Supporting Information

Chain Transfer Agents for the Catalytic Ring Opening Metathesis Polymerization of Norbornenes

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Materials and Instruments

Materials
(2E, 4E)-5-phenylpenta-2, 4-dienoic acid (CTA15) was purchased from Fluorochem. (2E,4E)-5-(benzo[d][1,3]dioxol-5-yl)penta-2,4-dienoic acid (CTA16), Piperine (CTA22), (1E,3E,5E)-1,6-diphenylhexa-1,3,5-triene (CTA26) and Norbornene (M2) were purchased from Sigma-Aldrich. Methoxy poly (ethylene glycol) was purchased from TCI. All other reagents were purchased from either Sigma-Aldrich or Acros organics. All of them were used without further purification. Deuterated solvents (CD$_2$Cl$_2$, CDCl$_3$, and DMSO-D$_6$) were purchased from Cambridge Isotope Laboratories, Inc. Grubbs 3rd generation catalyst (G3) was prepared as reported previously.  

Instruments
All $^1$H NMR, $^{13}$C NMR, and DOSY NMR spectra were recorded on a Bruker Avance DPX (400 MHz and 300 MHz) FT NMR spectrometer. Chemical shifts for $^1$H and $^{13}$C were given in ppm relative to the residual solvent peak (CDCl$_3$: 7.27 for $^1$H; CDCl$_3$: 77.16 for $^{13}$C and CD$_2$Cl$_2$: 5.32 for $^1$H; CD$_2$Cl$_2$: 53.84 for $^{13}$C). HR MALDI FT-ICR mass spectra were measured on a Bruker FTMS 4.7T BioAPEX II in positive mode using trans-2-[3-(tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix and sodium trifluoroacetate (NaTFA) or silver trifluoroacetate (AgTFA) as the counter ion source. HR-MS (ESI+) mass spectra were measured on a Bruker FTMS 4.7T BioAPEX II and Thermo Scientific LTQ Orbitrap XL equipped with a static nanospray ion source. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) with either chloroform or DMF as eluent with a flow rate of 1 mL/min at 40°C and 60°C, respectively. The chloroform GPC system was calibrated with polystyrene standards, and the DMF GPC system was calibrated with poly (ethylene oxide) calibration standards in a range from 10$^3$ to 3×10$^6$ Da. The Chloroform GPC is an automated PSS security System (Agilent Technologies 1260 infinity II) with a set of two MZ-Gel SDplus linear columns (300 x 8 mm, 5 μm particle size). The DMF GPC is an automated Agilent 1260 Infinity II HPLC system equipped with one Agilent PolarGel M guard column (particle size = 8 μm) and two Agilent PolarGel M columns (ID = 7.5 mm, L = 300 mm, particle size = 8 μm). Signals were recorded by an interferometric refractometer (Agilent 1260 series). Samples were run using DMF + 0.05M LiBr as the eluent. All polymer samples were filtered through a PTFE syringe membrane filter (0.45 μm pore size, VWR) before GPC measurements. Electron impact ionization mass spectra (EI-MS) were run on a gas chromatography –mass spectrometry (GC-MS) instrument of Agilent 8890 series GC system and Agilent5977B GC/MSD.
Synthesis of Chain Transfer Agents (CTAs):

CTA1 (methyl (E)-2-(4-(buta-1,3-dien-1-yl)-2-methoxyphenoxy)acetate)

4-Acetoxy-3-methoxycinnamaldehyde, predominantly trans (22.72 mmol, 5 g), was dissolved in 50 mL methanol in a round bottom flask. 50 mL water and 50 mL saturated sodium bicarbonate solution was added to it. Then, 15 mL 1 (M) aqueous sodium hydroxide was added in one portion, and the mixture was stirred overnight at room temperature. Complete consumption of starting material was observed. Next, the solution was concentrated and acidified under an ice bath with a concentrated hydrochloric acid solution until pH reached to 3. The aqueous mixture was extracted three times with ethyl acetate. The combined organics were mixed and dried over magnesium sulfate and further concentrated under reduced pressure to give a yellow solid (4 g, 22.46 mmol, 99% yield) as I1. The crude product was used for the next step without any further purification.

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) ppm: 3.96 (s, 3 H), 5.99 (s, 1 H), 6.60 (dd, \(J=15.83, 7.76\) Hz, 1 H), 6.97 (d, \(J=8.19\) Hz, 1 H), 7.03 - 7.19 (m, 2 H), 7.41 (d, \(J=15.89\) Hz, 1 H), 9.66 (d, \(J=7.70\) Hz, 1 H)

\(^13\)C NMR (CDCl\(_3\), 101 MHz) \(\delta\) ppm: 56.0, 76.6, 77.2, 77.3, 109.4, 114.9, 124.0, 126.4, 126.6, 146.9, 148.9, 153.0, 193.5.

In an oven-dried round bottom flask, I1 (1 equiv., 22.47 mmol, 4 g) and potassium carbonate (1.5 equiv., 33.72 mmol, 4.66 g) were dissolved in 50 mL dimethylformamide (DMF). Next, methyl bromoacetate (1.2 equiv., 27 mmol, 2.56 mL) was added to the DMF mixture dropwise at room temperature and stirred for 30 mins. Then, the mixture was concentrated in the rotary evaporator, and the concentrated solution was extracted three times with ethyl acetate and brine. The organics were combined, dried over magnesium sulfate, and concentrated under reduced pressure to give I2 as a white solid (5.22 g, 20.85 mmol, 93% yield). The crude product was pure enough to use directly in the next step.
$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 3.79 (s, 4 H), 3.91 (s, 3 H), 4.74 (s, 2 H), 6.60 (dd, $J$=15.89, 7.70 Hz, 1 H), 6.75 - 6.89 (m, 1 H), 7.04 - 7.17 (m, 2 H), 7.39 (d, $J$=15.89 Hz, 1 H), 9.65 (d, $J$=7.70 Hz, 1 H) $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 52.2, 55.9, 65.8, 76.6, 77.3, 110.7, 113.3, 122.7, 127.2, 128.3, 149.7, 149.8, 152.3, 168.7, 193.3.

Methyltriphenylphosphonium bromide (1.2 equiv., 10.55 mmol, 3.77 g) was dissolved in 40 mL THF and cooled to 0°C. Solid potassium tert-butoxide (1.2 equiv., 10.55 mmol, 1.18 g) was added in one shot, and the THF solution immediately became yellow. The solution was stirred at 0°C for 10 mins. I$_2$ (1 equiv., 8.79 mmol, 2.2 g) was dissolved in 5 mL THF and added slowly to the precooled mixture. Then, the resulting solution was stirred at room temperature for 15 mins. TLC showed complete consumption of starting material, but two close spots were observed. THF was evaporated under reduced pressure, and crude was dissolved in ethyl acetate and worked up against brine two times. The organic part was dried over magnesium sulfate, concentrated under reduced pressure, and further purified by column chromatography (5%-10% ethyl acetate-hexane) to obtain CTA1 as a yellow solid (1.1 g, 4.4 mmol, 50.45% yield) and I$_3$ as a bright yellow solid (400 mg, 1.7 mmol, 19.4% yield).

CTA1- $^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 3.80 (s, 3 H), 3.92 (s, 3 H), 4.71 (s, 2 H), 5.09 - 5.19 (m, 1 H), 5.27 - 5.39 (m, 1 H), 6.41 - 6.57 (m, 2 H), 6.60 - 6.71 (m, 1 H), 6.78 (d, $J$=8.31 Hz, 1 H), 6.92 (dd, $J$=8.31, 2.08 Hz, 1 H), 6.98 (d, $J$=2.08 Hz, 1 H) $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 52.2, 55.8, 66.4, 76.6, 77.2, 77.3, 109.5, 114.1, 117.0, 119.5, 128.5, 131.9, 132.3, 137.1, 147.0, 149.6, 169.3.

I$_3$- $^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 3.92 (s, 3 H), 4.59 (s, 2 H), 5.10 - 5.19 (m, 1 H), 5.26 - 5.38 (m, 1 H), 6.42 - 6.58 (m, 2 H), 6.65 (s, 1 H), 6.75 (d, $J$=8.31 Hz, 1 H), 6.86 - 7.00 (m, 2 H) $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 28.0, 55.9, 66.5, 76.6, 77.2, 77.3, 82.2, 109.5, 113.5, 116.8, 119.5, 128.3, 131.4, 132.4, 137.1, 147.2, 149.5, 167.8.
**CTA2 ((E)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene)**

Methyltriphenylphosphonium bromide (1.2 equiv., 14.8 mmol, 5.29 g) was dissolved in 30 mL THF and cooled to 0°C. Solid potassium tert-butoxide (1.2 equiv., 14.8 mmol, 1.66 g) was added in one shot, and the THF solution immediately became yellow. The solution was stirred at 0°C for 10 mins. Trans-p-methoxycinnamaldehyde (1 equiv., 12.33 mmol, 2 g) was dissolved in 10 mL THF and added slowly to the precooled mixture. Then, the resulting solution was stirred at room temperature for 15 mins. THF was evaporated under reduced pressure, and crude was dissolved in ethyl acetate and worked up against brine two times. The organic part was dried over magnesium sulfate, concentrated under reduced pressure, and further purified by column chromatography (5% ethyl acetate-hexane) to obtain **CTA2** as an off-white solid (1.7 g, 10.62 mmol, 86% yield).

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 3.83 (s, 3 H), 5.09 - 5.22 (m, 1 H), 5.32 (dt, J=16.75, 1.16 Hz, 1 H), 6.44 - 6.62 (m, 2 H), 6.62 - 6.78 (m, 1 H), 6.83 - 7.00 (m, 2 H), 7.30 - 7.49 (m, 2 H)

$^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 55.2, 76.6, 76.9, 77.3, 114.0, 116.3, 127.6, 129.8, 132.3, 137.3, 159.2.

**CTA3 ((E)-1-bromo-4-(buta-1,3-dien-1-yl)benzene)**

Methyltriphenylphosphonium bromide (1.2 equiv., 2.8 mmol, 1 g) was dissolved in 10mL THF and cooled to 0°C. Solid potassium tert-butoxide (1.2 equiv., 2.61 mmol, 319 mg) was added in one shot, and the THF solution immediately became yellow. The solution was stirred at 0°C for 10 mins. 3-(4-Bromophenyl) acrylaldehyde (1 equiv., 2.37 mmol, 500 mg) was dissolved in 2 mL THF and added slowly to the precooled mixture. Then, the resulting solution was stirred at room temperature for 15 mins. THF was evaporated under reduced pressure, and crude was dissolved in ethyl acetate and worked up against brine two times. The organic part was dried over magnesium sulfate, concentrated under reduced pressure, and further purified by column chromatography (2% ethyl acetate-hexane) to obtain **CTA3** as a colorless liquid (420 mg, 2 mmol, 85.2% yield).

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 5.12 - 5.27 (m, 1 H), 5.35 (ddt, 1 H), 6.39 - 6.58 (m, 2 H), 6.68 - 6.84 (m, 1 H), 7.19 - 7.30 (m, 2 H), 7.37 - 7.49 (m, 2 H)

$^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 76.6, 77.3, 118.3, 121.3, 127.8, 130.2, 131.5, 131.7, 136.0, 136.8.
CTA4 ((E)-2-(buta-1,3-dien-1-yl)furan)

Methyltriphenylphosphonium bromide (1.2 equiv., 4.93 mmol, 1.76 g) was dissolved in 10 mL THF and cooled to 0°C. Solid potassium tert-butoxide (1.2 equiv., 4.93 mmol, 554 mg) was added in one shot, and the THF solution immediately became yellow. The solution was stirred at 0°C for 10 mins. 3-(2-Furyl) acrolein (1 equiv., 4.1 mmol, 500 mg) was dissolved in 5 mL THF and added slowly to the precooled mixture. Then, the resulting solution was stirred at room temperature for 15 mins. THF was evaporated under reduced pressure, and crude was dissolved in ethyl acetate and worked up against brine two times. The organic part was dried over magnesium sulfate, concentrated under reduced pressure, and further purified by column chromatography (5% ethyl acetate-hexane) to obtain CTA4 as a colorless liquid (450 mg, 3.75 mmol, 91.6% yield).

1H NMR (300 MHz, CDCl3) δ ppm: 5.06 - 5.27 (m, 1 H), 5.27 - 5.45 (m, 1 H), 6.19 - 6.44 (m, 4 H), 6.50 (d, J=10.09 Hz, 1 H), 6.61 - 6.84 (m, 1 H), 7.37 (d, J=2.29 Hz, 1 H) 13C NMR (75 MHz, CDCl3) δ ppm: 76.5, 77.4, 108.5, 111.5, 117.7, 120.4, 128.1, 136.6, 142.1, 152.9.

CTA5 ((E)-9-(buta-1,3-dien-1-yl)anthracene)

Methyltriphenylphosphonium bromide (1.2 equiv., 5.16 mmol, 1.85 g) was dissolved in 20 mL THF and cooled to 0°C. Solid potassium tert-butoxide (1.5 equiv., 6.45 mmol, 725 mg) was added in one shot, and the THF solution immediately became yellow. The solution was stirred at 0°C for 10 mins. 3-(9-Anthryl) acrolein (1 equiv., 4.3 mmol, 1 g) was dissolved in 15mL THF and added slowly to the precooled mixture. Then, the resulting solution was stirred at room temperature for 15 mins. THF was evaporated under reduced pressure, and crude was dissolved in ethyl acetate and worked up against brine two times. The organic part was dried over magnesium sulfate, concentrated under reduced pressure, and further purified by column chromatography (only hexane) to obtain CTA5 as a bright yellow solid (800 mg, 3.48 mmol, 80.68% yield).

1H NMR (CDCl3, 400 MHz) δ ppm: 5.28 - 5.54 (m, 2 H), 6.69 (dd, J=15.83, 10.58 Hz, 1 H), 6.77 - 7.01 (m, 1 H), 7.36 - 7.64 (m, 5 H), 7.92 - 8.14 (m, 2 H), 8.25 - 8.51 (m, 3 H) 13C NMR (CDCl3,
In an oven-dried round bottom flask, 4-Hydroxybenzaldehyde (1 equiv., 57.32 mmol, 7 g) and potassium carbonate (1.6 equiv., 94 mmol, 13 g) were mixed, and 44 mL acetone was added to make a slurry. To the suspension, methyl bromoacetate (1.2 equiv., 68.82 mmol, 6.5 mL) was added dropwise, and the resulting solution was stirred at room temperature for 1 h. All the starting materials were consumed. The mixture was filtered, and the filtrate was concentrated and then worked up with ethyl acetate and brine. The organic part was dried over magnesium sulfate, concentrated under reduced pressure, and dried under a high vacuum to give 14 as a colorless viscous liquid (10.9 g, 56.18 mmol, 98%).

P.S. This compound causes eye irritation.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm: 3.75 (s, 4 H), 4.68 (s, 2 H), 6.95 (m, J=8.80 Hz, 2 H), 7.78 (m, J=8.80 Hz, 2 H), 9.83 (s, 1 H) $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ ppm: 25.3, 52.1, 64.8, 76.6, 77.3, 114.6, 130.5, 131.7, 162.3, 168.3, 190.4.
Allyltriphenylphosphonium bromide (1.2 equiv., 37.70 mmol, 14.45 g) was dissolved in 80 mL THF in a round bottom flask under an argon atmosphere. The solution was cooled to 0°C. Solid potassium tert-butoxide (1.2 equiv., 38.31 mmol, 4.3 g) was added quickly, and a yellow solution was observed. The mixture was stirred at that temperature for 10 mins. I4 (1 equiv., 31.41 mmol, 6.1 g) was dissolved in 15 mL THF and added to the precooled mixture dropwise; then, the flask was warmed to room temperature and stirred for 30 mins. All the starting materials were gone, and two very close spots were observed, presumably a mixture of cis and trans products. THF was evaporated under reduced pressure, added brine to the flask, and extracted three times with ethyl acetate. The combined organics were collected, dried over magnesium sulfate, and further purified by column chromatography (10%-20% ethyl acetate-hexane) to obtain a colorless viscous liquid as CTA6 (5.5 g, 25.2 mmol, 65.8%).

1H NMR (CDCl3, 400 MHz) δ ppm: 3.79 - 3.86 (m, 3 H), 4.62 - 4.69 (m, 2 H), 5.11 - 5.41 (m, 2 H), 6.21 (tt, J=11.31, 0.98 Hz, 1 H), 6.39 (d, J=11.37 Hz, 1 H), 6.44 - 6.56 (m, 1 H), 6.80 - 6.96 (m, 3 H), 7.24 - 7.38 (m, 3 H) 13C NMR (CDCl3, 101 MHz) δ ppm: 52.2, 65.3, 76.6, 77.2, 77.3, 114.3, 114.8, 116.8, 119.2, 127.7, 128.2, 129.6, 129.8, 130.3, 131.0, 131.1, 132.0, 133.1, 137.2, 156.8, 157.3, 169.3.

CTA7 (2-(4-(buta-1,3-dien-1-yl)phenoxy)ethyl 4-((tert-butoxycarbonyl)amino)benzoate)

To a mixture of 4-aminobenzoic acid (1 equiv., 36.45 mmol, 5.0 g) in dioxane (70 mL) and water (35 mL) were added trimethylamine (2 equiv., 73 mmol, 10.26 mL) followed by di-tert-
butyl dicarbonate (2 equiv., 73 mmol, 3.2 g). The reaction mixture was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation, and 3 (N) aqueous hydrochloric acid (30 mL) was added dropwise to the residue. A precipitate was obtained, collected, washed with water, and dried to provide 15 (8.16 g, 34.4 mmol, 94.3%) as a white solid.

$^1$H NMR (300 MHz, CDCl$_3$) δ ppm: 1.50 - 1.58 (m, 10 H), 6.68 - 6.87 (m, 1 H), 7.43 - 7.54 (m, 2 H), 7.98 - 8.11 (m, 2 H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ ppm: 28.2, 76.6, 77.2, 77.4, 81.4, 117.4, 123.3, 131.6, 143.4, 152.1, 170.4.

**CTA6** (1 equiv., 18.05 mmol, 3.940 g) was dissolved in 40 mL DCM and cooled to -78°C. To it, DIBAL-H (1M in THF) (2.2 equiv., 39.72 mmol, 39.72 mL) was added very slowly over 1 h. Then, the reaction mixture was brought to room temperature and kept stirring for 2 h. No starting materials were left afterward. The reaction was again cooled to -30°C and quenched by adding 20 mL of cold water. The resulting suspension was passed through celite, and the filtrate was extracted with ethyl acetate. The organics were combined, dried over magnesium sulfate, and purified by column chromatography (30% ethyl acetate-hexane). A white solid was obtained after drying overnight (3 g, 15.76 mmol, 87.36%).

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 2.14 - 2.40 (m, 1 H), 3.76 - 4.06 (m, 4 H), 5.01 - 5.31 (m, 2 H), 6.01 - 6.21 (m, 1 H), 6.21 - 6.50 (m, 1 H), 6.68 - 6.93 (m, 3 H), 7.06 - 7.33 (m, 2 H) $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 61.3, 69.1, 76.6, 77.3, 114.2, 114.6, 116.5, 119.0, 127.6, 127.8, 129.4, 129.7, 130.2, 130.4, 132.1, 133.1, 137.2, 157.6, 158.2.

I5 (1 equiv., 2.1 mmol, 500 mg), I6 (1 equiv., 2.1 mmol, 401 mg), and DMAP (0.1 equiv., 0.21 mmol, 25 mg) were dissolved in 15 mL DCM and cooled to 0°C. DCC (1.1 equiv., 2.5 mmol,
520 mg) was dissolved in 5 mL DCM and added to the mixture slowly. Then, the resulting solution was stirred at room temperature overnight. Next, it was filtered, and the filtrate was worked up with ethyl acetate and brine. The organic part dried over magnesium sulfate, concentrated and purified by column chromatography (10% ethyl acetate-hexane) to give CTA7 as a pure white solid (700 mg, 1.7 mmol, 82%).

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 1.54 (s, 9 H), 4.27 - 4.39 (m, 2 H), 4.59 - 4.72 (m, 2 H), 5.18 - 5.24 (m, 1 H), 5.26 - 5.40 (m, 1 H), 6.13 - 6.27 (m, 1 H), 6.35 - 6.45 (m, 1 H), 6.45 - 6.59 (m, 1 H), 6.59 - 6.73 (m, 1 H), 6.79 - 6.98 (m, 3 H), 7.28 - 7.31 (m, 1 H), 7.31 - 7.48 (m, 3 H), 7.93 - 8.07 (m, 2 H) $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 28.2, 63.1, 66.1, 76.6, 77.2, 77.3, 81.2, 114.4, 114.8, 117.3, 119.0, 127.6, 127.9, 129.5, 129.8, 130.3, 131.0, 132.2, 133.2, 137.3, 142.8, 166.1.

CTA8 (methyl 4-(buta-1,3-dien-1-yl)benzoate)

 Allyltriphénylphosphonium bromide (1.2 equiv., 30.90 mmol, 11.84 g) was dissolved in 50 mL THF in a round bottom flask under an argon atmosphere. The solution was cooled to 0°C. Solid potassium tert-butoxide (1.2 equiv., 30.90 mmol, 3.47 g) was added quickly, and a yellow solution was observed. The mixture was stirred at that temperature for 10 mins. Aldehyde (1 equiv., 25.75 mmol, 5.0 g) was dissolved in 20 mL THF and added to the precooled mixture dropwise; then, the flask was warmed to room temperature and stirred for 30 mins. THF was evaporated under reduced pressure, added brine to the flask, and extracted three times with ethyl acetate. The combined organics were collected, dried over magnesium sulfate, and further purified by column chromatography (slowly eluting 10% ethyl acetate-hexane) to obtain a colorless viscous liquid as CTA8 (3.65 g, 16.72 mmol, 65%).

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 3.85 - 3.96 (m, 3 H), 5.20 - 5.35 (m, 1 H), 5.35 - 5.48 (m, 1 H), 6.29 - 6.41 (m, 1 H), 6.41 - 6.63 (m, 1 H), 6.77 - 6.95 (m, 1 H), 7.35 - 7.48 (m, 2 H), 7.93 - 8.07 (m, 2 H) $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 51.9, 51.9, 76.6, 77.3, 119.2, 120.9, 126.1, 128.4, 128.8, 129.1, 129.4, 129.8, 131.6, 131.9, 132.4, 132.6, 136.7, 141.9, 166.7.
CTA8 (1 equiv., 5.31 mmol, 1 g) was dissolved in 10 mL methanol. Sodium hydroxide (10 equiv., 53.13 mmol, 2.1 g) was dissolved in 8.9 mL of water to give a 6M aqueous solution. This aqueous solution was added to methanol solution dropwise, and the resulting mixture was stirred overnight, upon which no starting material was left. Then, methanol was evaporated under reduced pressure, and water was added. The resulting solution was cooled in an ice bath. A concentrated HCl solution was added very slowly until pH reached 2. At that point, a white solid was precipitated. The solution was filtered, and the residue was extracted with ethyl acetate and brine two times. The organic part was dried over magnesium sulfate concentrated under reduced pressure to give I7 as a white solid (890 mg, 5.1 mmol, 96% yield). The crude was pure enough to use in the following steps.

$^{1}$H NMR (400 MHz, DMSO-d$_{6}$) δ ppm: 5.15 - 5.40 (m, 1 H), 5.40 - 5.63 (m, 1 H), 6.28 - 6.47 (m, 1 H), 6.47 - 6.64 (m, 1 H), 6.77 - 6.96 (m, 1 H), 7.36 - 7.51 (m, 2 H), 7.59 (d, J=7.95 Hz, 1 H), 7.81 - 8.09 (m, 2 H), 12.92 (br. s., 1 H) $^{13}$C NMR (101 MHz, DMSO-d$_{6}$) δ ppm: 39.0, 39.3, 39.7, 39.9, 40.1, 40.3, 119.9, 122.0, 126.5, 128.9, 129.0, 129.1, 129.3, 129.4, 129.6, 129.7, 129.9, 131.8, 132.2, 132.3, 132.7, 133.3, 133.5, 137.2, 141.2, 141.3, 167.2.
CTA9 (2-(4-(buta-1,3-dien-1-yl)phenoxy)ethyl 2-bromo-2-methylpropanoate)

A mixture of α-Bromoisobutyryl bromide (1.2 equiv., 2.52 mmol, 0.34 mL) and I6 (1.0 equiv., 2.1 mmol, 400 mg) in 20 mL dry DCM was cooled in an ice bath. Triethylamine (2.0 equiv., 4.2 mmol, 0.6 mL) was added dropwise at that temperature. The flask was stirred at room temperature overnight. Then, the mixture was diluted with water and extracted with DCM and brine. The organic part was combined, dried over magnesium sulfate, and further purified by column chromatography (5% ethyl acetate-hexane) to give CTA9 as a colorless liquid (630 mg, 1.86 mmol, 88.3% yield).

\(^1\)H NMR (CDCl\(_3\), 400 MHz) δ ppm: 1.91 - 1.99 (m, 6 H), 4.20 - 4.29 (m, 2 H), 4.48 - 4.59 (m, 2 H), 5.11 - 5.41 (m, 2 H), 6.21 (tt, J=11.31, 0.98 Hz, 1 H), 6.40 (d, J=11.49 Hz, 1 H), 6.44 - 6.55 (m, 1 H), 6.80 - 6.96 (m, 3 H), 7.22 - 7.40 (m, 2 H) \(^1\)C NMR (CDCl\(_3\), 101 MHz) δ ppm: 30.7, 55.4, 64.1, 65.6, 76.6, 77.2, 77.3, 114.5, 114.9, 116.6, 119.1, 127.6, 127.9, 129.6, 129.7, 130.3, 130.5, 130.6, 132.1, 133.2, 137.2, 157.5, 158.1, 171.6.

CTA10 (S-benzyl 4-(buta-1,3-dien-1-yl)benzothioate)

In an oven-dried round bottom flask, I7 (1.0 equiv., 1.43 mmol, 250 mg), benzyl mercaptan (1.1 equiv., 1.58 mmol, 196 mg), and DMAP (0.1 equiv., 0.14 mmol, 18 mg) were taken and dissolved in 6 mL dry DCM. The resulting solution was cooled to 0°C. Then, DCC (1.2 equiv., 1.72 mmol, 356 mg) was dissolved in 4 mL DCM and added to the mixture dropwise. Then the flask was warmed to room temperature and stirred overnight. Next, the solution was filtered, and the filtrate was concentrated under reduced pressure and further purified by column
chromatography (20% ethyl acetate-hexane) to give CTA10 as a colorless liquid (315 mg, 1.12 mmol, 78.3% yield). The product was stored at -20°C.

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 4.27 - 4.40 (m, 2 H), 5.24 - 5.37 (m, 1 H), 5.37 - 5.53 (m, 1 H), 6.28 - 6.42 (m, 1 H), 6.42 - 6.52 (m, 1 H), 6.76 - 6.96 (m, 1 H), 7.22 - 7.51 (m, 8 H), 7.88 - 8.03 (m, 2 H) $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 33.3, 76.6, 77.2, 77.3, 119.6, 121.2, 126.4, 127.3, 127.7, 128.6, 128.9, 129.0, 129.1, 131.4, 132.3, 132.6, 132.7, 135.1, 135.5, 136.7, 137.4, 142.2, 142.6, 190.6.

**CTA11 (1-(2-(4-((E)-buta-1,3-dien-1-yl)-2-methoxyphenoxy)ethyl) 10-(2-(4-((E)-buta-1,3-dien-1-yl)-3-methoxyphenoxy)ethyl) decanedioate)**

In an oven-dried round bottom flask, Ethyl 4-hydroxy-3-methoxycinnamate (1 equiv., 45.0 mmol, 10 g) and potassium carbonate (1.6 equiv., 72 mmol, 10 g) were mixed, and 50 mL acetone was added to it. To this suspension, methyl bromoacetate (1.2 equiv., 54 mmol, 5.12 mL) was added dropwise, and the resulting solution was stirred at room temperature overnight. All the starting materials were consumed. The mixture was filtered, and the filtrate was concentrated and then worked up with ethyl acetate and brine. The organic part was dried over magnesium sulfate, concentrated under reduced pressure, and dried under a high vacuum to give I8 (13.2 g, 44.8 mmol, 99%). The crude obtained was used in the next step without any further purification.

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 1.32 (t, $J=7.09$ Hz, 3 H), 3.74 - 3.87 (m, 4 H), 3.90 (s, 3 H), 4.24 (q, $J=7.09$ Hz, 2 H), 4.72 (s, 2 H), 6.31 (d, $J=15.89$ Hz, 1 H), 6.78 (d, $J=8.07$ Hz, 1 H), 6.97 - 7.13 (m, 2 H), 7.60 (d, $J=15.89$ Hz, 1 H) $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 14.1, 14.2, 20.9, 25.4, 52.2, 53.0, 55.8, 60.2, 60.3, 66.0, 76.6, 77.3, 110.4, 113.4, 116.6, 121.9, 128.8, 144.0, 149.0, 149.6, 166.9, 168.9.
I8 (1 equiv., 17 mmol, 5.00 g) was dissolved in 40 mL dry DCM and cooled to -78°C. To this solution, Diisobutylaluminum hydride solution (DIBAL-H) (1M in THF, 4.4 equiv., 75 mmol, 75 mL) was added dropwise over 1 h. The mixture was warmed to room temperature and stirred overnight, all the starting materials were consumed, and then the reaction was cooled to -30°C and quenched by adding cold water dropwise. Next, the flask was allowed to stir at room temperature for another 15 mins. The mixture was filtered over celite. The filtrate was worked up against ethyl acetate and brine three times. The combined organics were dried over magnesium sulfate and concentrated under reduced pressure to give I9 as a white solid (3.56 g, 15.8 mmol, 92.4% yield), which was used in the next step without any purification.

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 1.71 - 1.80 (m, 1 H), 2.82 (t, $J$=6.48 Hz, 1 H), 3.84 - 3.99 (m, 5 H), 4.09 - 4.17 (m, 2 H), 4.28 - 4.36 (m, 2 H), 6.25 (dt, $J$=15.86, 5.88 Hz, 1 H), 6.54 (dt, $J$=15.80, 1.57 Hz, 1 H), 6.82 - 6.98 (m, 3 H)

$^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 55.7, 61.2, 63.7, 71.3, 76.6, 77.3, 109.4, 114.5, 119.7, 127.0, 130.8, 130.9, 147.8, 149.7.

A solution of compound I9 (1 equiv., 15.87 mmol, 3.56 g) was dissolved in 90 mL dry DCM. To it, Manganese (IV) oxide (88% activated) (10 equiv., 158.7 mmol, 15.68 g) was added in one shot, and the resulting black solution was stirred at room temperature overnight. The mixture was filtered over celite the next day. The DCM solution was concentrated under reduced pressure, and the crude was purified by column chromatography (30% ethyl acetate-hexane) to obtain I10 as a white solid (3 g, 13.5 mmol, 85% yield).

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 2.44 (s, 1 H), 3.92 (s, 3 H), 3.95 - 4.07 (m, 2 H), 4.12 - 4.25 (m, 2 H), 6.63 (dd, $J$=15.83, 7.76 Hz, 1 H), 6.95 (d, $J$=8.31 Hz, 1 H), 7.05 - 7.22 (m, 2 H), 7.42 (d, $J$=15.89 Hz, 1 H), 9.68 (d, $J$=7.70 Hz, 1 H) $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 55.9, 61.1, 70.8, 76.6, 77.2, 77.3, 110.3, 113.5, 123.2, 127.0, 127.7, 149.9, 151.0, 152.5, 193.5.
In a 50mL oven-dried round bottom flask, sebacic acid (1 equiv., 0.5 mmol, 100 mg), I10 (2.1 equiv., 1.04 mmol, 231 mg), and DMAP (0.2 equiv., 0.1 mmol, 12 mg) were taken and dissolved in 10 mL dry DCM. The resulting solution was cooled to 0°C. Then, DCC (2.2 equiv., 1.09 mmol, 225 mg) was dissolved in 2 mL DCM and added to the mixture dropwise. Then the flask was warmed to room temperature and stirred overnight. Next, the solution was filtered. The filtrate was concentrated under reduced pressure and further purified by column chromatography (35%-45% ethyl acetate-hexane) to give I11 as a white solid (150 mg, 0.25 mmol, 50% yield).

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 1.22 - 1.33 (m, 10 H), 1.59 - 1.67 (m, 5 H), 2.34 (t, J=7.52 Hz, 4 H), 3.91 (s, 6 H), 4.24 - 4.38 (m, 4 H), 4.48 (t, J=4.95 Hz, 4 H), 6.64 (d, J=7.70 Hz, 1 H), 6.60 (d, J=7.70 Hz, 1 H), 6.94 (d, J=8.31 Hz, 2 H), 7.02 - 7.21 (m, 4 H), 7.44 (s, 1 H), 7.40 (s, 1 H), 9.67 (d, J=7.70 Hz, 2 H) $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 24.7, 29.0, 29.0, 34.0, 56.0, 62.3, 67.1, 76.6, 77.2, 77.3, 110.7, 113.3, 123.1, 127.0, 127.8, 149.9, 150.9, 152.5, 173.6, 193.5.

Methyltriphenylphosphonium bromide (2.4 equiv., 0.29 mmol, 104 mg) was dissolved in 3 mL THF and cooled to 0°C. Solid potassium tert-butoxide (2.5 equiv., 0.3 mmol, 34 mg) was added in one shot, and the THF solution immediately became yellow. The solution was stirred at 0°C for 10 mins. I11 (1 equiv., 0.12 mmol, 74 mg) was dissolved in 2 mL THF and added slowly to the precooled mixture. Then, the resulting solution was stirred at room temperature for 15 mins. THF was evaporated under reduced pressure, and crude was dissolved in ethyl acetate and worked up against brine two times. The organic part was dried over magnesium sulfate, concentrated under reduced pressure, and further purified by column chromatography (2% ethyl acetate-hexane) to obtain CTA11 as a white solid (25 mg, 0.04 mmol, 34% yield), which was stored at -20°C.
In an oven-dried round bottom flask, sebacic acid (1 equiv., 2.75 mmol, 556 mg), I6 (2.2 equiv., 6.04 mmol, 1.15 g), and DMAP (0.2 equiv., 0.55 mmol, 68 mg) were taken and dissolved in 12 mL dry DCM. The resulting solution was cooled to 0°C. Then, DCC (2.3 equiv., 6.32 mmol, 1.3 g) was dissolved in 3 mL DCM and added to the mixture dropwise. Then the flask was warmed to room temperature and stirred overnight. Next, the solution was filtered. The filtrate was concentrated under reduced pressure and further purified by column chromatography (10%-20% ethyl acetate-hexane) to give CTA12 a sticky, viscous liquid (900 mg 1.65 mmol, 60% yield). The product was further stored at -20°C freezer.

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 1.18 - 1.37 (m, 8 H), 1.55 - 1.72 (m, 4 H), 2.25 - 2.44 (m, 4 H), 4.06 - 4.26 (m, 4 H), 4.35 - 4.52 (m, 4 H), 5.10 - 5.40 (m, 4 H), 6.13 - 6.26 (m, 1 H), 6.34 - 6.59 (m, 3 H), 6.59 - 6.74 (m, 1 H), 6.81 - 6.99 (m, 5 H), 7.21 - 7.40 (m, 4 H) $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 24.8, 28.9, 28.9, 34.0, 62.5, 65.9, 76.6, 77.3, 114.3, 114.7, 116.5, 119.0, 127.6, 127.8, 129.5, 129.7, 130.2, 130.3, 130.4, 132.2, 133.2, 137.2, 157.5, 158.1, 173.6.
**CTA13 (tris(2-(4-(buta-1,3-dien-1-yl)phenoxy)ethyl) benzene-1,3,5-tricarboxylate)**

A mixture of 1,3,5-Benzenetricarbonyl trichloride (1 equiv., 1.0 mmol, 266 mg) and 16 (3.1 equiv., 3.1 mmol, 590 mg) in 20 mL dry DCM was cooled in an ice bath. Triethylamine (3.3 equiv., 3.3 mmol, 0.46 mL) was added dropwise at that temperature. The flask was stirred at room temperature for 1 h. Then, the mixture was diluted with water and extracted with DCM and brine. The organic part was combined, dried over magnesium sulfate, and further purified by column chromatography (15% ethyl acetate-hexane) to give CTA13 as a viscous liquid (450 mg, 0.62 mmol, 62% yield). The product was stored at -20°C, as in room temperature; after overnight, insoluble material was obtained, probably because of radical cross-linking.

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 4.30 - 4.39 (m, 6 H), 4.71 - 4.78 (m, 6 H), 5.11 - 5.41 (m, 6 H), 6.13 - 6.25 (m, 2 H), 6.40 (s, 1 H), 6.37 (s, 2 H), 6.43 - 6.58 (m, 1 H), 6.64 (s, 1 H), 6.78 - 6.96 (m, 9 H), 7.23 - 7.37 (m, 10 H), 8.82 - 8.95 (m, 3 H) $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 63.9, 65.8, 76.6, 77.2, 77.3, 114.4, 114.8, 116.6, 119.1, 127.7, 127.9, 129.6, 129.7, 130.3, 130.6, 131.0, 132.2, 133.2, 135.0, 135.0, 137.5, 157.5, 164.8.

**CTA14 (2,2-bis(4-(buta-1,3-dien-1-yl)benzoyl)oxy)methyl)propane-1,3-diy bis(4-(buta-1,3-dien-1-yl)benzoate)**

In an oven-dried round bottom flask, pentaerythritol (1 equiv., 0.47 mmol, 64.2 mg), 17 (4.2 equiv., 1.98 mmol, 345 mg), and DMAP (0.5 equiv., 0.24 mmol, 29 mg) were taken and dissolved in 5 mL dry DCM. The resulting solution was cooled to 0°C. Then, DCC (4.5 equiv., 2.12 mmol, 438 mg) was dissolved in 3 mL DCM and added to the mixture dropwise. Then the flask was warmed to room temperature and stirred overnight. Next, the solution was filtered, and the filtrate was concentrated under reduced pressure and further purified by column...
chromatography (20% ethyl acetate-hexane) to give CTA14 as a sticky, viscous liquid (250 mg, 0.33 mmol, 69.6% yield). The product was further stored at -20°C.

\[ ^1H \text{ NMR (CDCl}_3, 400 \text{ MHz) } \delta \text{ ppm: 4.64 - 4.79 (m, 8 H), 5.23 - 5.36 (m, 4 H), 5.36 - 5.50 (m, 4 H), 6.27 - 6.41 (m, 3 H), 6.41 - 6.51 (m, 3 H), 6.51 - 6.63 (m, 2 H), 6.74 - 6.94 (m, 4 H), 7.29 - 7.45 (m, 8 H), 7.87 - 8.05 (m, 8 H) \] 

\[ ^13C \text{ NMR (CDCl}_3, 101 \text{ MHz) } \delta \text{ ppm: 14.1, 43.1, 63.6, 76.6, 77.2, 77.3, 119.5, 121.2, 126.3, 127.6, 129.0, 129.0, 129.6, 130.0, 131.5, 132.3, 132.6, 132.7, 136.7, 142.4, 165.8. \]

CTA17 ((2E,4E)-N-methyl-5-phenylpenta-2,4-dienamide)

In a 50mL oven-dried round bottom flask, (2E, 4E)-5-phenylpenta-2, 4-dienoic acid (CTA15) (1 equiv., 2.87 mmol, 500 mg), methylation hydrochloride (1.1 equiv., 3.16 mmol, 213.5 mg), N-(3-Dimethylaminopropyl) -N'-ethylcarbodiimide hydrochloride (EDC.HCl) (1.2 equiv., 3.45 mmol, 661 mg) and 4-(Dimethylamino)pyridine (DMAP) (0.05 equiv., 0.15 mmol, 18 mg) were taken and then dissolved in 20 mL dry dichloromethane (DCM). The mixture was cooled in an ice bath under argon. Then, triethylamine (3.5 equiv., 9.9 mmol, 1.38 mL) was added to the flask dropwise. The ice bath was removed, and the mixture was stirred at room temperature overnight. The next day, the solution was diluted with DCM and washed one time with water and two times with brine. The combined organics were dried over magnesium sulfate and concentrated in a rotary evaporator. The crude was dissolved under a warm condition in a minimum amount of ethyl acetate and crystallized at room temperature to obtain white crystals (350 mg, 1.87 mmol, 65% yield), filtered, and dried under a high vacuum.

\[ ^1H \text{ NMR (CDCl}_3, 400 \text{ MHz) } \delta \text{ ppm: 2.92 (d, J=4.89 Hz, 3 H), 5.67 - 5.92 (m, 1 H), 5.99 (d, J=14.79 Hz, 1 H), 6.73 - 6.98 (m, 2 H), 7.24 - 7.53 (m, 6 H) \] 

\[ ^13C \text{ NMR (CDCl}_3, 101 \text{ MHz) } \delta \text{ ppm: 26.4, 76.6, 77.3, 123.7, 126.3, 126.9, 128.6, 128.7, 136.2, 139.1, 140.7, 166.7. } \]
In a 200 mL round bottom flask, potassium tert-butoxide (1.3 equiv., 21.24 mmol, 2.4 g) was dissolved in 80 mL tetrahydrofuran (THF) and cooled to 0°C. To it, trimethyl phosphonoacetate (1.3 equiv., 21.24 mmol, 3.45 mL) was added dropwise and stirred the resulting solution at 0°C for 15 mins. Then, 3-(2-Furyl) acrolein (1 equiv., 19.38 mmol, 2 g) was dissolved in 10 mL THF and added to the precooled solution dropwise over 15 mins. The flask was warmed to room temperature and stirred for 15 mins. Upon which no starting material was observed. Next, THF was removed under reduced pressure in a rotary evaporator, and the crude was dissolved in ethyl acetate and worked up against brine two times. The organic part was combined, concentrated, and further purified by column chromatography (5% ethyl acetate-hexane) to give a yellow solid (2.52 g, 14.15 mmol, 73% yield) mentioned above as I12.

I12 (1 equiv., 6.91 mmol, 1.23 g) was dissolved in 15 mL dry DCM and cooled to -78°C. To this solution, Diisobutylaluminum hydride solution (DIBAL-H) (1M in THF, 2.2 equiv., 15.18 mmol, 15.2 mL) was added dropwise over 30 mins. The mixture was warmed to room temperature and stirred for a further 3 h, almost all the starting materials were consumed, and then the reaction was cooled to -30°C and quenched by adding cold water dropwise. Next, the flask was allowed to stir at room temperature for another 15 mins. The mixture was filtered over celite. The filtrate was worked up against ethyl acetate and brine three times. The combined organics were dried over magnesium sulfate and concentrated under reduced pressure to give I13 as a white solid (1 g, 6.66 mmol, 96.5% yield), which was used in the next step without any purification.
**H NMR (CDCl₃, 400 MHz) δ ppm: 2.11 - 2.41 (m, 1 H), 4.21 (dt, J=5.90, 0.90 Hz, 2 H), 5.86 - 6.03 (m, 1 H), 6.18 - 6.48 (m, 4 H), 6.60 - 6.80 (m, 1 H), 7.36 (dd, J=1.77, 0.31 Hz, 1 H) \(^{13}\)C NMR (CDCl₃, 101 MHz) δ ppm: 63.0, 76.6, 77.3, 108.3, 111.5, 120.1, 126.7, 130.9, 132.6, 142.0, 152.9.

A solution of compound I13 (1 equiv., 5 mmol, 754 mg) was dissolved in 25 mL dry DCM. To it, Manganese (IV) oxide (88% activated) (10 equiv., 50.11 mmol, 4.36 g) was added in one shot, and the resulting black solution was stirred at room temperature overnight. The mixture was filtered over celite the next day. The DCM solution was concentrated under reduced pressure, and the crude was dissolved in ethyl acetate and kept at -20°C overnight to obtain yellow crystals of CTA18 (650 mg, 5.39 mmol, 87% yield).

\(^{1}\)H NMR (CDCl₃, 400 MHz) δ ppm: 6.18 - 6.35 (m, 1 H), 6.41 - 6.52 (m, 1 H), 6.55 (d, J=3.42 Hz, 1 H), 6.70 - 6.84 (m, 1 H), 6.84 - 6.99 (m, 1 H), 7.13 - 7.33 (m, 1 H), 7.43 - 7.58 (m, 1 H), 9.61 (d, J=7.95 Hz, 1 H) \(^{13}\)C NMR (CDCl₃, 101 MHz) δ ppm: 76.6, 76.9, 77.3, 112.3, 113.1, 124.4, 128.4, 131.4, 144.3, 151.4, 151.9, 193.3.

**CTA19 ((2E,4E)-5-(4-bromophenyl)penta-2,4-dienal)**

In an oven-dried Schlenk flask, (1,3-Dioxolan-2-ylmethyl) triphenylphosphonium bromide (2.6 equiv., 6.17 mmol, 2.65 g) was dissolved in 15 mL THF and cooled to 0°C. Potassium tert-butoxide (3 equiv., 7.11 mmol, 800 mg) was added, and the solution immediately turned yellow. The resulting solution was stirred at that temperature for 20 mins. Then 3-(4-Bromophenyl) acrylaldehyde (1 equiv., 2.37 mmol, 500 mg) was dissolved in 2 mL THF and added to the mixture dropwise over 10 mins. The flask was warmed to room temperature and stirred overnight. 5 mL water was added to the same flask, followed by 5 mL 2(M) HCl, and the solution was stirred for 2 more hours. Thin layer chromatography (TLC) showed the absence of starting material and generation of two very close spots suggesting probably cis and trans isomers. After that, THF was evaporated under reduced pressure, and the crude was dissolved in ethyl acetate and washed with brine two times. The organic part was dried over magnesium sulfate, concentrated, and further purified by column chromatography (5%-
10% ethyl acetate-hexane). Both isomers were isolated separately as white solid, and some mixtures contained both (335 mg, 1.42 mmol, overall yield of 60%).

Cis isomer - ¹H NMR (CDCl₃, 400 MHz) δ ppm: 5.99 (ddt, J=10.99, 7.29, 0.95 Hz, 1 H), 6.86 (d, J=15.28 Hz, 1 H), 6.92 - 7.12 (m, 1 H), 7.34 - 7.45 (m, 3 H), 7.45 - 7.60 (m, 3 H), 7.69 - 7.86 (m, 1 H), 10.27 (d, J=7.34 Hz, 1 H) ³¹C NMR (CDCl₃, 101 MHz) δ ppm: 76.68, 77.20, 77.31, 122.78, 123.69, 126.79, 127.32, 128.88, 132.06, 132.13, 134.55, 141.09, 146.45, 151.35, 190.09, 193.40.

Trans isomer - ¹H NMR (CDCl₃, 400 MHz) δ ppm: 6.30 (dd, J=15.16, 7.95 Hz, 1 H), 6.91 - 7.07 (m, 2 H), 7.19 - 7.31 (m, 2 H), 7.35 - 7.42 (m, 2 H), 7.49 - 7.58 (m, 2 H), 9.64 (d, J=7.95 Hz, 1 H) ³¹C NMR (CDCl₃, 101 MHz) δ ppm: 76.6, 77.2, 77.3, 123.7, 126.8, 128.8, 132.0, 132.1, 134.5, 140.8, 151.3, 193.4.

**CTA20 (2-chloroethyl (2E,4E)-5-phenylpenta-2,4-dienoate)**

![CTA20 reaction scheme](image)

In a 50mL oven-dried round bottom flask, (2E, 4E) -5-phenylpenta-2, 4-dienoic acid (CTA15) (1 equiv., 4.6 mmol, 800 mg), 2-chloroethanol (2 equiv., 9.2 mmol, 0.61 mL) and 4-(Dimethylamino) pyridine (DMAP) (1.2 equiv., 5.5 mmol, 674 mg) were taken and dissolved in 20 mL dry DCM. The resulting solution was cooled to 0°C. Then, N,N'-Dicyclohexylcarbodiimide (DCC) (1.5 equiv., 6.93 mmol, 1.43 g) was dissolved in 5 mL DCM and added to the mixture dropwise. Then the flask was warmed to room temperature and stirred overnight. Next, the solution was filtered. The filtrate was concentrated under reduced pressure and further purified by column chromatography (20% ethyl acetate-hexane) to give CTA20 as a white solid (810 mg, 3.43 mmol, 74.65% yield).

³¹H NMR (CDCl₃, 400 MHz) δ ppm: 3.75 (dd, J=6.24, 5.26 Hz, 2 H), 4.44 (dd, J=6.24, 5.26 Hz, 2 H), 6.03 (d, J=15.41 Hz, 1 H), 6.78 - 7.05 (m, 2 H), 7.30 - 7.43 (m, 3 H), 7.43 - 7.67 (m, 3 H).

**CTA21 ((3E,5E)-6-(4-bromophenyl)hexa-3,5-dien-2-one)**

![CTA21 reaction scheme](image)

3-(4-Bromophenyl) acrylaldehyde (1 equiv., 3.17 mmol, 670 mg) and 1-(triphenylphosphoranylidene)-2-propanone (1.5 equiv., 4.72 mmol, 1.5 g) were dissolved in 30 mL of toluene and heated at 85°C for overnight. TLC showed incomplete conversion of
starting material. Then, toluene was evaporated under reduced pressure and the crude purified by column chromatography (5% ethyl acetate-hexane) to give a white solid (555 mg, 2.22 mmol, 70% yield).

\[^1\text{H} \text{NMR}\ (\text{CDCl}_3, \ 400 \text{ MHz}) \delta \text{ ppm: } 2.32\ (s, 3 \text{ H}), \ 6.28\ (d, J=15.41 \text{ Hz}, 1 \text{ H}), \ 6.79 - 6.97\ (m, 2 \text{ H}), \ 7.21 - 7.40\ (m, 3 \text{ H}), \ 7.45 - 7.60\ (m, 2 \text{ H}).\]

\[^{13}\text{C} \text{NMR}\ (\text{CDCl}_3, \ 101 \text{ MHz}) \delta \text{ ppm: } 27.4, \ 76.6, \ 77.3, \ 123.1, \ 127.2, \ 128.5, \ 130.9, \ 132.0, \ 134.8, \ 139.7, \ 142.8, \ 198.2.\]

**CTA23 ((E)-(2-methylbuta-1,3-dien-1-yl)benzene)**

Methyltriphenylphosphonium bromide (1.2 equiv., 12.31 mmol, 4.4 g) was dissolved in 20 mL THF and cooled to 0°C. Solid potassium tert-butoxide (1.2 equiv., 12.31 mmol, 1.38 g) was added in one shot, and the THF solution immediately became yellow. The solution was stirred at 0°C for 10 mins. \(\alpha\)-Methyl-trans-cinnamaldehyde (1 equiv., 10.26 mmol, 1.44 mL) was dissolved in 5 mL THF and added slowly to the precooled mixture. Then, the resulting solution was stirred at room temperature for 15 mins. THF was evaporated under reduced pressure, and crude was dissolved in ethyl acetate and worked up against brine two times. The organic part was dried over magnesium sulfate, concentrated under reduced pressure, and further purified by column chromatography (2% ethyl acetate-hexane) to obtain CTA23 as a colorless liquid (1.3 g, 9.00 mmol, 88% yield).

\[^1\text{H} \text{NMR}\ (\text{CDCl}_3, \ 400 \text{ MHz}) \delta \text{ ppm: } 1.97 - 2.06\ (m, 3 \text{ H}), \ 5.10 - 5.21\ (m, 1 \text{ H}), \ 5.28 - 5.39\ (m, 1 \text{ H}), \ 6.45 - 6.67\ (m, 2 \text{ H}), \ 7.17 - 7.46\ (m, 5 \text{ H}).\]

\[^{13}\text{C} \text{NMR}\ (\text{CDCl}_3, \ 101 \text{ MHz}) \delta \text{ ppm: } 13.1, \ 76.6, \ 77.3, \ 112.9, \ 126.6, \ 128.1, \ 129.2, \ 131.6, \ 135.9, \ 137.7, \ 141.8.\]
CTA24 (1-methoxy-4-((1E)-penta-1,3-dien-1-yl)benzene)

Ethyltriphenylphosphonium bromide (1.2 equiv., 11.1 mmol, 4.1 g) was dissolved in 20 mL THF and cooled to 0°C. Solid potassium tert-butoxide (1.2 equiv., 11.1 mmol, 1.25 g) was added in one shot, and the THF solution immediately became yellow. The solution was stirred at 0°C for 10 mins. Trans-p-methoxycinnamaldehyde (1 equiv., 9.25 mmol, 1.5 g) was dissolved in 10 mL THF and added slowly to the precooled mixture. Then, the resulting solution was stirred at room temperature for 15 mins. THF was evaporated under reduced pressure, and crude was dissolved in ethyl acetate and worked up against brine two times. The organic part was dried over magnesium sulfate, concentrated under reduced pressure, and further purified by column chromatography (5% ethyl acetate-hexane) to obtain CTA24 as a colorless liquid (1.4 g, 8.0 mmol, 87% yield).

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 1.80 - 1.90 (m, 3 H), 3.80 - 3.85 (m, 3 H), 5.56 (ddt, $J$=10.71, 7.17, 1.02, 1.02 Hz, 1 H), 6.11 - 6.27 (m, 1 H), 6.49 (d, $J$=15.65 Hz, 1 H), 6.80 - 7.03 (m, 3 H), 7.29 - 7.43 (m, 2 H) $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 13.5, 18.3, 55.2, 76.6, 77.3, 114.0, 114.0, 122.2, 125.9, 127.2, 127.3, 127.4, 129.2, 129.7, 130.5, 131.3, 159.0.

CTA25 (1-((1E)-hexa-1,3-dien-1-yl)-4-methoxybenzene)

Propyltriphenylphosphonium bromide (1.2 equiv., 11.1 mmol, 4.3 g) was dissolved in 20 mL THF and cooled to 0°C. Solid potassium tert-butoxide (1.2 equiv., 11.1 mmol, 1.25 g) was added in one shot, and the THF solution immediately became yellow. The solution was stirred at 0°C for 10 mins. Trans-p-methoxycinnamaldehyde (1 equiv., 9.25 mmol, 1.5 g) was dissolved in 10 mL THF and added slowly to the precooled mixture. Then, the resulting solution was stirred at room temperature for 15 mins. THF was evaporated under reduced
pressure, and crude was dissolved in ethyl acetate and worked up against brine two times. The organic part was dried over magnesium sulfate, concentrated under reduced pressure, and further purified by column chromatography (5% ethyl acetate-hexane) to obtain CTA25 as a colorless liquid (1.5 g, 7.96 mmol, 88.2% yield).

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) ppm: 0.99 - 1.16 (m, 3 H), 2.24 - 2.40 (m, 2 H), 3.76 - 3.89 (m, 3 H), 5.49 (dtt, \(J=10.92, 7.47, 7.47, 1.01, 1.01\) Hz, 1 H), 6.05 - 6.26 (m, 1 H), 6.37 - 6.57 (m, 1 H), 6.80 - 7.02 (m, 3 H), 7.29 - 7.45 (m, 2 H) \(^13\)C NMR (CDCl\(_3\), 101 MHz) \(\delta\) ppm: 13.6, 14.3, 21.2, 25.8, 55.2, 76.6, 77.3, 114.0, 122.4, 127.2, 127.4, 28.2, 129.5, 129.6, 130.4, 131.5, 133.7, 136.1, 159.0.

PEG\(_{2k}\) macroinitiator

![PEG2k macroinitiator diagram]

Poly(ethylene glycol) methyl ether (M\(_n\)=2000 g/mol, 1 equiv., 4.96 mmol, 10 g), succinic anhydride (2.5 equiv., 12.4 mmol, 1.24 g), DMAP (1 equiv., 4.96 mmol, 607 mg) and triethyl amine (1 equiv., 4.96 mmol, 0.7 mL) were dissolved in 80 mL 1,4-dioxane. The resulting solution was heated at 40°C for 20 h. The reaction was cooled, and the dioxane was concentrated under reduced pressure. Then it was precipitated into cold diethyl ether two times to obtain carboxylic acid functional PEG (PEG\(_{2k}\) carboxylic acid) as a white solid (10 g, 4.3 mmol 95% yield).

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) ppm: 2.57 - 2.67 (m, 4 H), 3.36 (s, 3 H), 3.56 - 3.71 (m, 207 H), 4.22 - 4.26 (m, 2 H) \(^13\)C NMR (CDCl\(_3\), 101 MHz) \(\delta\) ppm: 29.2, 29.5, 39.3, 58.9, 63.6, 68.9, 70.5, 70.6, 71.8, 76.6, 77.2, 77.3, 106.3, 172.2, 174.2.

In an oven-dried round bottom flask, carboxylic acid functional PEG (1.0 equiv., .57 mmol, 1.23 g), I6 (10.0 equiv., 5.7 mmol, 1.08 g), and DMAP (1 equiv., 0.57 mmol, 70 mg) were taken and dissolved in 4 mL dry DCM. The resulting solution was cooled to 0°C. Then, DCC (10.0 equiv., 5.7 mmol, 1.18 g) was dissolved in 2 mL DCM and added to the mixture dropwise. Then the flask was warmed to room temperature and stirred overnight. Next, the solution was filtered. The filtrate was concentrated under reduced pressure and precipitated into cold diethyl ether
three times to obtain PEG$_{2k}$ macroinitiator as a white solid (1 g, 0.43 mmol, 75.1% yield). The product was stored at -20°C.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm: 2.63 - 2.72 (m, 4 H), 3.35 - 3.39 (m, 3 H), 3.41 - 3.50 (m, 2 H), 3.50 - 3.75 (m, 189 H), 3.75 - 3.89 (m, 2 H), 4.14 - 4.28 (m, 4 H), 4.39 - 4.49 (m, 2 H), 5.08 - 5.22 (m, 1 H), 5.34 (dt, $J$=16.87, 1.04 Hz, 1 H), 6.13 - 6.23 (m, 1 H), 6.32 - 6.46 (m, 1 H), 6.52 (s, 1 H), 6.79 - 6.93 (m, 3 H) $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ ppm: 24.6, 28.9, 58.9, 62.9, 63.8, 65.8, 68.9, 70.5, 70.7, 71.8, 76.6, 77.2, 77.3, 114.3, 114.7, 116.5, 119.0, 127.6, 127.8, 129.5, 129.7, 130.2, 130.5, 132.1, 133.1, 137.2, 157.4, 172.1.
**Synthesis of Monomers:**

**Synthesis of exo-MNI (M1)**

![Synthesis of exo-MNI (M1)](image)

Exo-N-methylnorbornene imide (exo-MNI) (M1) was synthesized according to the previously reported procedure\(^2\).

**Synthesis of endo, exo-bicyclo [2.2.1] hept-5-en-2-yl) methoxy) triisopropylsilane (M3)**

![Synthesis of endo, exo-bicyclo [2.2.1] hept-5-en-2-yl) methoxy) triisopropylsilane (M3)](image)

In an oven-dried Schlenk flask, bicyclo[2.2.1]hept-5-en-2-ylmethanol (exo and endo mixture) (1 equiv., 96.78 mmol, 12 g), triisopropylsilyl chloride (1.1 equiv., 106.45 mmol, 22.8 mL), imidazole (3 equiv., 291.2 mmol, 19.8 g) and DMAP (0.01 equiv., 0.97 mmol, 120 mg) were dissolved in 120 mL dry DCM. The resulting mixture was stirred overnight at room temperature. Then, the mixture was washed with water once and with brine two times. The organic part was dried over magnesium sulfate, concentrated, and purified by column chromatography (2% ethyl acetate-hexane) to give M3 as a colorless liquid (27g, 96.42 mmol, 99% yield).

\(^{1}\text{H NMR (CDCl}_3, 400 \text{ MHz}) \delta \text{ ppm: 0.42 - 0.53 (m, 1 H), 1.04 - 1.16 (m, 22 H), 1.24 - 1.40 (m, 2 H), 1.40 - 1.50 (m, 1 H), 1.71 - 1.87 (m, 1 H), 2.24 - 2.39 (m, 1 H), 2.74 - 2.88 (m, 1 H), 2.95 - 3.03 (m, 1 H), 3.24 (t, J=9.54 Hz, 1 H), 3.49 (dd, J=9.66, 6.24 Hz, 1 H), 5.98 (dd, J=5.75, 2.93 Hz, 1 H), 6.03 - 6.20 (m, 1 H).}\text{^{13}C NMR (CDCl}_3, 101 \text{ MHz}) \delta \text{ ppm: 11.7, 17.7, 28.2, 28.9, 41.2, 41.5, 41.9, 43.0, 43.4, 44.5, 49.0, 66.5, 67.4, 76.3, 76.6, 132.3, 136.2, 136.4, 136.5.}\)
1H NMR reactions:

The reaction of CTA1 with G3:

In an NMR tube, G3 (1 equiv., 0.01 mmol, 8 mg) and 1,3,5 trimethoxybenzene (as an internal standard) were dissolved in 0.5 mL dichloromethane-d\textsubscript{2} (DCM-d\textsubscript{2}), and 1H NMR was measured. CTA1 (1 equiv., 0.01 mmol, 2.63 mg) in 0.25 mL DCM-d\textsubscript{2} was added, and 1H NMR was measured immediately.

Fig. S1: 1H NMR (CD\textsubscript{2}Cl\textsubscript{2}, 300 MHz) of reaction of CTA1 (1 equiv.) with G3 (1 equiv.) in DCM-d\textsubscript{2} (CD\textsubscript{2}Cl\textsubscript{2}). NMR spectra were compared with CTA1 and styrene (measured independently in CDCl\textsubscript{3}). The peak at 6.05 ppm is from the internal standard. Peaks of CTA1 around 5.15 ppm
and 5.32 ppm are gone, and new peaks of **styrene** at 5.22-5.26 ppm and 5.73-5.79 ppm were observed.

**Scheme S1: Regioselective cross-metathesis**

We believe, minimal steric congestion of terminal 1,3 conjugated double bond as compared to internal double bond is responsible for the high regioselective cross-metathesis reaction. Grubbs’ ruthenium complex reacted regioselectively forming an electronically stable conjugated carbene rather than the methylidene complex.
End capping experiment:

**CTA1**

G3 (1 equiv., 0.0045 mmol, 4 mg) was dissolved in 0.5 mL dichloromethane-d$_2$ (CD$_2$Cl$_2$) in an NMR tube and to it exo-MNI (20 equiv., 0.09 mmol, 16 mg) in 0.2 mL CD$_2$Cl$_2$ was quickly added. $^1$H NMR was measured. Then, **CTA1** (2 equiv., 0.009 mmol, 2.24 mg) dissolved in 0.2 mL CD$_2$Cl$_2$ was added, and $^1$H NMR was measured over time. After that, the CD$_2$Cl$_2$ mixture was concentrated under reduced pressure at room temperature, and the formed polymer was precipitated in methanol. The polymer (P1) was obtained as a grey solid in quantitative yield.

![Diagram of the reaction](image)

**Fig. S2:** $^1$H NMR spectrum (CD$_2$Cl$_2$, 300 MHz) of end-capping reaction with **CTA1**.
**Fig. S3**: MALDI-ToF mass spectrum (DCTB, AgTFA) of **P1**.

**Catalytic polymerization in an NMR tube using CTA8:**

In an NMR tube, 1,3,5 trimethoxy benzene (as an internal standard), **G3** (1 equiv., 0.0026 mmol, 2 mg) and **CTA8** (20 equiv., 0.045 mmol, 8.5 mg) were mixed in 0.6 mL DCM-d$_2$ and $^1$H NMR were measured. Then, **M1** (200 equiv., 0.45 mmol, 80.13 mg) was added quickly, and $^1$H NMR was measured immediately. Complete consumption (see $^1$H NMR spectra below) of monomer and CTA was observed within the first measurement (5-8 mins). Next, a few drops of ethyl vinyl ether were added to the NMR tube, and the resulting solution was concentrated under reduced pressure. The concentrated mixture was precipitated into cold methanol. A white solid polymer (**P12**) was obtained further dried under a high vacuum.
General procedure for catalytic synthesis of Monotelechelic polymers:

In an oven dried Schlenk flask, monomer M1 was degassed three times and then dissolved in degassed dichloromethane (DCM) and kept under Argon. M2 and M3 were first dissolved in DCM and then degassed three times using a conventional freeze-thaw cycle. In a separate Schlenk flask, CTA was added and degassed three times. To it, dry, degassed DCM was added, followed by the addition of G3 that was already dissolved in degassed DCM. The resulting solution was stirred at room temperature for three mins. Then, the monomer solution was added quickly to the mixture of catalyst and CTA and stirred at room temperature for ten mins. Complete monomer consumption was observed by $^1$H NMR spectroscopy and/or thin layer chromatography. Next, a few drops of ethyl vinyl ether were added, and the resulting mixture was stirred for five more mins. The mixture was concentrated under reduced pressure and precipitated into cold methanol two times. A solid was obtained, filtered, and dried under a high vacuum. Respective yields of all the polymers were measured after drying under a high vacuum overnight.
**Table S1: Catalytically Synthesis of Monotelechelic polymers**

<table>
<thead>
<tr>
<th>Entry</th>
<th>CTA</th>
<th>Monomer (M)</th>
<th>G3:CTA: Monomer ratio</th>
<th>$M_n$ (Non-catalytic, M/G3) (kDa)</th>
<th>$M_n$ (Catalytic, M/CTA) kDa</th>
<th>$M_n$ ($^1$H NMR) kDa</th>
<th>$M_n$ (SEC, CHCl$_3$) kDa</th>
<th>$\bar{D}$</th>
<th>Polymer Yield (%)</th>
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<td>P2</td>
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<td>5</td>
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**P2:**

G3: 2 mg, CTA1: 22.5 mg, M1: 160 mg. Concentration (M1): 0.1 (M). DCM: 9 mL.

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 1.48 - 1.71, 2.00 - 2.22, 2.28, 2.64 - 2.76, 2.76 - 2.85, 2.90 - 3.13, 3.19 - 3.36, 3.80, 3.89 - 3.97, 4.69 - 4.72, 5.11 - 5.26, 5.45 - 5.59, 5.70 - 5.81, 5.83 - 6.00, 6.88 - 6.97, 7.32, 7.28. $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 24.7, 24.8, 24.8, 40.8, 45.6, 51.0, 51.1, 52.2, 52.6, 52.6, 55.9, 66.4, 76.6, 77.2, 77.3, 119.3, 131.8, 149.6, 178.3.

**P3:**

G3: 2 mg, CTA1: 22.5 mg, M1: 320 mg. Concentration (M1): 0.1 (M). DCM: 18 mL.

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 1.47 - 1.73, 2.01 - 2.21, 2.28, 2.66 - 2.86, 2.89 - 3.13, 3.18 - 3.36, 3.80, 3.90 - 3.96, 4.69 - 4.72, 5.10 - 5.25, 5.44 - 5.60, 5.69 - 5.82, 5.86 - 6.0, 6.87 - 6.97. $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 24.7, 24.8, 24.8, 40.8, 41.2, 41.4, 41.6, 41.6, 41.9, 42.0,

\[\text{entry} \quad \text{CTA} \quad \text{Monomer (M)} \quad \text{G3: CTA: Monomer ratio} \quad \text{M}_n \quad \text{(Non-catalytic, M/G3) (kDa)} \quad \text{M}_n \quad \text{(Catalytic, M/CTA) kDa} \quad \text{M}_n \quad \text{(1H NMR) kDa} \quad \text{M}_n \quad \text{(SEC, CHCl$_3$) kDa} \quad \bar{D} \quad \text{Polymer Yield (%)}
\]

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<th>Entry</th>
<th>CTA</th>
<th>Monomer (M)</th>
<th>G3: CTA: Monomer ratio</th>
<th>M$_n$ (Non-catalytic, M/G3) (kDa)</th>
<th>M$_n$ (Catalytic, M/CTA) kDa</th>
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<th>Polymer Yield (%)</th>
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\[\text{a= due to very high molecular weight of the polymer end group analysis could not be performed.}\]
42.4, 42.4, 42.7, 42.9, 43.1, 45.5, 45.6, 45.7, 45.8, 45.9, 46.0, 46.2, 46.8, 50.7, 50.9, 51.0, 51.1, 51.1, 51.3, 51.8, 52.2, 52.6, 52.9, 55.8, 66.4, 76.6, 77.2, 77.3, 114.1, 119.3, 131.3, 131.6, 131.7, 131.8, 131.9, 132.0, 132.0, 132.6, 133.4, 149.6, 169.3, 178.1, 178.3, 178.4.

P4:

G3: 2 mg, CTA1: 22.5 mg, M1: 480 mg. Concentration (M1): 0.1 (M). DCM: 27 mL.

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 2.00 - 2.23, 2.24 - 2.32, 3.80, 3.89 - 4.00, 4.65 - 4.74, 5.10 - 5.17, 5.17 - 5.27, 5.41 - 5.64, 5.64 - 5.86, 5.86 - 6.03, 6.47, 6.77, 6.83 - 6.93, 6.93 - 7.12. $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 24.7, 24.8, 24.8, 40.8, 40.8, 41.2, 41.4, 41.9, 42.0, 42.4, 42.7, 42.9, 45.5, 45.6, 46.2, 46.8, 50.9, 51.1, 51.3, 51.8, 52.2, 52.6, 53.0, 55.8, 66.4, 76.6, 77.2, 77.5, 114.2, 119.3, 131.6, 131.8, 132.0, 132.6, 133.4, 149.6, 169.3, 178.3, 178.4.

P5:

G3: 1 mg, CTA1: 56.2 mg, M1: 601 mg. Concentration (M1): 0.1 (M). DCM: 34 mL.

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 1.99 - 2.22, 2.23 - 2.31, 3.80, 3.87 - 3.99, 4.63 - 4.74, 5.07 - 5.27, 5.42 - 5.63, 5.63 - 5.83, 5.83 - 6.04, 6.34, 6.39 - 6.57, 6.66, 6.70 - 6.83, 6.83 - 7.12. $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 24.7, 24.7, 24.8, 40.8, 41.1, 41.4, 41.7, 41.9, 42.1, 42.4, 42.4, 42.7, 42.9, 43.1, 45.5, 45.6, 45.7, 45.7, 45.9, 46.0, 46.1, 46.2, 46.8, 50.7, 50.9, 50.9, 51.0, 51.0, 51.1, 51.3, 51.5, 51.8, 52.2, 52.5, 52.6, 52.9, 55.8, 66.4, 76.6, 77.2, 77.3, 109.4, 109.4, 114.1, 115.7, 119.3, 127.3, 131.4, 131.5, 131.7, 131.8, 131.8, 132.0, 132.0, 132.0, 132.6, 132.8, 133.4, 133.4, 138.7, 146.8, 149.6, 169.3, 177.9, 178.1, 178.3, 178.4.

P6:

G3: 1 mg, CTA2: 54.3 mg, M1: 601 mg. Concentration (M1): 0.1 (M). DCM: 34 mL.

$^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 1.43 - 1.73, 3.74 - 3.83, 5.06 - 5.25, 5.37 - 5.61, 5.66 - 5.95, 6.12 - 6.39, 6.39 - 6.53, 6.53 - 6.70, 6.79 - 6.88, 7.27 - 7.39. $^{13}$C NMR (CDCl$_3$, 101 MHz) δ ppm: 24.3, 24.3, 24.4, 40.4, 40.5, 40.8, 41.0, 41.0, 41.1, 41.2, 41.2, 41.4, 41.5, 41.6, 41.7, 41.9, 42.0, 42.3, 42.4, 42.5, 42.7, 43.2, 45.1, 45.2, 45.3, 45.3, 45.5, 45.6, 45.7, 45.8, 46.2, 46.4, 46.7, 50.3, 50.3, 50.5, 50.5, 50.6, 50.7, 50.8, 50.9, 51.1, 51.4, 51.7, 52.1, 52.1, 52.2, 52.2, 52.3, 52.5, 54.8, 76.3, 76.6, 76.8, 113.6, 115.3, 115.3, 125.9, 126.0, 127.0, 127.4, 129.6, 131.2, 131.3, 131.4, 131.4, 131.5, 131.6, 131.6, 131.7, 132.2, 132.5, 132.9, 132.9, 133.0, 133.0, 133.1, 138.3, 138.3, 158.7, 177.6, 177.7, 177.9, 177.5, 177.9, 178.0.

P7:

G3: 1 mg, CTA3: 23.6 mg, M1: 401 mg. Concentration (M1): 0.1 (M). DCM: 23 mL.
\[^1\text{H}\text{ NMR}\ (\text{CDCl}_3, 400 \text{ MHz}) \delta \text{ ppm} : 1.99 - 2.22, 2.24 - 2.31, 5.07 - 5.28, 5.40 - 5.64, 5.64 - 5.86, 5.86 - 6.06, 6.35 - 6.61, 6.73, 7.38 - 7.50. \[^{13}\text{C}\text{ NMR}\ (\text{CDCl}_3, 101 \text{ MHz}) \delta \text{ ppm} : 24.7, 24.8, 24.8, 40.8, 41.2, 41.4, 41.9, 42.1, 42.4, 42.7, 45.5, 45.5, 45.6, 45.7, 45.9, 46.0, 46.1, 46.2, 46.8, 50.9, 51.0, 51.1, 51.3, 51.8, 52.2, 52.6, 52.9, 76.5, 77.2, 77.3, 127.7, 131.6, 131.8, 132.0, 132.6, 133.4, 133.4, 178.1, 178.3, 178.3.\]

**P8:**

\[^{1}\text{H}\text{ NMR}\ (\text{CDCl}_3, 400 \text{ MHz}) \delta \text{ ppm} : 1.54 - 1.67, 1.82, 2.04 - 2.11, 2.12 - 2.17, 2.68 - 2.80, 2.91 - 3.12, 3.22 - 3.30, 3.47, 5.46 - 5.55, 5.71 - 5.78, 7.27. \[^{13}\text{C}\text{ NMR}\ (\text{CDCl}_3, 101 \text{ MHz}) \delta \text{ ppm} : 24.7, 24.8, 40.8, 41.2, 41.4, 41.9, 42.1, 42.4, 42.9, 45.6, 45.8, 45.9, 46.1, 46.2, 50.8, 50.9, 51.0, 51.1, 51.1, 51.8, 52.6, 53.0, 76.7, 77.2, 77.3, 131.6, 131.6, 131.7, 131.8, 131.9, 132.0, 132.1, 132.6, 133.4, 178.1, 178.3, 178.4.\]

**P9:**

\[^{1}\text{H}\text{ NMR}\ (\text{CDCl}_3, 400 \text{ MHz}) \delta \text{ ppm} : 2.00 - 2.22, 2.24 - 2.31, 5.07 - 5.28, 5.40 - 5.64, 5.64 - 5.86, 6.06, 6.14 - 6.43, 6.59 - 6.75, 7.32 - 7.40. \[^{13}\text{C}\text{ NMR}\ (\text{CDCl}_3, 101 \text{ MHz}) \delta \text{ ppm} : 24.7, 24.8, 24.9, 40.8, 41.2, 41.4, 41.9, 42.1, 42.4, 42.7, 42.9, 43.1, 45.6, 45.8, 45.9, 46.0, 46.2, 46.8, 50.7, 51.0, 51.1, 51.1, 51.3, 51.8, 52.2, 52.6, 52.9, 76.7, 77.2, 77.3, 108.2, 111.5, 115.8, 119.7, 131.1, 131.6, 131.7, 131.9, 132.0, 132.1, 132.7, 133.4, 142.1, 178.1, 178.3, 178.4.\]

**P10:**

\[^{1}\text{H}\text{ NMR}\ (\text{CDCl}_3, 400 \text{ MHz}) \delta \text{ ppm} : 2.00 - 2.22, 2.23 - 2.31, 5.09 - 5.28, 5.44 - 5.60, 5.62 - 5.83, 5.87 - 6.03, 6.53 - 6.81, 7.31 - 7.57, 7.93 - 8.07, 8.25 - 8.43. \[^{13}\text{C}\text{ NMR}\ (\text{CDCl}_3, 101 \text{ MHz}) \delta \text{ ppm} : 24.7, 24.8, 24.9, 40.8, 41.2, 41.4, 41.6, 42.4, 42.7, 42.9, 45.6, 45.6, 46.0, 46.2, 46.8, 50.7, 51.0, 51.1, 51.1, 51.3, 51.8, 52.7, 53.0, 76.7, 77.0, 77.2, 77.3, 115.8, 125.1, 125.4, 125.5, 126.0, 126.1, 126.4, 128.6, 129.5, 131.5, 131.5, 131.8, 132.0, 132.1, 132.6, 132.7, 133.4, 138.7, 178.3.\]
P11:

G3: 1 mg, CTA6: 24.7 mg, M1: 401 mg. Concentration (M1): 0.1 (M). DCM: 23 mL.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm: 2.00 - 2.23, 2.28, 3.82, 4.61 - 4.68, 5.13, 5.17 - 5.27, 5.39 - 5.64, 5.64 - 5.87, 5.87 - 6.04, 6.13 - 6.41, 6.81 - 6.94. $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ ppm: 24.7, 24.8, 41.2, 41.4, 41.9, 42.1, 42.4, 42.7, 42.9, 45.6, 45.6, 45.8, 46.0, 46.0, 46.2, 46.9, 47.9, 50.8, 51.0, 51.1, 51.4, 51.8, 52.3, 52.6, 52.7, 53.0, 65.3, 76.7, 77.2, 77.3, 114.3, 114.5, 114.8, 127.6, 130.3, 130.6, 131.6, 131.8, 132.1, 132.7, 133.4, 137.7, 178.3, 178.4.

P12:

G3: 2 mg, CTA8: 8.5 mg, M1: 80.1 mg. Concentration (M1): 0.4 (M). DCM-d$_2$: 1.1 mL.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm: 1.99 - 2.22, 2.23 - 2.31, 3.85 - 3.99, 5.08 - 5.27, 5.38 - 5.65, 5.65 - 5.85, 5.85 - 6.06, 6.34, 6.50 - 6.79, 7.33 - 7.57, 7.90 - 8.09. $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ ppm: 24.7, 24.8, 41.2, 41.4, 41.6, 41.8, 41.9, 42.1, 42.4, 42.7, 42.9, 43.1, 43.6, 45.5, 45.6, 45.8, 46.0, 46.1, 46.2, 46.6, 46.8, 50.7, 51.0, 51.1, 51.3, 51.3, 51.8, 52.0, 52.2, 52.6, 52.9, 76.7, 77.2, 77.3, 115.7, 115.7, 126.1, 126.3, 128.4, 128.5, 128.8, 129.0, 129.4, 129.5, 129.9, 130.0, 130.3, 131.2, 131.7, 131.8, 131.9, 132.0, 132.1, 132.6, 132.9, 133.1, 133.4, 138.7, 138.8, 166.8, 178.1, 178.3, 178.3, 178.4.

P13:

G3: 2 mg, CTA9: 76.7 mg, M1: 1.2 g. Concentration (M1): 0.2 (M). DCM: 34 mL.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm: 1.44 - 1.73, 3.14 - 4.31, 4.42 - 4.59, 5.11, 5.20, 5.35 - 5.62, 5.62 - 5.82, 5.82 - 6.01, 6.45, 6.79 - 6.96. $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ ppm: 24.7, 24.8, 30.6, 40.8, 41.1, 41.4, 41.6, 41.9, 42.0, 42.4, 42.7, 42.8, 43.1, 43.6, 45.5, 45.6, 45.7, 45.9, 46.0, 46.1, 46.2, 46.8, 50.7, 50.9, 51.1, 51.3, 51.8, 51.9, 52.1, 52.6, 52.9, 53.2, 64.1, 65.6, 76.7, 77.2, 77.3, 114.4, 114.5, 114.8, 115.7, 127.5, 130.2, 130.5, 131.6, 131.8, 131.8, 131.8, 132.0, 132.0, 132.1, 132.6, 132.9, 133.3, 133.4, 133.4, 133.8, 138.7, 171.6, 178.1, 178.3, 178.3, 178.4.

P14:

G3: 2 mg, CTA10: 12.7 mg, M1: 80.13 mg. Concentration (M1): 0.4 (M). DCM-d$_2$: 1.1 mL.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm: 2.00 - 2.22, 2.24 - 2.31, 4.26 - 4.39, 5.08 - 5.32, 5.40 - 5.64, 5.64 - 5.86, 5.86 - 6.07, 6.40, 6.49 - 6.77, 7.29 - 7.54, 7.85 - 8.03. $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ ppm: 24.7, 24.8, 24.8, 33.3, 40.8, 41.2, 41.4, 41.8, 42.1, 42.4, 42.7, 42.9, 45.6, 45.6, 45.7, 45.8, 45.9, 46.2, 46.8, 50.7, 50.9, 51.0, 51.1, 51.3, 51.8, 52.6, 52.7, 53.0, 76.7, 77.2, 77.3, 115.7, 126.3, 126.5, 127.2, 127.3, 127.7, 127.8, 128.6, 128.9, 129.1, 129.1, 129.3, 131.6, 131.8, 131.9, 132.0, 132.6, 133.2, 133.4, 178.3.
P15:

**G3:** 1 mg, **CTA2:** 18.1 mg, **M2:** 319.4 mg. Concentration (M2): 0.1 (M). DCM: 34 mL.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm: 1.24 - 1.51, 2.34 - 2.60, 2.71 - 2.94, 3.76 - 3.88, 4.85 - 4.93, 5.14 - 5.44, 5.69 - 5.89, 6.12 - 6.24, 6.35 - 6.55, 6.55 - 6.72, 6.82 - 6.91, 7.29 - 7.40. $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ ppm: 31.7, 31.8, 32.2, 32.4, 32.9, 33.1, 33.2, 38.4, 38.5, 38.7, 38.8, 39.1, 40.7, 41.4, 41.5, 41.9, 42.1, 42.8, 43.1, 43.2, 43.3, 43.4, 43.5, 43.8, 44.2, 44.5, 55.3, 76.7, 77.0, 77.2, 77.3, 112.2, 112.3, 112.3, 114.0, 127.3, 127.4, 127.5, 128.9, 130.5, 132.9, 133.0, 133.2, 133.7, 133.8, 133.8, 133.9, 134.0, 134.1, 143.3, 143.5.

P16:

**G3:** 2 mg, **CTA5:** 52.0 mg, **M2:** 534.0 mg. Concentration (M2): 0.2 (M). DCM: 29 mL.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm: 0.87 - 1.15, 4.84 - 5.03, 5.13 - 5.43, 5.74 - 5.92, 6.35 - 6.49, 6.49 - 6.65, 6.78 - 7.04, 7.31 - 7.54, 7.93 - 8.08, 8.24 - 8.44. $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ ppm: 32.2, 32.4, 32.9, 33.1, 33.1, 38.4, 38.7, 41.4, 42.1, 42.7, 42.8, 43.1, 43.4, 43.7, 76.7, 77.2, 77.3, 125.1, 125.1, 125.2, 125.3, 126.1, 128.6, 128.7, 131.5, 132.9, 133.0, 133.1, 133.7, 133.8, 133.8, 133.9, 134.0, 134.1.

P17:

**G3:** 2 mg, **CTA7:** 92.6 mg, **M2:** 534.0 mg. Concentration (M2): 0.2 (M). DCM: 28 mL.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm: 0.89 - 1.16, 1.54, 1.69 - 1.99, 2.31 - 2.57, 2.69 - 2.92, 4.25 - 4.38, 4.56 - 4.71, 4.83 - 4.92, 4.92 - 5.07, 5.14 - 5.44, 5.71 - 5.90, 6.53 - 6.74, 6.84 - 7.02, 7.36 - 7.47, 7.89 - 8.06. $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ ppm: 28.3, 32.2, 32.4, 32.9, 33.1, 33.1, 38.4, 38.7, 41.4, 42.1, 42.8, 43.1, 43.4, 50.9, 63.1, 76.7, 77.2, 77.3, 114.9, 117.3, 131.1, 132.9, 133.0, 133.1, 133.8, 133.8, 133.9, 134.0.

P18:

**G3:** 2 mg, **CTA9:** 77.0 mg, **M2:** 534.0 mg. Concentration (M2): 0.2 (M). DCM: 29 mL.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm: 0.94 - 1.16, 1.94 - 1.96, 4.13 - 4.33, 4.46 - 4.60, 4.86 - 5.03, 5.13 - 5.42, 5.71 - 5.89, 6.34 - 6.52, 6.79 - 7.03. $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ ppm: 30.7, 31.6, 31.8, 32.2, 32.4, 32.9, 33.1, 38.2, 38.4, 38.6, 40.7, 41.3, 41.4, 42.1, 42.7, 42.8, 42.9, 43.1, 43.4, 44.2, 44.5, 55.5, 64.2, 65.6, 76.7, 77.2, 77.3, 112.2, 112.3, 114.4, 114.5, 114.9, 127.3, 130.1, 130.4, 132.8, 133.0, 133.1, 133.5, 133.7, 133.8, 133.9, 134.0, 134.1, 143.3, 171.7.

P19:

**G3:** 2 mg, **CTA10:** 108.0 mg, **M2:** 724.0 mg. Concentration (M2): 0.2 (M). DCM: 40 mL.
Molecular weight determination by $^1$H NMR spectroscopy:

Fig. S5: Number average molecular weight ($M_n$) determination by end group analysis using $^1$H NMR (400 MHz) spectroscopy (olefinic region only, in CDCl$_3$). P2: red spectrum, P5: blue spectrum, P3: magenta spectrum, P4: green spectrum.
\(^1\)H NMR kinetics experiment:

In an NMR tube, 1,3,5 trimethoxy benzene (as an internal standard), \textbf{M1} (1000 equiv., 1.13 mmol, 200 mg), 3 bromopyridine (60 equiv., 0.067 mmol, 11 mg) and \textbf{CTA3} (50 equiv., 0.056 mmol, 11.8 mg) were mixed in 0.9 mL CDCl\(_3\) and \(^1\)H NMR were measured. Then, \textbf{G3} (1 equiv., 0.0011 mmol, 1 mg) dissolved in 0.2 mL was added quickly, and \(^1\)H NMR was measured overtime. Consumption of both \textbf{M1} and \textbf{CTA3} were observed overtime suggesting a kinetically controlled mechanism.
**Fig. S6**: $^1$H NMR (CDCl$_3$, 300 MHz) of reaction of CTA3 (50 equiv.), 3 bromopyridine (60 equiv.) and M1 (1000 equiv.) with G3 (1 equiv.) in CDCl$_3$ (CDCl$_3$).
In an NMR tube, 1,3,5 trimethoxy benzene (as an internal standard), G3 (1 equiv., 0.0011 mmol, 1 mg), 3 bromopyridine (60 equiv., 0.067 mmol, 11 mg) and CTA3 (50 equiv., 0.056 mmol, 11.8 mg) were mixed in 0.9 mL CDCl₃ and ¹H NMR were measured. Then, M2 (1000 equiv., 1.13 mmol, 106 mg) dissolved in 0.2 mL was added quickly, and ¹H NMR was measured overtime. Consumption of both M2 and CTA3 were observed overtime suggesting a kinetically controlled mechanism. As the rate of propagation of M2 is very high, almost full consumption of M2 was observed while CTA3 conversion was almost 90%.
Fig. S7: $^1$H NMR (CDCl$_3$, 300 MHz) of reaction of CTA3 (50 equiv.), 3 bromopyridine (60 equiv.) and M2 (1000 equiv.) with G3 (1 equiv.) in CDCl$_3$ (CDCl$_3$).
1H NMR Reactions:
The reaction of CTA11 with G3:

In an NMR tube, 1,3,5-trimethoxybenzene and CTA11 (1 equiv., 0.00165 mmol, 1 mg) was mixed in 0.5 mL DCM-d2, and 1H NMR was measured. A G3 stock solution of 5.83 mg (4 equiv., 0.0066 mmol) in 0.4 mL DCM-d2 was prepared. To the NMR tube, 0.1 mL of G3 stock solution (1 equiv.) was added, and 1H NMR was measured immediately. Quickly, another 0.11 mL (1.1 equiv.) of G3 stock solution was added, and 1H NMR was measured immediately. The terminal double bond proton of CTA11 (marked as 'a' in the above top spectrum) consumed 48.2% (theoretically 50%) after 1 equiv. of G3 was added, and simultaneously the same amount of styrene was generated, which should be a byproduct upon the reaction of G3 with CTA11. An equivalent amount of conjugated carbene was also observed (bottom spectra in blue). Adding
**Fig. S8**: $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) of reaction of CTA11 (1 equiv.) with G3 (2.1 equiv.).

1.1 equiv. more G3 catalyst gives complete consumption of CTA terminal double bond and integration of both styrene and conjugated carbene increased, which clearly proved attachment of two Ru complex to both chains ends of CTA11. A clear shift of methoxy proton (b) of CTA11 was also observed over time.

**$^1$H NMR Reaction using CTA13:**

In an NMR tube, 1,3,5-trimethoxybenzene and CTA13 (1 equiv., 0.00275 mmol, 2mg) were mixed in 0.6 mL DCM-d$_2$, and $^1$H NMR was measured. Then, G3 (3 equiv., 0.00825 mmol, 7.3 mg) was dissolved in 0.2 mL DCM-d$_2$ and added to the NMR tube, and again NMR was measured. Three equivalents of Ru complexes fully functionalized CTA to give a trifunctional initiator, and at the same time, styrene was generated in the process (See $^1$H NMR spectra below).
Fig. S9: $^1$H NMR (CD$_2$Cl$_2$, 300 MHz) of polymerization of M1 using CTA13.
A control $^1$H NMR tube polymerization reaction was performed where first G3 (1 equiv.) and CTA14 (20 equiv.) were dissolved in dichloromethane-d$_2$, and a $^1$H NMR spectrum was recorded (Figure S10, bottom, blue spectrum). Signals of the CTA14 protons were visible at 5.25 ppm (marked as "a") and 6.75-7.00 ppm (marked as "b"). A monomer (M1, 300 equiv.) solution in dichloromethane-d$_2$ was prepared beforehand and quickly added to the NMR tube. Immediate $^1$H NMR measurement revealed complete consumption of the monomer (no peak at 6.25 ppm) as well as CTA14 (disappearance of "a" protons and shift of "b" protons detected, also CTA14 peaks at 7.3 ppm and 8 ppm broadened significantly). At the same time, the polymer chain end protons (marked as "c" protons) and backbone protons (marked as "d" protons) were also visible. SEC measurement further verified the catalytic nature of the polymerization as the molecular weight obtained (P22, $M_n$, SEC (CHCl$_3$) = 4.5 kDa) was very close to that specified by the M1/CTA14 ($M_n$, M1/CTA14 = 3.4 kDa).

**Fig. S10**: $^1$H NMR (CD$_2$Cl$_2$, 300 MHz) of polymerization of M1 using CTA14.
## Table S2: Catalytically Synthesis of branched polymers-

<table>
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<tr>
<th>Entry</th>
<th>CTA</th>
<th>Monomer (M)</th>
<th>G3:CTA: Monomer ratio</th>
<th>$M_n$ (Non-catalytic, M/G3) (kDa)</th>
<th>$M_n$ (Catalytic, M/CTA) kDa</th>
<th>$M_n$ ($^1$H NMR) kDa</th>
<th>$M_n$ (SEC, CHCl₃) kDa</th>
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<th>Polymer Yield $^b$ (%)</th>
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<td>P20</td>
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<td>CTA13</td>
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<tr>
<td>P22</td>
<td>CTA14</td>
<td>M1</td>
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<td>3.2</td>
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<td>85</td>
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<tr>
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<td>- $^a$</td>
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<td>78</td>
</tr>
</tbody>
</table>

$^a$: due to very high molecular weight of the polymer end group analysis could not be performed.

$^b$: polymer yield is determined as follows-

\[
\text{Yield} (\%) = \frac{\text{amount of polymer obtained (in mg)}}{\text{amount of monomer used (in mg) + amount of CTA used (in mg)}} \times 100
\]

**P20:**

G3: 2 mg, CTA12: 62.0 mg, M1: 401.0 mg. Concentration (M1): 0.1 (M). DCM: 23 mL.
^1H NMR (CDCl$_3$, 400 MHz) δ ppm: 1.23 - 1.35, 2.31 - 2.37, 4.12 - 4.24, 4.38 - 4.47, 5.04 - 5.32, 5.45 - 5.61, 6.82 - 6.95.

P22:
G3: 2 mg, CTA14: 34.4 mg, M1: 122.0 mg. Concentration (M1): 0.5 (M). DCM-d$_2$: 1.3 mL.

^1H NMR (CDCl$_3$, 400 MHz) δ ppm: 2.00 - 2.23, 2.24 - 2.32, 4.59 - 4.82, 5.06 - 5.31, 5.43 - 5.67, 5.85 - 6.08, 6.23 - 6.47, 6.47 - 6.59, 6.59 - 6.89, 7.32 - 7.48, 7.90 - 8.06. ^13C NMR (CDCl$_3$, 101 MHz) δ ppm: 24.7, 24.8, 40.8, 41.4, 41.5, 41.8, 42.0, 43.1, 45.6, 46.8, 50.7, 50.7, 50.8, 51.0, 51.1, 51.1, 52.6, 76.7, 77.2, 77.3, 115.8, 129.0, 129.2, 129.6, 129.7, 130.0, 130.2, 131.6, 131.7, 131.8, 132.1, 132.7, 133.4, 138.7, 165.8, 178.3.

P23:
G3: 0.5 mg, CTA14: 8.6 mg, M1: 801.0 mg. Concentration (M1): 1 (M). DCM: 4.5 mL.

P24:
G3: 1.5 mg, CTA12: 93 mg, M2: 639.0 mg. Concentration (M2): 0.2 (M). DCM: 34 mL.

^1H NMR (CDCl$_3$, 400 MHz) δ ppm: 1.59 - 1.68, 2.29 - 2.38, 4.13 - 4.25, 4.36 - 4.49, 4.83 - 5.07, 5.13 - 5.42, 5.72 - 5.89, 6.04 - 6.30, 6.30 - 6.52, 6.52 - 6.71, 6.81 - 6.95. ^13C NMR (CDCl$_3$, 101 MHz) δ ppm: 24.8, 29.0, 29.0, 31.6, 31.8, 32.2, 32.4, 32.7, 32.9, 33.1, 33.1, 34.1, 38.4, 38.7, 40.7, 41.3, 41.4, 42.1, 42.7, 42.8, 43.1, 43.2, 43.3, 43.4, 44.2, 44.5, 62.6, 66.0, 66.0, 76.7, 77.2, 77.3, 112.2, 112.3, 112.3, 114.3, 114.4, 114.7, 115.1, 127.3, 127.5, 130.1, 130.3, 130.3, 130.4, 132.8, 132.9, 133.0, 133.1, 133.2, 133.7, 133.7, 133.8, 133.9, 134.0, 134.1, 143.3, 143.5, 173.7.

P25:
G3: 1 mg, CTA14: 55 mg, M3: 413.0 mg. Concentration (M3): 0.1 (M). DCM: 14.7 mL.

^1H NMR (CDCl$_3$, 400 MHz) δ ppm: 3.43 - 3.73 (m, 42 H), 4.59 - 4.81 (m, 8 H), 4.82 - 5.08 (m, 6 H), 5.17 - 5.47 (m, 37 H), 7.31 - 7.54 (m, 9 H), 7.91 - 8.08 (m, 9 H). ^13C NMR (CDCl$_3$, 101 MHz) δ ppm: 11.7, 12.0, 12.1, 12.3, 17.9, 18.1, 28.6, 35.6, 36.5, 40.9, 41.1, 41.5, 41.8, 42.0, 42.2, 42.4, 43.1, 43.7, 44.8, 45.0, 45.1, 47.1, 47.6, 48.3, 49.3, 63.6, 65.0, 66.8, 76.7, 77.2, 77.3, 121.2, 126.2, 126.3, 127.4, 127.7, 128.9, 129.0, 129.1, 129.1, 129.6, 129.6, 130.0, 130.1, 132.7, 133.4, 134.7, 136.9, 142.5, 165.8, 165.9.
End Capping Experiments:

**CTA6**

G3 (1 equiv., 0.0057 mmol, 5 mg) was dissolved in 0.5 mL dichloromethane-d$_2$ (CD$_2$Cl$_2$) in an NMR tube and to it exo-MNI (M1) (20 equiv., 0.12 mmol, 20 mg) in 0.2 mL CD$_2$Cl$_2$ was quickly added. $^1$H NMR was measured. Then, CTA6 (2 equiv., 0.012 mmol, 2.5 mg) dissolved in 0.2 mL CD$_2$Cl$_2$ was added, and $^1$H NMR was measured immediately. Thereafter, the CD$_2$Cl$_2$ mixture was concentrated under reduced pressure at room temperature, and the formed polymer was precipitated in methanol. The polymer (P26) was obtained as a grey solid in quantitative yield.

*Fig. S11:* $^1$H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of end-capping reaction with CTA6.
Fig. S12: MALDI-ToF mass spectrum (DCTB, AgTFA) of P26.
G3 (1 equiv., 0.0045 mmol, 4 mg) was dissolved in 0.5 mL dichloromethane-d$_2$ (CD$_2$Cl$_2$) in an NMR tube and to it M1 (20 equiv., 0.09 mmol, 16 mg) in 0.2 mL CD$_2$Cl$_2$ was quickly added. $^1$H NMR was measured. Then, CTA15 (10 equiv., 0.045 mmol, 7.9 mg) dissolved in 0.3 mL CD$_2$Cl$_2$ was added, and $^1$H NMR was measured over time. After 40 mins, the CD$_2$Cl$_2$ mixture was concentrated under reduced pressure at room temperature, and the formed polymer was precipitated in methanol. The polymer (P27) was obtained as a grey solid in quantitative yield.
Fig. S13: $^1$H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of end-capping reaction with CTA15. Full-spectrum is shown in the first image. The second and third spectra show zoomed regions corresponding to α proton (alkylidene region) and β proton to the Ru complex of G3, respectively.
Fig. S14: MALDI-ToF mass spectrum (DCTB, AgTFA) of P27.
**CTA17**

![CTA17 Reaction Scheme]

G3 (1 equiv., 0.0045 mmol, 4 mg) was dissolved in 0.7 mL dichloromethane-d$_2$ (CD$_2$Cl$_2$) in an NMR tube and to it (M1) (20 equiv., 0.09 mmol, 16 mg) in 0.2 mL CD$_2$Cl$_2$ was quickly added. $^1$H NMR was measured. Then, CTA17 (10 equiv., 0.045 mmol, 8.5 mg) dissolved in 0.2 mL CD$_2$Cl$_2$ was added, and $^1$H NMR was measured over time. After 40 mins, the CD$_2$Cl$_2$ mixture was concentrated under reduced pressure at room temperature, and the formed polymer was precipitated in methanol. The polymer (P28) was obtained as a grey solid in quantitative yield.

![NMR Spectra](https://example.com/fig15.png)

**Fig. S15:** $^1$H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of end-capping reaction with CTA17.
Fig. S16: MALDI-ToF mass spectrum (DCTB, AgTFA) of P28.

**CTA19**

G3 (1 equiv., 0.0045 mmol, 4 mg) was dissolved in 0.5 mL dichloromethane-d$_2$ (CD$_2$Cl$_2$) in an NMR tube and to it (M1) (20 equiv., 0.09 mmol, 16 mg) in 0.2 mL CD$_2$Cl$_2$ was quickly added. $^1$H NMR was measured. Then, CTA19 (10 equiv., 0.045 mmol, 10.7 mg) dissolved in 0.3 mL CD$_2$Cl$_2$ was added, and $^1$H NMR was measured over time. After 50 mins, the CD$_2$Cl$_2$ mixture
was concentrated under reduced pressure at room temperature, and the formed polymer was precipitated in methanol. The polymer (P29) was obtained as a grey solid in quantitative yield.

Fig. S17: $^1$H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of end-capping reaction with CTA19.
Fig. S18: MALDI-ToF mass spectrum (DCTB, AgTFA) of P29. The smaller distribution did not match with any possible non-regioselective metathesis.

**CTA21**

G3 (1 equiv., 0.0045 mmol, 4 mg) was dissolved in 0.5 mL dichloromethane-d$_2$ (CD$_2$Cl$_2$) in an NMR tube and to it (M1) (20 equiv., 0.09 mmol, 16 mg) in 0.2 mL CD$_2$Cl$_2$ was quickly added. $^1$H NMR was measured. Then, CTA21 (20 equiv., 0.045 mmol, 23.0 mg) dissolved in 0.3 mL CD$_2$Cl$_2$ was added, and $^1$H NMR was measured over time. After 50 mins, a few drops of ethyl vinyl ether was added, the CD$_2$Cl$_2$ mixture was concentrated under reduced pressure at room temperature, and the formed polymer was precipitated in methanol. The polymer (P30) was obtained as a grey solid in quantitative yield.
Fig. S19: $^1$H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of end-capping reaction with CTA21.

Although $^1$H NMR showed strictly regioselective chain transfer with CTA21, MALDI-ToF mass spectrum showed a minor distribution indicating another chain transfer. See following-
Fig. S20: MALDI-ToF mass spectrum (DCTB, AgTFA) of P30.

CTA24

G3 (1 equiv., 0.0045 mmol, 4 mg) was dissolved in 0.5 mL dichloromethane-d2 (CD2Cl2) in an NMR tube and to it (M1) (20 equiv., 0.09 mmol, 16 mg) in 0.2 mL CD2Cl2 was quickly added. 1H NMR was measured. Then, CTA24 (5 equiv., 0.022 mmol, 4.0 mg) dissolved in 0.2 mL CD2Cl2 was added, and 1H NMR was measured over time. After 20 mins, the CD2Cl2 mixture was concentrated under reduced pressure at room temperature, and the formed polymer was precipitated in methanol. The polymer (P31) was obtained as a grey solid in quantitative yield.

MALDI-ToF analyses (see below) of the precipitated polymer showed the main mass distribution bearing a phenyl group (G3) on one chain end and a methyl group (CTA24) on the other along with another smaller distribution suggesting a non-regioselective cross-metathesis between the propagating Ru carbene and the CTAs. We believe that the smaller distribution would have corresponded to the formation of a ruthenium alkylidene complex which was formed at concentrations too low to be observed by 1H NMR spectroscopy.
Fig. S21: $^1$H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of end-capping reaction with CTA24.
(1 equiv., 0.0045 mmol, 4 mg) was dissolved in 0.5 mL dichloromethane-d$_2$ (CD$_2$Cl$_2$) in an NMR tube and to it (M1) (20 equiv., 0.09 mmol, 16 mg) in 0.2 mL CD$_2$Cl$_2$ was quickly added. $^1$H NMR was measured. Then, CTA25 (5 equiv., 0.022 mmol, 4.25 mg) dissolved in 0.2 mL CD$_2$Cl$_2$ was added, and $^1$H NMR was measured over time. After 20 mins, the CD$_2$Cl$_2$ mixture was concentrated under reduced pressure at room temperature, and the formed polymer was precipitated in methanol. The polymer (P32) was obtained as a grey solid in quantitative yield.

MALDI-ToF analyses (see below) of the precipitated polymer showed the main mass distribution bearing a phenyl group (G3) on one chain end and an ethyl group (CTA25) on the other along with another smaller distribution suggesting a non-regioselective cross-metathesis between the propagating Ru carbene and the CTAs. We believe that the smaller distribution would have corresponded to the formation of a ruthenium alkylidene complex which was formed at concentrations too low to be observed by $^1$H NMR spectroscopy.
Fig. S23: $^1$H NMR spectrum (CD$_2$Cl$_2$, 300 MHz) of end-capping reaction with CTA25.

Fig. S24: MALDI-ToF mass spectrum (DCTB, AgTFA) of P32.
**1H NMR reactions:**

The reaction of CTA15-23 with G3:

![H NMR spectrum](image)

**Fig. S25:** 1H NMR (CD$_2$Cl$_2$, 400 MHz) of reaction of CTA15 (5 equiv.) with G3 (1 equiv.).
Fig. S26: $^1$H NMR (400 MHz) of reaction of CTA16 (10 equiv.) with G3 (1 equiv.) in THF-$d_8$.

Fig. S27: $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) of reaction of CTA17 (10 equiv.) with G3 (1 equiv.).
Fig. S28: $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) of reaction of CTA17 (1 equiv.) with G3 (1 equiv.). The regioselective cross-metathesis reaction produced a cinnamyl amide derivative as a side product upon reaction with G3, which could also be observed via $^1$H NMR spectroscopy (signal at 6.42 ppm).
**Fig. S29:** $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) of reaction of CTA19 (5 equiv.) with G3 (1 equiv.).

**Fig. S30:** $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) of reaction of CTA20 (5 equiv.) with G3 (1 equiv.).
**Fig. S31:** $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) of reaction of **CTA21** (20 equiv.) with **G3** (1 equiv.).

**Fig. S32:** $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) of reaction of **CTA22** (5 equiv.) with **G3** (1 equiv.).
Fig. S33: $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) of reaction of CTA23 (2 equiv.) with G3 (1 equiv.) in over 180 mins.

The reaction of CTA5 with G3:

In an NMR tube, G3 (1 equiv., 0.0034 mmol, 3 mg) and 1,3,5 trimethoxybenzene (as an internal standard) were dissolved in 0.5 mL dichloromethane-d$_2$ (DCM-d$_2$), and $^1$H NMR was measured. CTA5 (2 equiv., 0.0068 mmol, 1.56 mg) in 0.2 mL DCM-d2 was added, and $^1$H NMR was measured immediately.
Fig. S34: $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) of reaction of CTA5 (2 equiv.) with G3 (1 equiv.). The green line in the top spectrum shows only CTA5, and the blue spectrum is after adding G3 to it. The formation of styrene was clearly observed.
Mechanism of One-pot Heterotelechelic Polymer Synthesis:

The mechanism is as follows-

First, commercially available Grubbs 3rd generation catalyst (G3) was pre-functionalized using an excess of CTAs. Due to the aforementioned regioselective attack of G3 towards a given carbon-carbon double bond, the first reaction produced selectively only one type of ruthenium carbene complex. Upon introduction of a monomer, this conjugated ruthenium complex reacted immediately with monomers to produce a ruthenium alkylidene complex. As the rate of monomer propagation is way larger than the chain transfer with a CTA, the polymerization happened almost without any secondary metathesis. When all the monomer is consumed, propagating alkylidene species reacted with excess CTA present in situ in a similar regioselective manner to produce a heterotelechelic polymer.

Fig. S35: Mechanism of one-pot heterotelechelic polymer synthesis.
Polymerization in an NMR tube using CTA17:

G3 (1 equiv., 0.0045 mmol, 4 mg) was dissolved in 0.5 mL dichloromethane-d$_2$ (CD$_2$Cl$_2$) in an NMR tube and to it CTA17 (5 equiv., 0.023 mmol, 4.3 mg) in 0.2 mL CD$_2$Cl$_2$ was quickly added. $^1$H NMR was measured over time. After 20 mins, M1 (20 equiv., 0.09 mmol, 16 mg) dissolved in 0.2 mL CD$_2$Cl$_2$ was added, and $^1$H NMR was measured over time. After 80 mins, the CD$_2$Cl$_2$ mixture was concentrated under reduced pressure at room temperature, and the formed polymer was precipitated in methanol. The heterotelechelic polymer (P37) was obtained as a grey solid in quantitative yield.

Fig. S36: $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) of polymerization reaction of M1 using CTA17. Pre-functionalization of G3 was achieved fully within 20 mins using only 5 equiv. of CTA17 (spectrum in purple). The addition of monomer (M1) immediately formed polymer followed by chain transfer with in situ present excess CTA17 (Red spectrum followed by black).
General Procedure to synthesize one-pot heterotelechelic polymers:

A NMR tube was degassed and backfilled with argon. To the NMR tube, dichloromethane-d$_2$ solution of G3 and CTA was added sequentially. The ratio of CTA and G3 required to convert G3 to the new functional catalyst entirely depends on the CTA structure (as shown above). Complete pre-functionalization of G3 was confirmed via $^1$H NMR spectroscopy. Then, the prerequisite amount of monomer (M1 or M3) was dissolved in CD$_2$Cl$_2$ and added quickly to the same NMR tube. Complete monomer consumption was observed within 10 to 15 mins via $^1$H NMR spectroscopy. When all the propagating G3-alkylidene was converted to a conjugated carbene (sharp doublet), a few drops of ethyl vinyl ether were added to deactivate the G3. The resulting solution was concentrated under reduced pressure and precipitated using cold methanol to obtain the heterotelechelic polymer as a grey solid. Since the catalyst loading was stoichiometric, polymers obtained via this method were always colored.

Depending upon the reactivity of the CTA, different ratios of G3 to CTA were employed to synthesize the next heterotelechelic polymers as shown in the Table S3 below. All polymers showed isotopically resolved MALDI-ToF mass spectra matching the two expected end-groups.

To confirm the non-regioselective metathesis associated with a sterically congested CTA, CTA20 was utilized to synthesize a polymer (CTA20, P43, $M_n$, SEC(CHCl3) = 6.3 kDa, $\bar{D} = 1.22$) showing two mass distributions in MALDI-ToF mass spectrometry as predicted (Fig. S188). A slightly broader dispersity (1.19-1.37) was observed in all the above cases, which could be attributed to the known slower initiation rate of conjugated ruthenium complexes. CTA21 showed a non-regioselective reaction with G3; therefore, it was not used for synthesizing heterotelechelic polymer. Similarly, the reaction of CTA16 and CTA22 with G3 turned out to be extremely sluggish, and a large equivalent of both was required to pre-functionalize G3. Hence, they were also not used here.

Although heterotelechelic ROMP polymers can be obtained via this one-shot route, but the slow chain transfer of these CTAs during propagation stage of the polymerization strongly suggested they are not suitable for producing ROMP polymers catalytically.
### Table S3: One Pot Heterotelechelic Polymer Synthesis

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<th>Entry</th>
<th>CTA</th>
<th>Monomer (M)</th>
<th>G3: CTA:M</th>
<th>$M_n$ (Max, M/G3) (kDa)</th>
<th>$M_n$ (SEC, CHCl$_3$) kDa</th>
<th>$\tilde{D}$</th>
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<td>6.3</td>
<td>1.22</td>
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P33:

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm: 0.04 - 0.10, 1.12 - 1.40, 1.55 - 1.83, 2.00 - 2.22, 2.24 - 2.31, 2.57, 2.67 - 2.88, 2.89 - 3.15, 3.19 - 3.40, 5.44 - 5.65, 5.65 - 5.84, 6.21 - 6.41, 7.26 - 7.36. $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ 15.2, 24.7, 24.8, 24.9, 40.8, 41.2, 41.4, 41.9, 42.4, 45.6, 45.6, 46.0, 46.2, 51.0, 51.1, 51.8, 52.7, 53.0, 65.8, 76.7, 77.2, 77.3, 126.3, 128.6, 131.8, 132.1, 132.1, 132.7, 133.5, 178.3.

P37:

G3: 4 mg, CTA17: 4.23 mg, M1: 16.0 mg. Concentration (M1): 0.1 (M). DCM-d$_2$: 0.9 mL.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm: 1.36 - 1.74, 1.99 - 2.34, 2.67, 2.67 - 3.13, 3.17 - 3.23, 3.39 - 3.49, 5.35 - 5.65, 5.65 - 5.86, 6.03, 6.38, 6.47 - 6.64, 6.72 - 6.96, 7.19 - 7.25, 7.31 - 7.48. $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ 15.2, 24.7, 24.8, 24.9, 40.8, 41.2, 41.4, 41.9, 42.4, 45.6, 45.6, 46.0, 46.2, 51.0, 51.1, 51.8, 52.7, 53.0, 65.8, 76.7, 77.2, 77.3, 126.3, 128.6, 131.8, 132.1, 132.1, 132.7, 133.5, 178.3.

P38:

G3: 2 mg, CTA17: 23.5 mg, M1: 14.0 mg. Concentration (M1): 0.1 (M). DCM-d$_2$: 0.8 mL.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm: 0.04 - 0.10, 1.12 - 1.40, 1.55 - 1.83, 2.00 - 2.22, 2.24 - 2.31, 2.57, 2.67 - 2.88, 2.89 - 3.15, 3.19 - 3.40, 5.44 - 5.65, 5.65 - 5.84, 6.21 - 6.41, 7.26 - 7.36. $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ 15.2, 24.7, 24.8, 24.9, 40.8, 41.2, 41.4, 41.9, 42.4, 45.6, 45.6, 46.0, 46.2, 51.0, 51.1, 51.8, 52.7, 53.0, 65.8, 76.7, 77.2, 77.3, 126.3, 128.6, 131.8, 132.1, 132.1, 132.7, 133.5, 178.3.

P40:

G3: 2 mg, CTA19: 13.4 mg, M1: 20.0 mg. Concentration (M1): 0.1 (M). DCM-d$_2$: 1.13 mL.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm: 0.05 - 0.09, 1.46 - 1.74, 1.99 - 2.34, 2.67, 2.77 - 3.13, 3.17 - 3.36, 3.39 - 3.52, 5.42 - 5.62, 5.65 - 5.84, 7.20 - 7.46. $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ 15.2, 24.7, 24.8, 24.9, 40.8, 41.2, 41.4, 41.9, 42.4, 45.6, 45.6, 46.0, 46.2, 51.0, 51.1, 51.8, 52.7, 53.0, 65.8, 76.7, 77.2, 77.3, 126.3, 128.6, 131.8, 132.1, 132.7, 133.5, 178.3.
\(^1\text{H NMR reaction of (1E,3E,5E)-1,6-diphenylhexa-1,3,5-triene (CTA26) with G3:}\)

\[
\text{G3} + \text{Ph} = \text{Ph} \xrightarrow{\text{CDCl}_3} \text{Ph} \xrightarrow{\text{Ru}} + \text{Ph} \xrightarrow{\text{Ru}}
\]

\(\text{G3 (1 equiv., 0.0068 mmol, 6 mg)}\) was dissolved in 0.5 mL dichloromethane-d\(_2\) (\(\text{CD}_2\text{Cl}_2\)) in an NMR tube, and \(^1\text{H NMR was measured. Then, (1E,3E,5E)-1,6-diphenylhexa-1,3,5-triene (CTA26)}\) (10 equiv., 0.068 mmol, 16 mg) dissolved in 0.5 mL CD\(_2\text{Cl}_2\) was added and \(^1\text{H NMR was measured over time. As shown below, it took 150 mins to convert all the G3-benzylidene to a mixture of doublets.}\)

\(\text{Fig. S37: }^1\text{H NMR (CD}_2\text{Cl}_2, 300 MHz) of reaction of CTA26 (10 equiv.) with G3 (1 equiv.).}\)

\(\text{End capping experiment with CTA26:}\)

\(\text{G3 (1 equiv., 0.0068 mmol, 6 mg)}\) was dissolved in 0.5 mL CDCl\(_3\) (CDCl\(_3\)) in an NMR tube, and to it, \(\text{M1 (20 equiv., 0.136 mmol, 24 mg)}\) in 0.2 mL CDCl\(_3\) was quickly added. \(^1\text{H NMR was measured. Then, CTA26 (10 equiv., 0.068 mmol, 16 mg)}\) dissolved in 0.5 mL CDCl\(_3\) was added and \(^1\text{H NMR was measured over time. After 200 mins, the CDCl}_3\) mixture was concentrated under reduced pressure at room temperature, and the formed polymer was precipitated in methanol. The polymer (\(\text{P44}\)) was obtained as a yellow solid in quantitative yield.
Fig. S38: $^1$H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of end capping reaction with CTA26.
Fig. S39: MALDI-ToF mass spectrum (DCTB, AgTFA) of P44.
The macroinitiator P13 (1 equiv., 0.07073 mmol, 400 mg) and CuBr (1 equiv., 0.07073 mmol, 10.2 mg) were weighed inside the glovebox, mixed in a 10 mL Schlenk flask, and removed from the glovebox. The flask was kept under argon. Styrene was passed through basic alumina and further degassed via three freeze-thaw cycles. A stock solution of N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA) (30 µL in 0.4 mL DMF) was prepared and further degassed as before. Then, to the mixture of catalyst and macroinitiator, degassed styrene (500 equiv., 35.37 mmol, 3.76 mL) was added, followed by the addition of 0.2 mL of PMDETA (1 equiv., 0.07073 mmol, 15 µL) stock solution in DMF. The resulting mixture was stirred at 90°C for 19h. The reaction mixture was quenched by removing the hating and exposing it to air. The resulting mixture was diluted with dichloromethane, passed through basic alumina to remove copper salts, and concentrated under reduced pressure. The concentrated solution was then precipitated into cold methanol to obtain the block copolymer P13-b-PS as a white powder.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm: 0.82 - 1.12, 1.12 - 1.31, 1.36 - 1.56, 1.59, 1.61 - 1.63, 1.64 - 1.66, 1.78 - 1.95, 1.95 - 2.24, 2.28, 5.14, 5.40 - 5.64, 5.64 - 5.88, 6.19 - 6.43, 6.43 - 6.55, 6.55 - 6.85, 6.89 - 7.18, 7.18 - 7.24.
Block copolymer by Native Chemical Ligation (NCL)-

Commercially available poly (L-lactide) of 20,000 g/mol molecular weight (PLA$_{20k}$) (1 eq.) was dissolved in dry DCM. Then N-(tert-butoxycarbonyl)-S-trityl-L-cysteine (10 eq.) was added. After that, the solution was cooled in an ice bath, and DCC (12 eq.) was added slowly. After complete addition, DMAP (2 eq.) was added to the solution. The reaction mixture was stirred for 3 days under an argon atmosphere. Then it was filtered and extracted with DCM. Then the organic layer was concentrated and precipitated in cold diethyl ether 3 times. Then the precipitate was filtered and dried in a vacuum to obtain PLA$_{20k}$-Boc-Cys(Trt)-OH.

The polymer PLA$_{20k}$-Boc-Cys(Trt)-OH was stirred with 0.1 M TFA in DCM (10 mL) for 30 minutes with a few drops of triisopropylsilane. After that, a saturated sodium bicarbonate solution (20 mL) was added and extracted with DCM (3x 50 mL). Then the DCM layer was concentrated and precipitated into cold diethyl ether and used for the next step without further purifications. $^1$H NMR confirmed the absence of protons from Trityl and BoC groups. Kaiser amine test (showing intense blue color) was also performed to confirm the attachment of cysteine moiety with the polymers.

1eq. of the cysteine end functional polymer (PLA$_{20k}$-cysteine) was mixed with 1 eq. of thioester mono end functional polymer (P14) in dry DMF and chloroform (3:1). A few drops of triethylamine were added, and the mixture was stirred for 1 hour under an argon
atmosphere. After completion of the reaction (SEC monitoring), the solvent was evaporated in a vacuum, the solid residue redissolved in DCM, and then precipitated into methanol (10 fold excess) to give the corresponding conjugated polymer (P14-b-PLA).

**Fig. S41:** SEC (CHCl$_3$) trace of P14-b-PLA.
\[^1\text{H} \text{NMR Reaction of} \text{PEG}_{2k} \text{ macroinitiator with G3:}\]

G3 and PEG\(_{2k}\) macroinitiator stock solution was prepared in DCM-d\(_2\). Then, in an NMR tube, 1 equivalent of G3 and 1 equivalent of PEG\(_{2k}\) macroinitiator were mixed. \[^1\text{H} \text{NMR was measured immediately, which took around 4 to 5 mins. The spectrum is shown below (top spectrum, the blue one).}\]

\[^1\text{H} \text{NMR spectrum of PEG}_{2k} \text{ macroinitiator was measured separately in CDCl}_3 \text{ to avoid overlapping peaks (bottom spectrum, the green one). Clearly, chain-end protons of the macroinitiator vanished completely (marked as ‘a’ and ‘b’), and at the same time, styrene protons were visible. This simple experiment proved efficient end functionalization of a macroinitiator using an exactly stoichiometric amount of G3.}\]

\[\text{Fig. S42: Stacked} \:^{1}\text{H NMR (400 MHz) spectrum showing pre-functionalization of G3 using PEG}_{2k} \text{ macroinitiator.}\]
G3 and PEG<sub>2k</sub> macroinitiator stock solution was prepared in dry degassed dichloromethane and kept under argon in a Schlenk flask. In a separate Schlenk flask, MNI (M1) (200 equiv., 0.68 mmol, 120 mg) was degassed and then dissolved in 3.3 mL dichloromethane to give 0.2 M of monomer concentration. 1 equiv. of G3 (0.0034 mmol, 3 mg) (stock solution was prepared) and 1 equiv. of PEG<sub>2k</sub> macroinitiator (0.0034 mmol, 7.9 mg) (the stock solution was prepared) was mixed in an argon atmosphere, and the mixture was stirred at room temperature for 5 mins. Then, MNI solution was added quickly, and the resulting mixture was stirred for 10 mins, upon which no monomer was left as confirmed by <sup>1</sup>H NMR spectroscopy. The mixture was quenched by adding a few drops of ethyl vinyl ether, concentrated under vacuum, and precipitated from cold diethyl ether two times. A grey solid (83% yield, PEG<sub>2k</sub>-b-P(M1)) was obtained as a diblock copolymer.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ ppm: 1.99 - 2.22, 2.22 - 2.34, 3.39, 3.52 - 3.74, 5.44 - 5.64, 5.64 - 5.84. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz) δ ppm: 24.8, 24.8, 24.9, 40.8, 45.6, 45.8, 46.2, 51.0, 51.1, 52.7, 53.0, 70.6, 76.7, 77.2, 77.3, 131.9, 133.5, 178.3.
Fig. S43: SEC (DMF) trace of PEG\textsubscript{2k}-b-P(M1).
Table S4: Stability of Chain Transfer Agents-

Stability of purified chain transfer agents has been summarized as follows-

<table>
<thead>
<tr>
<th>CTA</th>
<th>Storage temperature</th>
<th>Time stable up to</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTA1-10, CTA23-25</td>
<td>-20°C</td>
<td>&gt;8 months</td>
</tr>
<tr>
<td>CTA11,12</td>
<td>-20°C</td>
<td>2 months</td>
</tr>
<tr>
<td>CTA13</td>
<td>room temperature</td>
<td>2-3 hours</td>
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<tr>
<td>CTA14</td>
<td>room temperature</td>
<td>60 minutes</td>
</tr>
<tr>
<td>CTA13,14</td>
<td>-20°C</td>
<td>24-48 hours</td>
</tr>
<tr>
<td>CTA15,17,26</td>
<td>room temperature</td>
<td>&gt;1 year</td>
</tr>
<tr>
<td>CTA18,19</td>
<td>-20°C</td>
<td>&gt;10 months</td>
</tr>
<tr>
<td>PEG_{2k} macroinitiator</td>
<td>-20°C</td>
<td>2-4 months</td>
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</table>
Table S5: Chemical shift data

<table>
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<tr>
<th>CTA</th>
<th>Solvent</th>
<th>Structure</th>
<th>Chemical Shift (ppm)</th>
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</thead>
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<tr>
<td>CTA15</td>
<td>CD$_2$Cl$_2$</td>
<td><img src="image1" alt="Structure Image" /></td>
<td>18.73</td>
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<tr>
<td>CTA16</td>
<td>C$_4$D$_8$O</td>
<td><img src="image2" alt="Structure Image" /></td>
<td>18.68</td>
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<tr>
<td>CTA17</td>
<td>CD$_2$Cl$_2$</td>
<td><img src="image3" alt="Structure Image" /></td>
<td>18.73</td>
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<tr>
<td>CTA18</td>
<td>CD$_2$Cl$_2$</td>
<td><img src="image4" alt="Structure Image" /></td>
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<td>-------</td>
</tr>
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<td>CTA1</td>
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<td>CTA6</td>
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<td>CTA8</td>
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<td><img src="image" alt="Chemical Structure" /></td>
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<td>CTA11</td>
<td>CD$_2$Cl$_2$</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>18.55</td>
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</table>
NMR Spectra of CTAs and Monomer:

Fig. S44: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of I1.

Fig. S45: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of I1.
Fig. S46: $^{1}$H NMR (CDCl$_3$, 400 MHz) spectrum of I2.

Fig. S47: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of I2.
Fig. S48: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA1.

Fig. S49: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA1.
Fig. S50: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of I$_3$.

Fig. S51: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of I$_3$. 
**Fig. S52:** $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA2.

**Fig. S53:** $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA2.
Fig. S54: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA3.

Fig. S55: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA3.
Fig. S56: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA4.

Fig. S57: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA4.
Fig. S58: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTAS.

Fig. S59: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTAS.
**Fig. S60:** $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of I4.

**Fig. S61:** $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of I4.
Fig. S62: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA6.

Fig. S63: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA6.
**Fig. S64:** $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of I5.

**Fig. S65:** $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of I5.
Fig. S66: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of I6.

Fig. S67: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of I6.
Fig. S68: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA7.

Fig. S69: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA7.
**Fig. S70**: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA8.

**Fig. S71**: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA8.
Fig. S72: $^1$H NMR (Dimethylsulfoxide-d$_6$, 400 MHz) spectrum of I7.

Fig. S73: $^{13}$C NMR (Dimethylsulfoxide-d$_6$, 101 MHz) spectrum of I7.
Fig. S74: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA9.

Fig. S75: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA9.
Fig. S76: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA10.

Fig. S77: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA10.
**Fig. S78:** $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of I8.

**Fig. S79:** $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of I8.
Fig. S80: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of I9.

Fig. S81: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of I9.
Fig. S82: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of I10.

Fig. S83: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of I10.
Fig. S84: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of I11.

Fig. S85: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of I11.
Fig. S86: $^{1}$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA11.

Fig. S87: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA11.
Fig. S88: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA12.

Fig. S89: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA12.
Fig. S90: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA13.

Fig. S91: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA13.
Fig. S92: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA14.

Fig. S93: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA14.
Fig. S94: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA17.

Fig. S95: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA17.
Fig. S96: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of I12.

Fig. S97: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of I12.
Fig. S98: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of I13. The peak at 3.76 corresponds to 4.5% unreacted methyl ester (starting material).

Fig. S99: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of I13.
Fig. S100: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA18.

Fig. S101: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA18.
Fig. S102: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA19 (Predominantly trans).

Fig. S103: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA19 (Predominantly trans).
Fig. S104: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA19 (Predominantly cis).

Fig. S105: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA19 (Predominantly cis).
Fig. S106: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA20.

Fig. S107: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA20.
Fig. S108: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA21.

Fig. S109: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA21.
Fig. S110: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA23.

Fig. S111: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA23.
Fig. S112: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA24.

Fig. S113: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA24.
Fig. S114: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of CTA25.

Fig. S115: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of CTA25.
Fig. S116: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of M3.

Fig. S117: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of M3.
NMR Spectra of polymers:

Fig. S118: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P2.

Fig. S119: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P2.
Fig. S120: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P3.

Fig. S121: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P3.
Fig. S122: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P4.

Fig. S123: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P4.
Fig. S124: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P5.

Fig. S125: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P5.
Fig. S126: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P6.

Fig. S127: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P6.
Fig. S128: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P7.

Fig. S129: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P7.
Fig. S130: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P8.

Fig. S131: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P8.
Fig. S132: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P9.

Fig. S133: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P9.
Fig. S134: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P10.

Fig. S135: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P10.
**Fig. S136:** $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P11.

**Fig. S137:** $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P11.
Fig. S138: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P12.

Fig. S139: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P12.
Fig. S140: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P13.

Fig. S141: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P13.
Fig. S142: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P14.

Fig. S143: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P14.
Fig. S144: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P15.

Fig. S145: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P15.
Fig. S146: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P16.

Fig. S147: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P16.
Fig. S148: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P17.

Fig. S149: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P17.
Fig. S150: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P18.

Fig. S151: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P18.
Fig. S152: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P20.

Fig. S153: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P22.
Fig. S154: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P22.

Fig. S155: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P23.
Fig. S156: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P23.

Fig. S157: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P24.
Fig. S158: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P24.

Fig. S159: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P25.
Fig. S160: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P25.

Fig. S161: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P37.
Fig. S162: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P37.

Fig. S163: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P38.
Fig. S164: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P40.

Fig. S165: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P13-b-PS.
Fig. S166: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of P13-b-PS.

Fig. S167: DOSY $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P13-b-PS.
Fig. S168: $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) spectrum of PLA$_{20k}$-Boc-Cys(Trt)-OH.

Fig. S169: $^{13}$C NMR (CD$_2$Cl$_2$, 101 MHz) spectrum of PLA$_{20k}$-Boc-Cys (Trt)-OH.
Fig. S170: $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) spectrum of PLA$_{20k}$-cysteine.

Fig. S171: $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) spectrum of P14-b-PLA.
**Fig. S172**: DOSY $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of a mixture of P14 and PLA$_{20k}$-Boc-Cys (Trt)-OH before coupling.

**Fig. S173**: DOSY $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P14-b-PLA.
Fig. S174: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of MeOPEG$_{2k}$ acid. DMAP as an impurity (peaks at around 3, 6.6, and 8.25 ppm).

Fig. S175: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of MeOPEG$_{2k}$ acid.
Fig. S176: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of PEG$_{2k}$ macroinitiator.

Fig. S177: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of PEG$_{2k}$ macroinitiator.
Fig. S178: $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of PEG$_{2k}$-b-P (M1).

Fig. S179: $^{13}$C NMR (CDCl$_3$, 101 MHz) spectrum of PEG$_{2k}$-b-P (M1).
Fig. S180: DOSY $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of PEG$_{2k}$-b-p (M1).
MALDI-ToF mass spectra of Polymers:

Sample preparation: A stock solution of a DCTB matrix of 20 mg/mL concentration in CHCl₃ was prepared. 1M solution of AgTFA (or NaTFA) salt in THF was also prepared. Then, 2 mg polymer solution was dissolved in 0.6 mL CHCl₃. In an Eppendorf tube, 20 μL of matrix solution, 2 μL of polymer solution, and 1 μL of salt solution were mixed homogeneously. Finally, from the mixture, 1 μL of the solution was spotted in a MALDI-ToF plate and kept for a few minutes to let the solvent evaporate. The polymer samples were calibrated against either using CSI₃ or using poly (styrene) standards.
Fig. S181: MALDI-ToF mass spectrum (DCTB, AgTFA) of P4.
Fig. S182: MALDI-ToF mass spectrum (DCTB, AgTFA) of P6. The tiny distribution corresponds to a broad spectrum, as shown above on the right-hand side, which did not match any possible non-regioselective metathesis reaction or chain end coupled products. This minimal broader peak was observed in the following spectrum too.
Fig. 5183: MALDI-ToF mass spectrum (DCTB, AgTFA) of P7.
Fig. S184: MALDI-ToF mass spectrum (DCTB, AgTFA) of P9.
Fig. S185: MALDI-ToF mass spectrum (DCTB, AgTFA) of P10.
Fig. S186: MALDI-ToF mass spectrum (DCTB, AgTFA) of P11.
**Fig. S187**: MALDI-ToF mass spectrum (DCTB, AgTFA) of P12.
**Fig. S188:** MALDI-ToF mass spectrum (DCTB, AgTFA) of P13. Elimination of HBr in high laser energy of MALDI machine, presumably, generates the above structure.
Fig. S189: MALDI-ToF mass spectrum (DCTB, AgTFA) of \textbf{P14}. 

Chemical Formula: \( \text{C}_{130}\text{H}_{148}\text{N}_{12}\text{O}_{23}\text{S}\text{Ag}^+ \)
Mono-isotopic Mass: 2511.94
Fig. S190: MALDI-ToF mass spectrum (DCTB, AgTFA) of P15.
Fig. S191: MALDI-ToF mass spectrum (DCTB, AgTFA) of P16.
Fig. S192: MALDI-ToF mass spectrum (DCTB, AgTFA) of P17 showing the difference in repeating unit of mass 94 (mass of norbornene) as isotopically resolved end group analysis was not possible (arguably, due to the presence of amineBoc group) due to unidentified degradation under MALDI-ToF high energy laser condition.
Fig. S193: MALDI-ToF mass spectrum (DCTB, AgTFA) of P18.
**Fig. S194:** MALDI-ToF mass spectrum (DCTB, AgTFA) of P19.
Fig. S195: MALDI-ToF mass spectrum (DCTB, AgTFA) of P20.

Chemical Formula: $C_{124}H_{181}N_3O_{24}Ag^+$
Exact Mass: 2246.91
Fig. S196: MALDI-ToF mass spectrum (DCTB, AgTFA) of P21.
**Fig. S197**: MALDI-ToF mass spectrum (DCTB, AgTFA) of P22.
**Fig. S198:** MALDI-ToF mass spectrum (DCTB, AgTFA) of P24.

Chemical Formula: C_{215}H_{350}O_{7}Ag<sup>+</sup>
Mono-isotopic Mass: 3099.24
Fig. 5199: MALDI-ToF mass spectrum (DCTB, AgTFA) of P25.
**Fig. S200**: MALDI-ToF mass spectrum (DCTB, AgTFA) of P34. The minor distribution matching with a methylene end group came from the ethyl vinyl ether (which was used to deactivate the ruthenium complex).

**Fig. S201**: MALDI-ToF mass spectrum (DCTB, AgTFA) of P37.
Fig. S202: MALDI-ToF mass spectrum (DCTB, AgTFA) of P38.
Fig. S203: MALDI-ToF mass spectrum (DCTB, NaTFA) of P39.
Fig. S204: MALDI-ToF mass spectrum (DCTB, NaTFA) of P42.
Fig. S205: MALDI-ToF mass spectrum (DCTB, NaTFA) of P43.
Fig. S206: MALDI-ToF mass spectrum (DCTB, AgTFA) of PEG$_{2k}$ carboxylic acid.
**Fig. S207:** MALDI-ToF mass spectrum (DCTB, AgTFA) of PEG$_{2k}$ macroinitiator. Shallow intensity peaks corresponded to monomethoxy PEG that could come from hydrolysis of PEG$_{2k}$ carboxylic acid during the reaction.
SEC traces of polymers:

**Fig. S208**: SEC (CHCl₃) trace for P1.

**Fig. S209**: SEC (CHCl₃) trace for P2.

**Fig. S210**: SEC (CHCl₃) trace for P3.
Fig. S211: SEC (CHCl₃) trace for P4.

Fig. S212: SEC (CHCl₃) trace for P5 (crude polymer).

Fig. S213: SEC (CHCl₃) trace for P5 (precipitated polymer).
Fig. S214: SEC (CHCl₃) trace for P6.

Fig. S215: SEC (CHCl₃) trace for P7.

Fig. S216: SEC (CHCl₃) trace for P8.
Fig. S217: SEC (CHCl₃) trace for P9.

Fig. S218: SEC (CHCl₃) trace for P10.

Fig. S219: SEC (CHCl₃) trace for P11.
Fig. S220: SEC (CHCl$_3$) trace for P12.

Fig. S221: SEC (CHCl$_3$) trace for P13.

Fig. S222: SEC (CHCl$_3$) trace for P14.
**Fig. S223:** SEC (CHCl$_3$) trace for P15.

**Fig. S224:** SEC (CHCl$_3$) trace for P16.

**Fig. S225:** SEC (CHCl$_3$) trace for P17.
Fig. S226: SEC (CHCl$_3$) trace for P18.

Fig. S227: SEC (CHCl$_3$) trace for P19.

Fig. S228: SEC (CHCl$_3$) trace for P20.
Fig. S229: SEC (CHCl₃) trace for P21.

Fig. S230: SEC (CHCl₃) trace for P22.

Fig. S231: SEC (CHCl₃) trace for P23.
Fig. S232: SEC (CHCl₃) trace for P24.

Fig. S233: SEC (CHCl₃) trace for P25.

Fig. S234: SEC (CHCl₃) trace for P28.
**Fig. S235**: SEC (CHCl₃) trace for P30.

**Fig. S236**: SEC (CHCl₃) trace for P31.

**Fig. S237**: SEC (CHCl₃) trace for P32.
Fig. S238: SEC (CHCl₃) trace for P33.

Fig. S239: SEC (CHCl₃) trace for P34.

Fig. S240: SEC (CHCl₃) trace for P35.
Fig. S241: SEC (CHCl$_3$) trace for P37.

Fig. S242: SEC (CHCl$_3$) trace for P38.

Fig. S243: SEC (CHCl$_3$) trace for P39.
Fig. S244: SEC (CHCl₃) trace for P40.

Fig. S245: SEC (CHCl₃) trace for P41.

Fig. S246: SEC (CHCl₃) trace for P42.
Fig. S247: SEC (CHCl₃) trace for P43.

Fig. S248: SEC (DMF) trace for PEG₂k macroinitiator.

Fig. S249: SEC (CHCl₃) trace for PLA₂₀k- Boc-Cys (Trt)-OH.
Fig. S250: SEC (DMF) trace for PEG$_{2k}$-b-P(M1).
High-Resolution Mass Spectrometric Data:

Fig. S251: HR-MS spectrum of CTA1.

Fig. S252: HR-MS spectrum of CTA3.
Fig. S253: HR-MS spectrum of CTAS.

Fig. S254: HR-MS spectrum of I6.
Fig. S255: HR-MS spectrum of CTA7.

Fig. S256: HR-MS spectrum of CTA9.
Fig. S257: HR-MS spectrum of CTA11.
Fig. S258: HR-MS spectrum of CTA12.

Fig. S259: HR-MS spectrum of CTA13.
Fig. S260: HR-MS spectrum of CTA23.

Fig. S261: HR-MS spectrum of CTA24.
Fig. S262: HR-MS spectrum of CTA25.
**Kinetic studies:**

**Determination of rate constants:**

The procedure is previously described in this work and is as follows- In an NMR tube, 1,3,5 trimethoxy benzene (as an internal standard), G3 (1 equiv., 0.0011 mmol, 1 mg), 3 bromopyridine (60 equiv., 0.067 mmol, 11 mg) and CTA3 (50 equiv., 0.056 mmol, 11.8 mg) were mixed in 0.9 mL CDCl₃ and ¹H NMR were measured. Then, M1 (1000 equiv., 1.13 mmol, 200 mg) dissolved in 0.2 mL was added quickly, and ¹H NMR was measured overtime (See Fig. S6). 3 bromopyridine was added to decrease the propagation as well as chain transfer events to measure the individual rate constants for CTA (CTA3) and monomer (M1) consumptions more precisely.

![化学反应图](image)

**Fig. S263:** Plot of ln(\(\{M_1\}_0/M_1\)) against time.

- **slope =** 0.01531
- **\(R^2 = 0.9967\)**
Here, \(\{M_1\}_0\) correspond to the initial concentration of monomer (\(M_1\)) and \(M_1\) represents the concentration of monomer at a given time. \(\ln(\{M_1\}_0/M_1)\) vs time provided a linear correlation and the slope of the linear regression corresponded to the rate constant for monomer consumption (\(k\)) under the given reaction conditions. Thus, \(k_{M_1} = 0.01531\ \text{min}^{-1}\). Similarly, rate constant for CTA consumption (\(k_{CTA}\)) was also determined utilizing the same reaction conditions as follows:

![Graph with slope 0.01434 and R² 0.9881](image)

**Fig. S264**: Plot of \(\ln(\{CTA3\}_0/CTA3)\) against time.

From the linear plot, slope i.e. CTA3 consumption rate constant (\(k_{CTA3}\)) is 0.01434 min\(^{-1}\).

Thus, as predicted, rate constants for the consumption of both monomer and CTA are of the same magnitude which definitively proved the proposed kinetically controlled chain transfer mechanism.

Additionally, the measured linear relation between \(\ln([S_0]/[S_i])\) (\(S=\) substrate) and time confirmed the first-order dependence in concentration of both monomer (\(M_1\)) and CTA (\(CTA3\)) as expected for a chain-growth process.
CTA concentration effects on kinetically controlled ROMP:

To understand how concentration of chain transfer agents influence kinetics the following \(^1\)H NMR experiments were conducted where concentration of G3 (1 equiv.), monomer (1000 equiv.) and 3 bromopyridine (60 equiv.) were kept constant and CTA concentration were varied (20 equiv./40 equiv. /50 equiv.).

General procedure is as follows-

In an NMR tube, 1,3,5 trimethoxy benzene (as an internal standard), M1 (1000 equiv., 1.13 mmol, 200 mg), 3 bromopyridine (60 equiv., 0.067 mmol, 11 mg) and CTA3 (xx equiv., xx mmol, xx mg) were mixed in 0.9 mL CDCl\(_3\) and \(^1\)H NMR were measured. Then, G3 (1 equiv., 0.0011 mmol, 1 mg) dissolved in 0.2 mL was added quickly, and \(^1\)H NMR was measured overtime.
Fig. S265: $^1$H NMR (CDCl$_3$, 300 MHz) of reaction of CTA3 (20 equiv.), 3 bromopyridine (60 equiv.) and M1 (1000 equiv.) with G3 (1 equiv.) in CDCl$_3$. 
Fig. S266: A plot of monomer (M1, 1000 equiv.) and CTA3 (20 equiv.) conversion vs. time determined by $^1$H NMR spectroscopy (CDCl$_3$, 300 MHz) showing both monomer and CTA were consumed at a similar rate during the polymerization, thus, suggesting a kinetically controlled mechanism.
Fig. S267: $^1$H NMR (CDCl$_3$, 300 MHz) of reaction of CTA3 (40 equiv.), 3 bromopyridine (60 equiv.) and M1 (1000 equiv.) with G3 (1 equiv.) in CDCl$_3$. 
Fig. S268: A plot of monomer (M1, 1000 equiv.) and CTA3 (40 equiv.) conversion vs. time determined by $^1$H NMR spectroscopy (CDCl$_3$, 300 MHz) showing both monomer and CTA were consumed at a similar rate during the polymerization, thus, suggesting a kinetically controlled mechanism.
Fig. S269: $^1$H NMR (CDCl$_3$, 300 MHz) of reaction of CTA3 (50 equiv.), 3 bromopyridine (60 equiv.) and M1 (1000 equiv.) with G3 (2.1 equiv.) in CDCl$_3$. 
Fig. S270: A plot of monomer (M1, 1000 equiv.) and CTA3 (50 equiv.) conversion vs. time determined by $^1$H NMR spectroscopy (CDCl$_3$, 300 MHz) showing both monomer and CTA were consumed at a similar rate during the polymerization, thus, suggesting a kinetically controlled mechanism.
Fig. S271: A plot of monomer (M1, 1000 equiv.) conversion vs. time at different concentration of CTA3 (20 equiv. /40 equiv. /50 equiv.) determined by $^1$H NMR spectroscopy (CDCl$_3$, 300 MHz) showing rate of consumption of M1 decreased with the increase in the concentration of CTA3.
Fig. S272: Plot of $\ln ([M_1]_0/M_1)$ against time at different CTA3 concentration.

Table S6: Data for the determination of $k_{M1}$ for different CTA3 concentration in CDCl₃:

<table>
<thead>
<tr>
<th>Degree of polymerization (DP)</th>
<th>G3:CTA3:M1⁰</th>
<th>Concentration of CTA3 (mmol/L)</th>
<th>R² value</th>
<th>$k_{M1}$ (1/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1:20:1000</td>
<td>20.00</td>
<td>0.9921</td>
<td>0.03235</td>
</tr>
<tr>
<td>25</td>
<td>1:40:1000</td>
<td>40.01</td>
<td>0.9795</td>
<td>0.01888</td>
</tr>
<tr>
<td>20</td>
<td>1:50:1000</td>
<td>50.02</td>
<td>0.9967</td>
<td>0.01531</td>
</tr>
</tbody>
</table>

a: 60 equiv. of 3 bromopyridine was used to decrease the overall rate of the polymerization.

Thus, as the concentration of the CTA3 increased, rate constant for the consumption of M1 ($k_{M1}$) decreased i.e. overall time for polymerization increases. In other words, rate of polymerization is inversely proportional to the concentration of the CTA.
Structure-property relationship for monosubstituted 1,3 diene CTAs

Hammett Plot:

To determine the Hammett plot, first an electro-neutral CTA (CTA27) was synthesized via following Wittig olefination reaction-

\[
\text{[Olefin]} + \text{MePPh}_3\text{Br}^- \xrightarrow{\text{KO}^1\text{Bu}} \text{[CTA]} \quad \text{(in THF)}
\]

Methyltriphenylphosphonium bromide (1.1 equiv., 58.26 mmol, 21 g) was dissolved in 100 mL THF and cooled to 0°C. Solid potassium tert-butoxide (1.1 equiv., 58.26 mmol, 6.5 g) was added in one shot, and the THF solution immediately became yellow. The solution was stirred at 0°C for 10 mins. trans-cinnamaldehyde (1 equiv., 52.97 mmol, 7 g, 6.65 mL) was added slowly to the precooled mixture. Then, the resulting solution was stirred at room temperature for 15 mins. THF was evaporated under reduced pressure, and crude was dissolved in dichloromethane and worked up against brine two times. The organic part was dried over magnesium sulfate, concentrated under reduced pressure, and further purified by column chromatography (only hexanes) to obtain CTA27 as a colorless liquid (6.6 g, 52.97 mmol, 96% yield).

Fig. S273: $^1$H NMR (CDCl$_3$, 300 MHz) spectrum of CTA27. The peaks in the aliphatic region (0.7-1.4 ppm) is from grease as the eluent for column chromatography was pure hexanes.
Fig. S274: $^{13}$C NMR (CDCl$_3$, 300 MHz) spectrum of CTA27.

CTAs considered for Hammett studies:

![CTA27](image1.png)  ![CTA2](image2.png)  ![CTA3](image3.png)  ![CTA8](image4.png)

In a 5 mL glass vial, M1 (30 equiv., 0.10 mmol, 18 mg), CTA8 (15 equiv., 0.05 mmol, 9.6 mg), CTA2 (15 equiv., 0.05 mmol, 8.1 mg), CTA3 (15 equiv., 0.05 mmol, 10.6 mg), CTA27 (15 equiv., 0.05 mmol, 6.6 mg) and n-decane (15 equiv., 0.05 mmol, 9.9 µL) were dissolved in 1.7 mL of CHCl$_3$. 80 µL of this solution was taken and injected for gas chromatography–mass spectrometry (GC-MS) measurement to give initial area ($A_0$) of the substrates. Then, G3 (1 equiv., 3.4 µmol, 3 mg) was weighed into a separate vial and the CHCl$_3$ mixture was added...
to the vial in one-shot. The resulting yellow solution was kept at room temperature for 5 mins. Then, 80 µL of the resulting solution was taken for another GC-MS measurement. The amount of CTA consumed in the process was determined by following GC-MS analysis with respect to n-decane.

It is noteworthy that initial attempts were made to study Hammett relationship using stoichiometric ratio of Grubbs’ catalyst which led to erroneous results. This may be because change in concentration of the mixture, after addition of catalyst, is significantly higher when stoichiometric amount of catalyst was used, thus affecting the overall area (concentration of unreacted species) measured via GC-MS.

![Chemical structure](image)

Table S7: Data analysis for Hammett plot

<table>
<thead>
<tr>
<th>Entry</th>
<th>GC-MS peak</th>
<th>Initial area (A_0)</th>
<th>Final area (A)</th>
<th>(\ln(A/A_0))</th>
<th>(\frac{\ln(A/A_0)}{\ln(A_H/A_{H0})} = K_{rel})</th>
<th>(\log K_{rel})</th>
<th>(\sigma_{para}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTA27 (H)</td>
<td>7.88</td>
<td>4813862</td>
<td>3213345</td>
<td>-0.404187</td>
<td>1</td>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>CTA2 (OMe)</td>
<td>10.47</td>
<td>7091024</td>
<td>3820190</td>
<td>-0.618529</td>
<td>1.53030</td>
<td>0.42546</td>
<td>-0.27</td>
</tr>
<tr>
<td>CTA3 (Br)</td>
<td>10.66</td>
<td>5131951</td>
<td>3607275</td>
<td>-0.352533</td>
<td>0.87220</td>
<td>-0.05938</td>
<td>0.23</td>
</tr>
<tr>
<td>CTA8 (CO(_2)Me)</td>
<td>11.55/12.01</td>
<td>6032684</td>
<td>4648163</td>
<td>-0.260719</td>
<td>0.64504</td>
<td>-0.19041</td>
<td>0.44</td>
</tr>
</tbody>
</table>
**Fig. S275:** Hammett plot ($\log K_{rel}$ vs $\sigma_{para}$) for differently para-substituted CTAs differing in electron donation capabilities.

From the slope, the reaction constant ($\rho$) is determined to be -0.88 which suggested the reaction builds positive charge during the metathesis mechanism. Therefore, electron-donation CTA (such as CTA2) will stabilise the transition state most (possessing highest $\log K_{rel}$ value) and CTA8 will destabilise the process. This further explain why electron rich substrates such as this kind of CTAs were extremely successful for this catalytic ROMP mechanism.

**Table S8: Synthesis of higher molecular weight polymers by catalytic ROMP:**

<table>
<thead>
<tr>
<th>Entry</th>
<th>CTA</th>
<th>Monomer (M)</th>
<th>G3:CTA: Monomer ratio</th>
<th>$M_n$ (Non-catalytic, M/G3) (kDa)</th>
<th>$M_n$ (Catalytic, M/CTA) kDa</th>
<th>$M_n$ (SEC, CHCl$_3$) kDa</th>
<th>$D$</th>
<th>Polymer Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P45</td>
<td>CTA2</td>
<td>M1</td>
<td>1:20:10000</td>
<td>1770</td>
<td>88.5</td>
<td>83.0</td>
<td>1.65</td>
<td>92</td>
</tr>
<tr>
<td>P46</td>
<td>CTA2</td>
<td>M1</td>
<td>1:20:20000</td>
<td>3540</td>
<td>177</td>
<td>165.0</td>
<td>1.68</td>
<td>92</td>
</tr>
</tbody>
</table>
P45:

G3: 1.0 mg, CTA2: 3.6 mg, M1: 2.0 g. Concentration (M1): 1 (M). DCM: 11.3 mL.

P46:

G3: 0.5 mg, CTA2: 1.8 mg, M1: 2.0 g. Concentration (M1): 1 (M). DCM: 11.3 mL.

P45 and P46 were prepared using the general procedure described before. In both cases, >99% conversion of monomer was observed as determined from crude $^1$H NMR spectroscopy from the polymerization mixture given below.

![Crude $^1$H NMR (CDCl$_3$, 400 MHz) spectra of polymerization mixture of P45 showing olefinic region. Absence of any peak at 6.26 ppm confirmed full consumption of M1.](image)
Fig. S277: Crude $^1$H NMR (CDCl$_3$, 400 MHz) spectra of polymerization mixture of P46 showing olefinic region.

SEC traces of P45 and P46:

Fig. S278: SEC (CHCl$_3$) trace for P45.
Fig. S279: SEC (CHCl₃) trace for P46.
Polymer pictures:

a) 

b) 

Fig. S280: a) Image of P15, b) Image of P16.

References

