^{-2} mmol) were charged in a vial, and the vial was purged with argon. The mixture was dissolved in toluene (0.3 mL). $\text{Sn}(\text{Oct})_2$ (2.4 mg, 0.60×10^{-2} mmol) was added to the mixture, and the solution was stirred at $110\text{ }^\circ\text{C}$ for 16 h. The reaction was quenched by an addition of acetic acid. The resulting solution was precipitated into cold methanol, filtered, and dried to yield **10** as a white solid.

Synthesis of **12**

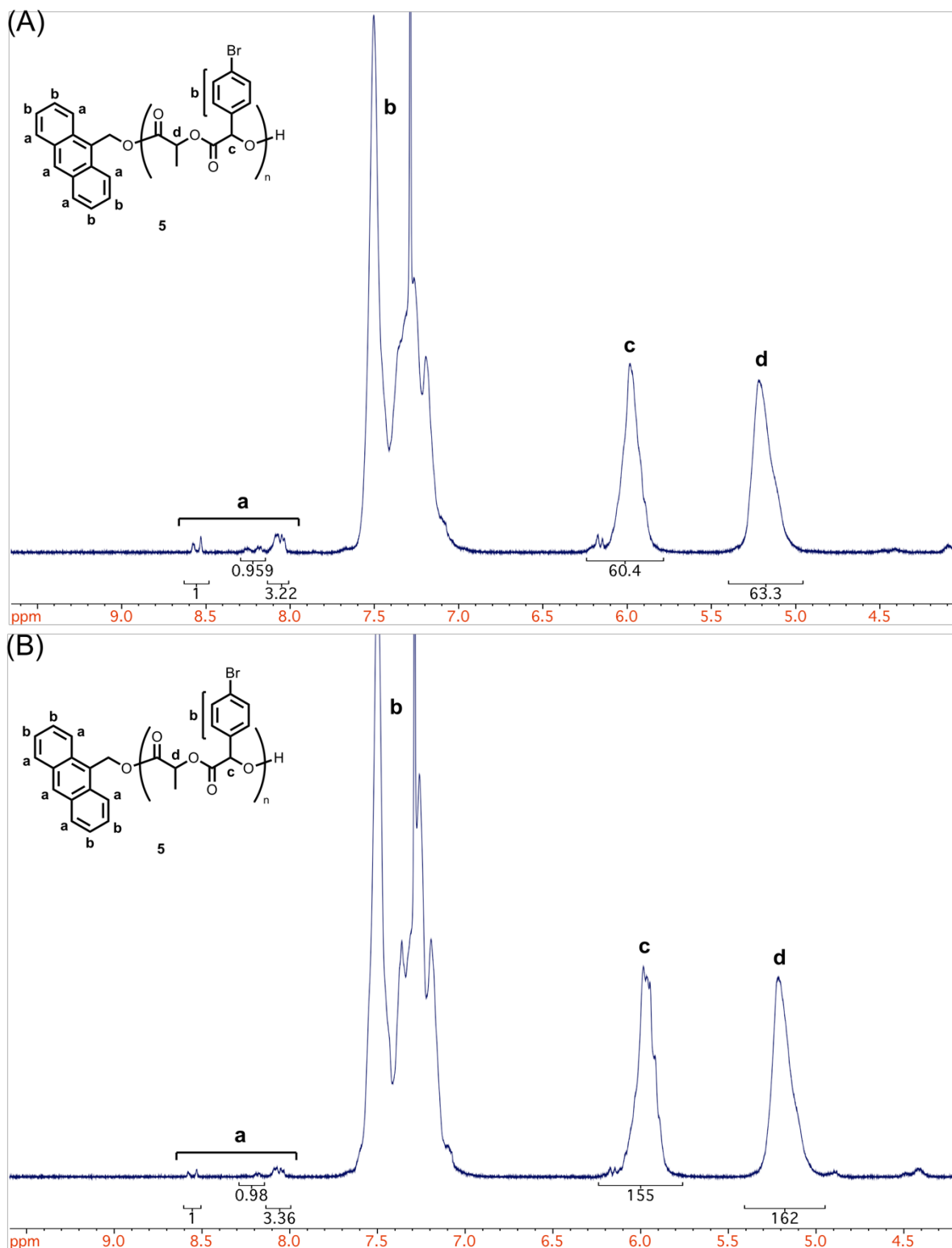


Following an adapted literature procedure,¹ **10** (26 mg, 0.08 mmol) and polymer-supported benzenboronic acid (330 mg, boronic acid content: 2.6–3.2 mmol/g) were charged in a round-bottomed flask with acetonitrile (2.5 mL) and aq. HCl (1 M, 0.27 mL). After stirring for 24 h, the solution was filtered, and the reaction solution was dialyzed against acetone for 24 h. Upon evaporation of the solvent, **12** was obtained as an off-white powder (17 mg, 87%).

Hydrolysis study of **5**



In a round-bottomed flask, **5** (20 mg, 0.07 mmol) was dispersed in acetonitrile (1.8 mL) with aq. HCl (1 M, 0.2 mL). To ensure full solubility of the polymer, THF (0.2 mL) was added. The solution was stirred over 96 h, and aliquots were taken in regular time intervals for SEC analysis.



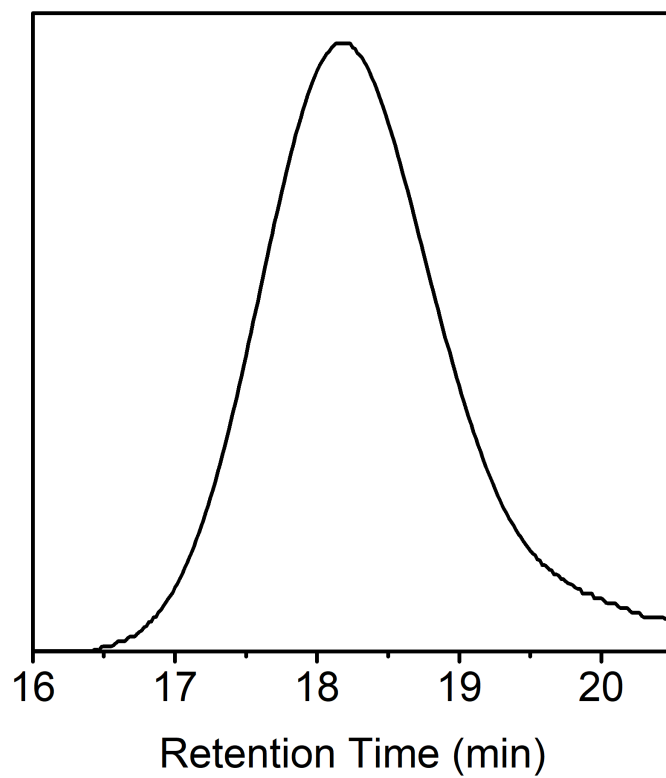


Figure S2. SEC chromatogram of **5** ($M_n = 7,300$ g/mol, $M_w/M_n = 1.11$)

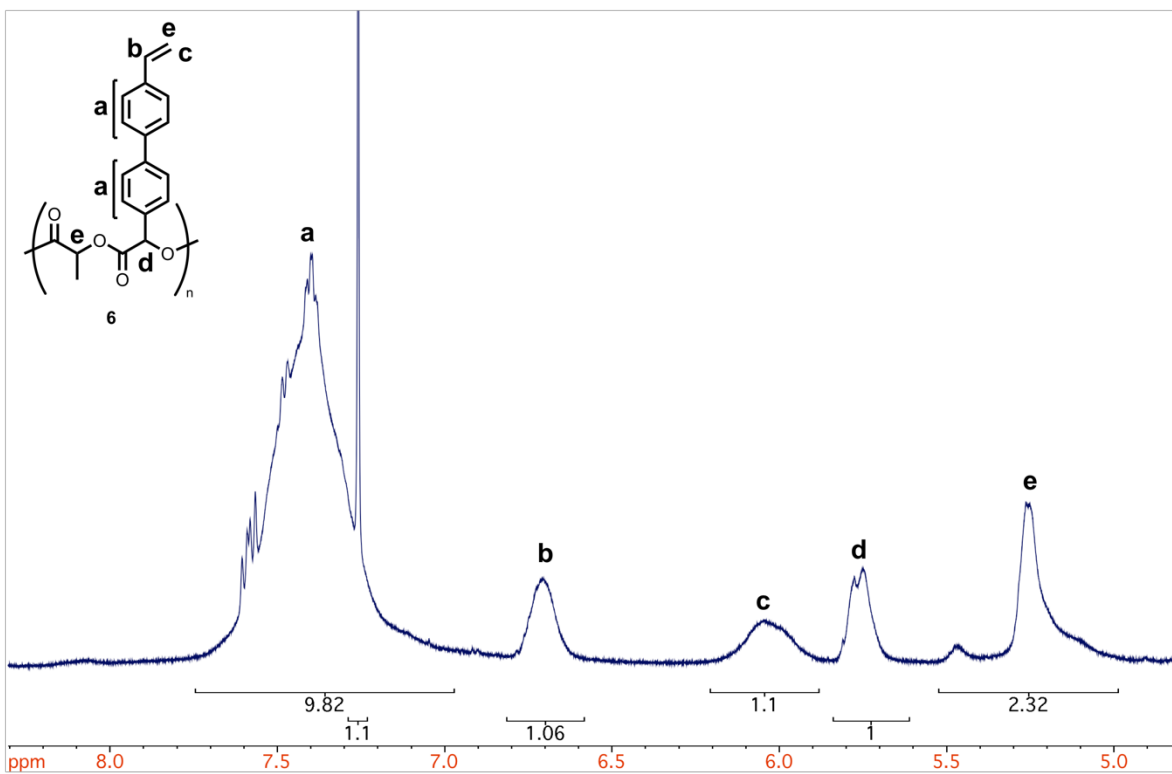


Figure S3. ^1H NMR spectrum of **6**

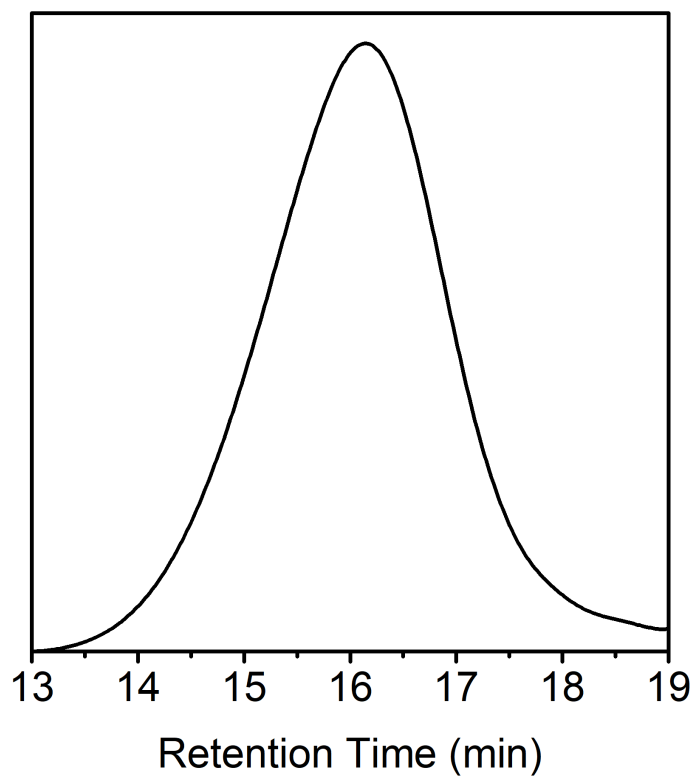


Figure S4. SEC chromatogram of **6** ($M_n = 7,400$ g/mol, $M_w/M_n = 1.55$)

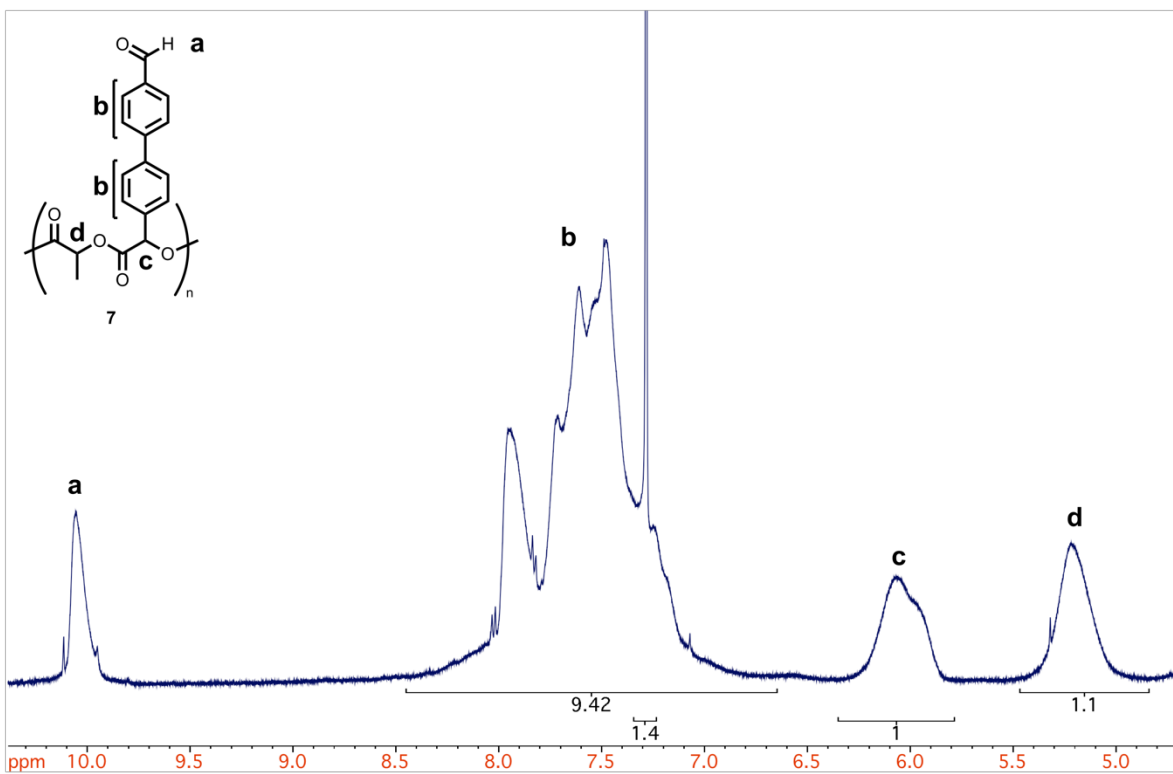


Figure S5. ^1H NMR spectrum of 7

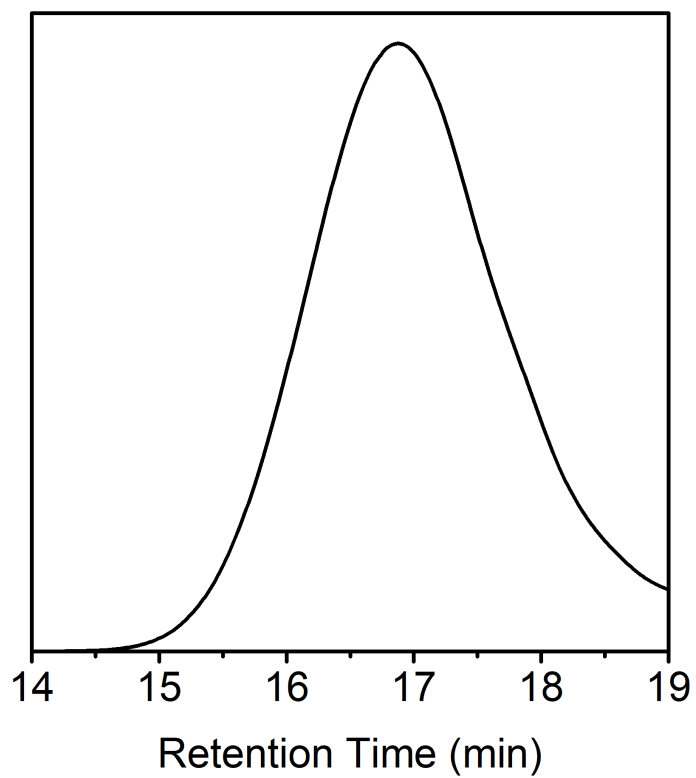


Figure S6. SEC chromatogram of 7 ($M_n = 5,900$ g/mol, $M_w/M_n = 1.27$)

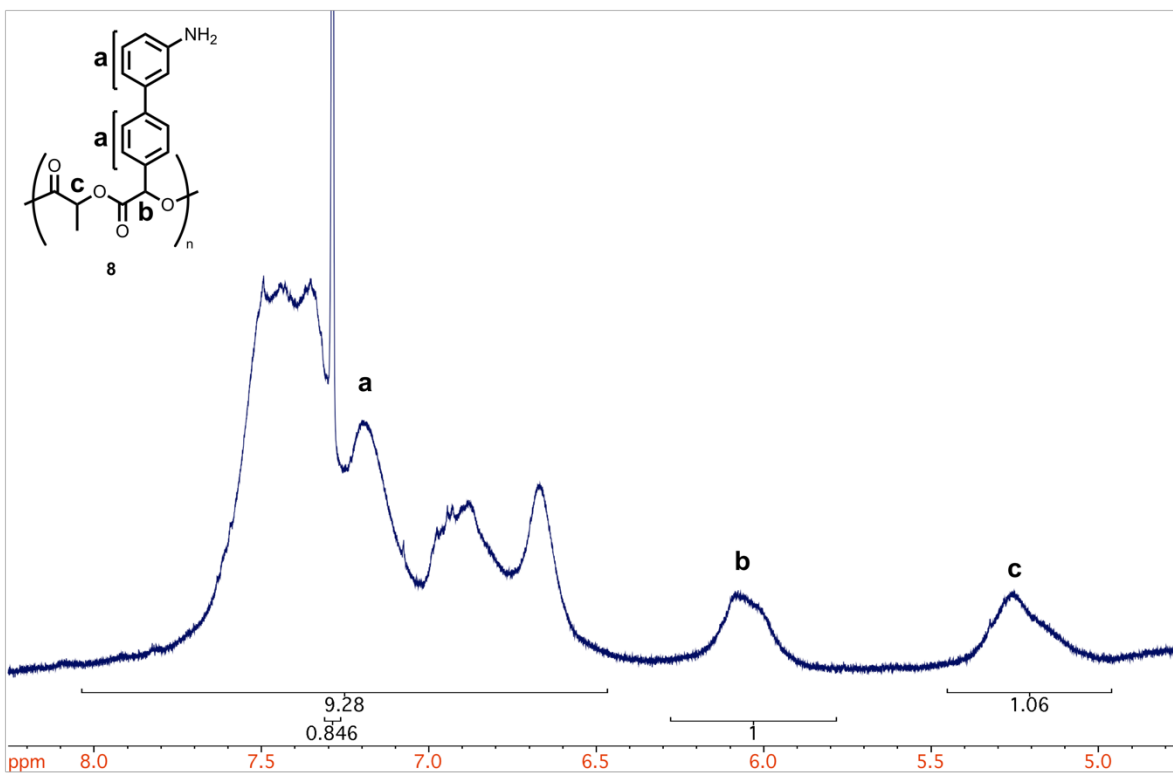


Figure S7. ^1H NMR spectrum of **8**

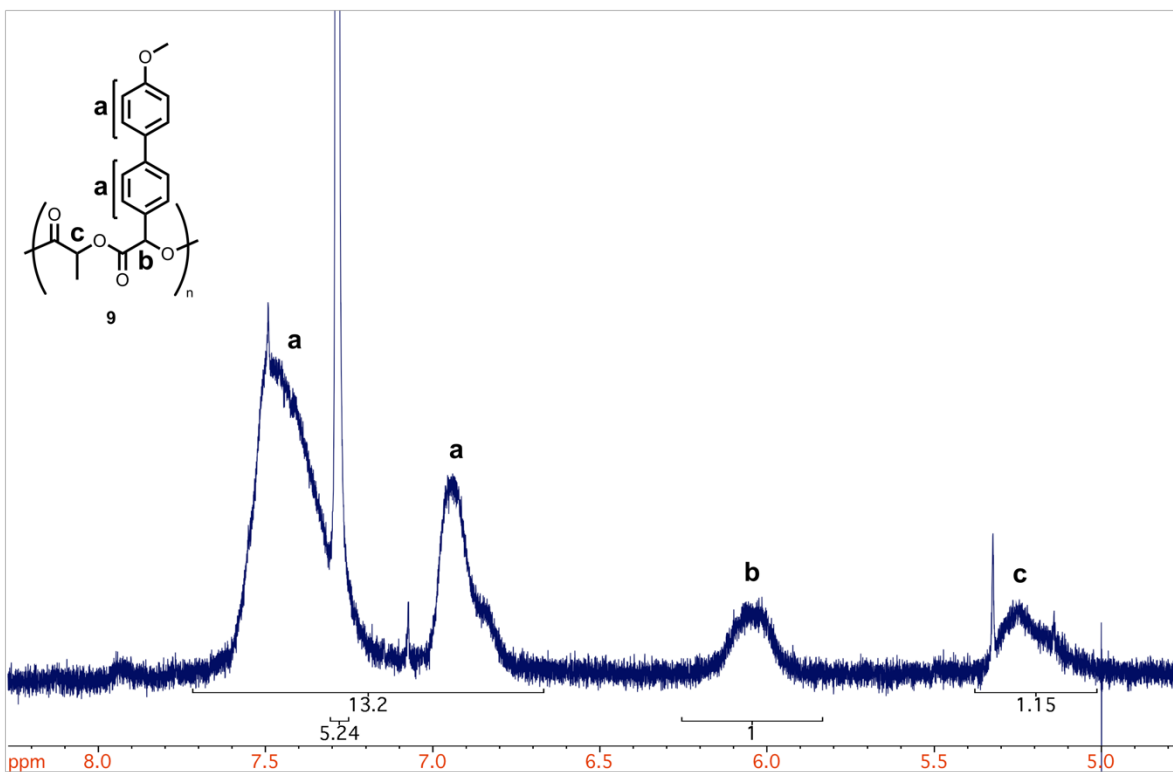


Figure S8. ^1H NMR spectrum of **9**

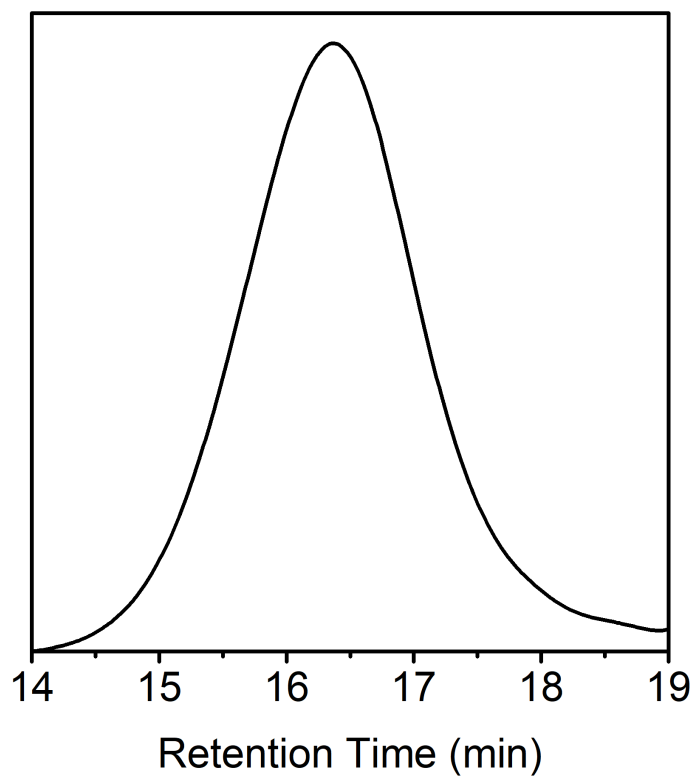


Figure S9. SEC chromatogram of **9** ($M_n = 6,600$ g/mol, $M_w/M_n = 1.36$)

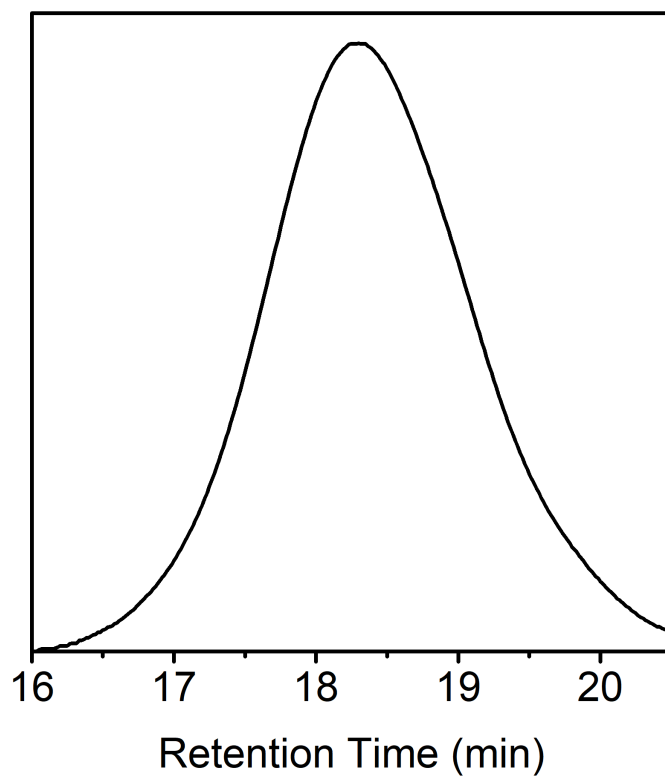


Figure S10. SEC chromatogram of **10** ($M_n = 6,700$ g/mol, $M_w/M_n = 1.22$)

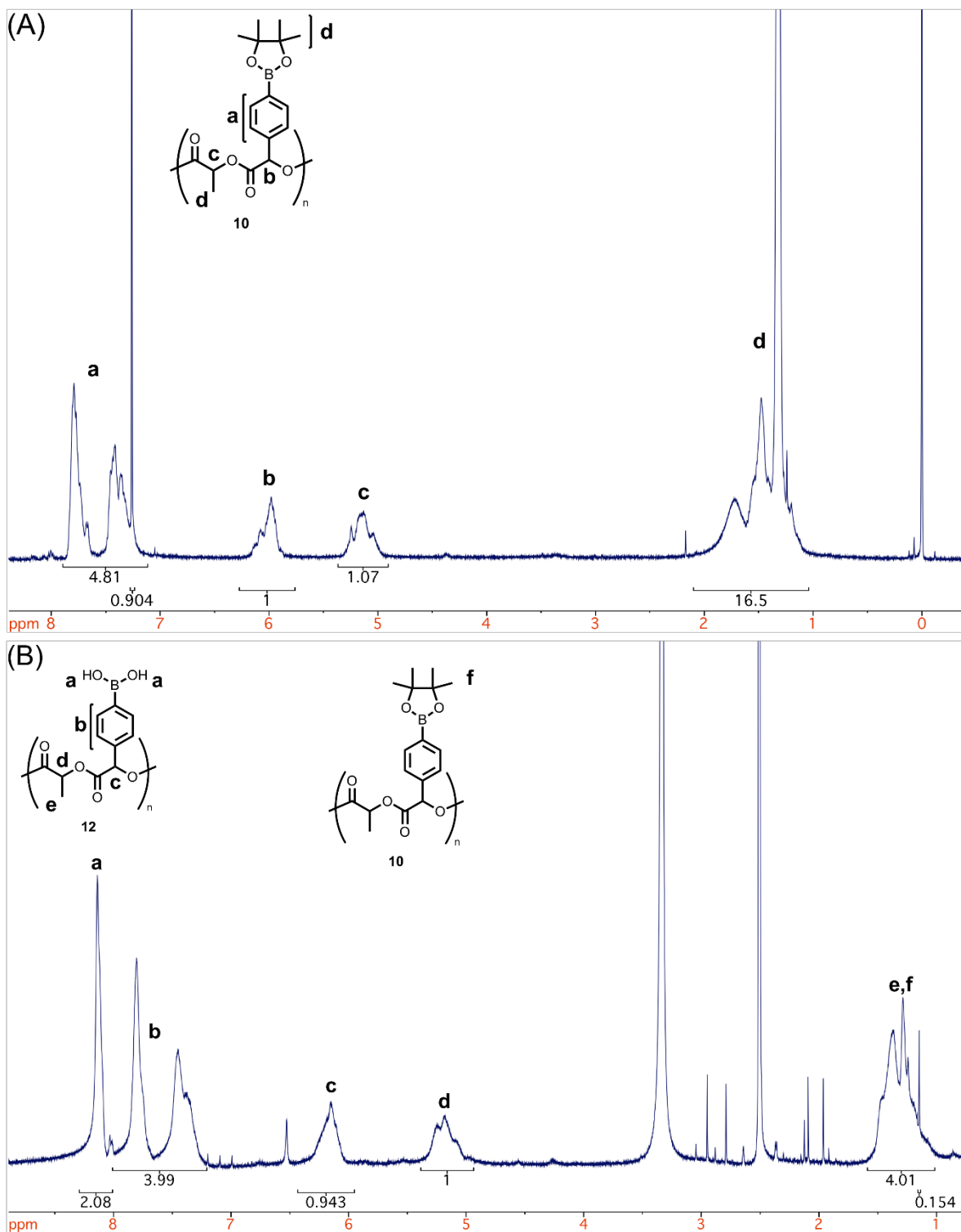


Figure S11. ^1H NMR spectrum of (A) **10** in CDCl_3 and (B) **12** in $\text{DMSO}-d_6$

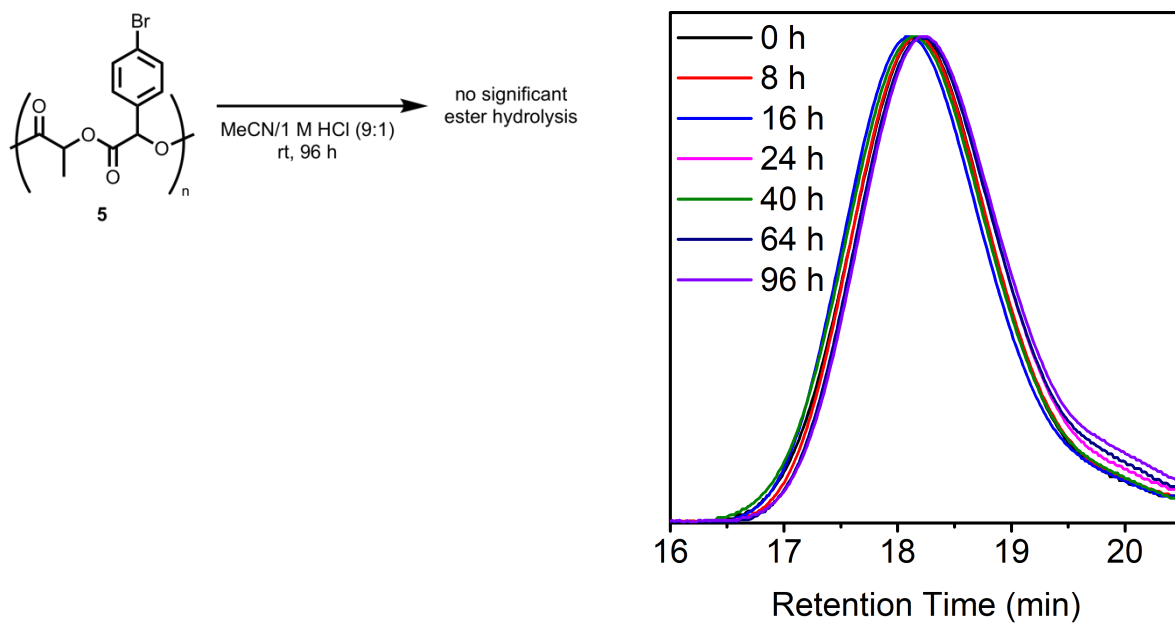


Figure S12. SEC study in which polymer **5** was subjected to a pinacol removal condition for 96 h.

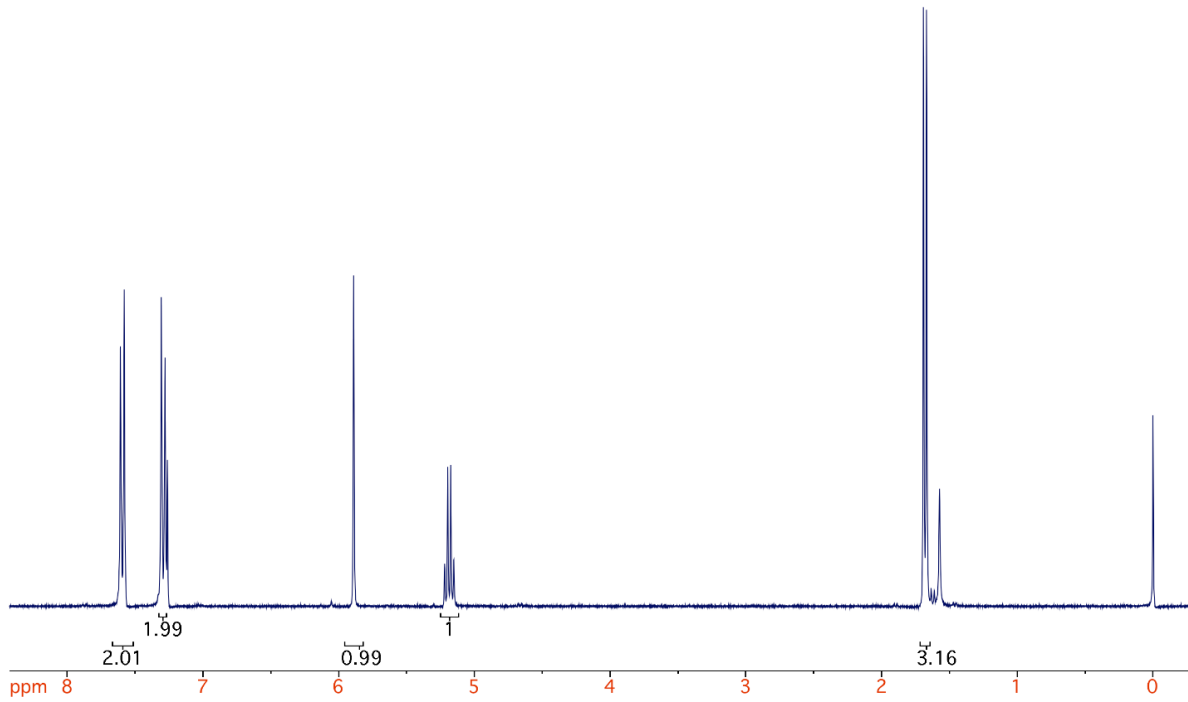


Figure S13. ^1H NMR spectrum of **4**

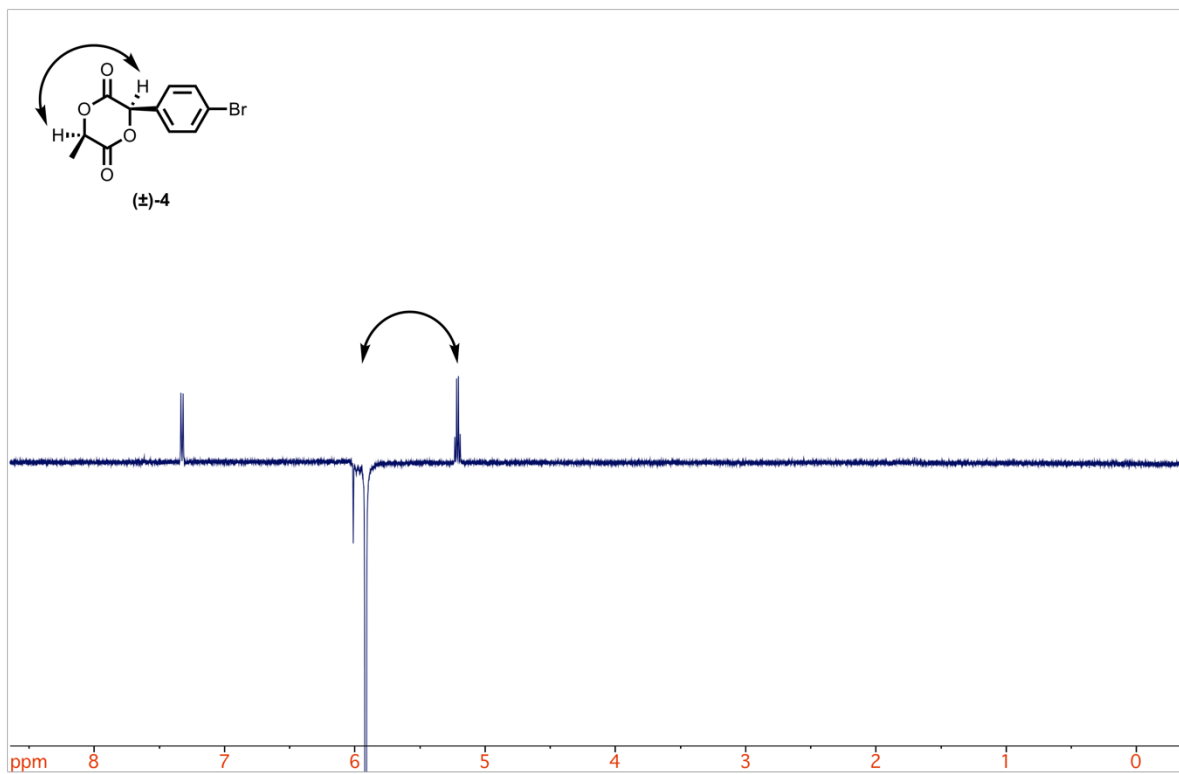


Figure S14. NOESY spectrum of **4**

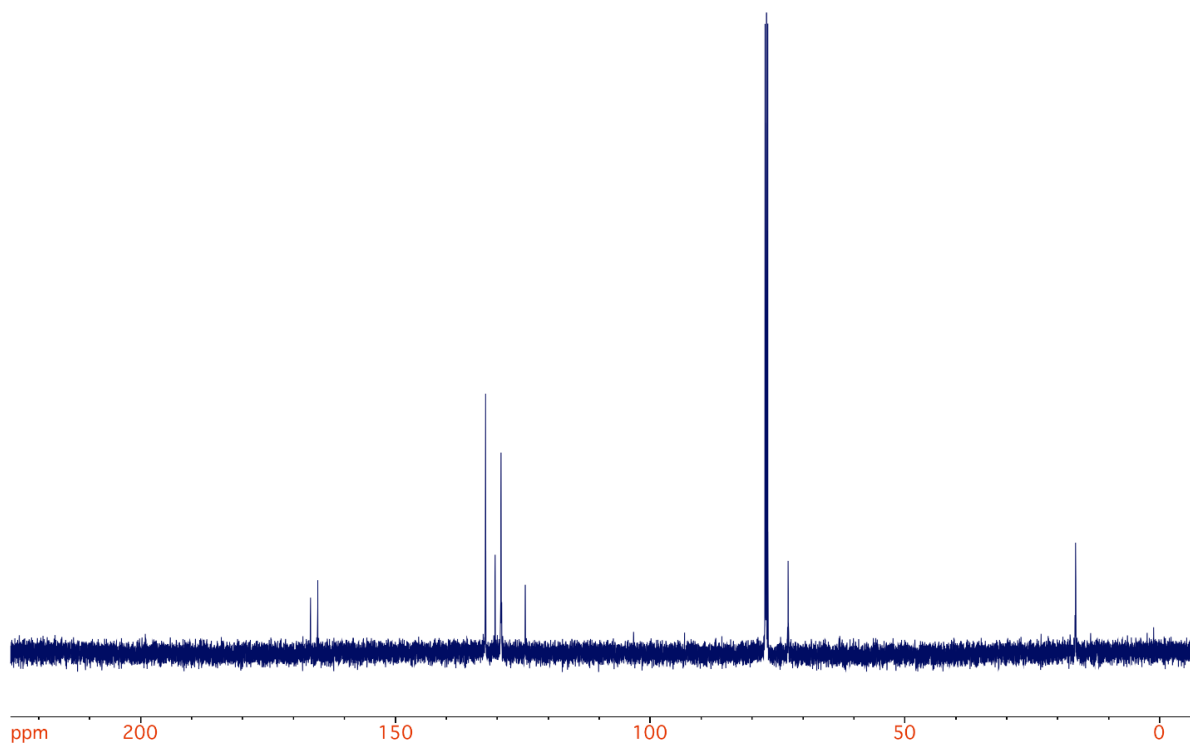


Figure S15. ^{13}C NMR spectrum of **4**

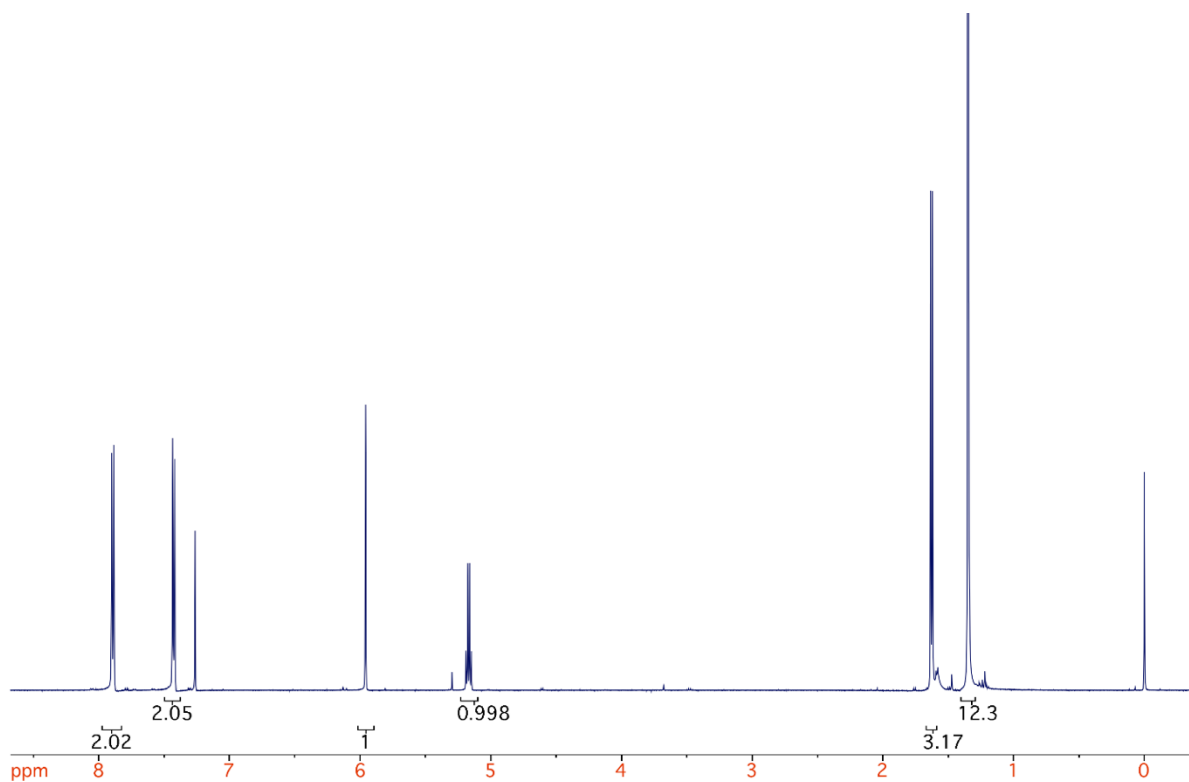


Figure S16. ^1H NMR spectrum of **11**

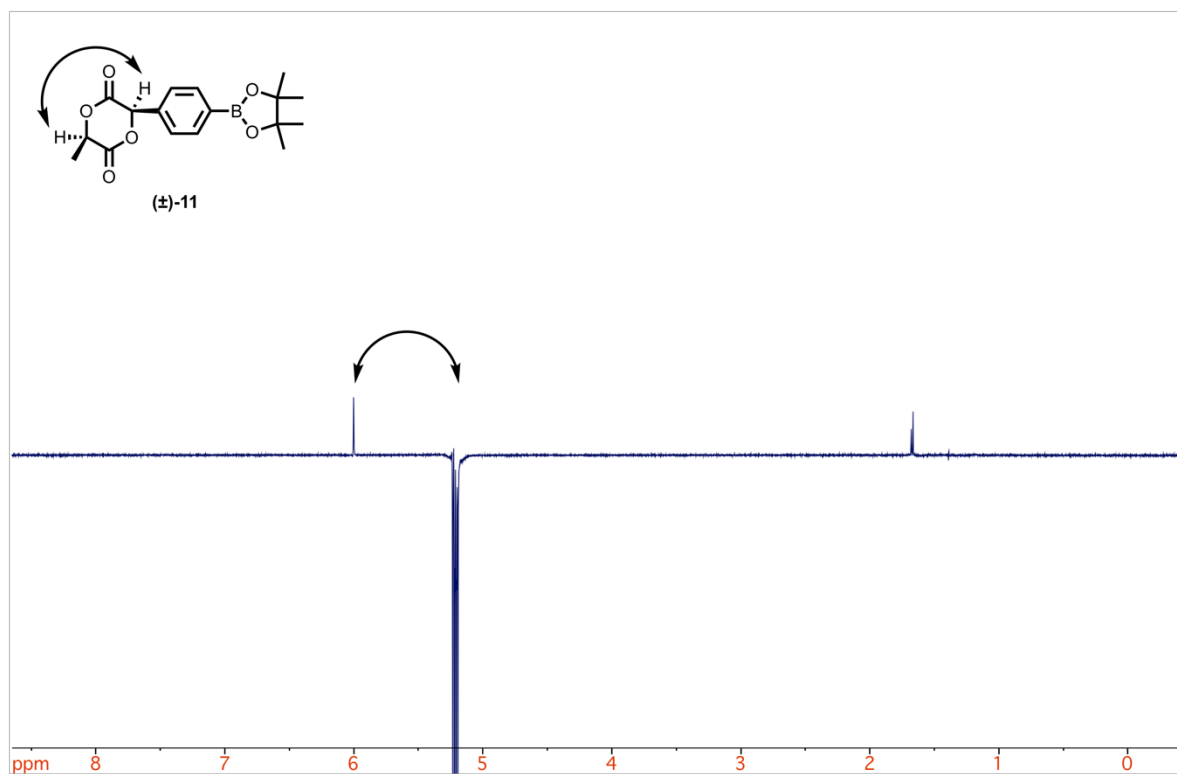


Figure S17. NOESY spectrum of **11**

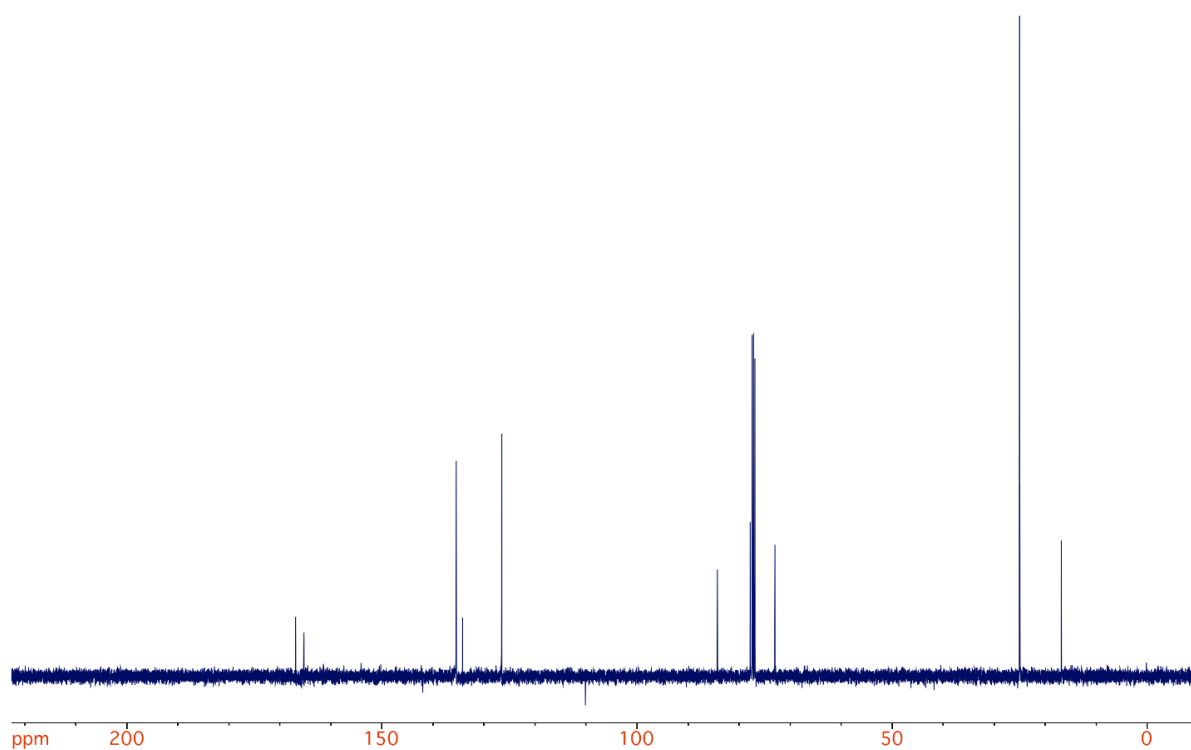


Figure S18. ^{13}C NMR spectrum of **11**

Reference:

1. T. E. Pennington, C. Kardiman and C. A. Hutton, *Tetrahedron Lett.*, 2004, **45**, 6657–6660.