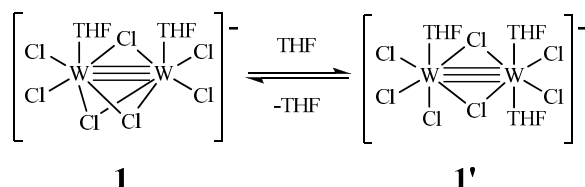
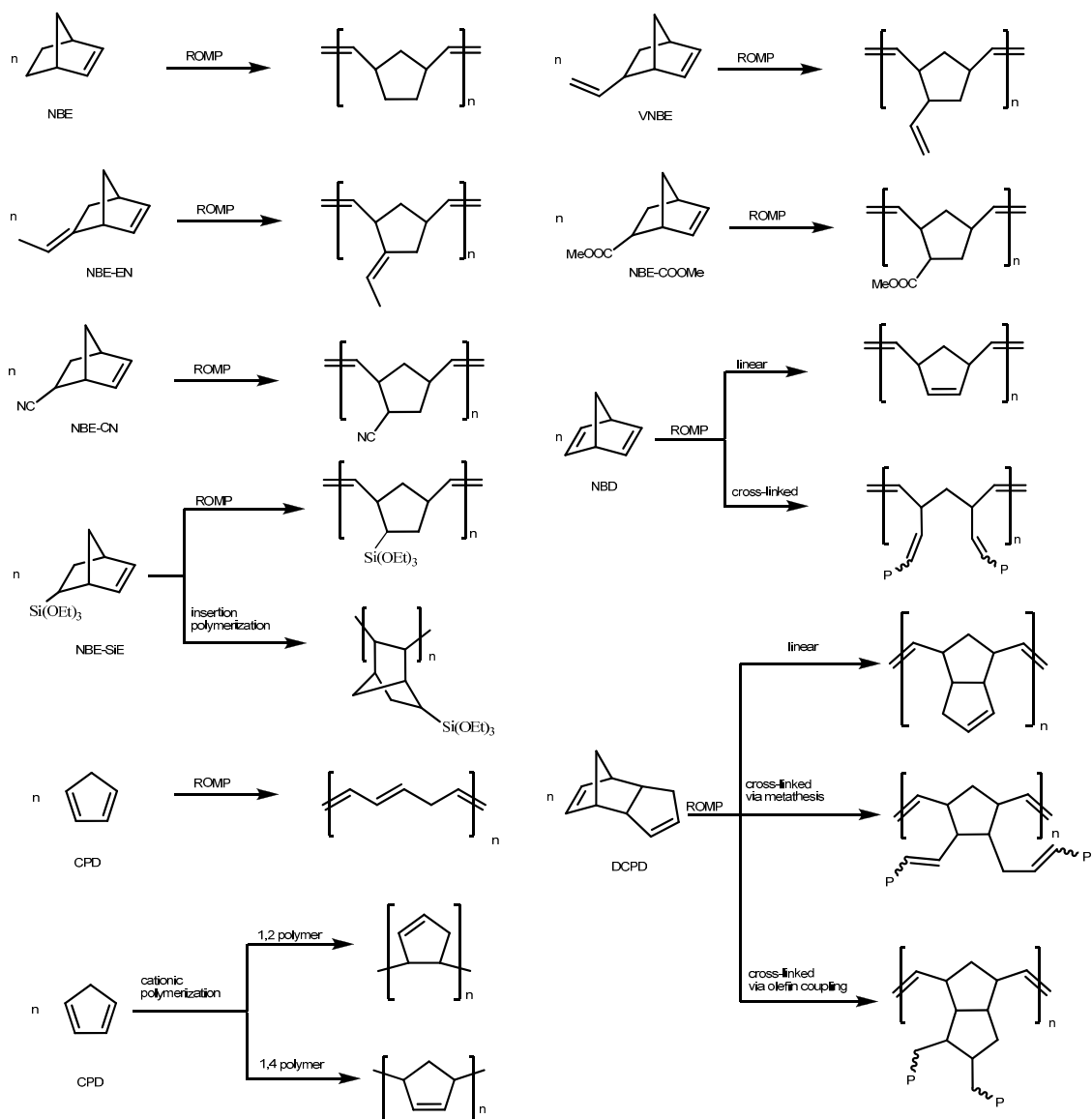


# Supporting Information: Exploring the Reactivity of $\text{Na}[\text{W}_2(\mu\text{-Cl})_3\text{Cl}_4(\text{THF})_2]\cdot(\text{THF})_3$ towards the Polymerization of Selected Cycloolefins

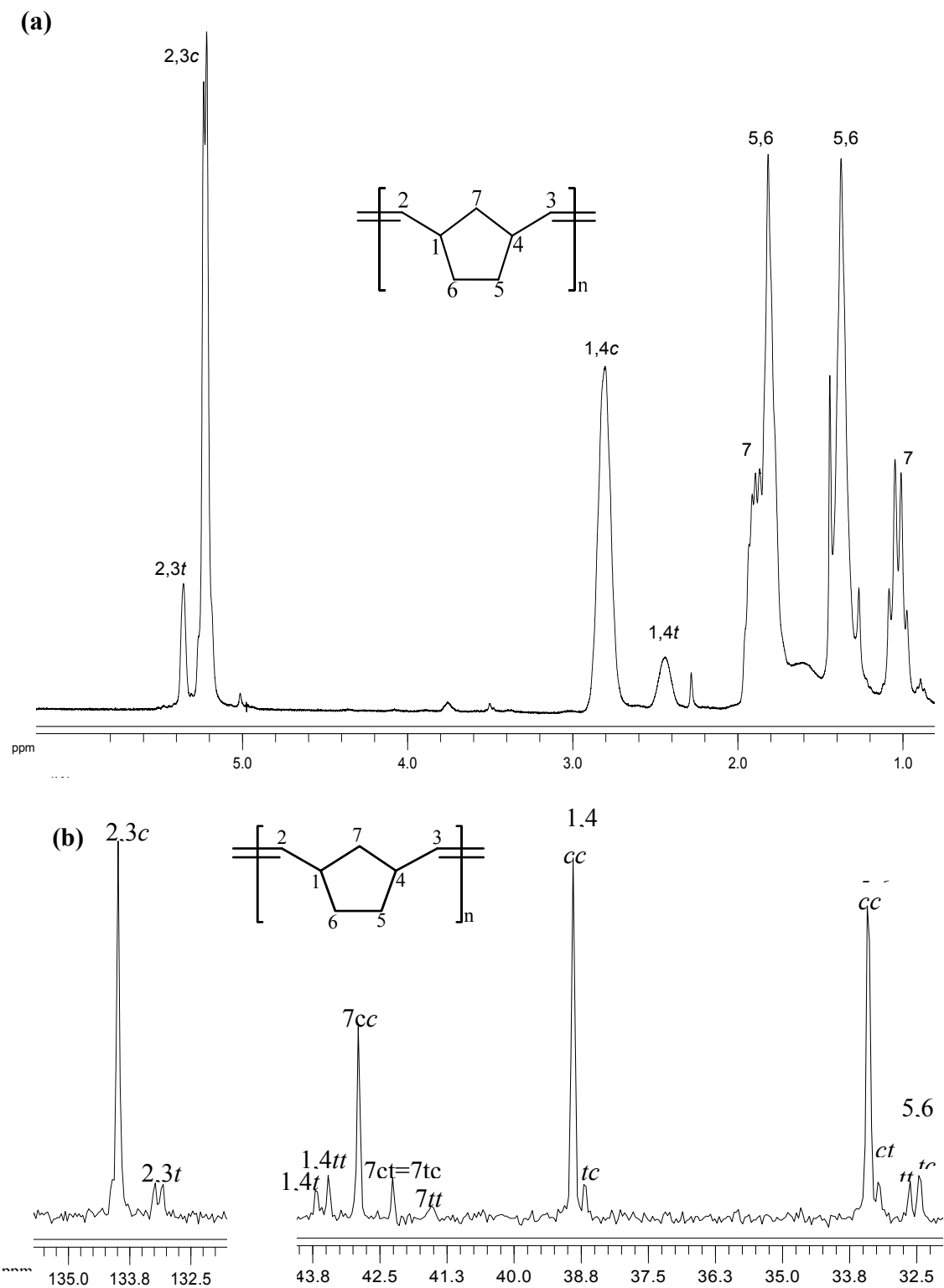
Nikolaos Saragas, Georgios Floros, Grigorios Raptopoulos, Marinos Pitsikalis, Patrina Paraskevopoulou and Konstantinos Mertis



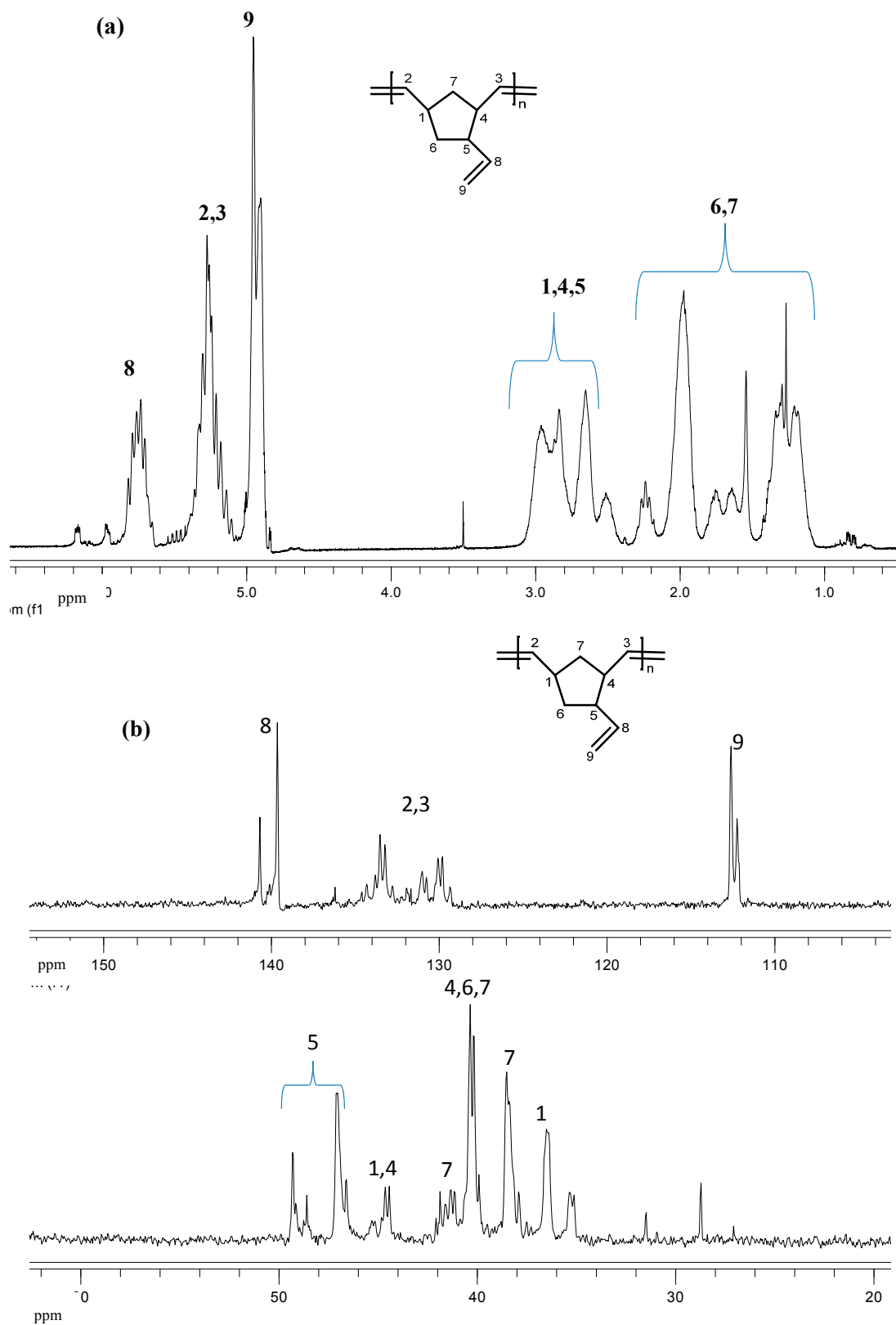
**Scheme S1.** Schematic representation of complex **1** and the equilibrium between **1** and **1'**.



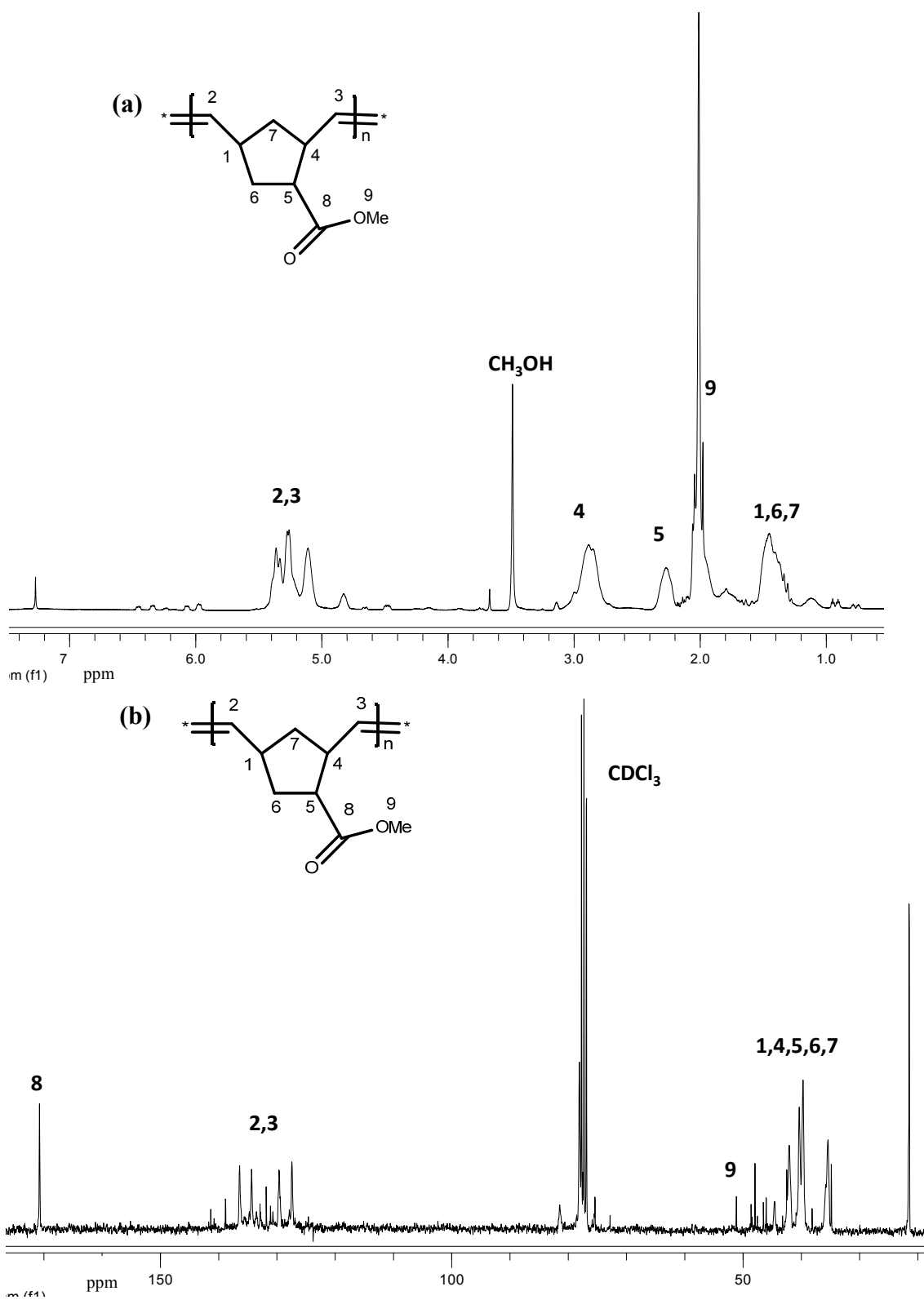
**Scheme S2.** Polymerization reactions of all monomers studied in this work.



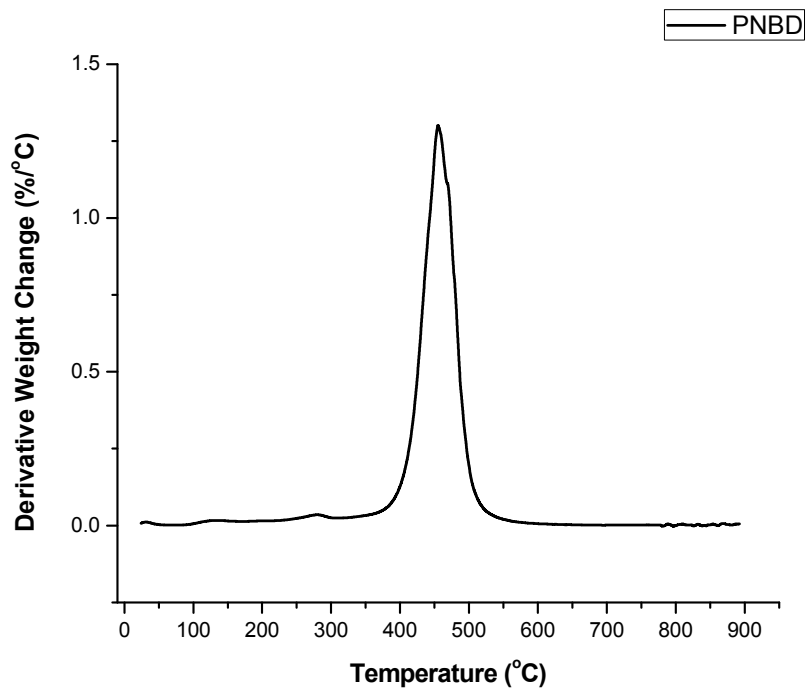
**Figure S1.** (a)  $^1\text{H}$ - and (b)  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra ( $\text{CDCl}_3$ ) of PNBE obtained from the reaction of **1**/PA/NBE in  $\text{CH}_2\text{Cl}_2$ .



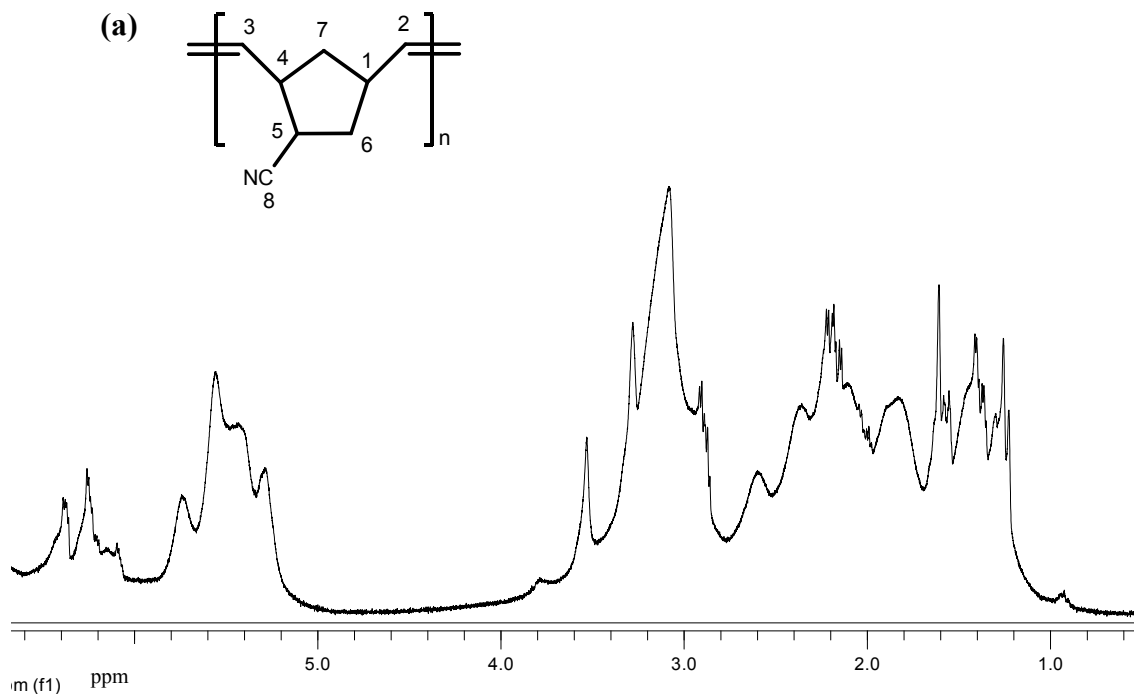
**Figure S2.** (a)  $^1\text{H}$ - and (b)  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra (CDCl<sub>3</sub>) of PVNBE obtained from the reaction of 1/PA/VNBE in CH<sub>2</sub>Cl<sub>2</sub>.



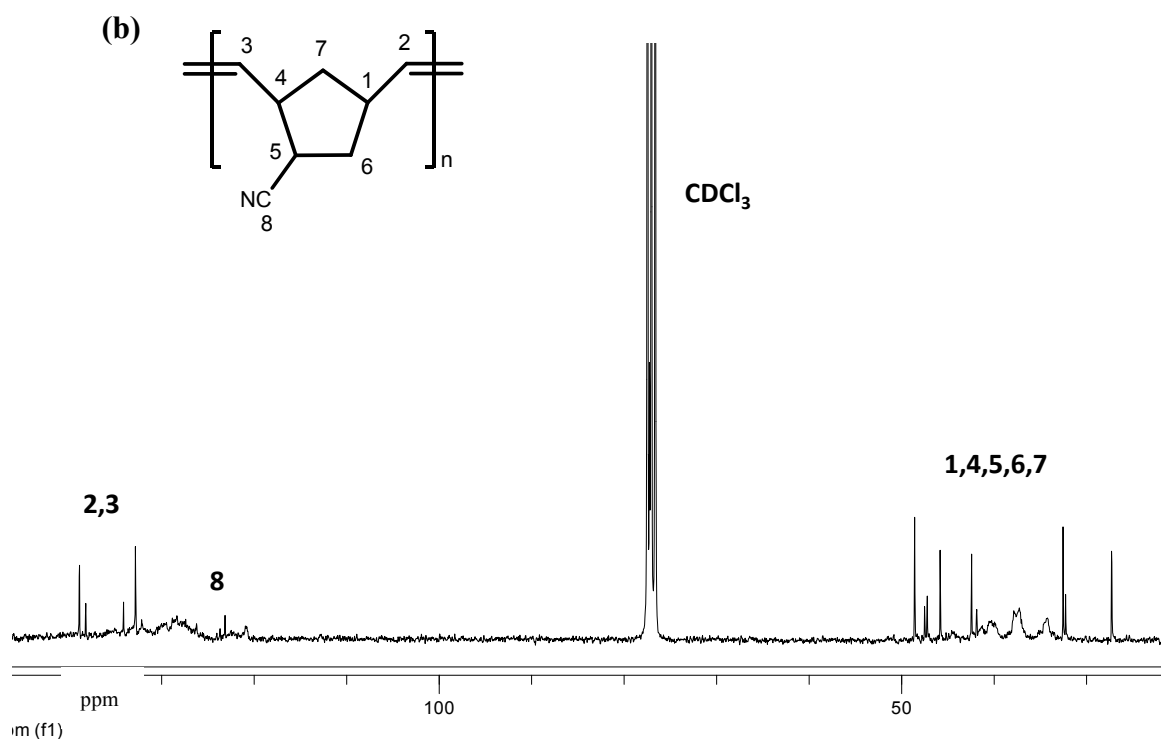
**Figure S3.** (a)  $^1\text{H}$ - and (b)  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra ( $\text{CDCl}_3$ ) of PNBE-COOMe obtained from the reaction of 1/PA/NBE-COOMe in  $\text{CH}_2\text{Cl}_2$ .



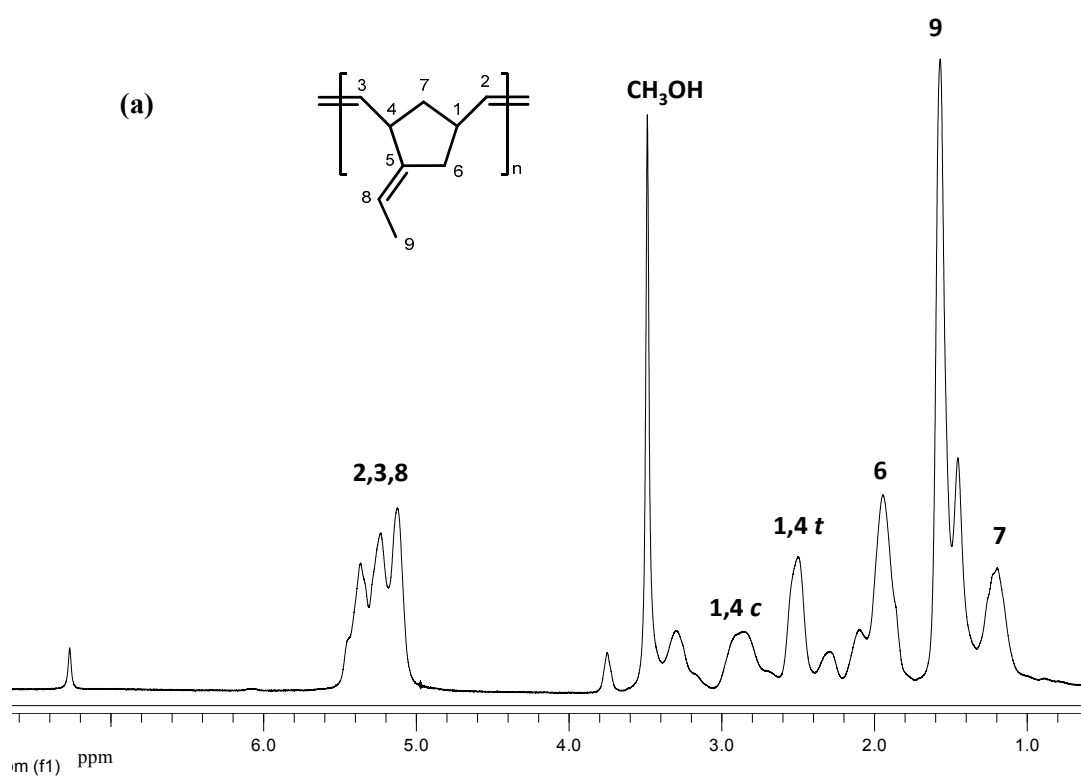
**Figure S4.** Derivative weight change with temperature of **PNBD** obtained from the reaction of **1/PA/NBD** in THF.



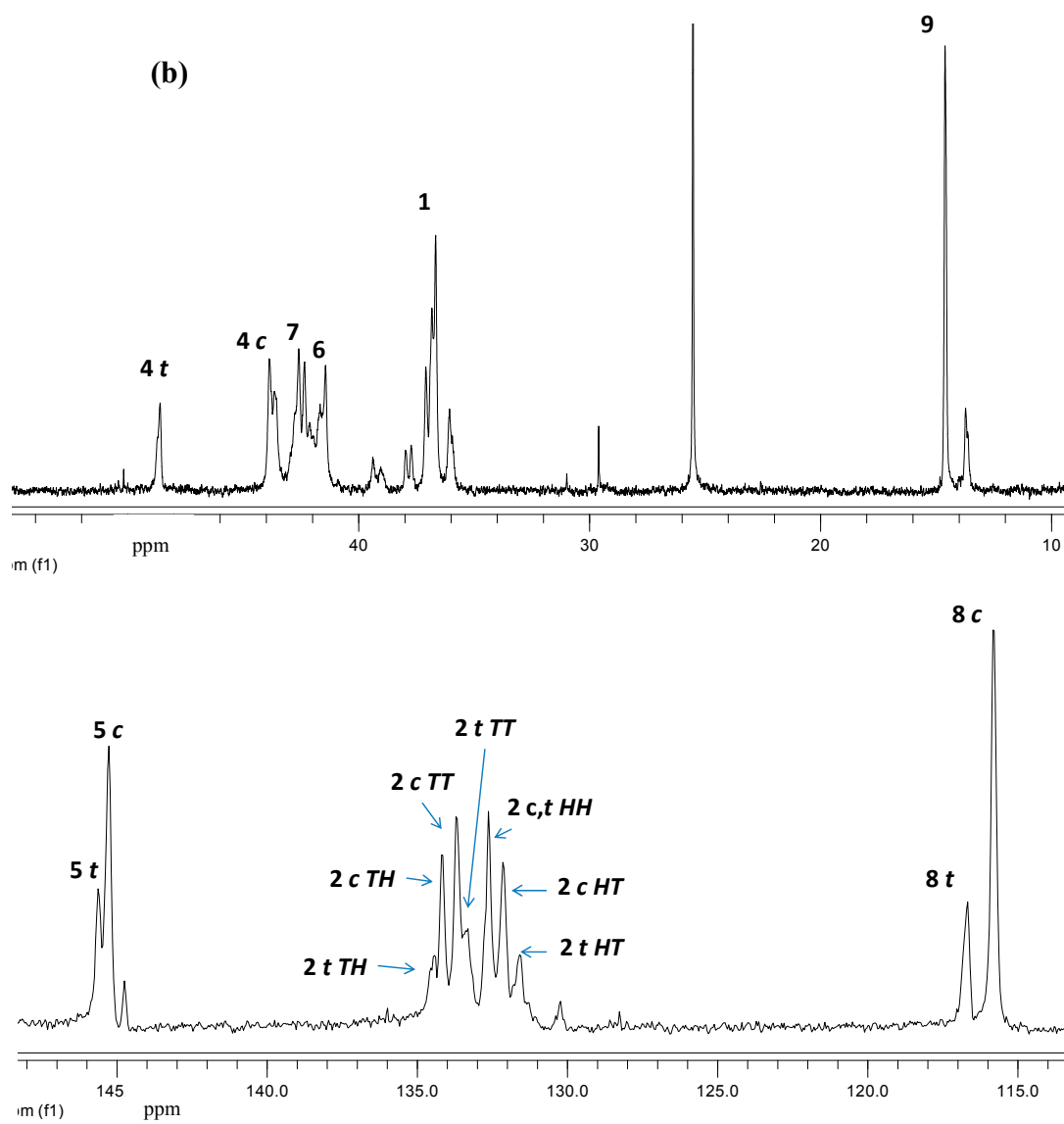
**Figure S5.** *Cont.*



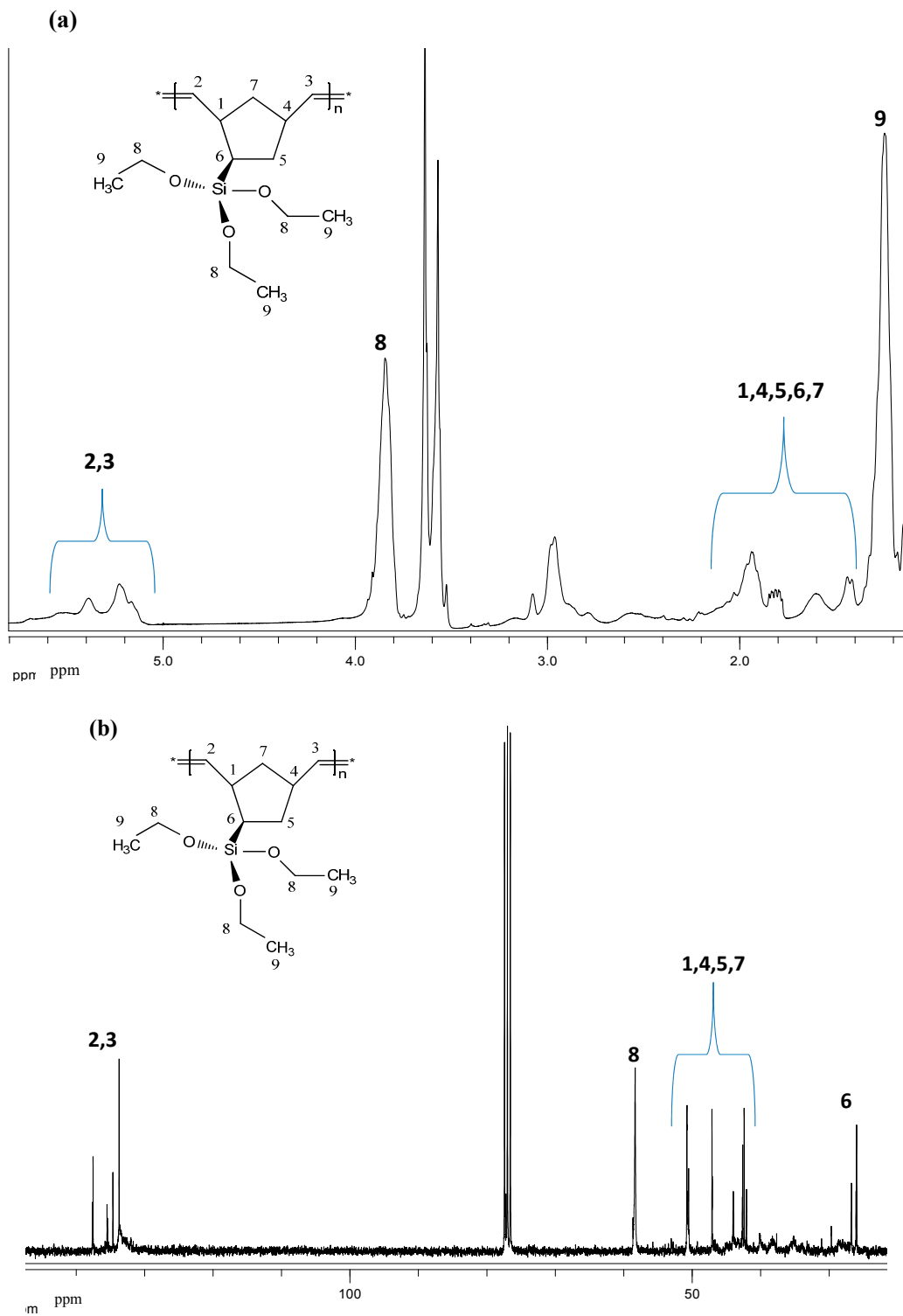
**Figure S5.** (a) <sup>1</sup>H- and (b) <sup>13</sup>C{<sup>1</sup>H}-NMR spectra (CDCl<sub>3</sub>) of PNBE-CN obtained from the reaction of 1/PA/NBE-CN in CH<sub>2</sub>Cl<sub>2</sub>.



**Figure S6.** *Cont.*

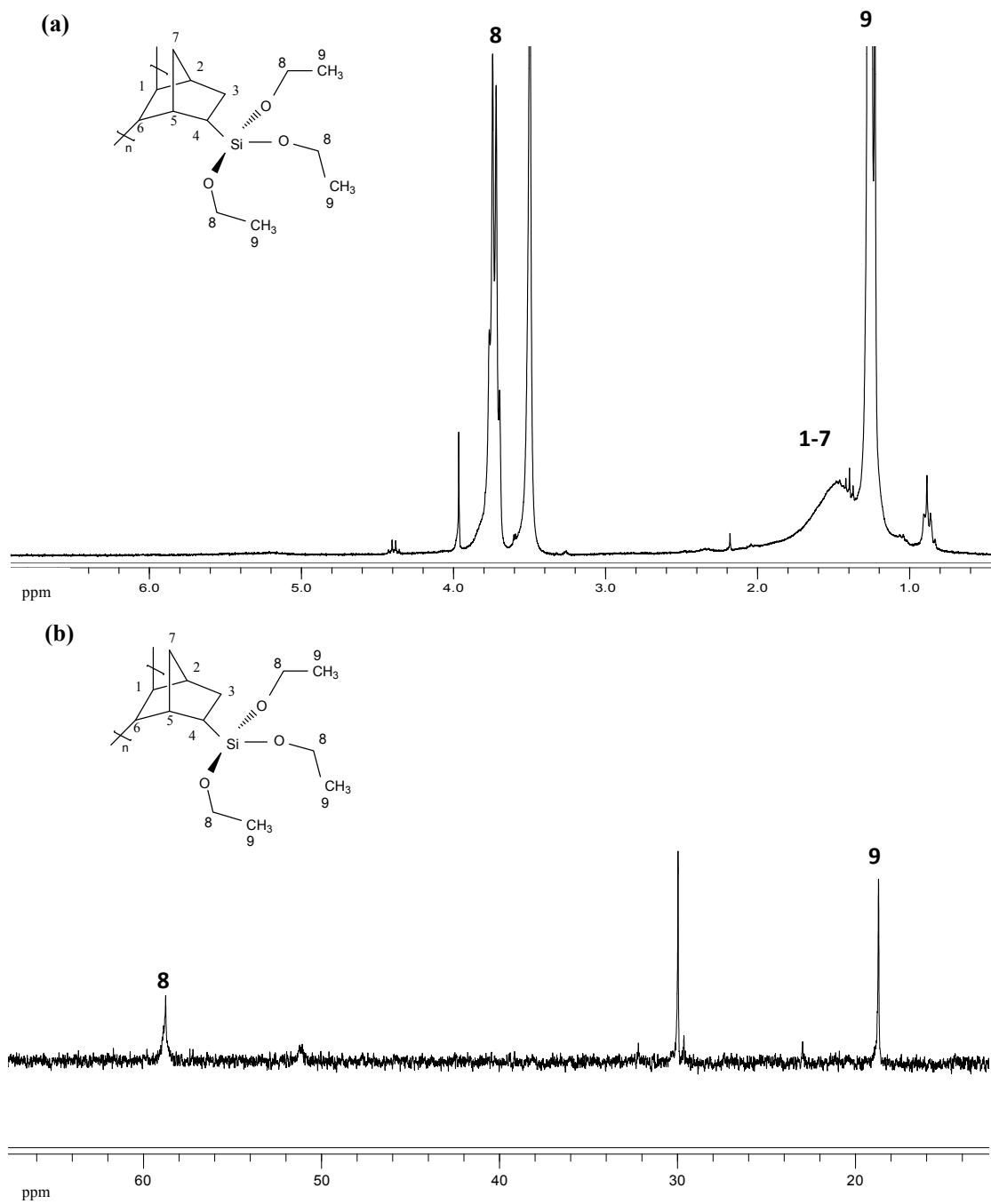


**Figure S6.** (a)  $^1\text{H}$ - and (b)  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra ( $\text{CDCl}_3$ ) of PNBE-EN obtained from the reaction of 1/PA/NBE-EN in  $\text{CH}_2\text{Cl}_2$ .



**Figure S7.** (a)  $^1\text{H}$ - and (b)  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra ( $\text{CDCl}_3$ ) of PNBE-SiE obtained from the reaction of 1/NBE-SiE in  $\text{CH}_2\text{Cl}_2$ .





**Figure S8.** (a)  $^1\text{H}$ - and (b)  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra ( $\text{CDCl}_3$ ) of PNBE-SiE obtained from the reaction of **1** and NBE-SiE in THF.

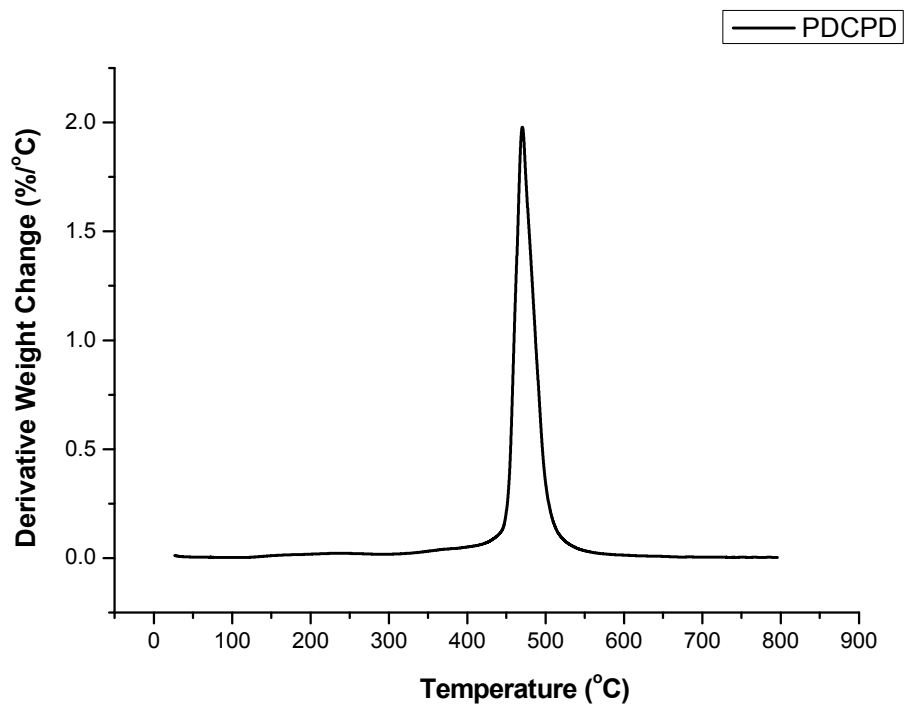


Figure S9. Derivative weight change with temperature of insoluble **PDCPD** obtained from the reaction of **1/PA/DCPD** in  $\text{CH}_2\text{Cl}_2$ .

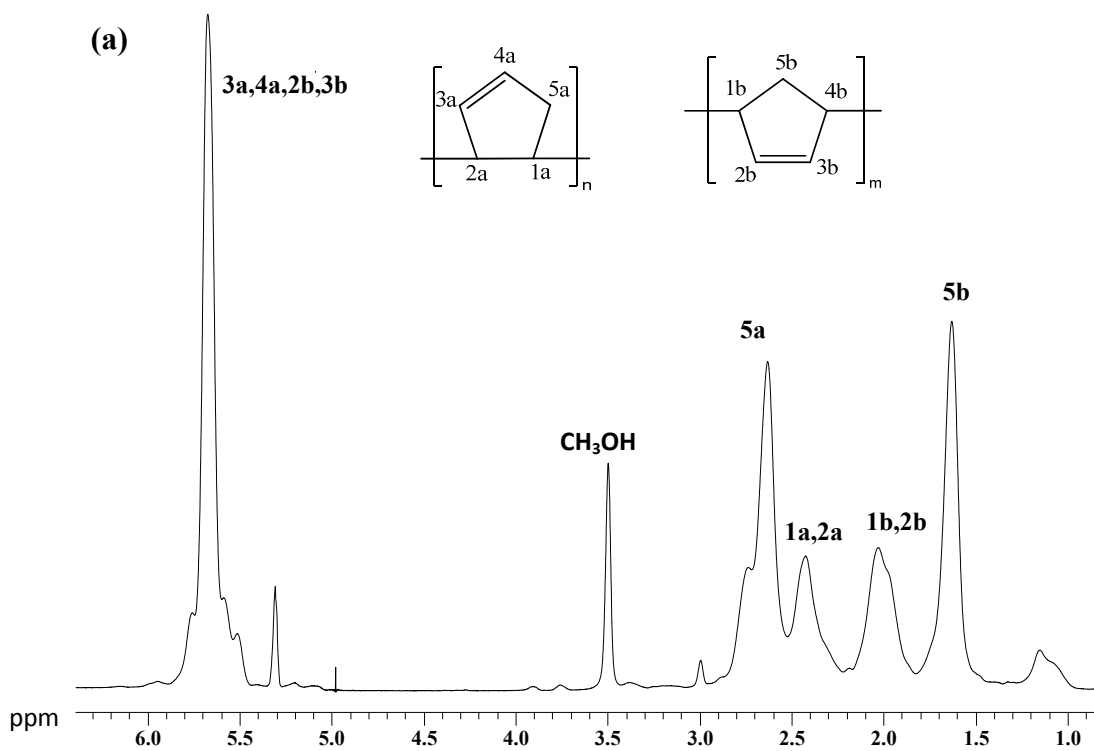
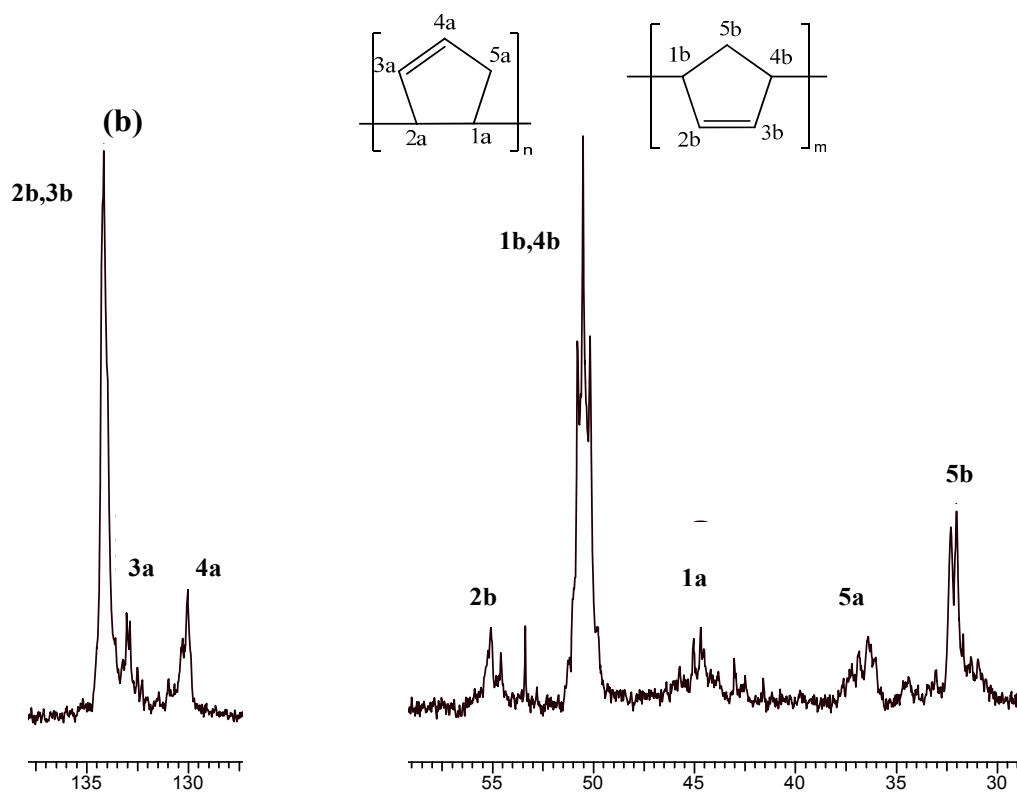


Figure S10. *Cont.*



**Figure S10.** (a)  $^1\text{H}$ - and (b)  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra (CDCl<sub>3</sub>) of PCPD obtained from the reaction of 1/CPD in CH<sub>2</sub>Cl<sub>2</sub>.