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Supporting Information

Rare-earth Metal-Catalyzed Highly 3,4-Regioselective Polymerization of Polar 1-Phenyl-1,3-Butadiene Derivates

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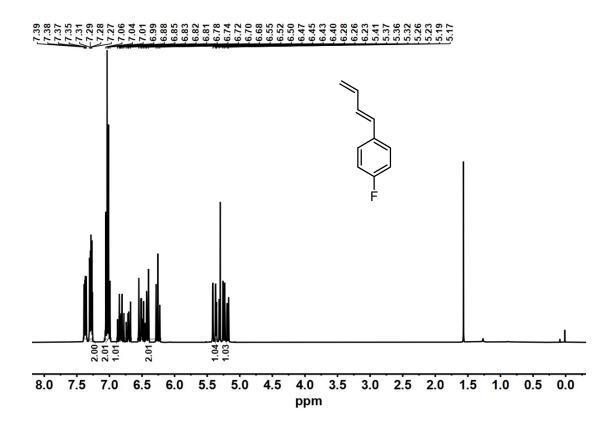


Figure S1. ¹H NMR spectrum of monomer *p*-FPB. (400 MHz, CDCl₃, 25 °C)

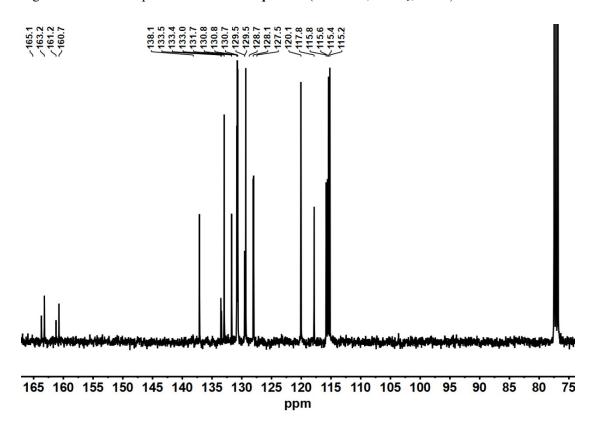


Figure S2. ¹³C NMR spectrum of monomer *p*-FPB. (400 MHz, CDCl₃, 25 °C)

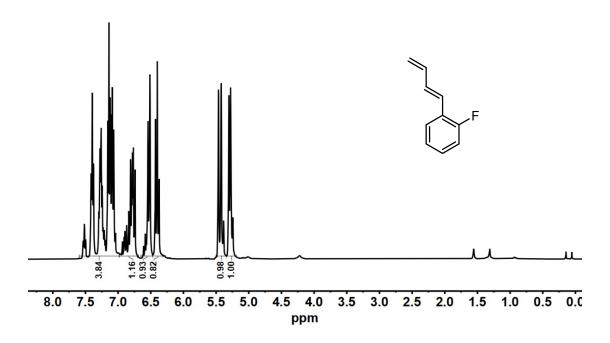


Figure S3. ¹H NMR spectrum of monomer *o-FPB*. (400 MHz, CDCl₃, 25 °C)

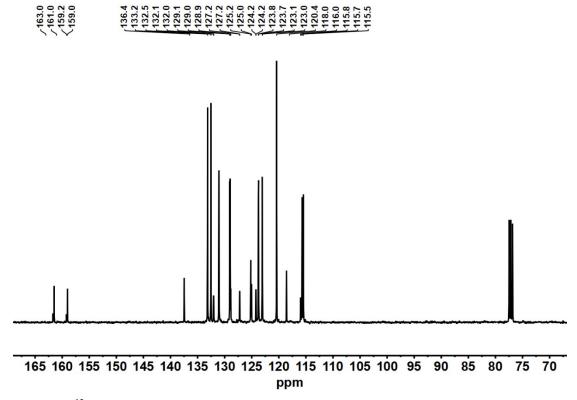


Figure S4. ¹³C NMR spectrum of monomer *o*-FPB. (400 MHz, CDCl₃, 25 °C)

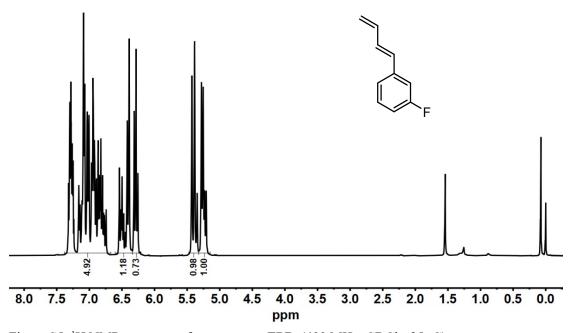


Figure S5. ¹H NMR spectrum of monomer *m*-FPB. (400 MHz, CDCl₃, 25 °C)

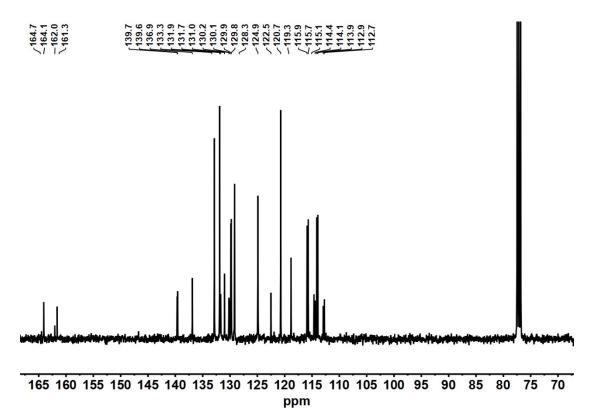


Figure S6. ¹³C NMR spectrum of monomer *m*-FPB. (400 MHz, CDCl₃, 25 °C)

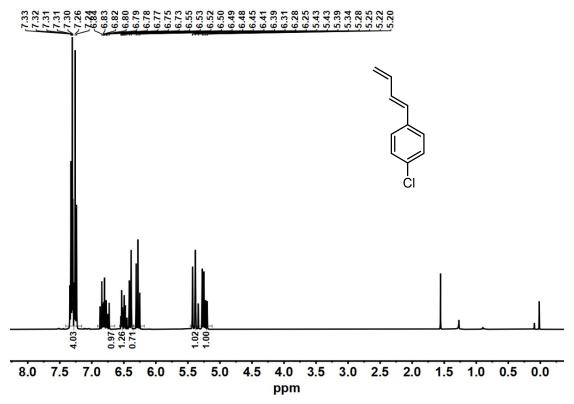


Figure S7. ¹H NMR spectrum of monomer *p*-CIPB. (400 MHz, CDCl₃, 25 °C)

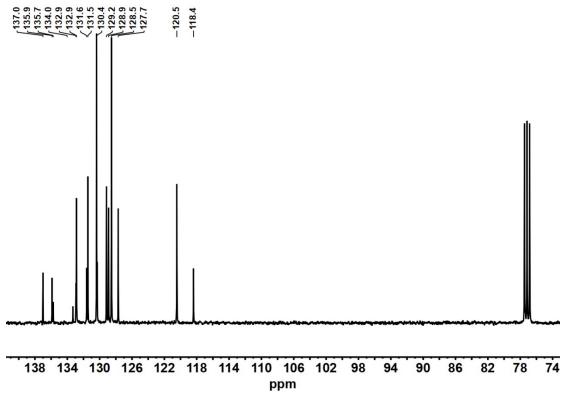


Figure S8. ¹³C NMR spectrum of monomer *p*-CIPB. (400 MHz, CDCl₃, 25 °C)

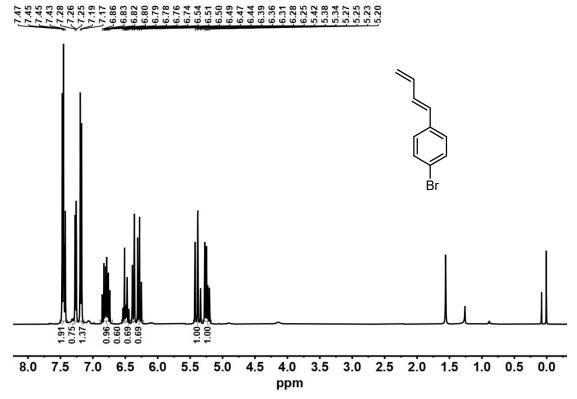


Figure S9. ¹H NMR spectrum of monomer *p*-BrPB. (400 MHz, CDCl₃, 25 °C)

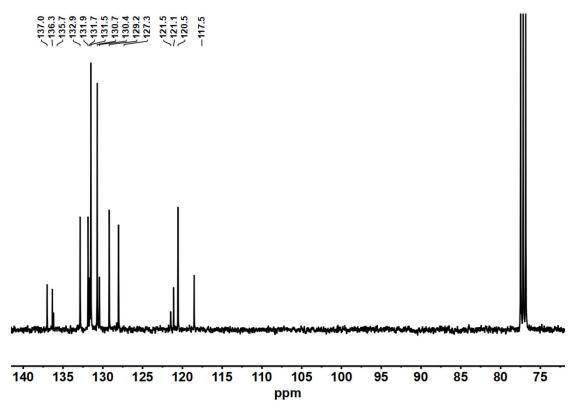


Figure S10. ¹³C NMR spectrum of monomer *p*-BrPB. (400 MHz, CDCl₃, 25 °C)

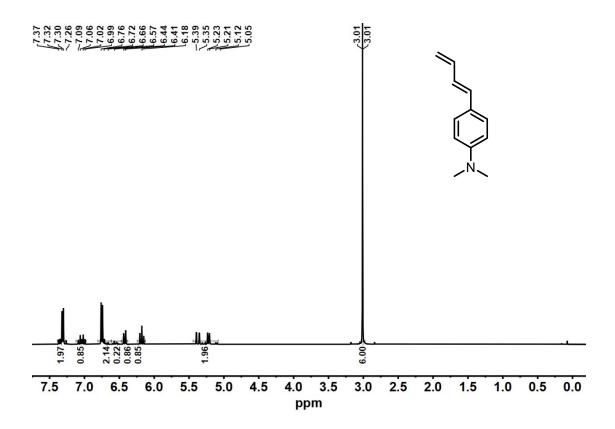


Figure S11. ¹H NMR spectrum of monomer *p*-NPB. (400 MHz, CDCl₃, 25 °C)

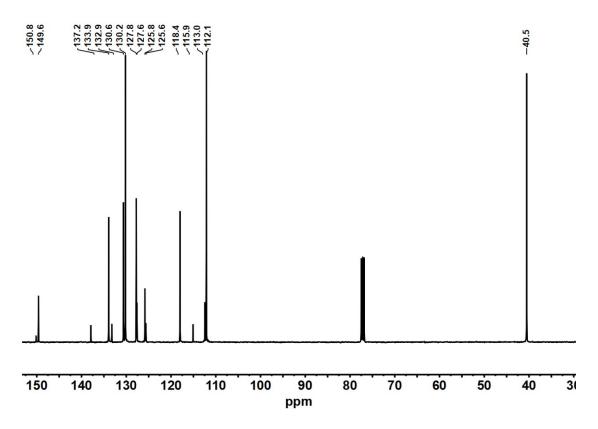


Figure S12. ¹³C NMR spectrum of monomer *p*-NPB. (400 MHz, CDCl₃, 25 °C)

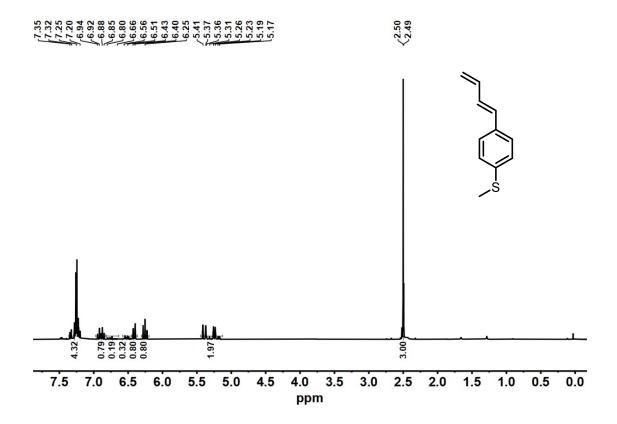


Figure S13. ¹H NMR spectrum of monomer *p*-SPB. (400 MHz, CDCl₃, 25 °C)

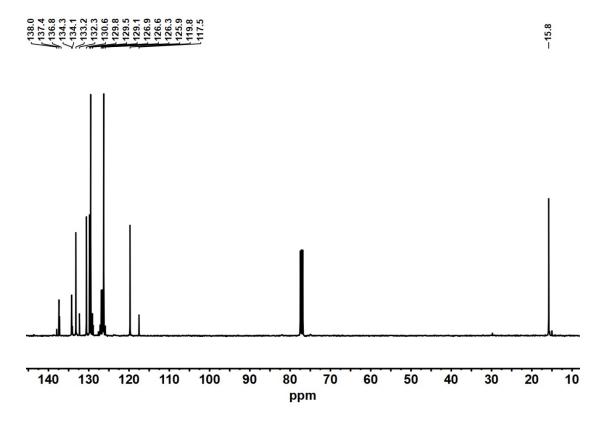


Figure S14. ¹³C NMR spectrum of monomer *p*-SPB. (400 MHz, CDCl₃, 25 °C)

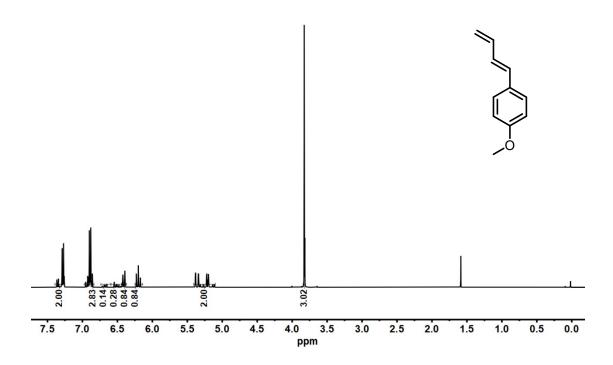


Figure S15. 1 H NMR spectrum of monomer p-OPB. (400 MHz, CDCl₃, 25 $^{\circ}$ C)

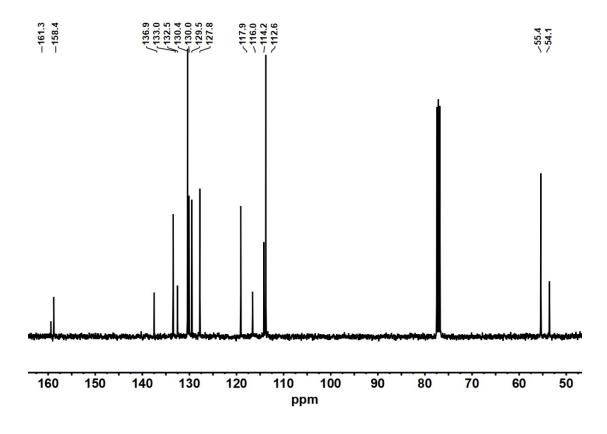


Figure S16. ¹³C NMR spectrum of monomer *p*-OPB. (400 MHz, CDCl₃, 25 °C)

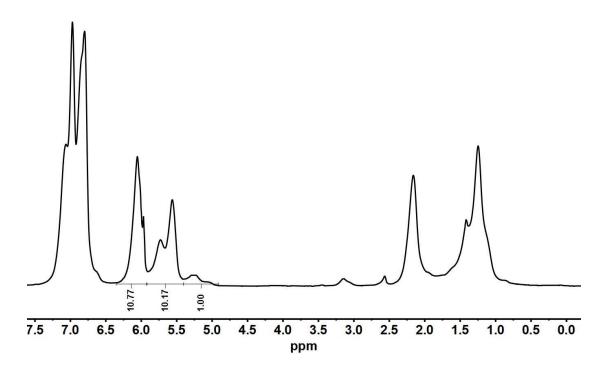


Figure S17. ¹H NMR spectrum of poly(*p*-FPB) prepared by complex 4. (Entry 5, Table 1)

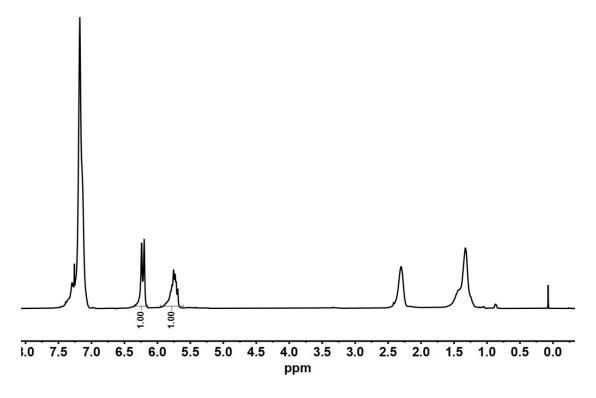


Figure S18. ¹H NMR spectrum of poly(**1PB**) prepared by complex **1**. (Entry 1, Table 2)

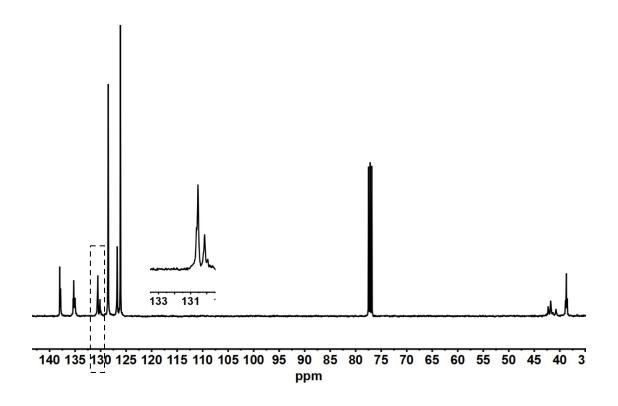


Figure S19. ¹³C NMR spectrum of poly(**1PB**) prepared by complex **1**. (Entry 1, Table 2)

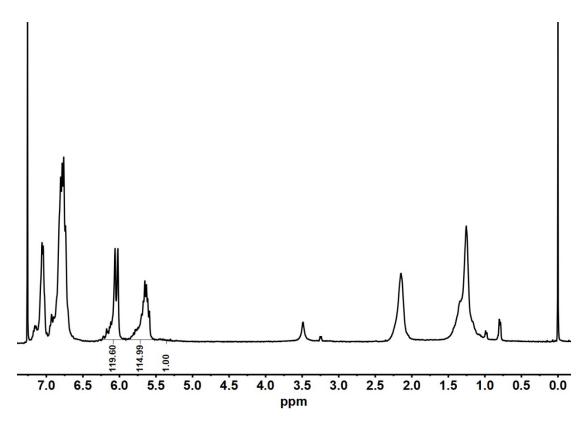


Figure S20 ¹H NMR spectrum of poly(*m*-FPB) prepared by complex 1. (Entry 2, Table 2)

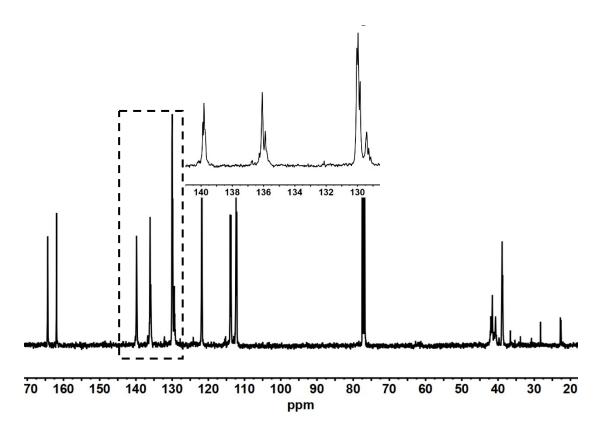


Figure S21. ¹³C NMR spectrum of poly(*m*-FPB) prepared by complex 1. (Entry 2, Table 2)

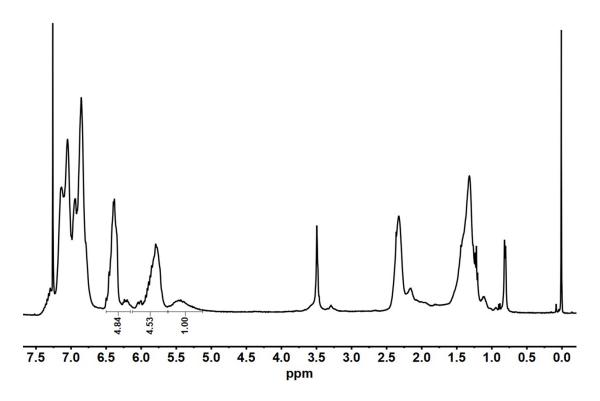


Figure S22. ¹H NMR spectrum of poly(*o*-FPB) prepared by complex 1. (Entry 3, Table 2)

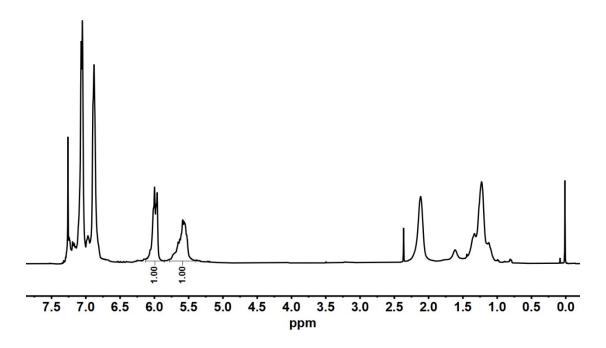


Figure S23. ¹H NMR spectrum of poly(*p*-ClPB) prepared by complex 1. (Entry 4, Table 2)

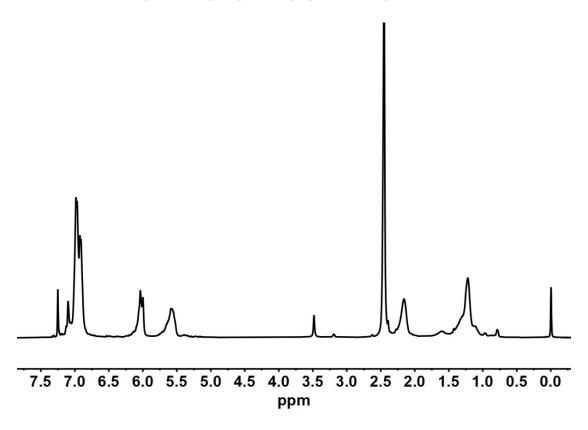


Figure S24. ¹H NMR spectrum of poly(*p*-SPB) prepared by complex 1. (Entry 4, Table 2)

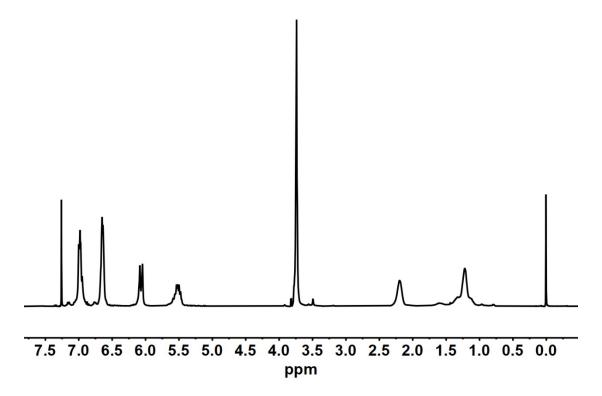


Figure S25. ¹H NMR spectrum of poly(*p*-OPB) prepared by complex 1. (Entry 4, Table 2)

Scheme S1. Homopolymerization of 1-(4-fluorophenyl)-1,3-butadiene (*p*-FPB) with bis(phosphinophenyl)amido yttrium complex.^a

Yield: 65.5% (3 h); $M_{\rm n}$ = 1.68 x 10⁴, $M_{\rm w}/M_{\rm n}$ = 1.25; 3,4-regularity: > 99%

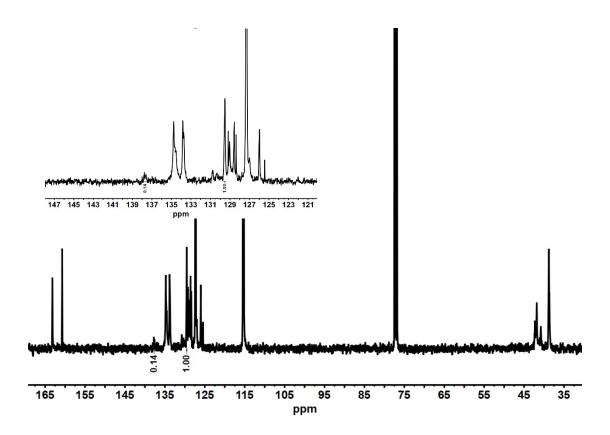


Figure S26. ¹³C NMR spectra of copolymer prepared by complex 1. (Entry 1, Table 3)

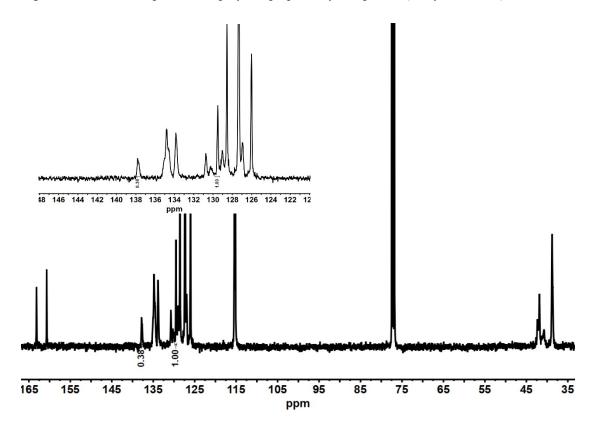


Figure S27. ¹³C NMR spectra of copolymer prepared by complex 1. (Entry 2, Table 3)

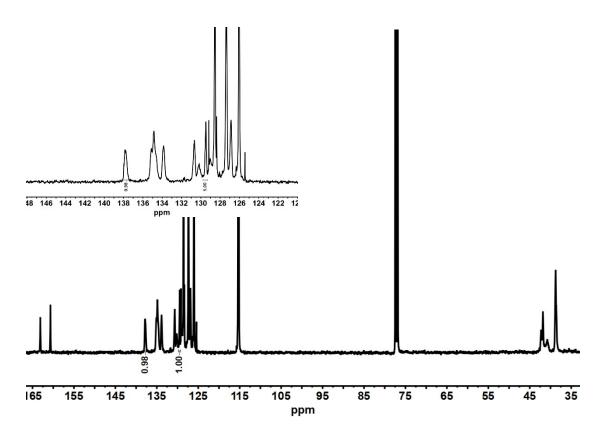


Figure S28. ¹³C NMR spectra of copolymer prepared by complex 1. (Entry 3, Table 3)

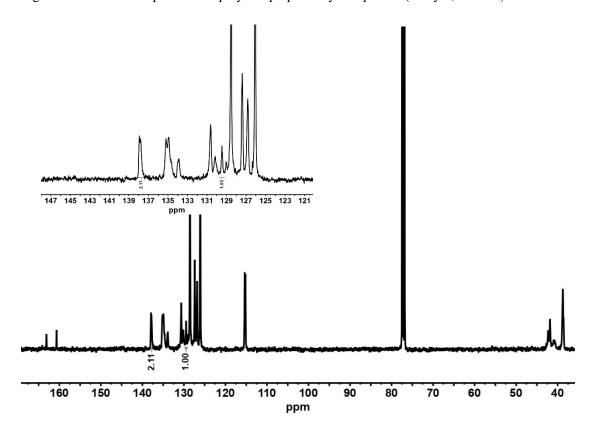


Figure S29. ¹³C NMR spectra of copolymer prepared by complex 1. (Entry 4, Table 3)

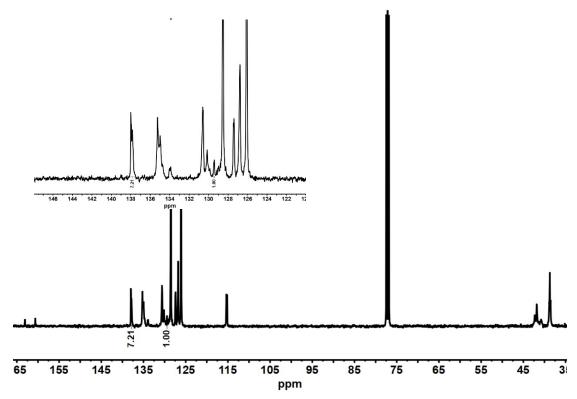


Figure S30. ¹³C NMR spectra of copolymer prepared by complex 1. (Entry 5, Table 3)

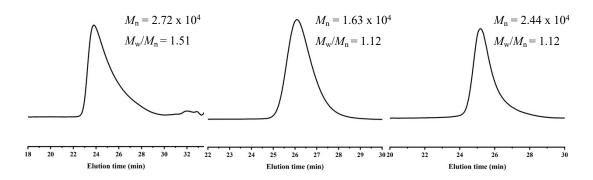


Figure S31. GPC curves of poly(*p*-FPB) prepared by complex 1. (From left to right: Entry 2, Table 1; Entry 8, Table 1; Entry 9, Table 1).

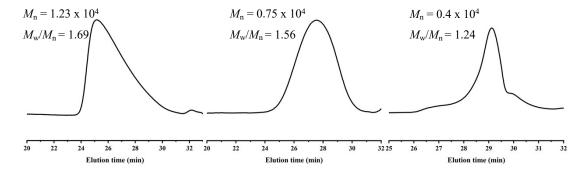


Figure S32. GPC curves of polymers with substitutents at the para position of the phenyl ring prepared by complex 1. (From left to right: Entry 2, Table 2; Entry 3, Table 2; c: Entry 4, Table 2).

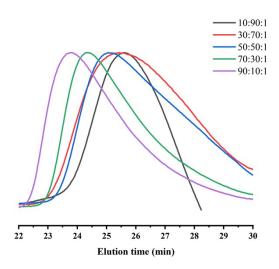


Figure S33 GPC curves of copolymers prepared by complex 1. (Entries in Table 3).

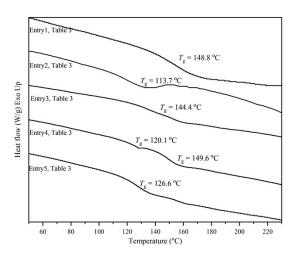


Figure S34. DSC curves of copolymers prepared by complex 1. (Entries in Table 3).

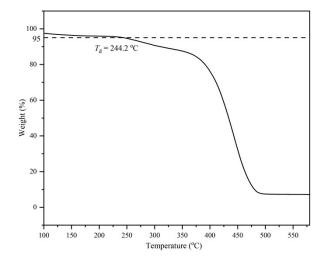


Figure S35. TGA curve of a poly(1PB) prepared by complex 1. (Entry 1, Table 2).

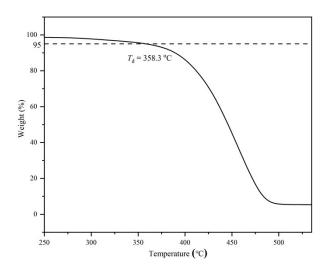


Figure S36. TGA curve of a poly(*p*-**FPB**) prepared by complex **1**. (Entry 7, Table 1).

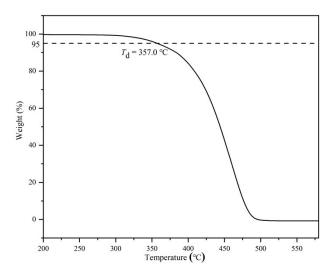


Figure S37. TGA curve of a poly(*m*-FPB) prepared by complex 1. (Entry 2, Table 2).

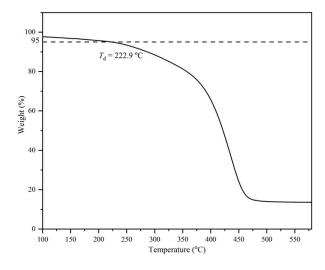


Figure S38. TGA curve of a poly(*o*-**FPB**) prepared by complex 1. (Entry 3, Table 2).

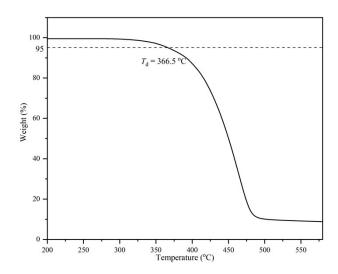


Figure S39. TGA curve of a poly(*p*-ClPB) prepared by complex 1. (Entry 4,Table 2).

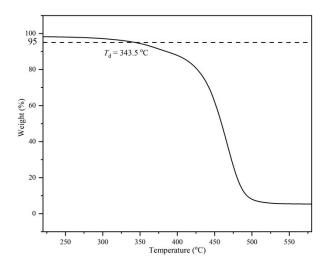


Figure S40. TGA curve of a poly(*p*-**NPB**) prepared by complex **1**. (Entry 6,Table 2).

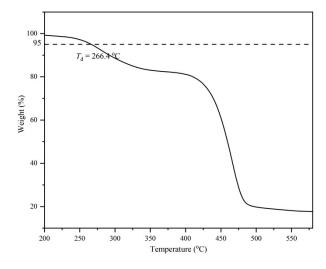


Figure S41. TGA curve of a poly(*p*-**OPB**) prepared by complex **1**. (Entry 7,Table 2).

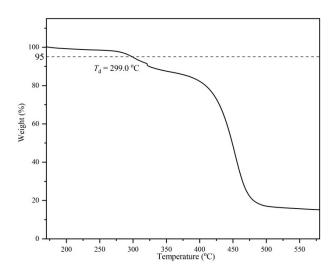


Figure S42. TGA curve of a poly(*p*-SPB) prepared by complex 1. (Entry 8,Table 2).