

Supporting Information

Ring-opening metathesis polymerization of norbornene-benzoladderene (macro)monomers

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Materials

All reagents and solvents were obtained from commercial vendors and used as received unless otherwise stated. CDCl_3 for all ROMPs was distilled at atmospheric pressure onto molecular sieves and was stored in a Strauss flask under nitrogen protected from light. ^1H NMR spectra were measured on an Agilent 400 MHz NMR spectrometer. Unless otherwise stated, ^1H and ^{13}C NMR chemical shifts are reported in ppm relative to internal solvent resonances. Yields refer to compounds as isolated after requisite purification unless otherwise stated. A Biotage Selekt flash purification system was used for automated silica gel column purification. Silica used for automated flash chromatography purifications was ZEOCHEM ZEOprep 60 HYD 40–63 μM pore size. Thin-layer chromatography (TLC) was performed on glass-backed silica plates and visualized by UV and I_2 unless otherwise stated. Size exclusion chromatography (SEC) was carried out in tetrahydrofuran (THF) at 1 mL min^{-1} at $30\text{ }^\circ\text{C}$ on two Agilent PLgel 10 μm MIXED-B columns connected in series with a Wyatt Dawn Heleos 2 light scattering detector and a Wyatt Optilab Rex refractive index detector. No calibration standards were used, and dn/dc values were obtained by assuming 100% mass elution from the columns unless otherwise stated. The known dn/dc for PS of 0.185 mL/g was used for all macromonomer and bottlebrush polymer samples.

Preparation of Grubbs' 3rd generation catalyst (G3)

Grubbs' 3rd generation catalyst (G3) was prepared freshly and used within 2 days following a modified version of published methods.¹⁻² First, pyridine and pentane were purified via passage through a short column of basic alumina. A one-dram vial was charged with a stir bar and 20 mg of Grubbs' 2nd generation catalyst ($\text{H}_2\text{IMes})(\text{PCy}_3)(\text{Cl})_2\text{Ru}=\text{CHPh}$). Next, purified pyridine (20 μL) was added to the vial, and the reaction mixture was stirred vigorously for 20–30 min until it had turned a vivid lime-green color. If the reaction mixture dried to a solid, additional pyridine (10 μL increments) was added, and solids were broken up manually with a spatula to allow for more stirring. Next, purified pentane (3 mL) was added to the vial to precipitate the catalyst. The pentane was decanted, and the solids were washed with additional purified pentane (3 mL). Once again, the pentane was decanted off, and the remaining solids were dried by blowing air over the vial for 1 min, then transferred to a clean vial, and then dried under vacuum overnight.

Monomer *exo*-norbornene benzoladderene [*xx*-NBL (**1**)]

Monomer *exo*-norbornene benzoladderene [*xx*-NBL (**1**)] was synthesized based on adaptations of a literature procedure.³ To an oven- and flame-dried, three-neck round-bottom flask (250 mL) equipped with a stir bar, septum, reflux condenser, and an adapter for N_2 , dioxane (65 mL) was added and degassed by bubbling with N_2 using a needle for 20 min. Next, cesium carbonate (10 g, 33 mmol), norbornadiene (30 g, 330 mmol), and 4-bromotoluene (5.6 g, 33 mmol) were added under gentle N_2 flow, followed by palladium acetate (0.28 g, 1.2 mmol) and triphenylphosphine (0.66 g, 2.5 mmol). The reaction mixture was stirred at rt for 5 min and then refluxed for 24 h. The reaction mixture was allowed to cool to rt, filtered through celite, and the filtrate was concentrated by rotary evaporation. The crude product, isolated as a yellow oil, was purified by automated flash chromatography on silica with hexanes as the mobile phase to yield a colorless oil. (1.40 g, 24 % yield). ^1H NMR (CDCl_3): δ 7.02 (m, 1H), 6.96 (m, 1H), 6.91 (m, 1H), 6.24–6.19 (m, 2H), 3.13–3.08 (m, 2H), 2.78–2.74 (m, 2H), 2.34 (s, 3H), 1.28 (m, 1H), 0.89 (m, 1H). ^{13}C NMR (CDCl_3): 146.28, 143.04, 136.83, 136.77, 127.83, 122.68, 121.60, 47.33, 47.14, 41.76, 41.68, 41.50, 22.17.

Compound (I): 2-(2'-bromobenzyloxy)tetrahydropyran

A round-bottom flask equipped with a stir bar was charged with 2-bromobenzyl alcohol (8.00 g, 42.8 mmol), CH₂Cl₂ (70 mL), 3,4-dihydro-2*H*-pyran (4.00 mL, 43.8 mmol), and *p*-toluenesulfonic acid (0.20 g, 1.2 mmol). The reaction mixture was stirred at rt and monitored by TLC (CH₂Cl₂) until 2-bromobenzyl alcohol was completely consumed, about 16 h, and then concentrated by rotary evaporation. The crude product, isolated as a yellow oil, was then purified by automated flash chromatography on silica with a hexanes/EtOAc gradient as the mobile phase to give compound **I** as a colorless oil (9.50 g, 82 % yield). ¹H NMR (CDCl₃): δ 7.56–7.46 (m, 2H), 7.30 (m, 1H), 7.13 (m, 1H), 4.81 (m, 1H), 4.76 (m, 1H), 4.56 (m, 1H), 3.96–3.86 (m, 1H), 3.60–3.52 (m, 1H), 1.88–1.55 (m, 6H). ¹³C NMR (CDCl₃): δ 138.4, 133.0, 129.4, 129.3, 127.9, 123.5, 98.9, 69.3, 62.5, 31.2, 26.0, 19.8. Both ¹H and ¹³C NMR spectra matched literature values.⁴

Compound (II): *exo*-norbornene benzoladderene-*ortho*-methoxytetrahydropyran

Compound **I** (9.50 g, 35 mmol) was added to an oven- and flame-dried three-neck round-bottom flask equipped with a stir bar, septum, reflux condenser, and adapter for N₂. Dioxane (100 mL) was added and degassed by bubbling with N₂ using a needle for 20 min. Cesium carbonate (11.0 g, 35 mmol) and norbornadiene (32.0 g, 350 mmol) were added to the round-bottom flask under gentle N₂ flow. Palladium acetate (390 mg, 1.8 mmol) and triphenylphosphine (920 mg, 3.5 mmol) were then added under N₂ flow. The reaction mixture was stirred at rt for 5 min and then refluxed for 24 h. The reaction mixture was allowed to cool to rt, filtered through celite, and the filtrate was concentrated by rotary evaporation. The crude product, isolated as a yellow oil, was purified by automated flash chromatography on silica with 2% EtOAc in hexanes as the mobile phase to yield a yellow oil. The oil was then distilled under reduced pressure to give compound **II** as a colorless oil (1.50 g, 15 % yield). ¹H NMR (CDCl₃): δ 7.20–7.11 (m, 2H), 6.97 (m, 1H), 6.23–6.19 (m, 2H), 4.74 (m, 1H), 4.68 (m, 1H), 4.47 (m, 1H), 3.96–3.84 (m, 1H), 3.54 (m, 1H), 3.16 (m, 1H), 3.13–3.08 (m, 1H), 2.87–2.79 (m, 1H), 2.76 (m, 1H), 1.86–1.54 (m, 6H).

Compound (xx-NBL-*o*-Br): *exo*-norbornene benzoladderene-*ortho*-2-bromo-2-methylpropanoate

Compound **II** (1.50 g, 5.3 mmol) was dissolved in methanol (50 mL) in a round-bottom flask equipped with a stir bar. Next, *p*-toluenesulfonic acid (0.20 g, 1.2 mmol) was added, and the reaction mixture was stirred at rt. Reaction progress was monitored by TLC (1:1 CH₂Cl₂:hexanes, visualization by a potassium permanganate stain) until compound **II** was completely consumed, about 2 h. The reaction mixture was concentrated by rotary evaporation, redissolved in CH₂Cl₂ (100 mL), and transferred to a separatory funnel. The organic solution was washed with saturated NaHCO₃ (3 x 20 mL) and brine (20 mL), dried over Na₂SO₄, and concentrated by rotary evaporation to yield a yellow oil. Crude compound **III** (1.05 g, >99 % yield) was used immediately in the following step.

An oven- and flame-dried two-neck round-bottom flask containing a stir bar, septum, and an N₂ adapter was charged with compound **III** (1.05 g, 5.31 mmol), NEt₃ (1.18 mL, 8.47 mmol), and dry THF (30 mL). The flask was placed in an ice bath, and once cooled, α -bromoisobutyryl bromide (1.83 mL, 14.8 mmol) was added dropwise under an N₂ atmosphere. The reaction mixture was stirred overnight, allowing the ice to melt and the contents of the flask to warm to rt. Reaction progress was monitored by TLC (CH₂Cl₂, visualization by a potassium permanganate stain) until compound **III** was completely consumed. The reaction mixture was filtered through filter paper, the filtrate was concentrated by rotary evaporation, and the crude product, recovered as a yellow

oil, was purified by automated flash chromatography on silica with an EtOAc/hexanes gradient as the mobile phase. The product, compound **xx-NBL-*o*-Br**, was obtained as a colorless oil (0.77 g, 42 % yield). ¹H NMR (CDCl₃): δ 7.24–7.16 (m, 2H), 7.05 (m, 1H), 6.23 (t, *J* = 1.8 Hz, 2H), 5.24–5.09 (m, 2H), 3.24–3.14 (m, 2H), 2.84 (m, 2H), 1.95 (m, 6H), 1.30 (m, 1H), 0.86 (m, 1H). ¹³C NMR (CDCl₃): δ 171.98, 146.87, 145.31, 137.09, 129.62, 128.13, 127.01, 122.35, 65.19, 56.13, 47.90, 47.35, 41.91, 41.85, 41.76, 31.29, 31.27.

Compound (V): *exo*-norbornene benzoladderene-*meta*-methoxycarbonyl

To an oven- and flame-dried three-neck round-bottom flask equipped with a stir bar, septum, reflux condenser, and an adapter for N₂, dioxane (40 mL) was added and degassed by bubbling with N₂ using a needle for 20 min. Cesium carbonate (4.2 g, 13 mmol), norbornadiene (13 mL, 130 mmol), and methyl 4-bromo-3-methylbenzoate (**IV**, 3.0 g, 13 mmol) were added to the round-bottom flask under gentle N₂ flow. Palladium acetate (0.15 g, 0.67 mmol) and triphenylphosphine (0.35 g, 1.3 mmol) were then added to the reaction mixture under N₂ flow. The reaction mixture was stirred at rt for 5 min and then refluxed for 24 h. The reaction mixture was cooled to rt, and the solids were removed by filtration through celite. The filtrate was concentrated by rotary evaporation, and the crude product was purified by automated flash chromatography on silica, eluting with 2% EtOAc in hexanes to yield compound **V** as a colorless oil (1.25 g, 40 % yield). ¹H NMR (CDCl₃): δ 7.75 (m, 1H), 7.55 (m, 1H), 6.25–6.23 (m, 2H), 3.89 (s, 3H), 3.16–3.11 (m, 2H), 2.84–2.78 (m, 2H), 2.26 (t, *J* = 0.6 Hz, 3H), 1.54 (s, 1H), 1.32–1.26 (m, 1H), 0.82 (m, 1H). ¹³C NMR (CDCl₃): δ 168.30, 150.79, 146.16, 137.13, 137.00, 132.35, 130.37, 129.94, 120.70, 52.36, 47.18, 47.03, 41.78, 41.08.

Compound (VI): *exo*-norbornene benzoladderene-*meta*-methanol

LiAlH₄ (0.078 g, 2.06 mmol) was suspended in dry THF (1.4 mL) at 0 °C in an oven- and flame-dried three-neck round-bottom flask equipped with a stir bar, an adapter for N₂, a septum, and a reflux condenser. Compound **V** (0.330 g, 1.37 mmol) was dissolved in dry THF in a vial (1.4 mL) and added dropwise to the LiAlH₄ suspension via syringe. The reaction mixture was brought to rt and then heated to reflux in an oil bath for 12 h. The reaction mixture was then cooled to rt and placed in an ice bath again. Once cooled to 0 °C, water (0.78 mL) was added dropwise slowly, followed by a 15% aqueous NaOH solution (0.78 mL) and then water again (2.34 mL) until no more foaming was observed. Brine (~5 mL) was added to the solution until two separate layers formed, and then the mixture was transferred to a separatory funnel. The top organic layer was collected and dried over Na₂SO₄ and was concentrated by rotary evaporation. The crude product, isolated as a yellow oil, was purified by automated flash chromatography on silica, eluting with 5% EtOAc in hexanes to yield compound **VI** as a colorless oil (0.195 g, 67 % yield). ¹H NMR (CDCl₃): δ 6.99 (m, 1H), 6.94–6.90 (m, 1H), 6.24–6.21 (m, 2H), 4.62 (d, *J* = 5.5 Hz, 2H), 3.12–3.06 (m, 2H), 2.83–2.74 (m, 2H), 2.22 (s, 3H), 1.58 (m, 1H), 1.28 (m, 1H), 0.86 (m, 1H). ¹³C NMR (CDCl₃): δ 146.18, 144.33, 140.58, 136.77, 136.71, 132.18, 127.30, 118.33, 66.37, 46.75, 46.43, 41.57, 41.51, 40.92, 16.82.

Compound (xx-NBL-*m*-Br): *exo*-norbornene benzoladderene-*meta*-2-bromo-2-methylpropanoate

An oven- and flame-dried, two-neck round-bottom flask containing a stir bar and an adapter for N₂ was charged with compound **VI** (0.195 g, 0.919 mmol), NEt₃ (0.166 mL, 1.19 mmol), and dry THF (5 mL). The flask was placed in an ice bath. Once cooled, α-bromoisobutyryl

bromide (0.170 mL, 1.38 mmol) was added dropwise under an N₂ atmosphere. The reaction mixture was stirred overnight, allowing the ice to melt and the contents of the flask to warm to rt. Reaction progress was monitored by TLC (CH₂Cl₂, visualization by potassium permanganate stain) until compound **VI** was consumed. The reaction mixture was concentrated by rotary evaporation, and the crude product, isolated as a yellow oil, was purified by automated flash chromatography on silica eluting with CH₂Cl₂ as the mobile phase. The product was obtained as a colorless oil (0.133 g, 40 % yield). ¹H NMR (CDCl₃): δ 6.99 (m, 1H), 6.92 (m, 1H), 6.22 (m, 2H), 5.15–5.12 (m, 2H), 3.09 (d, *J* = 1.1 Hz, 2H), 2.82–2.74 (m, 2H), 2.22 (m, 3H), 1.94 (s, 6H), 1.28 (m, 1H), 0.85 (m, 1H). ¹³C NMR (CDCl₃): δ 171.71, 146.13, 145.02, 136.77, 136.73, 134.84, 132.17, 128.25, 119.21, 68.65, 56.04, 46.77, 46.49, 41.59, 41.49, 40.88, 30.94, 16.84.

Synthesis of Polystyrene Macromonomers

A representative styrene polymerization procedure to prepare MM *xx*-NBL-*m*-PS (**3**) was as follows: Initiator **xx-NBL-*m*-Br** (0.085 g, 0.24 mmol), styrene (7.3 mL, 64 mmol), CuBr (17 mg, 0.12 mmol), and CuBr₂ (26 mg, 0.12 mmol) were added to a 100 mL Schlenk tube equipped with a stir bar. The mixture in the Schlenk tube was deoxygenated by three freeze–pump–thaw cycles and then backfilled with N₂. The Schlenk tube was submerged in an oil bath at 90 °C, and after ~10 min, *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) (0.050 mL, 0.24 mmol) was injected under N₂ flow. The reaction mixture was heated in an oil bath maintained at 90 °C for about 3 h. An aliquot was removed via N₂-purged syringe and analyzed via ¹H NMR spectroscopy to ensure that ~10% conversion had been reached. At this point, the reaction was terminated by removing the Schlenk tube from the oil bath and exposing its contents to air. The reaction mixture was diluted with EtOAc (50 mL) and washed with water (3 x 20 mL) in a separatory funnel, and then the EtOAc layer was concentrated by rotary evaporation. The resultant PS-MM was dissolved in a small volume of THF and then purified by four successive precipitations into MeOH. Before the final precipitation, the product was purified further via passage through a short column of basic alumina using THF as the mobile phase. After the last precipitation, the polymer was recovered via filtration as a white solid and then dried under vacuum overnight (0.171 g). MM *xx*-NBL-*m*-PS (**2**) was prepared following the same procedure.

Evaluation of Propagation Rates of ROMP

A representative ROMP procedure is as follows: MM *xx*-NBL-*m*-PS (**3**) (25 mg, 100 equiv) was dissolved in CDCl₃ (0.317 mL) in a vial equipped with a stir bar. A stock solution of **G3** in CDCl₃ at a concentration of 0.61 mg/mL was prepared, and 0.1 mL of this solution (to achieve 0.061 mg of G3, 1 equiv) was then added rapidly to the first vial to make the final concentration of MM = 20 mM. Polymerizations were conducted under air with the capping of the vials in between aliquot removals. Aliquots (20 μL) were withdrawn periodically via micropipette at pre-determined time points and added to 1.5 mL Eppendorf microcentrifuge tubes containing CDCl₃ (0.1 mL) and ethyl vinyl ether (2 μL) to terminate the polymerizations. Each aliquot was then analyzed by ¹H NMR spectroscopy or SEC after solvent evaporation under a stream of air for about 1 min. The same procedure was used for the ROMP of MM *xx*-NBL-*o*-PS (**2**).

Macromonomer and Diluent Monomer Copolymerizations

A representative procedure is as follows: MM *xx*-NBL-*m*-PS (**3**) (10 mg, 100 equiv) and *x*-IM₂E'P (5.19 mg, 500 equiv) were dissolved in CDCl₃ (1 mL) in a vial equipped with a stir bar. A stock solution of **G3** in CDCl₃ at a concentration of 0.24 mg/mL was prepared, and 0.1 mL of this solution (to achieve 0.024 mg of **G3**, 1 equiv) was then added rapidly to the first vial to make the final concentration of norbornene = 20 mM. Polymerizations were conducted under air with the capping of the vials in between aliquot removals. Aliquots (0.11 mL each) were withdrawn periodically via micropipette at pre-determined time points and added to 1.5 mL Eppendorf microcentrifuge tubes containing 0.1 mL CDCl₃ and ethyl vinyl ether (2 μL) to terminate the polymerizations. Each aliquot was concentrated under a stream of air for about 1 min, redissolved in THF, and then analyzed by SEC. The same procedure was used for ROMP of MM *xx*-NBL-*o*-PS (**2**) with *x*-IM₂E'P.

Monomer and Small Molecule Characterization:

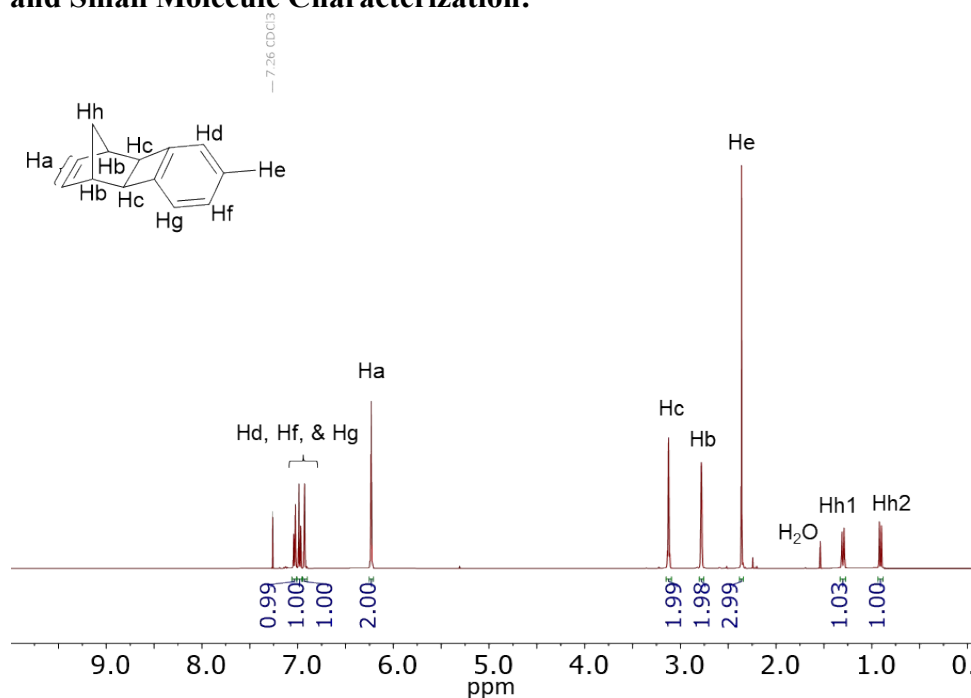


Figure S1. ¹H NMR spectrum of compound *xx*-NBL (**1**).

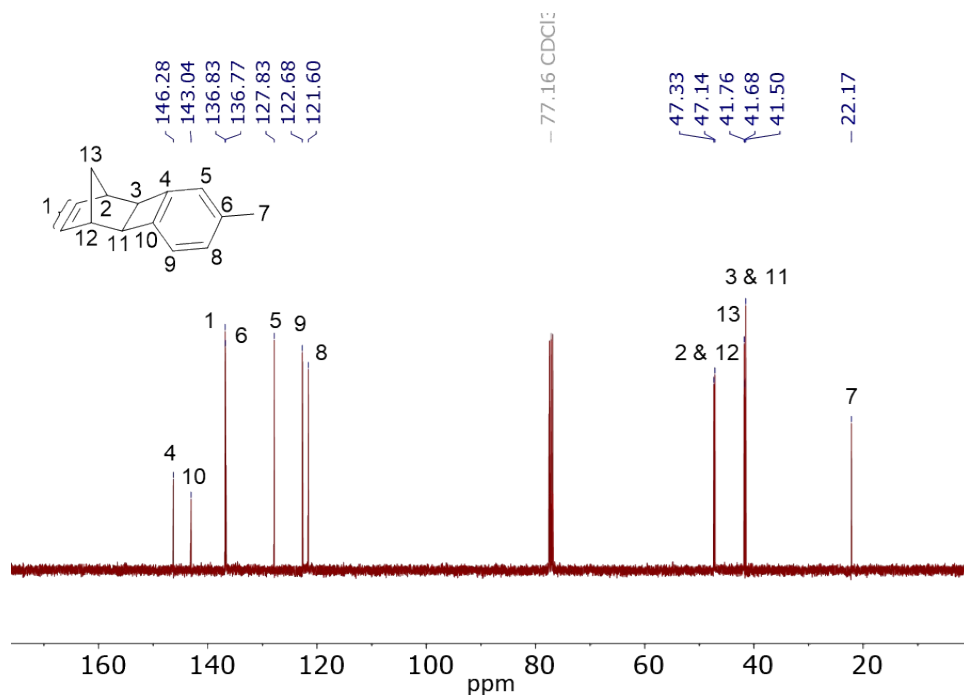


Figure S2. ^{13}C NMR spectrum of compound **xx-NBL (1)**.

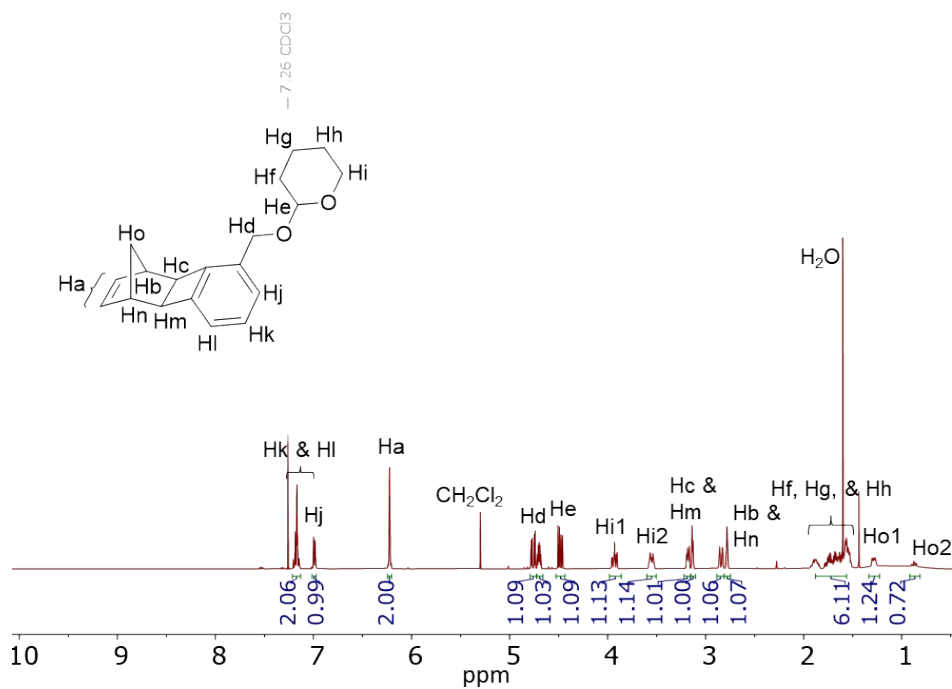


Figure S3. ^1H NMR spectrum of compound **II**.

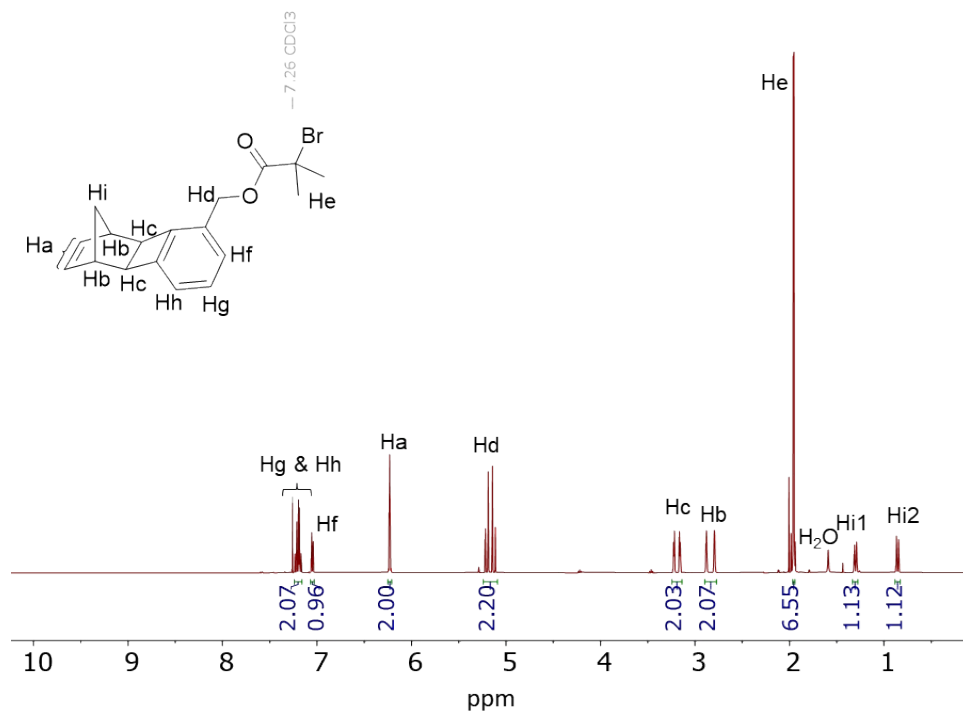


Figure S4. ¹H NMR spectrum of compound **xx-NBL-o-Br**.

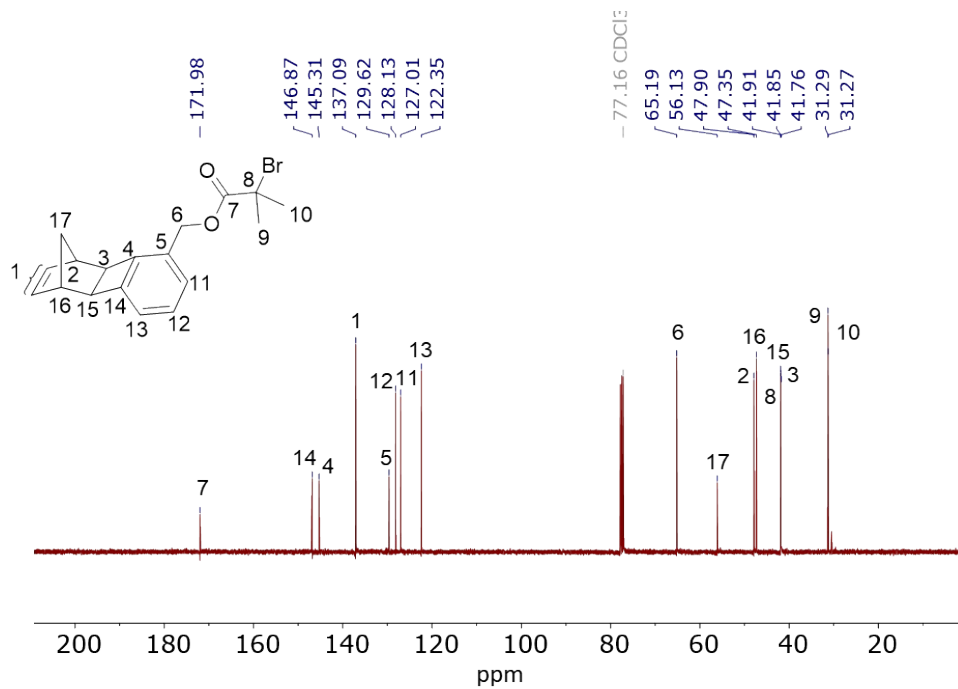


Figure S5. ¹³C NMR spectrum of compound **xx-NBL-o-Br**.

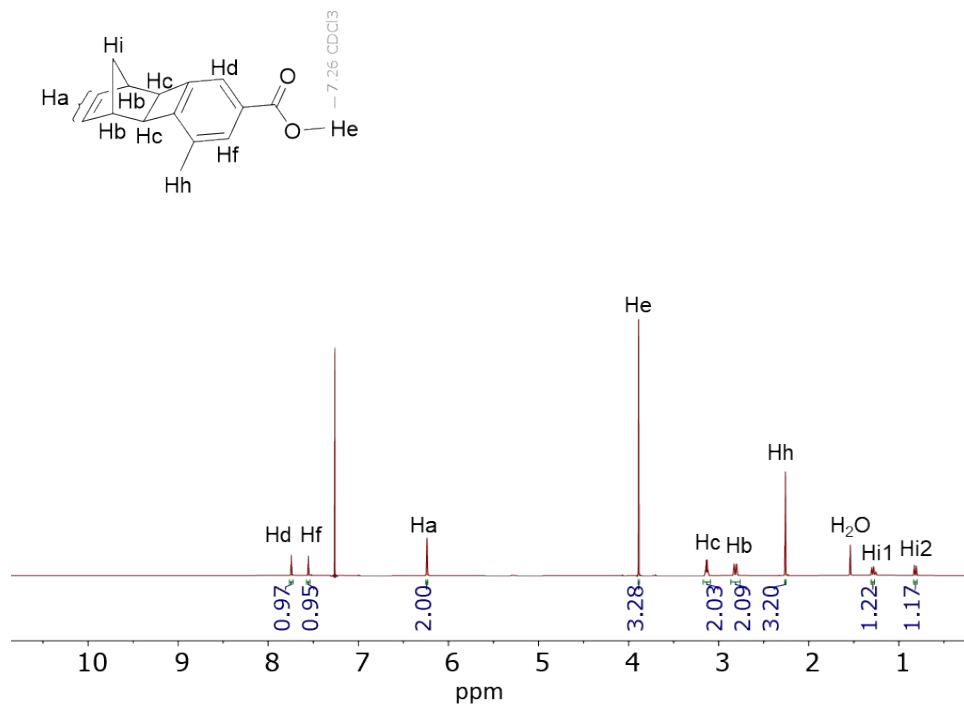


Figure S6. ^1H NMR spectrum of compound V.

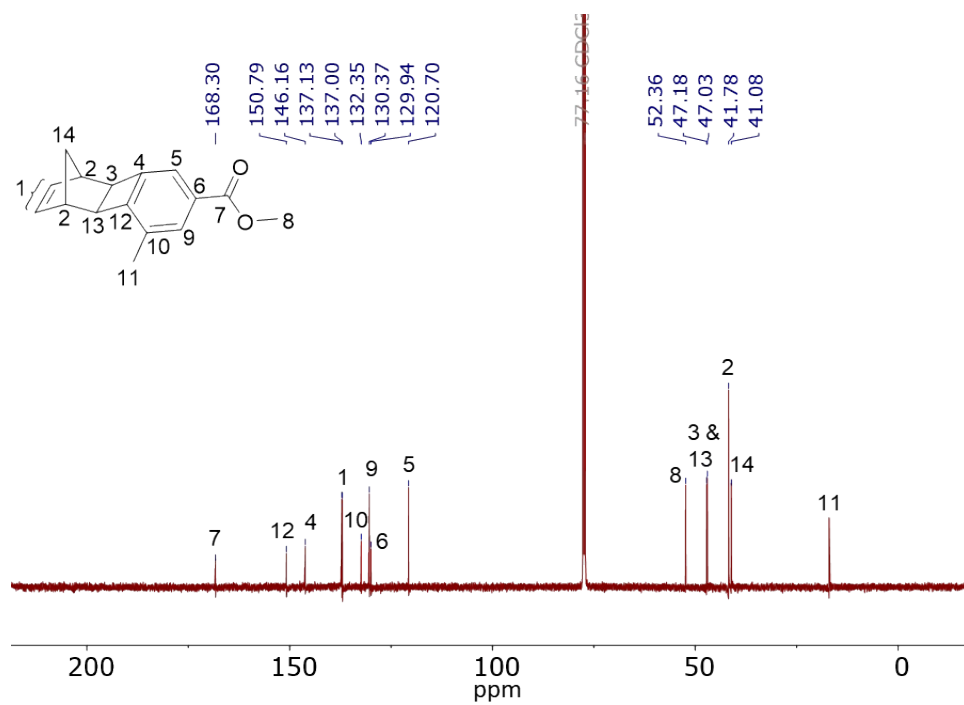


Figure S7. ^{13}C NMR spectrum of compound V.

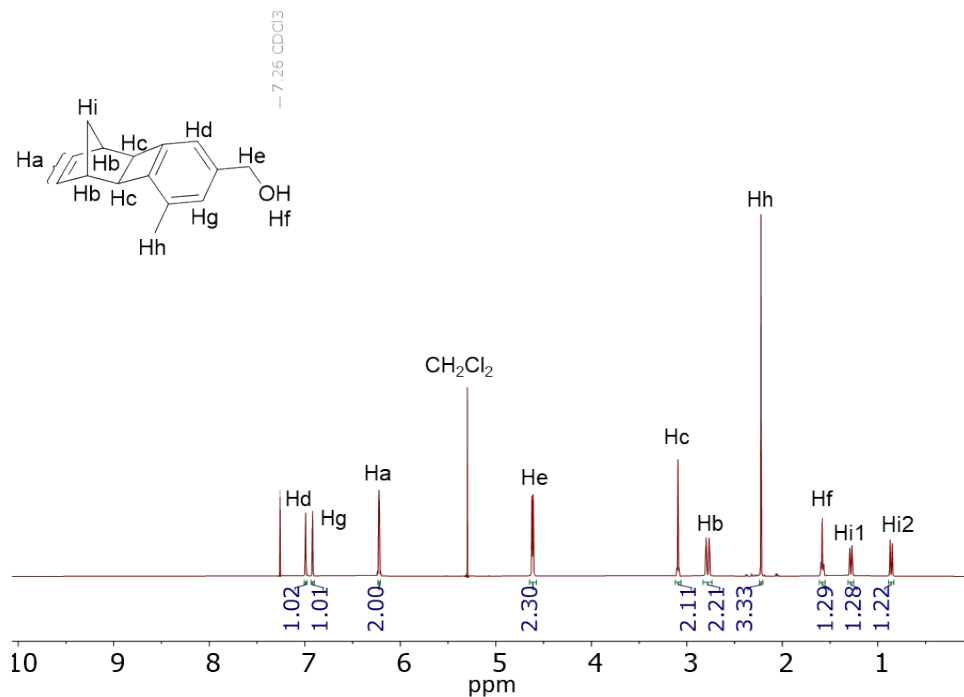


Figure S8. ^1H NMR spectrum of compound VI.

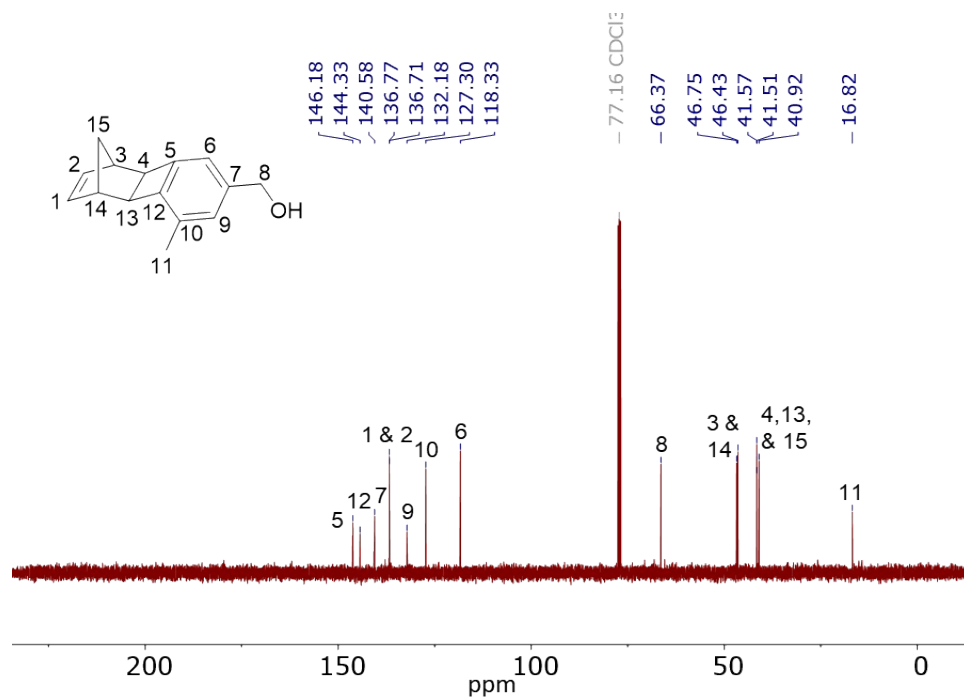


Figure S9. ^{13}C NMR spectrum of compound VI.

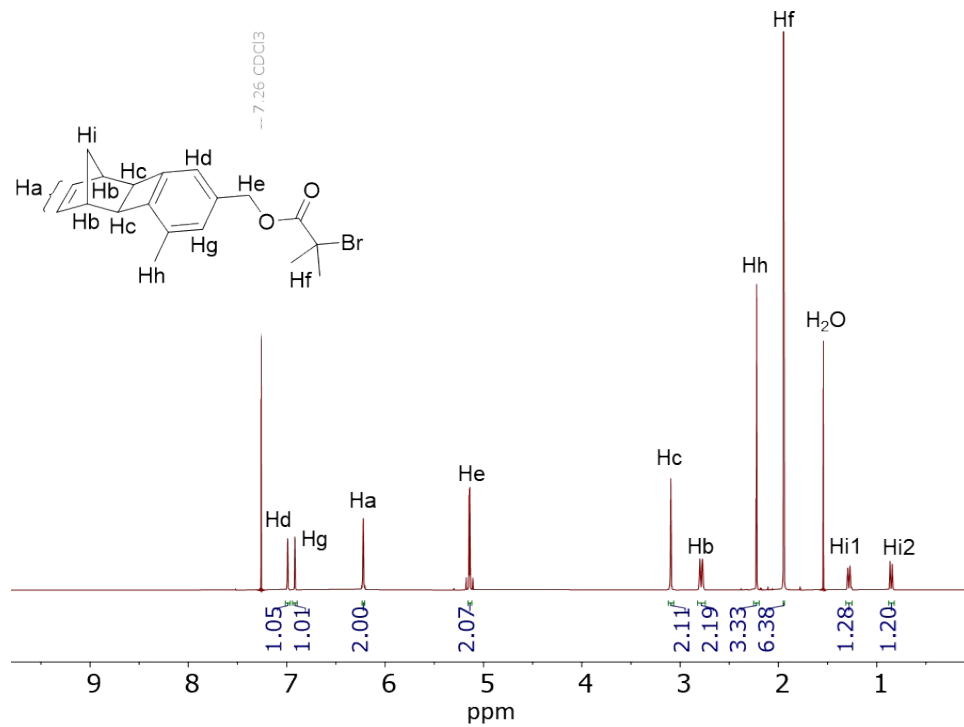


Figure S10. ¹H NMR spectrum of compound **xx-NBL-*m*-Br**.

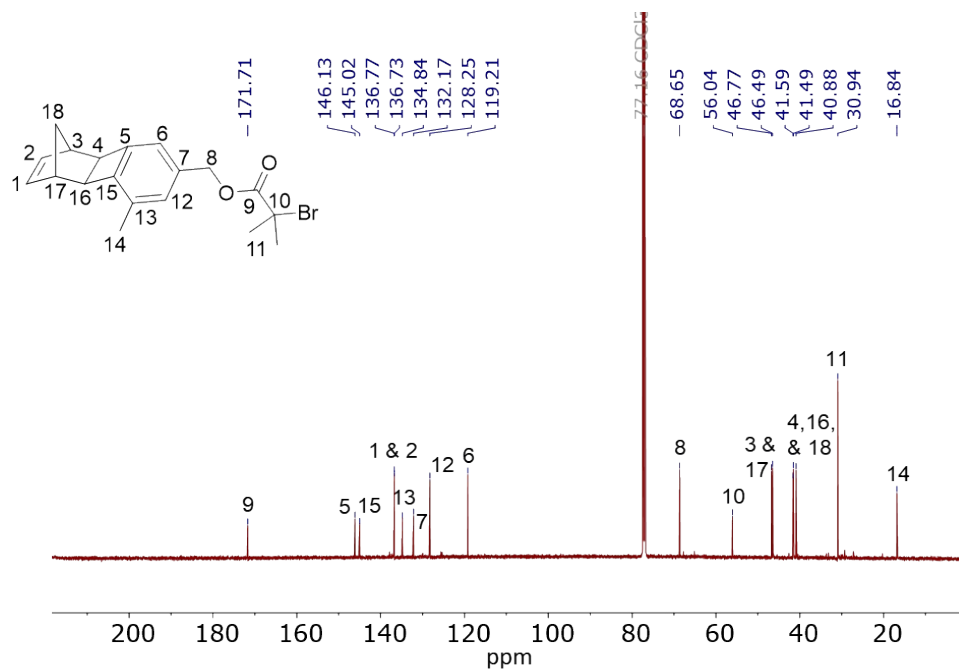


Figure S11. ¹³C NMR spectrum of compound **xx-NBL-*m*-Br**.

^1H NMR and SEC Analysis of MMs

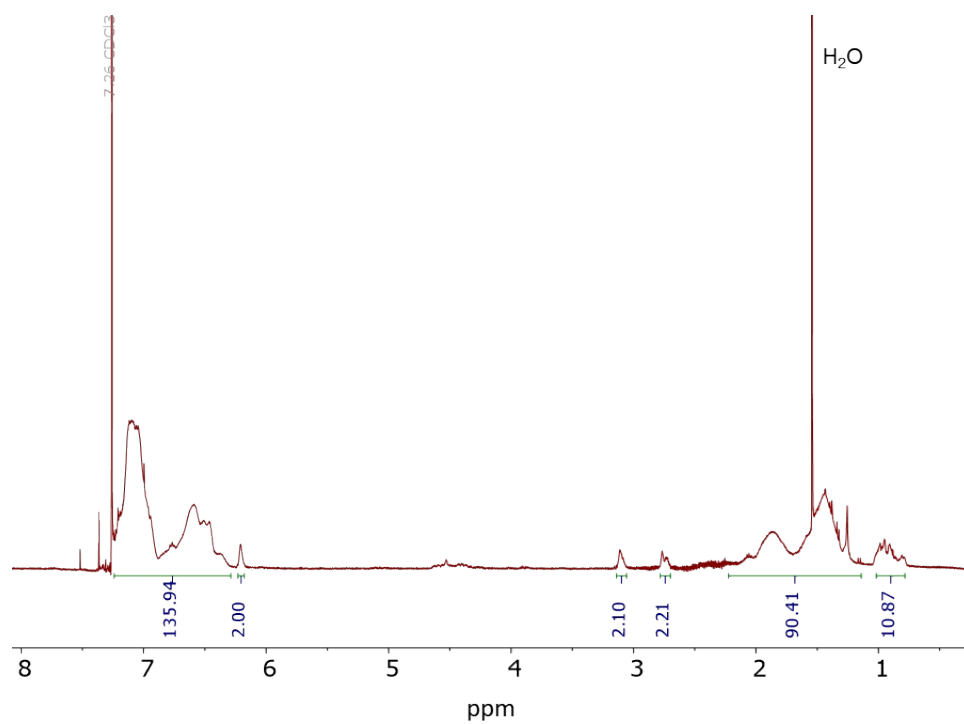


Figure S12. ^1H NMR spectrum of MM *xx*-NBL-*o*-PS (2).

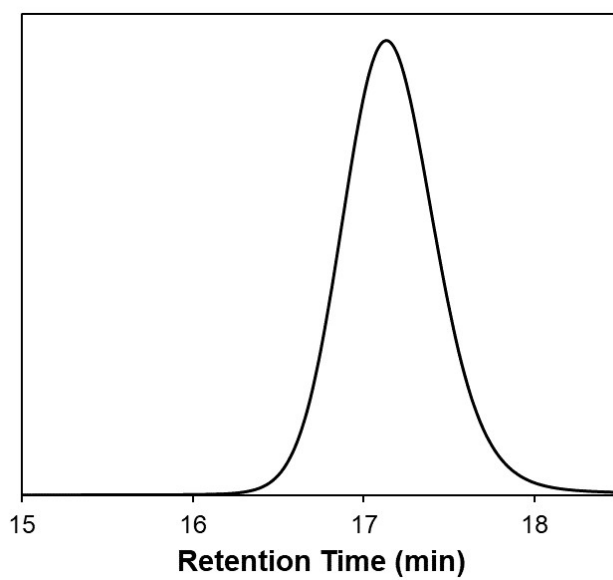


Figure S13. SEC trace (dRI signal) of MM *xx*-NBL-*o*-PS (2).

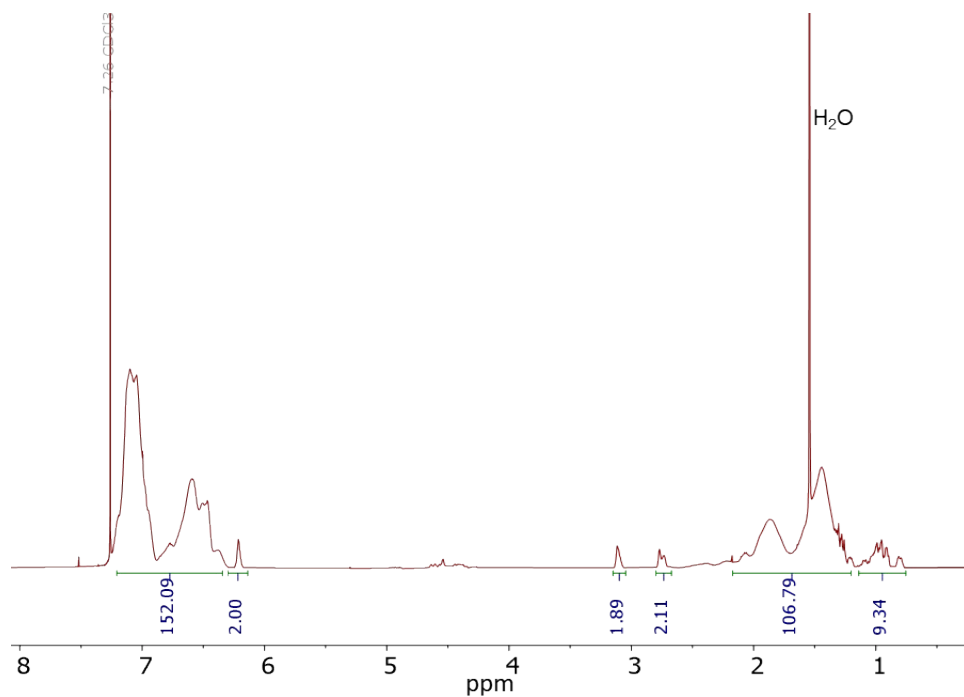


Figure S14. ¹H NMR spectrum of MM *xx*-NBL-*m*-PS (3).

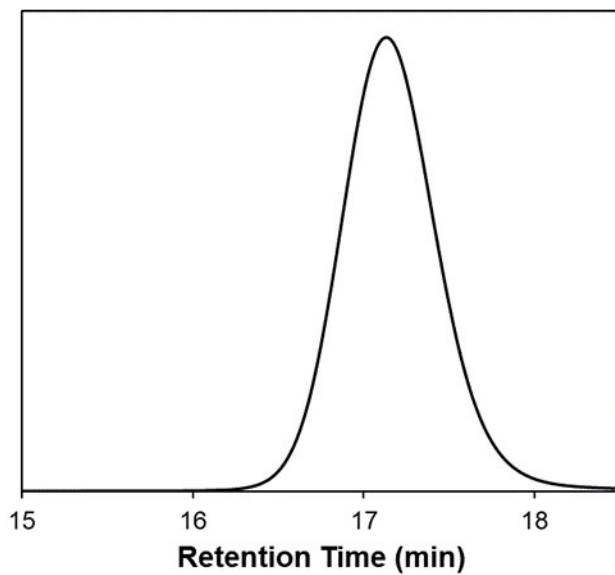


Figure S15. SEC trace (dRI signal) of MM *xx*-NBL-*m*-PS (3).

ROMP Kinetics Analysis

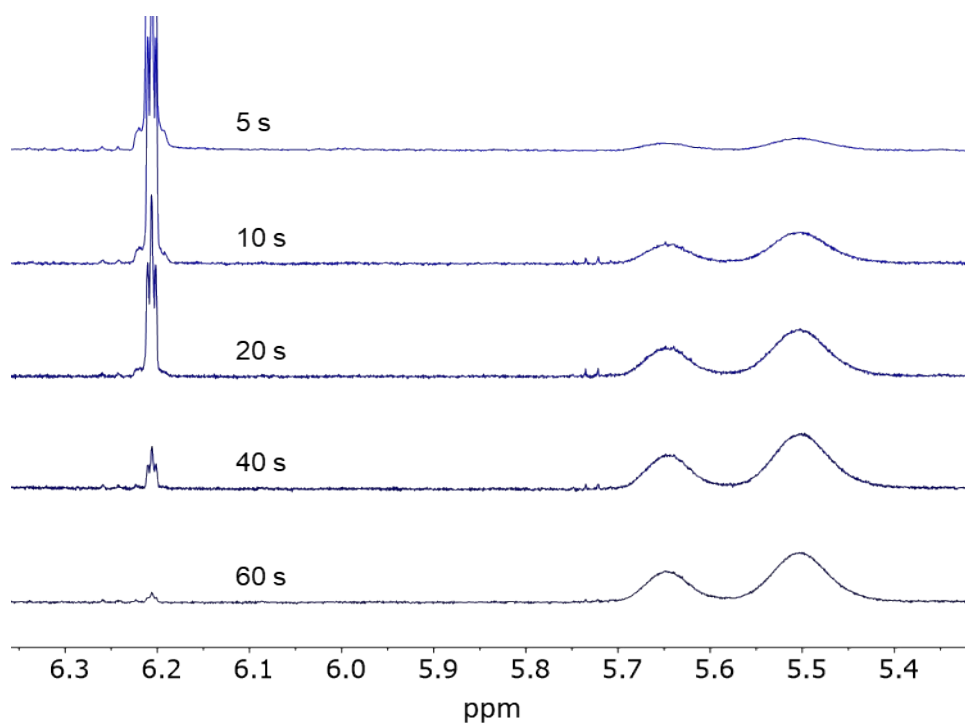


Figure S16. Representative spectra for ¹H NMR kinetics experiment of the ROMP of monomer *xx*-NBL (**1**). As the polymerization proceeds, the norbornene olefin resonance at ~6.2 ppm decreases in intensity, and the polymer backbone resonance at 5.4–5.7 ppm increases in intensity.

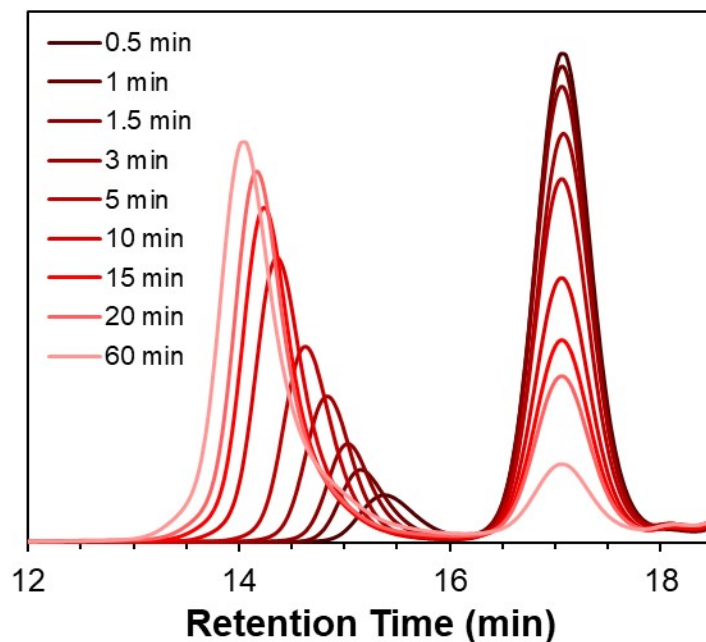


Figure S17. Representative SEC traces (dRI signal) of the ROMP of MM *xx*-NBL-*o*-PS (**2**) at an [MM]/[G3] ratio of 100:1. As the polymerization proceeds, the MM signal centered at 17.2 min decreases in intensity and the bottlebrush polymer signal increases in intensity and shifts in peak retention time from 15.4 min to 14.0 min.

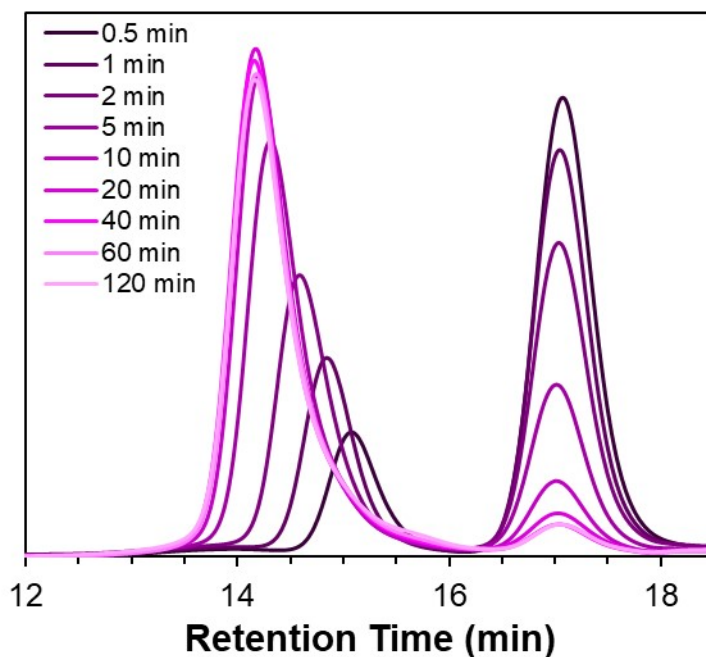


Figure S18. Representative SEC traces (dRI signal) of the ROMP of MM *xx*-NBL-*m*-PS (**3**) at an [MM]/[G3] ratio of 100:1. As the polymerization proceeds, the MM signal centered at 17.2 min decreases in intensity and the bottlebrush polymer signal increases in intensity and shifts in peak retention time from 15.2 min to 14.1 min.

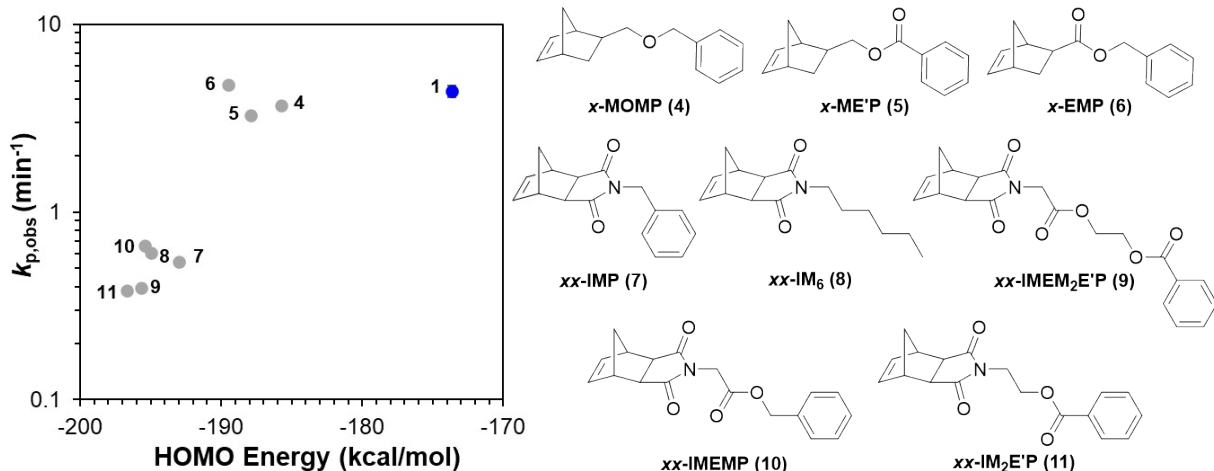


Figure S19. Measured $k_{p,obs}$ values versus HOMO energy for monomer *xx*-NBL (1) (blue circle) compared to published small molecule *exo*-norbornene monomers with various anchor groups (grey circles).⁵

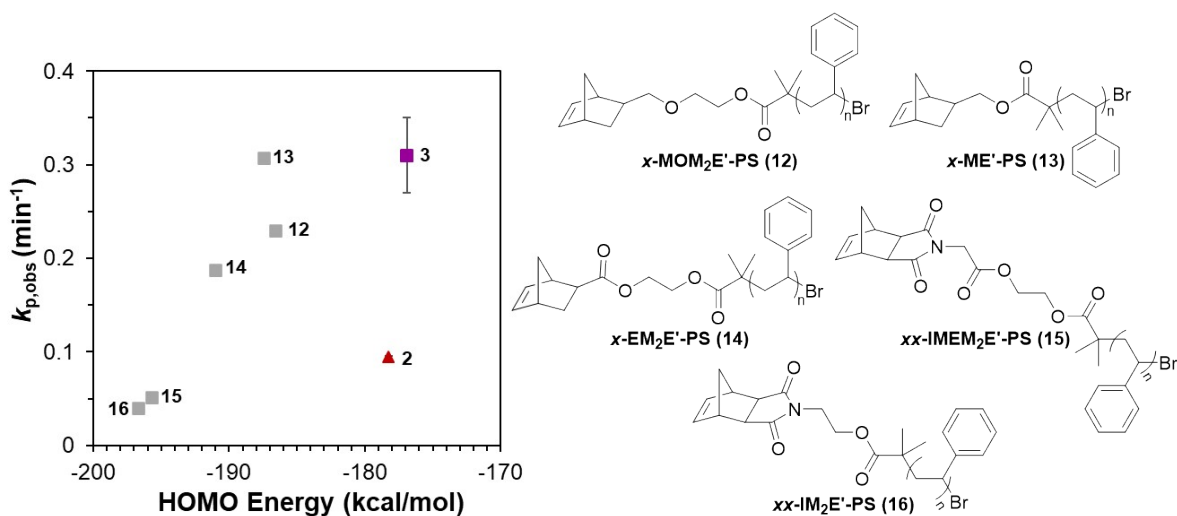


Figure S20. Measured $k_{p,obs}$ values versus HOMO energy for MM *xx*-NBL-*o*-PS (2) (red triangle) and MM *xx*-NBL-*m*-PS (3) (purple square) compared to published MMs (grey squares).⁶

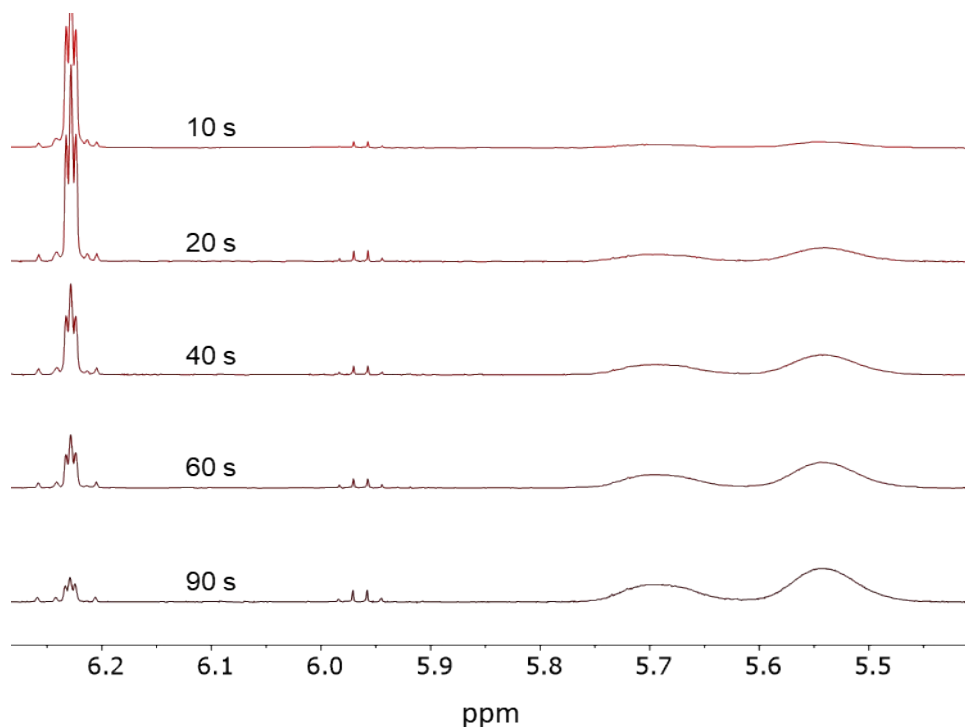


Figure S21. Spectra for ^1H NMR kinetics experiment of the ROMP of monomer **xx-NBL-*o*-Br**. As the polymerization proceeds, the norbornene olefin resonance at ~ 6.2 ppm decreases in intensity, and the polymer backbone resonance at 5.45–5.75 ppm increases in intensity.

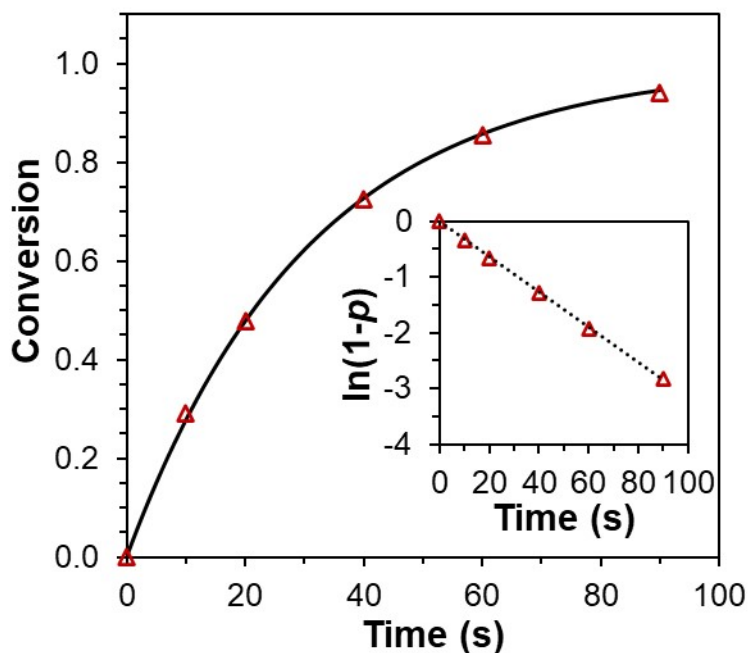


Figure S22. First-order ROMP kinetics analysis of monomer **xx-NBL-*o*-Br** in CDCl_3 at a $[\text{monomer}]/[\text{G3}]$ ratio of 100:1 and $[\text{monomer}] = 20$ mM. The solid line represents the fit to the averaged conversion data based on the equation $p = 1 - e^{(-k_{obs}t)}$ where p = fractional conversion.

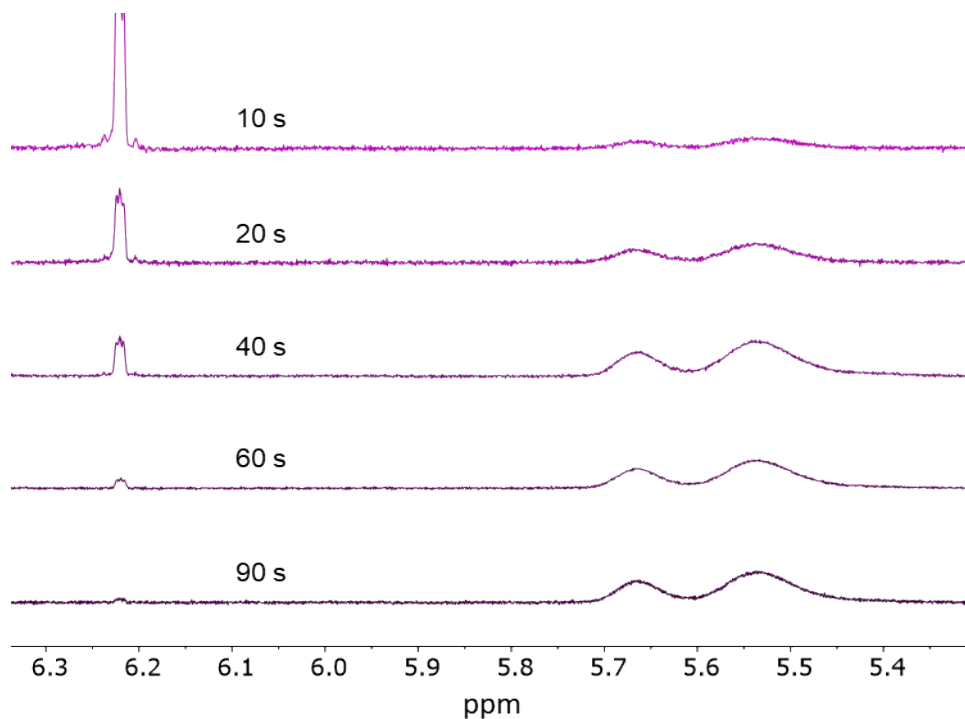


Figure S23. Spectra for ^1H NMR kinetics experiment of the ROMP of monomer **xx-NBL-*m*-Br**. As the polymerization proceeds, the norbornene olefin resonance at ~ 6.2 ppm decreases in intensity and the polymer backbone resonance at 5.45–5.70 ppm increases in intensity.

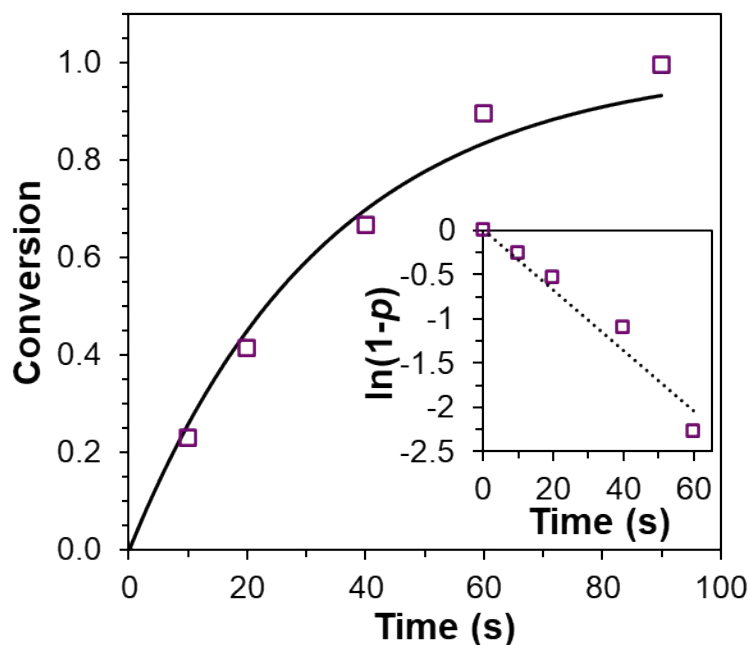


Figure S24. First-order ROMP kinetics analysis of monomer **xx-NBL-*m*-Br** in CDCl_3 at a $[\text{monomer}]/[\text{G3}]$ ratio of 100:1 and $[\text{monomer}] = 20$ mM. The solid line represents the fit to the averaged conversion data based on the equation $p = 1 - e^{(-k_{obs}t)}$ where p = fractional conversion.

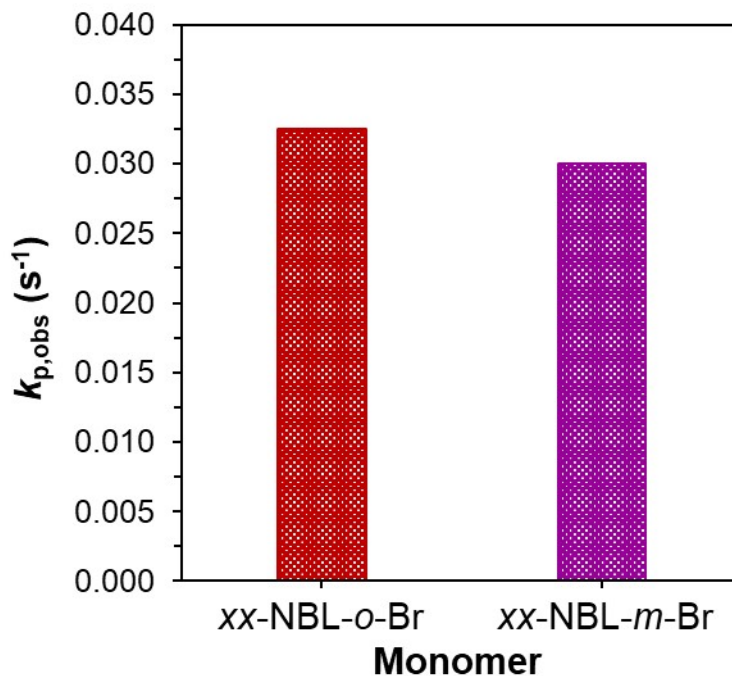


Figure S25. Measured $k_{p,obs}$ values for ROMP of compounds **xx-NBL-*o*-Br** and **xx-NBL-*m*-Br**.

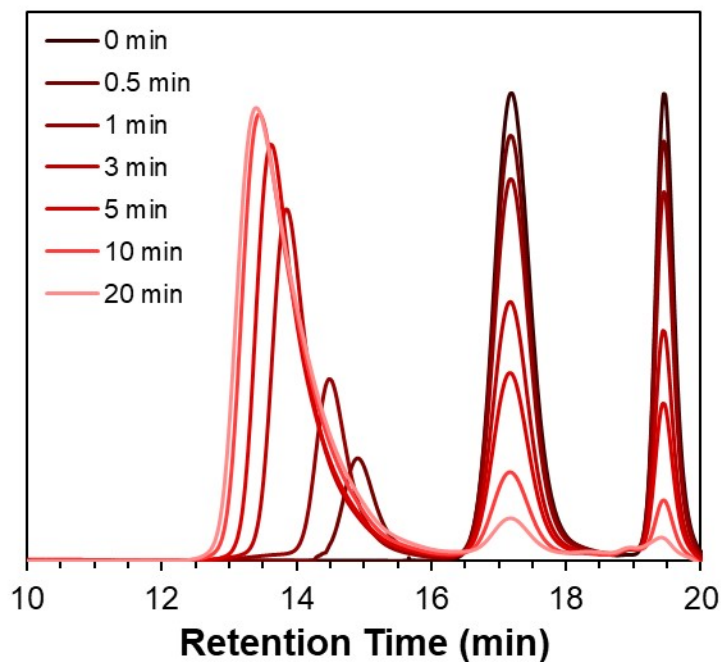


Figure S26. Representative SEC traces (dRI signal) of the copolymerization of MM **xx-NBL-*o*-PS (2)** with small molecule diluent monomer **xx-IM₂E'P** at an [MM]/[diluent]/[G3] ratio of 100:500:1. As the polymerization proceeds, the MM signal at 17.2 min and the diluent monomer signal at 19.5 decrease in intensity and the bottlebrush polymer signal increases in intensity and shifts in retention time from 15.2 min to 13 min.

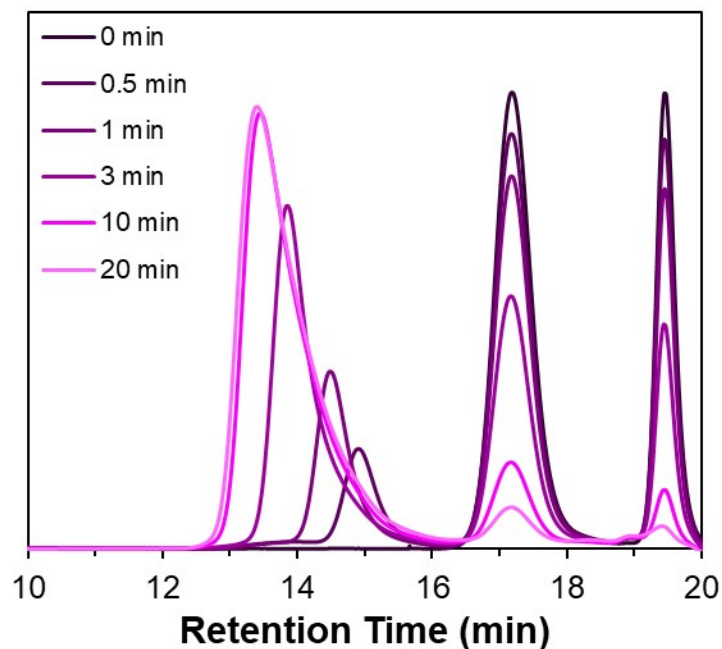


Figure S27. Representative SEC traces (dRI signal) of the copolymerization of MM *xx*-NBL-*m*-PS (**3**) with small molecule diluent monomer *xx*-IM₂E'P at an [MM]/[diluent]/[G3] ratio of 100:500:1. As the polymerization proceeds, the MM signal at 17.2 min and the diluent monomer signal at 19.5 decrease in intensity and the bottlebrush polymer signal increases in intensity and shifts in retention time from 15 min to 13 min.

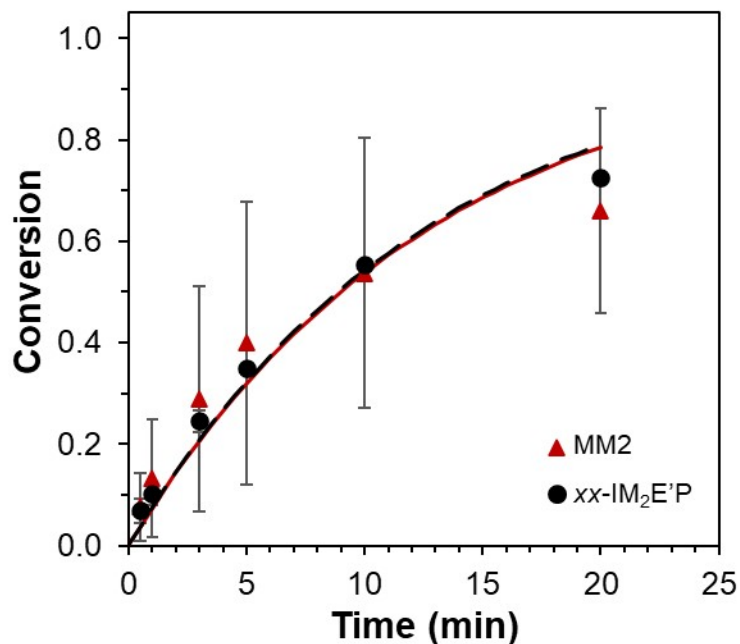


Figure S28. First-order ROMP kinetics analysis of MM *xx*-NBL-*o*-PS (**2**, red triangles) and small molecule diluent monomer ***xx*-IM₂E'P** (black circles) in CDCl₃ at an [MM]/[diluent]/[G3] ratio of 100:500:1 and [norbornene] = 20 mM. The lines represent the fits to the averaged conversion data for MM *xx*-NBL-*o*-PS (**2**, red solid line) and monomer ***xx*-IM₂E'P** (black dashed line) based on the equation $p = 1 - e^{(-k_{obs}t)}$ where p = fractional conversion.

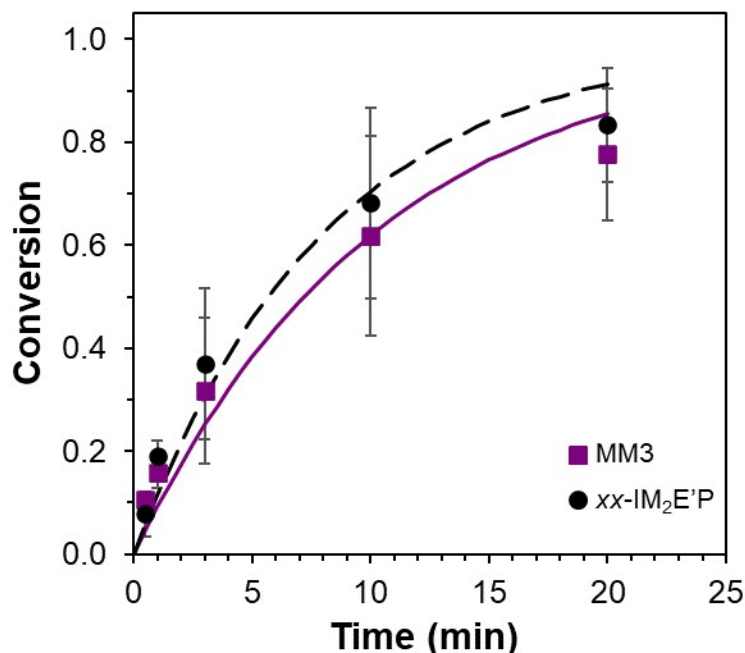


Figure S29. First-order ROMP kinetics analysis of MM *xx*-NBL-*m*-PS (**3**, purple squares) and small molecule diluent monomer *xx*-IM₂E'P (black circles) in CDCl₃ at an [MM]/[diluent]/[G3] ratio of 100:500:1 and [norbornene] = 20 mM. The lines represent the fits to the averaged conversion data for MM *xx*-NBL-*m*-PS (**3**, purple solid line) and monomer *xx*-IM₂E'P (black dashed line) based on the equation $p = 1 - e^{(-k_{obs}t)}$ where p = fractional conversion.

Theoretical Calculations

All density functional theory calculations were performed using the Gaussian 09⁷ suite of software. The M06-2X functional and def2-TZVP basis set were used to optimize the geometries with PCM solvation (chloroform) and an ultrafine integration grid. HOMO energies were obtained with the optimum structures.

Monomer *xx*-NBL (**1**)

Pi Energy (homo): -0.27673 Pi* energy (lumo+1): 0.02947

C	-7.848675	-2.677772	-0.056966
C	-8.665584	-2.316980	-1.107189
C	-8.803345	-3.096618	-2.246480
C	-8.127229	-4.289203	-2.396608
C	-7.294592	-4.661935	-1.336526
C	-7.144728	-3.884708	-0.184975
C	-9.650763	-1.266377	-1.590012
C	-11.087009	-1.281667	-0.995539
C	-11.557303	-2.707738	-1.336440
C	-11.310692	-2.549773	-2.848280
C	-9.807550	-2.155906	-2.889140
C	-12.036848	-1.236403	-3.096913
C	-11.904631	-0.487555	-2.003058

C	-6.213699	-4.326114	0.913304
H	-12.473155	-0.942362	-4.041622
H	-12.210874	0.541494	-1.874288
H	-12.611182	-2.855545	-1.107878
H	-10.962578	-3.492588	-0.871202
H	-9.258167	-0.259401	-1.723283
H	-9.513765	-1.705355	-3.836054
H	-11.155468	-0.967923	0.043083
H	-11.582106	-3.385519	-3.488386
H	-8.217933	-4.918312	-3.273555
H	-6.739677	-5.590771	-1.403871
H	-7.736179	-2.074810	0.837485
H	-5.302314	-3.724318	0.913654
H	-6.679770	-4.210394	1.892494
H	-5.925289	-5.369298	0.791821

MM *xx*-NBL-*o*-PS₁ (2)

Pi energy (homo): -0.28408 Pi* energy (lumo+3): 0.02207

C	-3.984952	-0.431662	-1.593606
C	-2.472298	-0.226770	-1.797990
C	-1.890061	-0.768266	-0.463106
C	-2.865003	-1.965399	-0.121762
C	-3.859113	-1.940930	-1.316760
C	-3.005629	-2.354990	-2.506816
C	-2.188358	-1.342157	-2.792272
C	-2.372150	-0.132656	0.824977
H	-3.003544	-3.341490	-2.949578
H	-1.383560	-1.334318	-3.514890
H	-4.549790	-0.228583	-2.501533
H	-4.400708	0.137522	-0.763323
H	-0.825900	-0.993306	-0.518782
H	-2.413609	-2.943663	0.035740
H	-2.136068	0.771162	-2.068898
H	-4.778777	-2.498878	-1.159848
C	-3.228863	-1.181544	1.128544
C	-4.030573	-1.180965	2.251317
C	-3.923067	-0.054057	3.072567
C	-3.062132	0.996854	2.767724
C	-2.258182	0.990091	1.621471
H	-4.703327	-1.990825	2.503325
H	-4.518256	0.007055	3.974975
C	-1.373424	2.157141	1.302583
O	-0.381094	1.730577	0.366528
H	-1.945083	2.977716	0.862051
H	-0.884904	2.541694	2.199315
C	0.526766	2.647586	0.008432

O	0.504914	3.776799	0.425214
C	1.564467	2.079061	-0.950073
C	2.323680	0.979712	-0.175569
C	0.839791	1.493421	-2.169262
C	2.495279	3.208434	-1.380571
C	3.464399	0.318167	-0.954581
H	2.733995	1.411075	0.743471
H	1.610197	0.209595	0.127171
H	3.204164	2.846323	-2.124533
H	1.925766	4.025943	-1.822364
H	3.050822	3.606041	-0.530776
H	1.563345	1.206884	-2.932196
H	0.254476	0.615780	-1.895070
H	0.168050	2.232023	-2.611252
C	4.092612	-0.786013	-0.145448
H	3.083755	-0.093254	-1.891627
H	4.224620	1.059190	-1.206429
C	5.187307	-0.533723	0.677460
C	5.739150	-1.541562	1.457537
C	5.200295	-2.820880	1.425556
C	4.107207	-3.084259	0.609562
C	3.559418	-2.073044	-0.167588
H	5.612928	0.463295	0.703339
H	6.592583	-1.328109	2.088555
H	5.630373	-3.608485	2.030534
H	3.682600	-4.079591	0.576575
H	2.706935	-2.283278	-0.804629
H	-3.011029	1.843932	3.442772

MM *xx*-NBL-*m*-PS₁ (**3**)

Pi energy (homo): -0.28194 Pi* energy (lumo+3): 0.02287

C	-3.250997	1.715444	1.335284
C	-2.879550	2.417370	0.015902
C	-3.239599	1.333473	-1.038416
C	-4.520910	0.652975	-0.406561
C	-4.708593	1.449237	0.915558
C	-5.105381	2.841377	0.447761
C	-4.025553	3.412989	-0.083177
C	-2.575220	-0.026684	-0.916804
H	-6.114979	3.228601	0.451889
H	-3.974951	4.361159	-0.600496
H	-3.188394	2.389624	2.187485
H	-2.674924	0.812513	1.533184
H	-3.337171	1.736436	-2.045173
H	-5.422045	0.627878	-1.018104
H	-1.873647	2.820959	-0.069299

H	-5.360667	0.976636	1.646070
C	-3.697870	-0.621953	-0.361848
C	-3.737699	-1.948647	0.025212
C	-2.544346	-2.651633	-0.188495
C	-1.408665	-2.066445	-0.748743
C	-1.403329	-0.718716	-1.131696
C	-4.949675	-2.585805	0.639877
H	-2.498723	-3.698844	0.092584
C	-0.167621	-2.885929	-0.949259
H	-0.515473	-0.274784	-1.567425
O	0.872499	-2.314513	-0.137510
H	-0.317877	-3.925015	-0.656092
H	0.162499	-2.868472	-1.989097
H	-4.834072	-3.666120	0.715636
H	-5.125083	-2.192135	1.643271
H	-5.841692	-2.373496	0.048658
C	2.101641	-2.814903	-0.302530
O	2.338935	-3.722080	-1.058516
C	3.127938	-2.090361	0.559494
C	3.135904	-0.618315	0.093051
C	2.695802	-2.204975	2.027567
C	4.487614	-2.751320	0.356651
C	4.177622	0.270109	0.779692
H	3.314684	-0.589534	-0.987213
H	2.144114	-0.192761	0.261364
H	5.223501	-2.306643	1.026132
H	4.430489	-3.817880	0.572905
H	4.833137	-2.634234	-0.671147
H	3.461817	-1.782007	2.677176
H	1.757101	-1.680964	2.204389
H	2.566171	-3.251906	2.307990
C	4.048330	1.696267	0.312627
H	4.043369	0.231016	1.862594
H	5.182856	-0.092801	0.560128
C	4.787968	2.162485	-0.771221
C	4.633829	3.463635	-1.232039
C	3.732635	4.319569	-0.612940
C	2.988141	3.865405	0.468609
C	3.146011	2.563970	0.924673
H	5.494540	1.498195	-1.256409
H	5.220346	3.810031	-2.073534
H	3.613138	5.334753	-0.968511
H	2.285957	4.527180	0.959742
H	2.563941	2.213660	1.770147

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