

Expanded Functionality of Polymers Prepared using Metal-Free Ring-Opening Metathesis Polymerization

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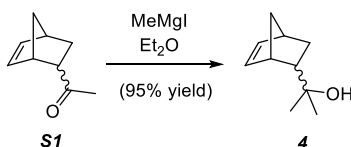
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Materials and Methods. For reactions set up inside the glovebox CH₂Cl₂ was obtained from a solvent purification system and stored inside the glovebox. For reactions set up outside the glovebox, CH₂Cl₂ was dried over 4Å molecular sieves before use. All polymerizations were carried out in standard borosilicate glass vials purchased from Fisher Scientific with magnetic stirring unless otherwise noted. Irradiation of photochemical reactions was done using a 2 W Miracle blue LED indoor gardening bulb purchased from Amazon. Norbornene (**1**) was sublimed prior to use. The alcohols used for the additive studies were dried over 4A molecular sieves prior to use. Pyridine and THF were obtained from a solvent purification system. All other reagents and solvents were obtained from commercial sources and used as received unless otherwise noted. ¹H and ¹³C NMR spectra were recorded on Bruker AVance 300 MHz or 500 MHz spectrometers. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the residual protio-solvent as an internal standard (CDCl₃, ¹H: 7.26 ppm and ¹³C: 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd= doublet of doublets, br = broad, m = multiplet), coupling constants (Hz) and integration. Gel permeation chromatography (GPC) was performed using a GPC setup consisting of: a Shimadzu pump, 3 in-line columns, and Wyatt light scattering and refractive index detectors with tetrahydrofuran (THF) as the mobile phase. Number-average molecular weights (*M_n*) and weight-average molecular weights (*M_w*) were calculated from light scattering. *T_g* values were determined using either a Perkin-Elmer DMA 8000 or a TA instruments Discovery DSC. For DMA, analysis was performed on powdered samples held within material pockets supplied by Perkin-Elmer. Samples were analyzed using the Single-Cantilever Geometry Fixture with the following settings: heating rate = 3.0 °C/min, frequency = 1 Hz, static force = 1.0 N. Reported *T_g* values refer to the temperature corresponding to the peak of the tan delta curve. For *T_g* values below room temperature, samples were analyzed by DSC at a rate of 10 °C/min. The pyrylium tetrafluoroborate salt was prepared according to literature procedure.¹ TGA analysis was performed using a TA Instruments Q50 TGA.

Preparation of Monomers

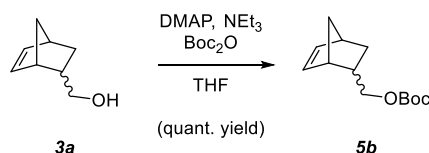
Monomers **3**, **5a**, and **5e** were prepared using known procedures starting from the commercially available mixture of 5-norbornene-2-carboxylic acid diastereomers.^{2,3,4} Monomers **5f**, **5g**, and **5h** were prepared using reported procedures.^{5,6,7} Compound **5h** was obtained as a 1.8:1 mixture of *endo:exo* diastereomers.⁸

Preparation of tertiary alcohol **4**.



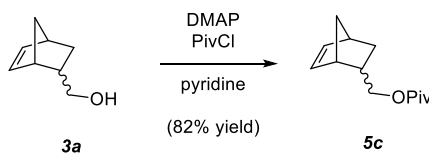
To a solution of **S1** (2.75 mL, 20.29 mmol) in Et₂O (100 mL) at 0 °C was added a solution of MeMgI (35 mL, 1.06 M, 36.95 mmol). The reaction mixture was stirred for 2 h and then saturated NH₄Cl (aq) solution and water (50 mL each) were added to the mixture. The mixture was extracted with EtOAc (2 × 60 mL) and the combined organics were then washed with brine (50 mL), and then dried over MgSO₄. Purification of the desired product by flash chromatography on silica gel (1:1 hexanes:Et₂O eluent) provided 2.92 g (95% yield) of alcohol **4**. Spectral data matched those previously reported.⁹

Preparation of carbonate **5b**.



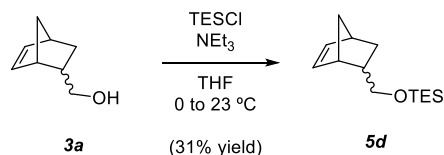
To a solution of alcohol **3a** (2.48 g, 19.97 mmol, 1 equiv) in THF (20 mL) was added triethylamine (8.5 mL, 60.98 mmol, 3 equiv), DMAP (245.1 mg, 2.01 mmol, 0.1 equiv), and di-*tert*-butyl dicarbonate (8.62 g, 39.50 mmol, 2 equiv). After 17 hours, water (5 mL) and Et₂O (75 mL) were added. This mixture was washed successively with H₂O (40 mL), 5% HCl (40 mL), sat. aq. NaHCO₃ (50 mL), and brine (50 mL). The organic layer was dried over MgSO₄. The crude product was purified by flash chromatography (9:1 hexane:Et₂O eluent) to give the desired product (4.47 g, quantitative yield) as a 4.2:1 ratio of diastereomers. ¹H-NMR (major isomer) (CDCl₃, 300 MHz) 6.21–6.15 (*m*, 1H), 5.98 (*dd*, *J* = 5.6, 2.6, 1H), 3.95–3.65 (*m*, 2H), 2.94 (*s*, 1H), 2.84 (*s*, 1H), 2.53–2.37 (*m*, 1H), 1.94–1.82 (*m*, 1H), 1.50 (*s*, 9H), 1.32–1.23 (*m*, 2H), 0.62–0.53 (*m*, 1H); ¹³C-NMR (major isomer) (CDCl₃, 75 MHz) 153.8, 137.7, 132.3, 81.0, 70.5, 49.5, 43.9, 42.3, 37.9, 29.0, 27.9; MS-ESI (*m/z*) [*M* + NH₄⁺] calcd for C₁₃H₂₄NO₃, 242.2, found, 242.2.

Preparation of pivalate **5c**.



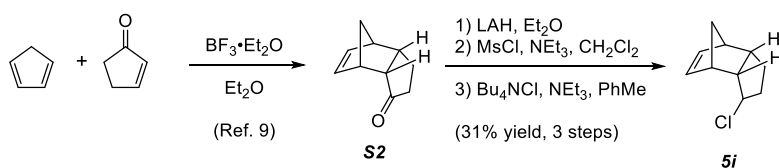
To a flask containing a stir bar was added alcohol **3a** (1.56 g, 12.56 mmol, 1 equiv), pyridine (62 mL), and DMAP (308.6 mg, 2.53 mmol, 0.2 equiv). The pivaloyl chloride (1.9 mL, 15.44 mmol, 1.2 equiv) was added dropwise, and the reaction stirred for 4.5 hours. Water (100 mL) was added and the reaction extracted with EtOAc (2 x 75 mL). The combined organic layers were washed consecutively with 1M HCl (2 x 50 mL), 1M NaOH (50 mL), saturated aq. NaHCO₃ (50 mL), brine (50 mL), and then dried over MgSO₄. The crude product was purified by flash chromatography (12:1 hexane:EtOAc eluent) to give the desired product (2.17 g, 82%) as a 3.9:1 *endo:exo* mixture of diastereomers. ¹H-NMR (major isomer) (CDCl₃, 300 MHz) 6.14 (*dd*, *J* = 5.4, 2.8, 1H), 5.92 (*dd*, *J* = 5.4, 2.6, 1H), 3.84 (*dd*, *J* = 10.7, 6.8, 1H), 3.62 (*app. t*, *J* = 10.2, 1H), 2.84 (*d*, *J* = 17.0, 1H), 2.52–2.33 (*m*, 1H), 1.88–1.76 (*m*, 1H), 1.48–1.31 (*m*, 3H), 1.20 (*s*, 9H), 0.55 (*ddd*, *J* = 11.6, 4.0, 2.5, 1H); ¹³C-NMR (CDCl₃, 125 MHz) 178.5, 137.5, 132.3, 67.8, 49.4, 44.0, 42.3, 38.9, 37.9, 28.9, 27.3; MS-ESI (*m/z*) [*M* + Na⁺] calcd for C₁₃H₂₀O₂Na, 231.1; found 231.0.

Preparation of TES ether **5d**.



To a flame dried flask was added THF (11 mL) and triethylamine (1.50 mL, 10.5 mmol, 1.3 equiv). The reaction was cooled to 0 °C and triethylsilyl chloride (1.80 mL, 10.5 mmol, 1.3 equiv) was added rapidly. A solution of 5-norbornene-2-methanol (1.00 g, 8.06 mmol, 1.0 equiv) in THF (8 mL) was added dropwise and the reaction mixture was warmed to room temperature. After 2 hrs. water (20 mL) was added and the mixture extracted with hexanes (4 x 20 mL). The combined organic layers were then washed with water (40 mL), brine (40 mL) and dried over MgSO₄. The solvent was evaporated to give the crude product as a yellow oil which was passed through a silica plug using hexanes to give **3c** as an oil (0.602 g, 31%). Spectral data matched those previously reported.¹⁰

Preparation of chlorinated monomer **5i**.



Monomer **5i** was prepared from Diels-Alder adduct **S2**, which was obtained using a known procedure.¹¹ To a flask containing a slurry of lithium aluminum hydride (1.80 g, 47.4 mmol) in Et₂O (150 mL) at 0 °C was added over 5 minutes **S2** (4.62 g, 31.17 mmol, 1 equiv) as a solution in 10 mL Et₂O. The reaction was allowed to gradually warm to room temperature. After 90 minutes, the flask was cooled to 0 °C, and MeOH (20 mL) was added gradually (*add MeOH slowly with a vent needle present on the flask to avoid pressure buildup*) followed by 30% aq.

Rochelle's salt (75 mL). After stirring for an additional 60 minutes, the solution was extracted with Et₂O (3 x 75 mL), and the combined organic layers dried over MgSO₄. Evaporation under reduced pressure afforded the crude alcohol, which was used directly in the next step.

To a solution of the crude alcohol and triethylamine (6.5 mL, 46.64 mmol, 1.5 equiv) in CH₂Cl₂ (130 mL) at 0 °C was added methanesulfonyl chloride (2.7 mL, 34.88 mmol, 1.1 equiv) dropwise over 2 minutes. After 3.5 hours, the reaction mixture was transferred to a separatory funnel was washed successively with H₂O (60 mL), 10% aq. HCl (60 mL), sat. aq. NaHCO₃ (75 mL), and brine (75 mL). The organic layer was then dried over MgSO₄. Evaporation under reduced pressure afforded the crude mesylate, which was further purified by flash chromatography (1:1 hexane:Et₂O) to give the desired mesylate (4.51 g, 63% yield, 2 steps) which was used directly in the next step.

To a flame-dried flask containing anhydrous tetrabutylammonium chloride (8.2 g, 29.5 mmol, 1.5 equiv), toluene (50 mL), and triethylamine (6 mL, 43.05 mmol, 2.2 equiv) was added the mesylate as a solution in toluene (2 mL). The flask was placed in an oil bath at 50 °C for 22 hours. After cooling to room temperature, the reaction mixture was diluted with Et₂O (75 mL) and washed with H₂O (4 x 100 mL) and brine (100 mL) and the organic layer dried over MgSO₄. Evaporation under reduced pressure afforded the crude product, which was purified by flash chromatography (hexane eluent) to afford chloride **5i** (1.63 g, 49% yield) as a colorless oil. ¹H-NMR (CDCl₃, 300MHz) 6.21–6.09 (*m*, 2H), 3.70 (*app. q*, *J* = 5.9, 1H), 2.96 (*s*, 1H), 2.89–2.81 (*m*, 2H), 2.78 (*s*, 1H), 2.15–2.07 (*m*, 1H), 1.91–1.76 (*m*, 2H), 1.59 (*d*, *J* = 8.2, 1H), 1.44 (*d*, *J* = 8.2, 1H), 1.08–1.00 (*m*, 1H); ¹³C-NMR (CDCl₃, 75 MHz) 137.2, 135.8, 62.0, 57.7, 53.4, 47.0, 46.2, 44.7, 41.1, 27.0; GC-MS (*m/z*) calcd for C₁₀H₁₃Cl, 168.1; found 168.1.

General Procedure for Polymerizations Set Up Inside the Glovebox

A 2 dram vial containing a magnetic stirbar and *p*-OMeTPT (1.1 mg, 0.002 mmol, 0.05 equivs) was taken into a glovebox maintained under nitrogen atmosphere. To this vial was added norbornene (**1**, 424 mg 4.5 mmol, 100 equiv). Dichloromethane (2 mL) was added, followed by ethyl propenyl ether (5 µL, 0.045 mmol, 1 equiv). The vial was capped, removed from the glovebox, and irradiated with blue LEDs (λ = 450–480 nm, 2 W) for 90 minutes. A small scoop of hydroquinone was added to the vial and an aliquot taken for analysis to determine conversion. The contents of the vial were then diluted with CH₂Cl₂ and filtered over neutral alumina to remove any remaining *p*-OMeTPT. This CH₂Cl₂ mixture was concentrated down to ~5 mL and added slowly to MeOH (70 mL) causing the polymer to precipitate. The solids were collected by filtration, washed with MeOH and acetone, and dried under reduced pressure to give the final polymer.

General Procedure for (Co)Polymerizations Set Up Outside the Glovebox

To a 2 dram vial containing a magnetic stirbar was added *p*-OMeTPT (1.1 mg, 0.002 mmol, 0.05 equivs) followed by norbornene and any comonomers (total 4.5 mmol, 100 equiv). Dichloromethane (2 mL) was added, followed by ethyl propenyl ether (5 µL, 0.045 mmol, 1 equiv). The vial was capped and irradiated with blue LEDs (λ = 450–480 nm, 2 W) for 90

minutes. A small scoop of hydroquinone was added to the vial and an aliquot taken for analysis to determine conversion of each monomer. The contents of the vial were then diluted with CH₂Cl₂ and filtered over neutral alumina to remove any remaining *p*-OMeTPT. This CH₂Cl₂ mixture was concentrated down to approximately 5 mL and added slowly into MeOH (70 mL) causing the polymer to precipitate. The solids were collected by filtration, washed successively with MeOH and acetone, and then dried under reduced pressure to give the final polymer.

Method for Determining Conversion for (Co)polymerizations

Conversions were approximated using ¹H-NMR spectroscopy (CDCl₃) by comparing the relative integrations of the following signals. In cases where monomer and polymer signals overlapped, the polymer integration was determined by subtracting the monomer signals from the total integration:

Polymerization of norbornene: The monomer peak at 5.99 ppm was integrated against the region from 3.0–2.3 ppm, which contained signals corresponding 2H from the monomer and 2H from the polymer.

Copolymerization of methyl ether monomer 5a and norbornene: The norbornene monomer signal at 5.99 ppm (2H) and the methyl ether monomer signals from 6.2–5.90 (2H) were integrated against the region from 3.15–2.30 ppm, which contains signals corresponding to 2H from norbornene monomer, 5H from methyl ether monomer, and 4H from the polymer.

Copolymerization of Boc carbonate monomer 5b and norbornene: The norbornene monomer signal at 5.99 ppm (2H) and the Boc monomer signal from 6.20–5.90 (2H) were integrated against the region from 3.0–2.25 ppm, which contained signals corresponding to 2H from norbornene monomer, 3H from Boc carbonate monomer, and 4H from the polymer.

Copolymerization of pivalate monomer 5c and norbornene: The norbornene monomer peak at 5.99 ppm (2H) and pivalate monomer peaks at 6.2–5.9 ppm (2H) were integrated against the region from 3.0–2.2 ppm, which contains signals corresponding to 2H from norbornene monomer, 3H from pivalate monomer, and 4H from the polymer.

Polymerization of TBS ether monomer 5e: The monomer peaks at 6.15–5.9 ppm (2H) were integrated against the region from 3.0–2.3 ppm, which contains signals corresponding to 2H from the monomer and 2H from the polymer.

Copolymerization of TBS ether monomer 5e and norbornene: The monomer peaks at 6.15–5.9 ppm (4H total) were integrated against the region from 3.0–2.3 ppm, which contains signals corresponding to 4H from the monomers, and 4H from the polymer.

Copolymerization of exo-dihydroDCPD monomer 5f and norbornene: The norbornene monomer peaks at 5.99 ppm (2H) and the *exo*-dihydroDCPD monomer peak at 6.1 ppm (2H) were integrated against the region from 1.25–0.90 ppm, which contains signals corresponding to 3H from norbornene monomer, 2H from *exo*-dihydroDCPD monomer and 2H from the polymer.

Copolymerization of benzannulated monomer 5g and norbornene: The norbornene monomer peak at 5.99 ppm (2H) and the benzannulated monomer peak at 6.8 ppm (2H) were integrated against the region from 1.22–0.95 ppm, which contains signals corresponding to 3H from norbornene monomer and 2H from the polymer.

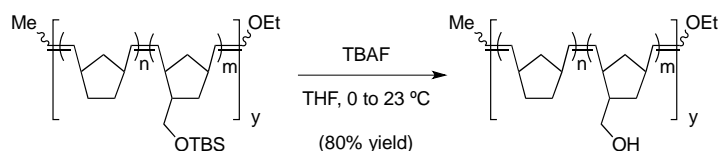
Copolymerization of TMS monomer 5h and norbornene: The monomer peaks at 6.15–5.90 ppm (4H total) were integrated against the region from 1.25–0.8 ppm, which contains signals corresponding to 6H from the monomers and 3H from the polymer.

Polymerization of chlorinated monomer 5i: For larger scale polymerization in CH₂Cl₂ (NMR analysis in CDCl₃), the monomer peaks at 6.17 ppm (2H) were integrated against the region from 4.3–3.65 ppm, which contains signals corresponding to 1H from the monomer and 1H from the polymer. For NMR-scale kinetics experiment in CD₂Cl₂, olefinic regions for monomer and polymer were directly compared.

Table S1. Comparison of Norbornene Polymerizations Set Up Inside vs. Outside of Glovebox

Atmosphere	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Avg.
N ₂	82%	79%	78%	80%	80%	81%	80 ± 1%
Ambient air	88%	85%	89%	86%	88%	85%	87 ± 2%
O ₂	72%	65%	73%	-	-	-	70 ± 4%

Example Removal of TBS Ether from Copolymer



To a solution of the TBS ether-containing copolymer (169.7 mg, TBS content = 20% by ¹H-NMR) in THF (15 mL) at 0 °C was added TBAF (1.0 M in THF, 850 μL, 0.85 mmol) dropwise. The reaction was removed from the ice bath and allowed to gradually warm to room temperature. After 3.5 hours, the reaction mixture was concentrated to ~5 mL under reduced pressure, and then added dropwise to MeOH (50 mL) causing the polymer to precipitate. The solids were collected by filtration, washed with MeOH and acetone and dried under reduced pressure to give the final polymer (109.9 mg, 80% yield, TBS content = 3% by ¹H-NMR spectroscopy).

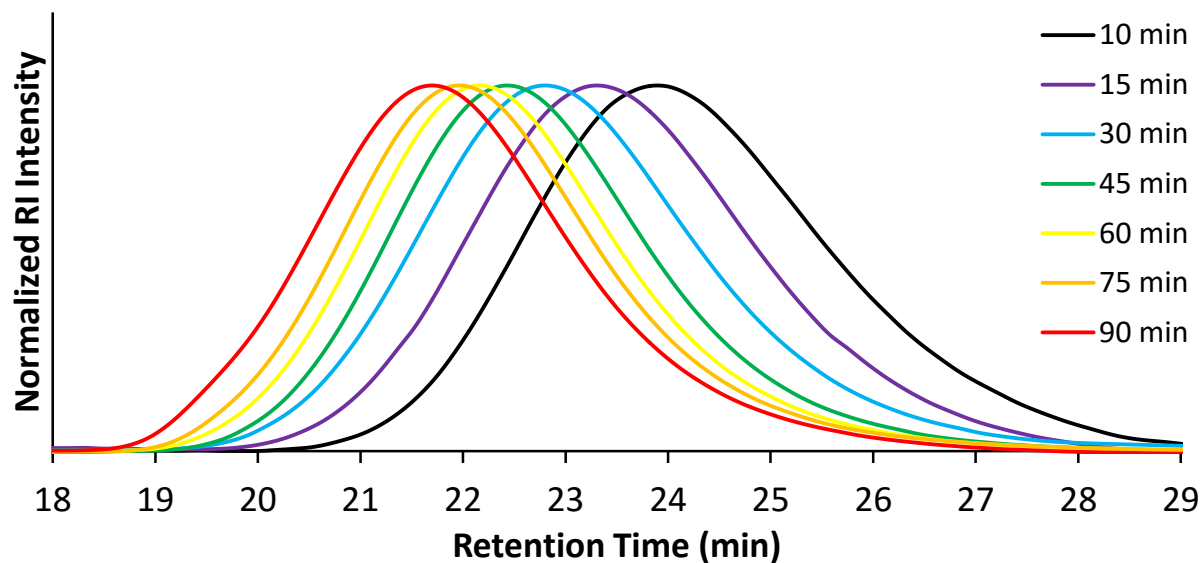
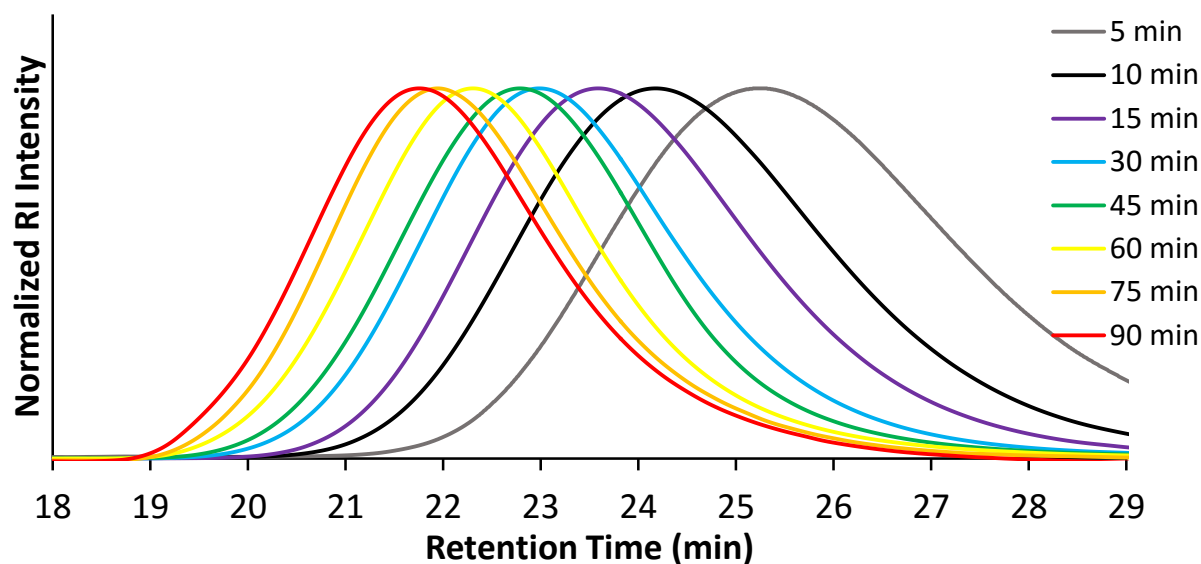


Figure S1. GPC traces taken during the copolymerization of **1** and **5e** with an initial 1:1 feed ratio. (top) GPC traces of crude aliquots. (bottom) GPC traces of polymer samples isolated by precipitation into MeOH at each time point.

Table S2. GPC data from copolymerization of **1** and **5e** relating to Figure S1.

Time (min)	Crude polymer data			Precipitated polymer data		
	M_w (kDa)	M_n (kDa)	\bar{D}	M_w (kDa)	M_n (kDa)	\bar{D}
10	11.7	9.4	1.3	7.7	5.8	1.3
15	11.7	9.9	1.2	12.8	11.4	1.1
30	12.8	11.1	1.2	15.9	14.9	1.1
45	14.9	12.8	1.2	17.8	16.5	1.1
60	16.8	14.6	1.2	19.3	17.3	1.1
75	22.3	20.8	1.1	19.9	16.6	1.2
90	21.9	18.9	1.2	23.0	19.8	1.2

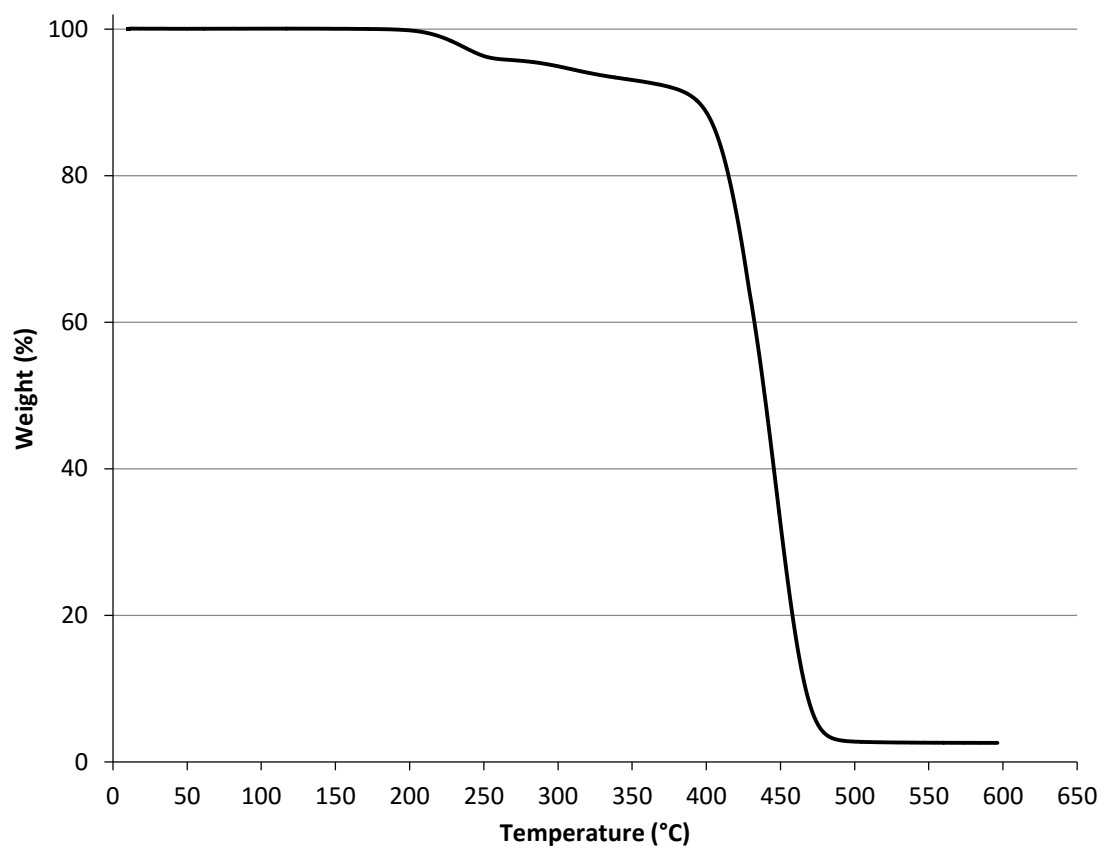
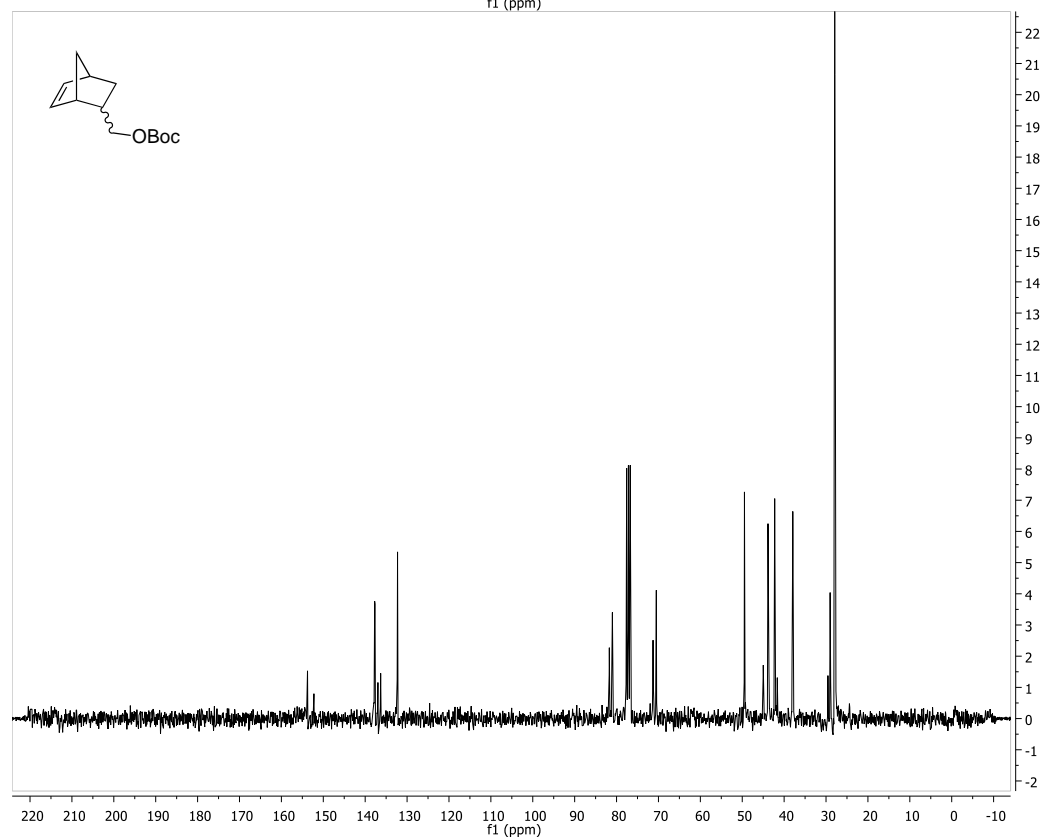
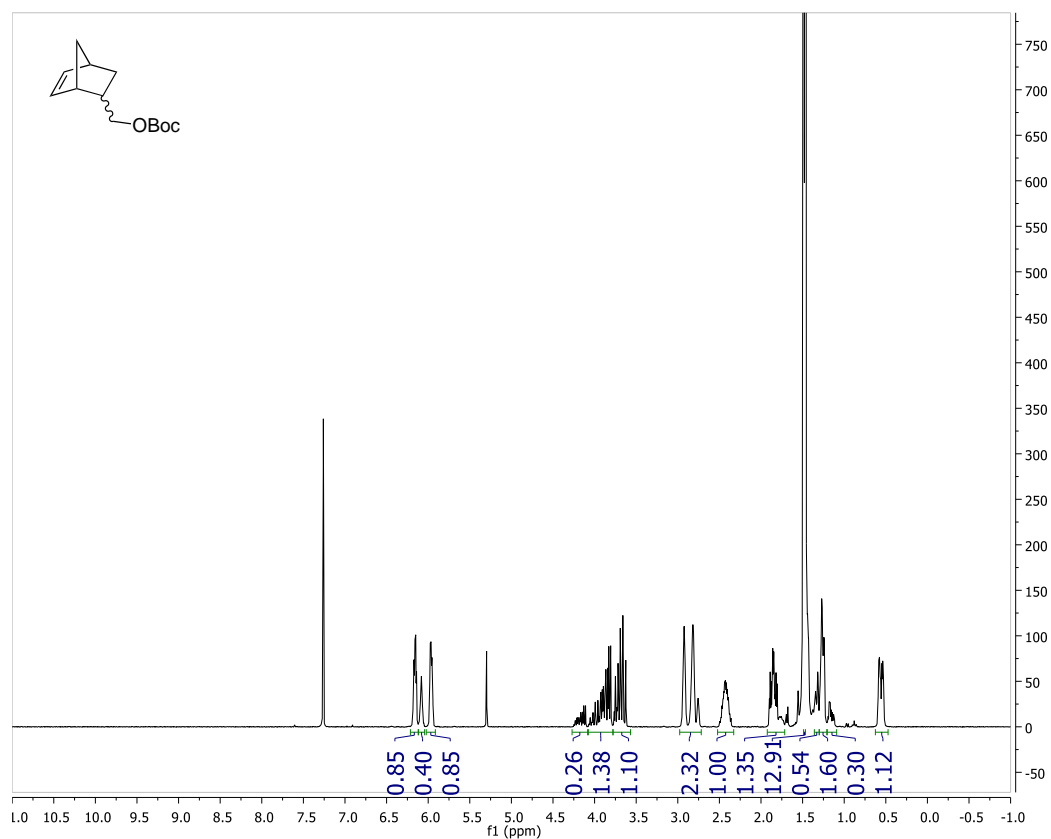
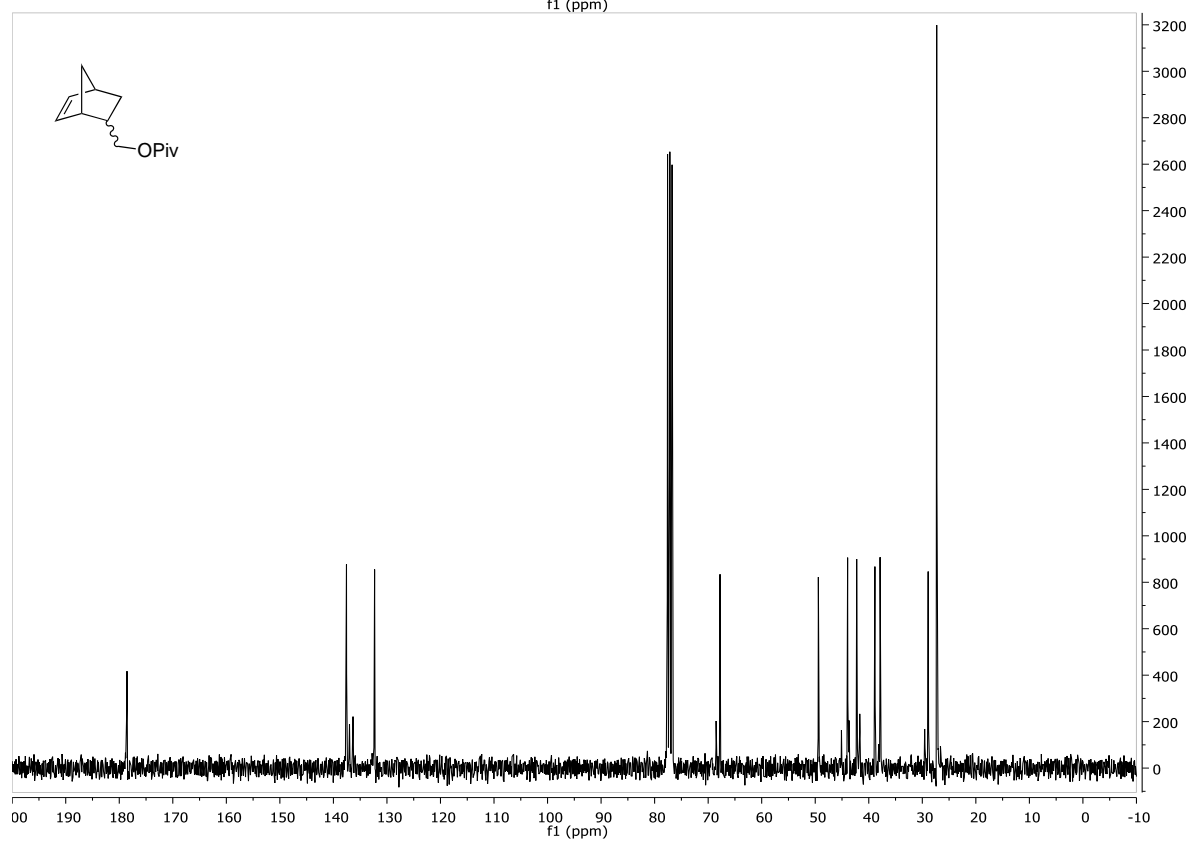
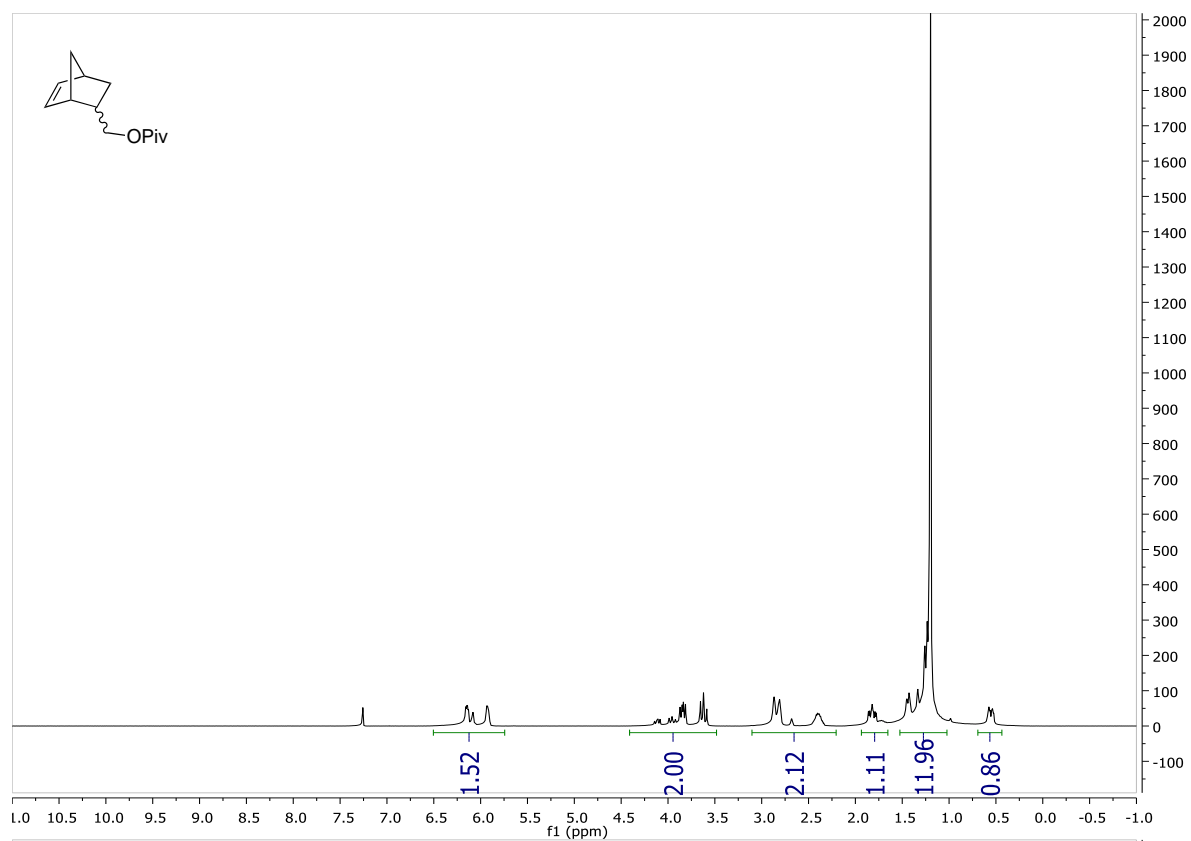
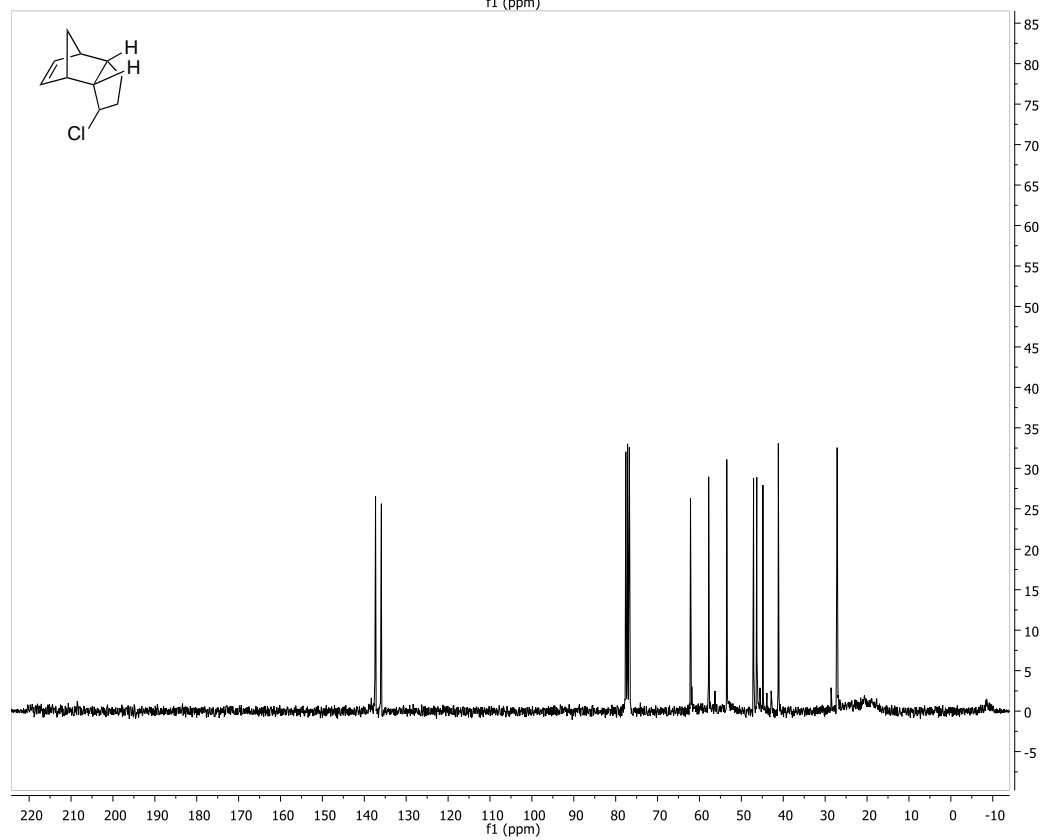
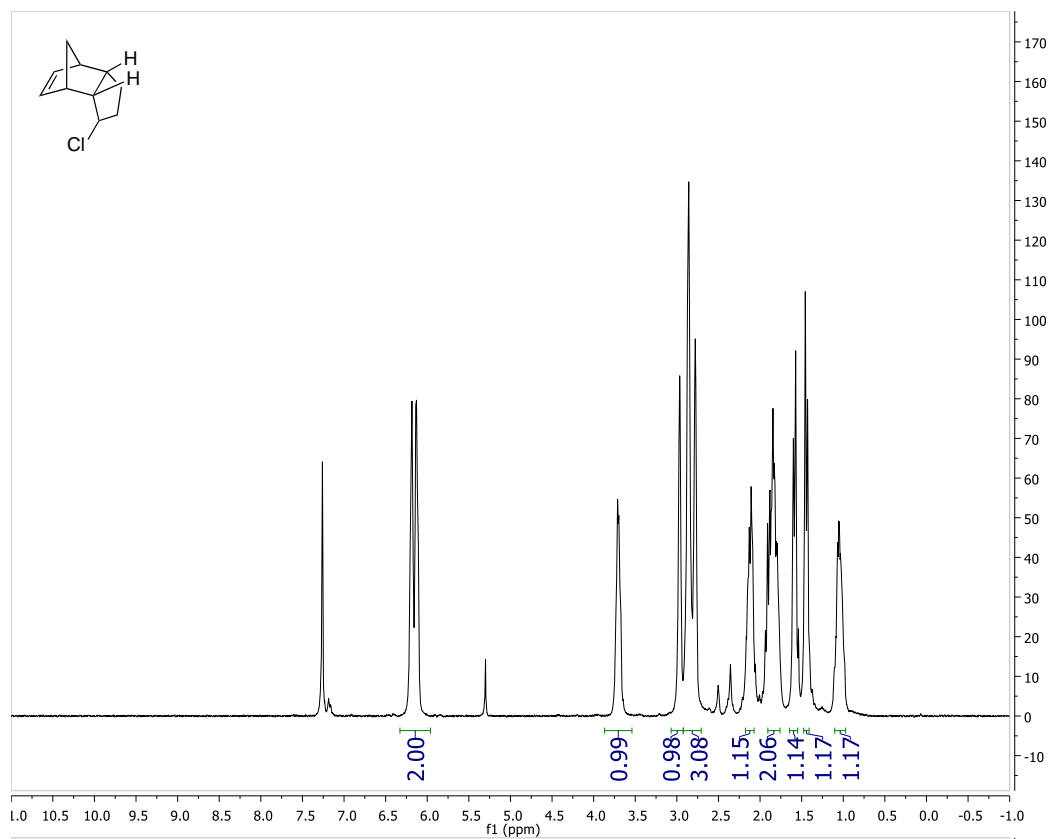


Figure S2. Thermogravimetric analysis of poly(1-co-5b). Heating rate = 10 °C/min, N₂ atmosphere.

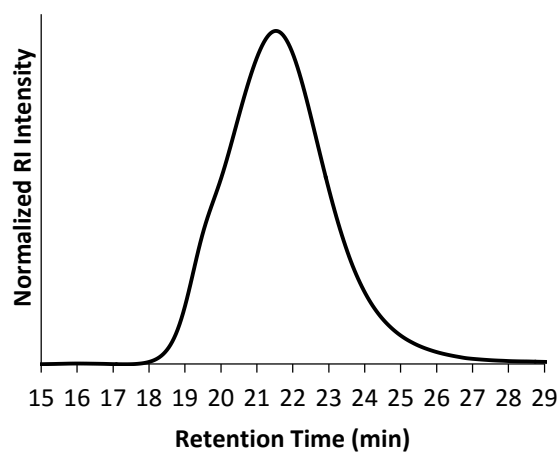
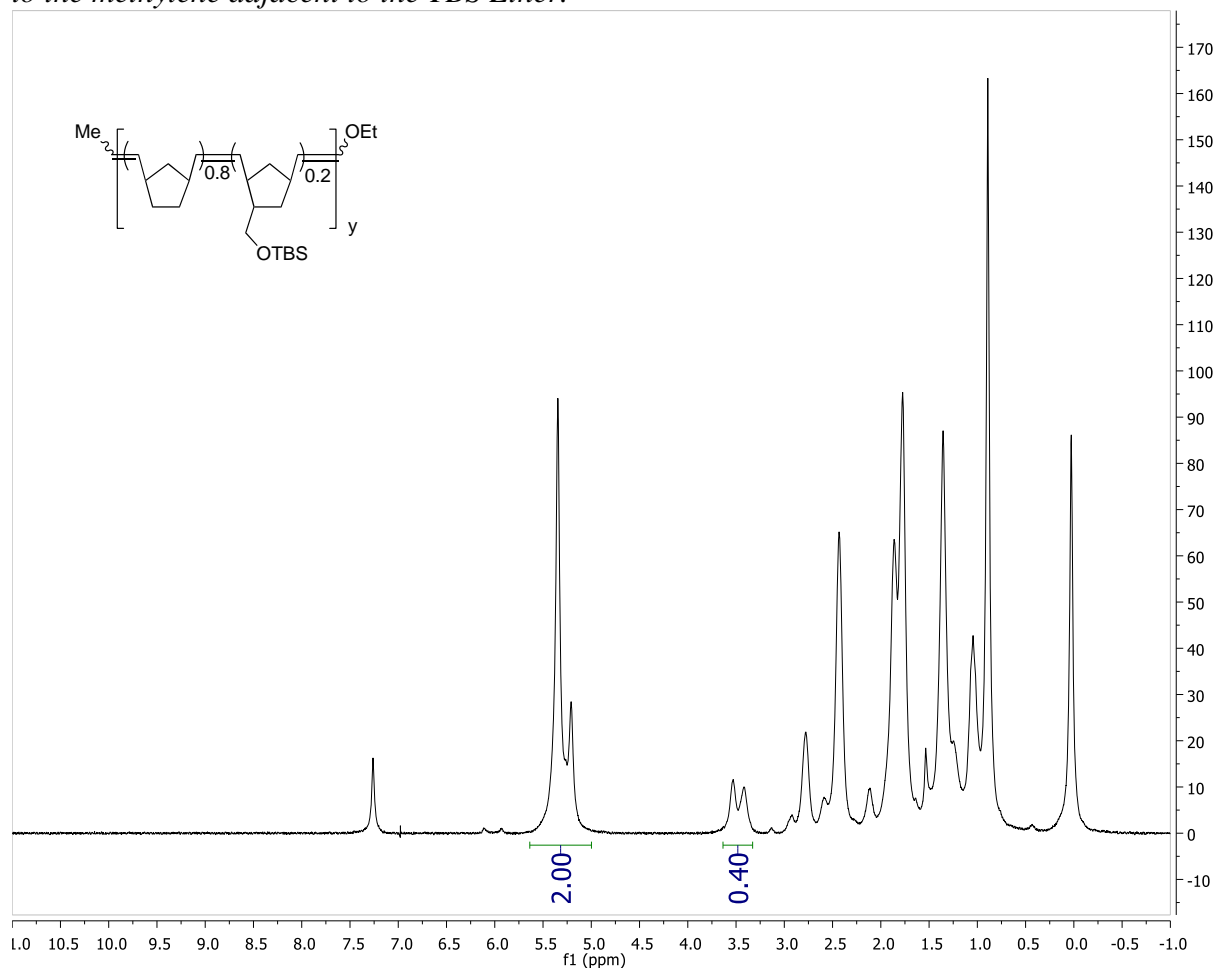
¹H-NMR and GPC Data



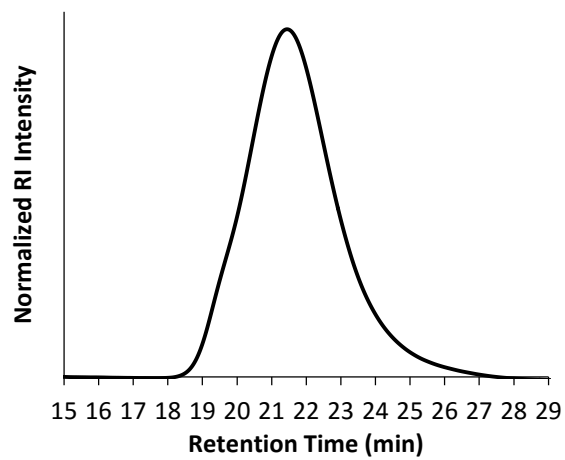
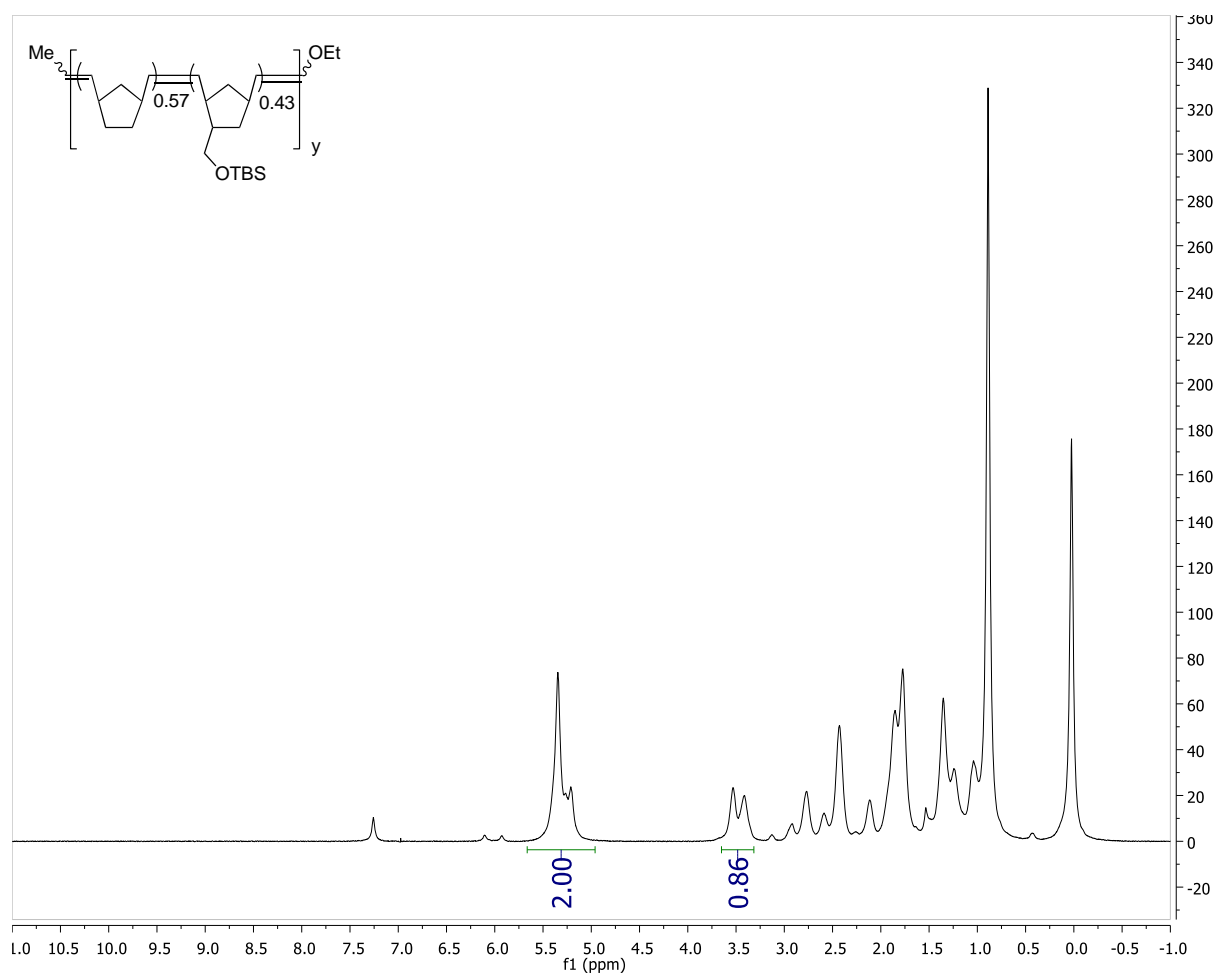




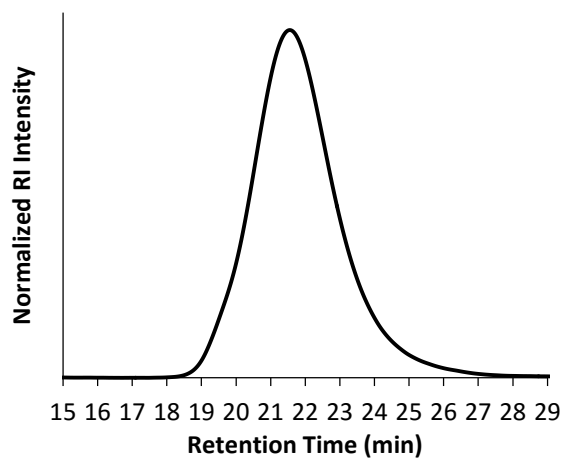
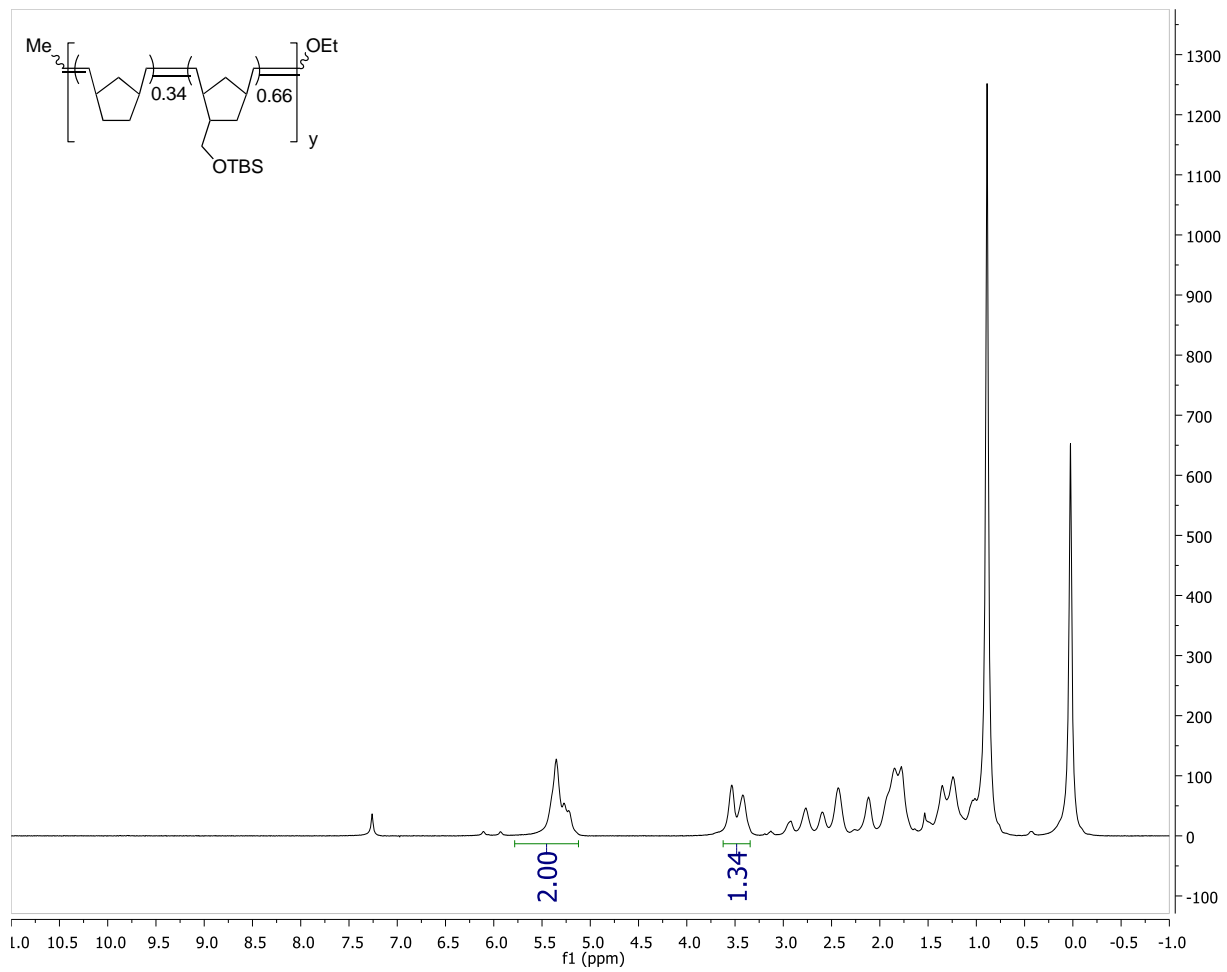
Copolymers of Norbornene and TBS Ether Monomer 5e – The ratio was determined by ^1H -NMR spectroscopy by comparing the peaks corresponding to the olefins with the peaks corresponding to the methylene adjacent to the TBS Ether.

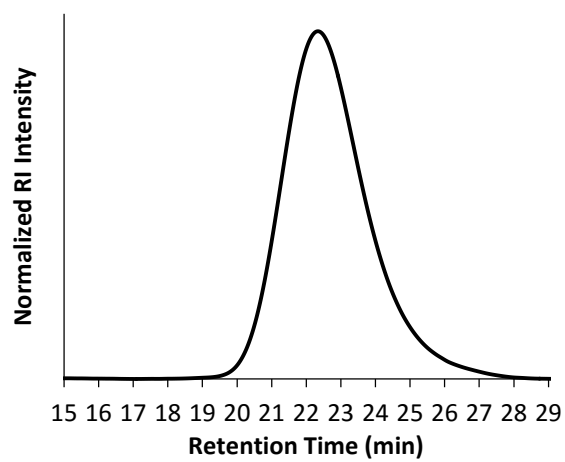
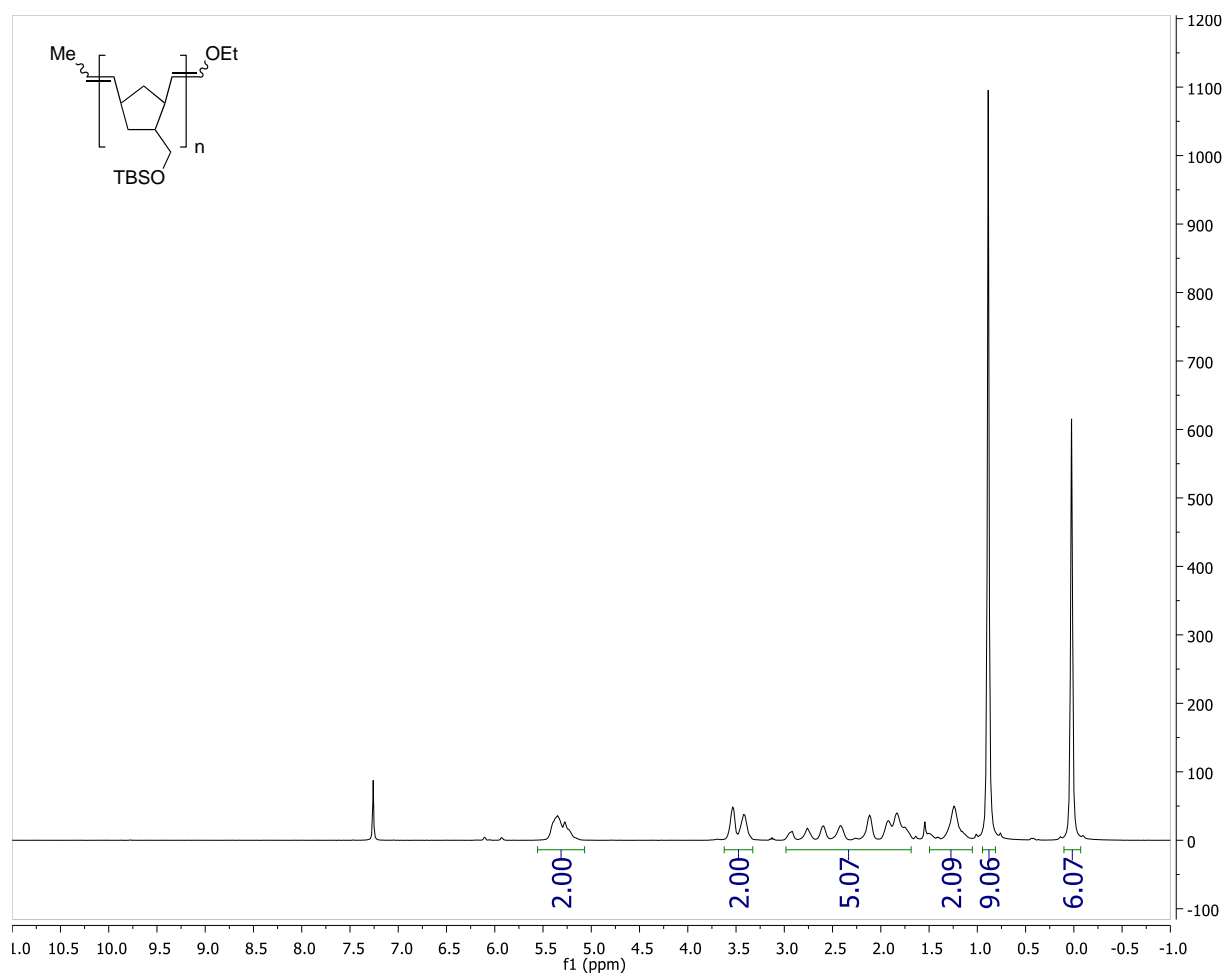


$M_n = 17.7$ kDa; $M_w = 27.0$ kDa; $D = 1.5$; $T_g = 29$ °C (DMA)



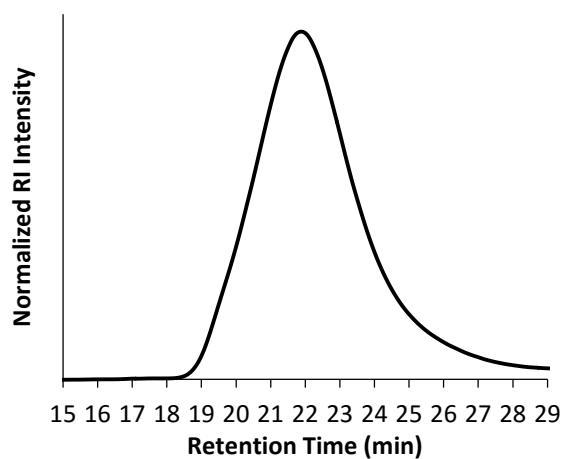
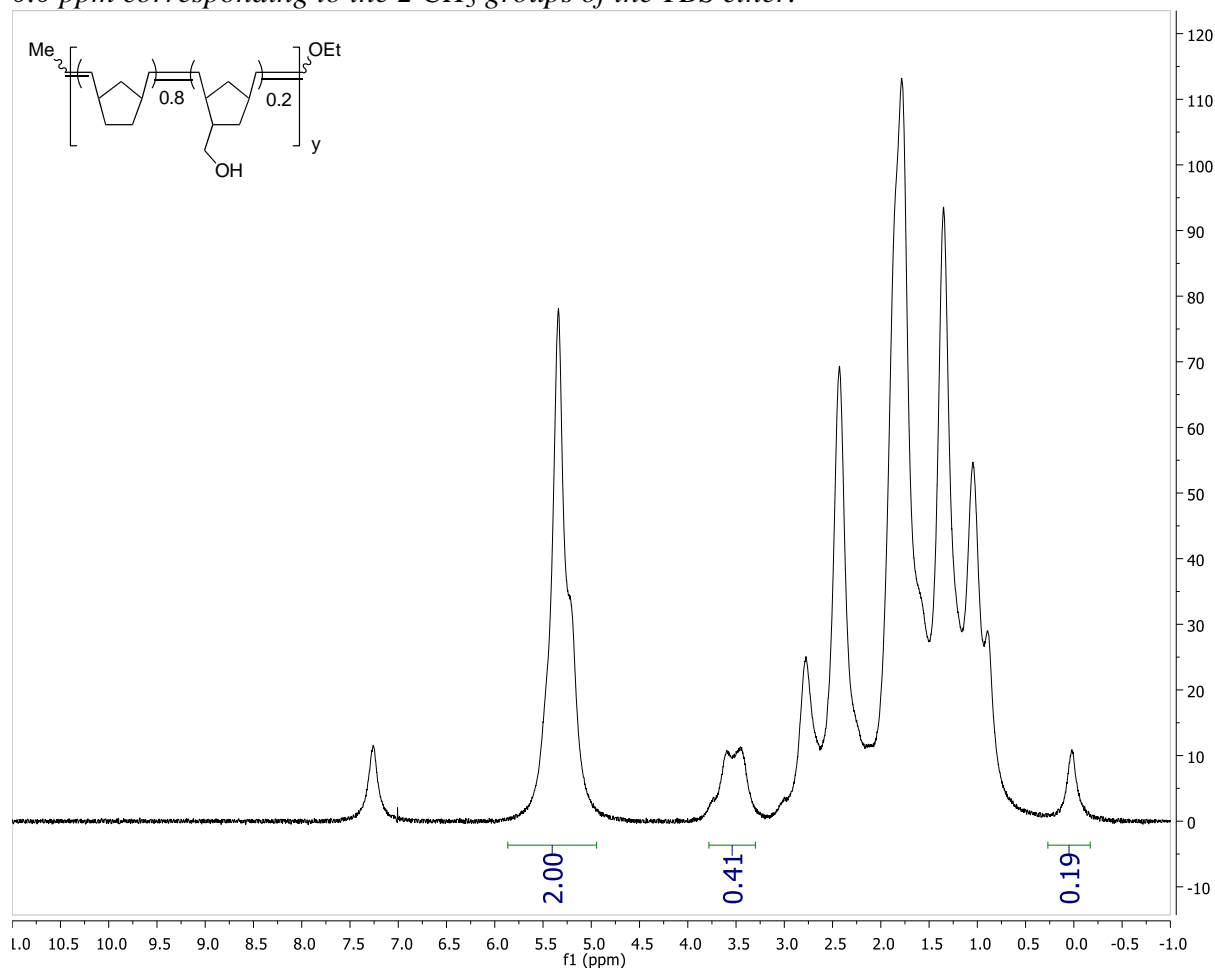
$M_n = 23.4$ kDa; $M_w = 30.0$ kDa; $D = 1.3$; $T_g = -14.4$ °C (DSC)


$$M_n = 21.3 \text{ kDa}; M_w = 28.0 \text{ kDa}; \bar{D} = 1.3; T_g = -3.9^\circ\text{C} \text{ (DSC)}$$



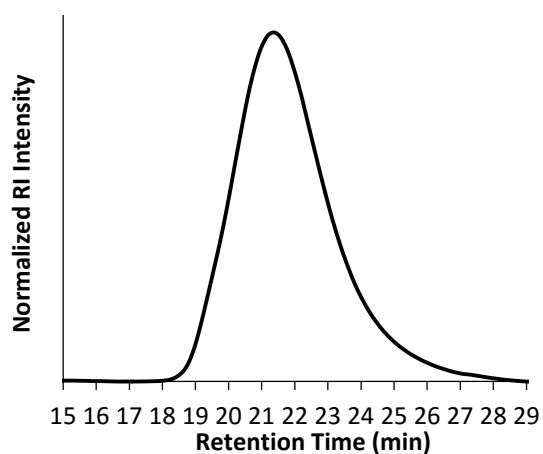
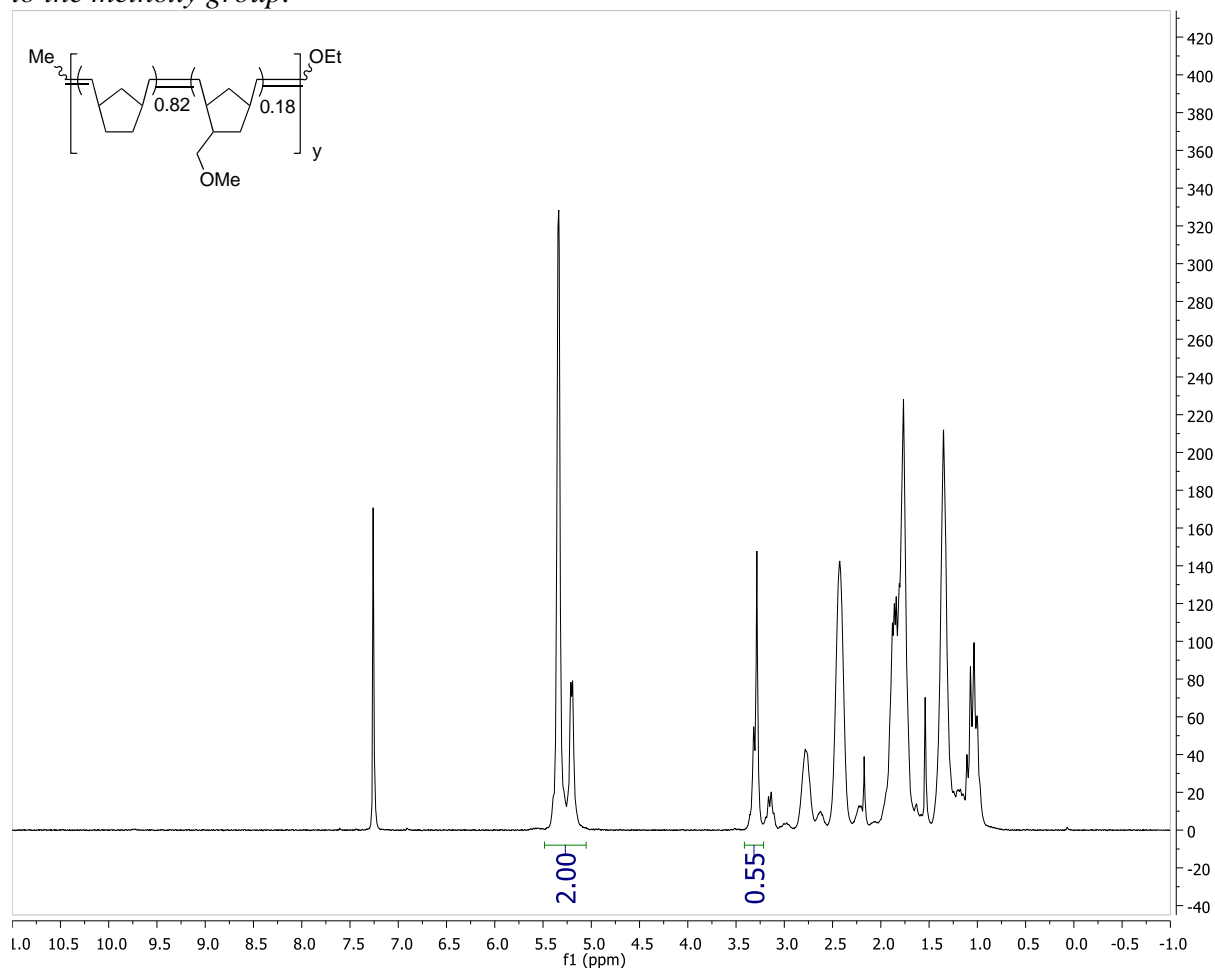
$M_n = 15.4$ kDa; $M_w = 18.8$ kDa; $\bar{D} = 1.2$

Removal of TBS Group from Copolymer – The amount of TBS ether remaining was determined by ^1H -NMR spectroscopy by comparing the peaks corresponding to the olefins with the peak at 0.0 ppm corresponding to the 2 CH_3 groups of the TBS ether.



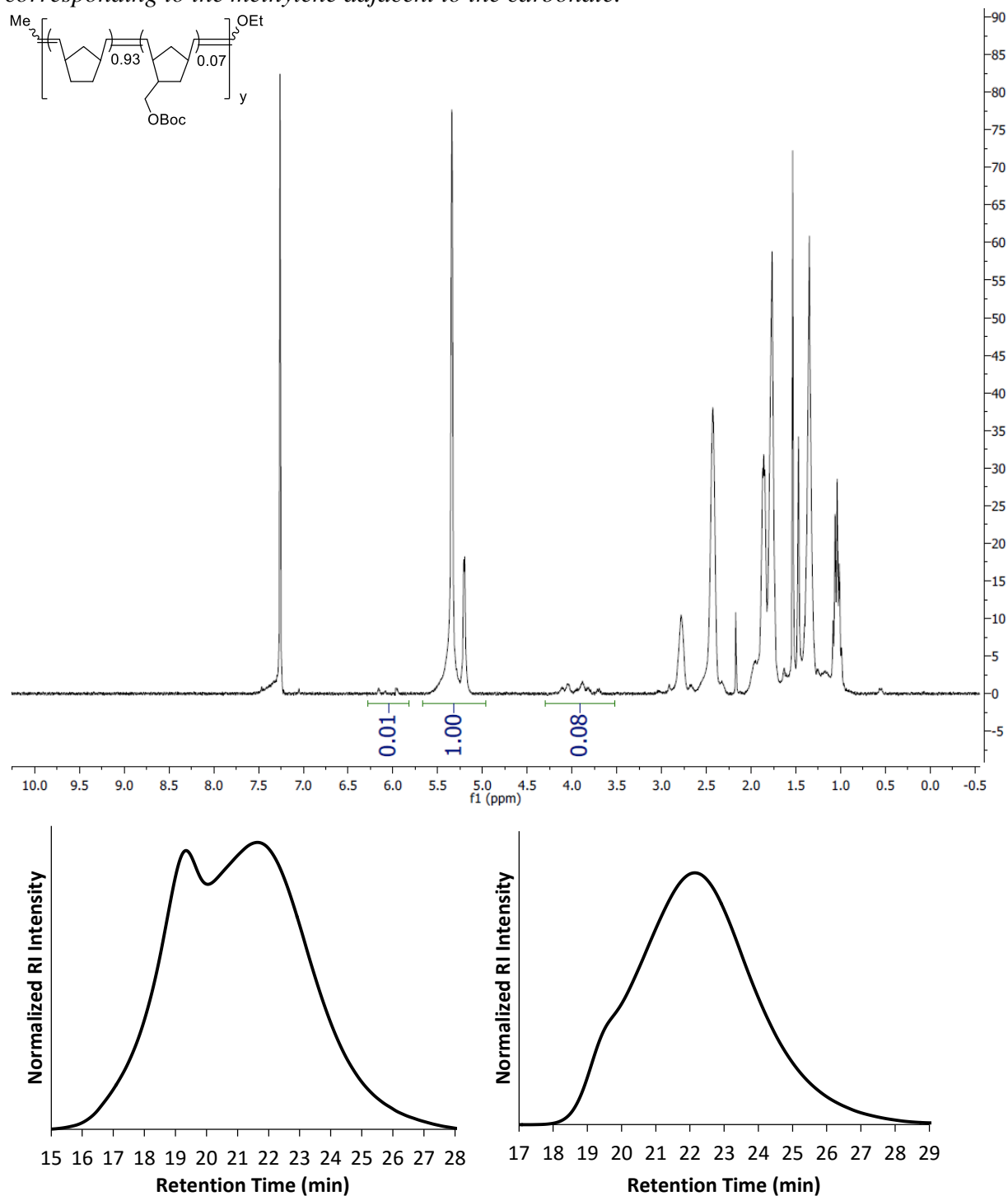
$M_n = 20.2$ kDa; $M_w = 25.5$ kDa; $D = 1.3$; $T_g = 47$ °C

Copolymer of Norbornene and methyl ether monomer 5a – The ratio was determined by ^1H -NMR spectroscopy by comparing the peaks corresponding to the olefins with the peaks corresponding to the methoxy group.



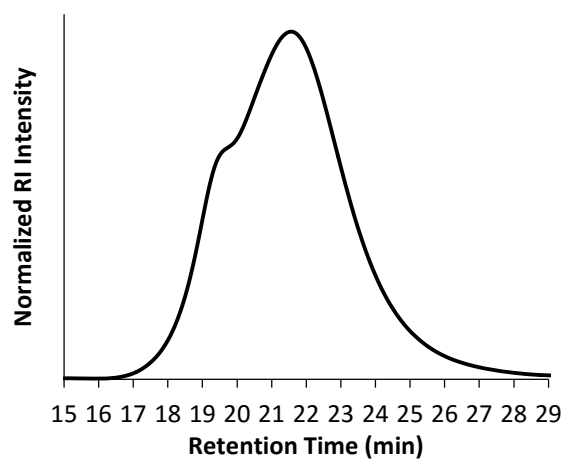
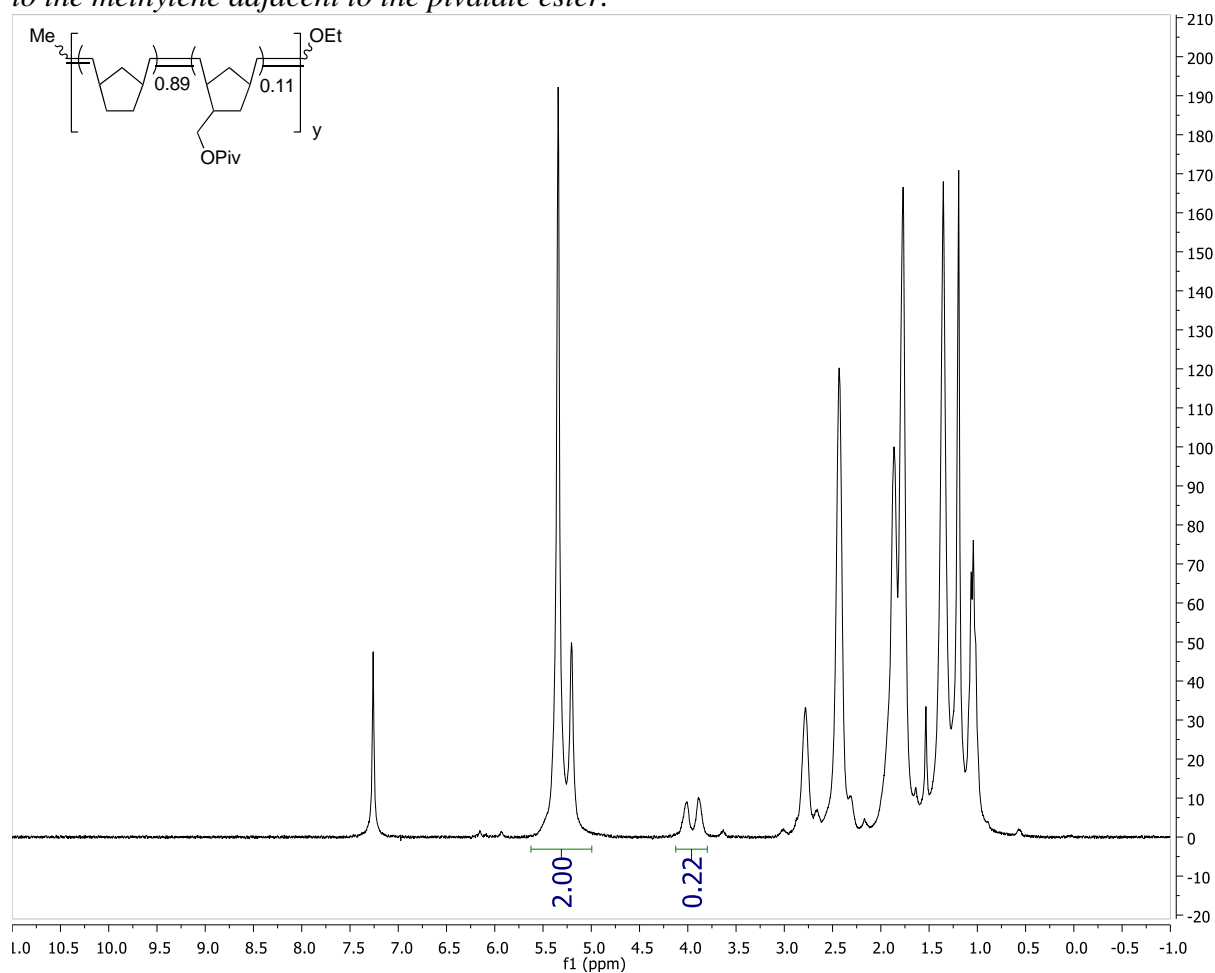
$M_n = 15.1 \text{ kDa}$, $M_w = 20.3 \text{ kDa}$; $\bar{D} = 1.4$; $T_g = 45^\circ\text{C}$ (DMA)

*Copolymer of Norbornene and Boc carbonate monomer **5b** – The ratio was determined by ^1H -NMR spectroscopy by comparing the peaks corresponding to the olefins with the peaks corresponding to the methylene adjacent to the carbonate.*



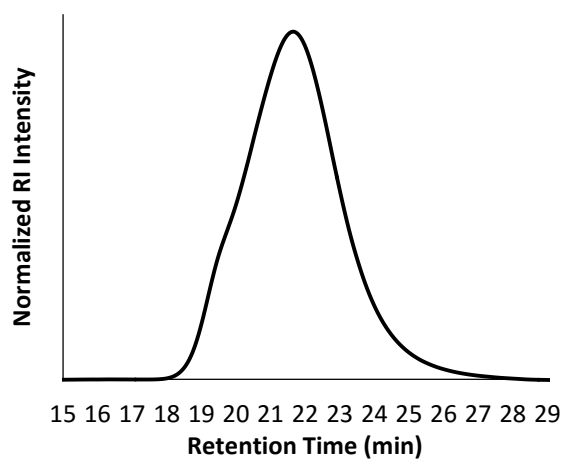
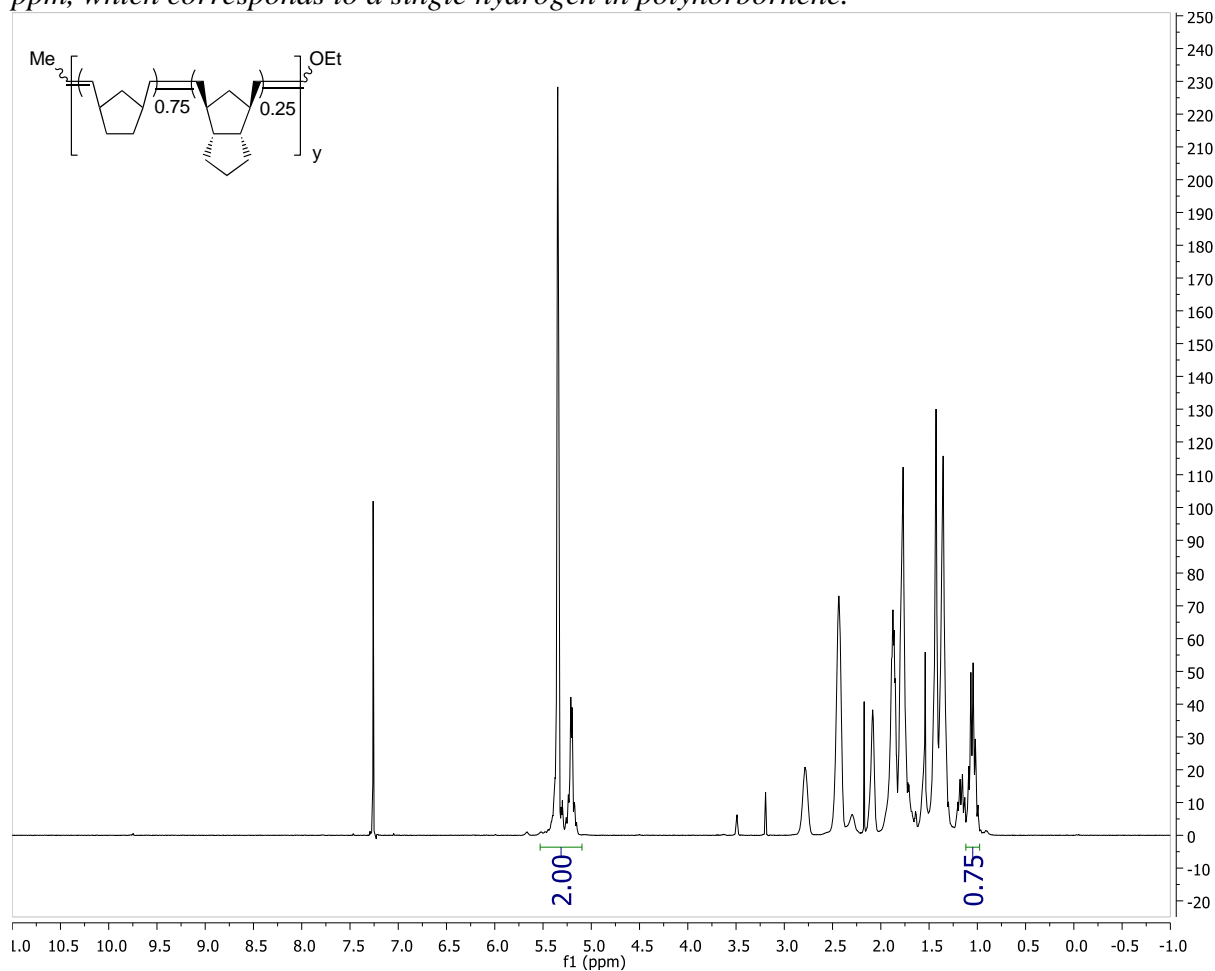
(left) Polymerization in CH_2Cl_2 : $M_n = 25.7$ kDa; $M_w = 95.0$ kDa; $D = 3.7$; $T_g = 51^\circ\text{C}$ (DMA)
 (right) Polymerization in CHCl_3 : $M_n = 11.3$ kDa; $M_w = 18.9$ kDa; $D = 1.7$; $T_g = 51^\circ\text{C}$ (DMA)

Copolymer of Norbornene and Pivalate Monomer 5c - The ratio was determined by ^1H -NMR spectroscopy by comparing the peaks corresponding to the olefins with the peaks corresponding to the methylene adjacent to the pivalate ester.



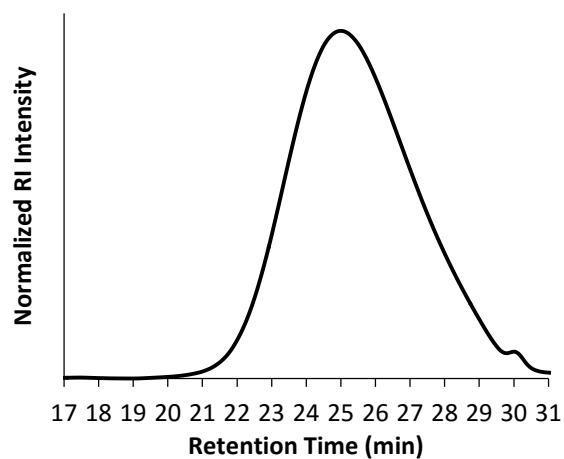
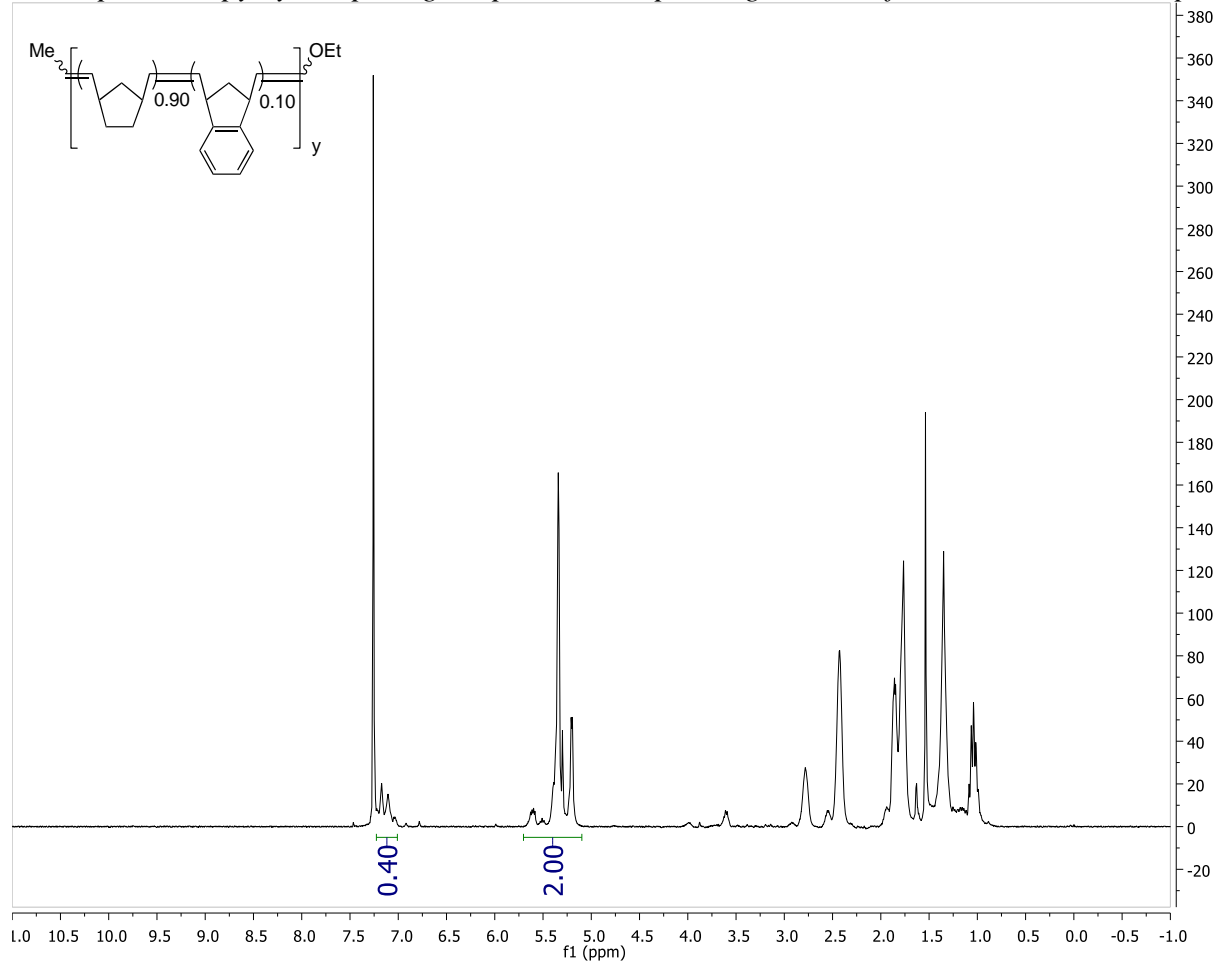
$M_n = 16.9$ kDa; $M_w = 37.2$ kDa; $D = 2.2$; $T_g = 36$ °C (DMA)

Copolymer of Norbornene and exo-DihydroDCPD Monomer 5f - The ratio was determined by ^1H -NMR spectroscopy by comparing the peaks corresponding to the olefins with the peak at 1.05 ppm, which corresponds to a single hydrogen in polynorbornene.



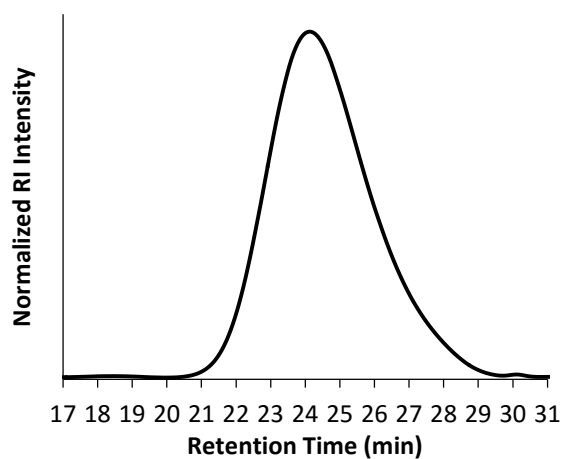
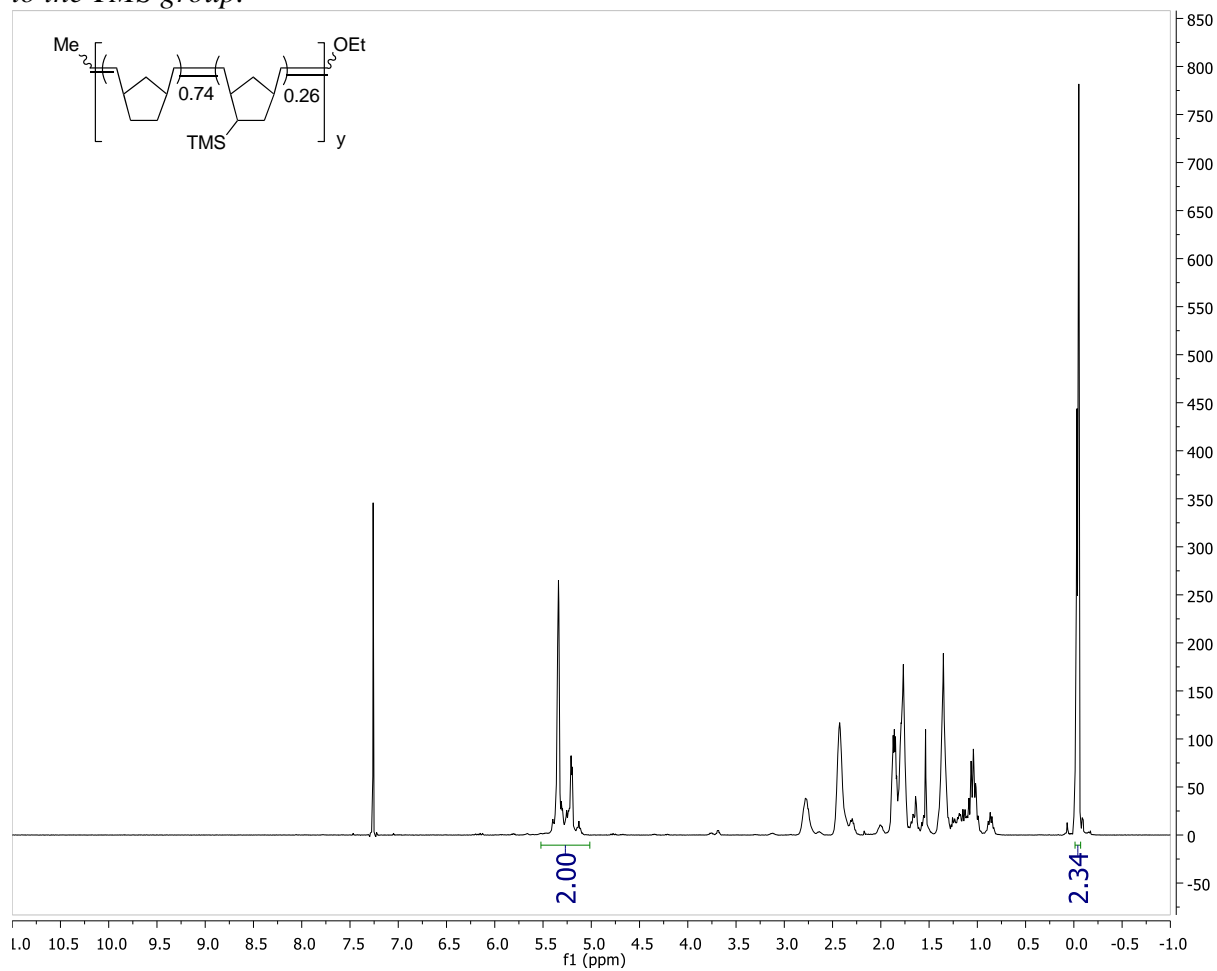
$M_n = 15.4 \text{ kDa}$; $M_w = 22.7 \text{ kDa}$; $D = 1.5$; $T_g = 74 \text{ }^\circ\text{C}$ (DMA)

Copolymer of Norbornene and Benzannulated Monomer 5g - The ratio was determined by ^1H -NMR spectroscopy by comparing the peaks corresponding to the olefins with the aromatic peaks.

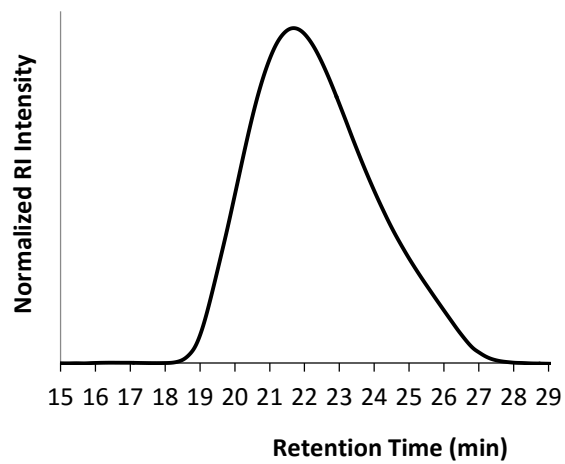
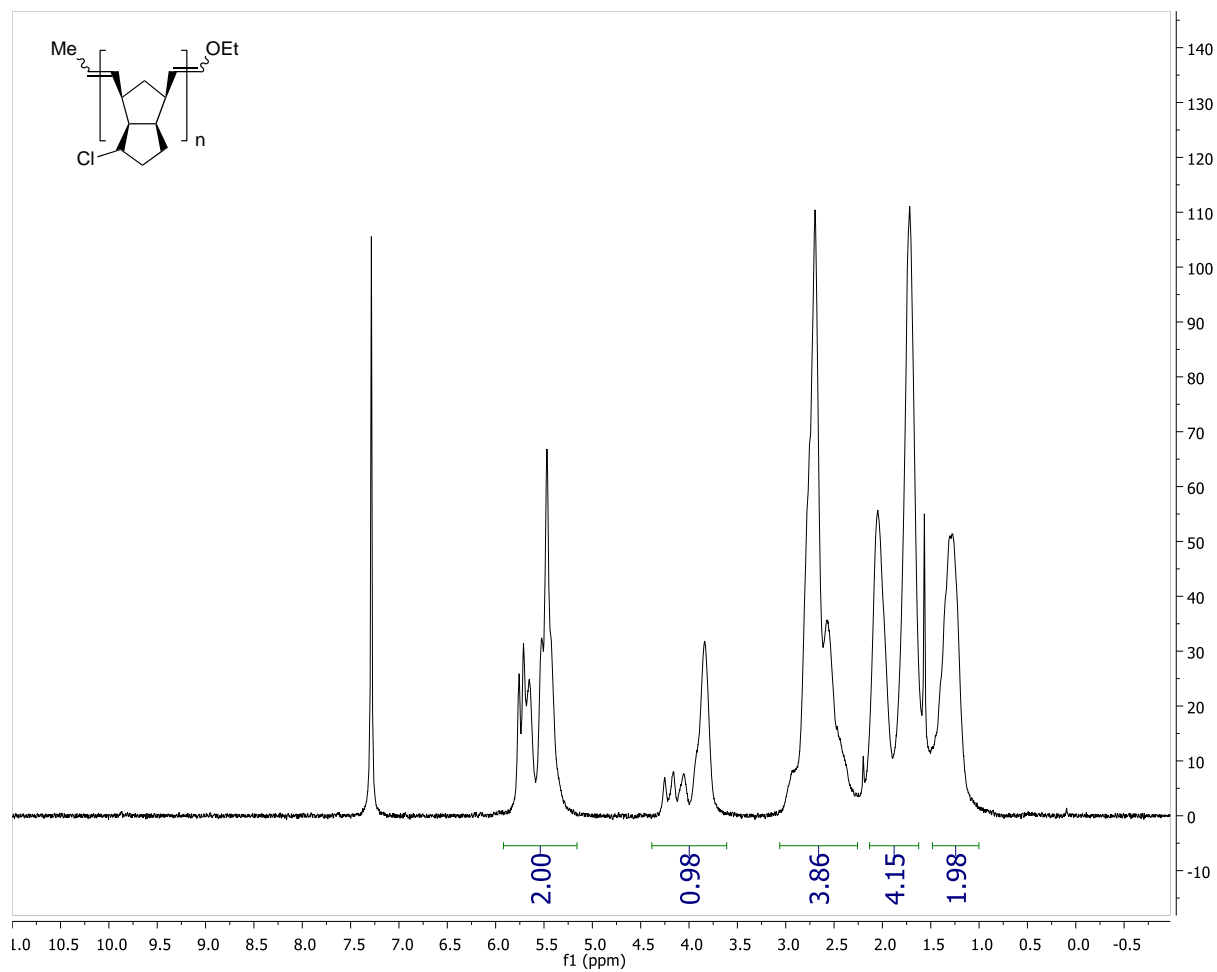


$M_n = 4.2 \text{ kDa}$; $M_w = 5.3 \text{ kDa}$; $\bar{D} = 1.3$; $T_g = 42 \text{ }^\circ\text{C}$ (DMA)

*Copolymer of Norbornene and Silyl Monomer **5h** - The ratio was determined by ^1H -NMR spectroscopy by comparing the peaks corresponding to the olefins with the peak corresponding to the TMS group.*



$M_n = 6.5 \text{ kDa}$; $M_w = 7.9 \text{ kDa}$; $D = 1.2$; $T_g = 55 \text{ }^\circ\text{C}$ (DMA)



$M_n = 17.8$ kDa, $M_w = 27.7$ kDa; $D = 1.6$; $T_g = 170$ °C (DMA)

Supporting Information References

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