Synthesis of Polyisobutylene Bottlebrush Polymers *via* Ring-Opening Metathesis Polymerization

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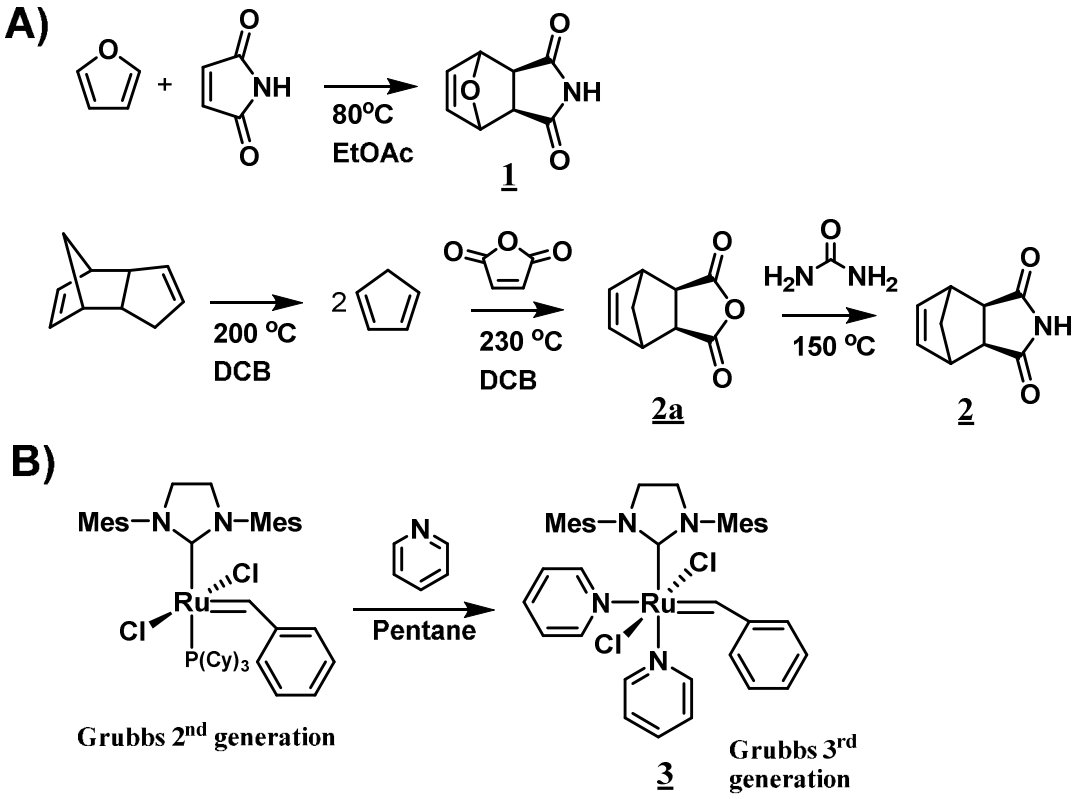
Supporting Information



Scheme S1. Synthesis of A) *exo*-7-oxanorbornene-2,3-dicarboximide and *exo*-5-norbornene-2,3-dicarboximide, and B) third generation Grubbs catalyst.

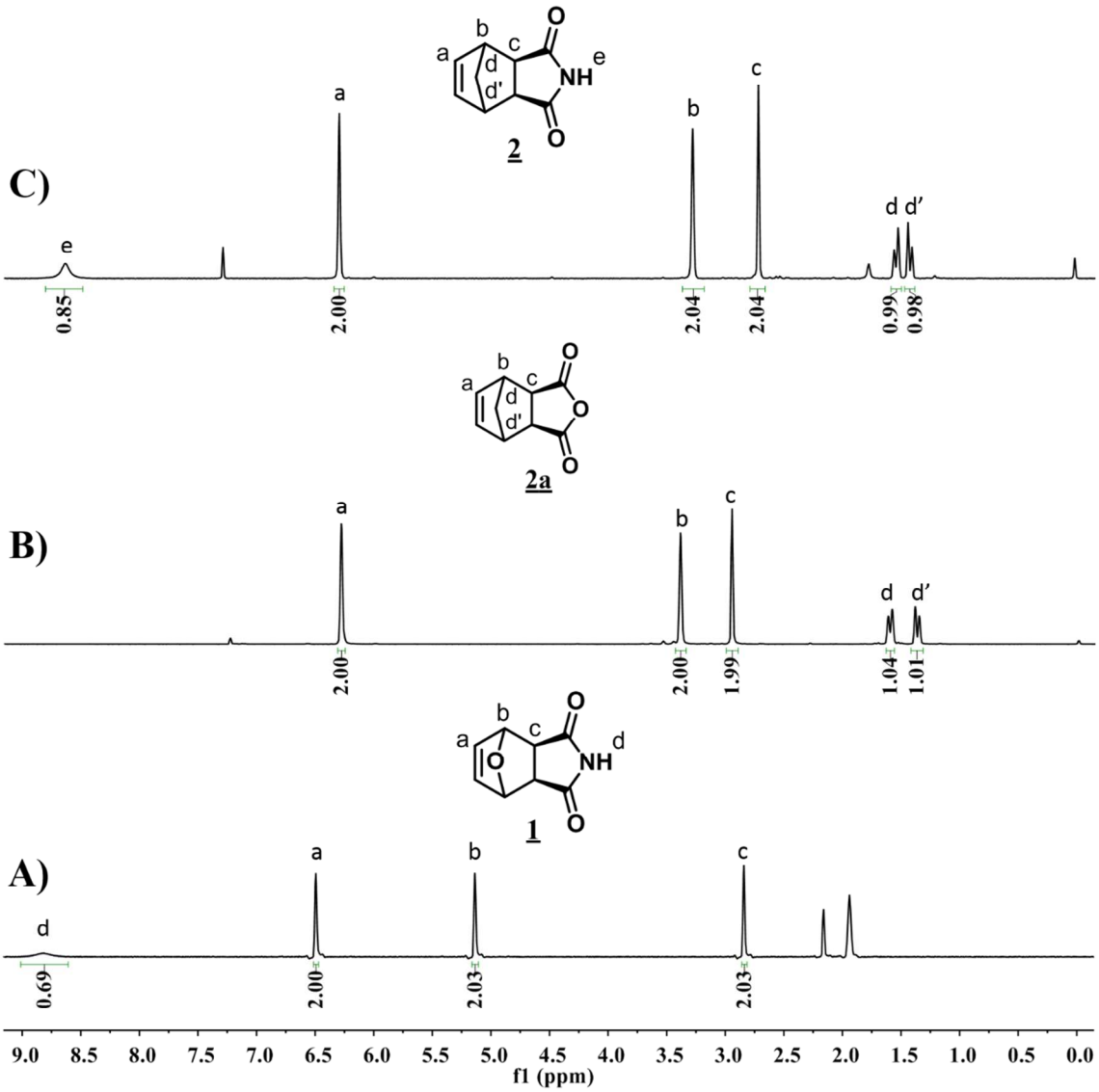


Figure S1. ^{1}H NMR spectra (300 MHz, 25^{o}C) of A) *exo*-7-oxanorbornene-2,3-dicarboximide (**1**) in CD_3CN, B) *exo*-5-norbornene-2,3-dicarboxylic anhydride (**2a**) in $CDCl_3$, and C) *exo*-5-norbornene-2,3-dicarboximide (**2**) in $CDCl_3$.

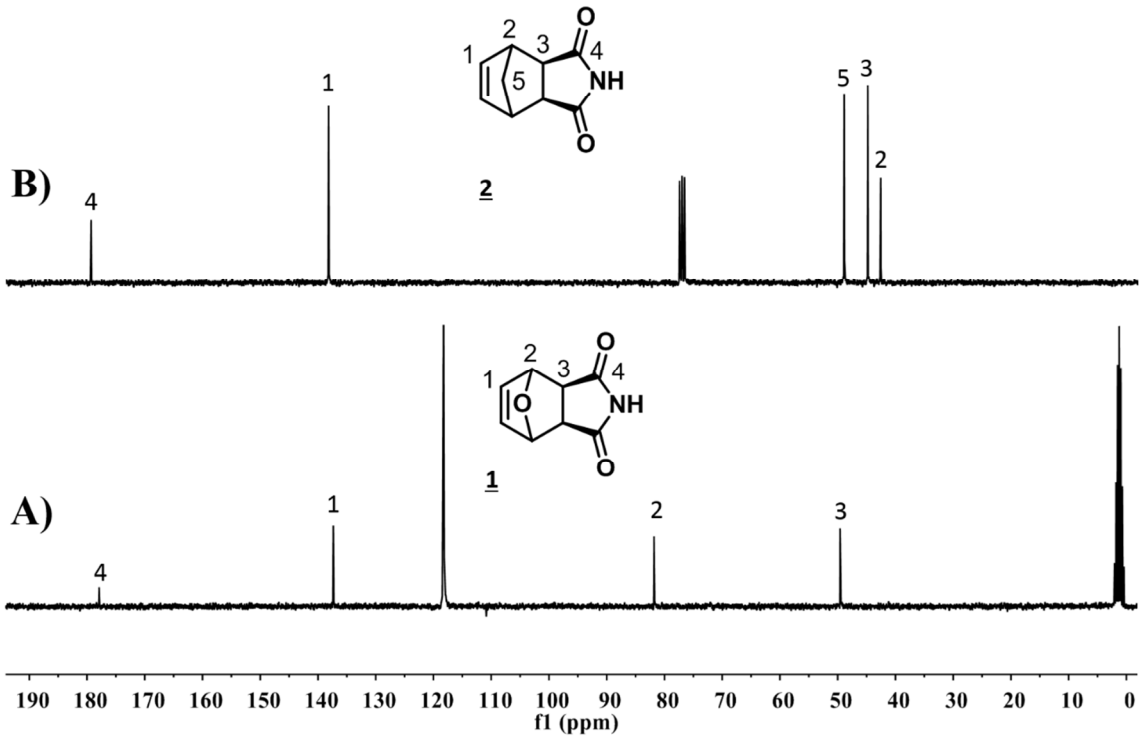


Figure S2. ^{13}C NMR spectra (75 MHz, 25°C) of A) *exo*-7-oxanorbornene-2,3-dicarboximide (**1**) in CD_3CN and B) *exo*-5-norbornene-2,3-dicarboximide (**2**) in $CDCl_3$.

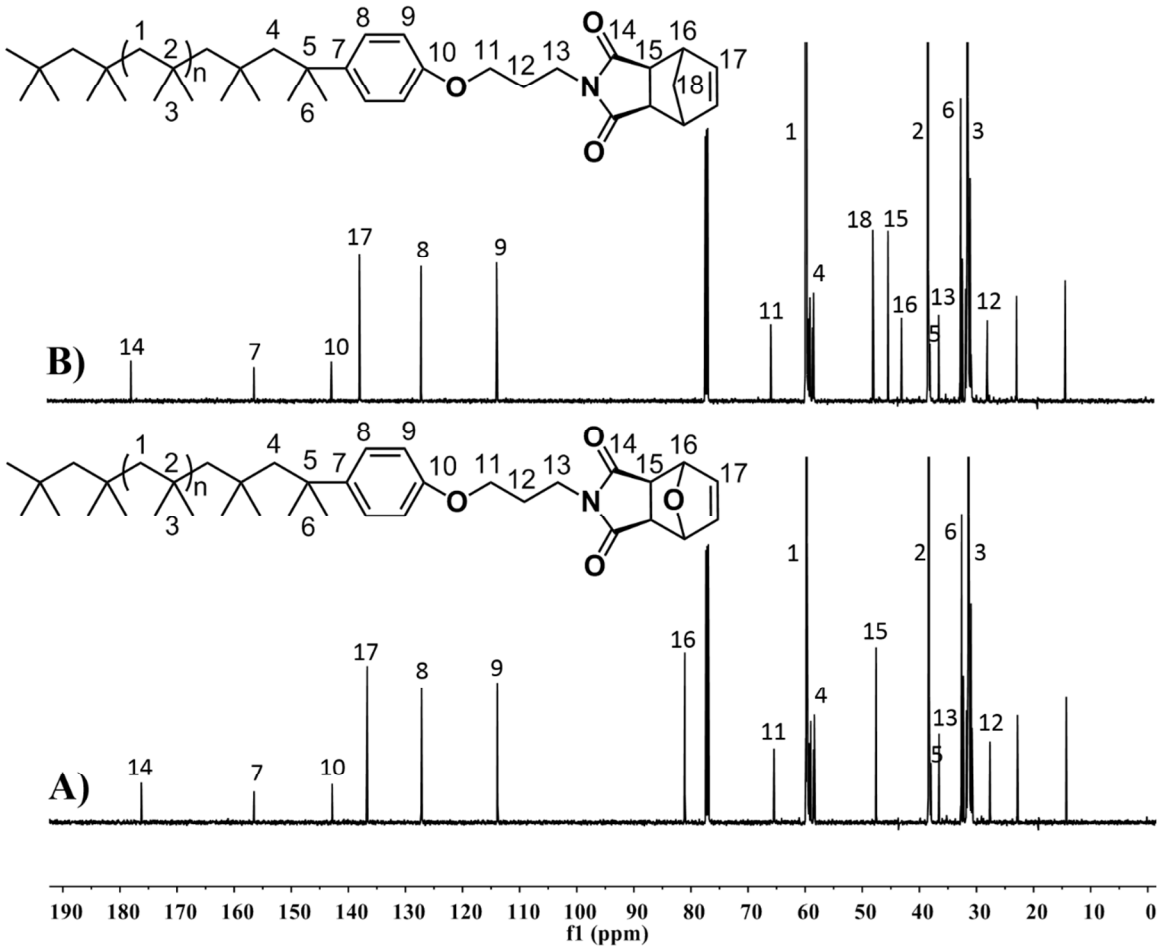


Figure S3. ^{13}C NMR spectra (150 MHz, 25°C, $CDCl_3$) of monofunctional A) PIB oxanorbornene macromonomer (PIB MM1), and B) PIB norbornene macromonomer (PIB MM2).

Table S1. Molecular weight and dispersity of 4K mono-functional PIB oxanorbornene and PIB norbornene macromonomers

Sample	Funct.	$M_{n,NMR}$ (g/mol)	$M_{n,SEC}$ (g/mol)	Đ
4K PIB Br	1	4,040	4,200	1.23
4K PIB oxanorbornene	1	4,420	4,500	1.22
4K PIB norbornene	1	4,400	4,500	1.21

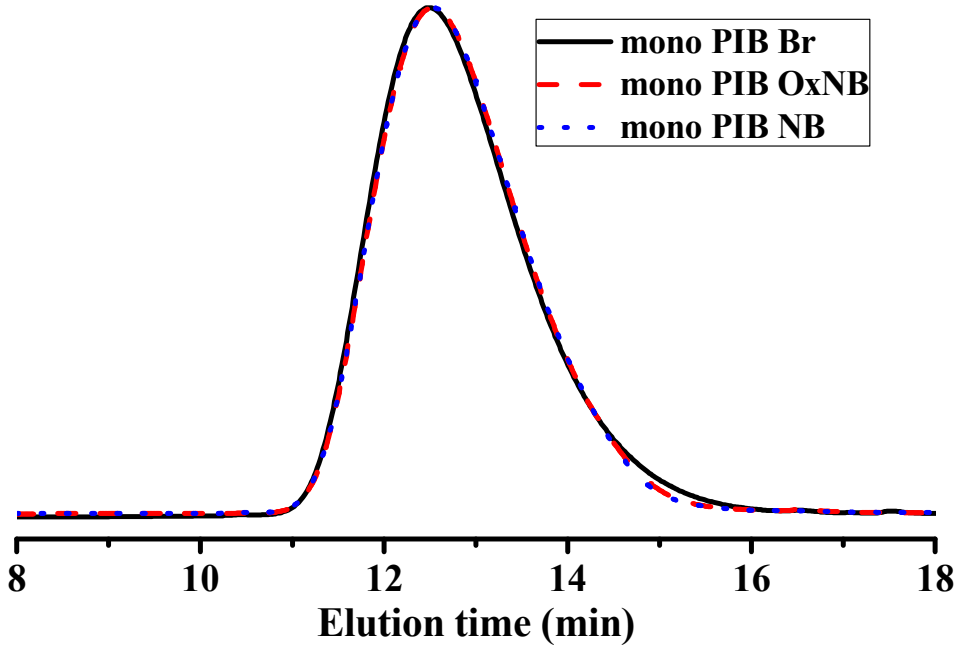


Figure S4. SEC refractive index traces of mono-functional PIB Br (solid) and PIB oxanorbornene (dashed) and PIB norbornene (dot) macromonomers.

Table S2. MALDI-TOF MS data for mono-functional PIB oxanorbornene and PIB norbornene macromonomers

Sample	MW_{theo} f×EG+I+C[a]	MW_{exp} f×EG+I+C	Diff. (%)	M_n (Da x10^{-3})	Đ	M_{ru}[b] (Da)
4K PIB oxanorbornene	518.15	509.06	1.8	1,621	1.14	56.12
4K PIB norbornene	516.17	519.26	0.60	1,996	1.13	56.11

[a] f = chain end functionality = 1; EG = end group; I = initiator (2,4,4-trimethylpent-2-yl, C_8H_{17}); C = ^{107}Ag cation.

[b] ru = repeat unit.

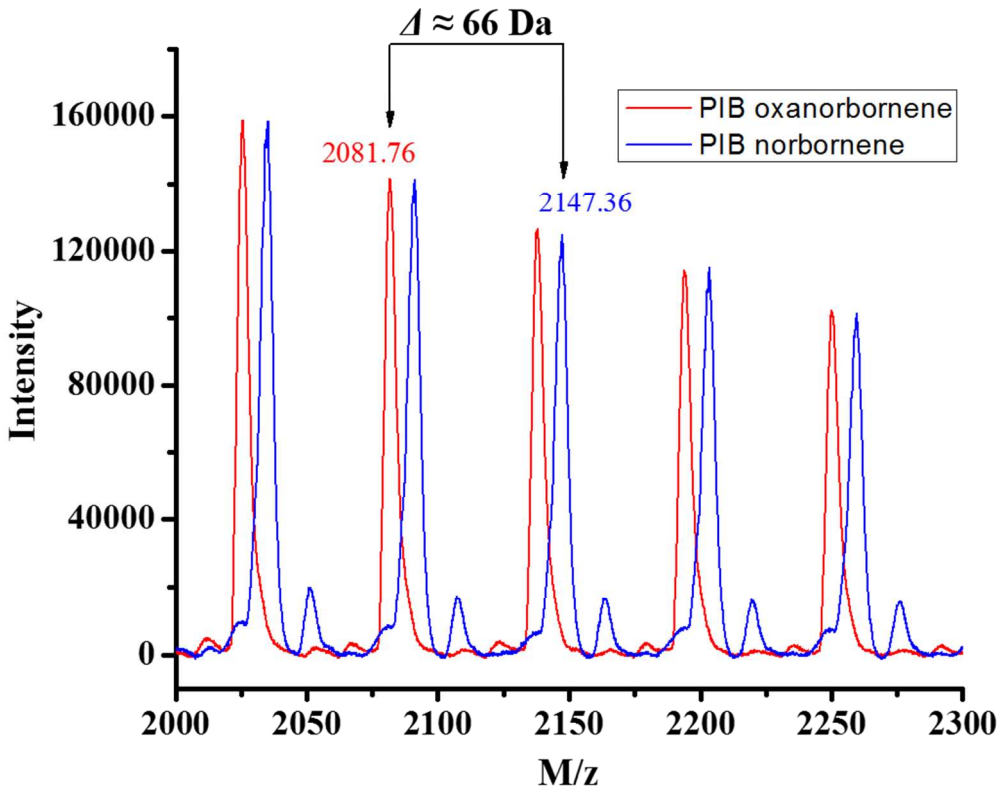


Figure S5. Overlaid MALDI-TOF mass spectra of PIB oxanorbornene (red) and PIB norbornene (blue). We postulate that the PIB oxanorbornene undergoes retro Diels Alder fragmentation during the MALDI-TOF MS experiment to produce the corresponding PIB maleimide. PIB maleimide is lower in mass by one unit of cyclopentadiene (66.05 Da) compared to PIB norbornene. The representative peaks selected above differ by about 66 Da and represent PIB norbornene (blue) and PIB maleimide (red) each possessing a DP = 29.

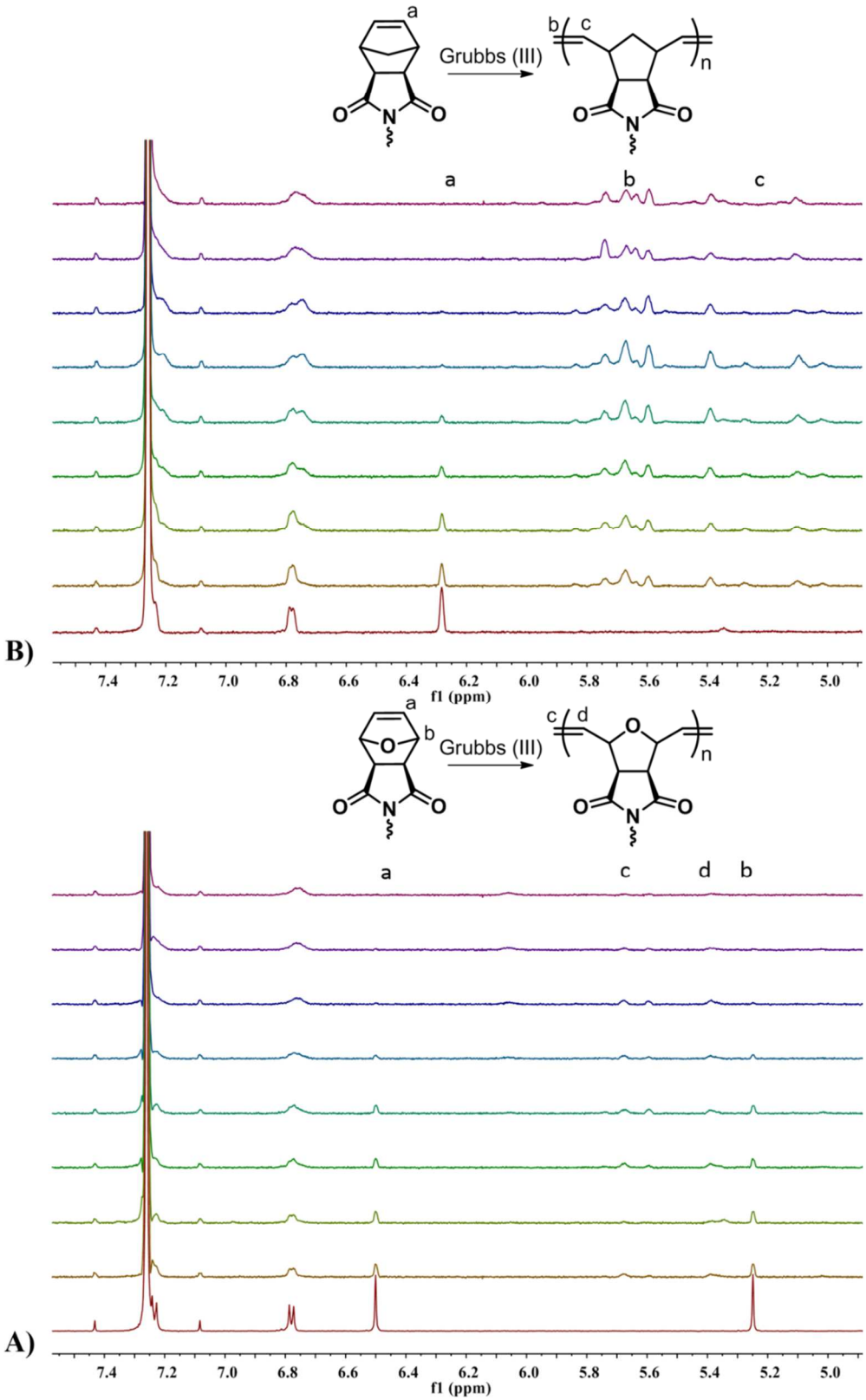


Figure S6. ^{1}H NMR spectral overlay of aliquots taken during ROMP of A) PIB oxonorbornene and B) PIB norbornene MMs at various reaction times.