Supplementary Information (SI) for Polymer Chemistry.

Boron-Based Poly(Asymmetric Substituted Glycolide) Nanospheres

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Table of Contents

I. ATR-FTIR Spectra of 4-6, 9-14, I-VI and 16-21 2
II. NMR Spectra of 4-6, 9-14, I-V, 16-20 and HRMS Spectra of I-VI.....6
III. UV/Vis Spectra of 15-22 27
IV. Particle Size Distribution Graphs of 16-21.....34

I. ATR-FTIR Spectra of 4-6, 9-14, I-VI and 16-21

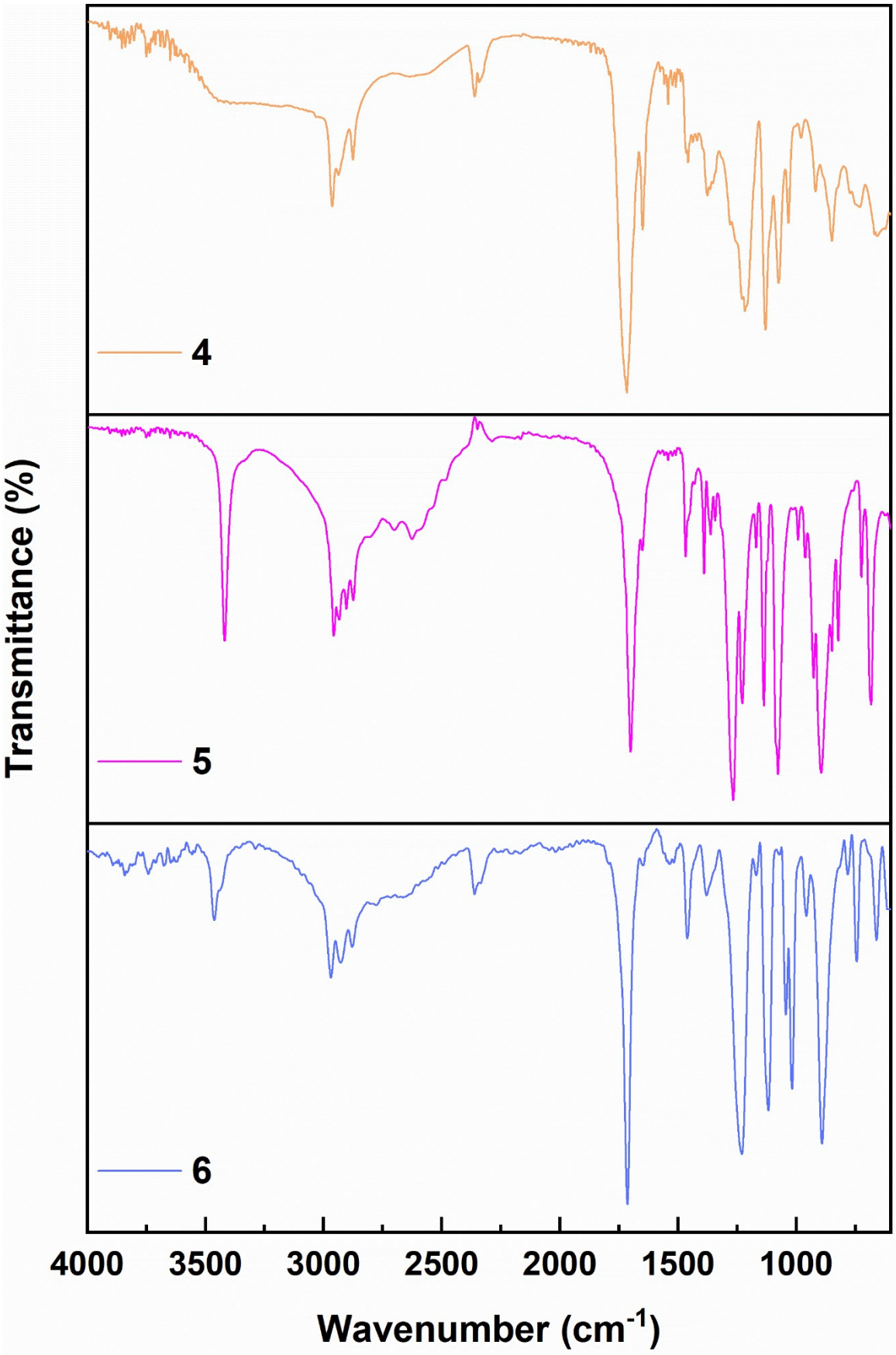

Figure S1. ATR-FTIR spectra of hydroxy acids **4-6**

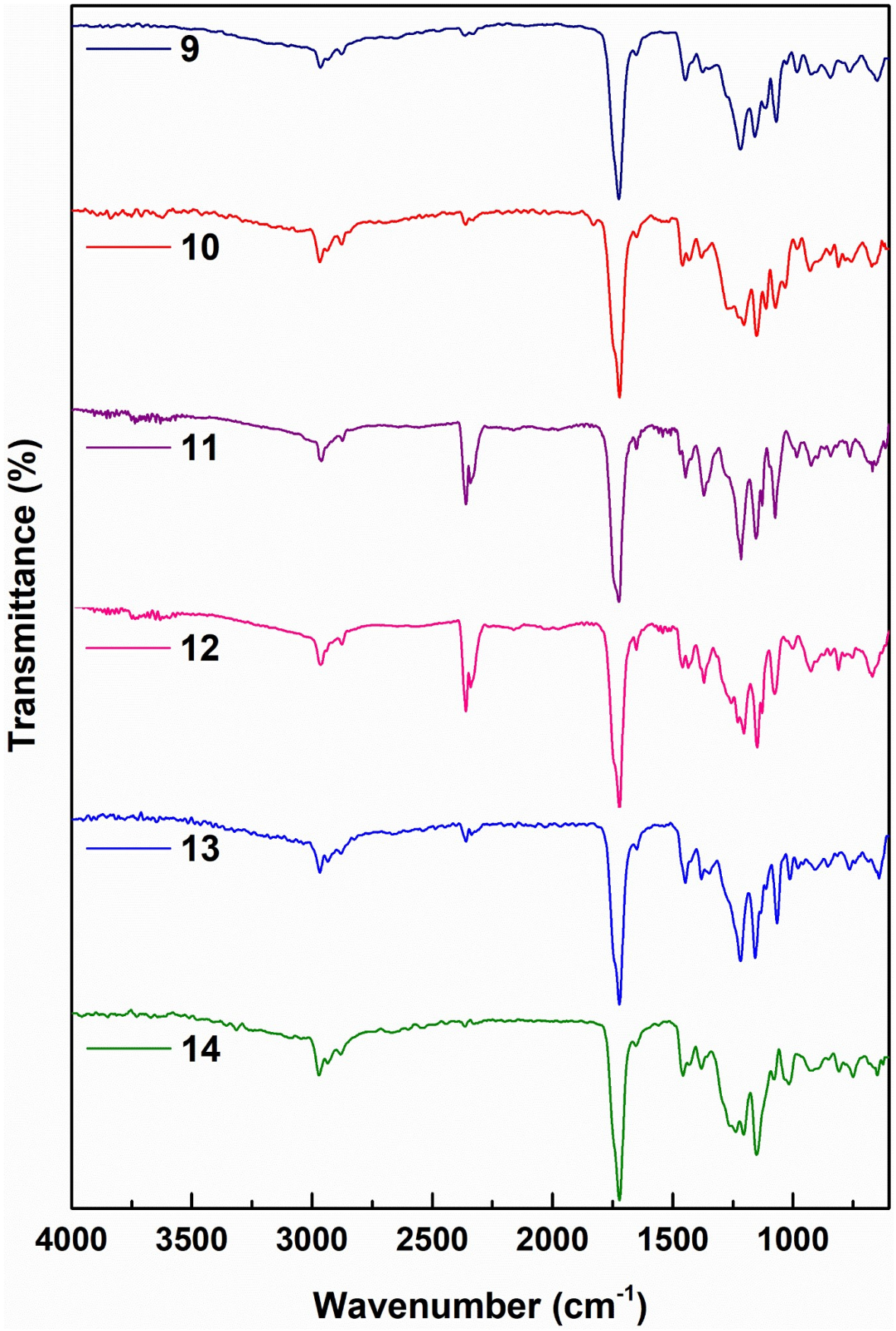

Figure S2. ATR-FTIR spectra of intermediates **9-14**

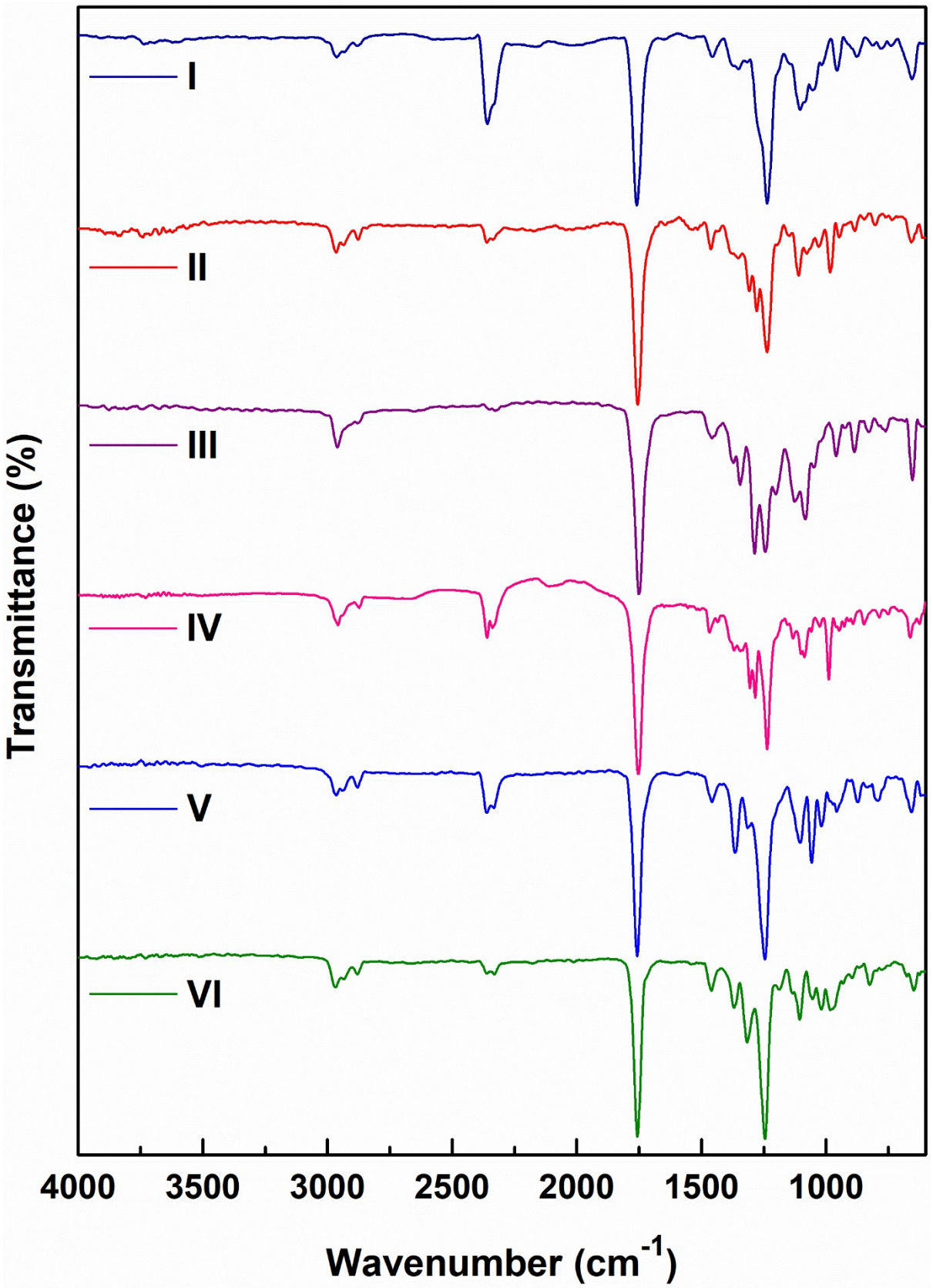

Figure S3. ATR-FTIR spectra of ASGs **I-VI** monomers

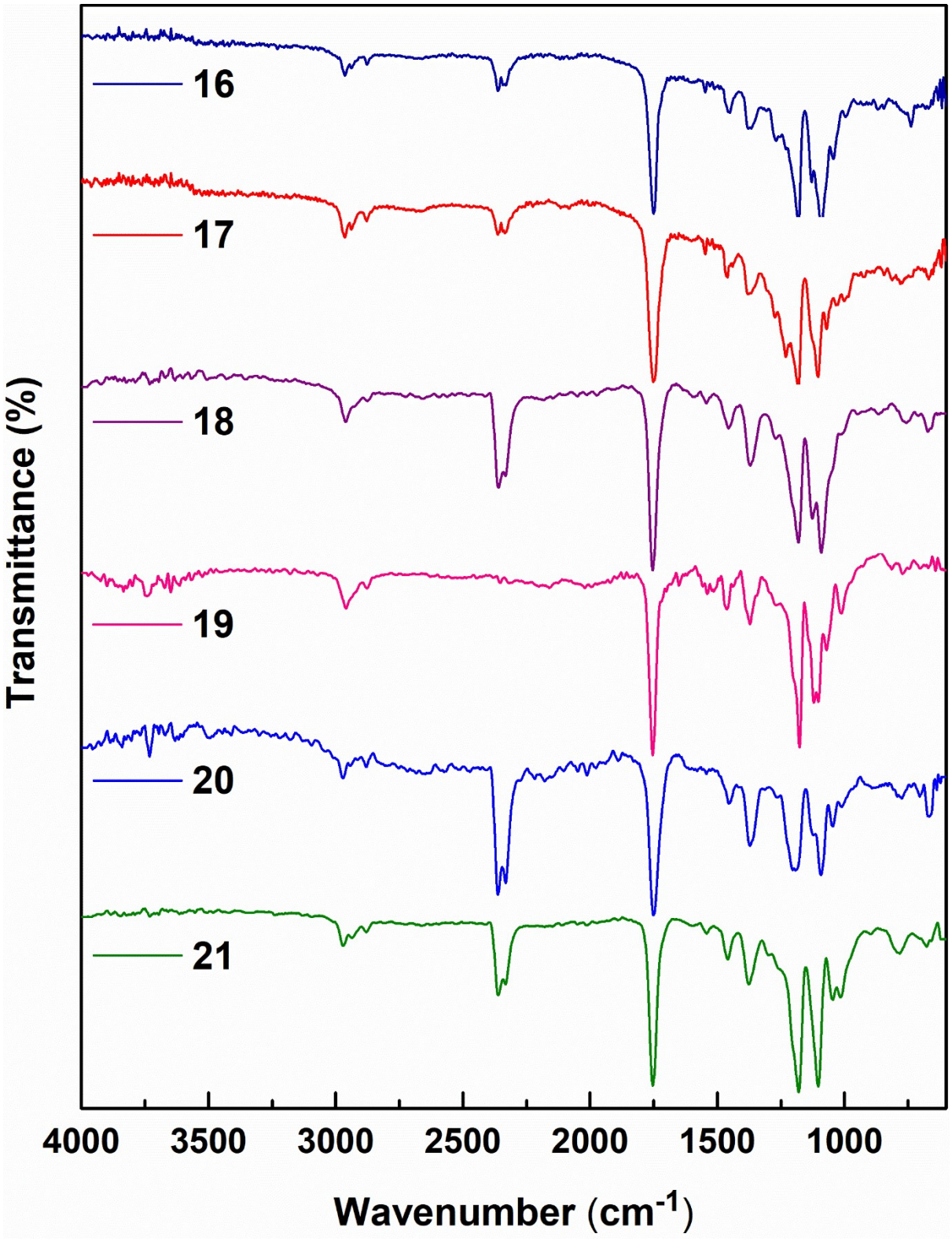

Figure S4. ATR-FTIR spectra of boron based BF_2I-PASGs **16-21** homopolymers

II. NMR Spectra of 4-6, 9-14, I-V, 16-20 and HRMS Spectra of I-VI

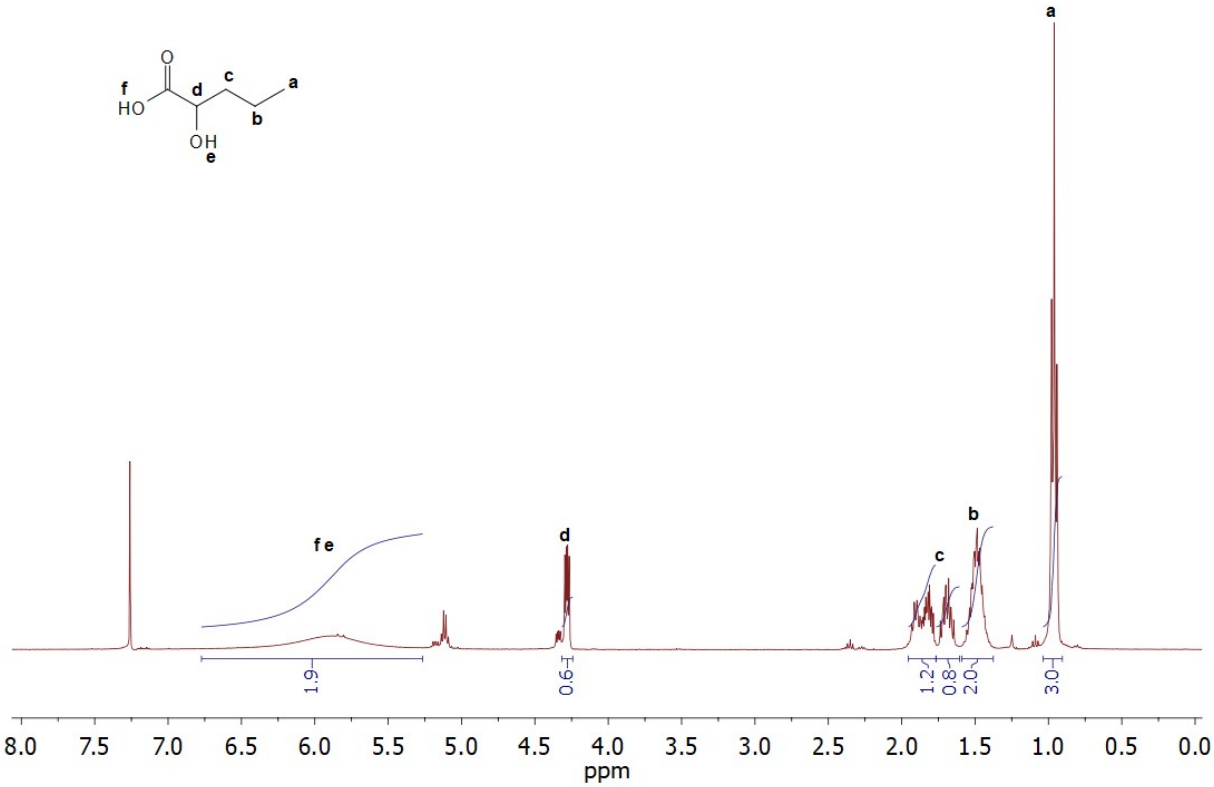

Figure S5. ^{1}H NMR spectrum of hydroxy acid **4**

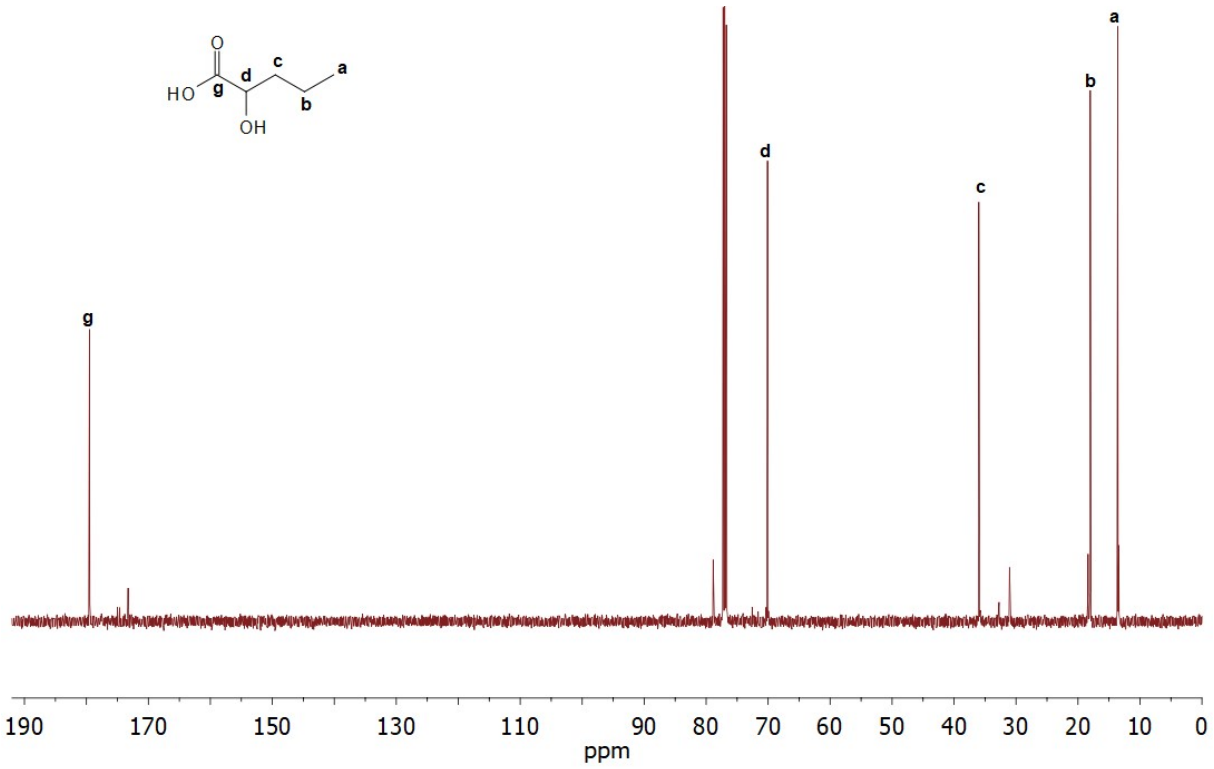

Figure S6. ^{13}C NMR spectrum of hydroxy acid **4**

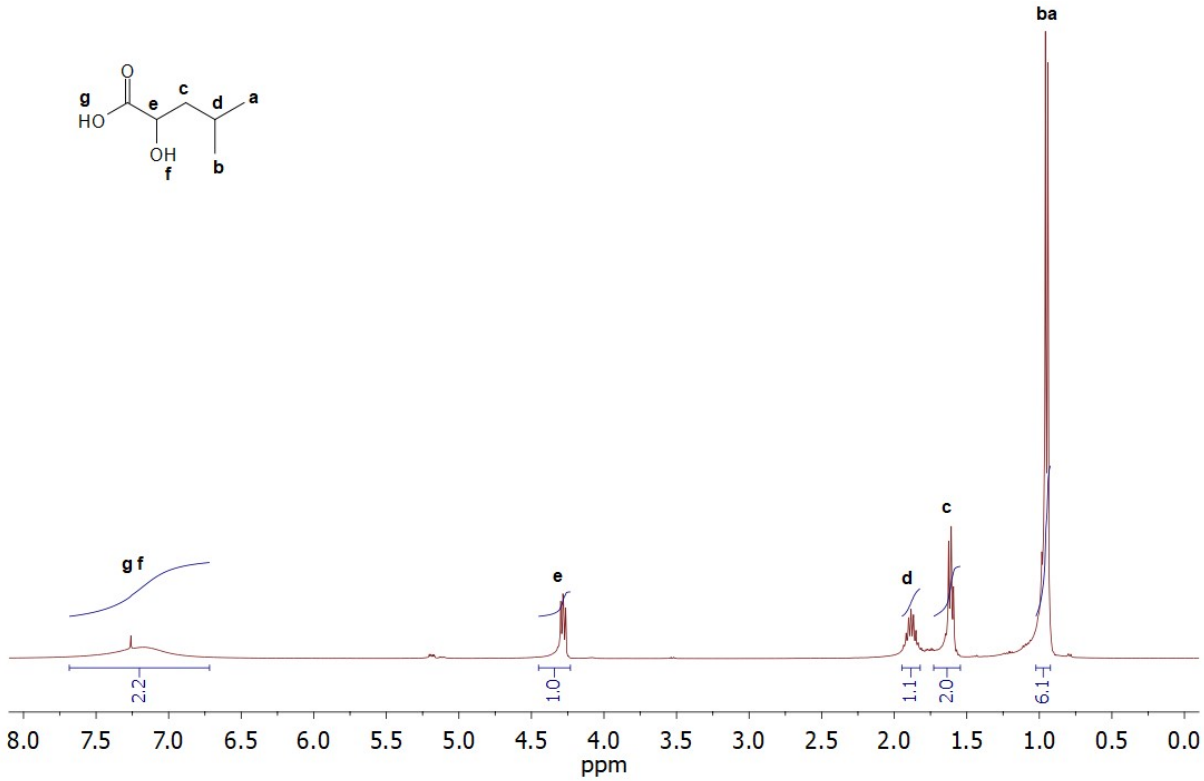

Figure S7. [1]H NMR spectrum of hydroxy acid **5**

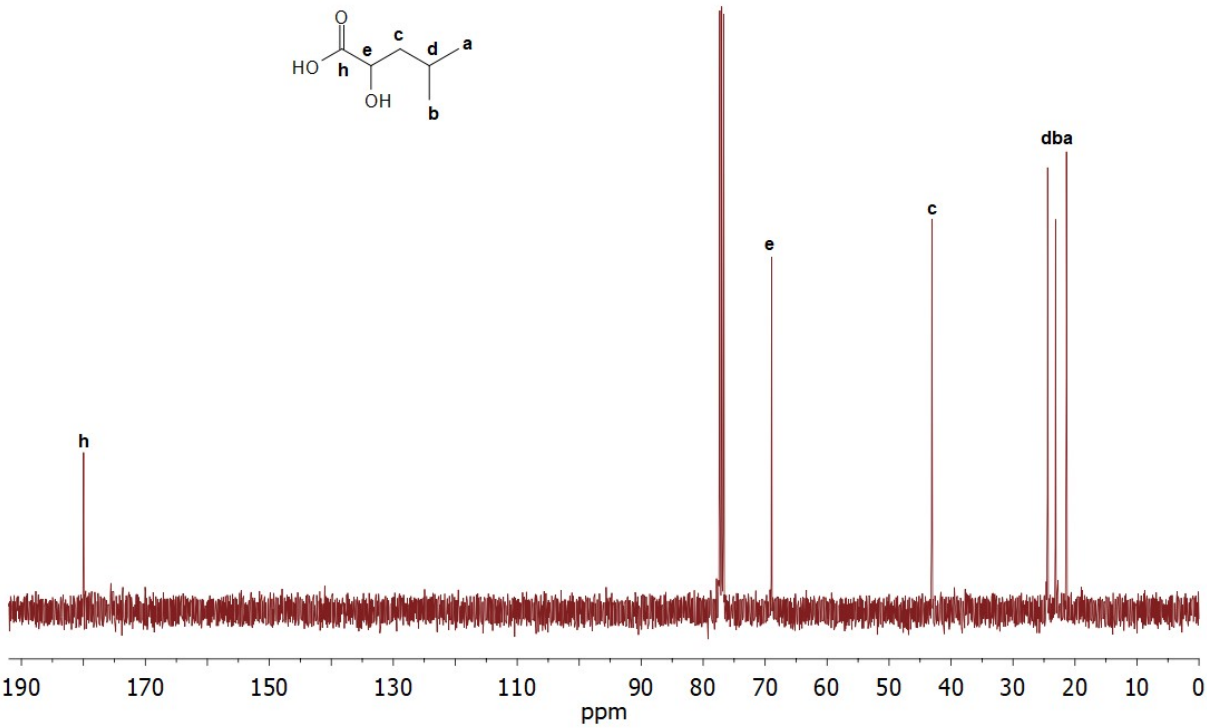

Figure S8. [13]C NMR spectrum of hydroxy acid **5**

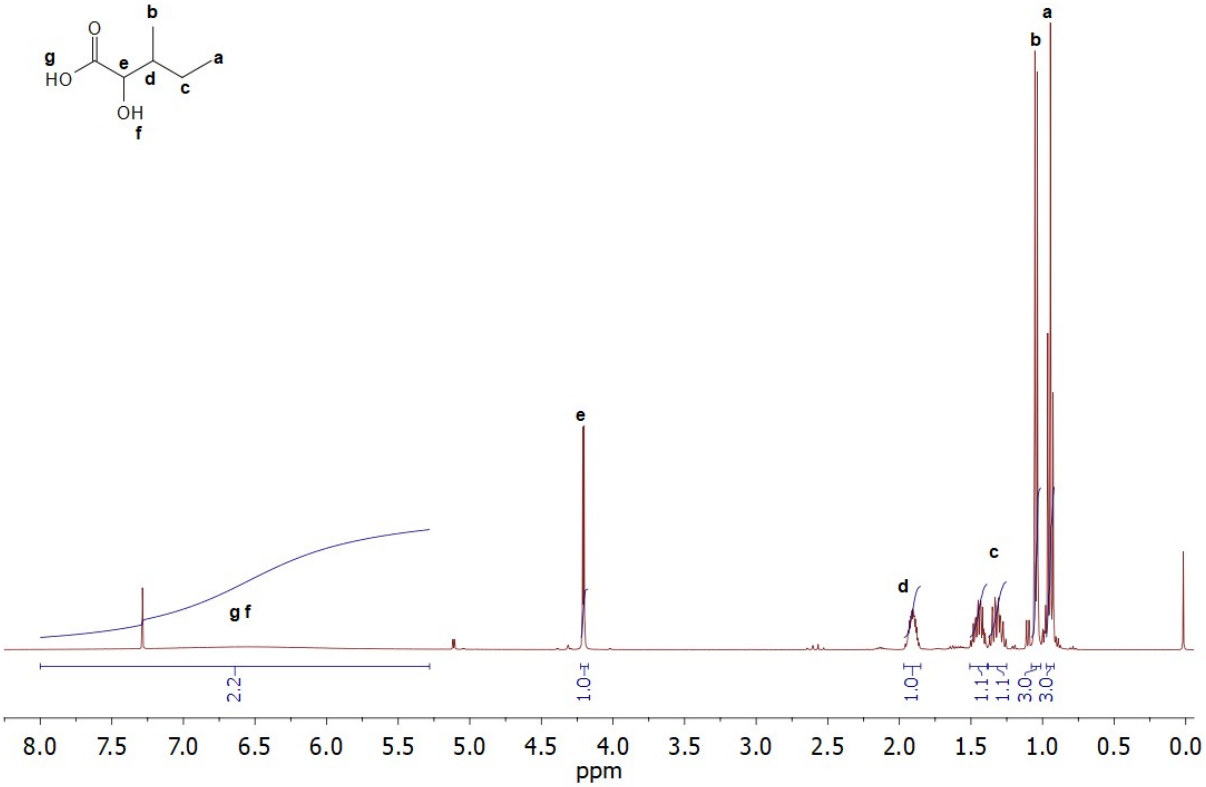

Figure S9. ^{1}H NMR spectrum of hydroxy acid **6**

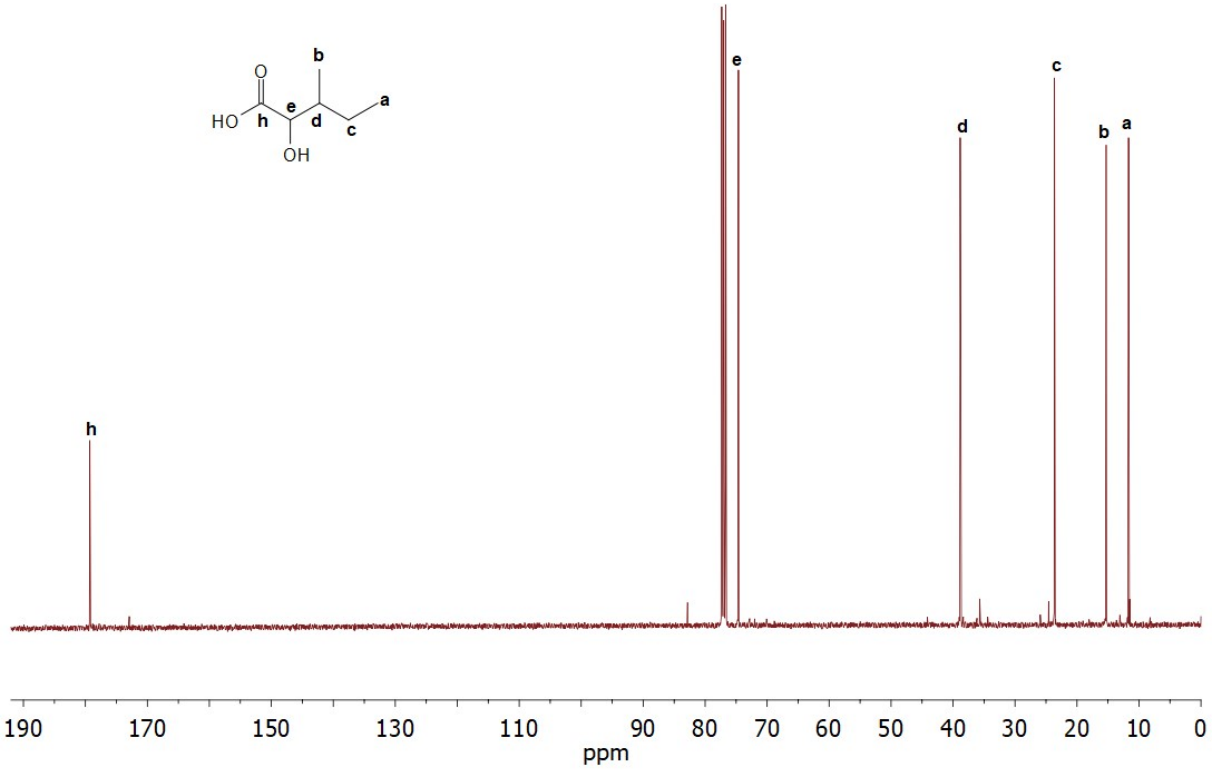

Figure S10. ^{13}C NMR spectrum of hydroxy acid **6**

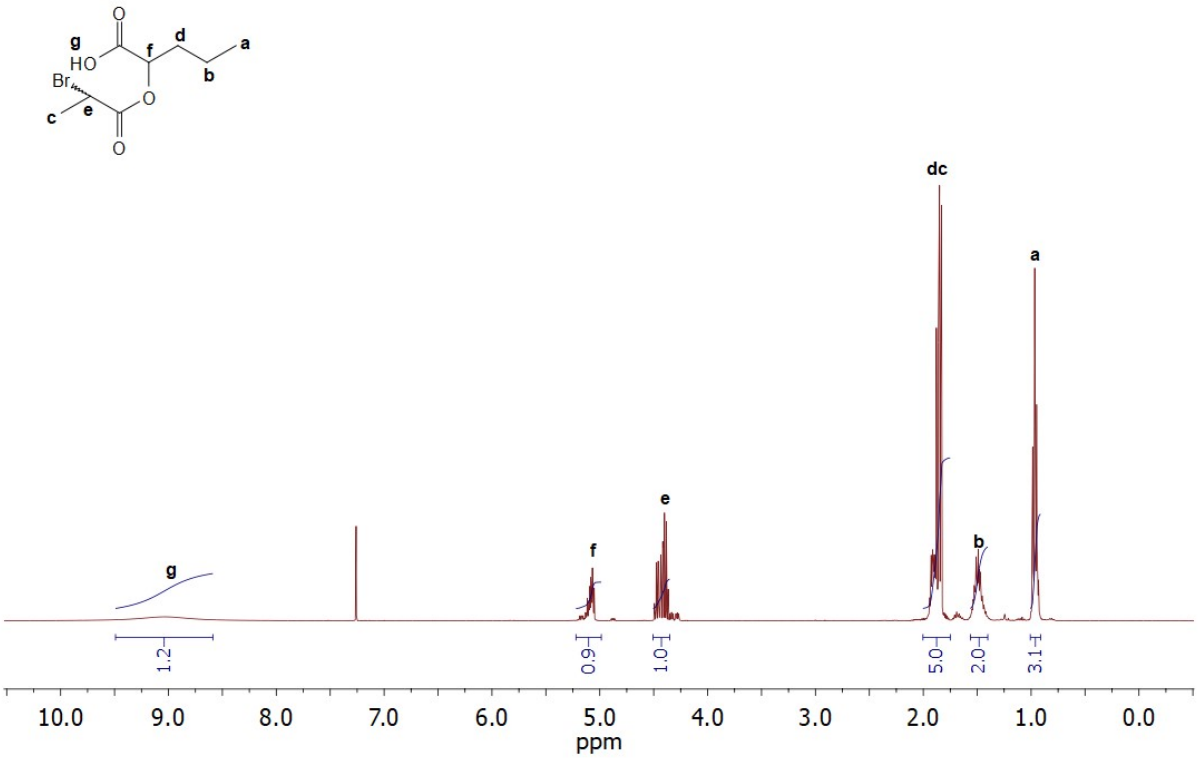

Figure S11. [1]H NMR spectrum of intermediate **9**

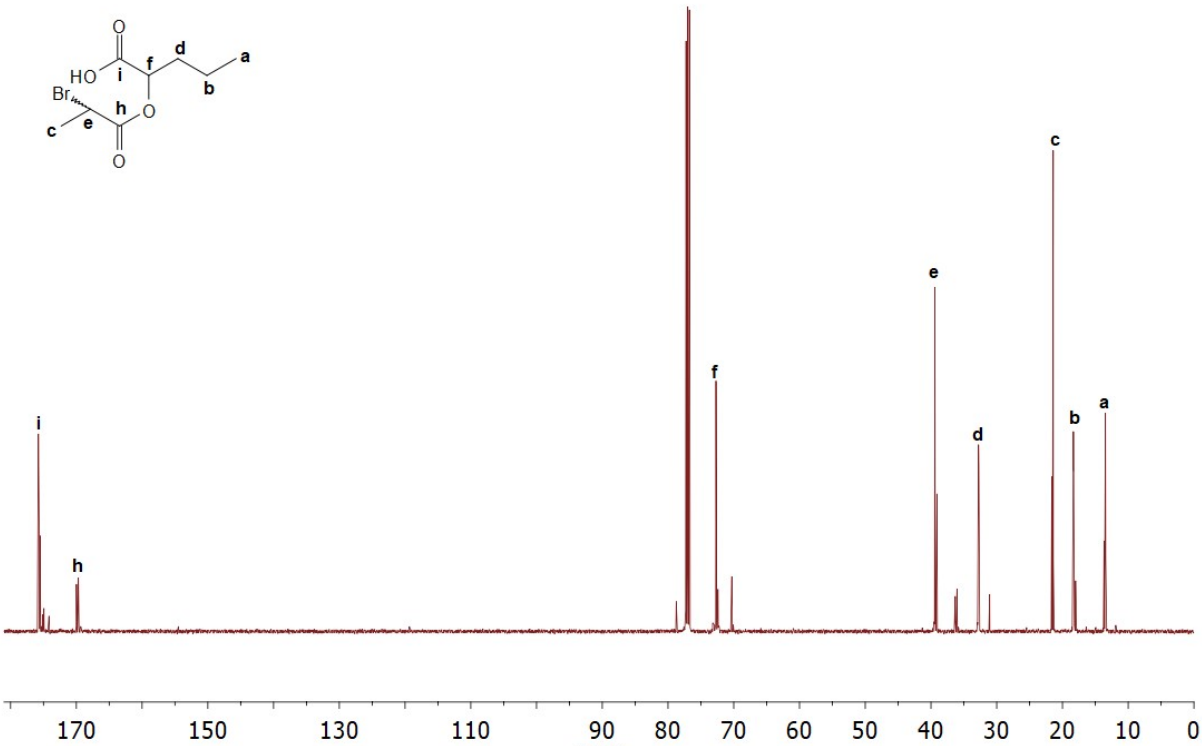

Figure S12. [13]C NMR spectrum of intermediate **9** (a mixture of diastereomers)[1]

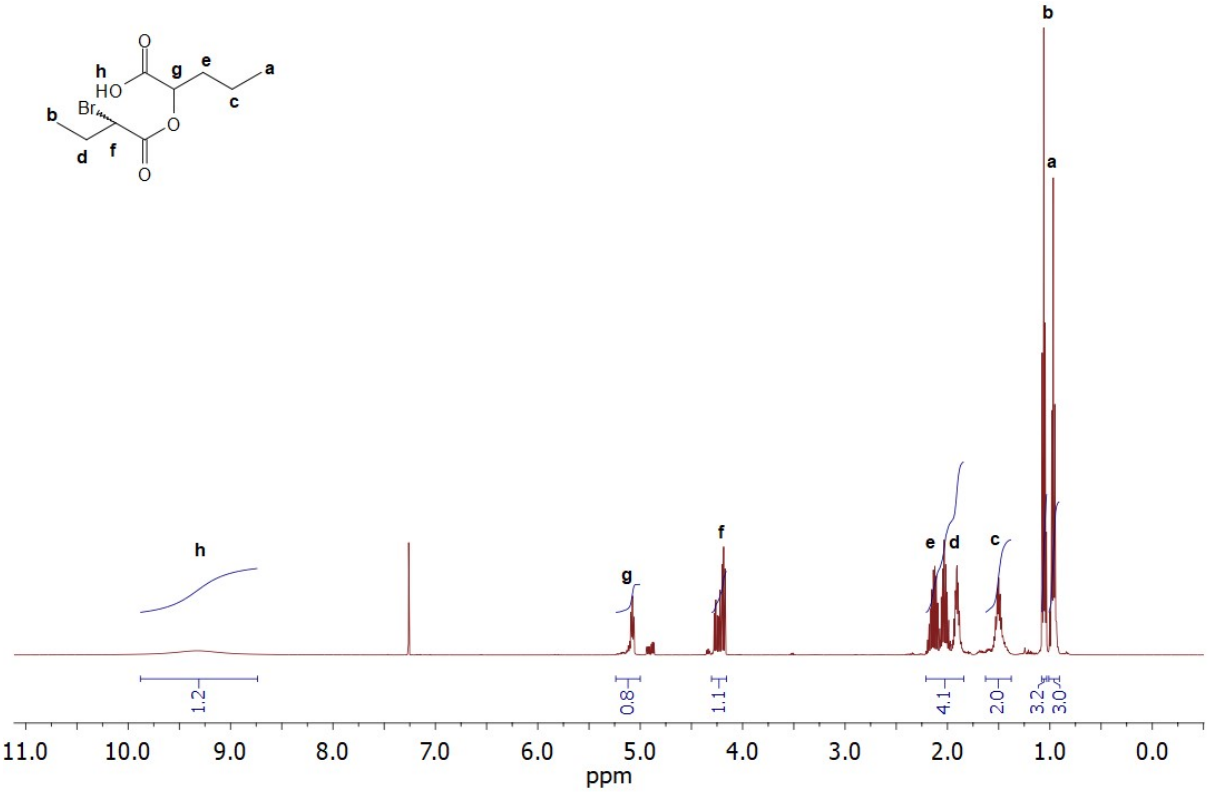

Figure S13. [1]H NMR spectrum of intermediate **10**

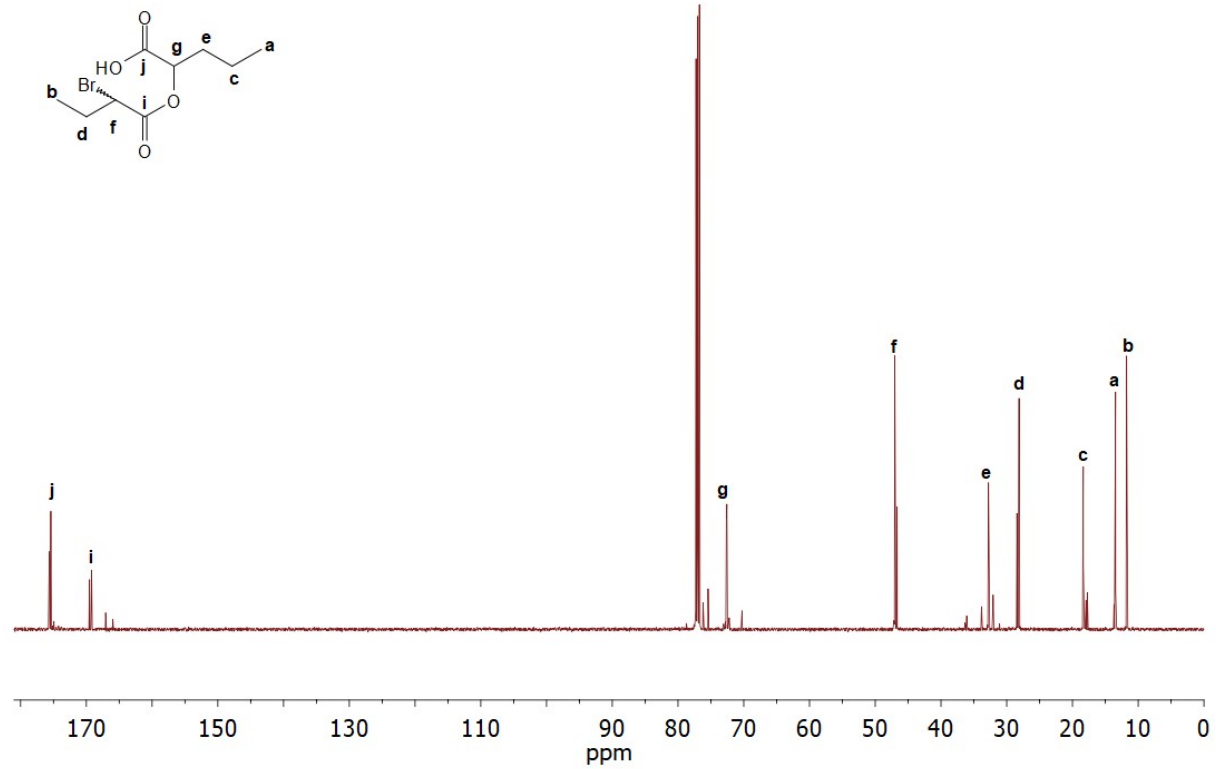

Figure S14. [13]C NMR spectrum of intermediate **10** (a mixture of diastereomers)[1]

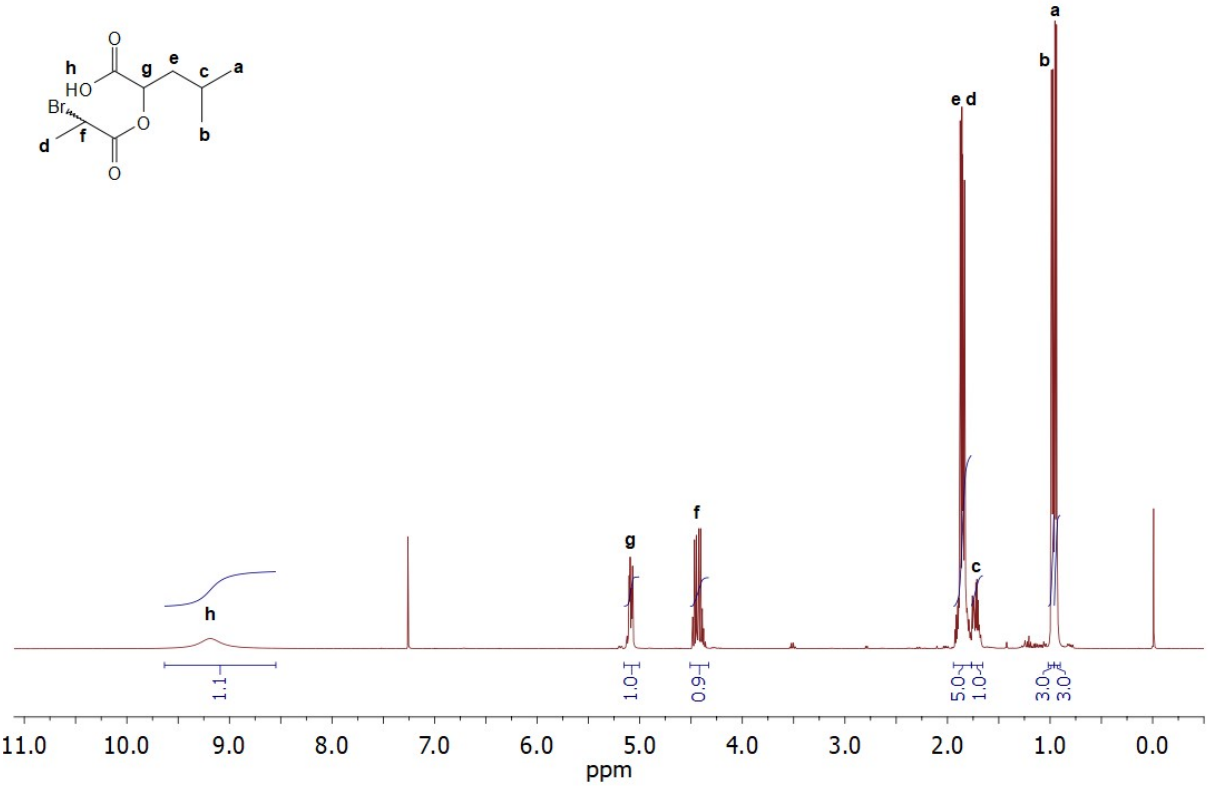

Figure S15. [1]H NMR spectrum of intermediate **11**

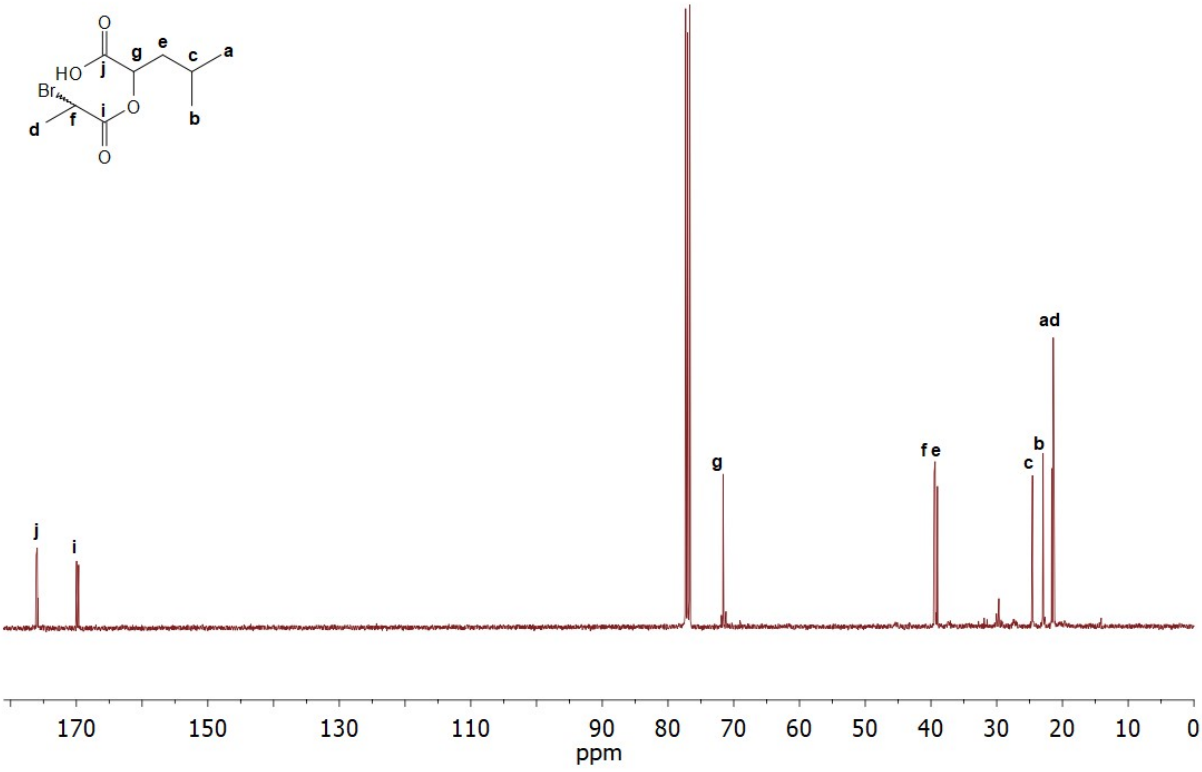

Figure S16. [13]C NMR spectrum of intermediate **11** (a mixture of diastereomers)[1]

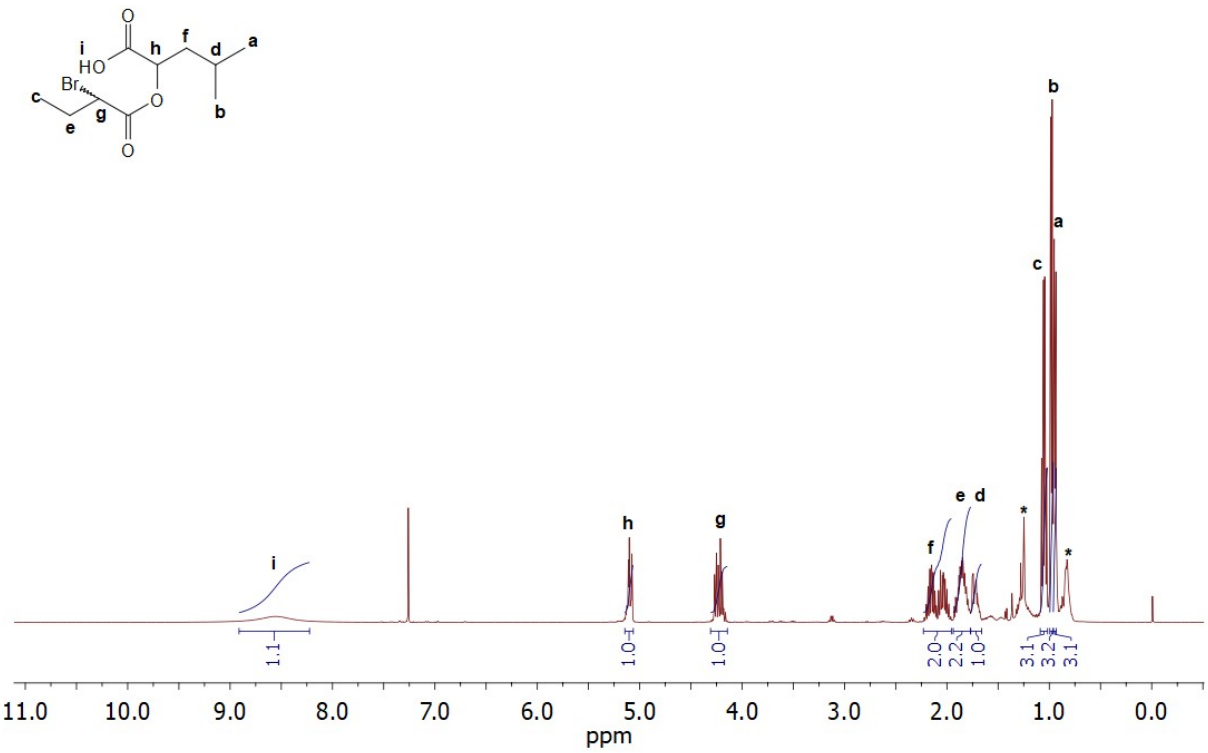

Figure S17. [1]H NMR spectrum of intermediate **12** (* indicates impurity)

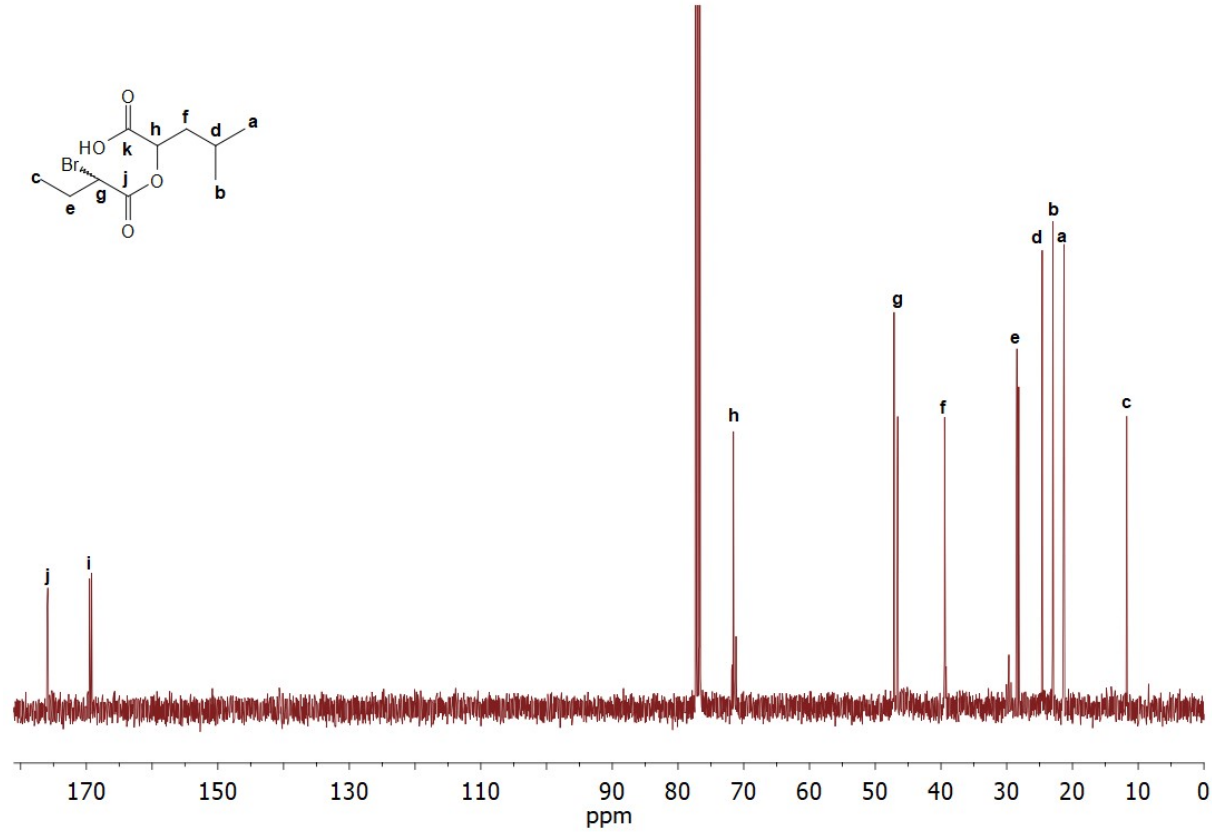

Figure S18. [13]C NMR spectrum of intermediate **12** (a mixture of diastereomers)[1]

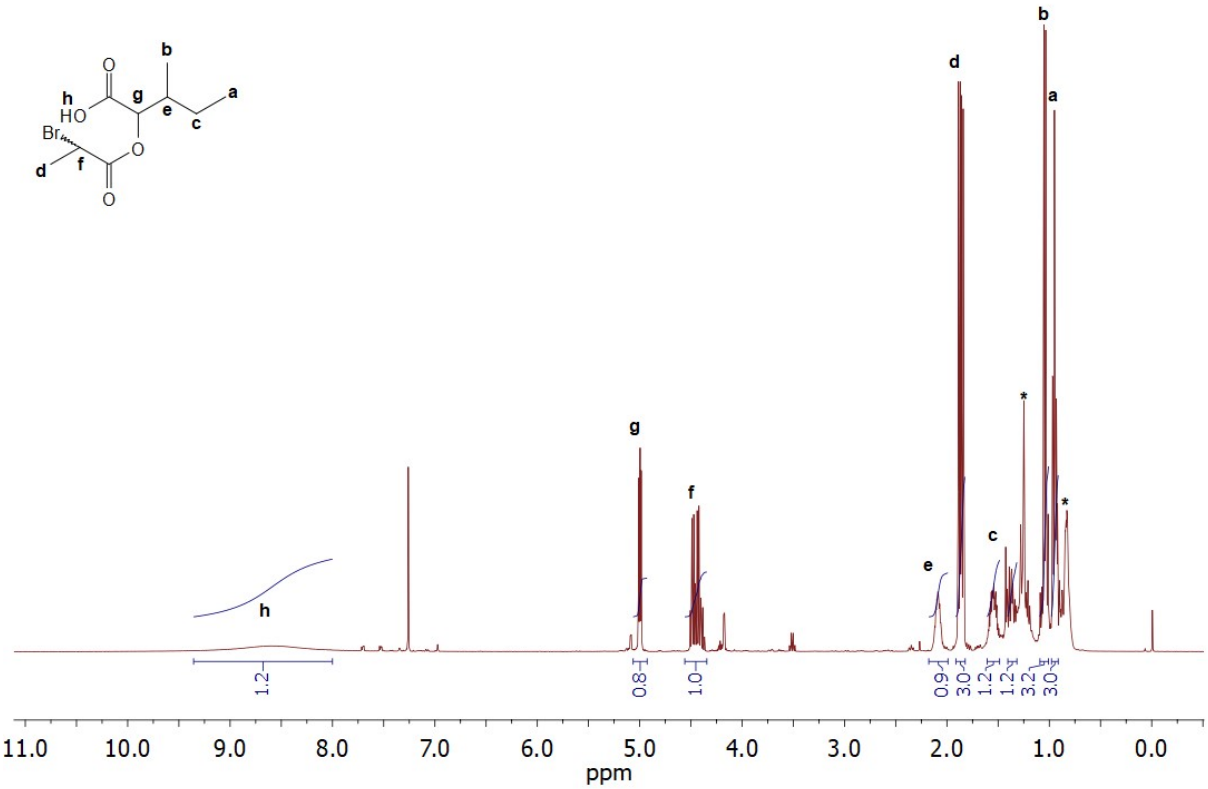

Figure S19. [1]H NMR spectrum of intermediate **13** (* indicates impurity)

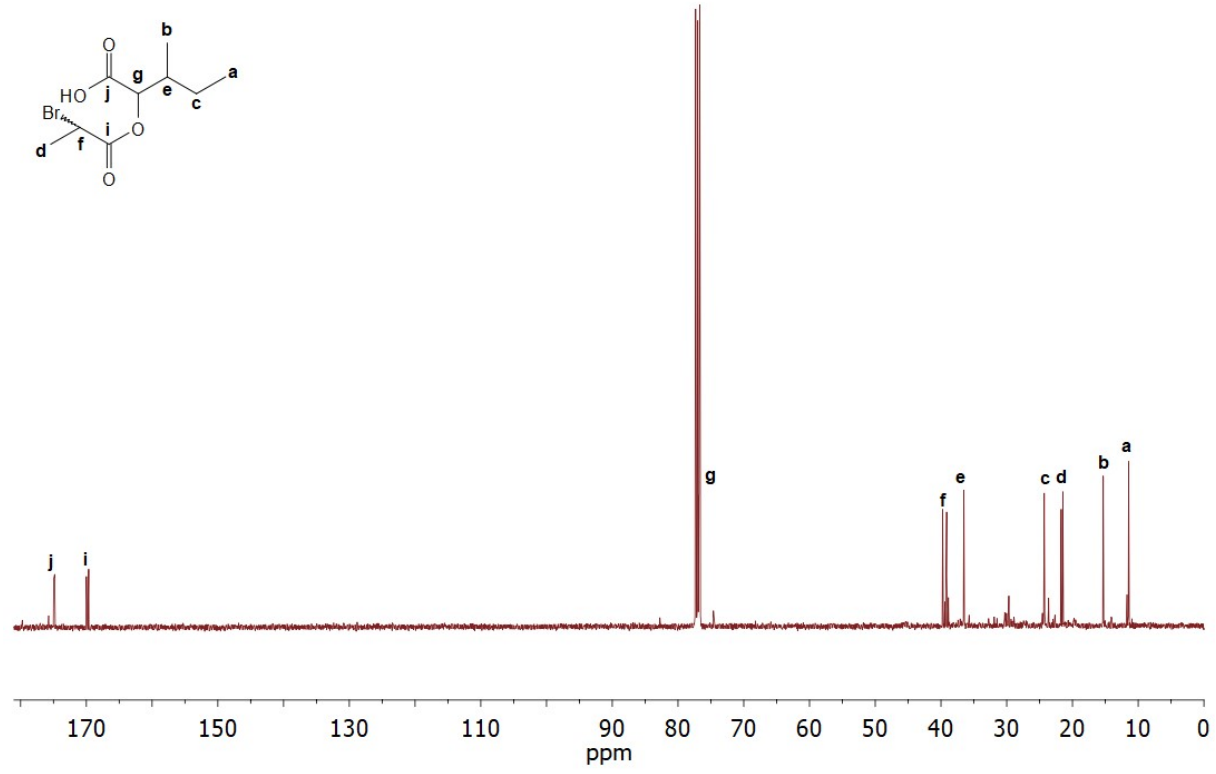

Figure S20. [13]C NMR spectrum of intermediate **13** (a mixture of diastereomers)[1]

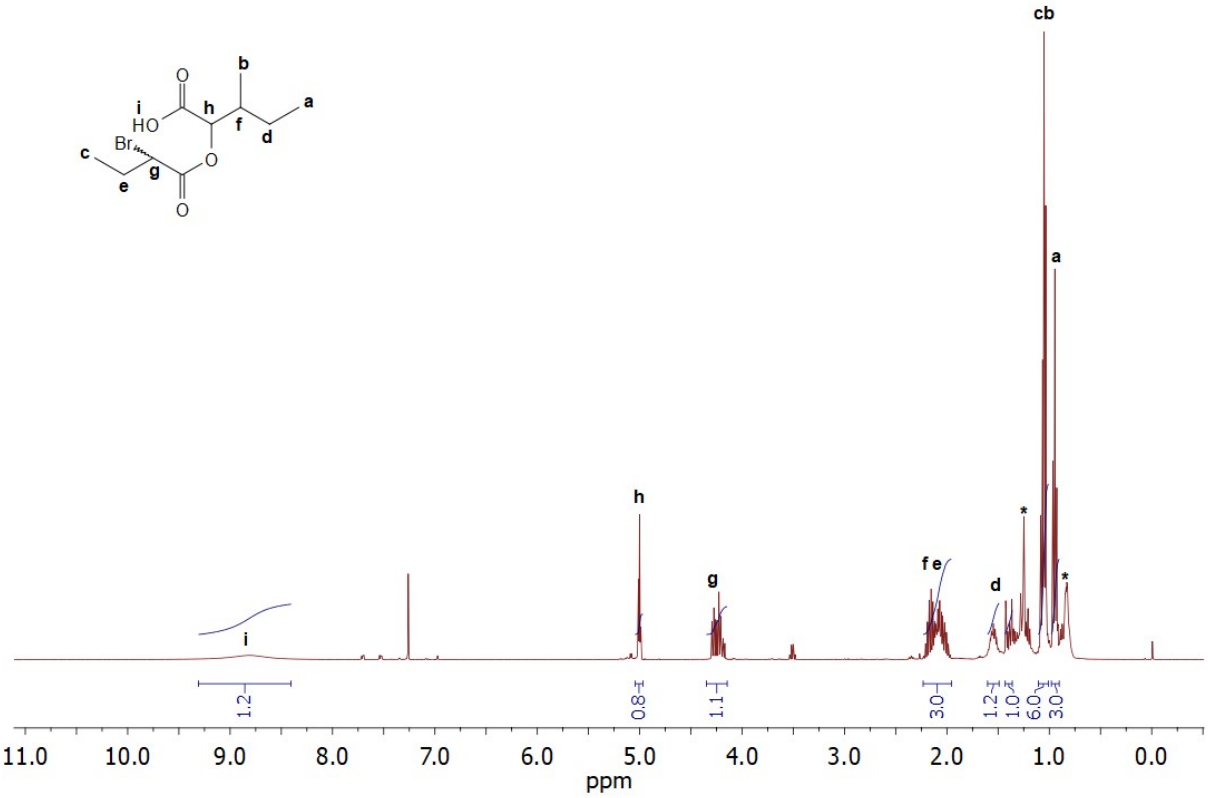

Figure S21. [1]H NMR spectrum of intermediate **14** (* indicates impurity)

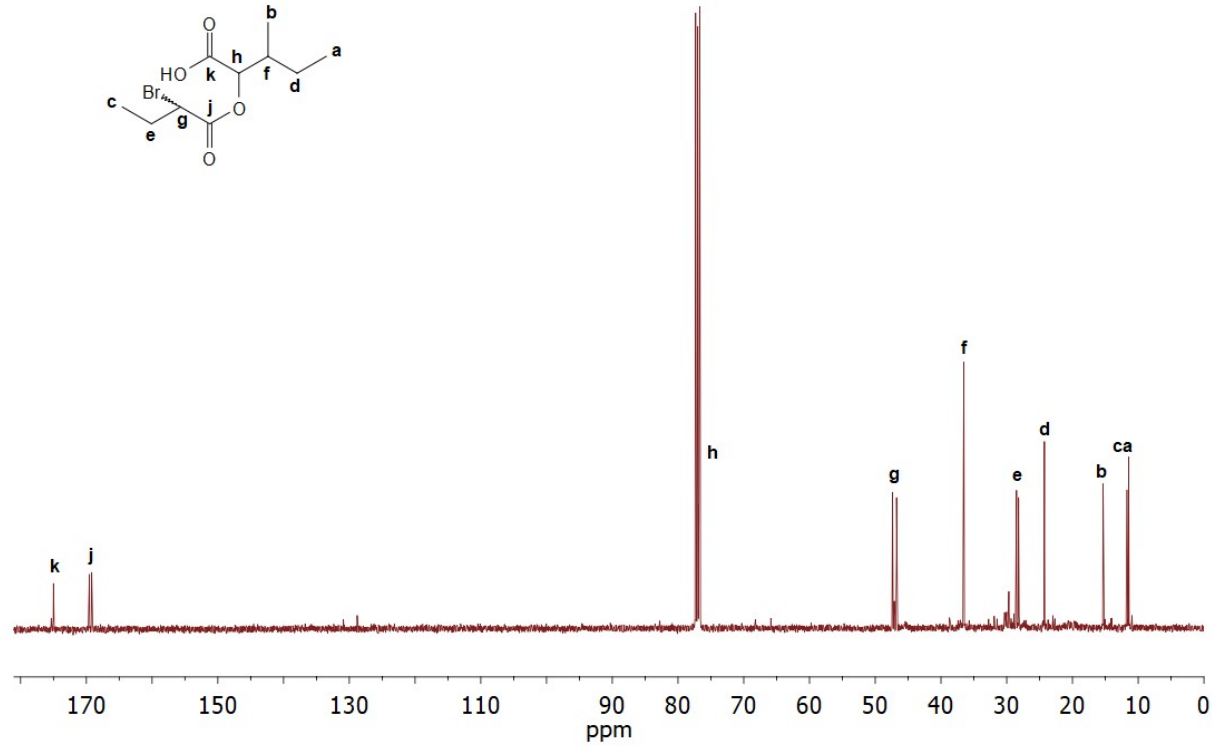

Figure S22. [13]C NMR spectrum of intermediate **14** (a mixture of diastereomers)[1]

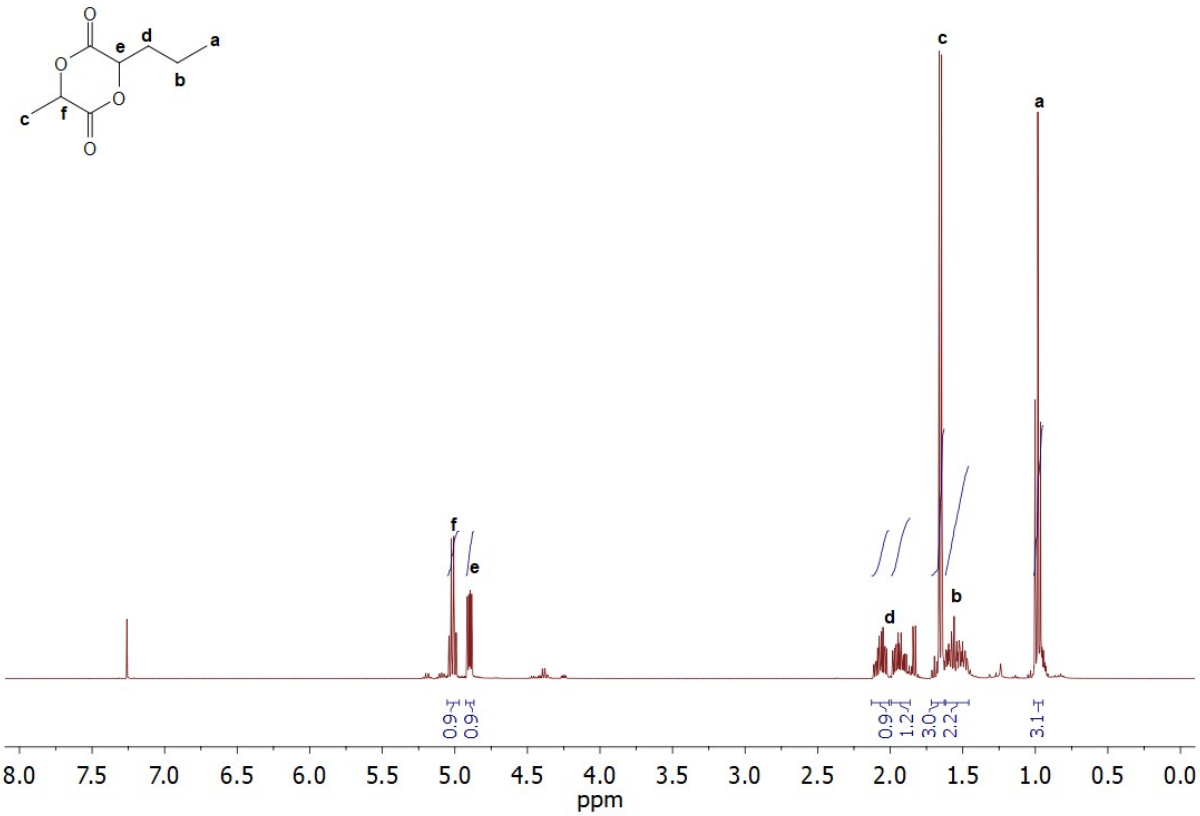

Figure S23. ^{1}H NMR spectrum of **I (PMG)**

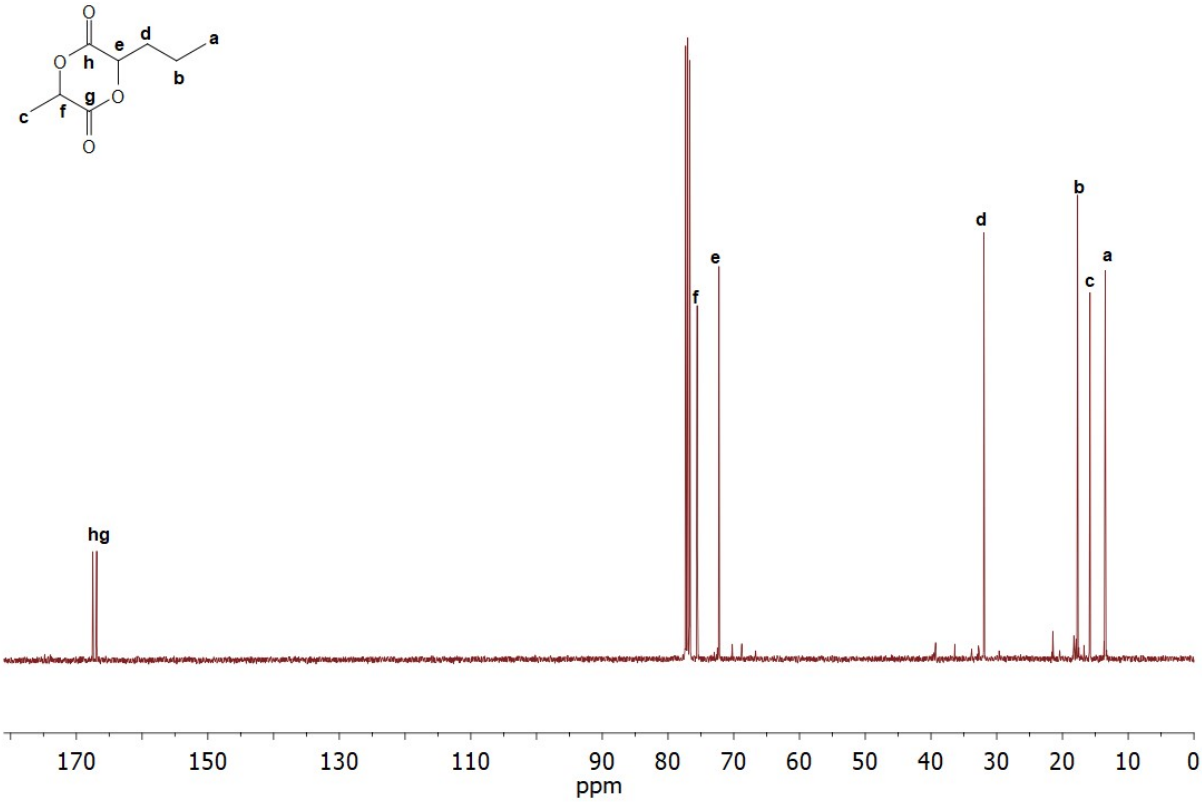

Figure S24. ^{13}C NMR spectrum of **I (PMG)** (a mixture of diastereomers)[1]

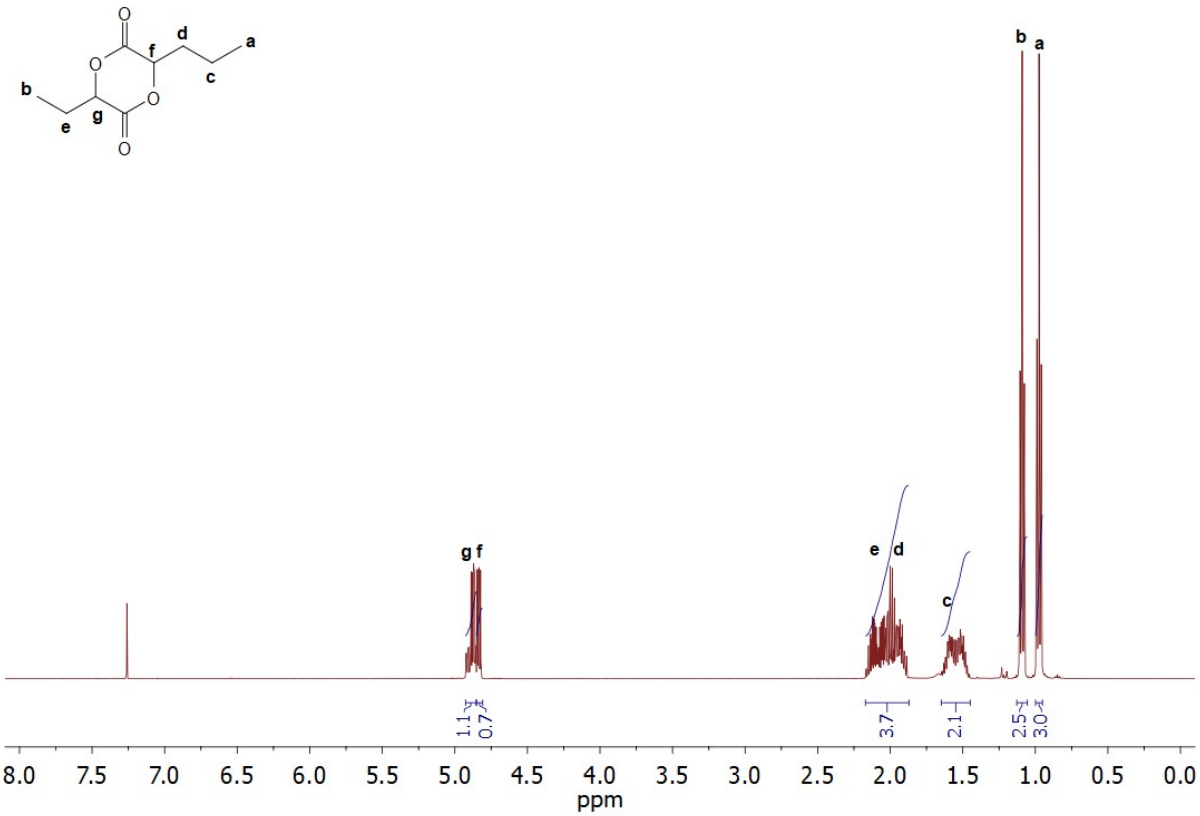

Figure S25. ^{1}H NMR spectrum of **II (PEG)**

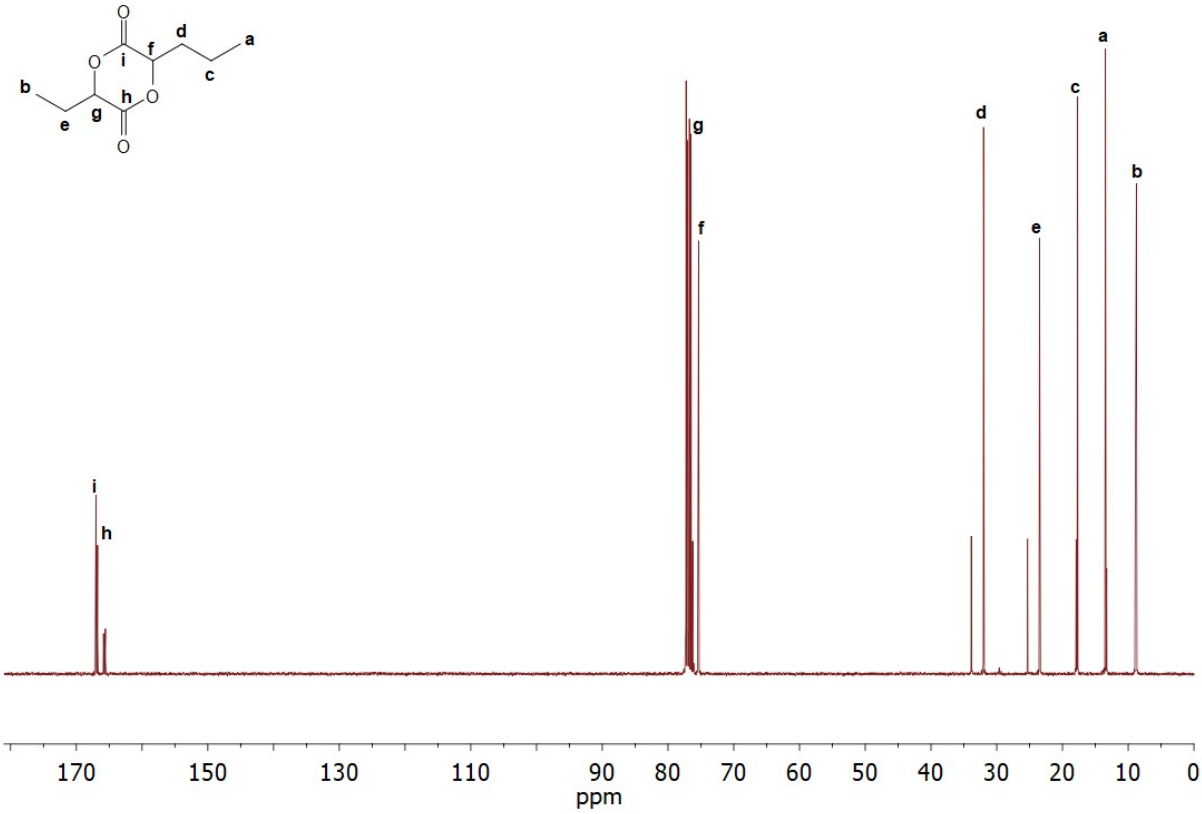

Figure S26. ^{13}C NMR spectrum of **II (PEG)** (a mixture of diastereomers)[1]

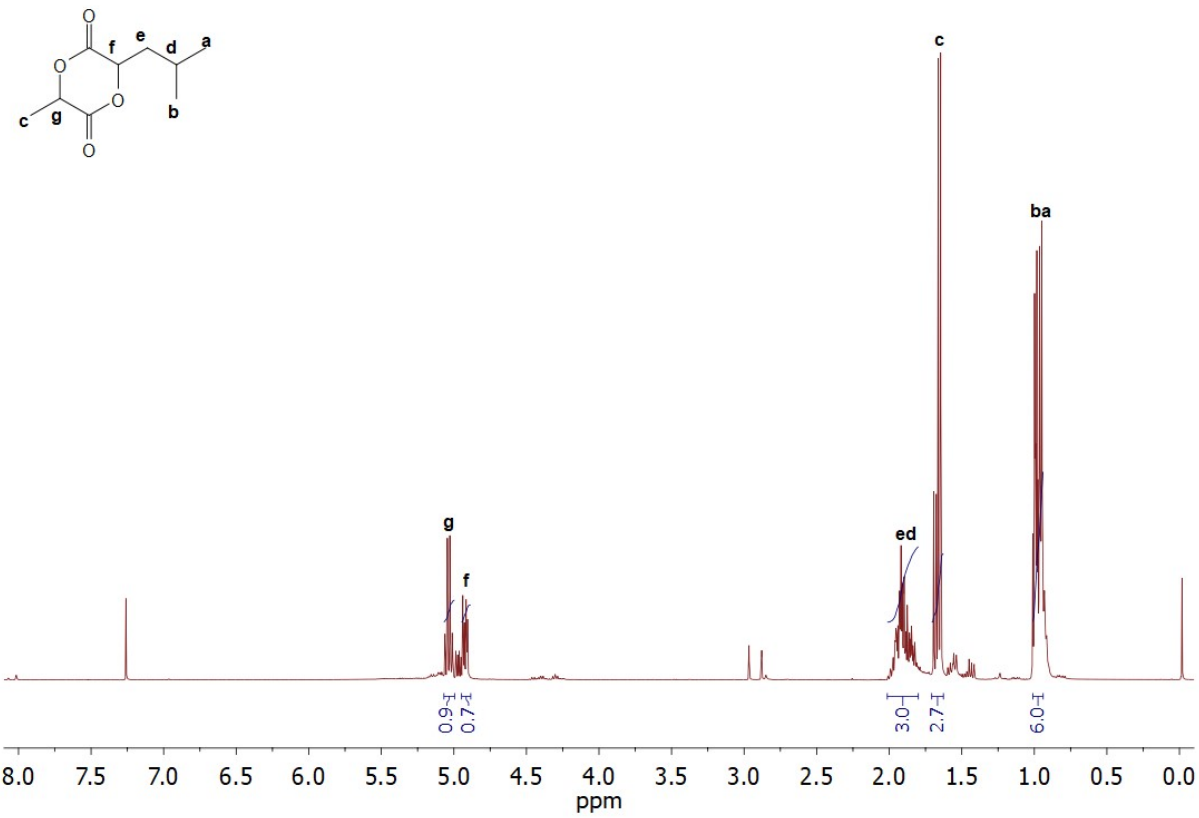

Figure S27. [1]H NMR spectrum of **III (IBMG)**

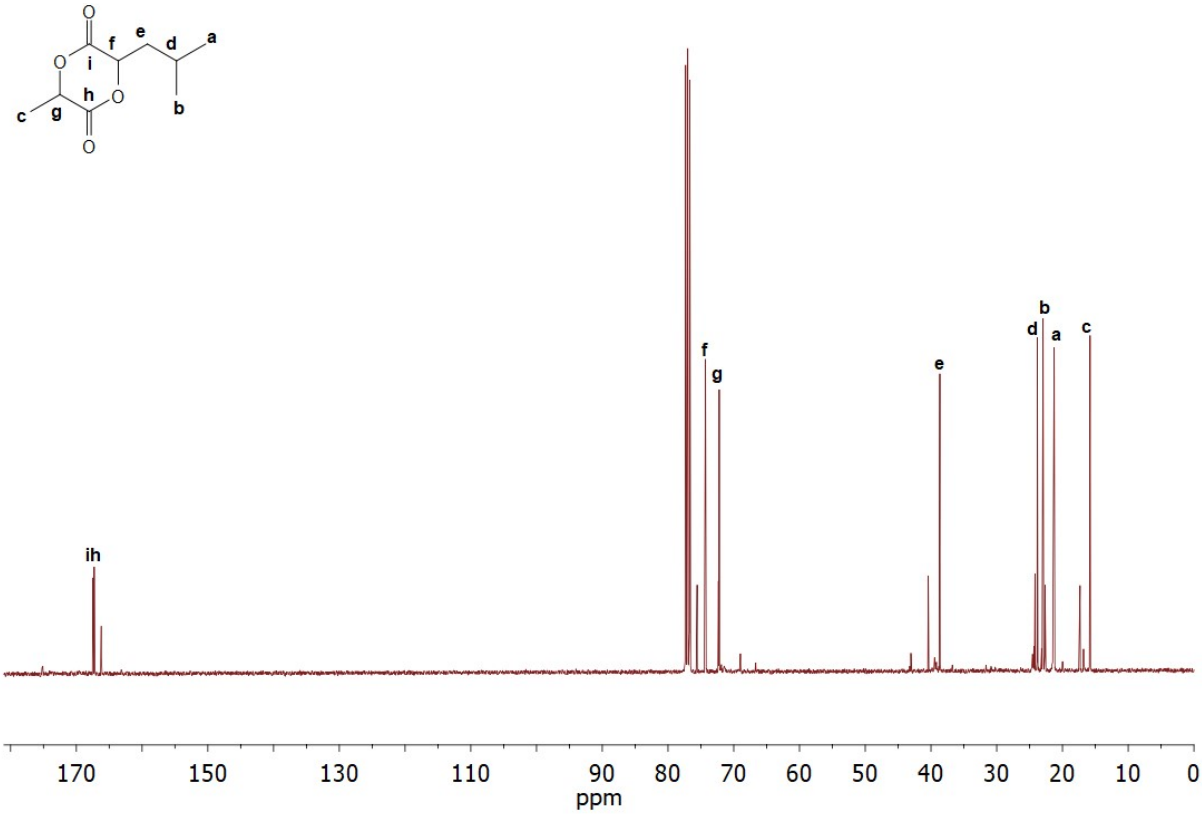

Figure S28. [13]C NMR spectrum of **III (IBMG)** (a mixture of diastereomers)[1]

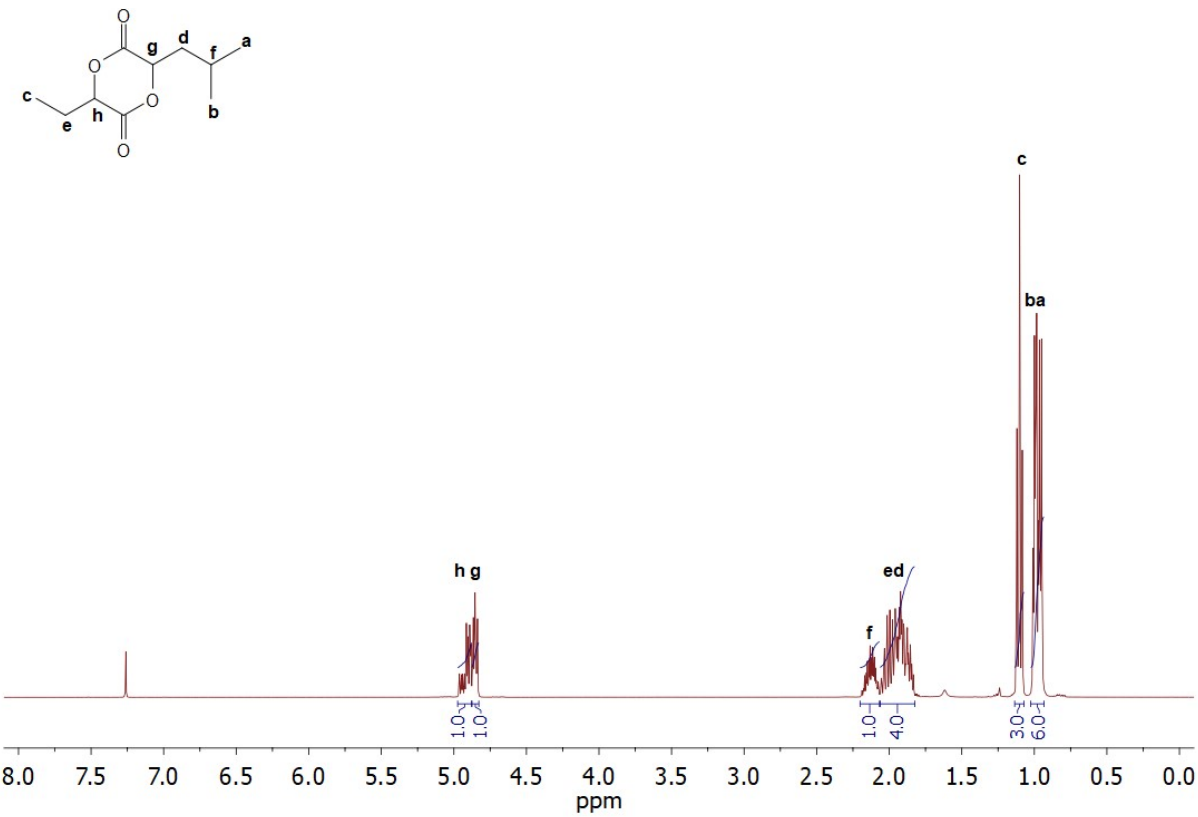

Figure S29. [1]H NMR spectrum of **IV (IBEG)**

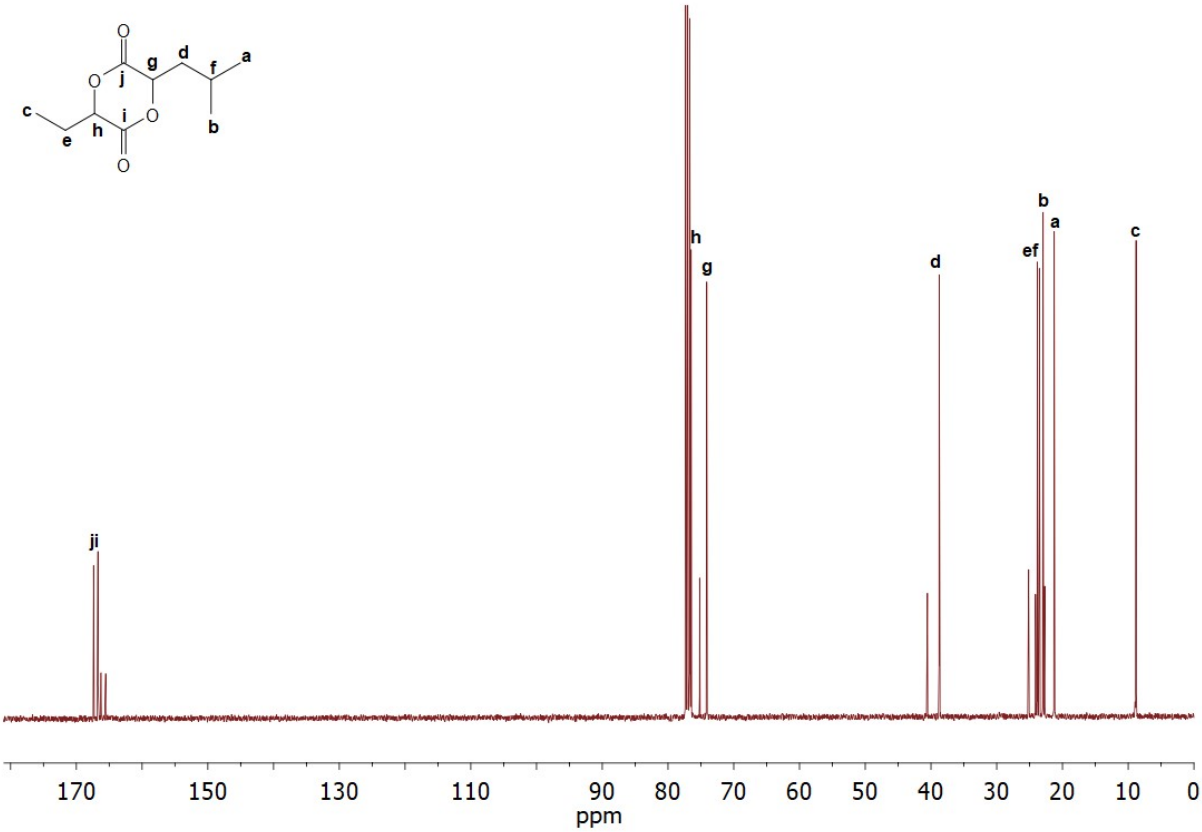

Figure S30. [13]C NMR spectrum of **IV (IBEG)** (a mixture of diastereomers)[1]

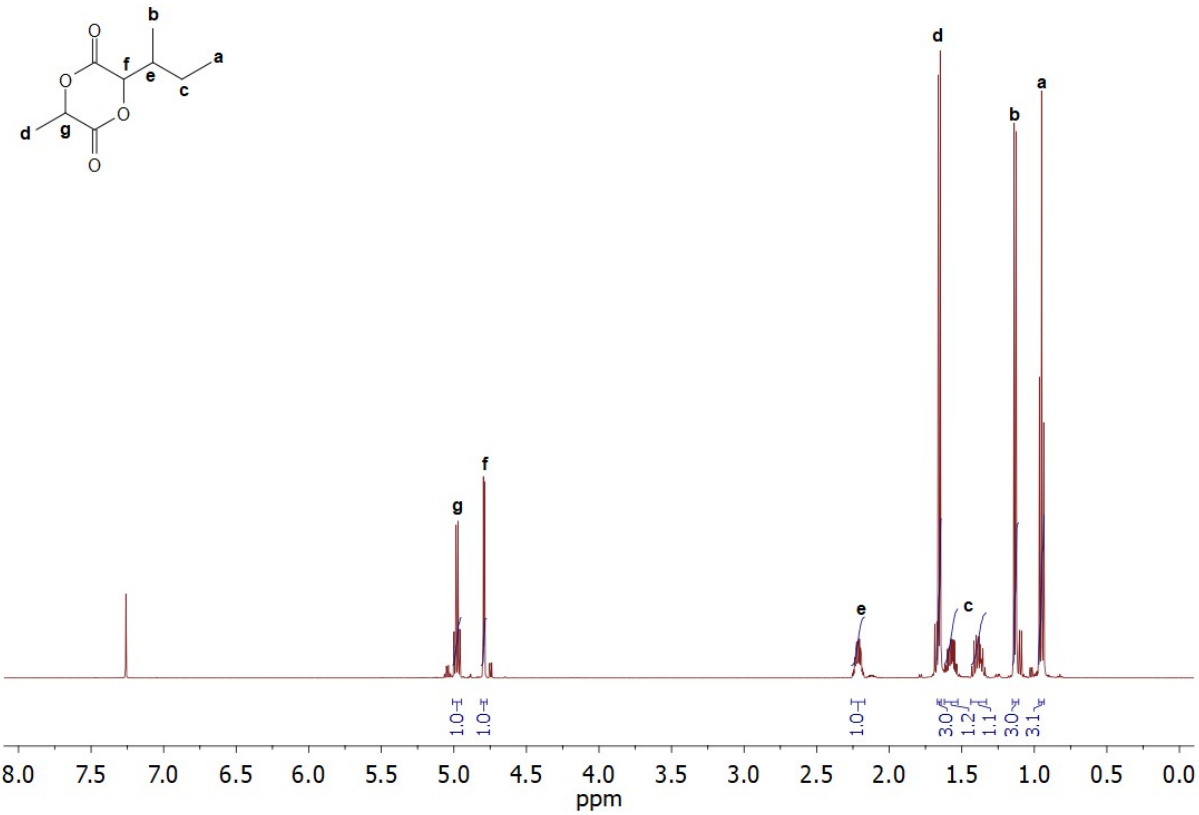

Figure S31. ^{1}H NMR spectrum of **V (ILMG)**

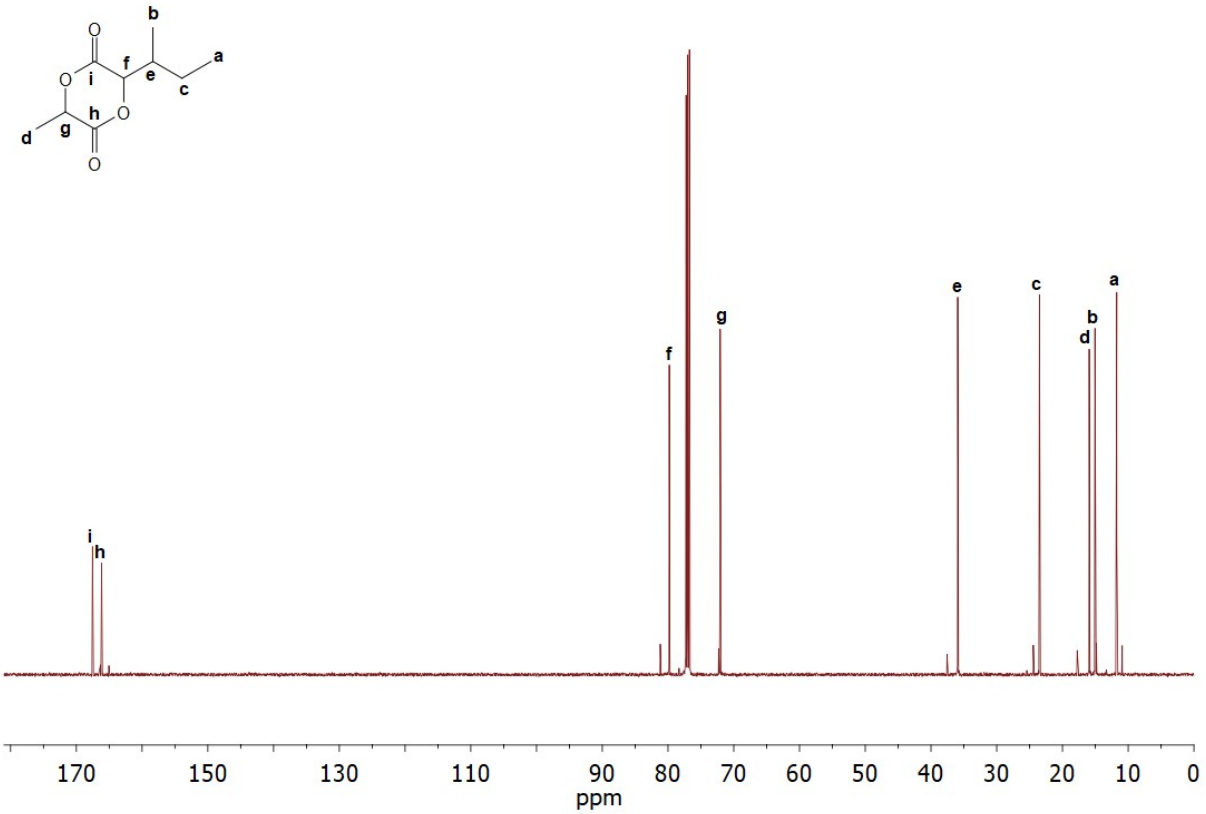

Figure S32. ^{13}C NMR spectrum of **V (ILMG)** (a mixture of diastereomers)[1]

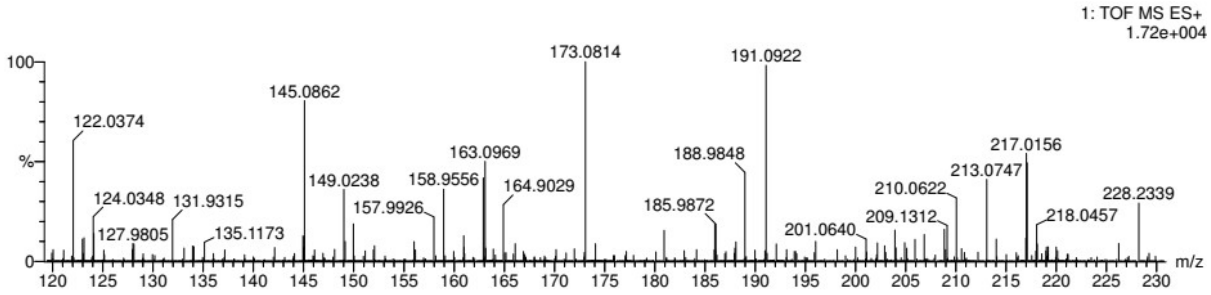

Figure S33. HRMS spectrum of **I (PMG)**

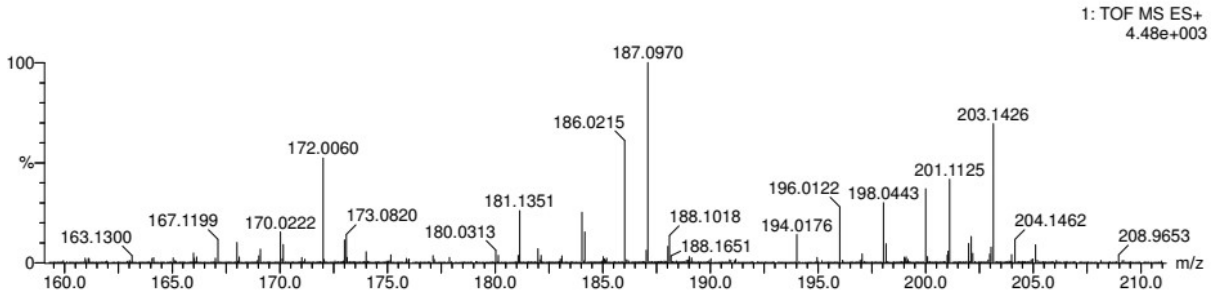

Figure S34. HRMS spectrum of **II (PEG)**

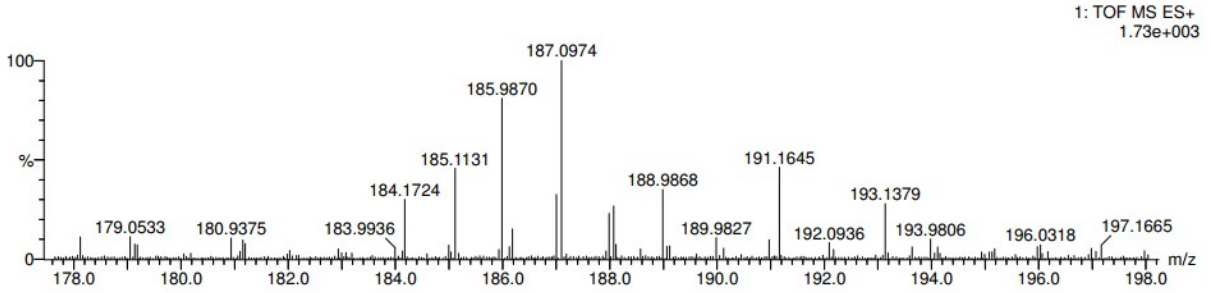

Figure S35. HRMS spectrum of **III (IBMG)**

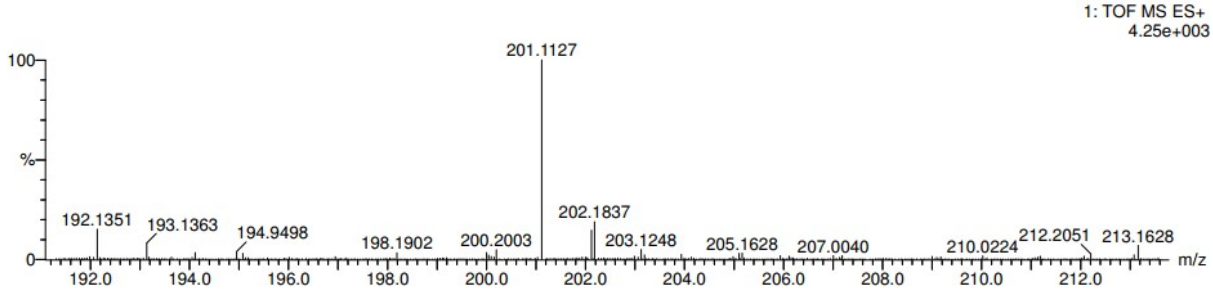

Figure S36. HRMS spectrum of **IV (IBEG)**

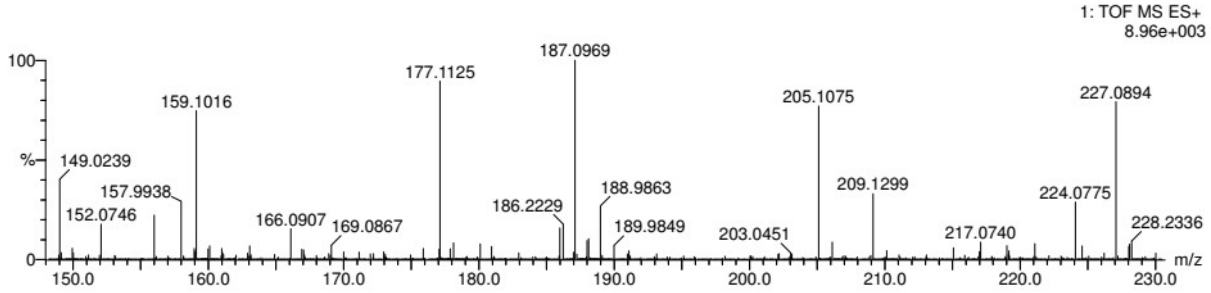

Figure S37. HRMS spectrum of **V (ILMG)**

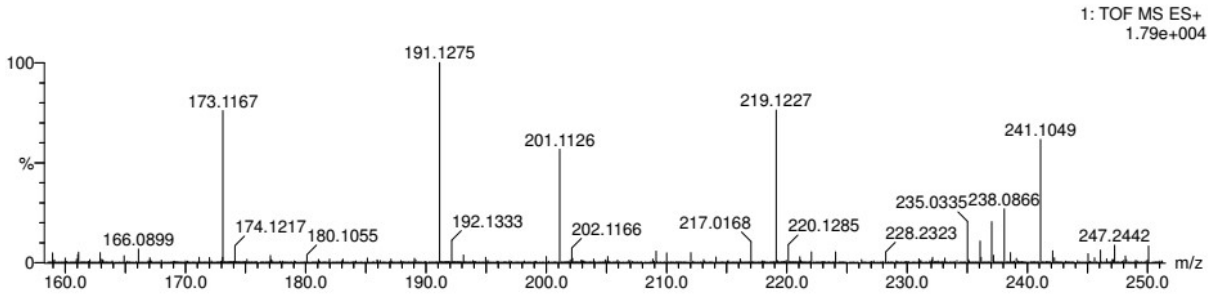

Figure S38. HRMS spectrum of **VI (ILEG)**

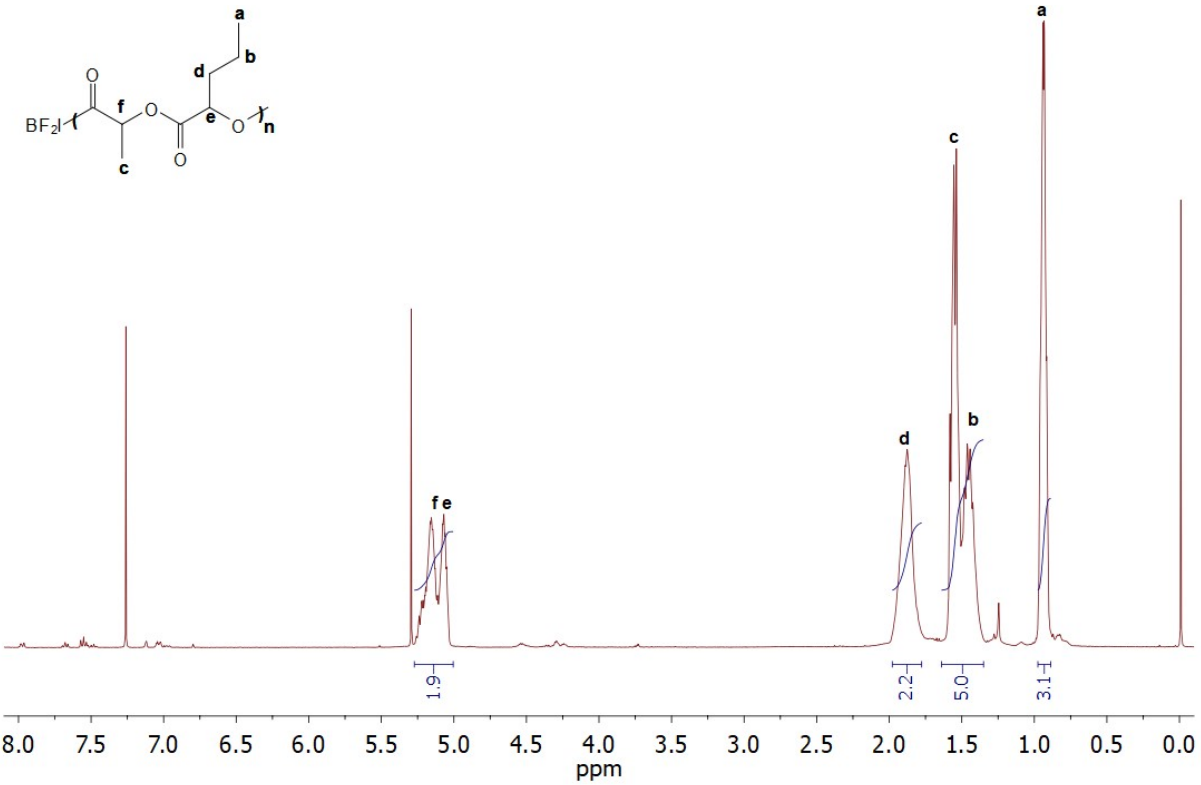

Figure S39. ^{1}H NMR spectrum of **16** (**BF_2I-PPMG)**

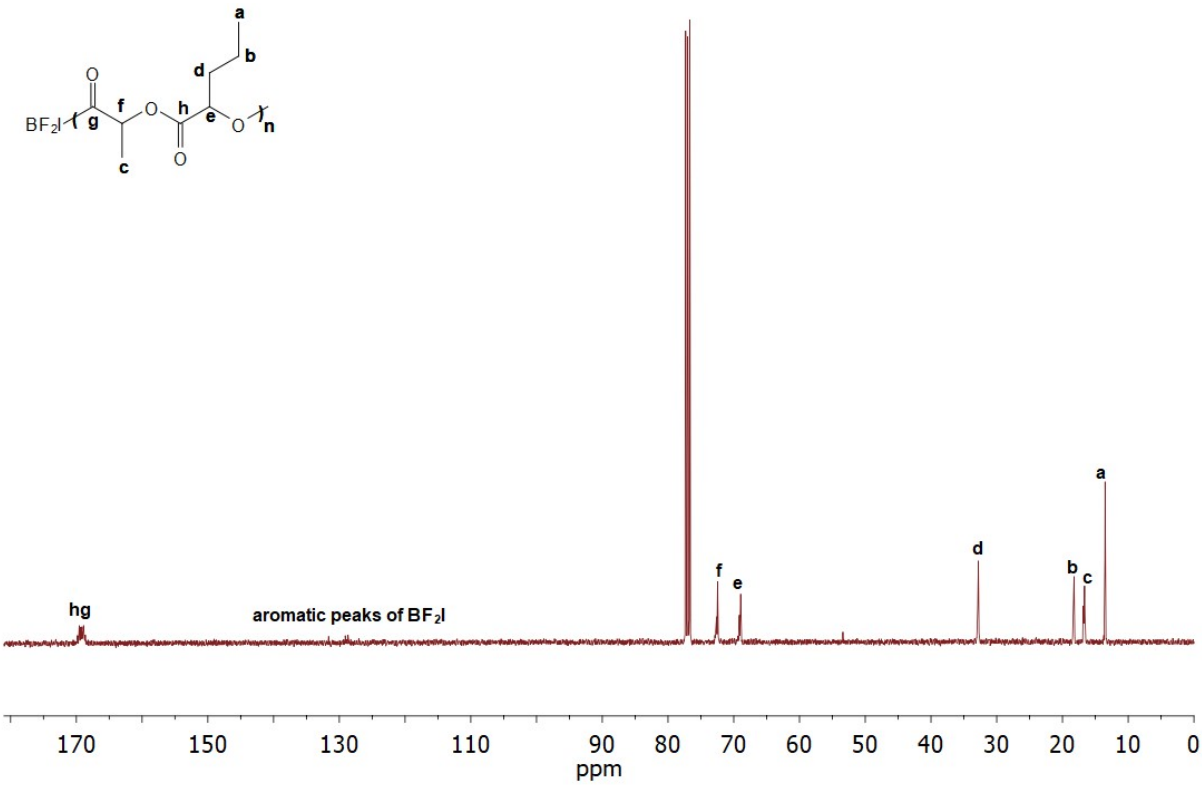

Figure S40. ^{13}C NMR spectrum of **16 (BF_2I-PPMG)**

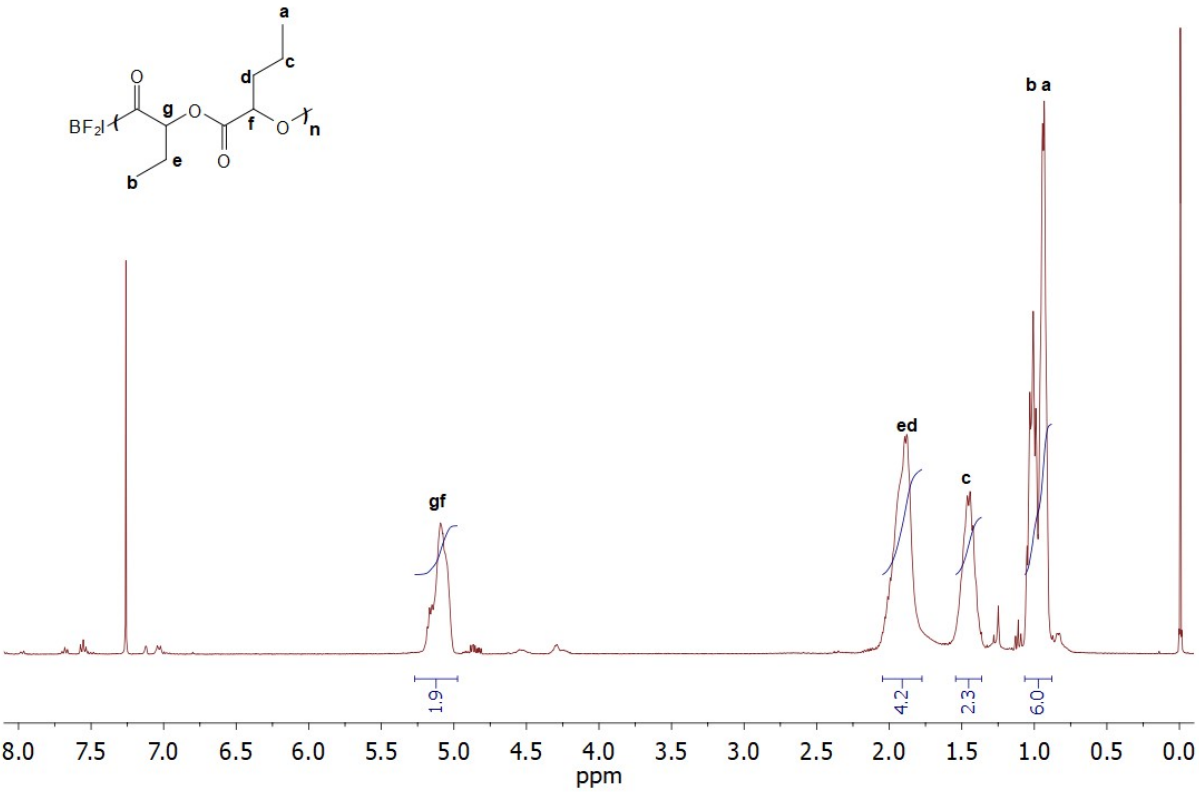

Figure S41. ^{1}H NMR spectrum of **17 (BF_2I-PPEG)**

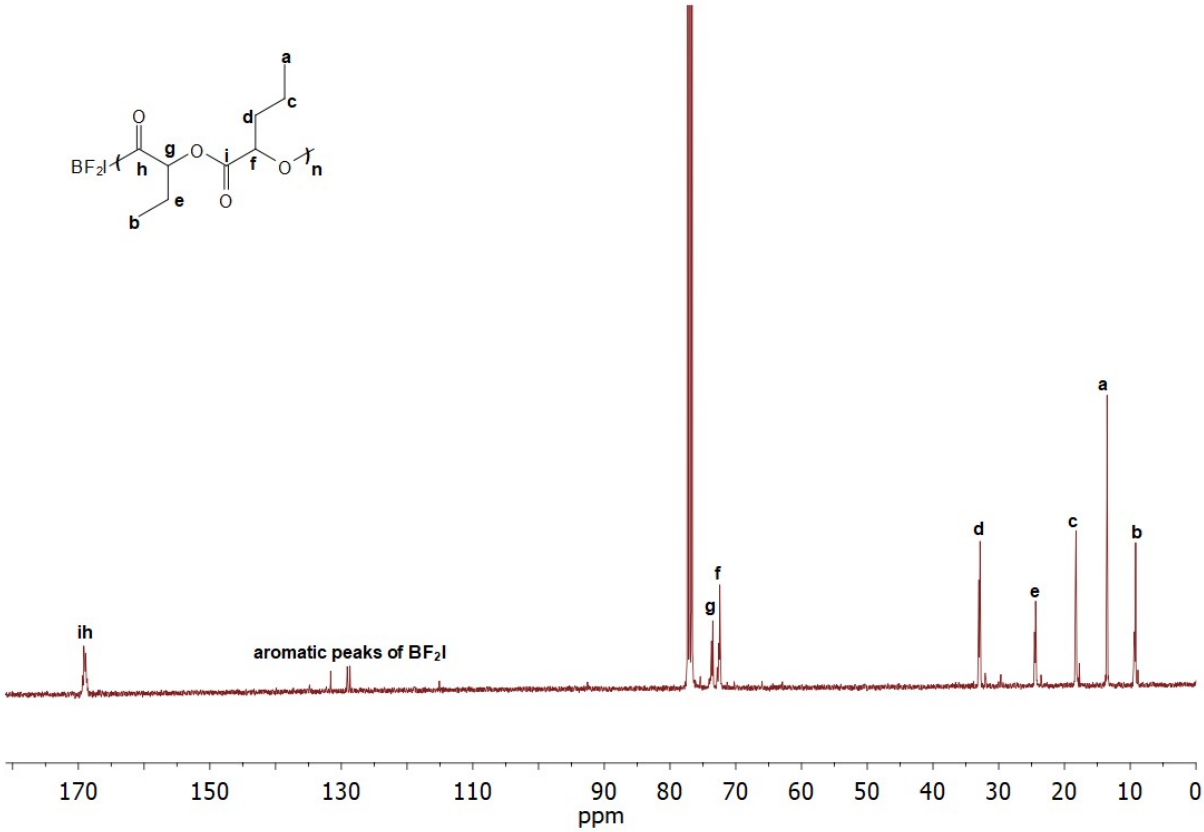

Figure S42. ^{13}C NMR spectrum of **17 (BF_2I-PPEG)**

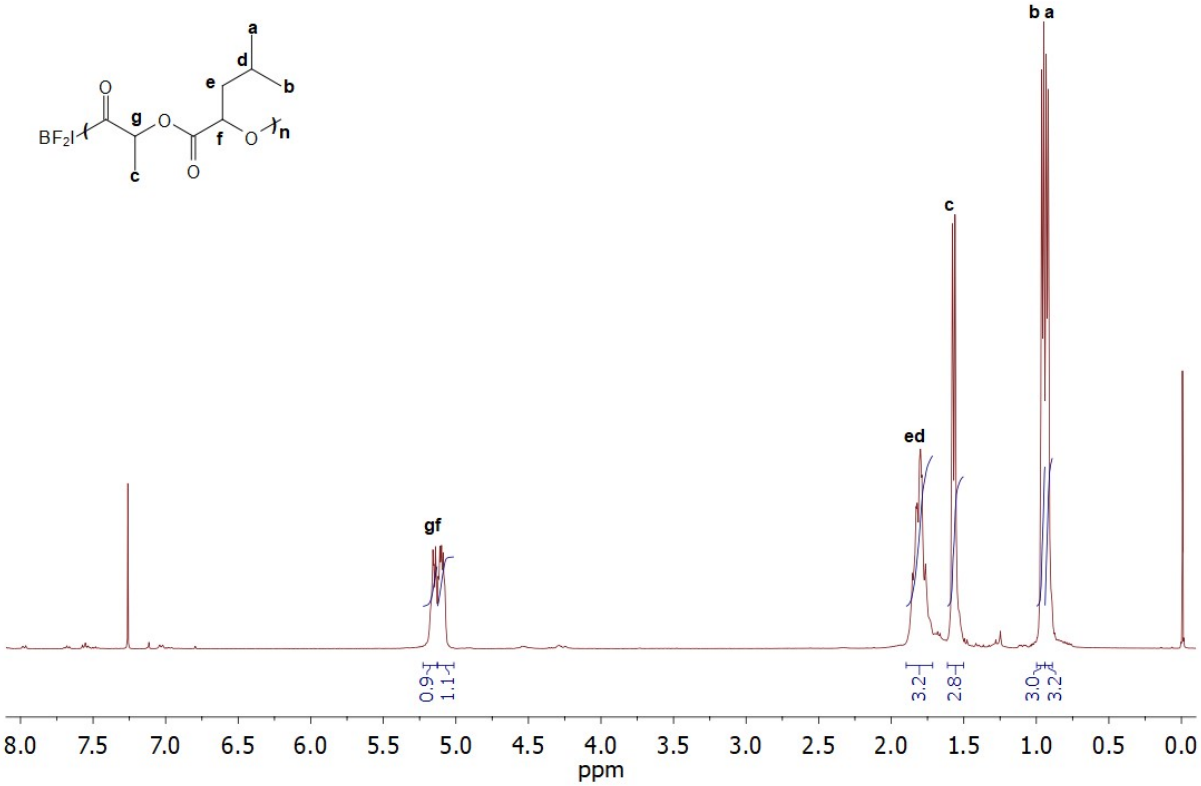

Figure S43. ^{1}H NMR spectrum of **18 (BF_2I-PIBMG)**

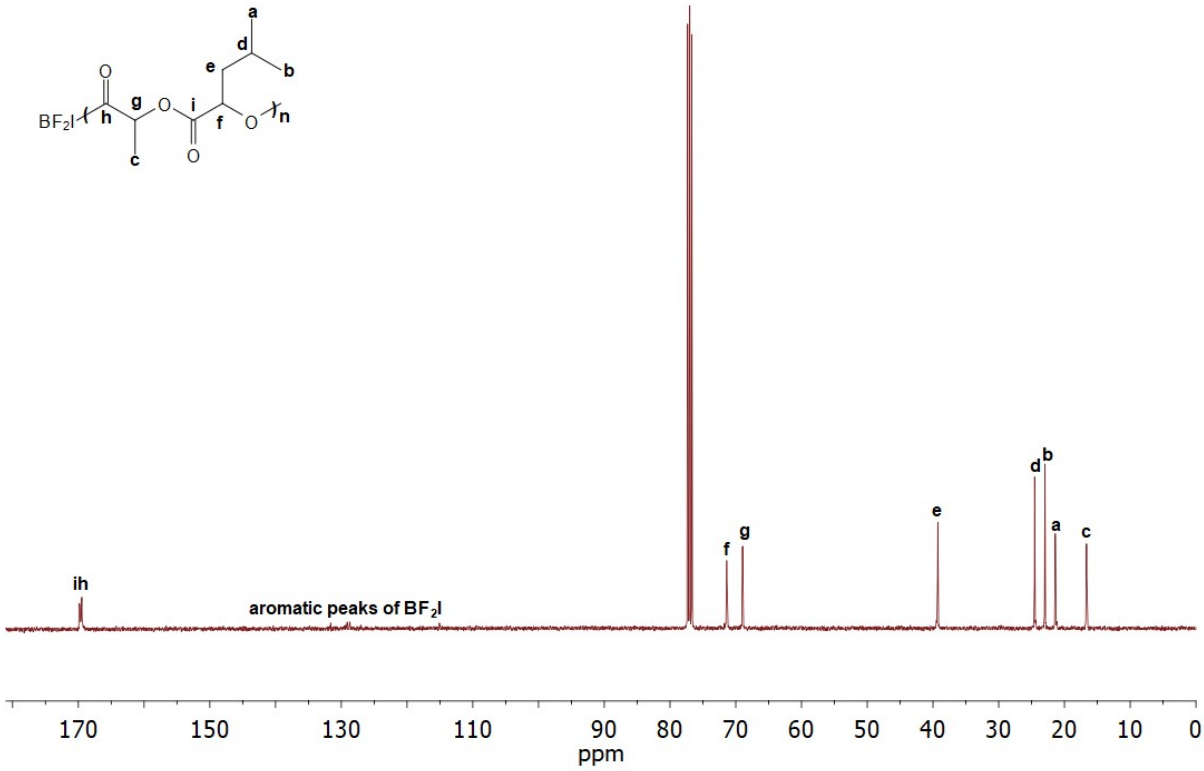

Figure S44. ^{13}C NMR spectrum of **18 (BF_2I-PIBMG)**

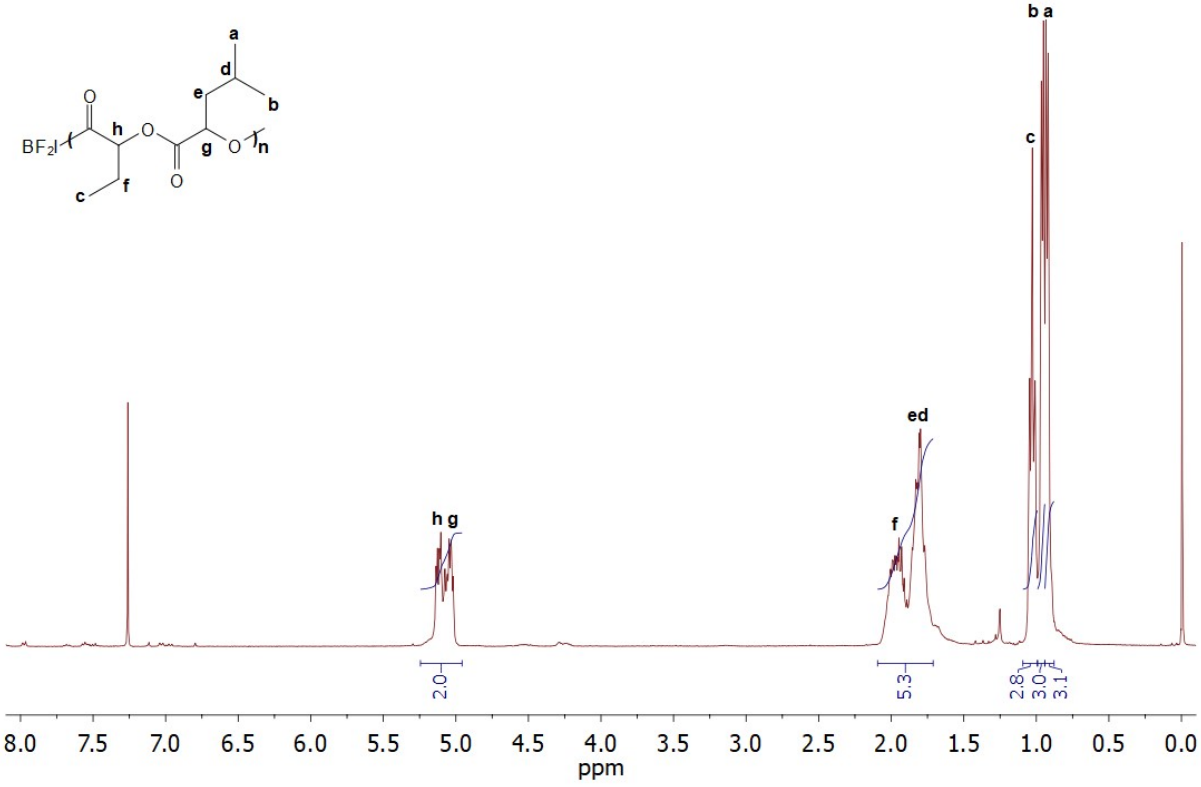

Figure S45. ^{1}H NMR spectrum of **19 (BF_2I-PIBEG)**

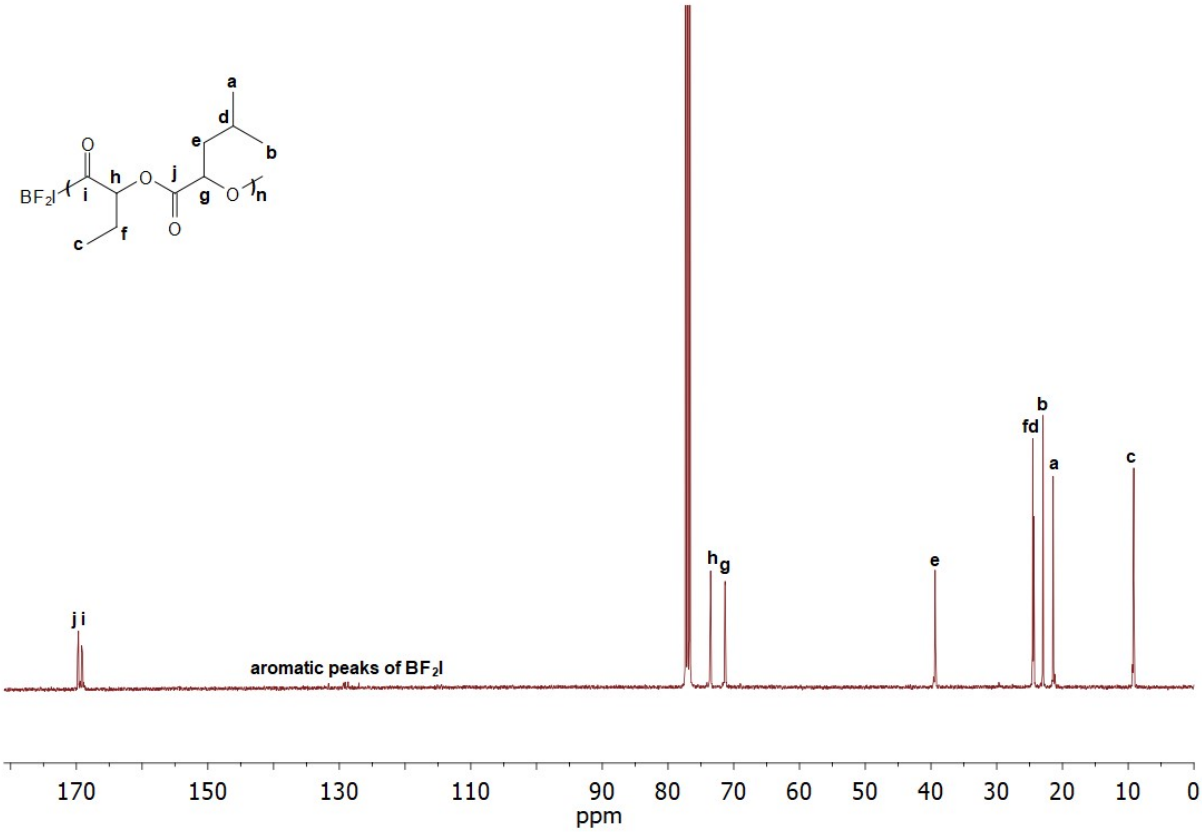

Figure S46. ^{13}C NMR spectrum of **19** (**BF_2I-PIBEG)**

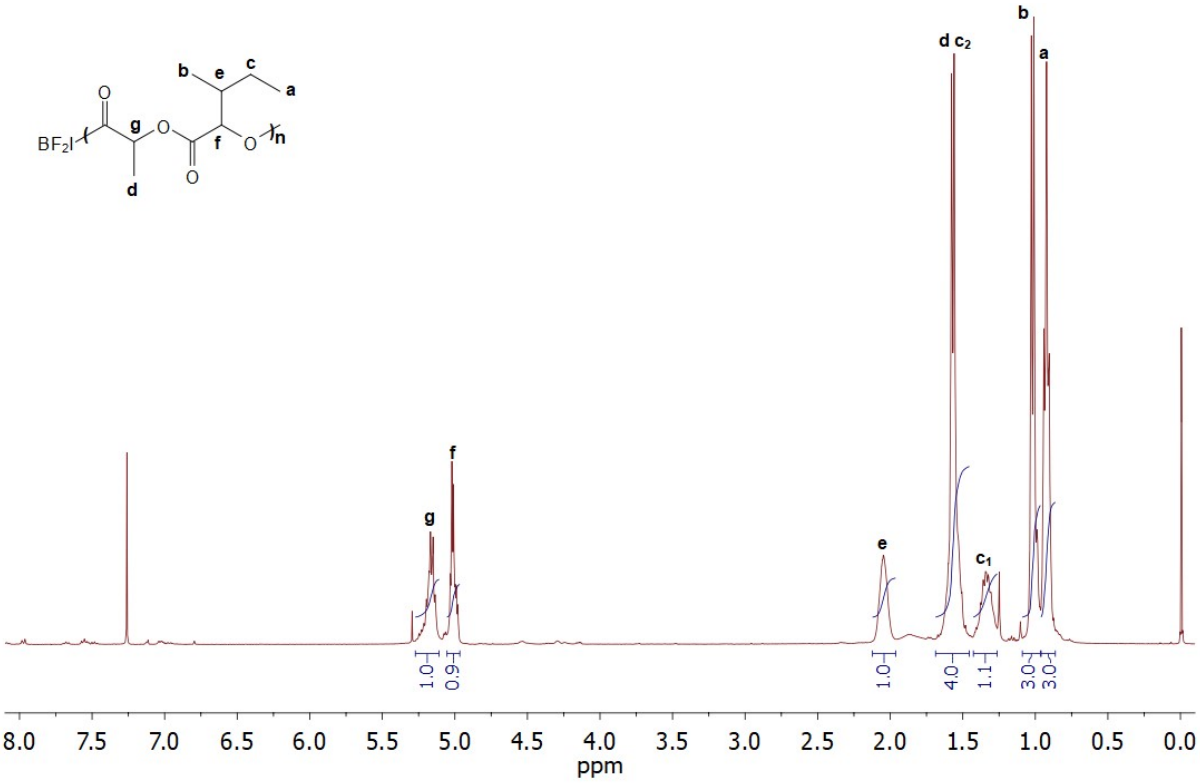

Figure S47. ^{1}H NMR spectrum of **20** (**BF_2I-PILMG)**

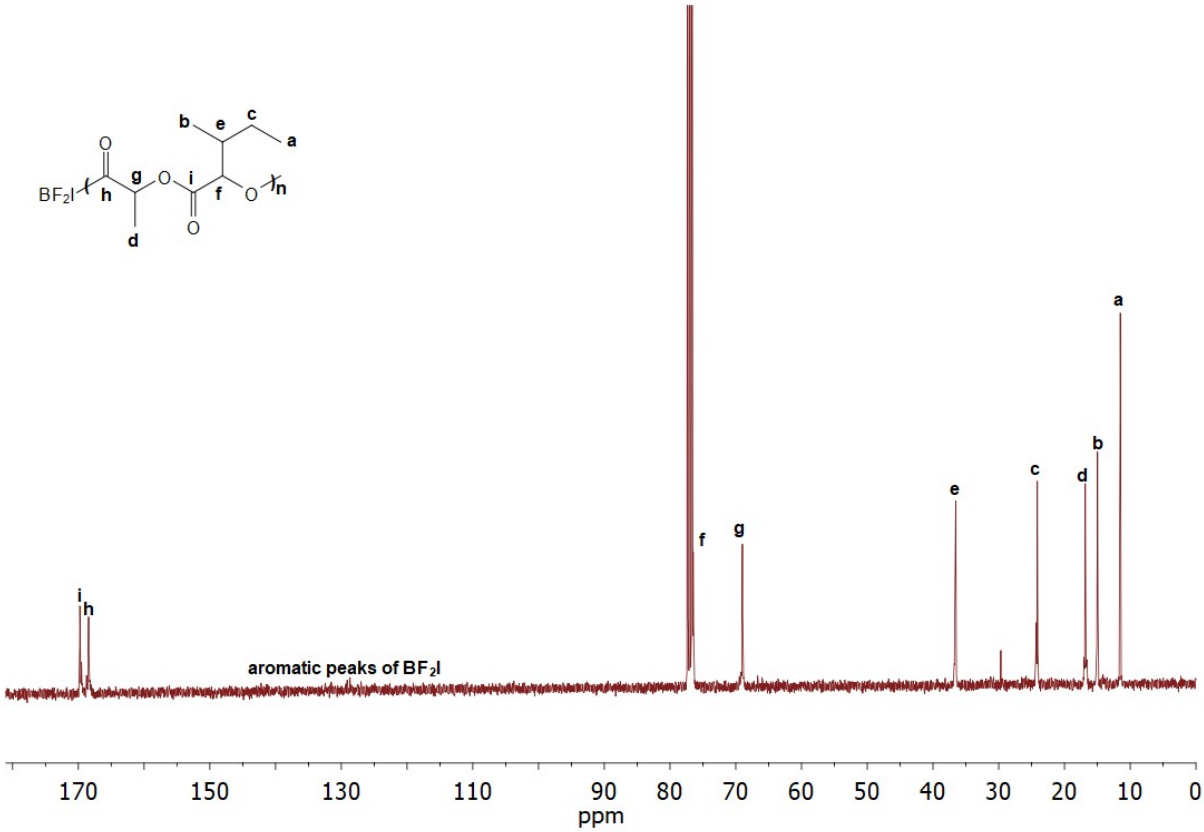

Figure S48. ^{13}C NMR spectrum of **20** (**BF_2I-PILMG)**

III. UV/Vis Spectra of 15-22

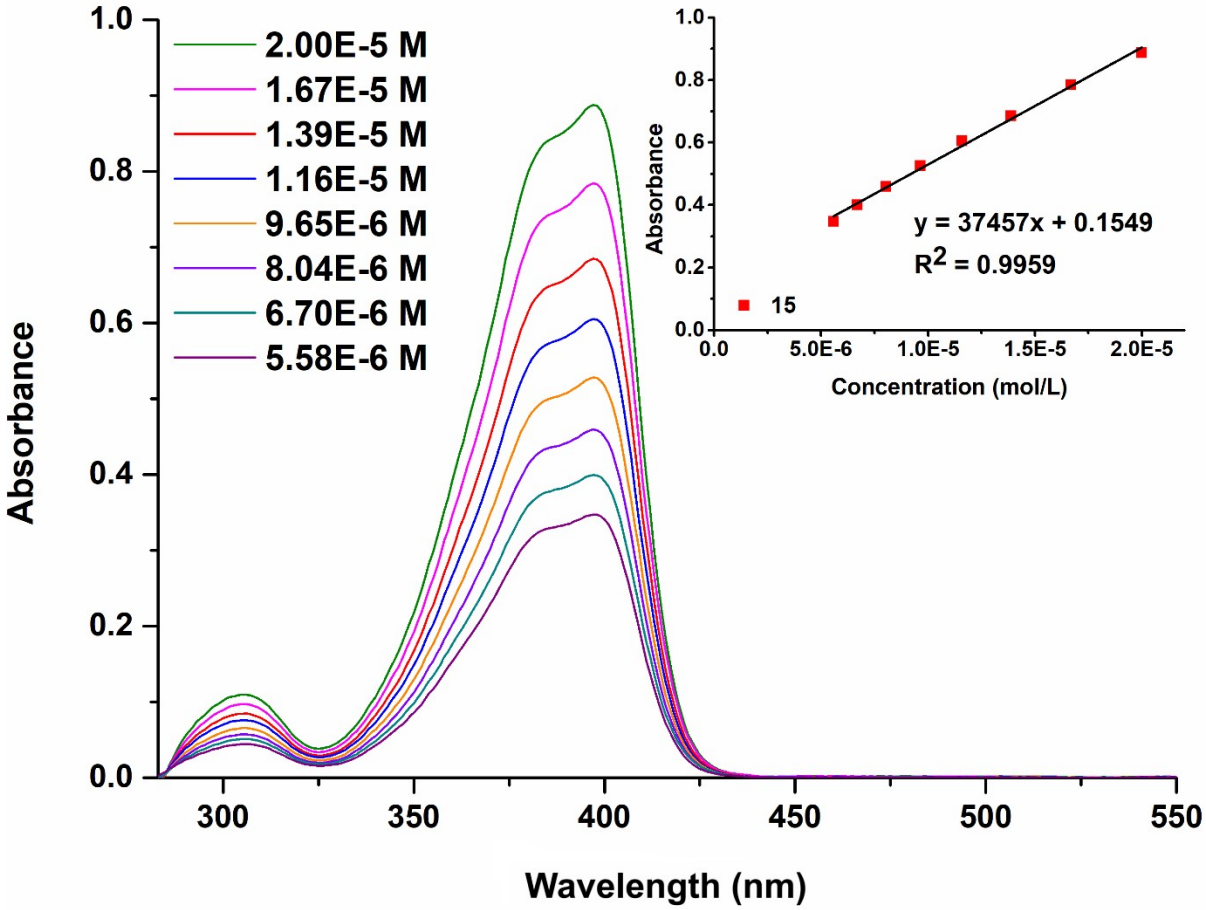

Figure S49. Wavelength-absorption change at different concentrations, and concentration-absorption change (inlet) for boron **BF_2I 15** initiator

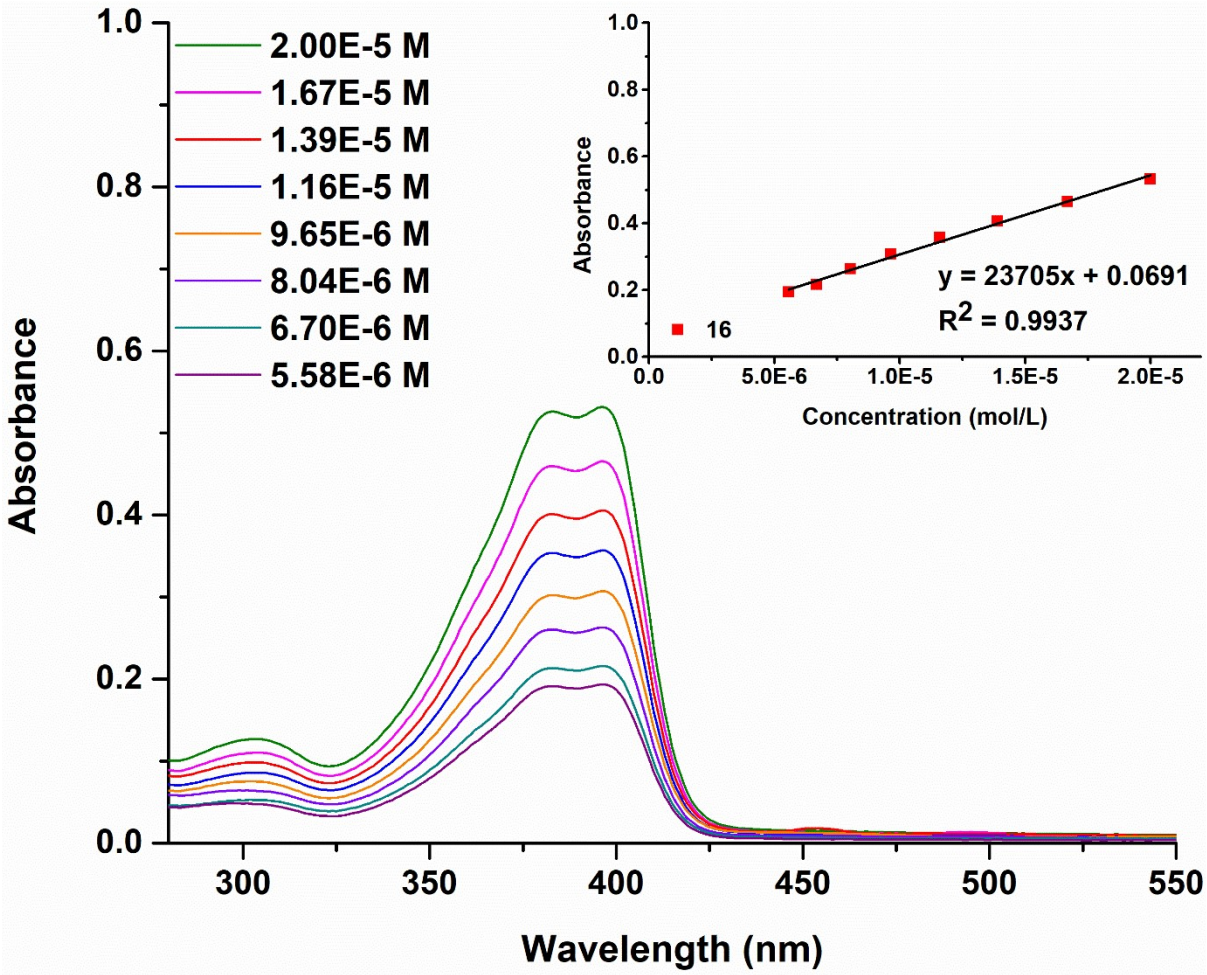

Figure S50. Wavelength-absorption change at different concentrations, and concentration-absorption change (inlet) for **BF_2I-PPMG 16**

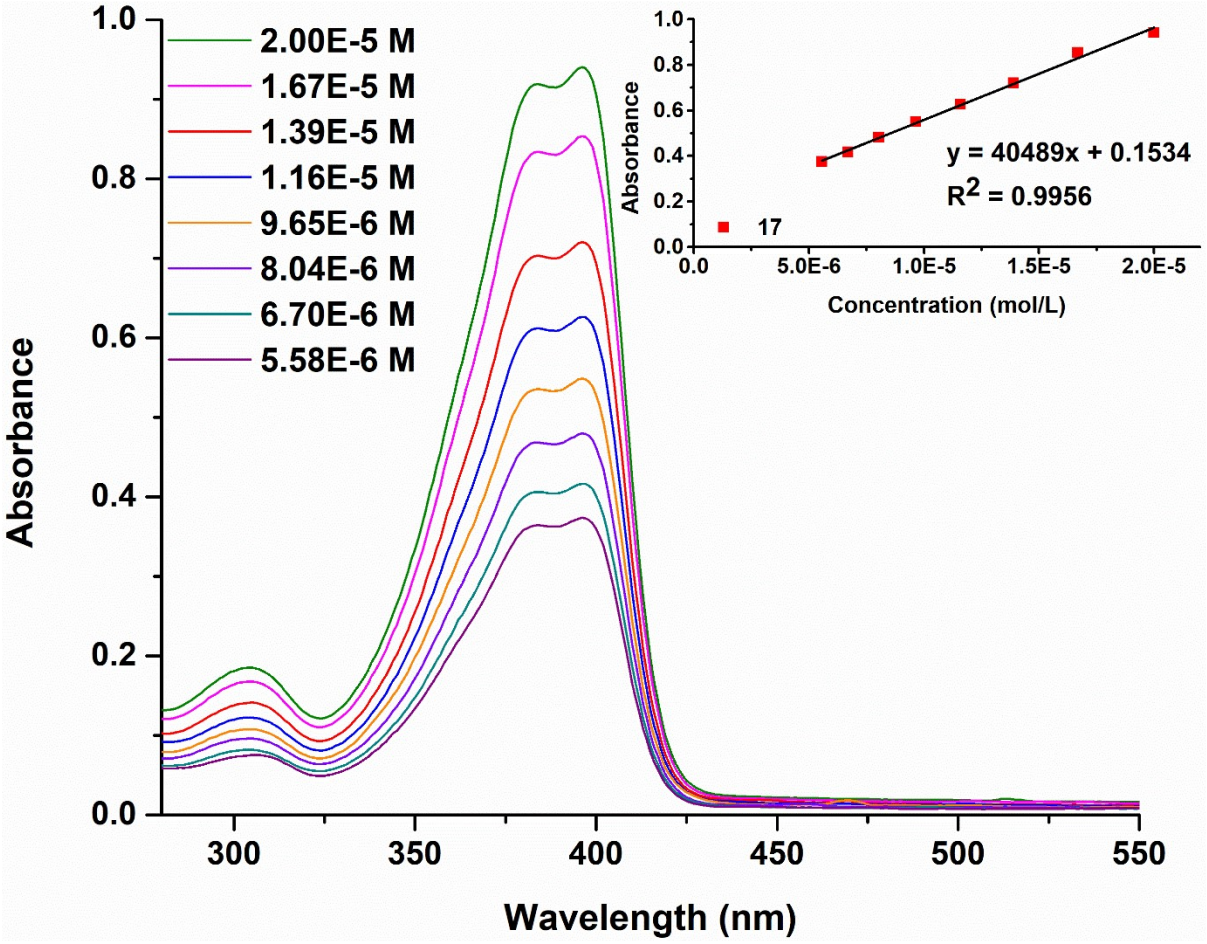

Figure S51. Wavelength-absorption change at different concentrations, and concentration-absorption change (inlet) for **BF_2I-PPEG 17**

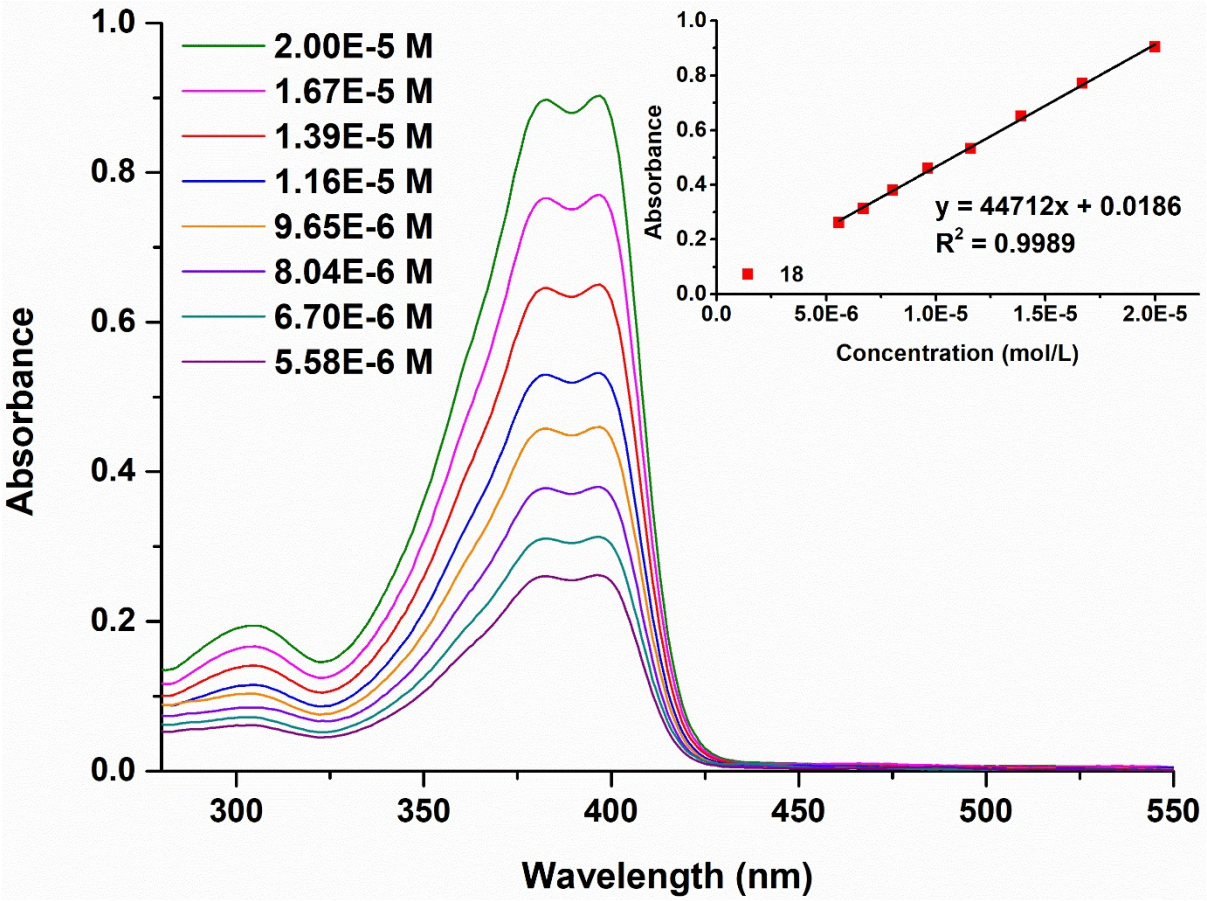

Figure S52. Wavelength-absorption change at different concentrations, and concentration-absorption change (inlet) for **BF_2I-PIBMG 18**

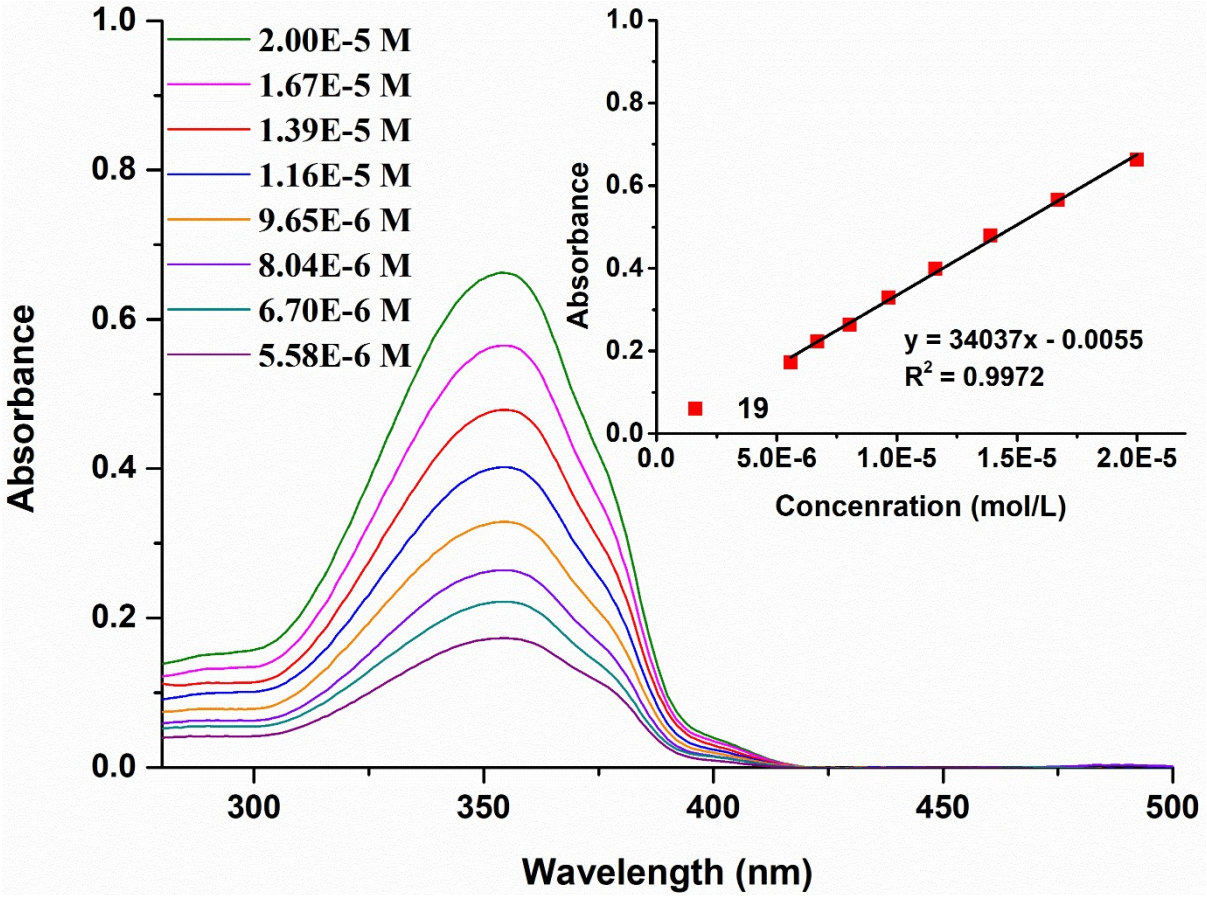

Figure S53. Wavelength-absorption change at different concentrations, and concentration-absorption change (inlet) for **BF_2I-PIBEG 19**

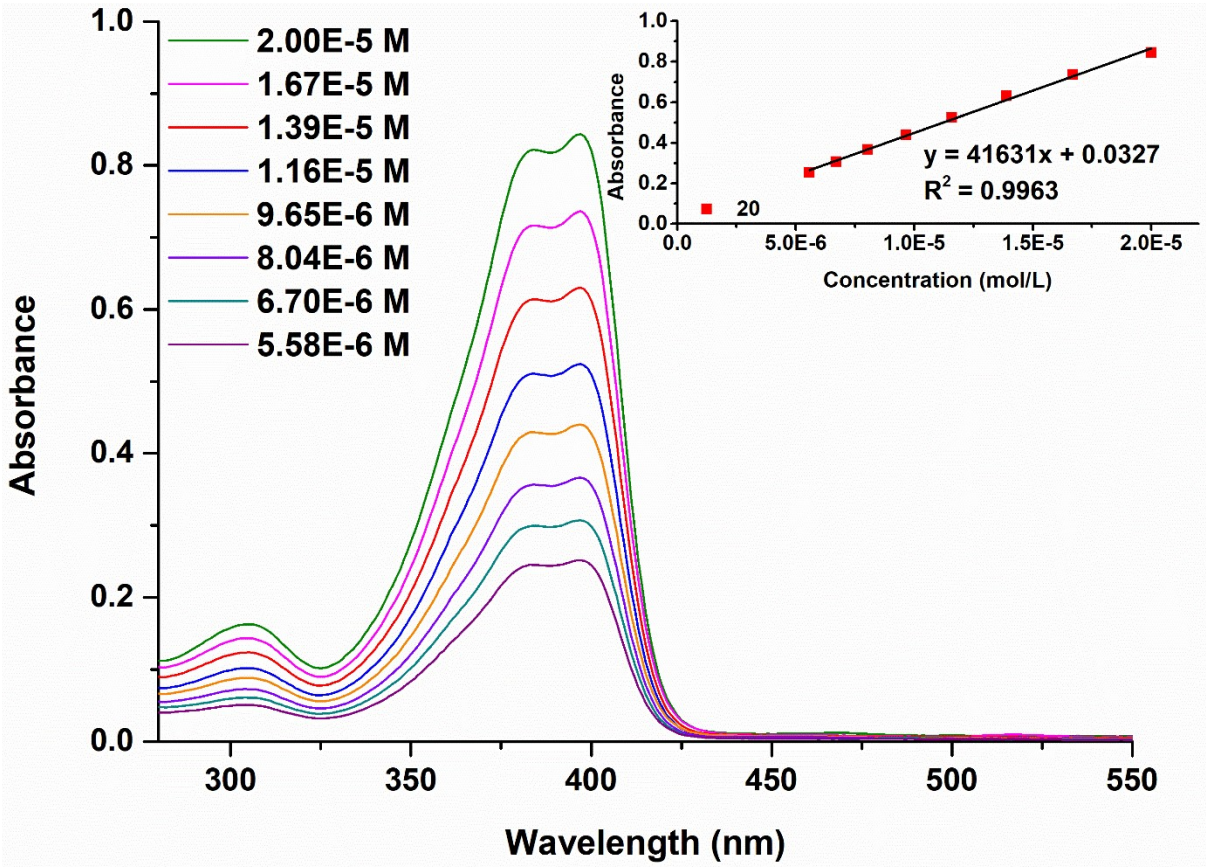

Figure S54. Wavelength-absorption change at different concentrations, and concentration-absorption change (inlet) for **BF_2I-PILMG 20**

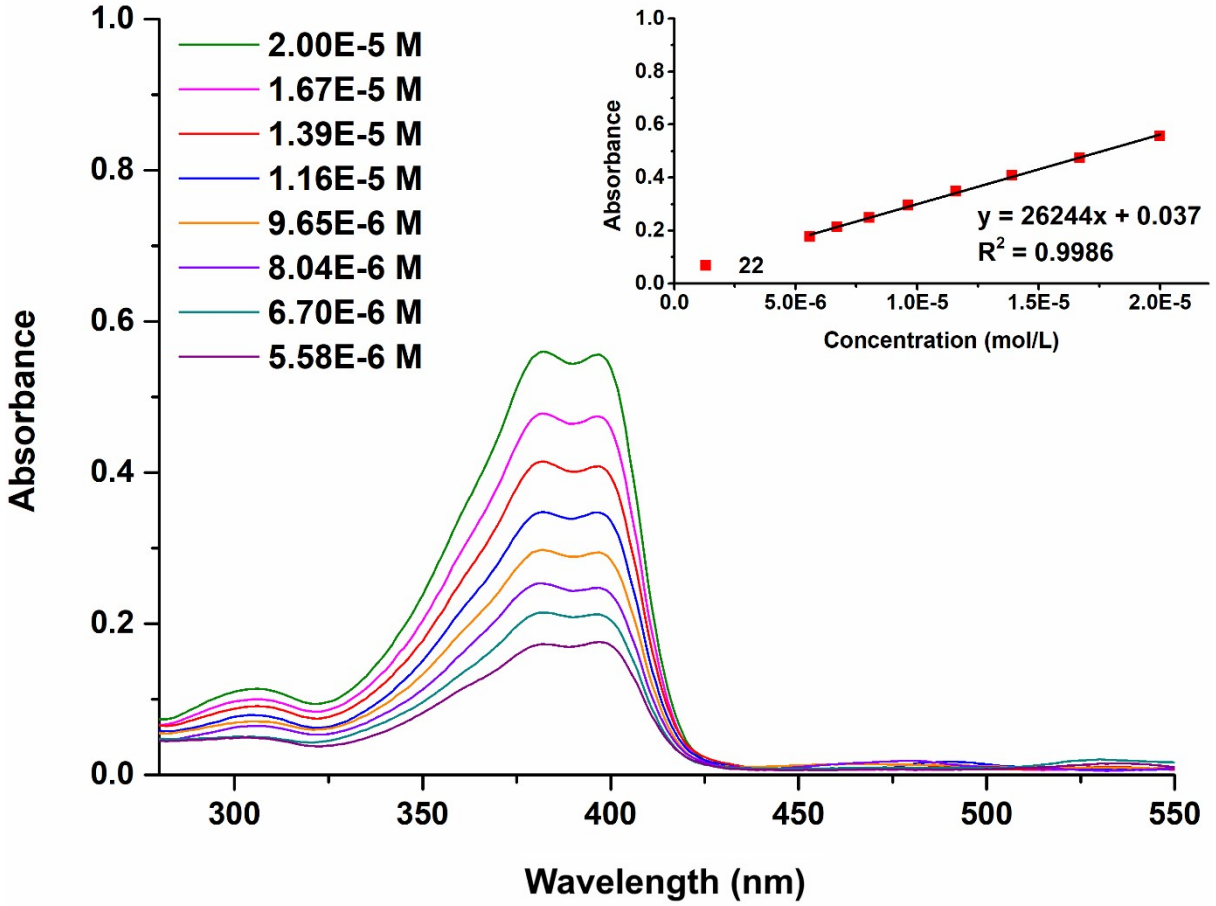

Figure S55. Wavelength-absorption change at different concentrations, and concentration-absorption change (inlet) for **BF_2I-PLA 22**

IV. Particle Size Distribution Graphs of 16-21

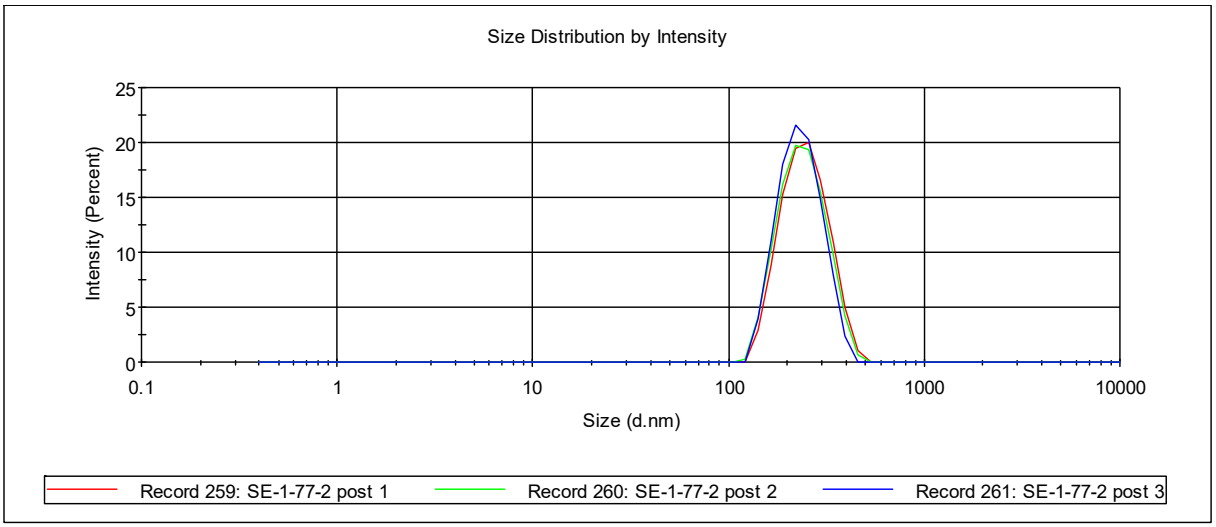

Figure S56. Intensity-size graph of PTX-BF_2I-PPMG-NP **16**

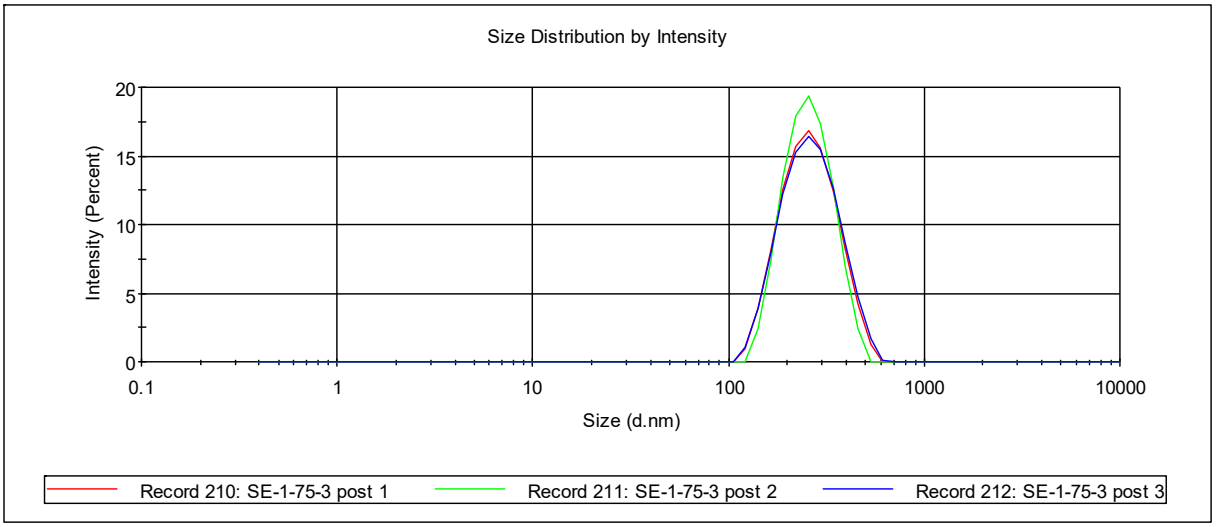

Figure S57. Intensity-size graph of PTX-BF_2I-PPEG-NP **17**

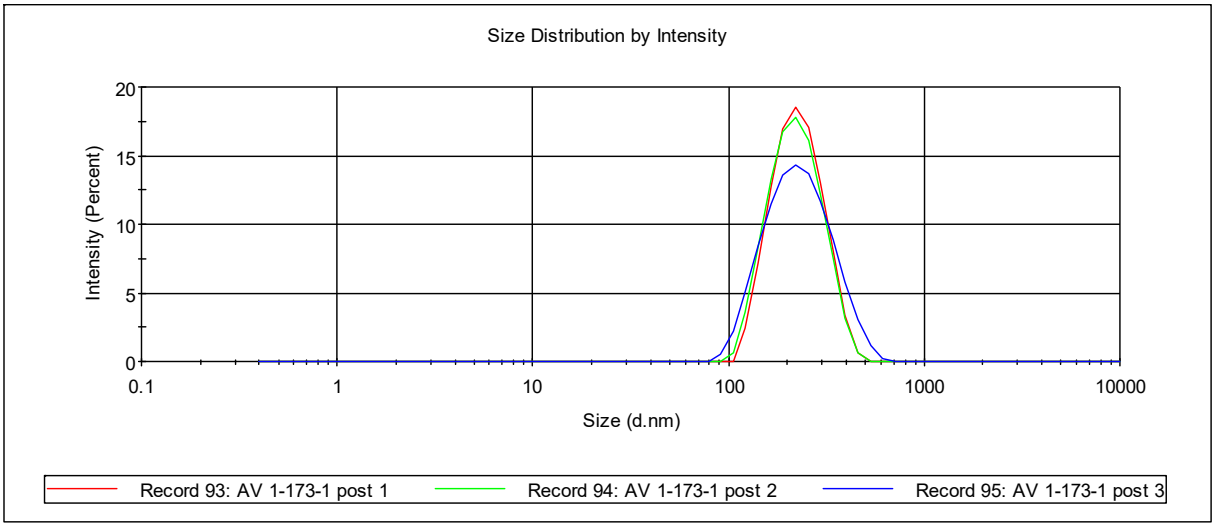

Figure S58. Intensity-size graph of PTX-BF_2I-PIBMG-NP **18**

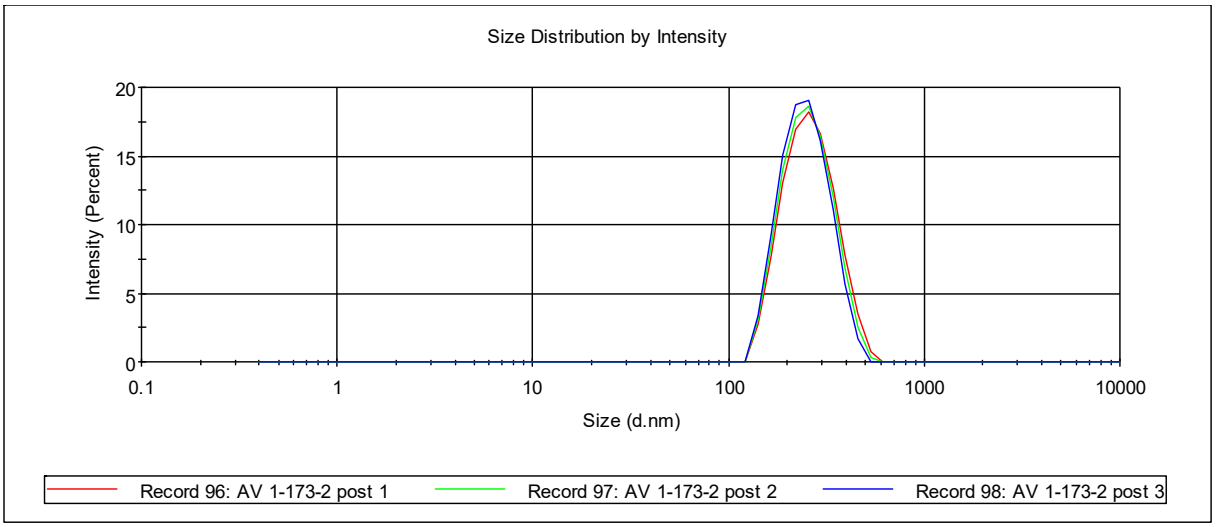

Figure S59. Intensity-size graph of PTX-BF_2I-PIBEG-NP **19**

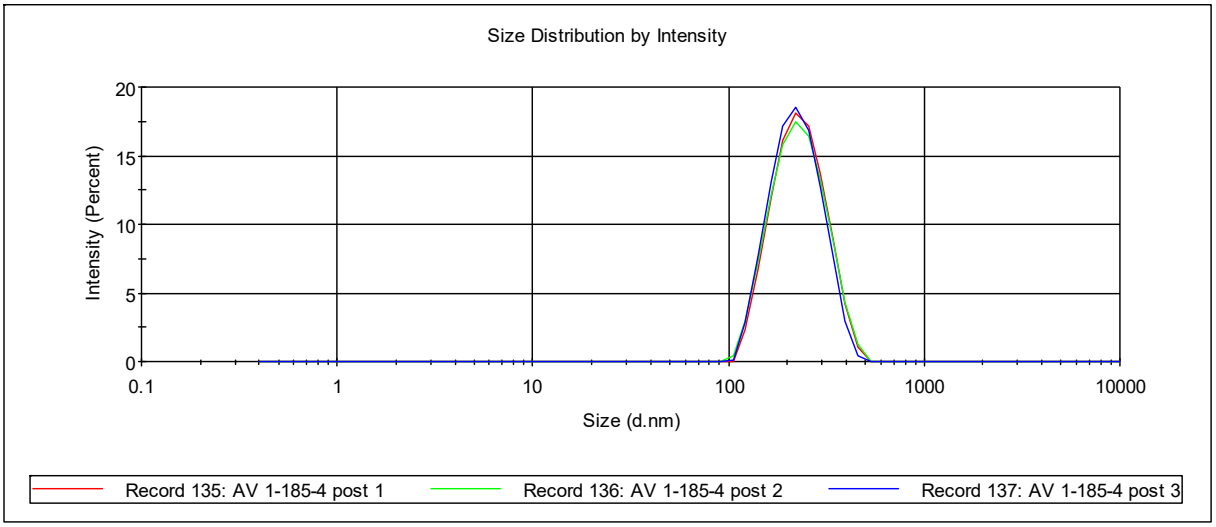

Figure S60. Intensity-size graph of PTX-BF_2I-PILMG-NP **20**

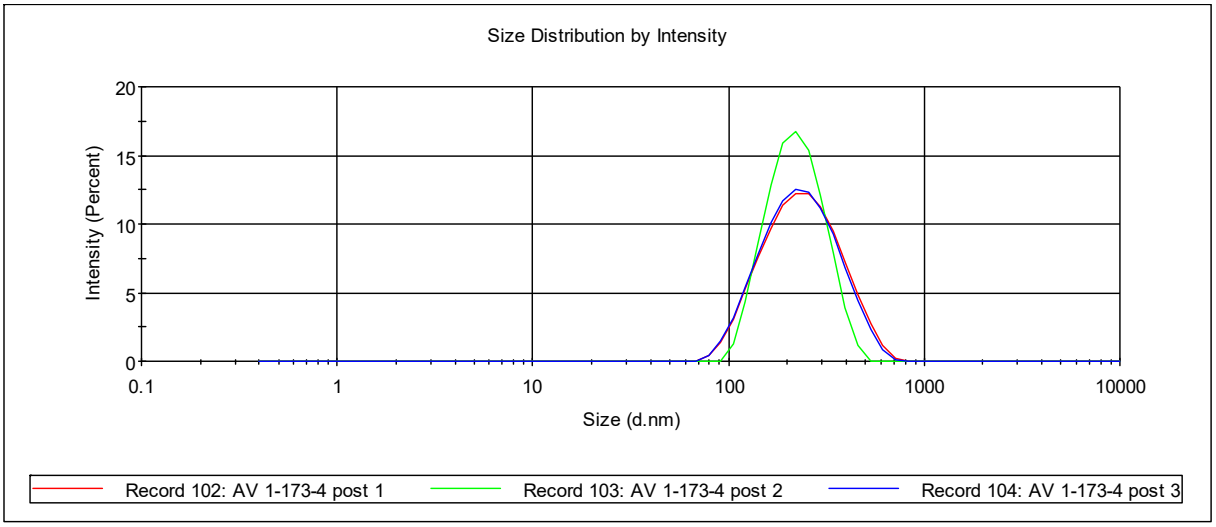

Figure S61. Intensity-size graph of PTX-BF_2I-PILEG-NP **21**

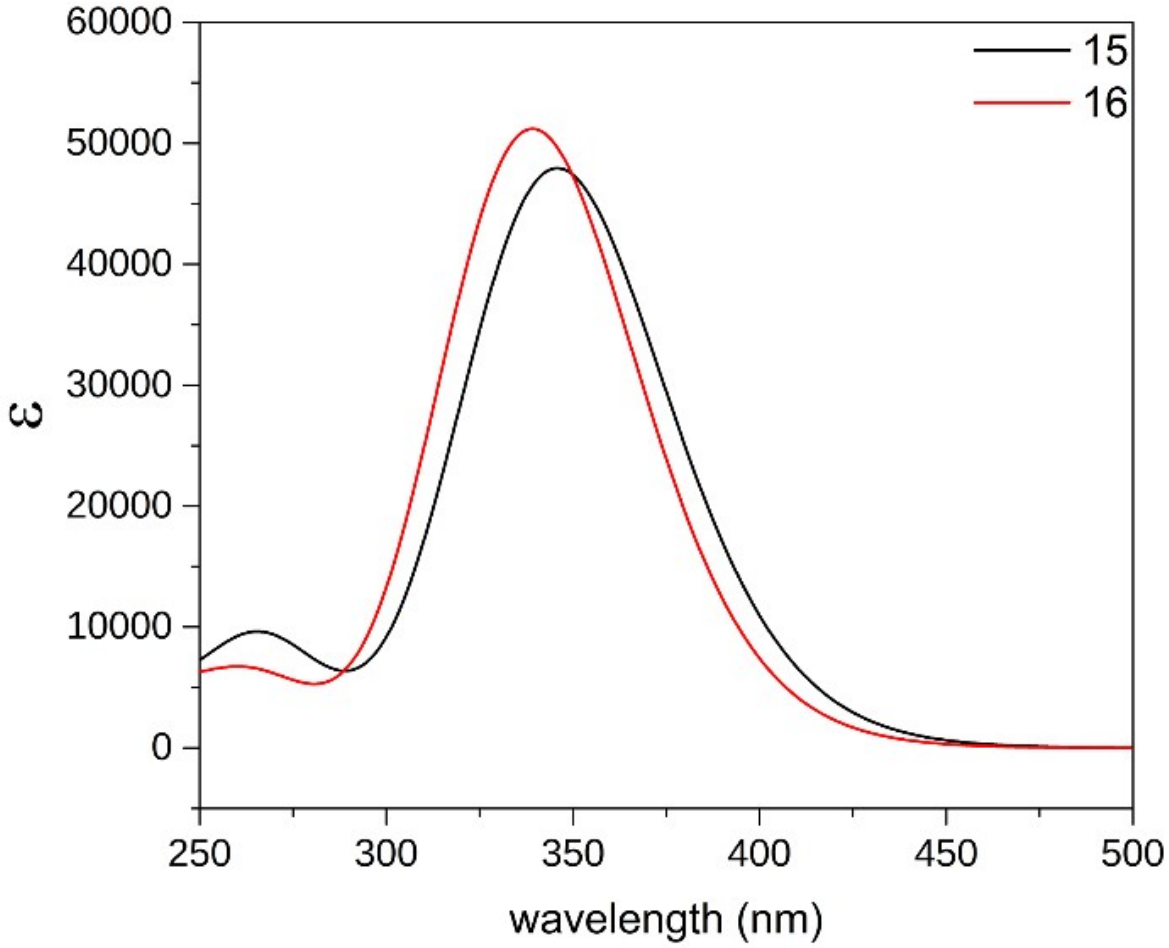

Figure S62. Calculated UV absorption spectra of **15** and **16**

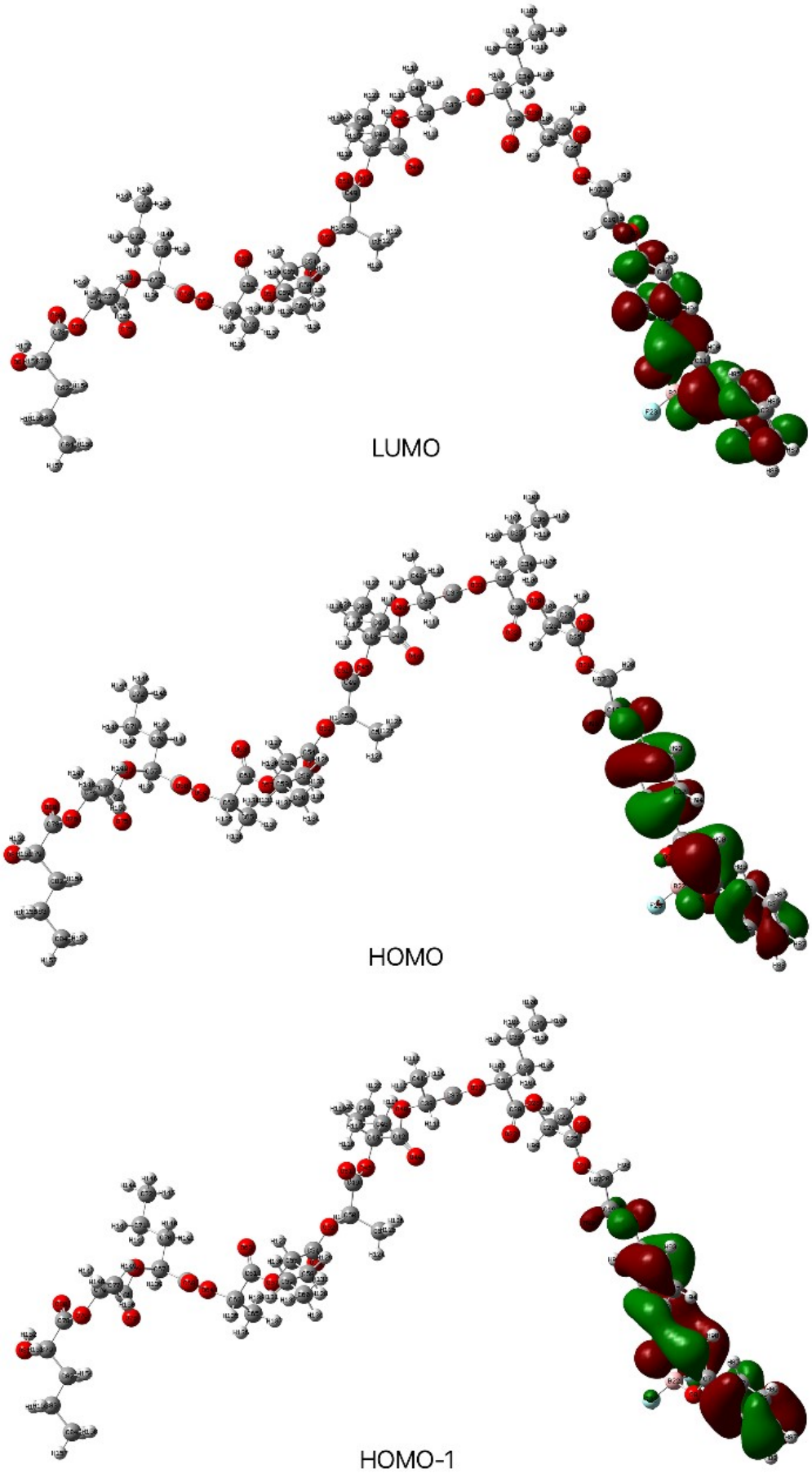

Figure S63. Computed frontier molecular orbitals of **16**

REFERENCES

(1) Yin, M.; Baker, G. L. Preparation and Characterization of Substituted Polylactides. *Macromolecules* **1999**, *32* (23), 7711-7718.