Supplementary Information for:

Functional Hyperbranched Polymers using Ring Opening Metathesis Polymerization of Dicyclopentadiene with Monoterpenes

Robert T. Mathers,[*†] *Krishnan Damodaran,*[§] *Matthew G. Rendos,*[†] *Michael S. Lavrich*[†]

Department of Chemistry, Pennsylvania State University, New Kensington, PA 15068.

Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

Table of Contents

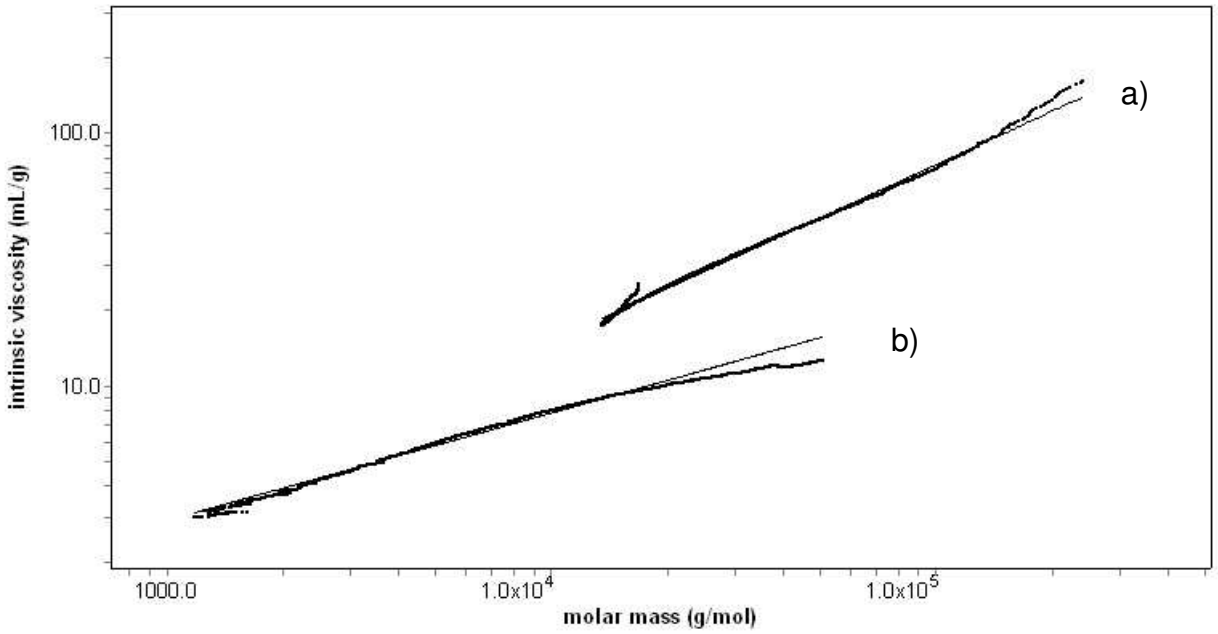

Figure S1. Mark-Houwink-Sakarada plots for the gel permeation chromatography (GPC) data (light scattering and viscometer detectors) obtained for the ring-opening metathesis polymerization (ROMP) of a) norbornene (1.3 M in *d*-limonene; MHS a value = 0.70) and b) dicyclopentadiene (0.3 M in *d*-limonene; MHS a value = 0.53). The polymerizations were run with a second generation ruthenium catalyst ([monomer]/[catalyst] = 800) for 1 h.

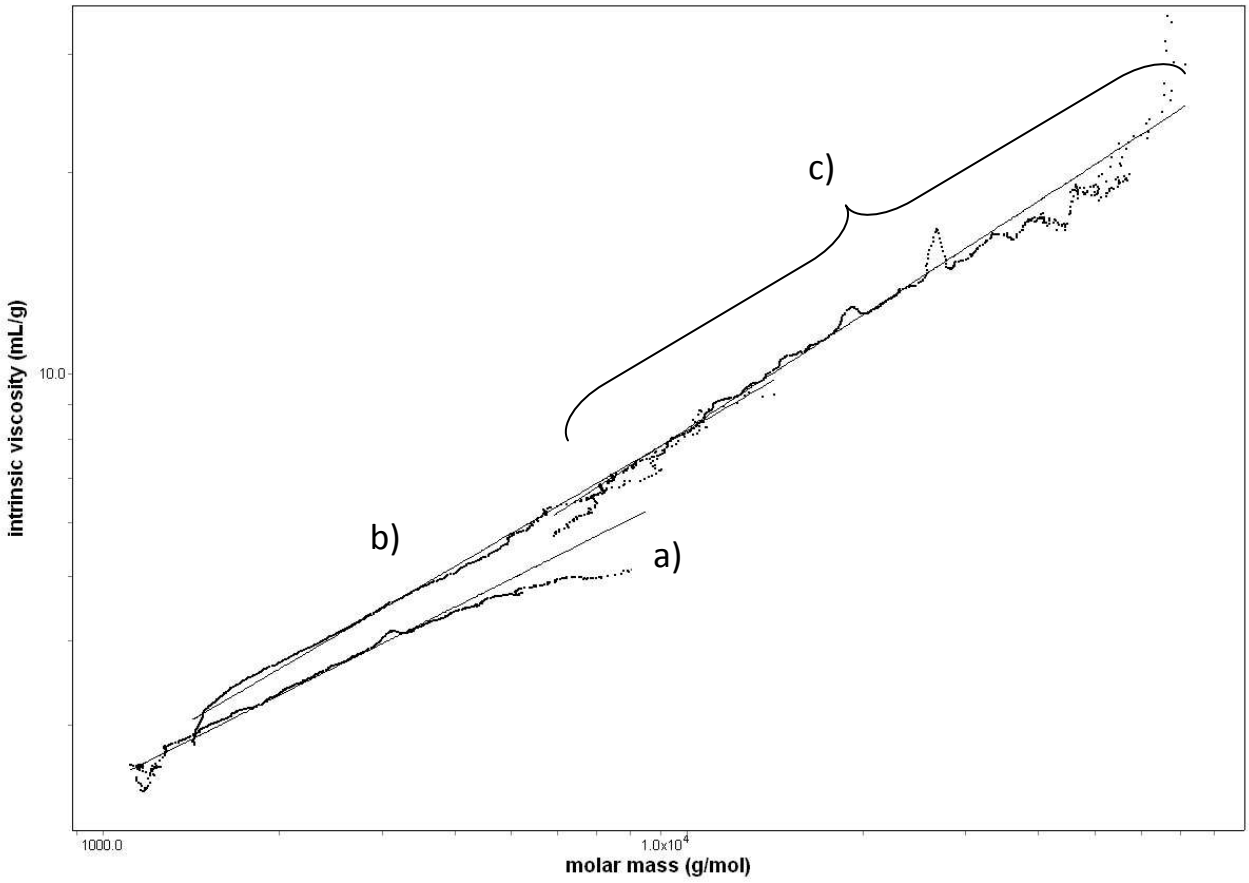

Figure S2. Mark-Houwink-Sakarada plots for the gel permeation chromatography (GPC) data (light scattering and viscometer detectors) obtained for the ring-opening metathesis polymerizations (ROMP) of dicyclopentadiene (0.3 M). The polymerizations were run with a second generation ruthenium catalyst for 1 h at 50° C using a) neat β-pinene and [monomer]/[catalyst] = 200, b) neat β-pinene and [monomer]/[catalyst] = 1000, and c) stoichiometric amounts of β-pinene ([monomer]/[β-pinene] = 5) in toluene and [monomer]/[catalyst] = 1000.

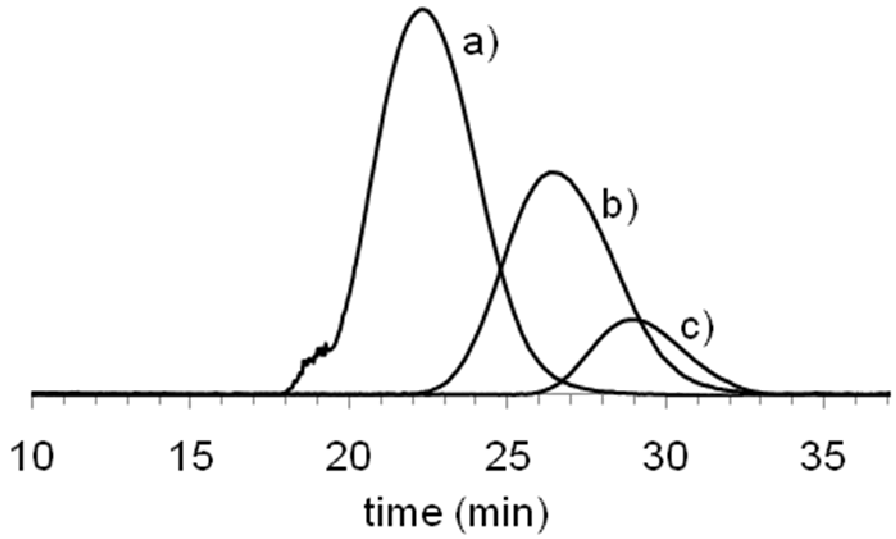

Figure S3. Gel permeation chromatography (GPC) data (light scattering detector) for the polymerization of norbornene with the 2nd generation Grubbs catalyst ([NB]/[catalyst] = 1000) in a) toluene, b) *d*-limonene and c) β-pinene. The polymerizations were run for 1 h at 50° C under nitrogen.

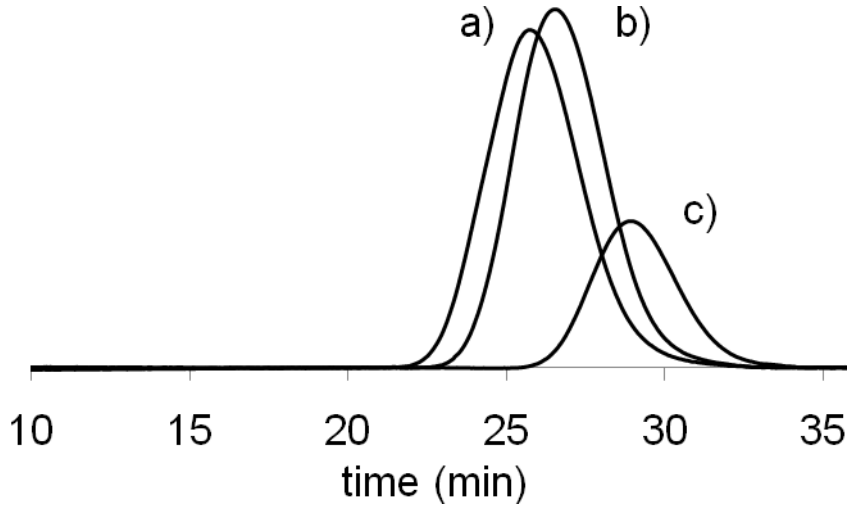

Figure S4. Gel permeation chromatography (GPC) data (light scattering detector) for the polymerization of dicyclopentadiene (DCPD) in toluene with stoichiometric amounts of β-pinene: a) [DCPD]/[β-pinene] = 40, b) [DCPD]/[β-pinene] = 20 and c) [DCPD]/[β-pinene] = 5. The polymerizations were run for 1 h at 50° C under nitrogen with the 2nd generation Grubbs catalyst ([DCPD]/[catalyst] = 1000).

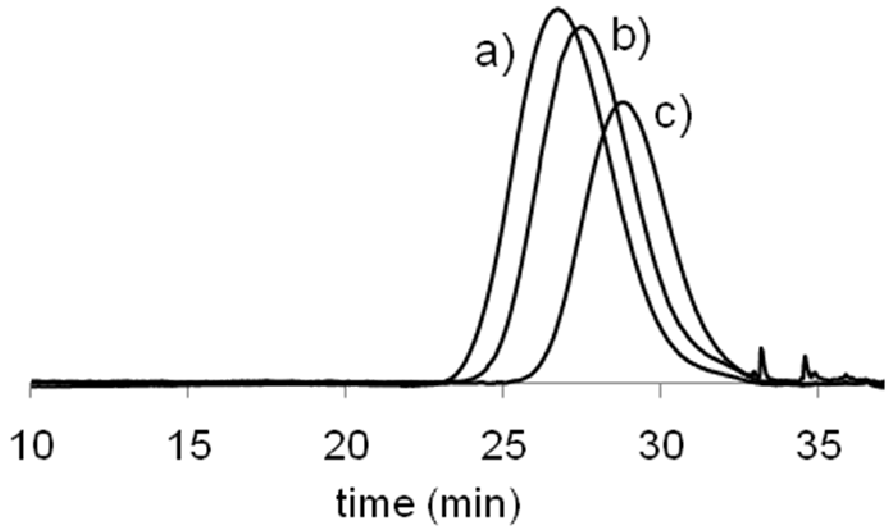

Figure S5. Gel permeation chromatography (GPC) data (light scattering detector) for the polymerization of dicyclopentadiene (DCPD) in toluene with stoichiometric amounts of limonene oxide: a) [DCPD]/[limonene oxide] = 40, b) [DCPD]/[limonene oxide] = 20 and c) [DCPD]/[limonene oxide] = 5. The polymerizations were run for 1 h at 50° C under nitrogen with the 2nd generation Grubbs catalyst ([DCPD]/[catalyst] = 1000).

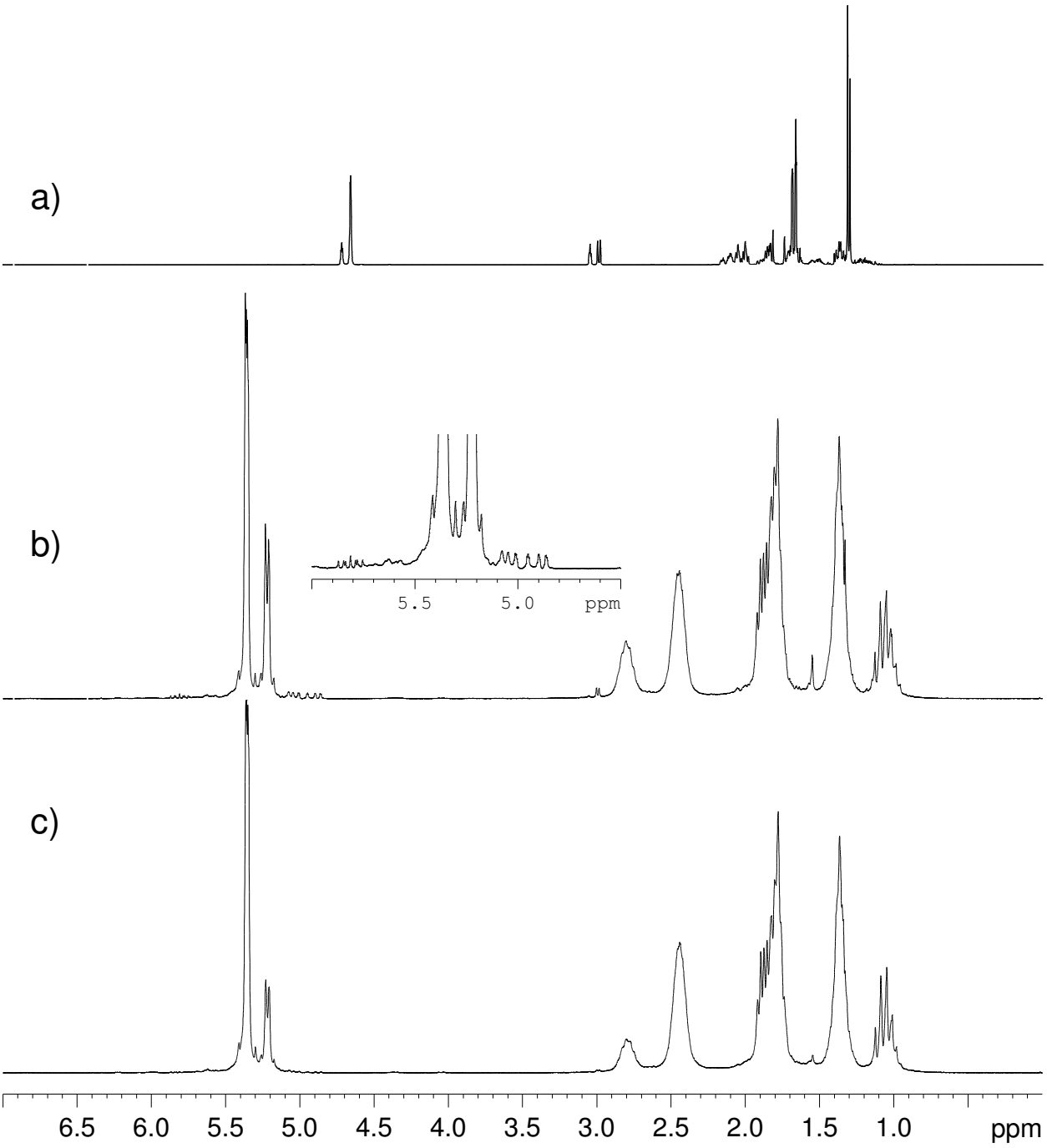

Figure S6. ^{1}H NMR (300 MHz, $CDCl_3$) spectra for a) limonene oxide, b) polymerization of norbornene at 50° C for 1 h with [NB]/[limonene oxide] = 3 (M_w = 7800 g/mol; M_w/M_n = 1.3) and c) polymerization of norbornene at 50° C for 1 h with [NB]/[limonene oxide] = 40 (M_w = 24300 g/mol; M_w/M_n = 1.3).

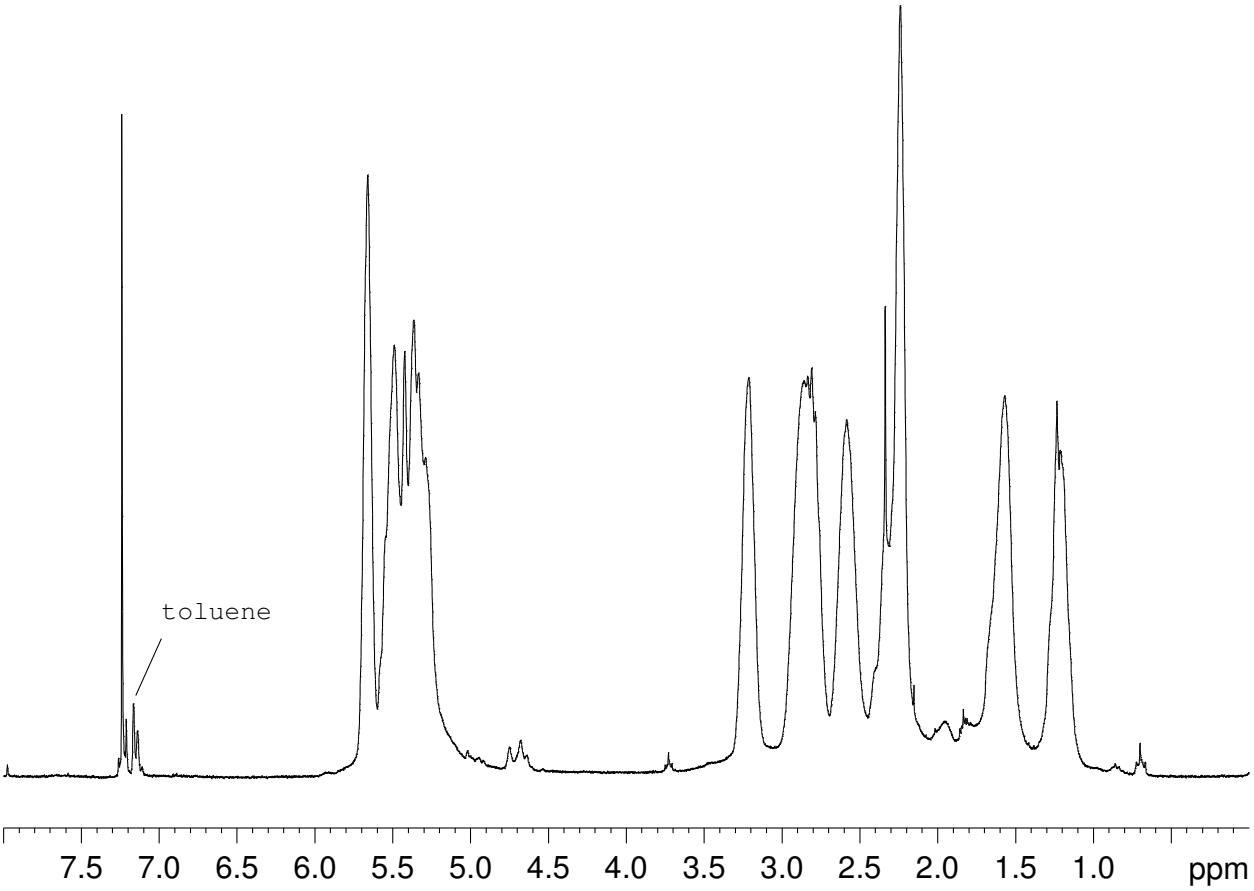

Figure S7. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for polymerization of dicyclopentadiene (0.3 M) in toluene with β-pinene ([DCPD]/[β-pinene] = 40) for 1 h at 50° C using [DCPD]/[catalyst] = 1000.

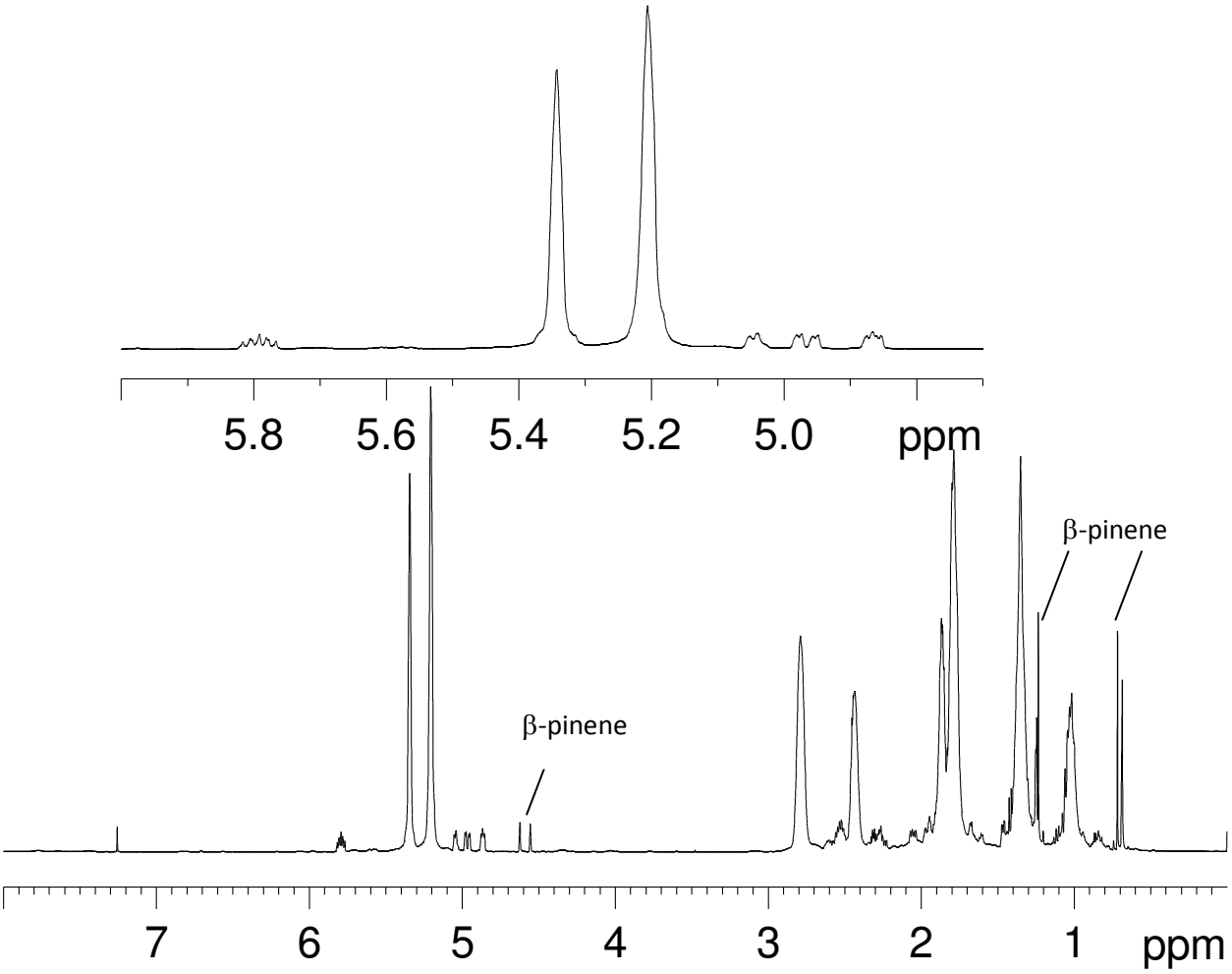

Figure S8. ^{1}H NMR (700 MHz, $CDCl_3$) spectrum and expanded view of alkene region for polymerization of norbornene (0.3 M) at 50° C for 1 h with neat β-pinene.

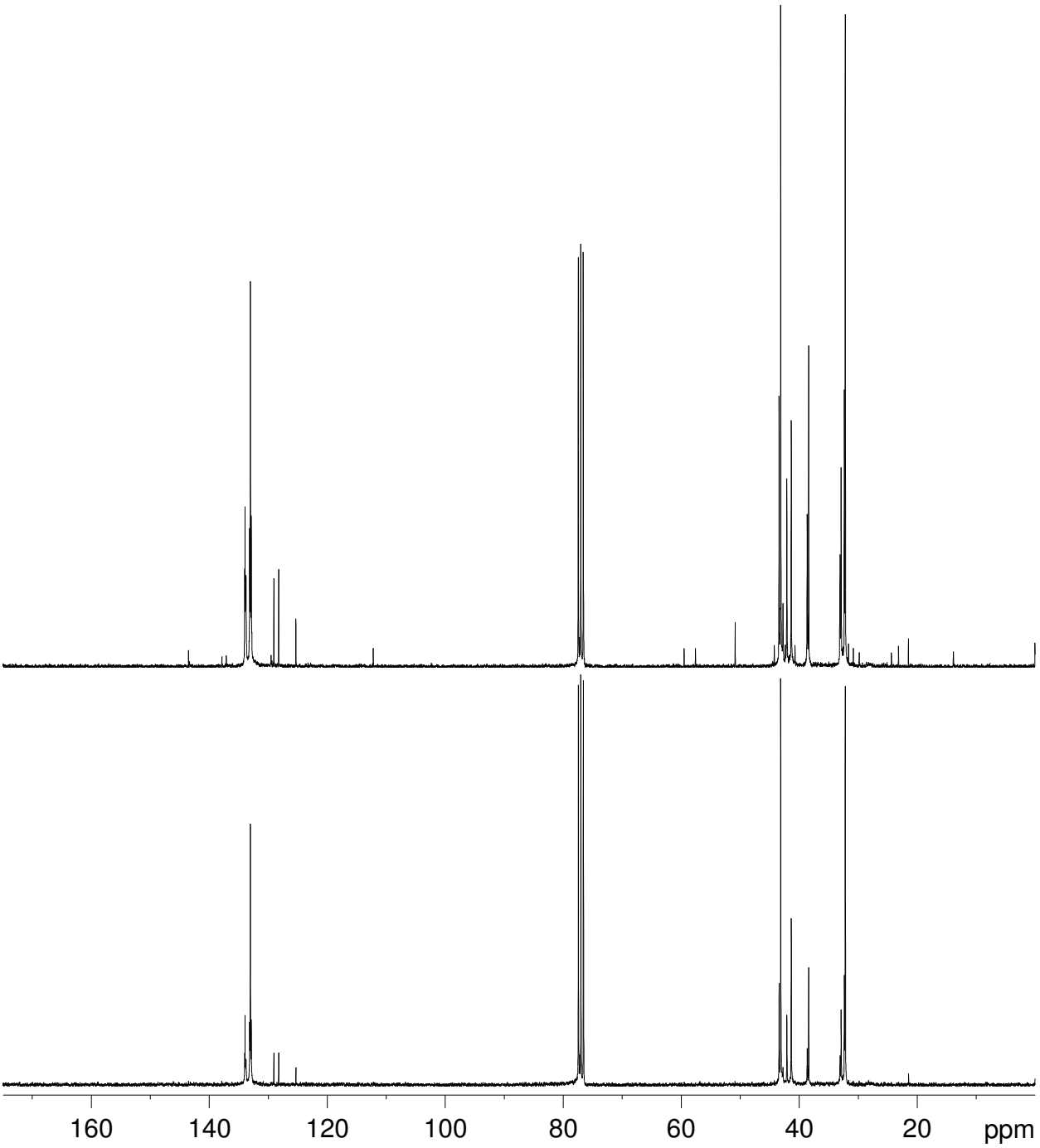

Figure S9. ^{13}C NMR (75 MHz, $CDCl_3$) spectra for the polymerization of norbornene at 50° C for 1 h with a) [NB]/[limonene oxide] = 3 (M_w = 7800 g/mol; M_w/M_n = 1.3) and b) [NB]/[limonene oxide] = 40 (M_w = 24300 g/mol; M_w/M_n = 1.3).

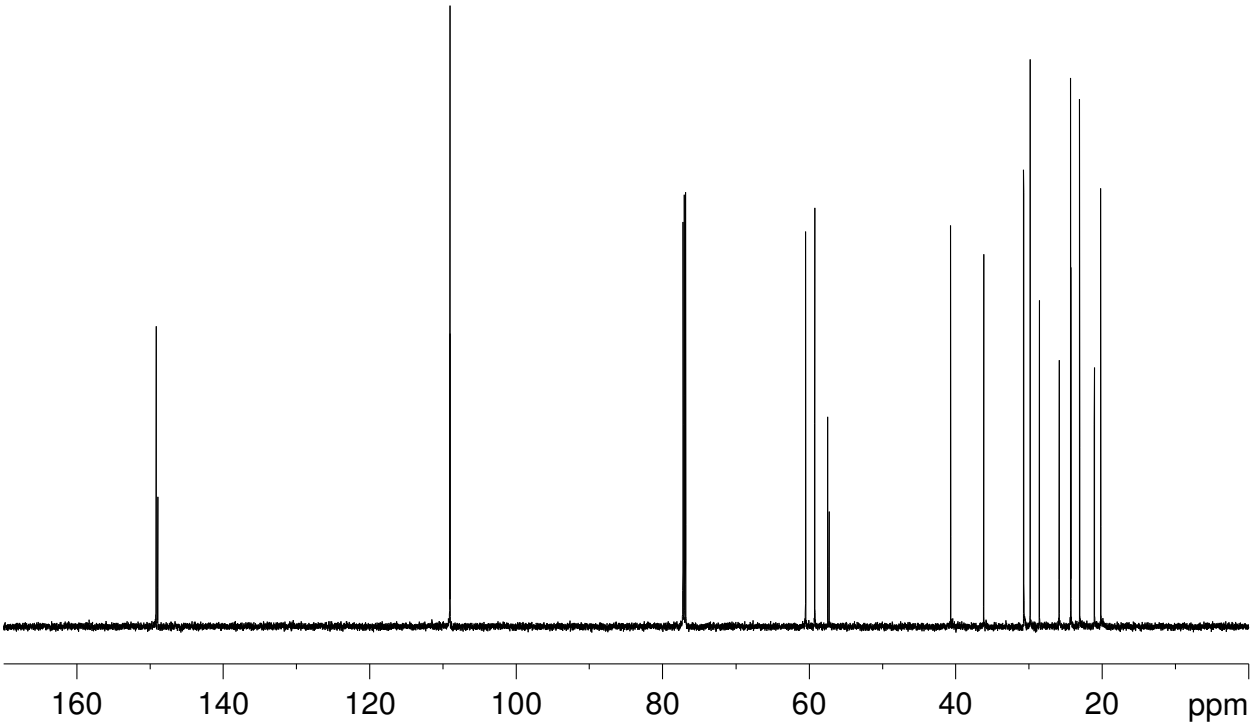

Figure S10. ^{13}C NMR (176 MHz, $CDCl_3$) spectrum for limonene oxide.

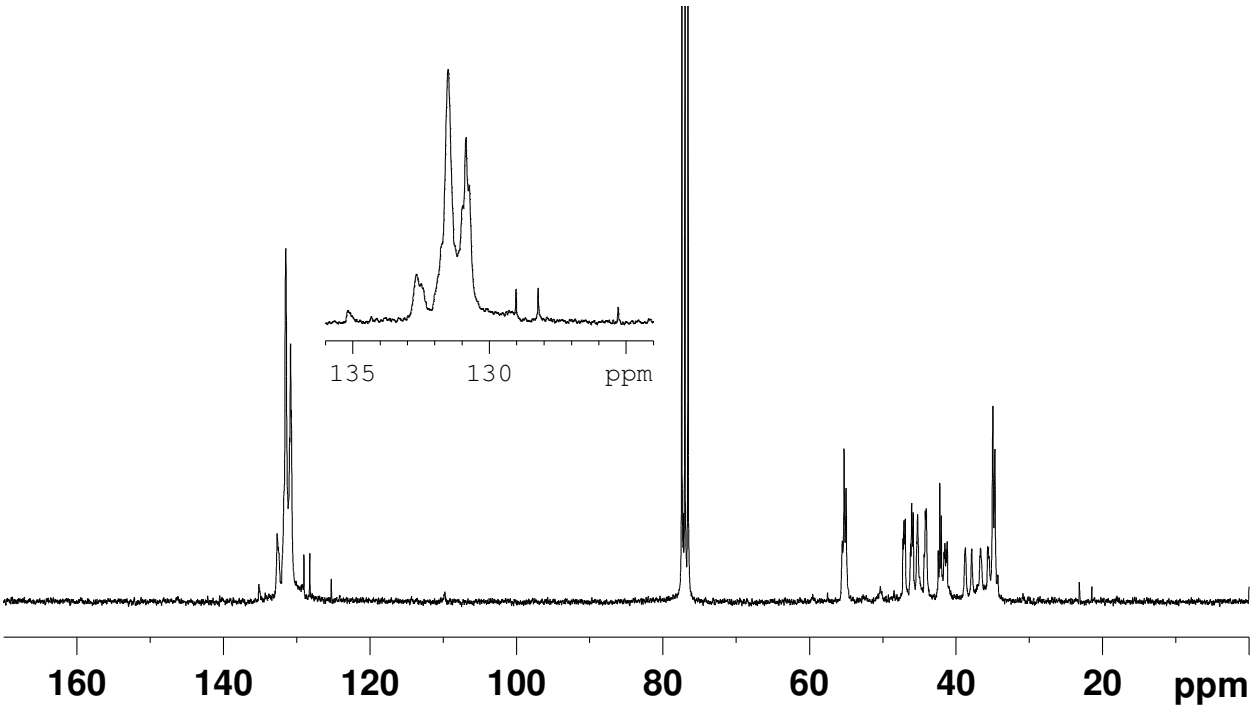

Figure S11. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for the polymerization of dicyclopentadiene (0.3 M) in toluene with limonene oxide ([dicyclopentadiene]/[limonene oxide] = 5) after 1 h at 50° C using a second generation ruthenium catalyst ([dicyclopentadiene]/[catalyst] = 1000).

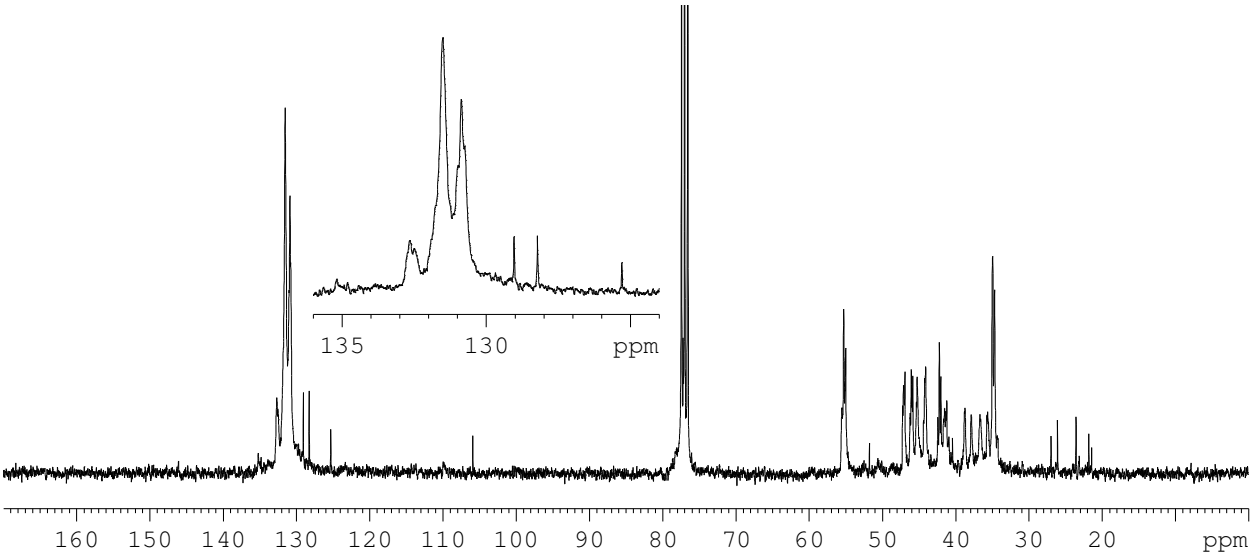

Figure S12. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for the polymerization of dicyclopentadiene (0.3 M) in toluene with β-pinene ([dicyclopentadiene]/[β-pinene] = 5) after 1 h at 50° C using a second generation ruthenium catalyst ([dicyclopentadiene]/[catalyst] = 1000).