Supporting Information

Metal-Free Ring-Opening Metathesis Polymerization

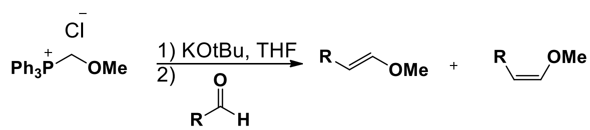
Kelli A. Ogawa, Adam E. Goetz, and Andrew J. Boydston*

Department of Chemistry, University of Washington, Seattle, WA 98195

Materials and Methods. Acetonitrile (CH_3CN) and nitromethane (CH_3NO_2) were dried over calcium hydride and distilled prior to use. Dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) were obtained from a solvent purification system. ^{1}H and ^{13}C 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 ($CDCl_3$, ^{1}H: 7.27 ppm and ^{13}C: 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. UV-visible spectroscopy data were collected on an Agilent 8453 UV-vis spectrophotometer. 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. All polymerizations were carried out under an inert atmosphere of nitrogen 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. Electrochemical experiments were performed on a CH Instruments 1100B potentiostat using a 25 mL 3-neck round bottom flask as an undivided cell. Cyclic voltammetry experiments were done using a glassy carbon working electrode (3 mm diameter), Pt counter electrode (Premier Lab Supply), and Ag/0.01 M $AgNO_3$ (0.1 M tetrabutylammonium tetrafluoroborate in CH_3CN) reference electrode. Electro-organic ROMP experiments were done using a carbon fiber (Zoltek) working electrode, carbon fiber counter electrode, and Ag/0.01 M $AgNO_3$ (0.1 M tetrabutylammonium tetrafluoroborate in CH_3CN) reference electrode. T_g values were determined using a Perkin-Elmer DMA 8000. 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 ºC/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. Norbornene (**1**) was purchased from Aldrich and sublimed prior to use. Initiators **2a** and **2b** were prepared according to literature procedures.[1] The pyrylium tetrafluoroborate (**3a**) and perchlorate (**3b**) salts were prepared according to literature procedures.[2,3] All other reagents and solvents were obtained from commercial sources and used as received unless otherwise noted.

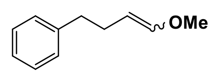
General procedure for the preparation of initiators 2a and 2b. Procedures for the synthesis of enol ether initiators as reported by Stambuli were used.

Scheme S1. Preparation of initiators **2a** and **2b**.



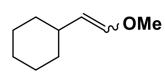
A solution of potassium *tert*-butoxide (5.1 g, 45.0 mmol, 1.5 equiv.) in 10 mL of dry THF was slowly added to a solution of (methoxymethyl)triphenylphosphonium chloride (15.4 g, 45.0 mmol, 1.5 equiv.) in 40 mL of dry THF. After stirring the red solution at 23 °C for 45 min, a solution of the corresponding aldehyde (30.0 mmol, 1.0 equiv.) in 10 mL of dry THF was slowly added and allowed to stir at 23 °C for an additional 2 h. The solvent was removed under vacuum and the residue was diluted with hexanes. The organic layer was washed with water (3 x 100 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting residue was purified by filtering through a plug of silica with diethyl ether as the eluent. In some cases, residual triphenylphosphine was removed by stirring overnight with 10 equiv of iodomethane and filtration through a plug of silica with diethyl ether as the eluent.

1-methoxy-4-phenyl butene (2a).

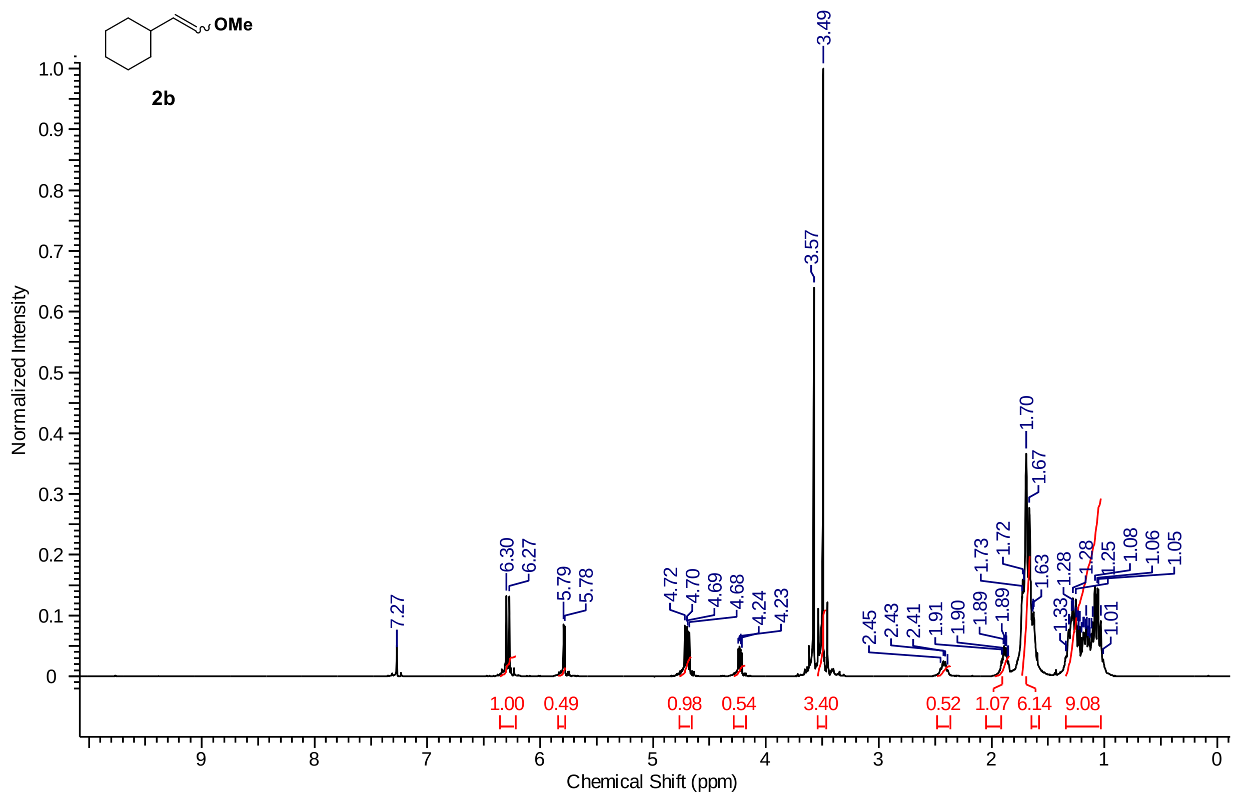


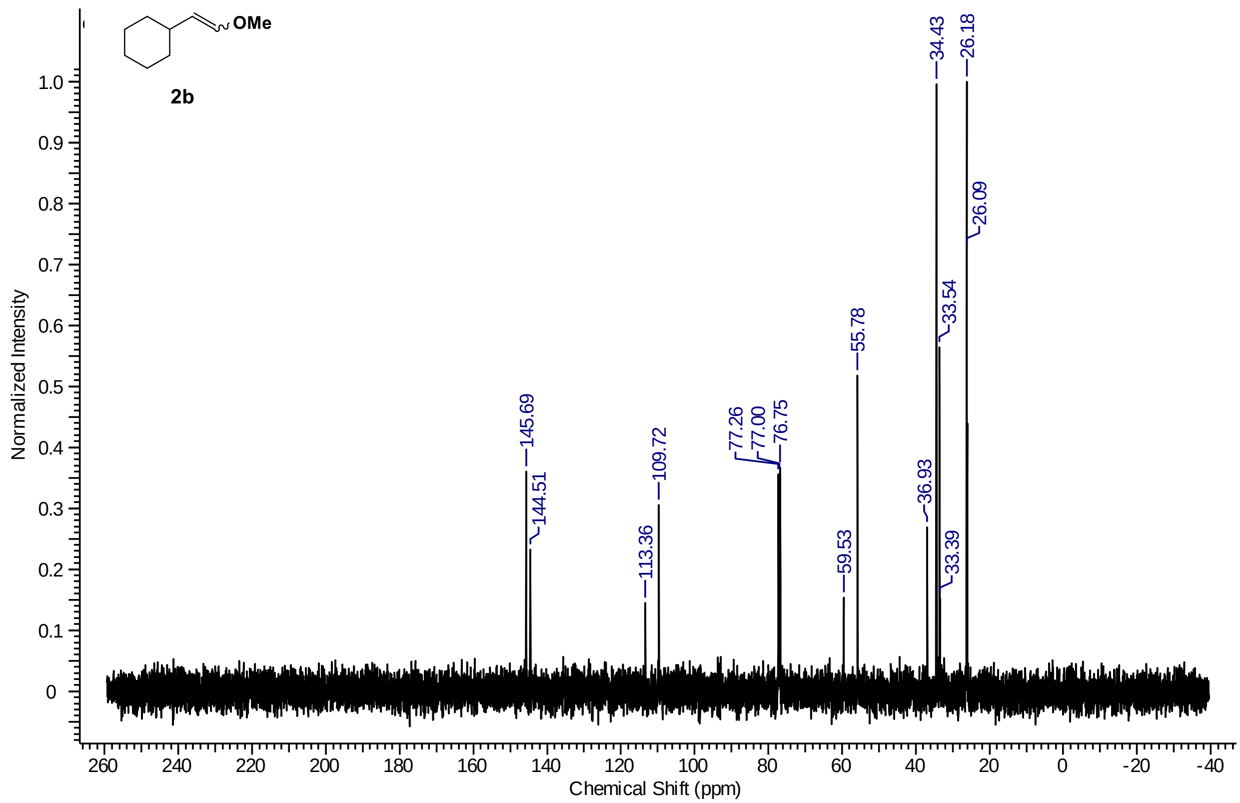
Prepared according to the above procedure in 92% yield (1:2 *cis* to *trans* ratio); spectral data were consistent with literature values.[4]

2-cyclohexyl-1-methoxyethylene (2b).

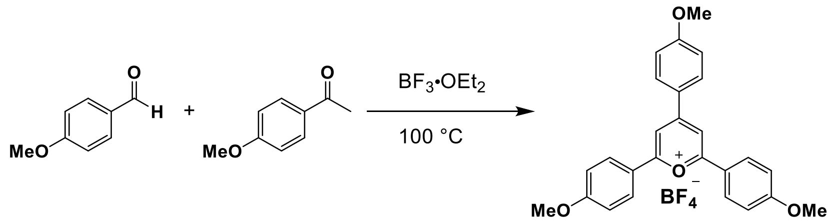


Prepared according to above procedures in 82% yield (1:2 *cis* to *trans* ratio). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.29 (d, *J* = 12 Hz, 1 H, *trans*) 5.79 (d, *J* = 6.0 Hz, 0.5 H, *cis*) 4.70 (dd, *J* = 6.0 Hz, 9 Hz, 1 H, *trans*) 4.24 (dd, *J* = 3 Hz, 6 Hz, 0.5 H, *cis*) 3.58 (s, 1.5 H, *cis*) 3.50 (s, 3 H, *trans*) 2.42 (m, 0.5 H, *cis*) 1.88 (m, 1 H, *trans*) 1.68 (m, 4 H, *cis/trans*) 1.16 (m, 9 H, *cis/trans*). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 145.7, 144.5, 113.4, 109.7, 59.5, 55.8, 36.9, 34.4, 35.4, 33.4, 26.2, 26.1, 26.0


OMe
2b
Normalized Intensity
Chemical Shift (ppm)
7.27
6.30
6.27
5.79
5.78
4.72
4.70
4.69
4.68
4.24
4.23
3.57
3.49
2.45
2.43
2.41
1.91
1.90
1.89
1.89
1.73
1.72
1.70
1.67
1.63
1.33
1.28
1.28
1.25
1.08
1.06
1.05
1.01
1.00
0.49
0.98
0.54
3.40
0.52
1.07
6.14
9.08

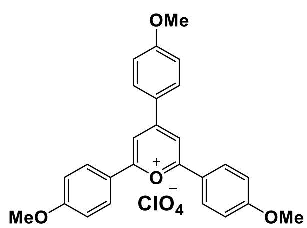

OMe
2b
Normalized Intensity
Chemical Shift (ppm)
145.69
144.51
113.36
109.72
77.26
77.00
76.75
59.53
55.78
36.93
34.43
33.54
33.39
26.18
26.09

Scheme S2. Preparation of 2,4,6-tri-(*p*-methoxyphenyl) pyrylium tetrafluoroborate (**3a**)



To a flask containing *p*-anisaldehyde (6.1mL, 50.3 mmol, 1 equiv) and *p*-acetylanisole (15.07g, 100.4 mmol, 2 equiv) was added BF_3•Et_2O (15.0mL, 121.5 mmol, 2.4 equiv) dropwise over 5 min. The solution was heated in an oil bath set to 100 °C. After 2 h, the reaction was removed from heat. Once at room temperature, the crude material was diluted with acetone (200 mL) and Et_2O (250 mL) and filtered to give a rust-colored solid. The solids were washed with warm acetone (175 mL) and dried under vacuum to give the pyrylium tetrafluoroborate as an orange solid (5.01 g, 20%). Spectral data matched those previously reported.[2]

Preparation of 2,4,6-tri-(*p*-methoxyphenyl) pyrylium perchlorate (3b).



Prepared according to literature procedures in 10% yield, spectral data were consistent with literature values.[5]

General procedure for cyclic voltammetry of initiators 2a – 2c. Representative cyclic voltammograms are depicted in Figures S1 – S3. The general procedure was as follows: In a drybox, a 3-neck round bottom flask was charged with a magnetic stir bar, anhydrous CH_3NO_2 (15 mL), and lithium perchlorate (15.0 mmol). The indicated initiator (0.075 mmol) was then added to the mixture. The flask was equipped with a glassy carbon anode (3 mm diameter), Pt basket cathode, and Ag/$AgNO_3$ reference electrode (0.01 M $AgNO_3$/0.1 M tetrabutylammonium tetrafluoroborate in CH_3CN) and then the apparatus was sealed using rubber septa. The electrochemical cell was then removed from the drybox and the solution was placed under a positive pressure of N_2 and stirred at room temperature. Stirring was stopped prior to connecting to the potentiostat. The cyclic voltammograms for the initiators were typically taken from 0.5 V to 2.5 V vs. Ag/$AgNO_3$ with a sweep rate of 0.10 V/s. Ferrocene (0.15 mmol) was added as an internal standard after each voltammogram.[6] All potentials are reported in V vs. SCE.

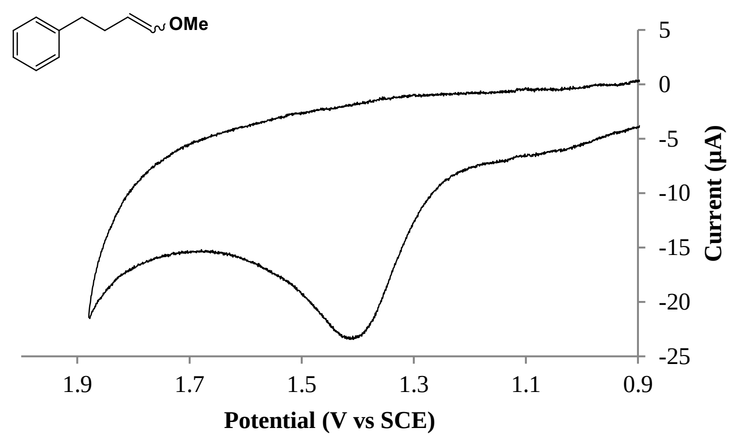


Figure S1. Cyclic voltammogram of initiator **2a**.

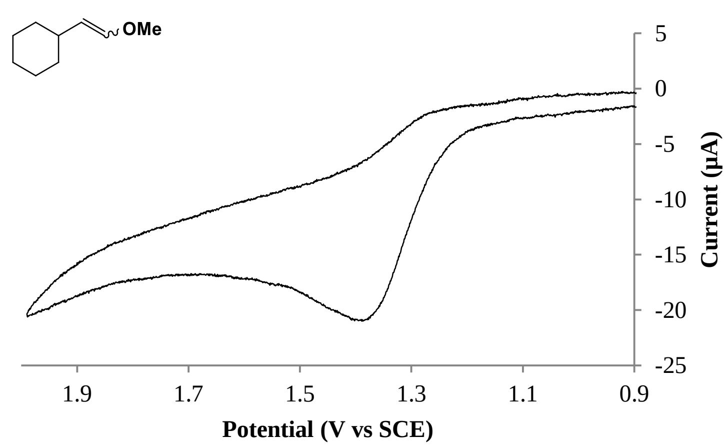


Figure S2. Cyclic voltammogram of initiator **2b**.

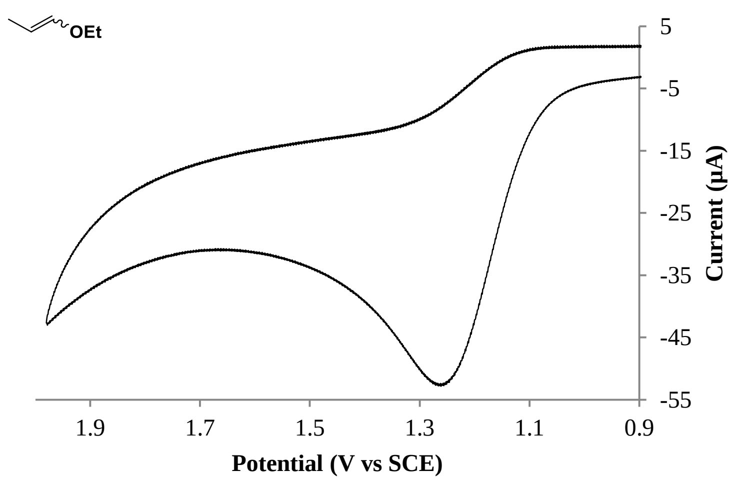


Figure S3. Cyclic voltammogram of initiator **2c**.

General procedure for electro-organic ROMP. Electro-organic ROMP experiments were done using a carbon fiber (Zoltek) working electrode, carbon fiber counter electrode, and Ag/0.01 M $AgNO_3$ (0.1 M tetrabutylammonium tetrafluoroborate in CH_3CN) reference electrode in a double junction chamber. The carbon fiber electrodes were 40 mm in length (excluding the copper lead) and 15 mm of the carbon fiber was submerged in the electrolyte solution during electrolysis. In the drybox, a 3-neck round bottom flask was charged with a magnetic stir bar, lithium perchlorate (15.0 mmol) and CH_3NO_2 (15 mL). To the solution was added norbornene (23.2 mmol, 100 equiv.) and initiator (0.23 mmol, 1 equiv.). The electrodes were attached onto the cell and the apparatus was sealed using rubber septa. The electrochemical cell was then removed from the dry box and placed under a positive pressure of N_2. The electrodes were connected to the potentiostat and bulk electrolysis with a constant potential of 1.43 V vs SCE was started with constant stirring. After the current reached background levels, the electrolysis was stopped and hydroquinone (2.3 mmol, 10 equiv) was then added to the solution. The carbon fiber electrodes were removed and soaked in THF. The quenched solution and electrode soaks were added to rapidly stirring methanol to precipitate the polymer. The resulting solids were redissolved in THF, passed through a syringe filter (2 μm) to remove any carbon fiber particulates, and reprecipitated into methanol. The resulting solids were dried under vacuum and analyzed by ^{1}H NMR spectroscopy and GPC.

a) 

b) 

Figure S4. a) Undivided electrochemical cell with carbon fiber working and counter electrodes, double junction chamber (for the reference electrode), and Ag/$AgNO_3$ reference electrode. b) Carbon fiber electrode with copper lead bound with Teflon tape.

General procedure for photoredox mediated ROMP. All polymerizations were set up in a drybox under an inert atmosphere of nitrogen. Irradiation of the sealed vials with blue LEDs was done outside of the drybox. A 2-dram vial was equipped with a magnetic stir-bar, 2,4,6-tri-(*p*-methoxyphenyl) pyrylium tetrafluoroborate (**3a**, 3.0 – 25.0 mol %), and norbornene (48 – 1000 equiv. relative to **2**). The solvent, CH_2Cl_2 (1.2 – 5.3 M), and initiator **2** (1 equiv.) were added to the vial. The vial was sealed with a Teflon-coated screw cap and brought out of the drybox. The mixture was irradiated for the indicated period of time. The reaction progress and M_n were monitored by ^{1}H NMR spectroscopy and GPC, respectively. Upon completion, hydroquinone (5 equiv.) was added to the reaction mixture, which was then passed through a short plug of alumina. The polymer solution was then added dropwise into an excess of methanol (MeOH) or dry acetonitrile (CH_3CN) to cause precipitation of the polymer. *Note: As a control, the same setup was performed outside the drybox, and then the reaction mixture was sparged with N_2 for 15 minutes before irradiation. This led to a significant decrease in polymer formation (only ~ 30 % conversion of monomer as determined by ^1H NMR spectroscopy) compared to reactions setup inside the drybox.*

NMR Spectra for Structural Comparisons:

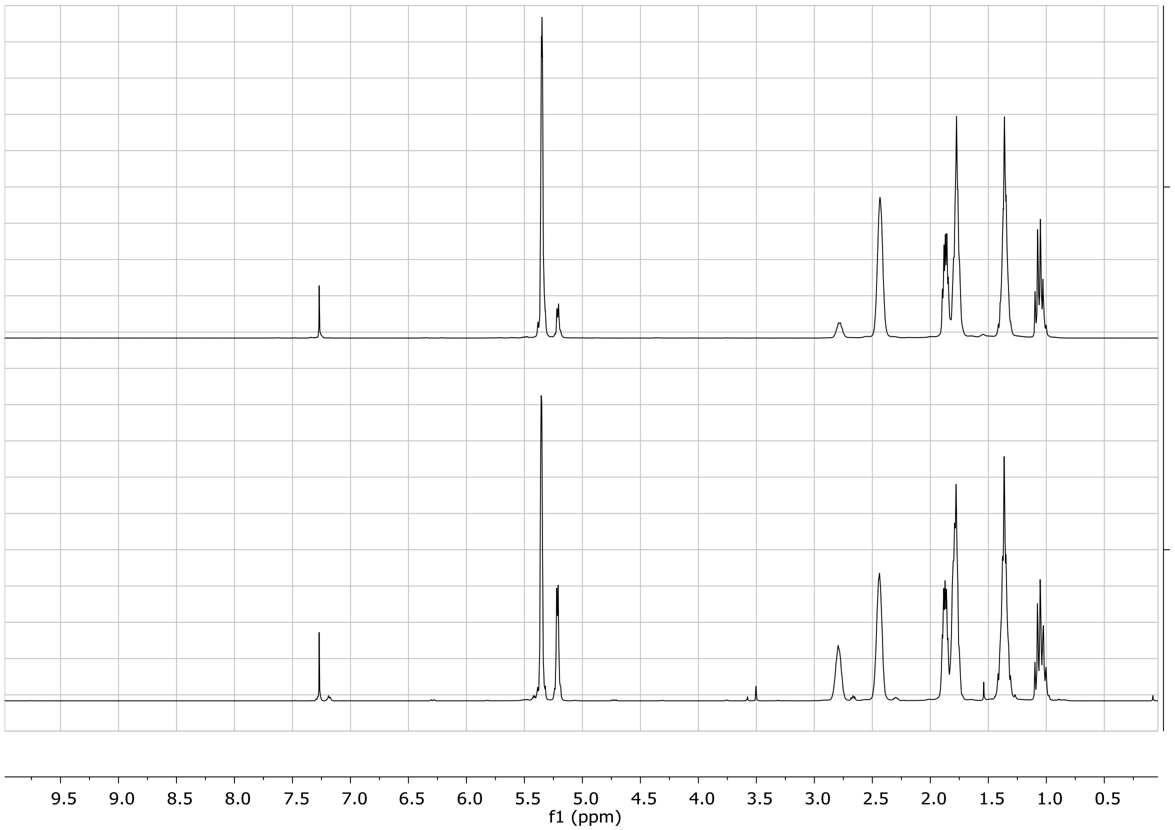


Figure S5. ^{1}H NMR spectra of (top) polynorbornene (M_n = 49.3 kDa; Đ = 1.2, *cis*/*trans* = 1:8) synthesized using Grubbs 1st-generation initiator, and (bottom) polynorbornene (M_n = 10.1 kDa; Đ = 1.5 by GPC analysis and M_n = 12.7 kDa by ^{1}H NMR analysis; *cis*/*trans* = 1:2) synthesized via metal-free ROMP using initiator **2a**.

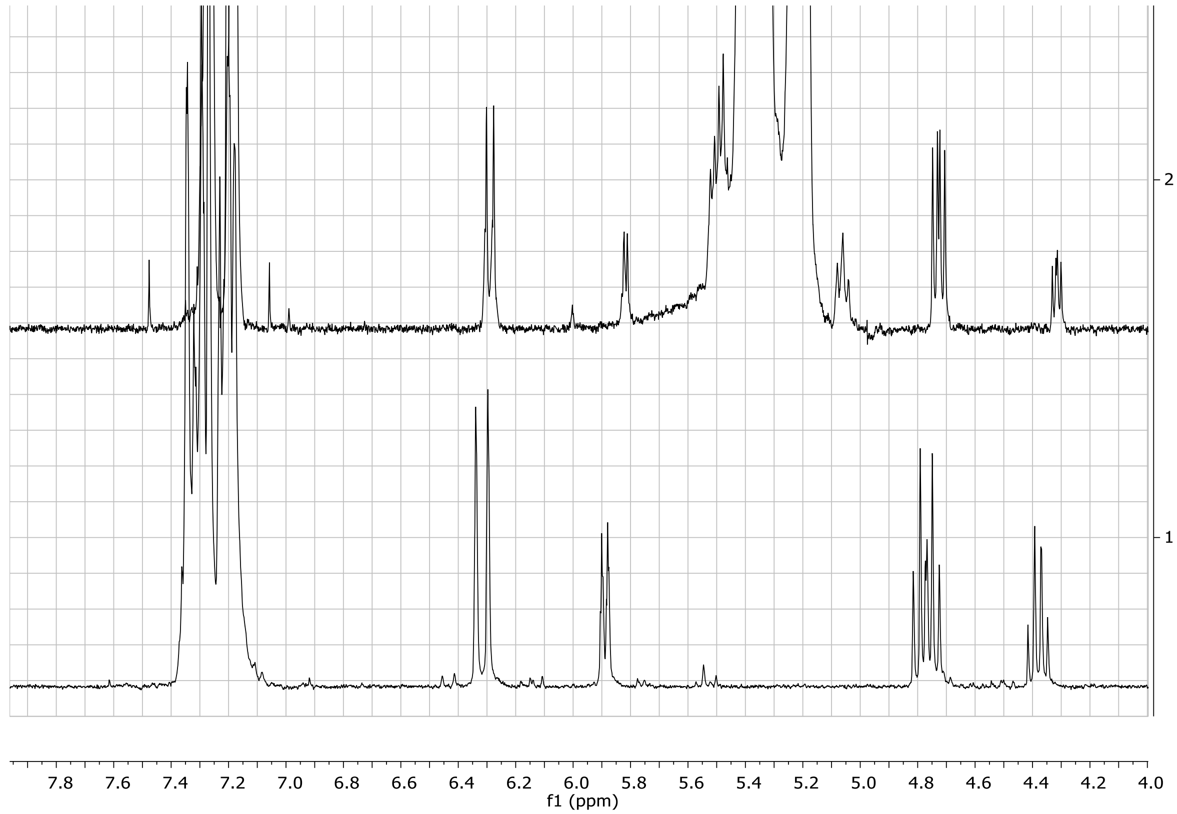


Figure S6. Zoomed in ^{1}H NMR spectra of (top) polynorbornene (M_n = 10.1 kDa; Đ = 1.5) synthesized via metal-free ROMP using initiator **2a**, and (bottom) initiator **2a**.

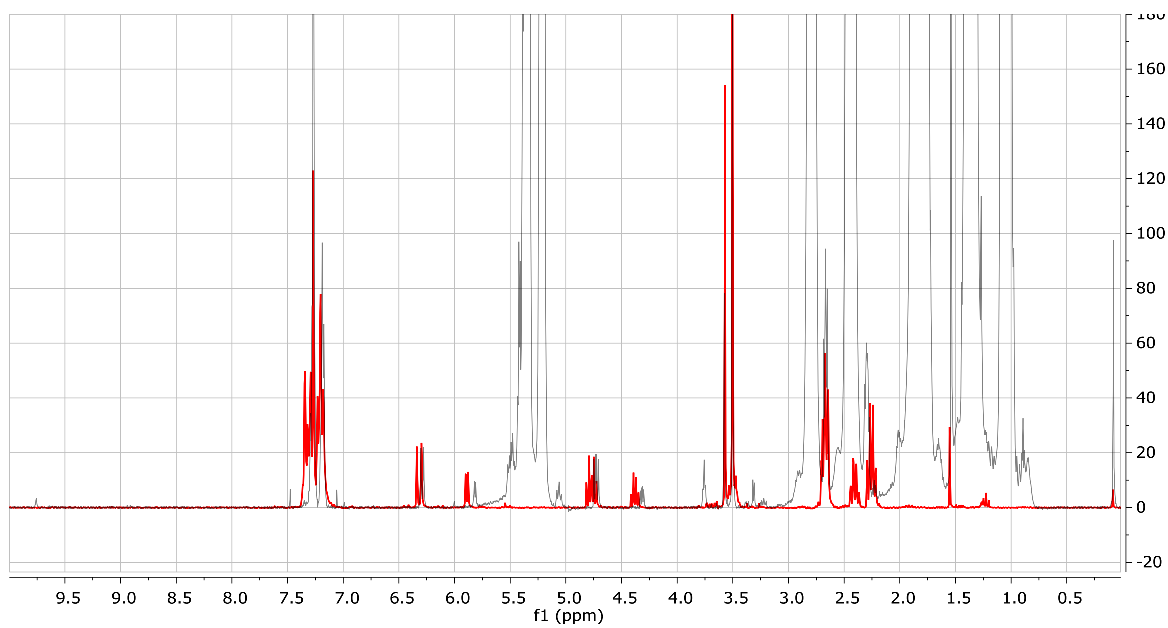


Figure S7. ^{1}H NMR spectra of (black) polynorbornene (M_n = 10.1 kDa; Đ = 1.5) synthesized via metal-free ROMP using initiator **2a**, and (red) initiator **2a**.

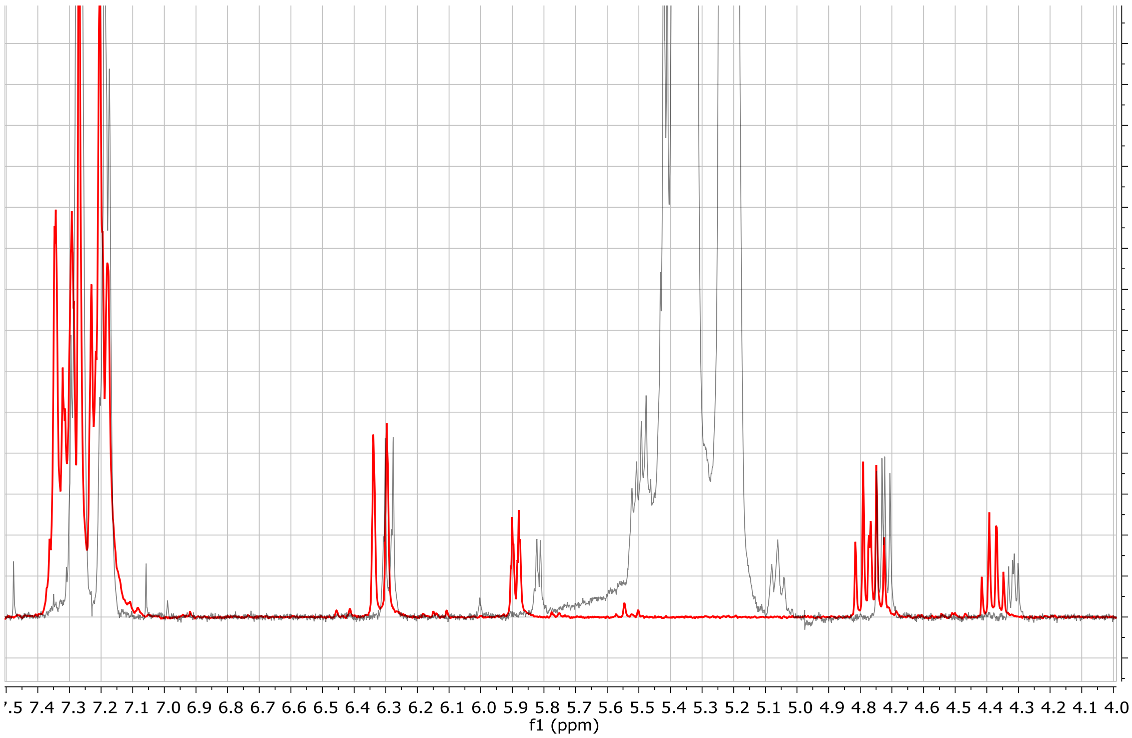


Figure S8. Zoomed in [1]H NMR spectra of (black) polynorbornene (M_n = 10.1 kDa; Đ = 1.5) synthesized via metal-free ROMP using initiator **2a**, and (red) initiator **2a**.

Representative GPC traces:

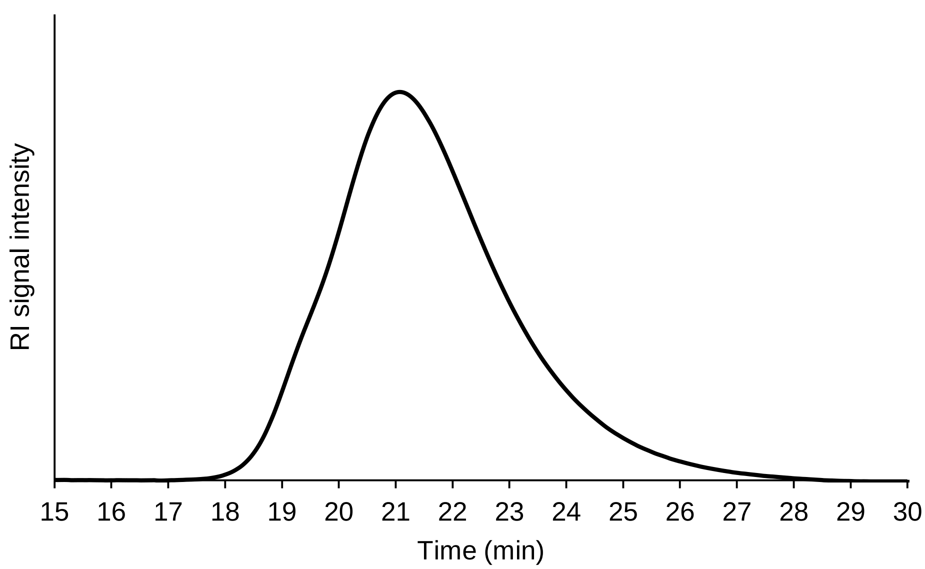


Figure S9. GPC trace of polymer corresponding to Table 1, entry 1 of the main text.

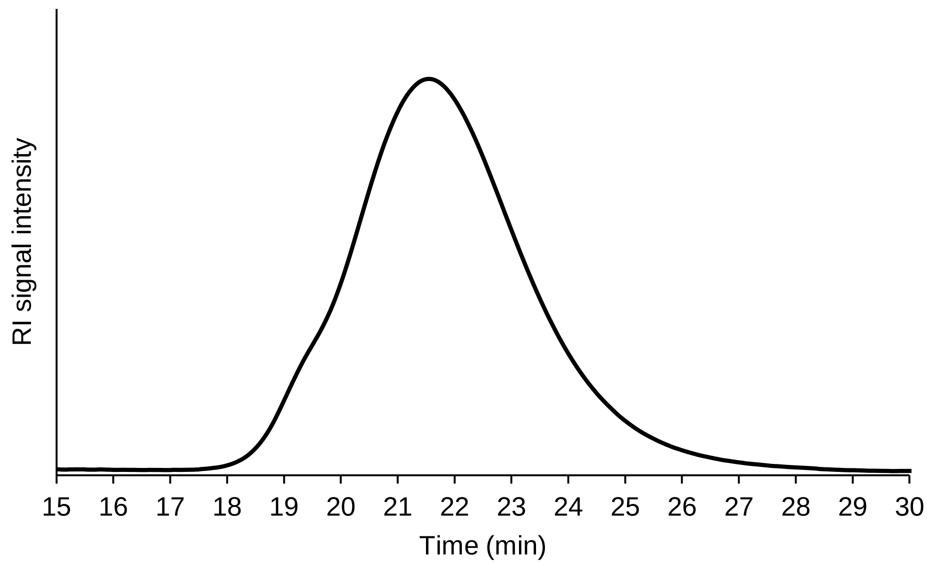


Figure S10. GPC trace of polymer corresponding to Table 1, entry 2 of the main text.

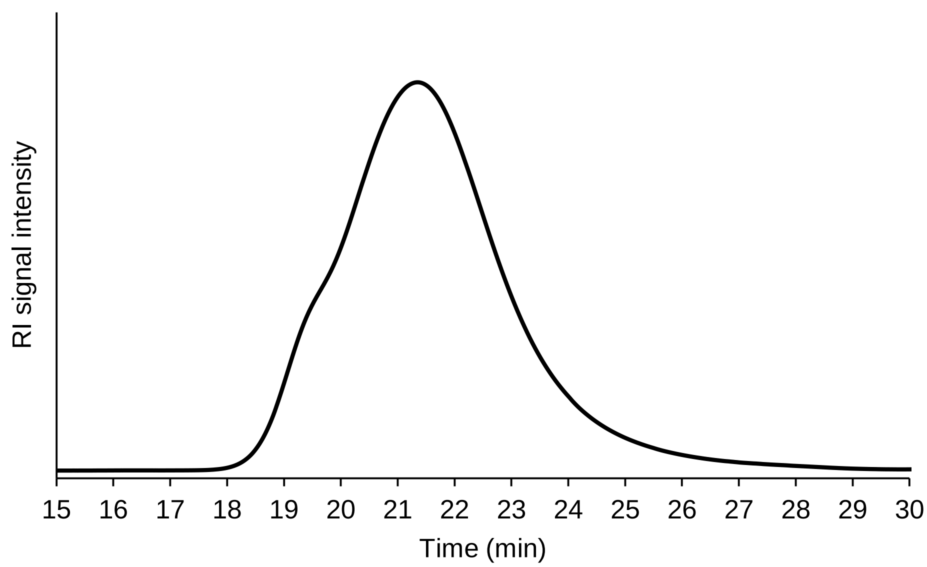


Figure S11. GPC trace of polymer corresponding to Table 1, entry 3 of the main text.

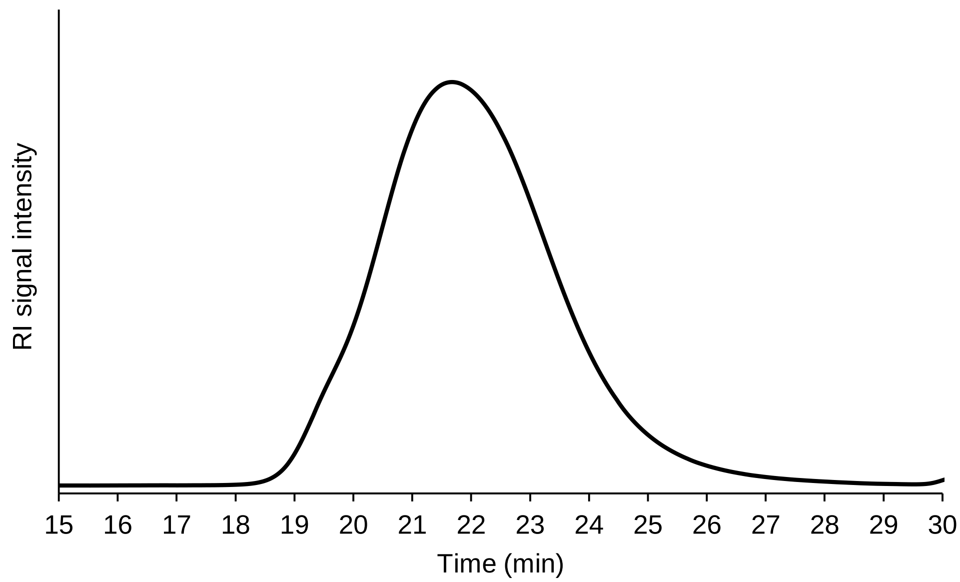


Figure S12. GPC trace of polymer corresponding to Table 1, entry 4 of the main text.

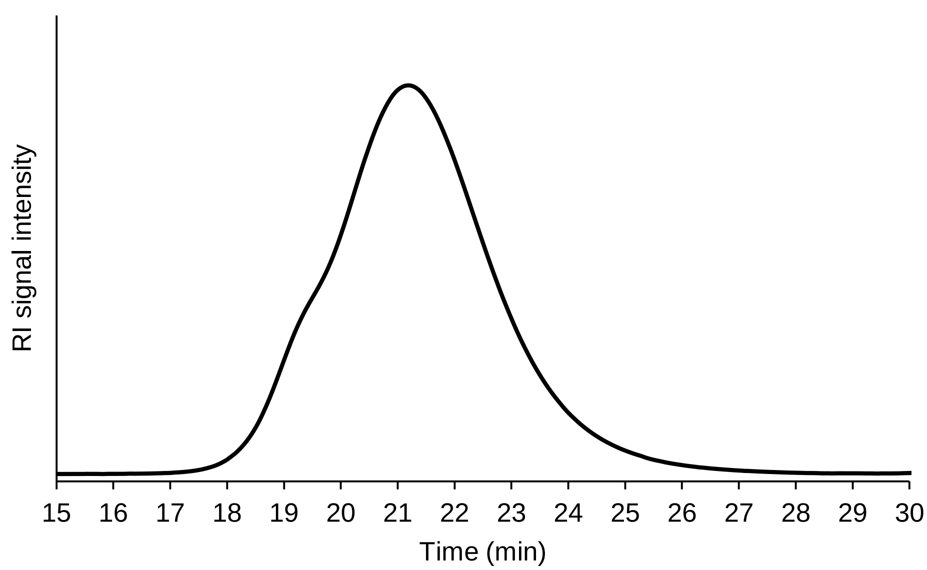


Figure S13. GPC trace of polymer corresponding to Table 1, entry 5 of the main text.

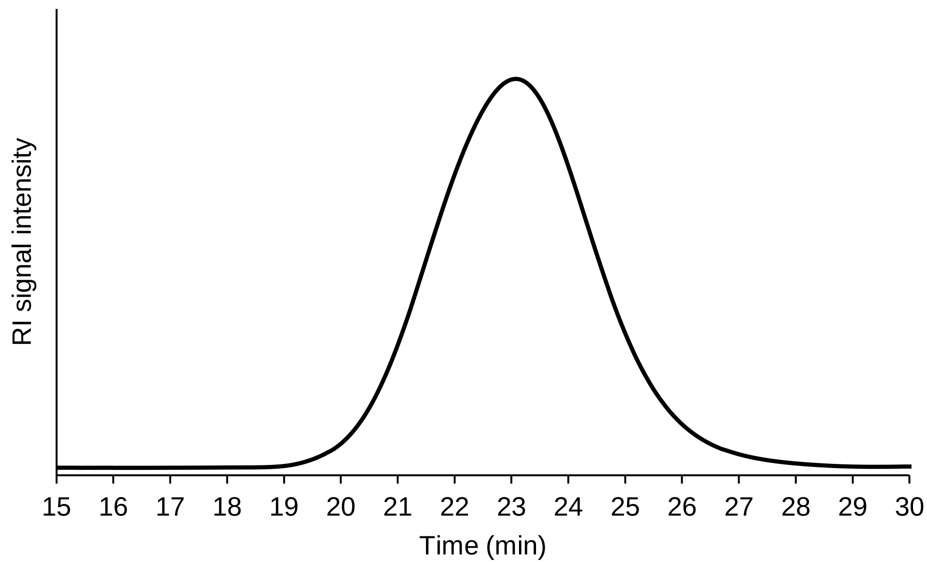


Figure S14. GPC trace of polymer corresponding to Table 1, entry 6 of the main text.

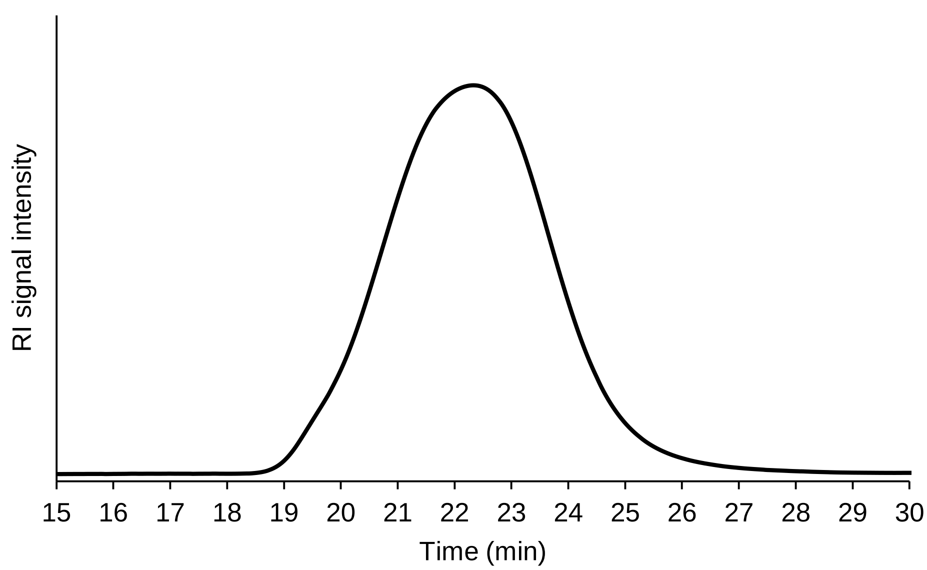


Figure S15. GPC trace of polymer corresponding to Table 1, entry 7 of the main text.

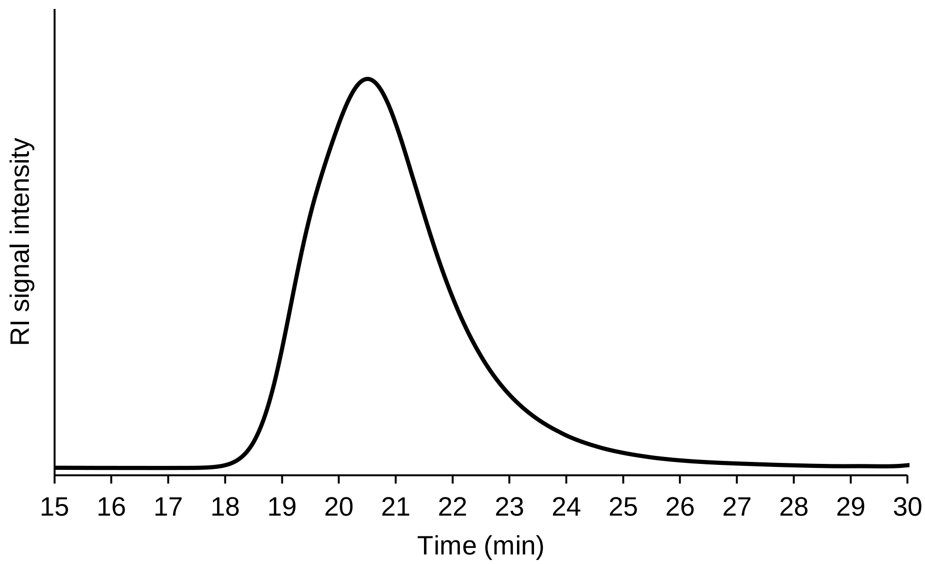


Figure S16. GPC trace of polymer corresponding to Table 1, entry 8 of the main text.

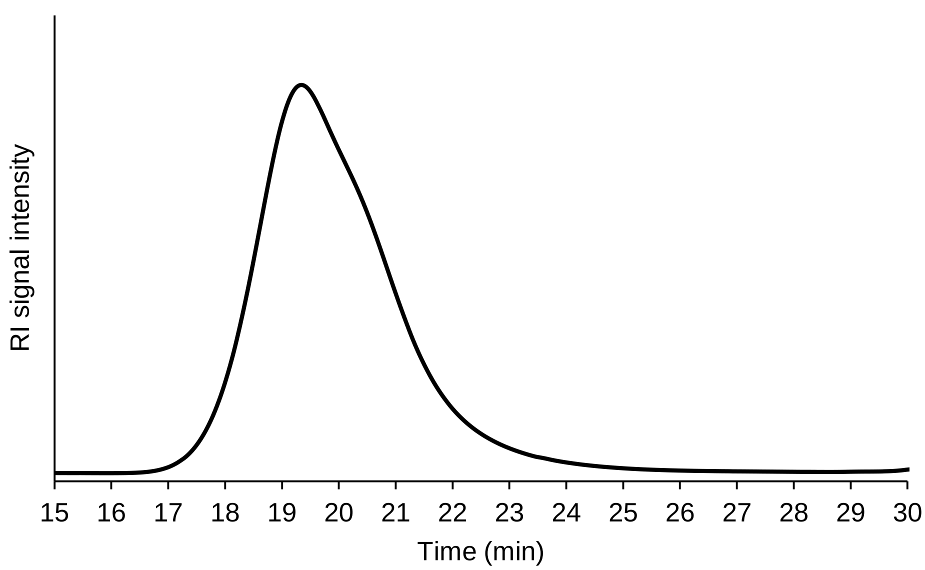


Figure S17. GPC trace of polymer corresponding to Table 1, entry 9 of the main text.

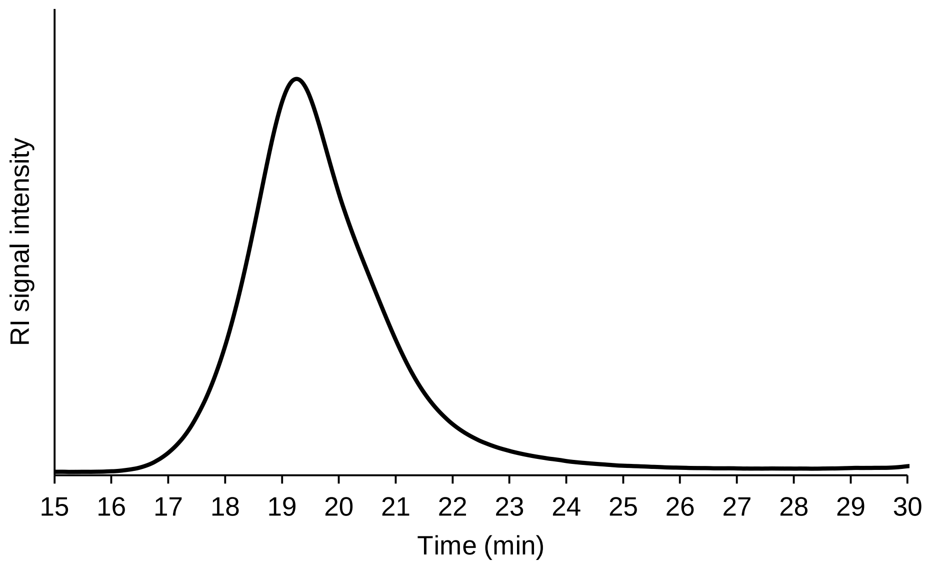


Figure S18. GPC trace of polymer corresponding to Table 1, entry 10 of the main text.

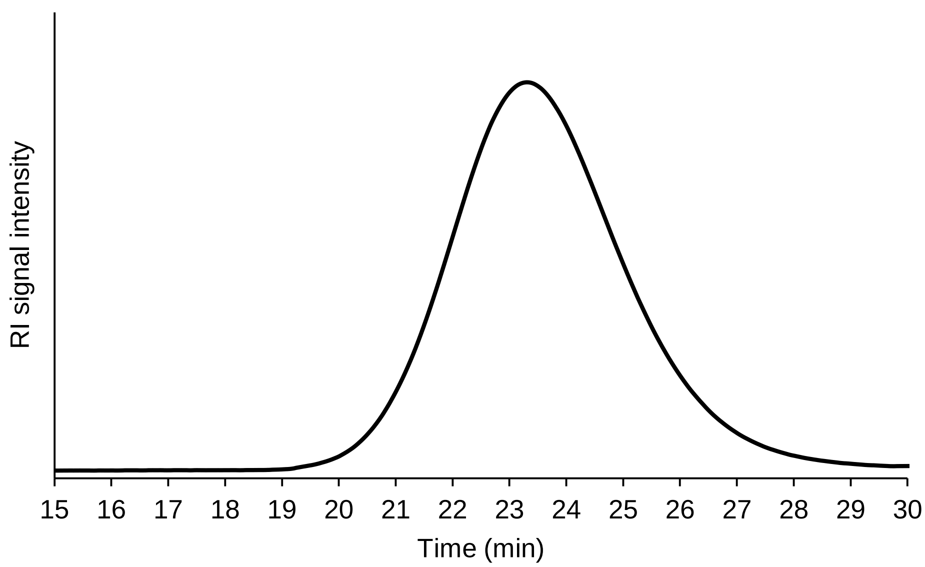


Figure S19. GPC trace of polymer corresponding to Table 1, entry 11 of the main text.

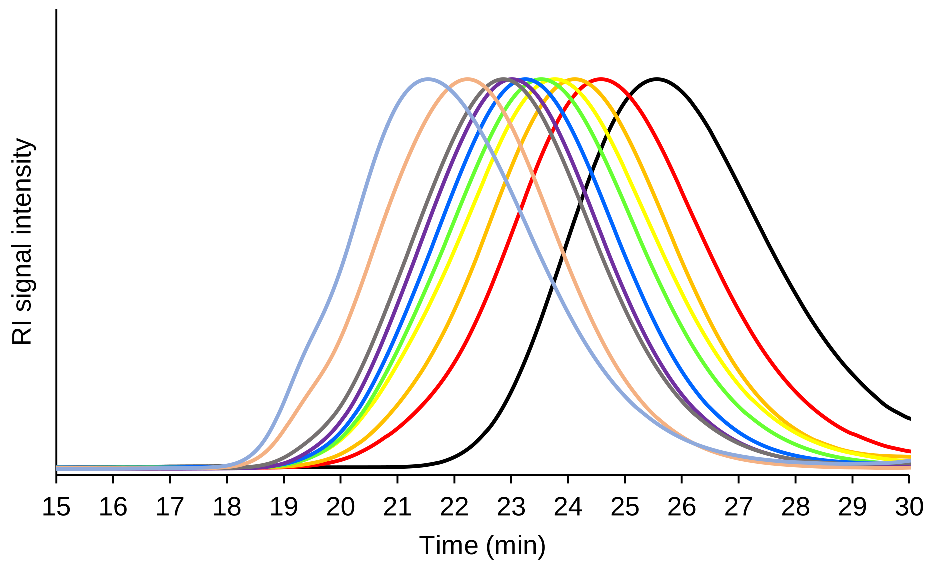


Figure S20. Each GPC trace corresponds to a data point in Figure 3, top, from the main text. From right (longest retention time) to left (shortest retention time), the sequence of GPC traces corresponds to increased % conversion of monomer as shown in Figure 3, top.

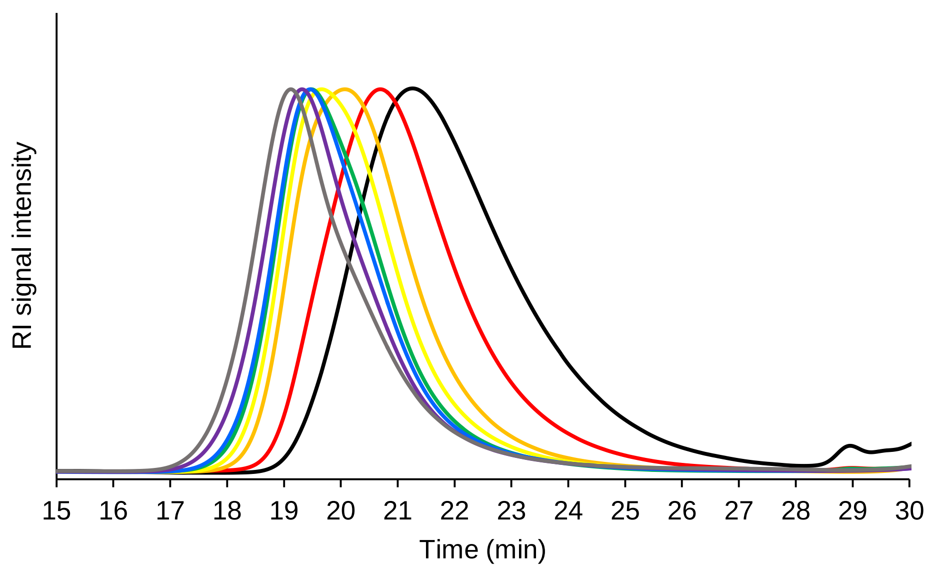


Figure S21. Each GPC trace corresponds to a data point in Figure 3, bottom, from the main text. From right (longest retention time) to left (shortest retention time), the sequence of GPC traces corresponds to increased % conversion of monomer as shown in Figure 3, bottom.

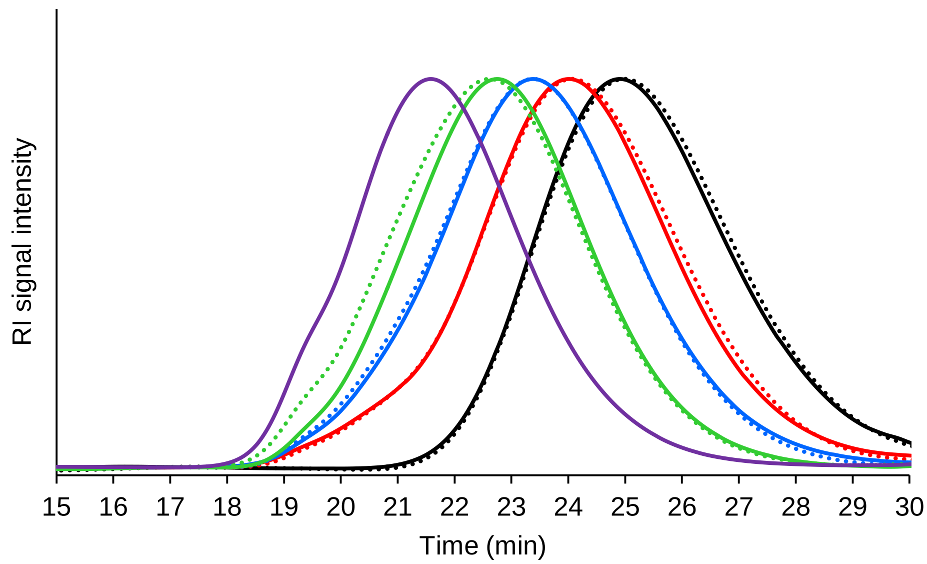


Figure S22. Each GPC trace corresponds to a data point in Figure 4 from the main text. Solid lines indicate GPC traces after a period of blue LED light exposure. The dotted lines indicate GPC traces after the period in the dark immediately following (colors are coordinated). From right (longest retention time) to left (shortest retention time), the sequence of GPC traces corresponds to increased % conversion of monomer as shown in Figure 4.

UV-Visible Spectroscopy Data:

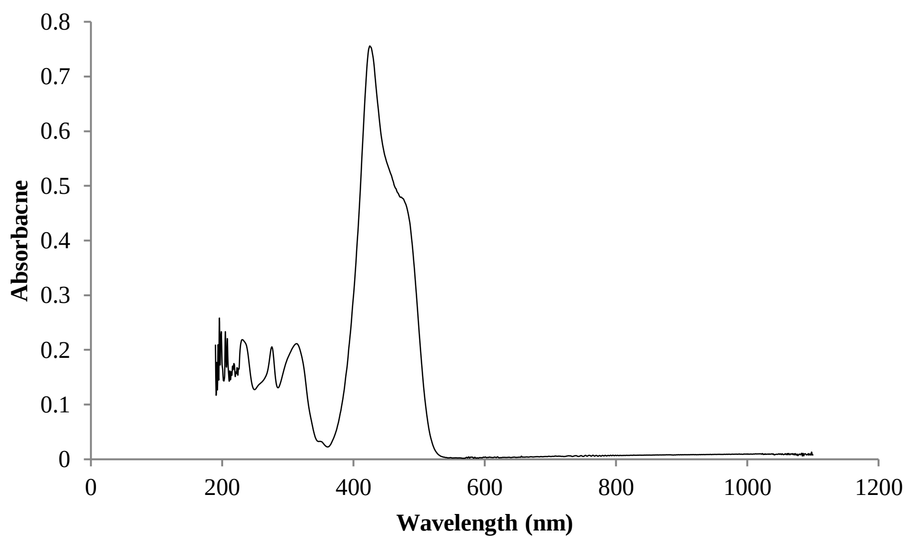


Figure S23. UV-visible spectrum of a $1.4*10^{-4}$ M solution of pyrylium **3a**. Measurements were taken in dichloromethane using a quartz cuvette with a 1 cm pathlength. The measured extinction coefficient of **3a** was 5400 M^{-1} cm^{-1}.

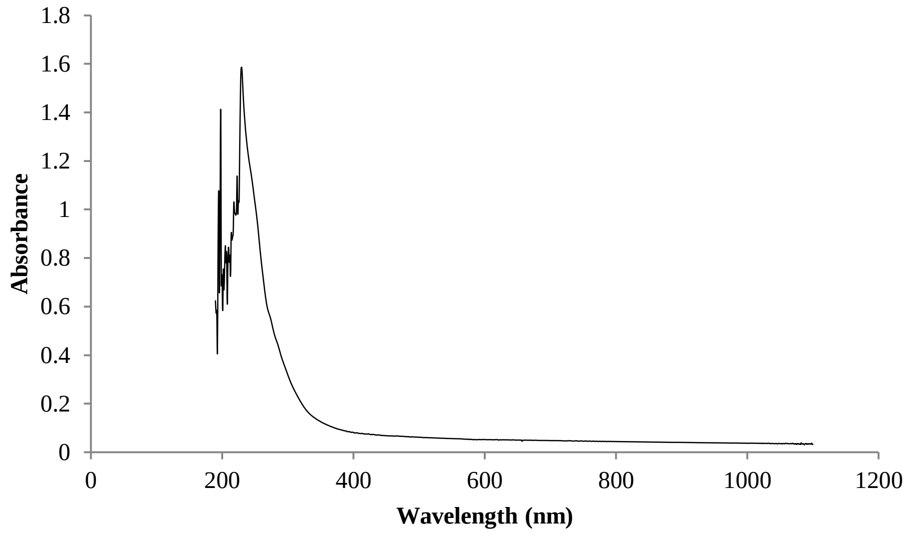


Figure S24. UV-visible spectrum of polynorbornene synthesized via metal-free ROMP using initiator **2b**. Measurements were taken in dichloromethane using a quartz cuvette with a 1 cm pathlength.

1) Lauer, M. G.; Henderson, W. H.; Awad, A.; Stambuli, J. P. *Org. Lett.* **2012**, *14*, 6000–6003.
2) Martiny, M.; Steckhan, E.; Esch, T. *Chem. Ber.* **1993**, *126*, 1671–1682.
3) VanAllan, J. A.; Reynolds, G. A. *J. Org. Chem.* **1968**, *33*, 1102–1105.
4) Miura, T.; Kim, S.; Kitano, Y.; Tada, M.; Chiba, K. *Angew. Chem. Int. Ed.* **2006**, *45*, 1461–1463.
5) Ye, J.; Zhang, X.; Deng, D.; Ning, G.; Liu, T.; Zhuang, M.; Yang, L.; Gong, W.; Lin, Y. *RSC Adv.* **2013**, *3*, 8232–8235.
6) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877–910.