

Supporting Information

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

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Materials and Instruments

Materials

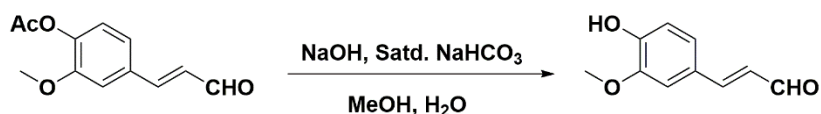
(2E, 4E) -5-phenylpenta-2, 4-dienoic acid (**CTA15**) was purchased from Fluorochem. (2E,4E)-5-(benzo[d][1,3]dioxol-5-yl)penta-2,4-dienoic acid (**CTA16**), Piperine (**CTA22**), (1E,3E,5E)-1,6-diphenylhexa-1,3,5-triene (**CTA26**) and Norbornene (**M2**) were purchased from Sigma-Aldrich. Methoxy poly (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_2Cl_2 , CDCl_3 , and DMSO-D_6) were purchased from Cambridge Isotope Laboratories, Inc. Grubbs 3rd generation catalyst (**G3**) was prepared as reported previously.¹

Instruments

All ^1H 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 ^1H and ^{13}C were given in ppm relative to the residual solvent peak (CDCl_3 : 7.27 for ^1H ; CDCl_3 : 77.16 for ^{13}C and CD_2Cl_2 : 5.32 for ^1H ; CD_2Cl_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):

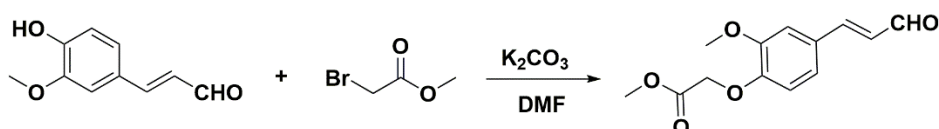
CTA1 (methyl (E)-2-(4-(buta-1,3-dien-1-yl)-2-methoxyphenoxy)acetate)



I1

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.

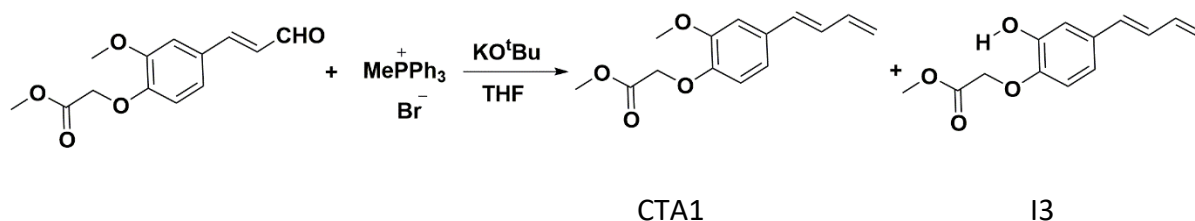
^1H NMR (CDCl_3 , 400 MHz) δ ppm: 3.96 (s, 3 H), 5.99 (s, 1 H), 6.60 (dd, $J=15.83$, 7.76 Hz, 1 H), 6.97 (d, $J=8.19$ Hz, 1 H), 7.03 - 7.19 (m, 2 H), 7.41 (d, $J=15.89$ Hz, 1 H), 9.66 (d, $J=7.70$ Hz, 1 H)
 ^{13}C NMR (CDCl_3 , 101 MHz) δ ppm: 56.0, 76.6, 77.2, 77.3, 109.4, 114.9, 124.0, 126.4, 126.6, 146.9, 148.9, 153.0, 193.5.



I2

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.

^1H 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.

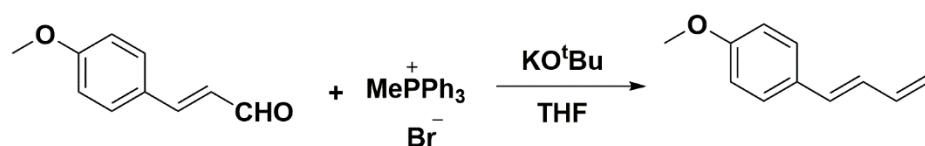


Methyltriphenylphosphonium bromide (1.2 equiv., 10.55 mmol, 3.77 g) was dissolved in 40 mL THF and cooled to 0°C . Solid potassium tert-butoxide (1.2 equiv., 10.55 mmol, 1.18 g) was added in one shot, and the THF solution immediately became yellow. The solution was stirred at 0°C for 10 mins. I2 (1 equiv., 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 I3 as a bright yellow solid (400 mg, 1.7 mmol, 19.4% yield).

CTA1- ^1H 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.

I3- ^1H 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.

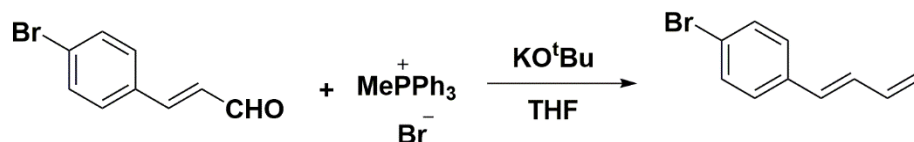
CTA2 ((E)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene)



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).

¹H NMR (CDCl₃, 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) ¹³C NMR (CDCl₃, 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.

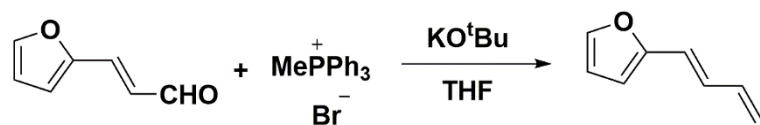
CTA3 ((E)-1-bromo-4-(buta-1,3-dien-1-yl)benzene)



Methyltriphenylphosphonium bromide (1.2 equiv., 2.8 mmol, 1 g) was dissolved in 10 mL 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).

¹H NMR (CDCl₃, 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) ¹³C NMR (CDCl₃, 101 MHz) δ ppm: 76.6, 77.3, 118.3, 121.3, 127.8, 130.2, 131.5, 131.7, 136.0, 136.8.

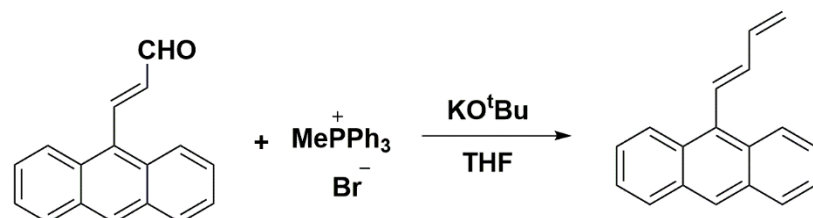
CTA4 ((E)-2-(buta-1,3-dien-1-yl)furan)



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)

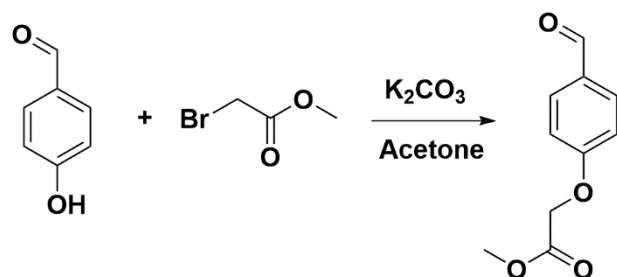


Methyltriphenylphosphonium bromide (1.2 equiv., 5.16 mmol, 1.85 g) was dissolved in 20 mL THF and cooled to 0°C. Solid potassium tert-butoxide (1.5 equiv., 6.45 mmol, 725 mg) was added in one shot, and the THF solution immediately became yellow. The solution was stirred at 0°C for 10 mins. 3-(9-Anthryl) 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,

101 MHz) δ ppm: 76.3, 76.6, 117.7, 124.7, 125.0, 125.5, 126.1, 128.3, 128.5, 129.1, 131.1, 132.0, 136.8, 137.9.

CTA6 (methyl 2-(4-(buta-1,3-dien-1-yl)phenoxy)acetate)

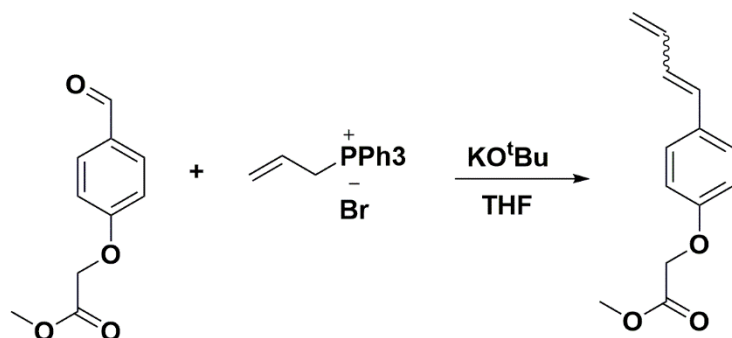


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In an oven-dried round bottom flask, 4-Hydroxybenzaldehyde (1 equiv., 57.32 mmol, 7 g) and potassium carbonate (1.6 equiv., 94 mmol, 13 g) were mixed, and 44 mL acetone was added to make a slurry. To the suspension, methyl bromoacetate (1.2 equiv., 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.

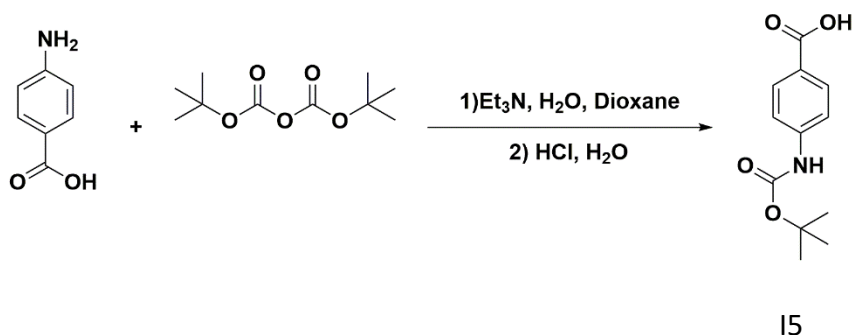
1H NMR ($CDCl_3$, 400 MHz) δ ppm: 3.75 (s, 4 H), 4.68 (s, 2 H), 6.95 (m, $J=8.80$ Hz, 2 H), 7.78 (m, $J=8.80$ Hz, 2 H), 9.83 (s, 1 H) ^{13}C NMR ($CDCl_3$, 101 MHz) δ ppm: 25.3, 52.1, 64.8, 76.6, 77.3, 114.6, 130.5, 131.7, 162.3, 168.3, 190.4.



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.

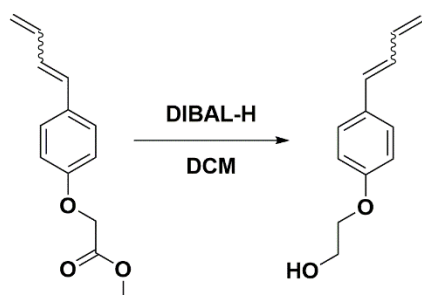
CTA7 (2-(4-(buta-1,3-dien-1-yl)phenoxy)ethyl 4-((tert-butoxycarbonyl)amino)benzoate)



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.

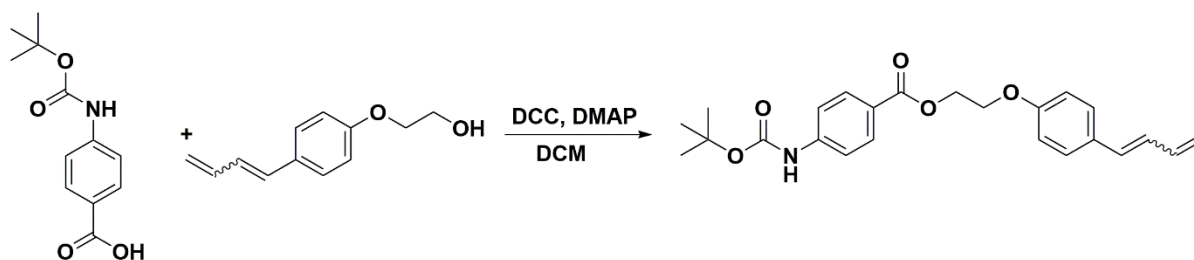
^1H NMR (300 MHz, CDCl_3) δ ppm: 1.50 - 1.58 (m, 10 H), 6.68 - 6.87 (m, 1 H), 7.43 - 7.54 (m, 2 H), 7.98 - 8.11 (m, 2 H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm: 28.2, 76.6, 77.2, 77.4, 81.4, 117.4, 123.3, 131.6, 143.4, 152.1, 170.4.



16

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%).

^1H 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.

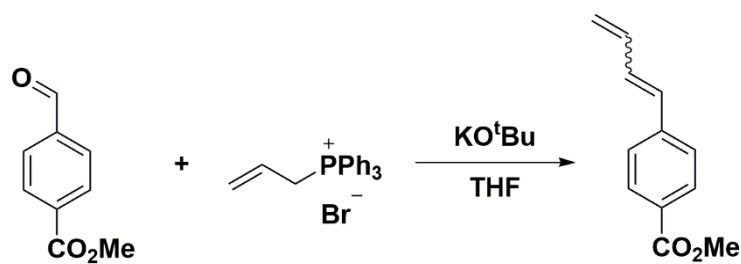


15 (1 equiv., 2.1 mmol, 500 mg), 16 (1 equiv., 2.1 mmol, 401 mg), and DMAP (0.1 equiv., 0.21 mmol, 25 mg) were dissolved in 15 mL DCM and cooled to 0°C . DCC (1.1 equiv., 2.5 mmol,

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%).

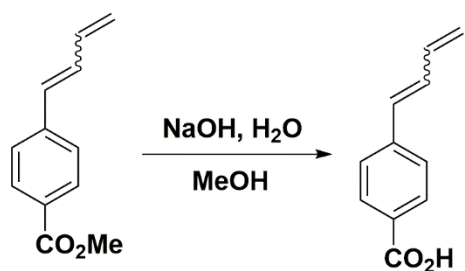
^1H NMR (CDCl_3 , 400 MHz) δ ppm: 1.54 (s, 9 H), 4.27 - 4.39 (m, 2 H), 4.59 - 4.72 (m, 2 H), 5.18 - 5.24 (m, 1 H), 5.26 - 5.40 (m, 1 H), 6.13 - 6.27 (m, 1 H), 6.35 - 6.45 (m, 1 H), 6.45 - 6.59 (m, 1 H), 6.59 - 6.73 (m, 1 H), 6.79 - 6.98 (m, 3 H), 7.28 - 7.31 (m, 1 H), 7.31 - 7.48 (m, 3 H), 7.93 - 8.07 (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)



Allyltriphenylphosphonium 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%).

^1H 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.

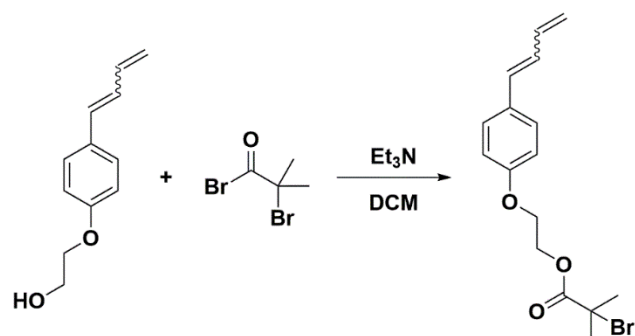


17

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 **17** as a white solid (890 mg, 5.1 mmol, 96% yield). The crude was pure enough to use in the following steps.

¹H 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) ¹³C 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.

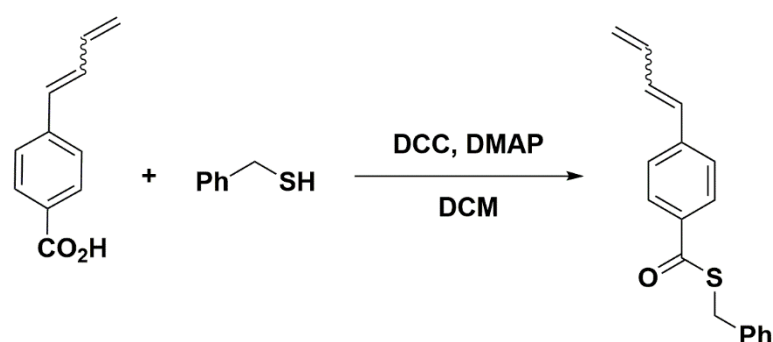
CTA9 (2-(4-(buta-1,3-dien-1-yl)phenoxy)ethyl 2-bromo-2-methylpropanoate)



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).

^1H 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) ^{13}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)

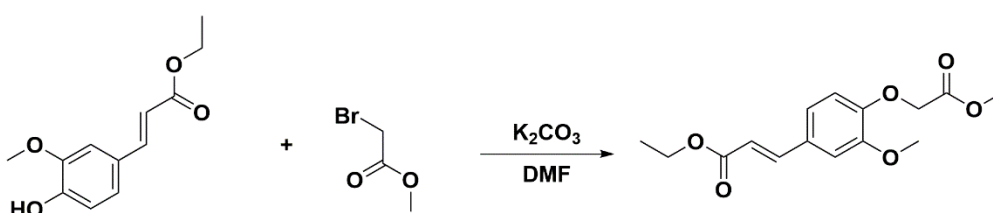


In an oven-dried round bottom flask, I7 (1.0 equiv., 1.43 mmol, 250 mg), benzyl mercaptan (1.1 equiv., 1.58 mmol, 196 mg), and DMAP (0.1 equiv., 0.14 mmol, 18 mg) were taken and dissolved in 6 mL dry DCM. The resulting solution was cooled to 0°C . Then, DCC (1.2 equiv., 1.72 mmol, 356 mg) was dissolved 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.

¹H NMR (CDCl₃, 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) ¹³C NMR (CDCl₃, 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.

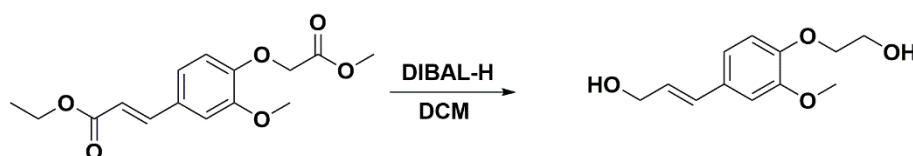
CTA11 (1-(2-(4-((E)-buta-1,3-dien-1-yl)-2-methoxyphenoxy)ethyl) 10-(2-(4-((E)-buta-1,3-dien-1-yl)-3-methoxyphenoxy)ethyl) decanedioate)



18

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 18 (13.2 g, 44.8 mmol, 99%). The crude obtained was used in the next step without any further purification.

¹H NMR (CDCl₃, 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) ¹³C NMR (CDCl₃, 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.



19

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.

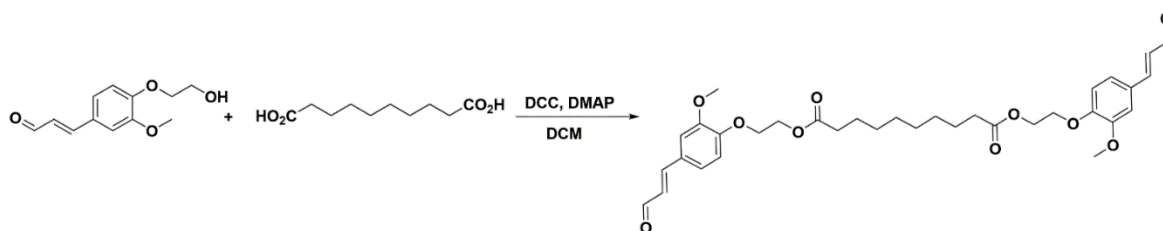
^1H NMR (CDCl_3 , 400 MHz) δ ppm: 1.71 - 1.80 (m, 1 H), 2.82 (t, $J=6.48$ Hz, 1 H), 3.84 - 3.99 (m, 5 H), 4.09 - 4.17 (m, 2 H), 4.28 - 4.36 (m, 2 H), 6.25 (dt, $J=15.86$, 5.88 Hz, 1 H), 6.54 (dt, $J=15.80$, 1.57 Hz, 1 H), 6.82 - 6.98 (m, 3 H) ^{13}C NMR (CDCl_3 , 101 MHz) δ ppm: 55.7, 61.2, 63.7, 71.3, 76.6, 77.3, 109.4, 114.5, 119.7, 127.0, 130.8, 130.9, 147.8, 149.7.



I10

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).

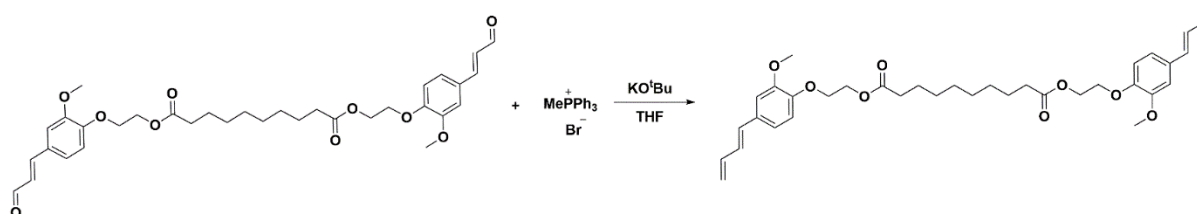
^1H NMR (CDCl_3 , 400 MHz) δ ppm: 2.44 (s, 1 H), 3.92 (s, 3 H), 3.95 - 4.07 (m, 2 H), 4.12 - 4.25 (m, 2 H), 6.63 (dd, $J=15.83$, 7.76 Hz, 1 H), 6.95 (d, $J=8.31$ Hz, 1 H), 7.05 - 7.22 (m, 2 H), 7.42 (d, $J=15.89$ Hz, 1 H), 9.68 (d, $J=7.70$ Hz, 1 H) ^{13}C NMR (CDCl_3 , 101 MHz) δ ppm: 55.9, 61.1, 70.8, 76.6, 77.2, 77.3, 110.3, 113.5, 123.2, 127.0, 127.7, 149.9, 151.0, 152.5, 193.5.



111

In a 50 mL oven-dried round bottom flask, sebacic acid (1 equiv., 0.5 mmol, 100 mg), 110 (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 111 as a white solid (150 mg, 0.25 mmol, 50% yield).

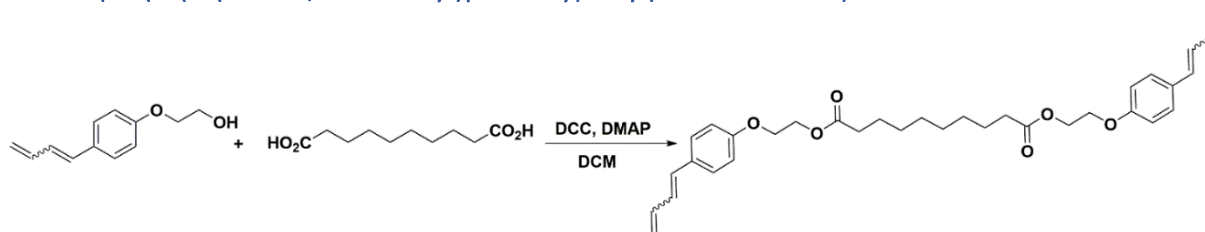
¹H NMR (CDCl₃, 400 MHz) δ ppm: 1.22 - 1.33 (m, 10 H), 1.59 - 1.67 (m, 5 H), 2.34 (t, *J*=7.52 Hz, 4 H), 3.91 (s, 6 H), 4.24 - 4.38 (m, 4 H), 4.48 (t, *J*=4.95 Hz, 4 H), 6.64 (d, *J*=7.70 Hz, 1 H), 6.60 (d, *J*=7.70 Hz, 1 H), 6.94 (d, *J*=8.31 Hz, 2 H), 7.02 - 7.21 (m, 4 H), 7.44 (s, 1 H), 7.40 (s, 1 H), 9.67 (d, *J*=7.70 Hz, 2 H) ¹³C NMR (CDCl₃, 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. 111 (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.

^1H NMR (CDCl_3 , 400 MHz) δ ppm: 1.22 - 1.36 (m, 10 H), 1.58 - 1.67 (m, 4 H), 2.33 (t, $J=7.58$ Hz, 4 H), 3.83 - 3.95 (m, 6 H), 4.24 (dd, $J=5.56, 4.34$ Hz, 4 H), 4.34 - 4.52 (m, 4 H), 5.07 - 5.22 (m, 2 H), 5.22 - 5.38 (m, 2 H), 6.42 - 6.59 (m, 4 H), 6.59 - 6.74 (m, 2 H), 6.81 - 6.89 (m, 2 H), 6.89 - 7.04 (m, 4 H) ^{13}C NMR (CDCl_3 , 101 MHz) δ ppm: 24.8, 29.0, 34.1, 55.9, 62.6, 67.3, 76.6, 77.2, 77.3, 109.5, 114.2, 116.8, 119.7, 128.2, 131.3, 132.4, 137.1, 147.8, 149.8, 173.7.

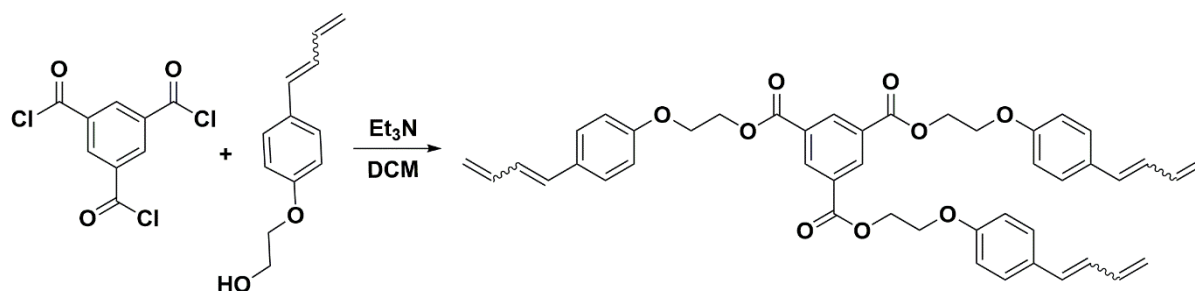
CTA12 (bis(2-(4-(buta-1,3-dien-1-yl)phenoxy)ethyl) decanedioate)



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.

^1H 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.

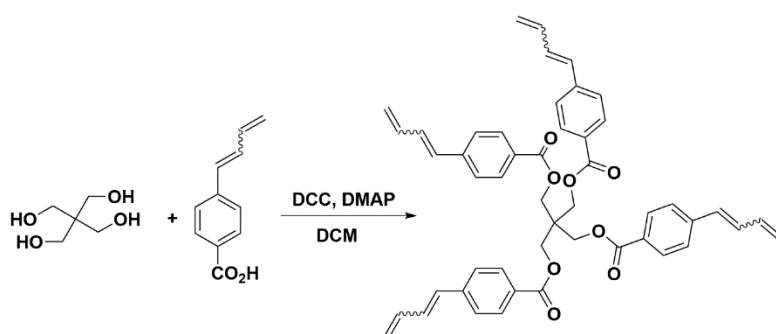
CTA13 (tris(2-(4-(buta-1,3-dien-1-yl)phenoxy)ethyl) benzene-1,3,5-tricarboxylate)



A mixture of 1,3,5-Benzenetricarbonyl trichloride (1 equiv., 1.0 mmol, 266 mg) and I6 (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.

^1H 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, 137.2, 157.5, 164.8.

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

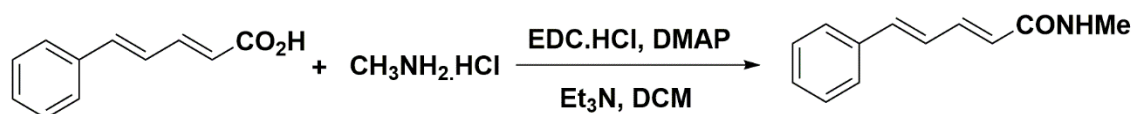


In an oven-dried round bottom flask, pentaerythritol (1 equiv., 0.47 mmol, 64.2 mg), I7 (4.2 equiv., 1.98 mmol, 345 mg), and DMAP (0.5 equiv., 0.24 mmol, 29 mg) were taken and dissolved in 5 mL dry DCM. The resulting solution was cooled to 0°C . Then, DCC (4.5 equiv., 2.12 mmol, 438 mg) was dissolved 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 NMR (CDCl₃, 400 MHz) δ 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 NMR (CDCl₃, 101 MHz) δ 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.

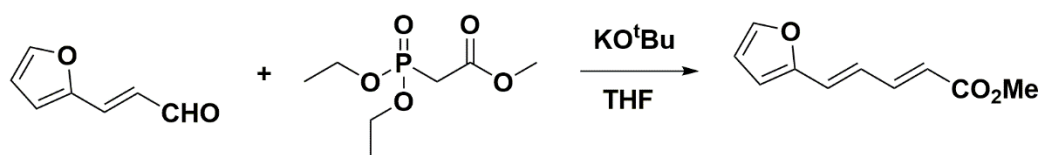
CTA17 ((2E,4E)-N-methyl-5-phenylpenta-2,4-dienamide)



In a 50mL oven-dried round bottom flask, (2E, 4E) -5-phenylpenta-2, 4-dienoic acid (**CTA15**) (1 equiv., 2.87 mmol, 500 mg), methylamine 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 NMR (CDCl₃, 400 MHz) δ 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 NMR (CDCl₃, 101 MHz) δ 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.

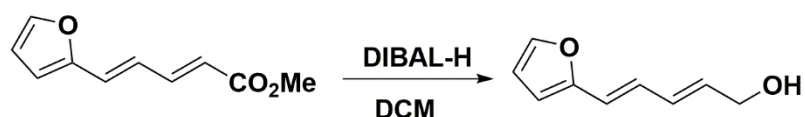
CTA18 ((2E,4E)-5-(furan-2-yl)penta-2,4-dienal)



I12

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 15mins. 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 15mins. 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.

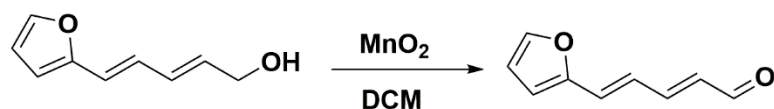
¹H NMR (300 MHz, CDCl₃) δ ppm: 3.77 (s, 3 H), 5.99 (dt, *J*=15.27, 0.71 Hz, 1 H), 6.45 (dd, *J*=2.20, 1.28 Hz, 2 H), 6.62 - 6.87 (m, 2 H), 7.32 - 7.50 (m, 2 H) ¹³C NMR (75 MHz, CDCl₃) δ ppm: 51.5, 76.5, 77.2, 77.4, 111.8, 112.1, 120.6, 124.5, 127.0, 143.6, 144.3, 152.1, 167.4.



I13

I12 (1 equiv., 6.91 mmol, 1.23 g) was dissolved in 15mL 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.

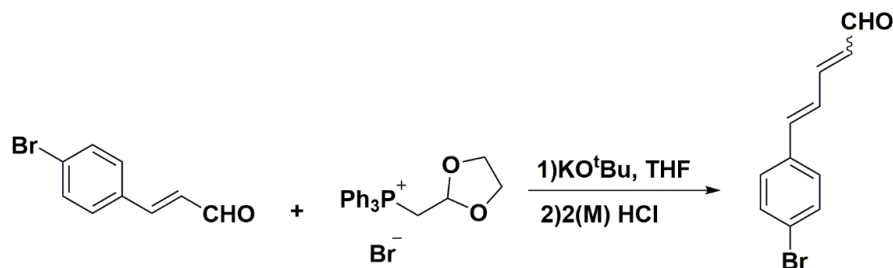
^1H NMR (CDCl_3 , 400 MHz) δ ppm: 2.11 - 2.41 (m, 1 H), 4.21 (dt, $J=5.90, 0.90$ Hz, 2 H), 5.86 - 6.03 (m, 1 H), 6.18 - 6.48 (m, 4 H), 6.60 - 6.80 (m, 1 H), 7.36 (dd, $J=1.77, 0.31$ Hz, 1 H) ^{13}C NMR (CDCl_3 , 101 MHz) δ ppm: 63.0, 76.6, 77.3, 108.3, 111.5, 120.1, 126.7, 130.9, 132.6, 142.0, 152.9.



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** (650mg, 5.39mmol, 87% yield).

^1H NMR (CDCl_3 , 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 (CDCl_3 , 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)



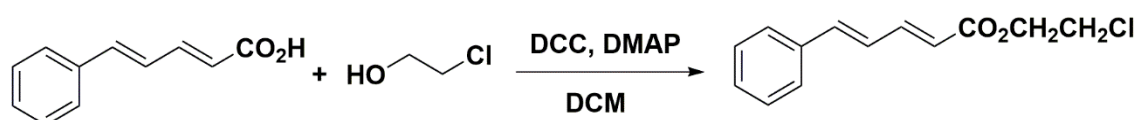
In an oven-dried Schlenk flask, (1,3-Dioxolan-2-ylmethyl) triphenylphosphonium bromide (2.6 equiv., 6.17 mmol, 2.65 g) was dissolved in 15mL THF and cooled to 0°C . Potassium tert-butoxide (3 equiv., 7.11 mmol, 800 mg) was added, and the solution immediately turned yellow. The resulting solution was stirred at that temperature for 20 mins. Then 3-(4-Bromophenyl) acrylaldehyde (1 equiv., 2.37 mmol, 500 mg) was dissolved in 2mL THF and added to the mixture dropwise over 10 mins. The flask was warmed to room temperature and stirred overnight. 5mL water was added to the same flask, followed by 5mL 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 (CDCl_3 , 400 MHz) δ ppm: 5.99 (ddt, $J=10.99, 7.29, 0.95, 0.95$ 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) ^{13}C NMR (CDCl_3 , 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 (CDCl_3 , 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) ^{13}C NMR (CDCl_3 , 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.

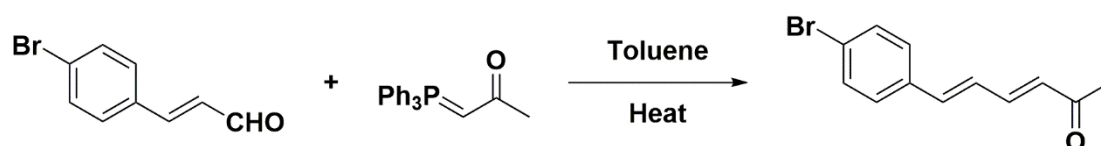
CTA20 (2-chloroethyl (2E,4E)-5-phenylpenta-2,4-dienoate)



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).

^1H NMR (CDCl_3 , 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)

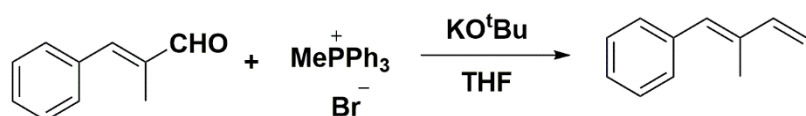


3-(4-Bromophenyl) acrylaldehyde (1 equiv., 3.17 mmol, 670 mg) and 1-(triphenylphosphoranylidene)-2-propanone (1.5 equiv., 4.72 mmol, 1.5 g) were dissolved in 30 mL of toluene and heated at 85°C for overnight. TLC showed incomplete conversion of

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).

^1H NMR (CDCl_3 , 400 MHz) δ ppm: 2.32 (s, 3 H), 6.28 (d, $J=15.41$ Hz, 1 H), 6.79 - 6.97 (m, 2 H), 7.21 - 7.40 (m, 3 H), 7.45 - 7.60 (m, 2 H). ^{13}C NMR (CDCl_3 , 101 MHz) δ 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.

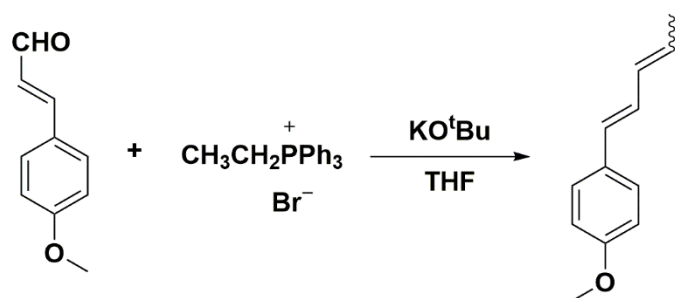
CTA23 ((E)-(2-methylbuta-1,3-dien-1-yl)benzene)



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. α -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).

^1H NMR (CDCl_3 , 400 MHz) δ ppm: 1.97 - 2.06 (m, 3 H), 5.10 - 5.21 (m, 1 H), 5.28 - 5.39 (m, 1 H), 6.45 - 6.67 (m, 2 H), 7.17 - 7.46 (m, 5 H). ^{13}C NMR (CDCl_3 , 101 MHz) δ ppm: 13.1, 76.6, 77.3, 112.9, 126.6, 128.1, 129.2, 131.6, 135.9, 137.7, 141.8.

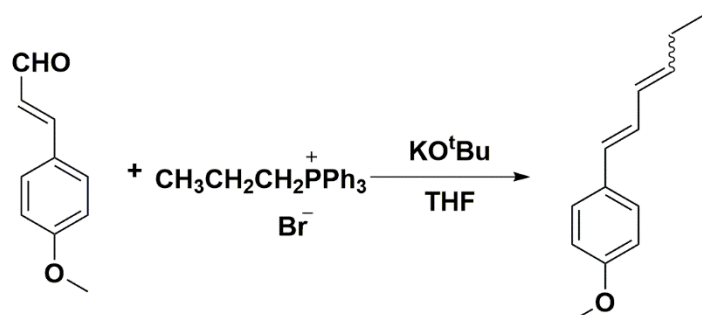
CTA24 (1-methoxy-4-((1E)-penta-1,3-dien-1-yl)benzene)



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).

¹H NMR (CDCl₃, 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) ¹³C NMR (CDCl₃, 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)

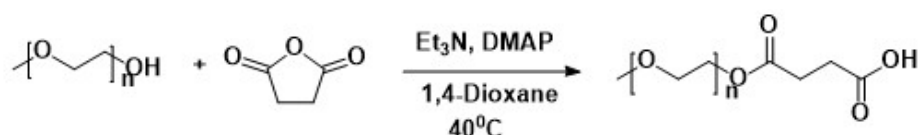


Propyltriphenylphosphonium bromide (1.2 equiv., 11.1 mmol, 4.3 g) was dissolved in 20 mL THF and cooled to 0°C. Solid potassium tert-butoxide (1.2 equiv., 11.1 mmol, 1.25 g) was added in one shot, and the THF solution immediately became yellow. The solution was stirred at 0°C for 10 mins. Trans-p-methoxycinnamaldehyde (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).

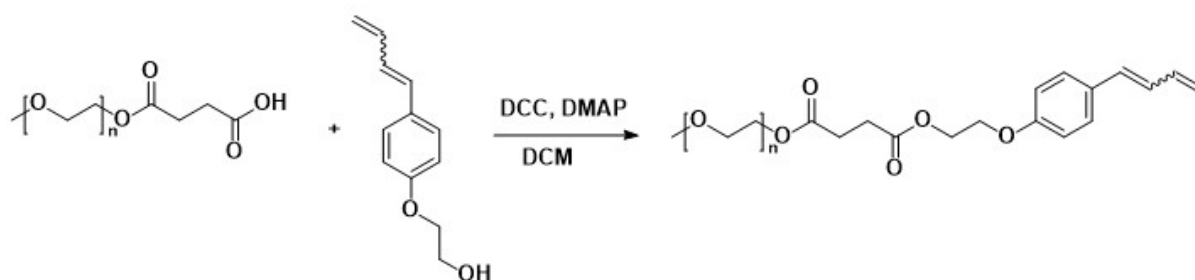
^1H NMR (CDCl_3 , 400 MHz) δ ppm: 0.99 - 1.16 (m, 3 H), 2.24 - 2.40 (m, 2 H), 3.76 - 3.89 (m, 3 H), 5.49 (dtt, $J=10.92$, 7.47, 7.47, 1.01, 1.01 Hz, 1 H), 6.05 - 6.26 (m, 1 H), 6.37 - 6.57 (m, 1 H), 6.80 - 7.02 (m, 3 H), 7.29 - 7.45 (m, 2 H) ^{13}C NMR (CDCl_3 , 101 MHz) δ ppm: 13.6, 14.3, 21.2, 25.8, 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



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).

^1H NMR (CDCl_3 , 400 MHz) δ 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) δ 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.



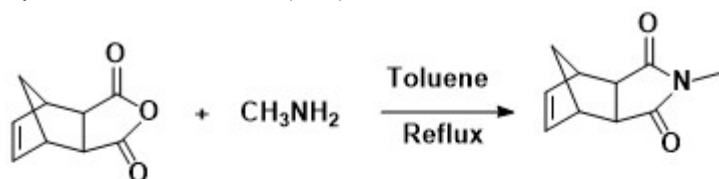
In an oven-dried round bottom flask, carboxylic acid functional PEG (1.0 equiv., .57 mmol, 1.23 g), I6 (10.0 equiv., 5.7 mmol, 1.08 g), and DMAP (1 equiv., 0.57 mmol, 70 mg) were taken and dissolved in 4 mL dry DCM. The resulting solution was cooled to 0°C. Then, DCC (10.0 equiv., 5.7 mmol, 1.18 g) was 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.

¹H NMR (CDCl₃, 400 MHz) δ 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) ¹³C NMR (CDCl₃, 101 MHz) δ 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.

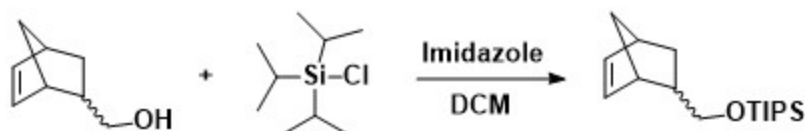
Synthesis of Monomers:

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



Exo-N-methylnorbornene imide (*exo*-MNI) (**M1**) was synthesized according to the previously reported procedure².

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



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 (3equiv., 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).

¹H NMR (CDCl_3 , 400 MHz) δ 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). ¹³C NMR (CDCl_3 , 101 MHz) δ ppm: 11.7, 17.7, 28.2, 28.9, 41.2, 41.5, 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-d₂ (DCM-d₂), and ¹H NMR was measured. **CTA1** (1 equiv., 0.01 mmol, 2.63 mg) in 0.25 mL DCM-d₂ was added, and ¹H NMR was measured immediately.

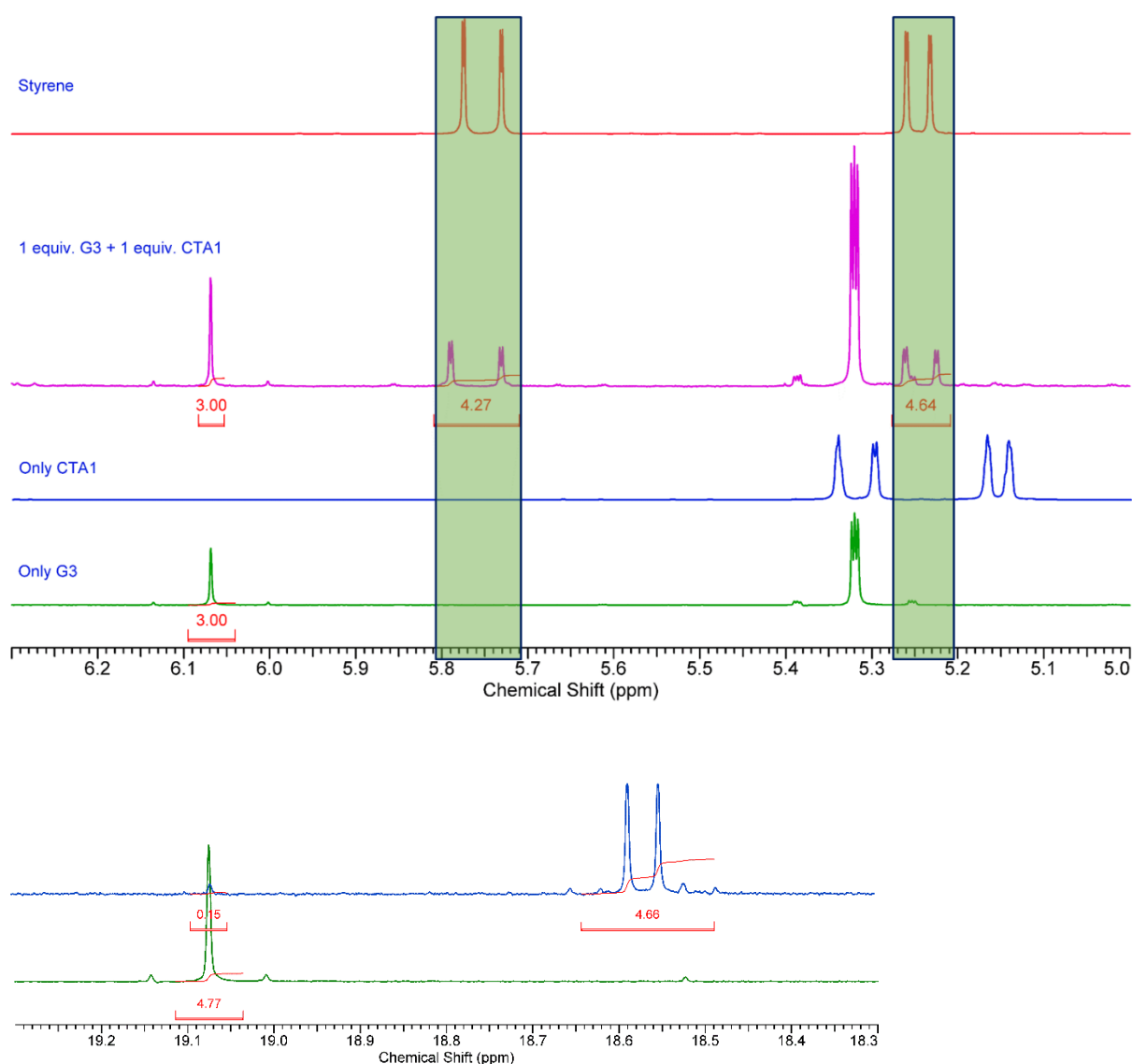
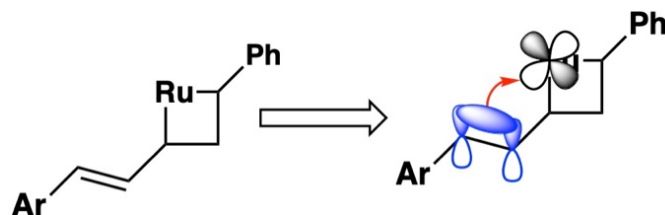
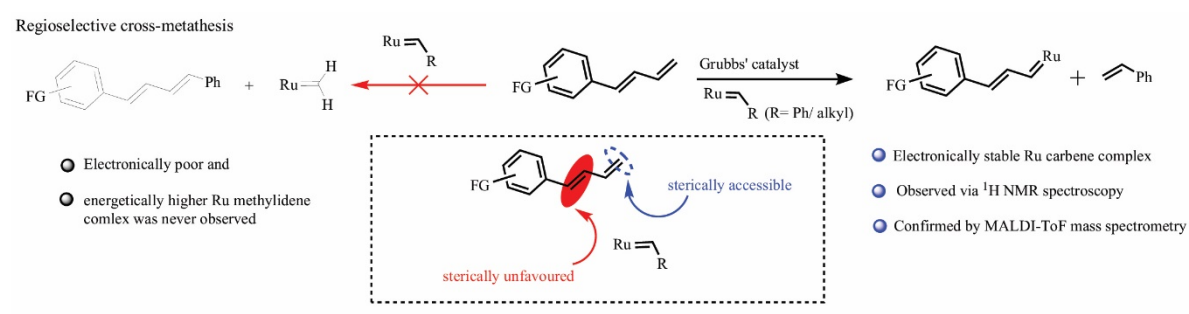


Fig. S1: ¹H NMR (CD₂Cl₂, 300 MHz) of reaction of **CTA1** (1 equiv.) with **G3** (1 equiv.) in DCM-d₂ (CD₂Cl₂). NMR spectra were compared with **CTA1** and styrene (measured independently in CDCl₃). The peak at 6.05 ppm is from the internal standard. Peaks of **CTA1** around 5.15 ppm

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

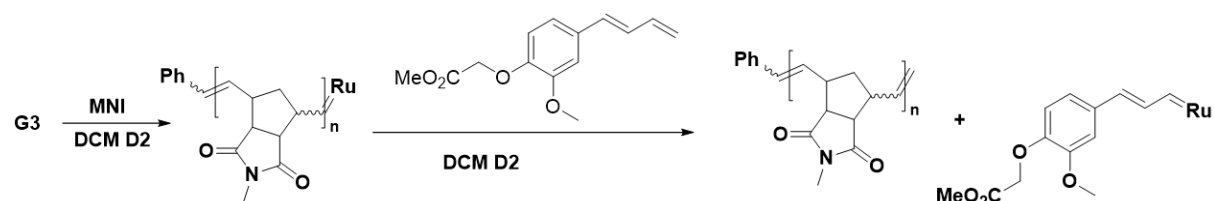
We believe, minimal steric congestion of terminal 1,3 conjugated double bond as compared to internal double bond is responsible for the high regioselective cross-metathesis reaction. Grubbs' ruthenium complex reacted regioselectively forming an electronically stable conjugated carbene rather than the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



π -electron donation of extra double bond of conjugated CTA to the vacant and diffused d-orbital of Ru led to stabilisation of four membered metallacyclobutane. This maybe a plausible explanation for observed regioselectivity as well as fast reactivity of conjugated diene CTAs.

End capping experiment:

CTA1



G3 (1 equiv., 0.0045 mmol, 4 mg) was dissolved in 0.5 mL dichloromethane-d₂ (CD₂Cl₂) in an NMR tube and to it exo-MNI (20 equiv., 0.09 mmol, 16 mg) in 0.2 mL CD₂Cl₂ was quickly added. ¹H NMR was measured. Then, **CTA1** (2 equiv., 0.009 mmol, 2.24 mg) dissolved in 0.2 mL CD₂Cl₂ was added, and ¹H NMR was measured over time. After that, the CD₂Cl₂ 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.

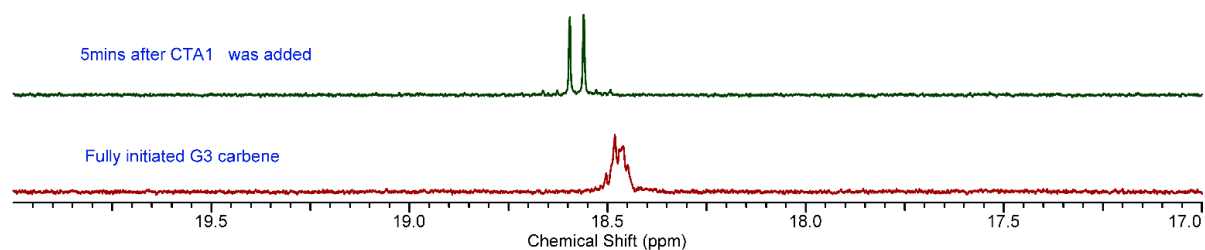


Fig. S2: ¹H NMR spectrum (CD₂Cl₂, 300 MHz) of end-capping reaction with **CTA1**.

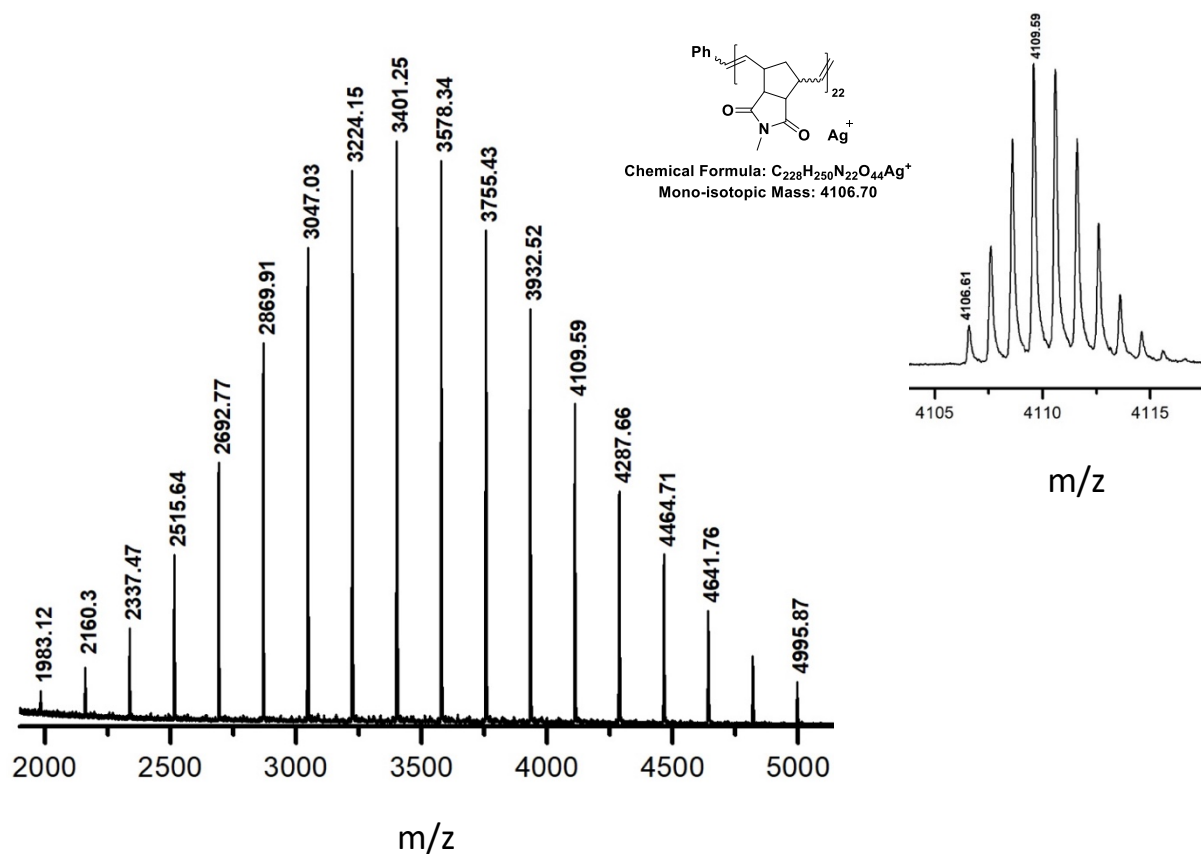
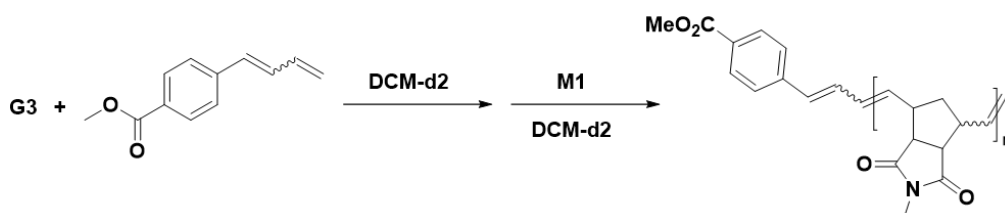


Fig. S3: MALDI-ToF mass spectrum (DCTB, AgTFA) of P1.

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 1H NMR were measured. Then, **M1** (200 equiv., 0.45 mmol, 80.13 mg) was added quickly, and 1H NMR was measured immediately. Complete consumption (see 1H 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.

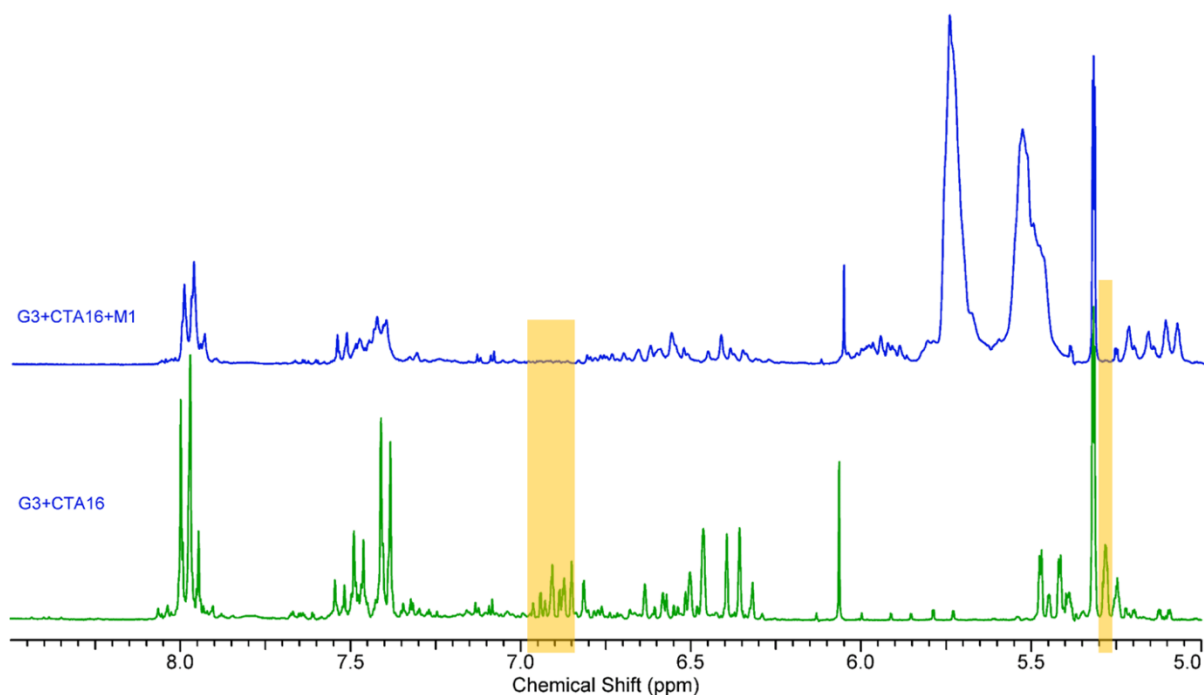


Fig. S4: ^1H NMR (400 MHz) of polymerization of **M1** using **CTA8** in DCM-d_2 (CD_2Cl_2). Peaks from **CTA8** (Bottom spectra, green line) disappeared (top spectra, blue line, yellow shaded region), and no peaks from monomer (**M1**) were observed.

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 ^1H 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-

Entry	CTA	Monomer (M)	G3:CTA: Monomer ratio	M _n (Non-catalytic, M/G3) (kDa)	M _n (Catalytic, M/CTA) kDa	M _n (¹ H NMR) kDa	M _n (SEC, CHCl ₃) kDa	Đ	Polymer Yield (%)
P2	CTA1	M1	1:40:400	71	2.0	2.7	2.6	1.77	88
P3	CTA1	M1	1:40:800	141	3.7	4.4	5.4	1.74	85
P4	CAT1	M1	1:40:1200	212	5.5	6.2	8.2	1.59	91
P5	CTA1	M1	1:200:3000	531	2.9	3.1	3.6	1.68	84
P6	CTA2	M1	1:300:3000	531	1.9	2.2	2.5	1.72	91
P7	CTA3	M1	1:100:2000	354	3.8	3.6	3.9	1.95	92
P8	CTA3	M1	1:50:10000	1770	35.5	- ^a	44.0	1.80	90
P9	CTA4	M1	1:100:1500	265	2.8	3.5	4.4	1.76	88
P10	CTA5	M1	1:200:2000	354	2.0	2.1	2.3	1.78	86.5
P11	CTA6	M1	1:100:2000	354	3.7	4	6.5	1.60	87
P12	CTA8	M1	1:20:200	35	2	2.6	3.4	1.66	84
P13	CTA9	M1	1:100:3000	531	5.7	6.1	7.9	1.72	87.6
P14	CTA10	M1	1:100:2000	354	3.8	4.0	5	1.80	88

Entry	CTA	Monomer (M)	G3: CTA: Monomer ratio	M _n (Non-catalytic, M/G3) (kDa)	M _n (Catalytic, M/CTA) kDa	M _n (¹ H NMR) kDa	M _n (SEC, CHCl ₃) kDa	Đ	Polymer Yield (%)
P15	CTA2	M2	1:100:3000	282	3.0	4.0	7.2	2.09	85
P16	CTA5	M2	1:100:2500	235	2.6	3.7	8.8	1.98	90
P17	CTA7	M2	1:100:2500	235	2.7	3.6	8.8	2.10	84
P18	CTA9	M2	1:100:2500	235	2.7	4.1	8.2	2.10	80
P19	CTA10	M2	1:170:3400	320	2.1	3.5	7.0	2.10	88

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

P2:

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

¹H NMR (CDCl₃, 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. ¹³C NMR (CDCl₃, 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.

¹H NMR (CDCl₃, 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. ¹³C NMR (CDCl₃, 101 MHz) δ ppm: 24.7, 24.8, 24.8, 40.8, 41.2, 41.4, 41.6, 41.6, 41.9, 42.0,

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.

¹H NMR (CDCl₃, 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. ¹³C NMR (CDCl₃, 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, 45.7, 45.9, 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, 77.3, 77.5, 114.2, 119.3, 131.6, 131.8, 132.0, 132.6, 133.4, 149.6, 178.3, 178.3, 178.4.

P5:

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

¹H NMR (CDCl₃, 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. ¹³C NMR (CDCl₃, 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.

¹H NMR (CDCl₃, 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. ¹³C NMR (CDCl₃, 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, 45.3, 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, 52.1, 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.

^1H NMR (CDCl_3 , 400 MHz) δ 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, 6.39 - 6.61, 6.73, 7.38 - 7.50. ^{13}C NMR (CDCl_3 , 101 MHz) δ 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, 76.6, 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:

G3: 1 mg, **CTA3:** 11.8 mg, **M1:** 2.0 g. Concentration (**M1**): 1 (M). DCM: 11.3 mL.

^1H NMR (CDCl_3 , 400 MHz) δ 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}C NMR (CDCl_3 , 101 MHz) δ ppm: 24.7, 24.8, 24.8, 40.8, 41.2, 41.4, 41.9, 42.1, 42.4, 42.9, 45.6, 45.6, 45.8, 45.9, 46.0, 46.1, 46.2, 50.8, 50.9, 51.0, 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:

G3: 2 mg, **CTA4:** 27.20 mg, **M1:** 601 mg. Concentration (**M1**): 0.1 (M). DCM: 34 mL.

^1H NMR (CDCl_3 , 400 MHz) δ ppm: 2.00 - 2.22, 2.24 - 2.31, 5.07 - 5.21, 5.21 - 5.25, 5.39 - 5.64, 5.68 - 5.83, 5.84 - 6.00, 6.14 - 6.43, 6.59 - 6.75, 7.32 - 7.40. ^{13}C NMR (CDCl_3 , 101 MHz) δ 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, 45.6, 45.8, 45.9, 46.0, 46.2, 46.8, 50.7, 51.0, 51.0, 51.1, 51.1, 51.1, 51.3, 51.8, 52.2, 52.6, 52.6, 52.6, 53.0, 76.7, 77.2, 77.3, 108.2, 111.5, 115.8, 119.7, 131.1, 131.6, 131.7, 131.9, 131.9, 132.0, 132.0, 132.1, 132.7, 133.4, 142.1, 178.1, 178.3, 178.4.

P10:

G3: 1 mg, **CTA5:** 52.0 mg, **M1:** 401 mg. Concentration (**M1**): 0.1 (M). DCM: 23 mL.

^1H NMR (CDCl_3 , 400 MHz) δ 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}C NMR (CDCl_3 , 101 MHz) δ 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, 46.0, 46.2, 46.8, 50.7, 51.0, 51.1, 51.1, 51.3, 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.

^1H NMR (CDCl_3 , 400 MHz) δ 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) δ ppm: 24.7, 24.8, 40.8, 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, 51.1, 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.

^1H NMR (CDCl_3 , 400 MHz) δ 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) δ ppm: 24.7, 24.8, 24.8, 40.8, 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, 45.9, 46.0, 46.1, 46.2, 46.2, 46.8, 50.7, 51.0, 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, 132.0, 132.1, 132.6, 132.9, 133.1, 133.4, 138.7, 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.

^1H NMR (CDCl_3 , 400 MHz) δ ppm: 1.44 - 1.73, 4.14 - 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) δ 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, 45.7, 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, 178.4.

P14:

G3: 2 mg, **CTA10:** 12.7 mg, **M1:** 80.13 mg. Concentration (**M1**): 0.4 (M). DCM-d_2 : 1.1 mL.

^1H NMR (CDCl_3 , 400 MHz) δ 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) δ 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, 51.1, 51.3, 51.8, 52.6, 53.0, 76.7, 77.2, 77.3, 115.7, 126.3, 126.5, 127.2, 127.3, 127.3, 127.7, 127.8, 128.6, 128.9, 129.1, 129.1, 129.3, 131.6, 131.8, 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.

¹H NMR (CDCl₃, 400 MHz) δ 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. ¹³C NMR (CDCl₃, 101 MHz) δ 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, 41.5, 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.

¹H NMR (CDCl₃, 400 MHz) δ 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. ¹³C NMR (CDCl₃, 101 MHz) δ 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, 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.

¹H NMR (CDCl₃, 400 MHz) δ 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. ¹³C NMR (CDCl₃, 101 MHz) δ 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.

¹H NMR (CDCl₃, 400 MHz) δ 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. ¹³C NMR (CDCl₃, 101 MHz) δ 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 ^1H NMR spectroscopy:

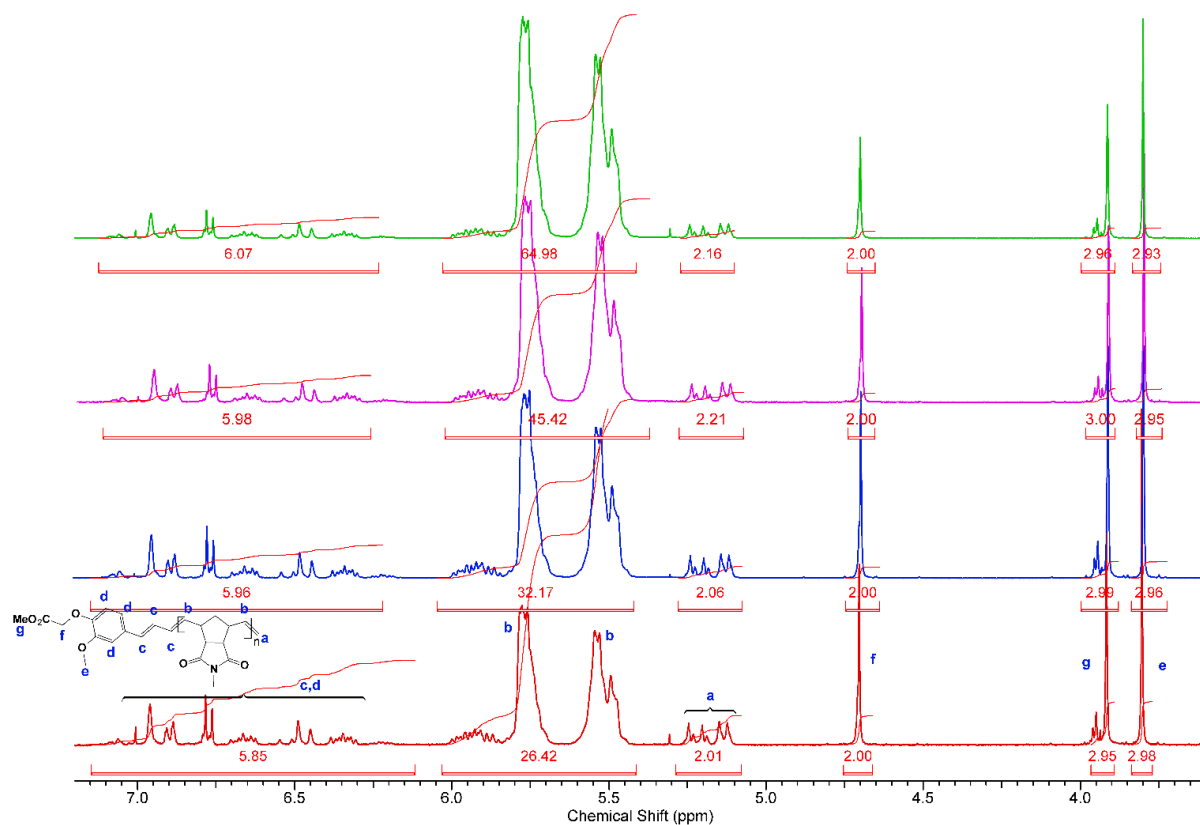
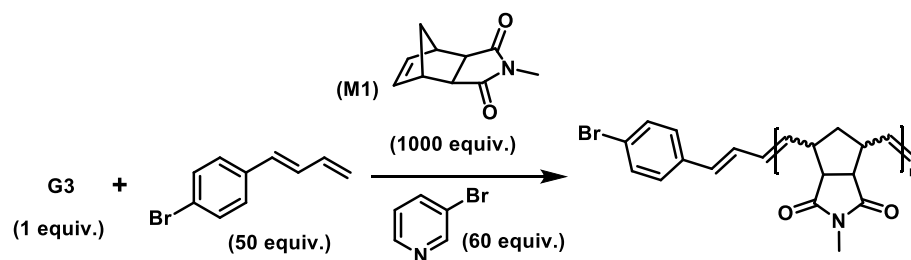


Fig. S5: Number average molecular weight (M_n) determination by end group analysis using ^1H NMR (400 MHz) spectroscopy (olefinic region only, in CDCl_3). **P2:** red spectrum, **P5:** blue spectrum, **P3:** magenta spectrum, **P4:** green spectrum.

¹H NMR kinetics experiment:



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** (50 equiv., 0.056 mmol, 11.8 mg) were mixed in 0.9 mL CDCl₃ and ¹H NMR were measured. Then, **G3** (1 equiv., 0.0011 mmol, 1 mg) dissolved in 0.2 mL was added quickly, and ¹H NMR was measured overtime. Consumption of both **M1** and **CTA3** were observed overtime suggesting a kinetically controlled mechanism.

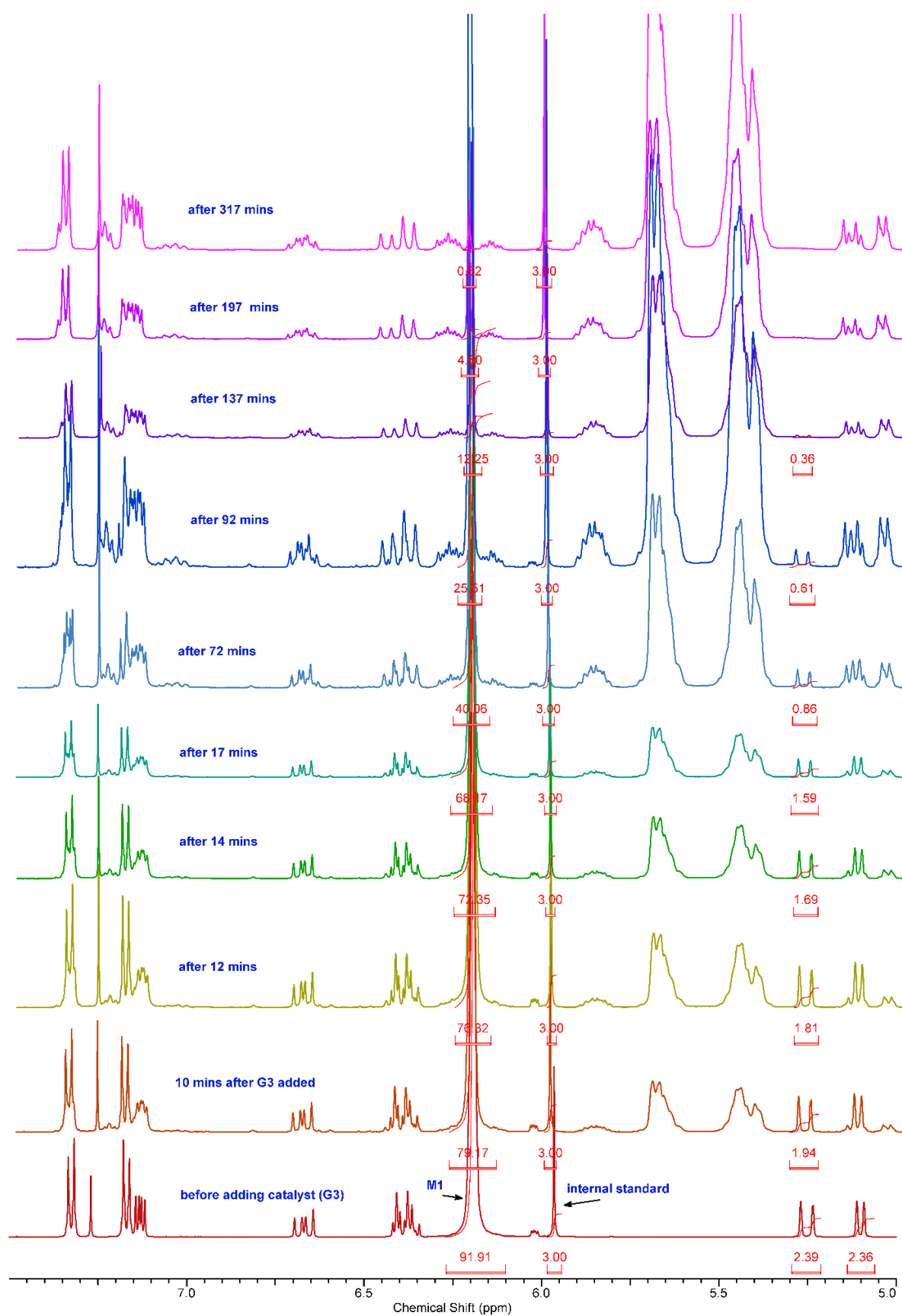
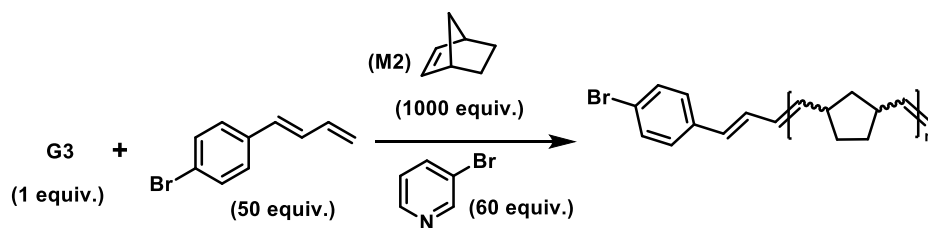


Fig. S6: ¹H NMR (CDCl₃, 300 MHz) of reaction of **CTA3** (50 equiv.), 3 bromopyridine (60 equiv.) and **M1** (1000 equiv.) with **G3** (1 equiv.) in CDCl₃ (CDCl₃).



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%.

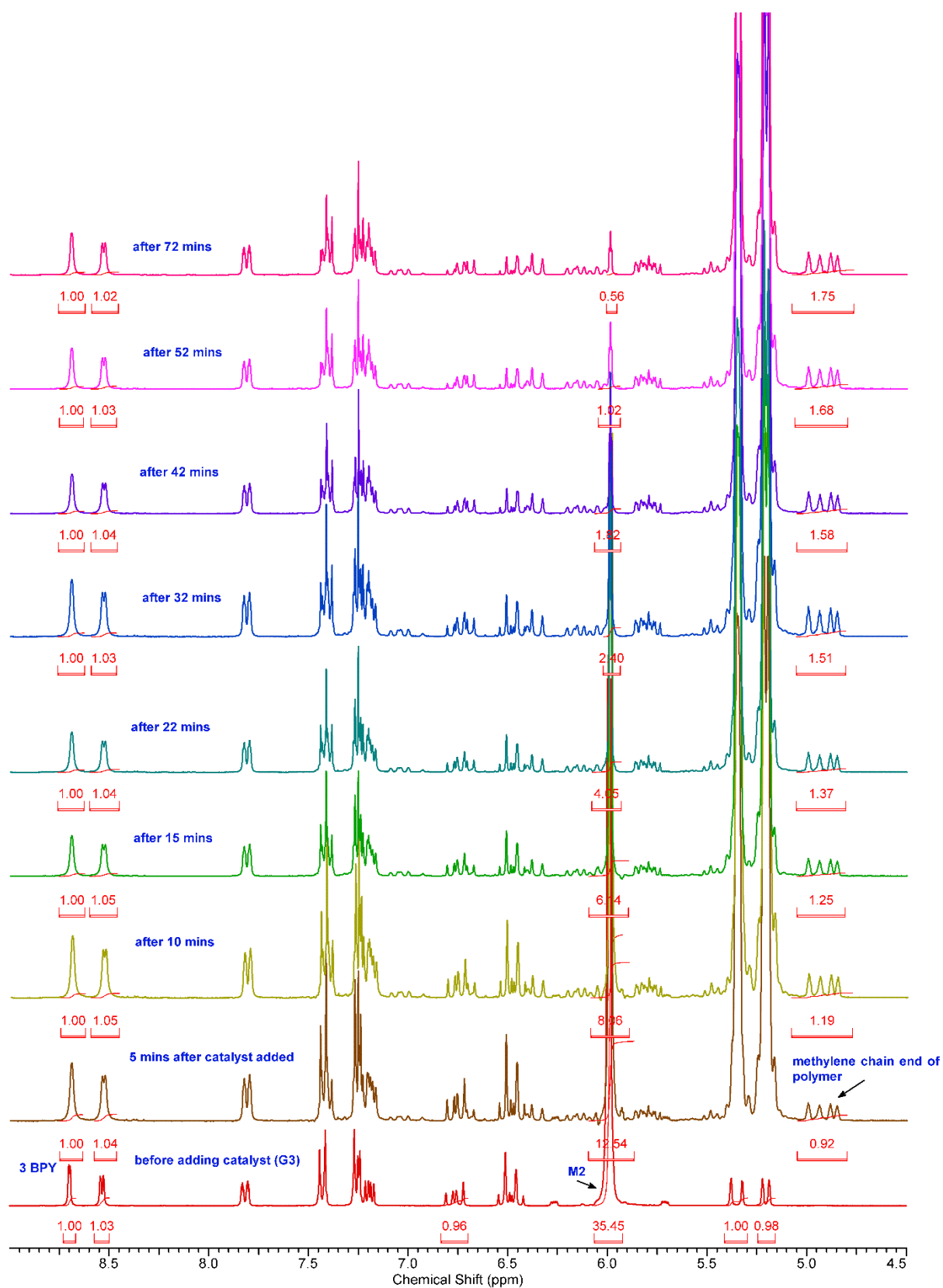
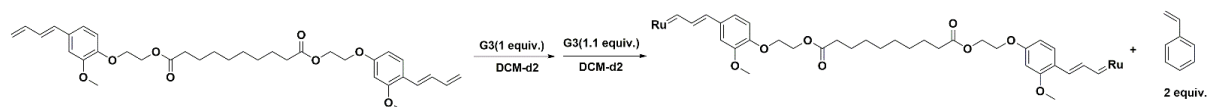


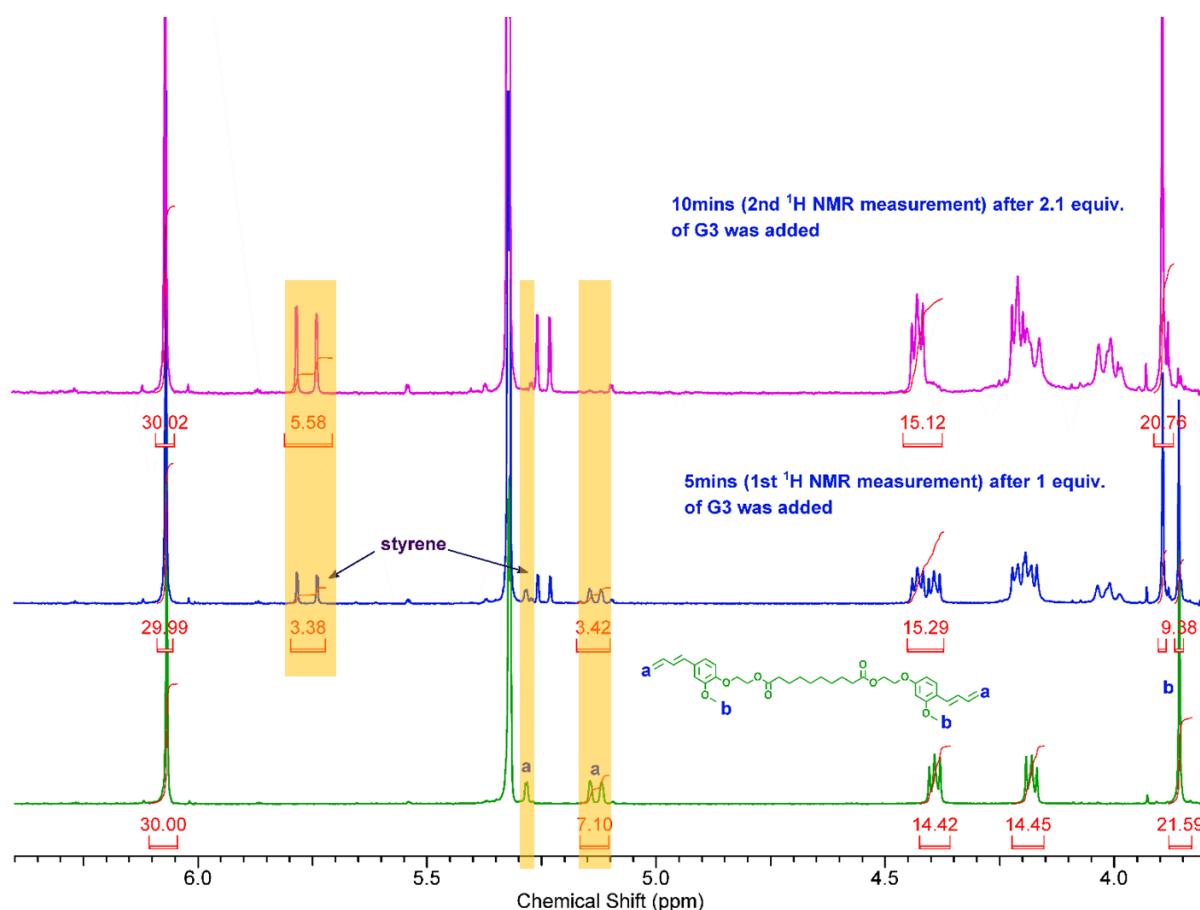
Fig. S7: ¹H NMR (CDCl₃, 300 MHz) of reaction of **CTA3** (50 equiv.), 3 bromopyridine (60 equiv.) and **M2** (1000 equiv.) with **G3** (1 equiv.) in CDCl₃ (CDCl₃).

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



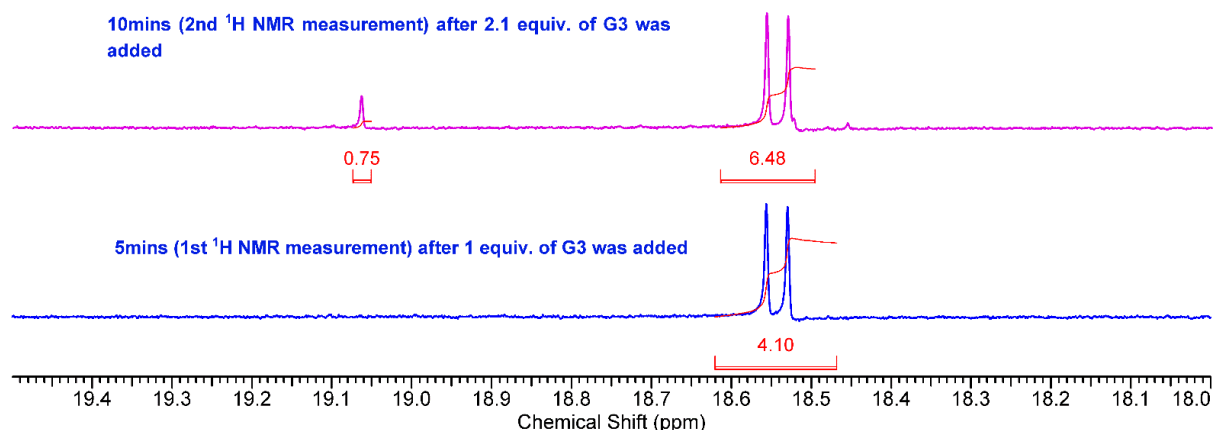
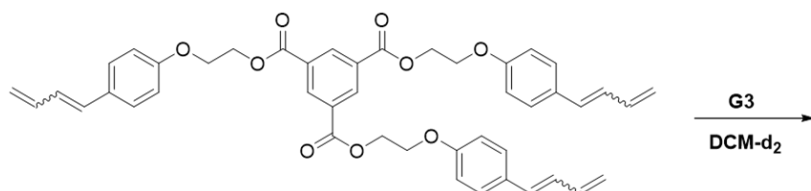


Fig. S8: ^1H NMR (CD_2Cl_2 , 400 MHz) of reaction of **CTA11** (1 equiv.) with **G3** (2.1 equiv.).

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.

^1H 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 ^1H 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 ^1H NMR spectra below).

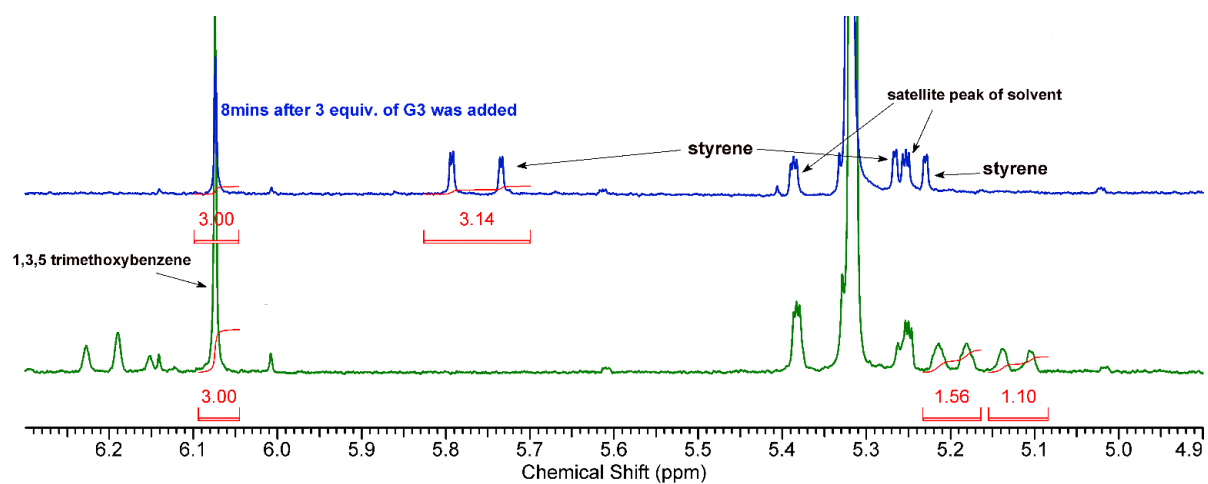


Fig. S9: ^1H NMR (CD_2Cl_2 , 300 MHz) of polymerization of **M1** using **CTA13**.

¹H NMR polymerization reaction monitoring using CTA14:

A control ¹H NMR tube polymerization reaction was performed where first **G3** (1 equiv.) and **CTA14** (20 equiv.) were dissolved in dichloromethane-d₂, and a ¹H 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-d₂ was prepared beforehand and quickly added to the NMR tube. Immediate ¹H 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 (CHCl₃)} = 4.5 kDa) was very close to that specified by the **M1/CTA14** (M_{n, M1/CTA14} = 3.4 kDa).

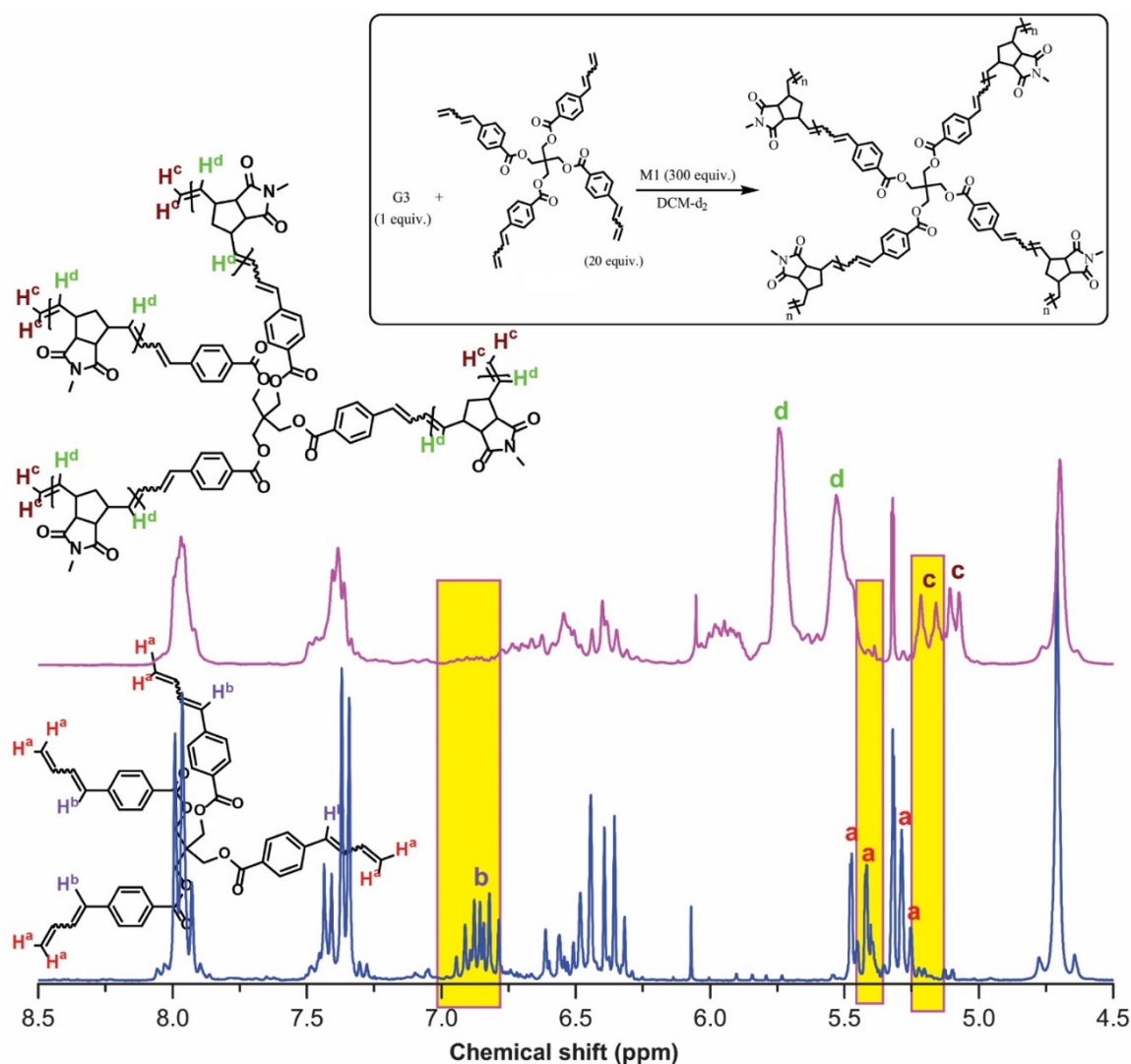


Fig. S10: ¹H NMR (CD₂Cl₂, 300 MHz) of polymerization of **M1** using **CTA14**.

Table S2: Catalytically Synthesis of branched polymers-

Entry	CTA	Monomer (M)	G3:CTA: Monomer ratio	M _n (Non-catalytic, M/G3) (kDa)	M _n (Catalytic, M/CTA) kDa	M _n (¹ H NMR) kDa	M _n (SEC, CHCl ₃) kDa	Đ	Polymer Yield ^b (%)
P20	CTA12	M1	1:50:1000	177	4.0	5.0	6.8	1.52	85
P21	CTA13	M1	1:100:2000	354	4.3	4.0	4.6	1.72	82
P22	CTA14	M1	1:20:300	53.5	3.4	3.2	4.5	1.47	85
P23	CTA14	M1	1:20:8000	1416	71	- ^a	70	1.72	88
P24	CTA12	M2	1:100:4000	376.5	4.3	4.8	7.7	2.0	85
P25	CTA14	M3	1:64:1300	365.4	6.4	6.2	6.5	1.45	78

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

b= polymer yield is determined as follows-

Yield (%) = [amount of polymer obtained (in mg) / (amount of monomer used (in mg) + amount of CTA used (in mg))] * 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. ^{13}C 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, 51.0, 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. ^{13}C 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.

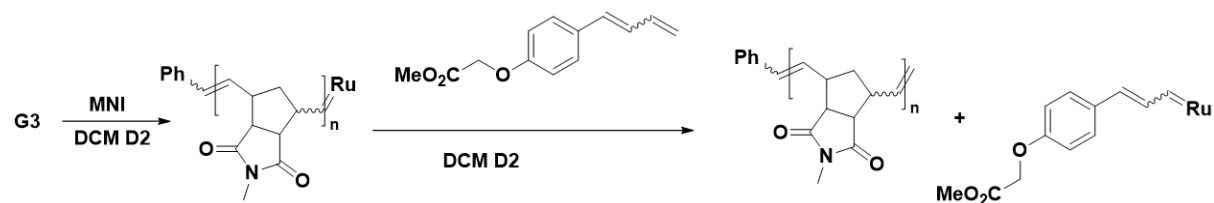
P25:

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). ^{13}C 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-d₂ (CD₂Cl₂) in an NMR tube and to it exo-MNI (**M1**) (20 equiv., 0.12 mmol, 20 mg) in 0.2 mL CD₂Cl₂ was quickly added. ¹H NMR was measured. Then, **CTA6** (2 equiv., 0.012 mmol, 2.5 mg) dissolved in 0.2 mL CD₂Cl₂ was added, and ¹H NMR was measured immediately. Thereafter, the CD₂Cl₂ 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.

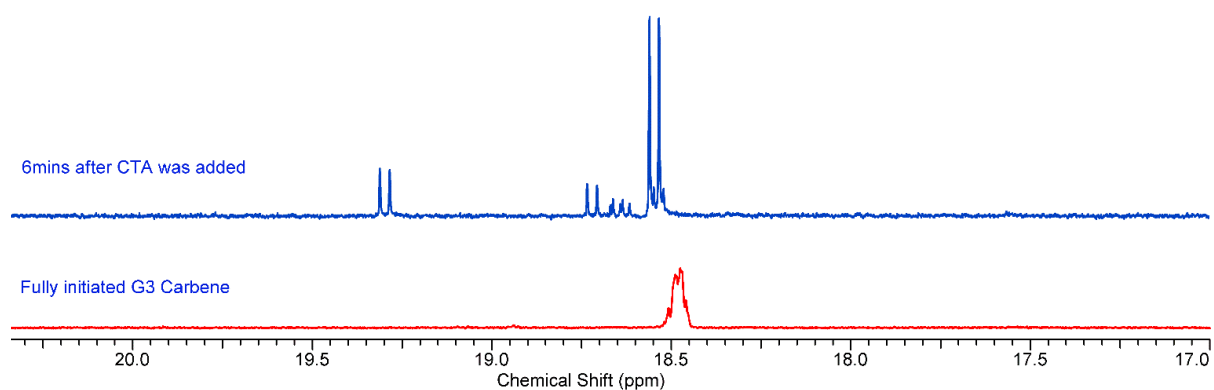
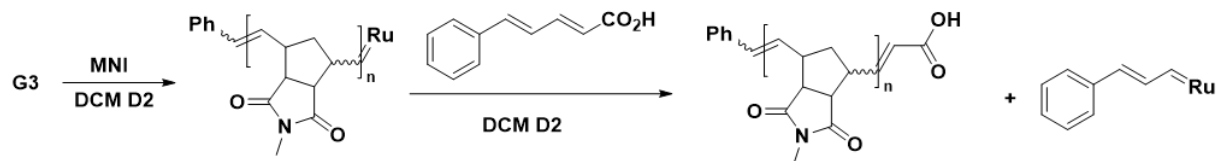
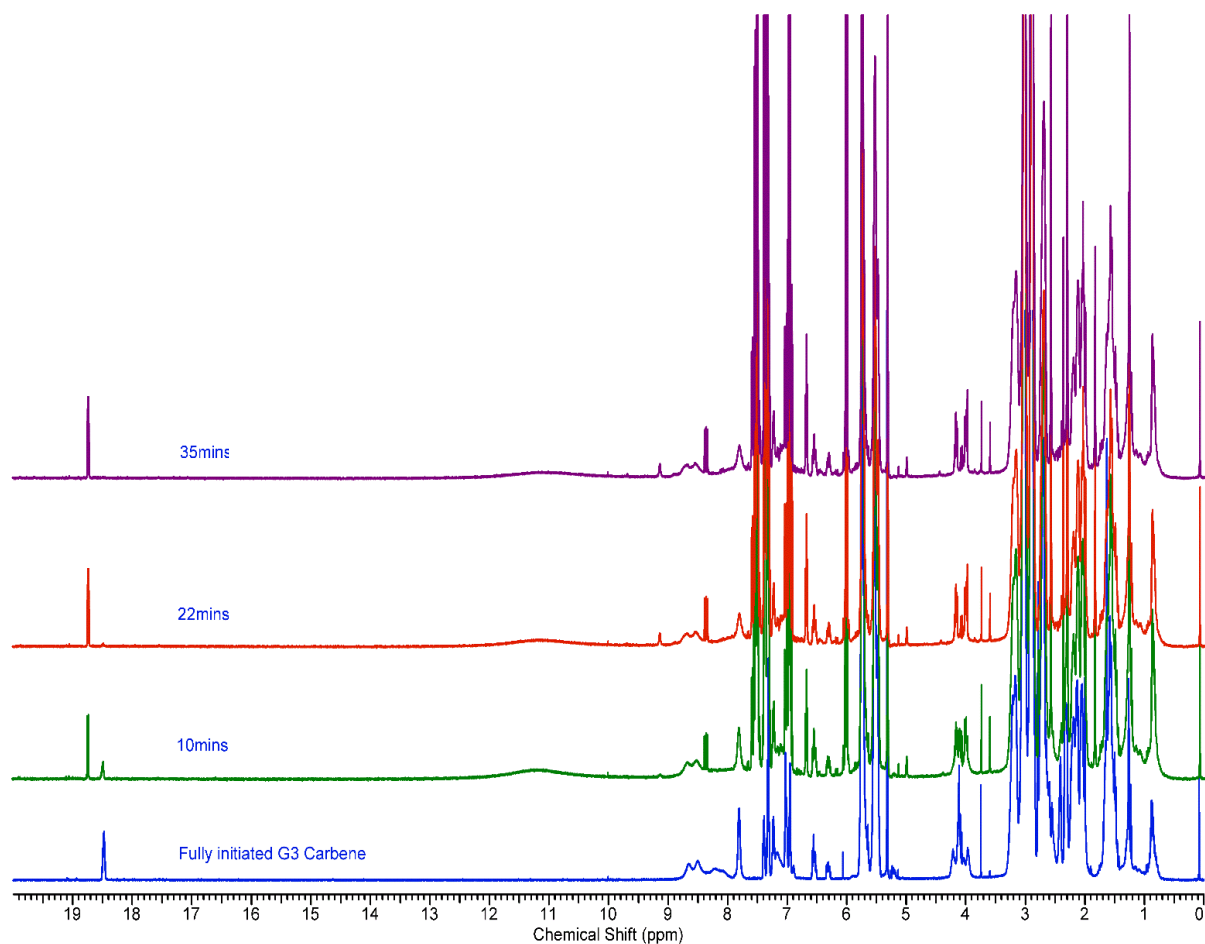


Fig. S11: ¹H NMR spectrum (CD₂Cl₂, 400 MHz) of end-capping reaction with **CTA6**.

CTA15



G3 (1 equiv., 0.0045 mmol, 4 mg) was dissolved in 0.5 mL dichloromethane- d_2 (CD_2Cl_2) in an NMR tube and to it **M1** (20 equiv., 0.09 mmol, 16 mg) in 0.2 mL CD_2Cl_2 was quickly added. ^1H NMR was measured. Then, **CTA15** (10 equiv., 0.045 mmol, 7.9 mg) dissolved in 0.3 mL CD_2Cl_2 was added, and ^1H NMR was measured over time. After 40 mins, the CD_2Cl_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.



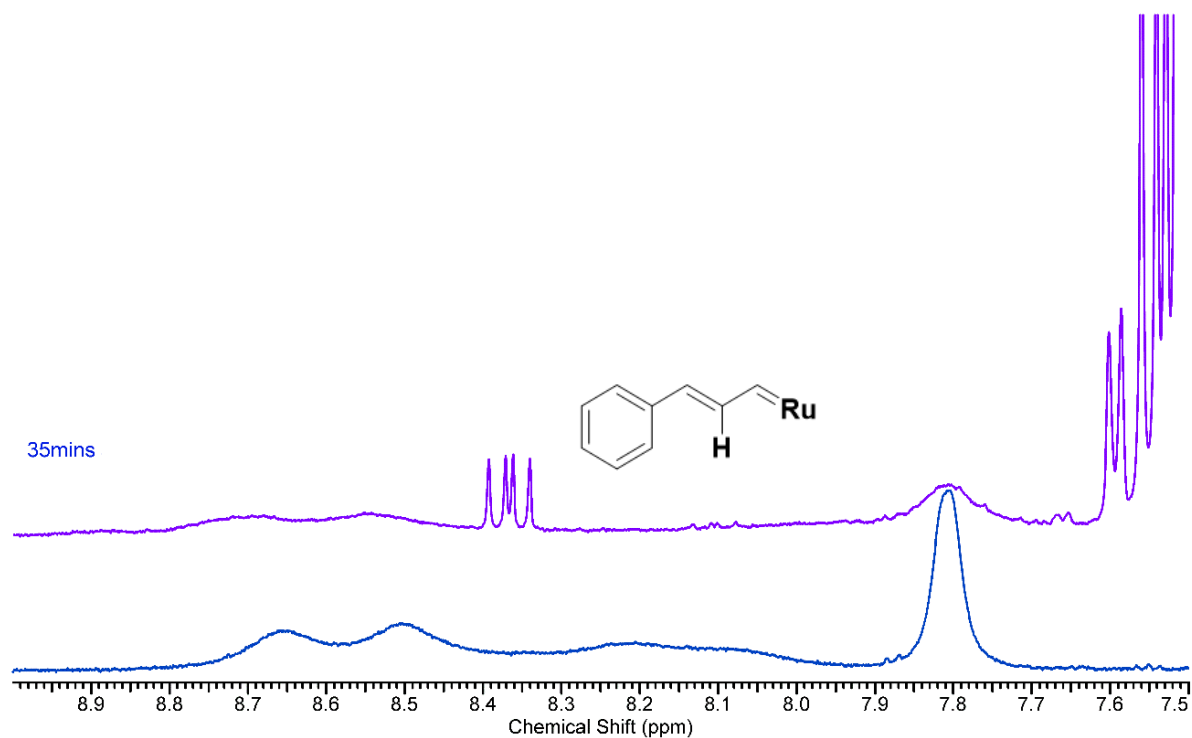
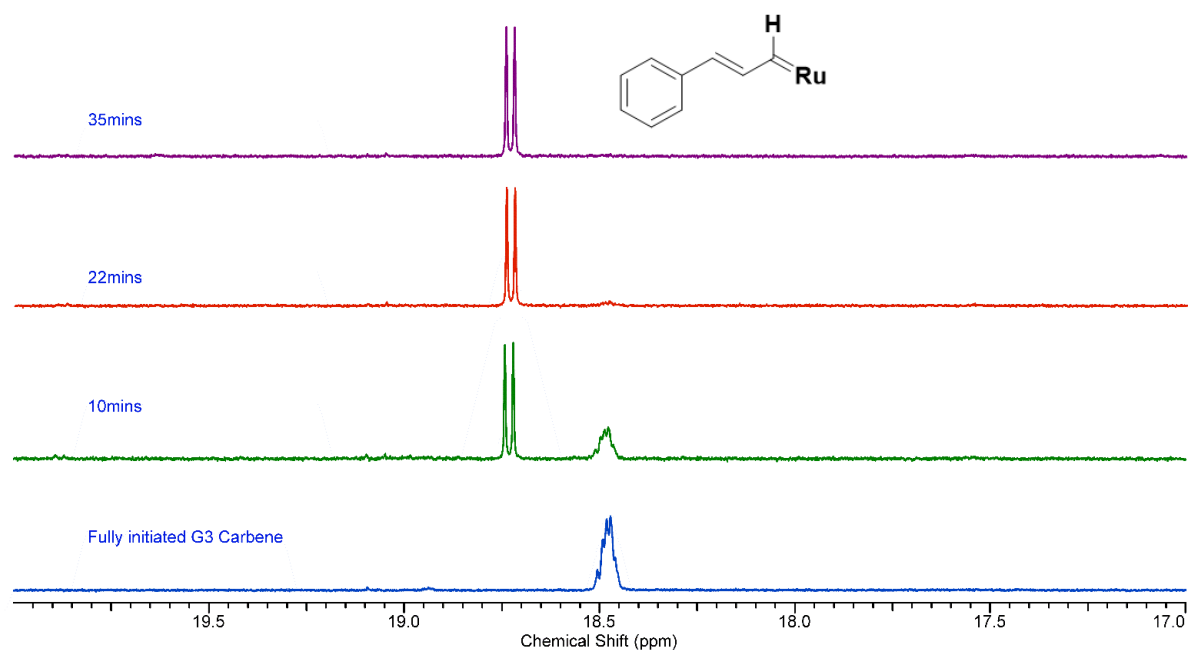


Fig. S13: ¹H NMR spectrum (CD₂Cl₂, 400 MHz) of end-capping reaction with **CTA15**. Full-spectrum is shown in the first image. The second and third spectra show zoomed regions corresponding to α proton (alkylidene region) and β proton to the Ru complex of **G3**, respectively.

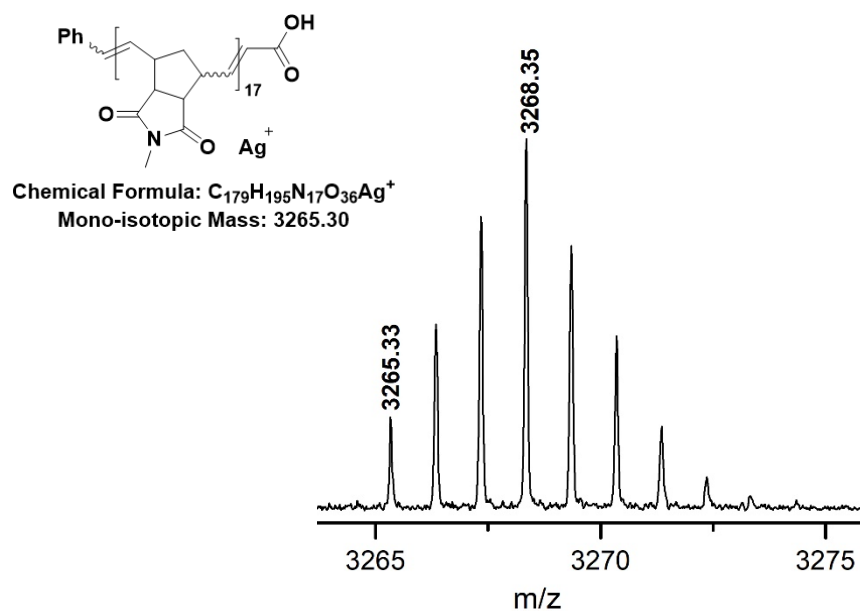
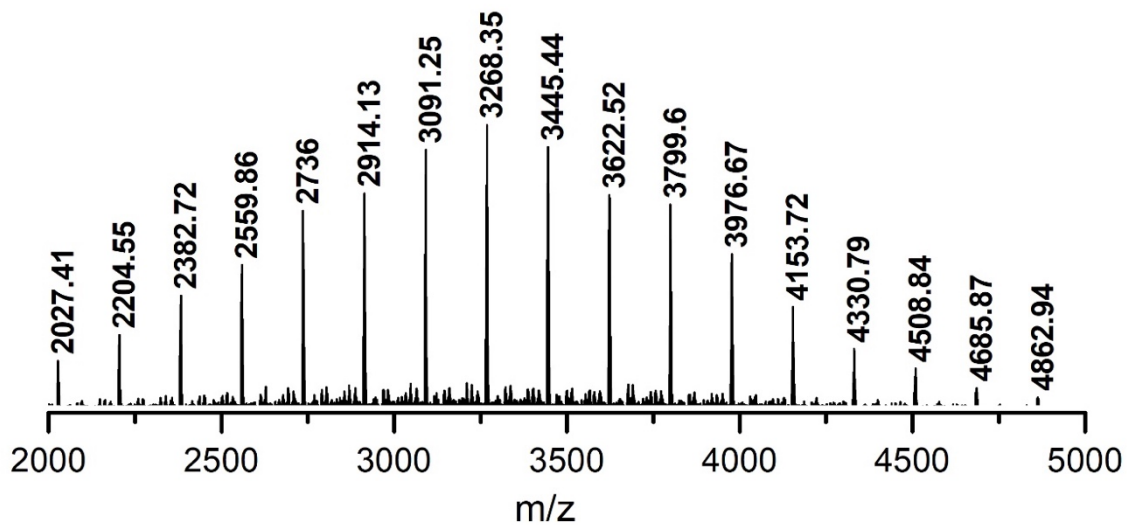
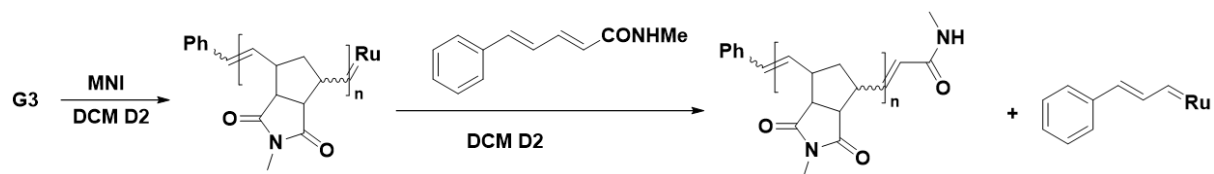


Fig. S14: MALDI-ToF mass spectrum (DCTB, AgTFA) of **P27**.

CTA17



G3 (1 equiv., 0.0045 mmol, 4 mg) was dissolved in 0.7 mL dichloromethane- d_2 (CD_2Cl_2) in an NMR tube and to it (**M1**) (20 equiv., 0.09 mmol, 16 mg) in 0.2 mL CD_2Cl_2 was quickly added. 1H NMR was measured. Then, **CTA17** (10 equiv., 0.045 mmol, 8.5 mg) dissolved in 0.2 mL CD_2Cl_2 was added, and 1H NMR was measured over time. After 40 mins, the CD_2Cl_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.

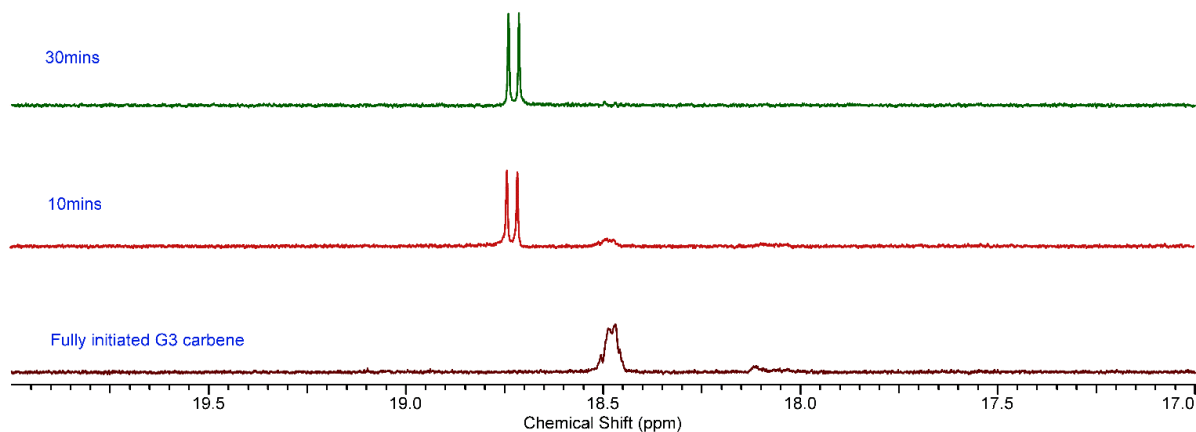


Fig. S15: 1H NMR spectrum (CD_2Cl_2 , 400 MHz) of end-capping reaction with **CTA17**.

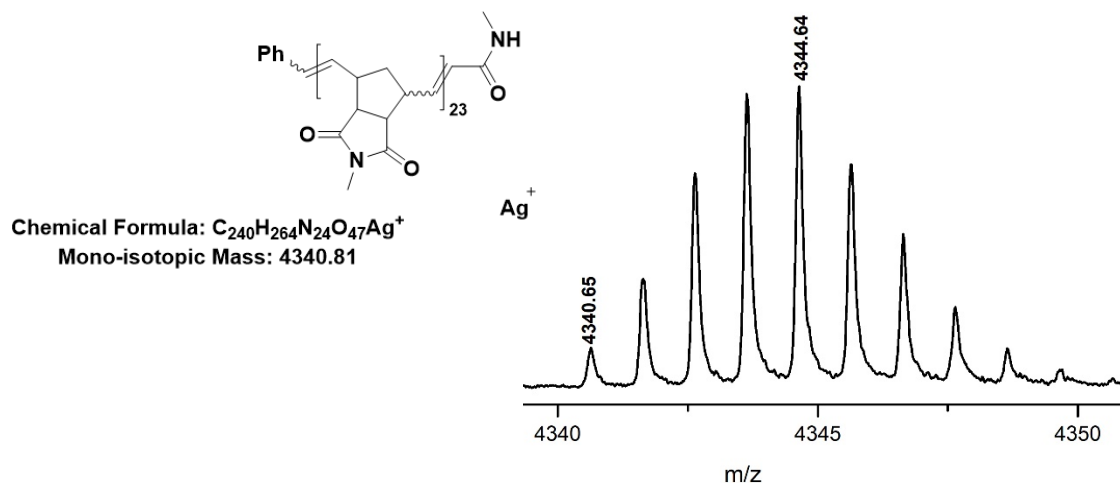
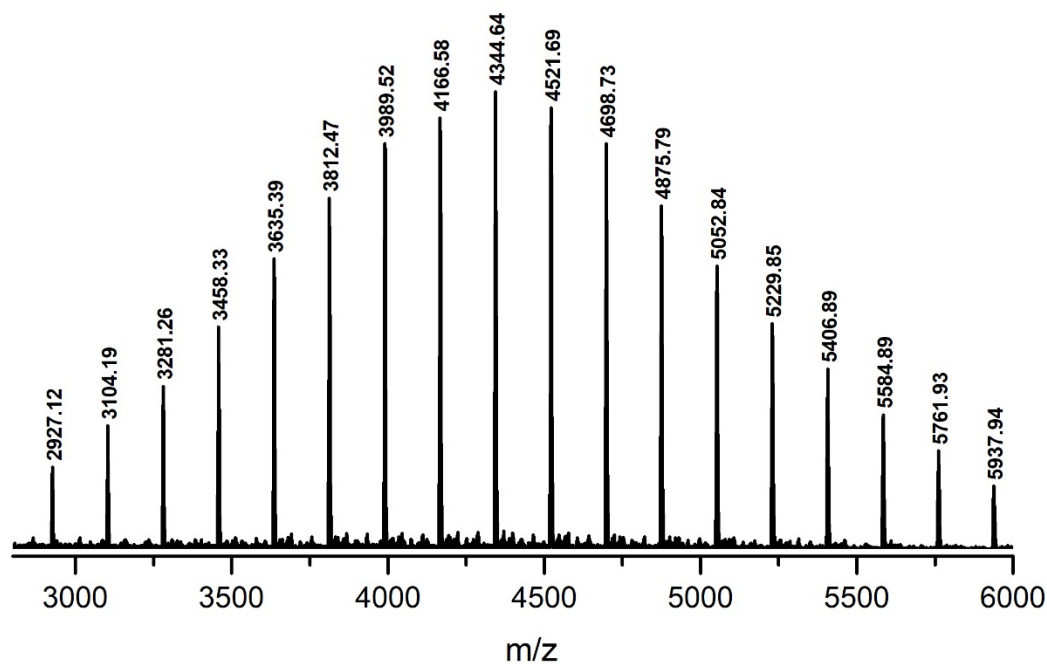
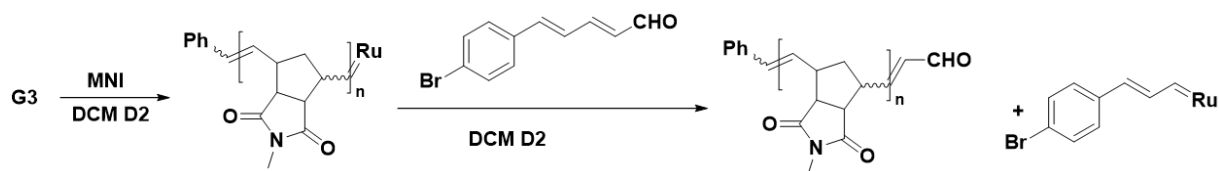


Fig. S16: MALDI-ToF mass spectrum (DCTB, AgTFA) of **P28**.

CTA19



G3 (1 equiv., 0.0045 mmol, 4 mg) was dissolved in 0.5 mL dichloromethane-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, **CTA19** (10 equiv., 0.045 mmol, 10.7 mg) dissolved in 0.3 mL CD₂Cl₂ was added, and ¹H NMR was measured over time. After 50 mins, the CD₂Cl₂ 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.

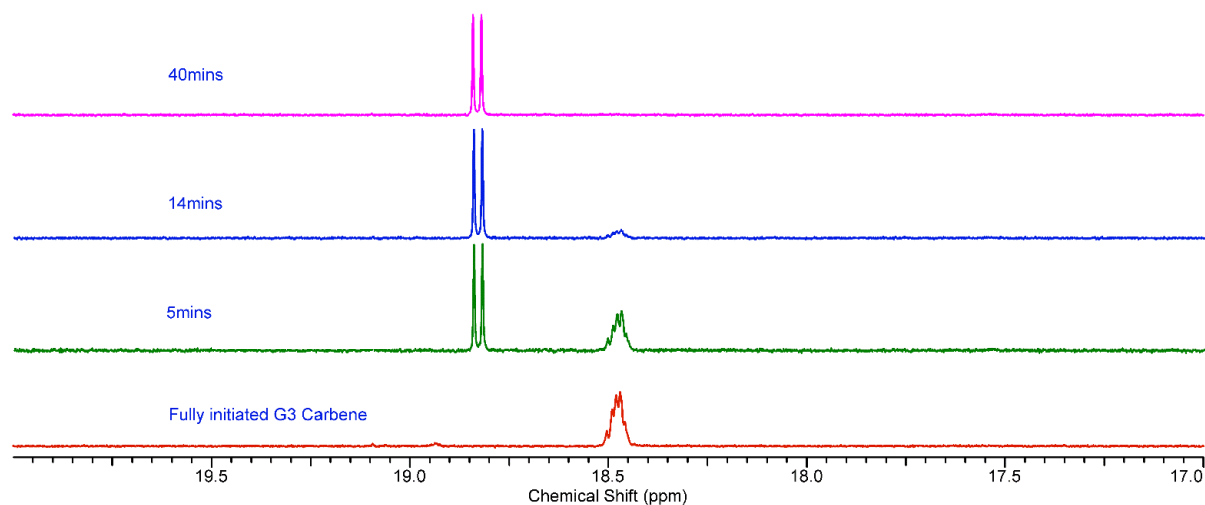
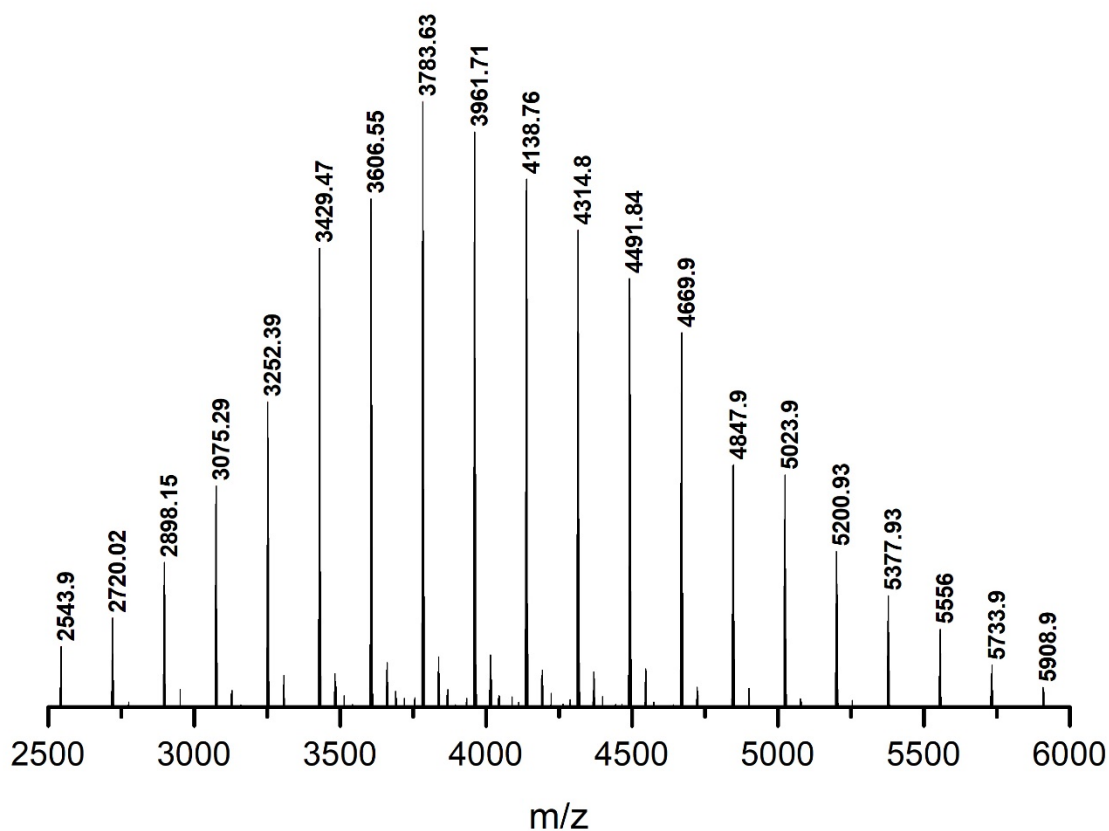


Fig. S17: ¹H NMR spectrum (CD₂Cl₂, 400 MHz) of end-capping reaction with **CTA19**.



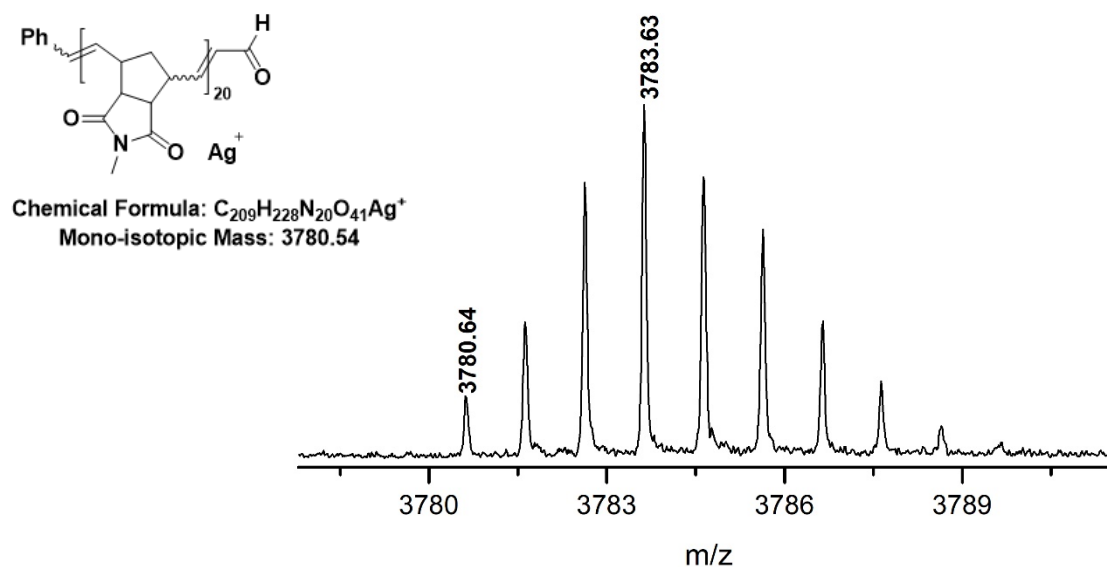
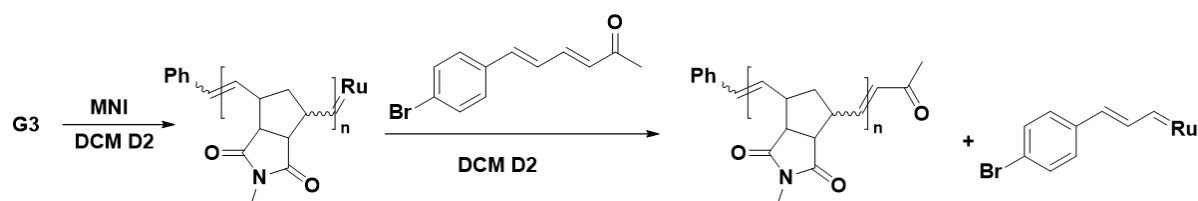


Fig. S18: MALDI-ToF mass spectrum (DCTB, AgTFA) of **P29**. The smaller distribution did not match with any possible non-regioselective metathesis.

CTA21



G3 (1 equiv., 0.0045 mmol, 4 mg) was dissolved in 0.5 mL dichloromethane- d_2 (CD_2Cl_2) in an NMR tube and to it (**M1**) (20 equiv., 0.09 mmol, 16 mg) in 0.2 mL CD_2Cl_2 was quickly added. 1H NMR was measured. Then, **CTA21** (20 equiv., 0.045 mmol, 23.0 mg) dissolved in 0.3 mL CD_2Cl_2 was added, and 1H NMR was measured over time. After 50 mins, a few drops of ethyl vinyl ether was added, the CD_2Cl_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.

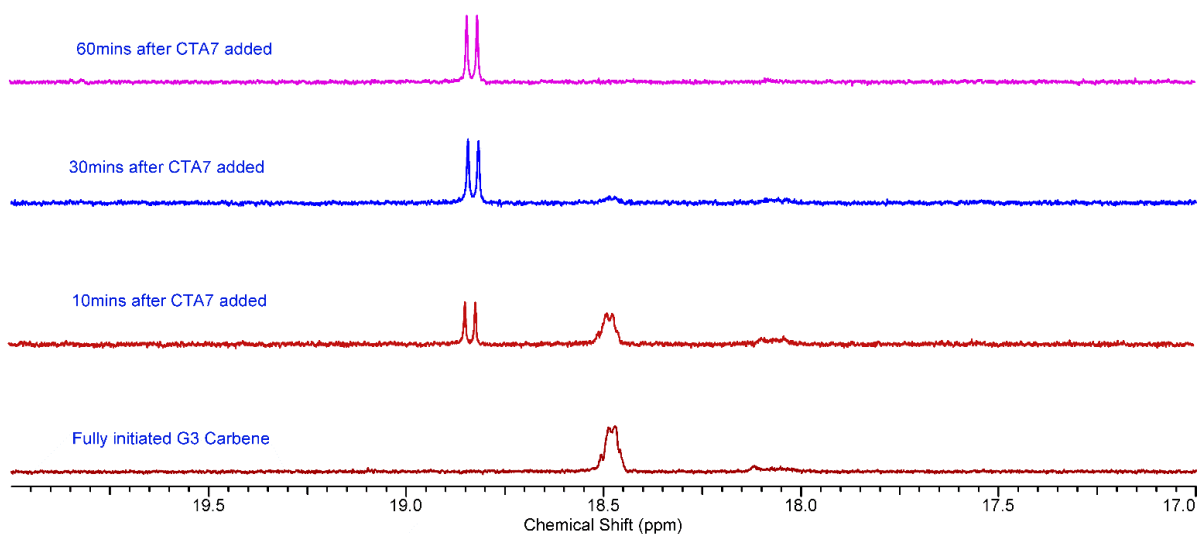
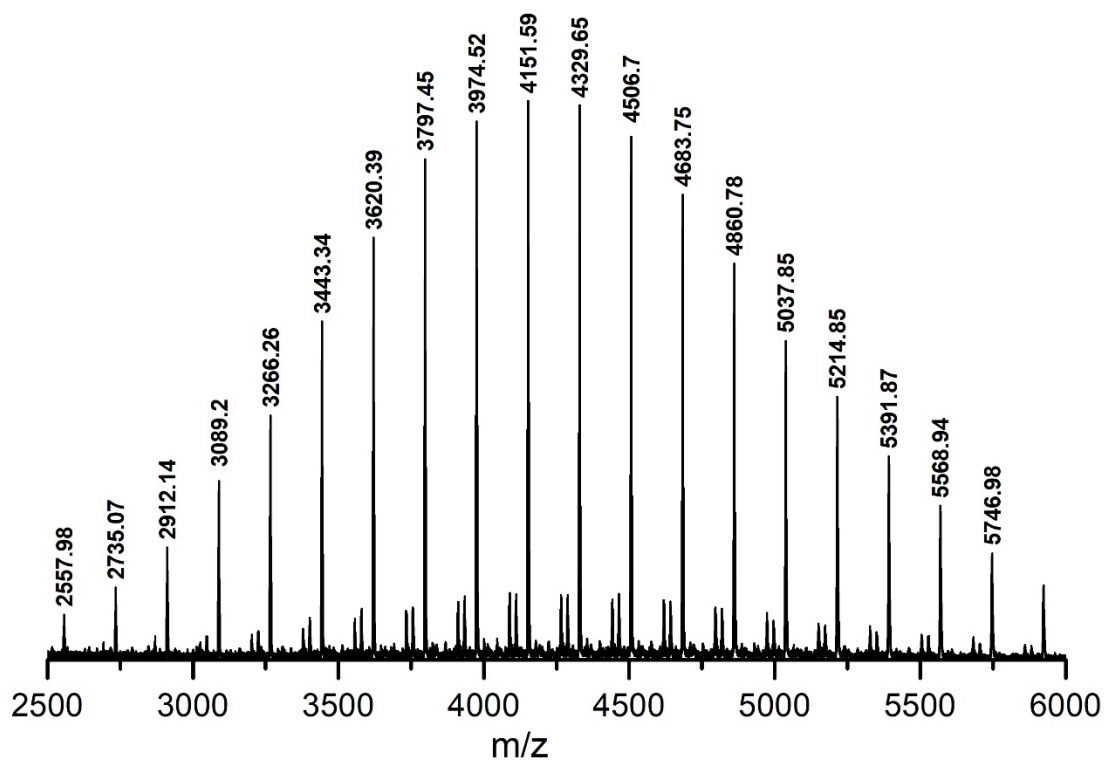


Fig. S19: ^1H NMR spectrum (CD_2Cl_2 , 400 MHz) of end-capping reaction with **CTA21**.

Although ^1H NMR showed strictly regioselective chain transfer with **CTA21**, MALDI-ToF mass spectrum showed a minor distribution indicating another chain transfer. See following-



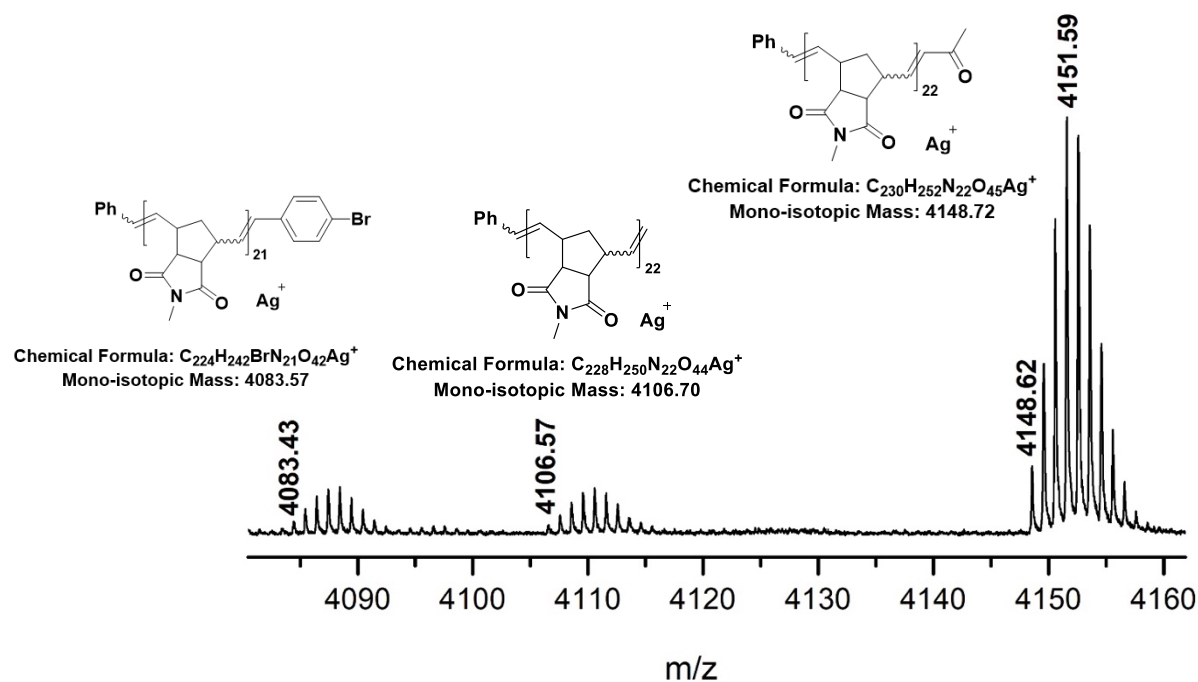
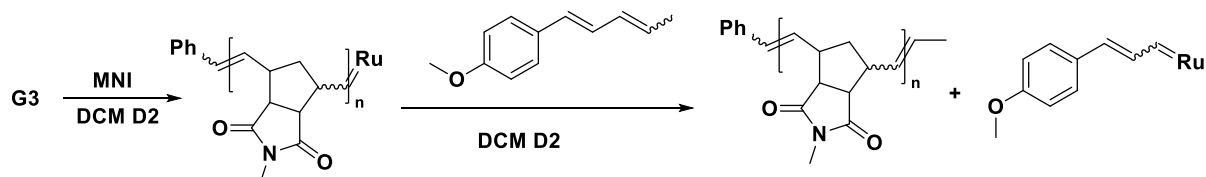


Fig. S20: MALDI-ToF mass spectrum (DCTB, AgTFA) of **P30**.

CTA24



G3 (1 equiv., 0.0045 mmol, 4 mg) was dissolved in 0.5 mL dichloromethane- d_2 (CD_2Cl_2) in an NMR tube and to it (**M1**) (20 equiv., 0.09 mmol, 16 mg) in 0.2 mL CD_2Cl_2 was quickly added. 1H NMR was measured. Then, **CTA24** (5 equiv., 0.022 mmol, 4.0 mg) dissolved in 0.2 mL CD_2Cl_2 was added, and 1H NMR was measured over time. After 20 mins, the CD_2Cl_2 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.

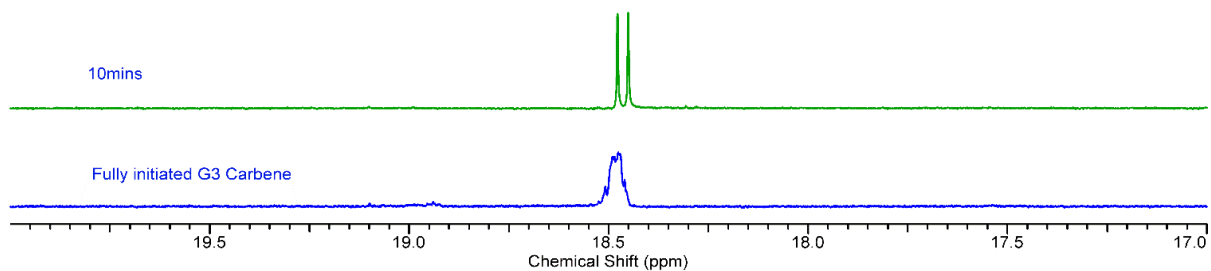
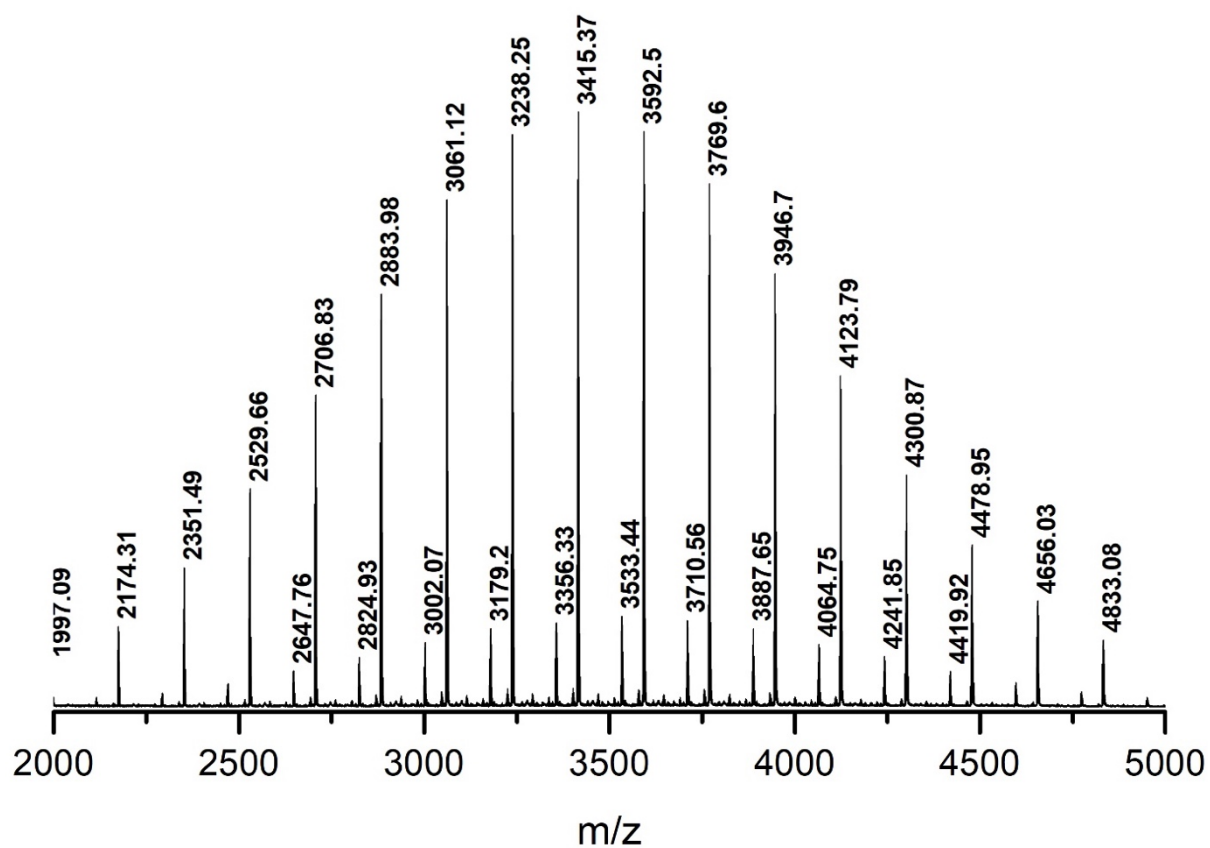


Fig. S21: ¹H NMR spectrum (CD₂Cl₂, 400 MHz) of end-capping reaction with **CTA24**.



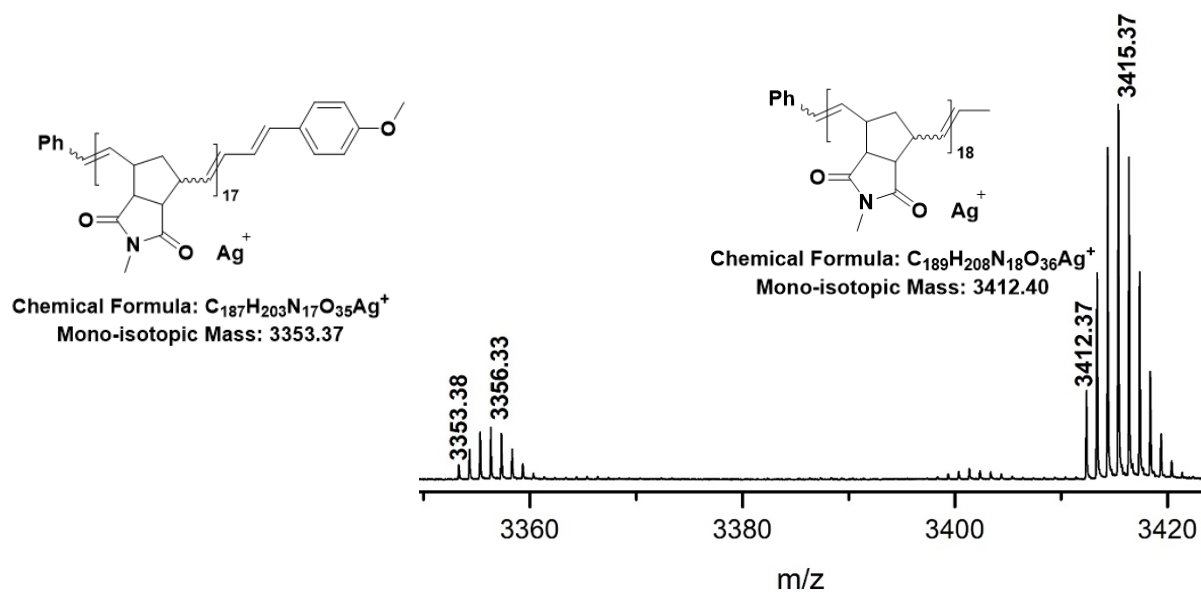
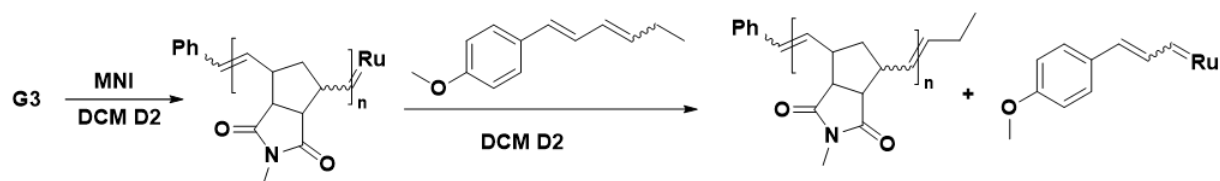


Fig. S22: MALDI-ToF mass spectrum (DCTB, AgTFA) of **P31**.

CTA25



G3 (1 equiv., 0.0045 mmol, 4 mg) was dissolved in 0.5 mL dichloromethane- d_2 (CD_2Cl_2) in an NMR tube and to it (**M1**) (20 equiv., 0.09 mmol, 16 mg) in 0.2 mL CD_2Cl_2 was quickly added. 1H NMR was measured. Then, **CTA25** (5 equiv., 0.022 mmol, 4.25 mg) dissolved in 0.2 mL CD_2Cl_2 was added, and 1H NMR was measured over time. After 20 mins, the CD_2Cl_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 1H NMR spectroscopy.

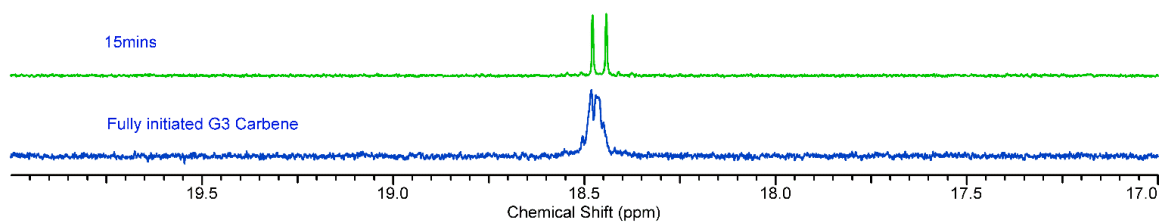


Fig. S23: ^1H NMR spectrum (CD_2Cl_2 , 300 MHz) of end-capping reaction with CTA25.

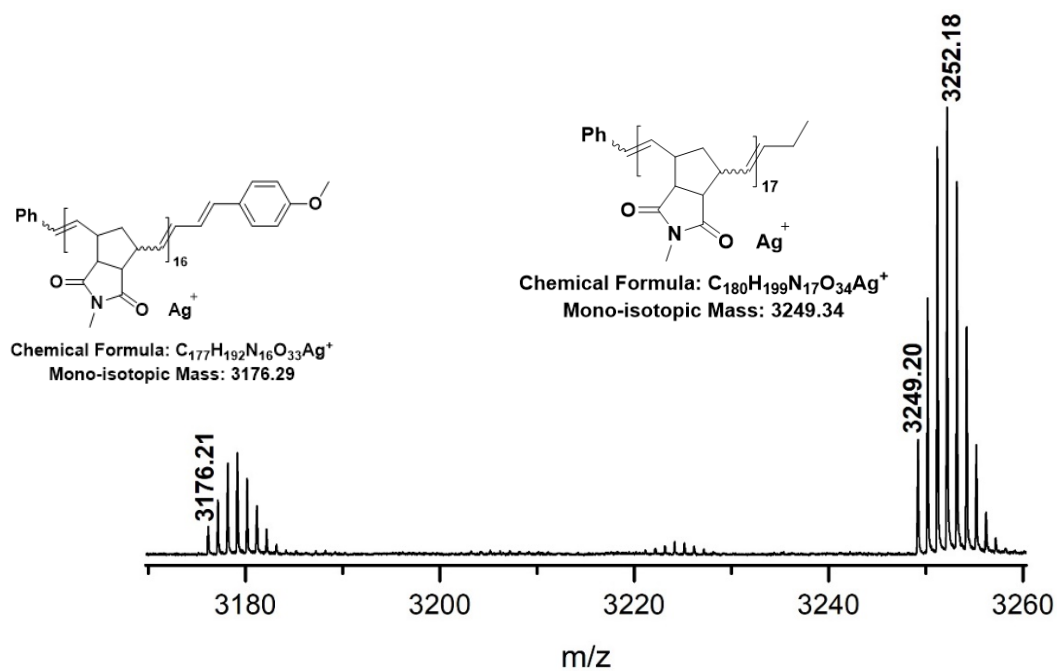
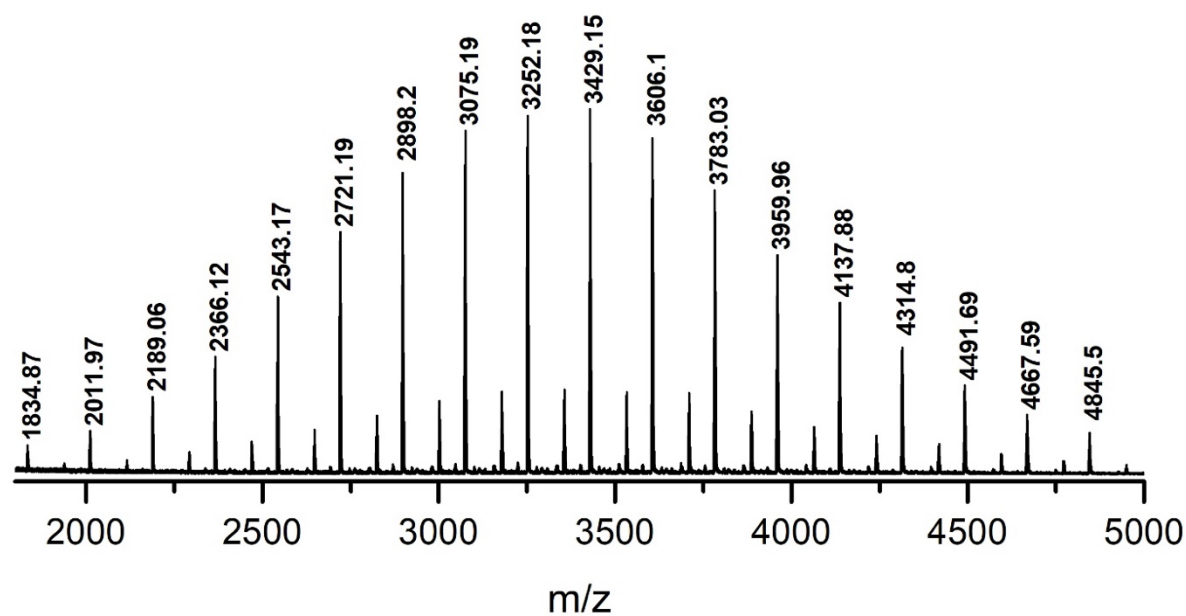


Fig. S24: MALDI-ToF mass spectrum (DCTB, AgTFA) of P32.

¹H NMR reactions:

The reaction of CTA15-23 with G3:

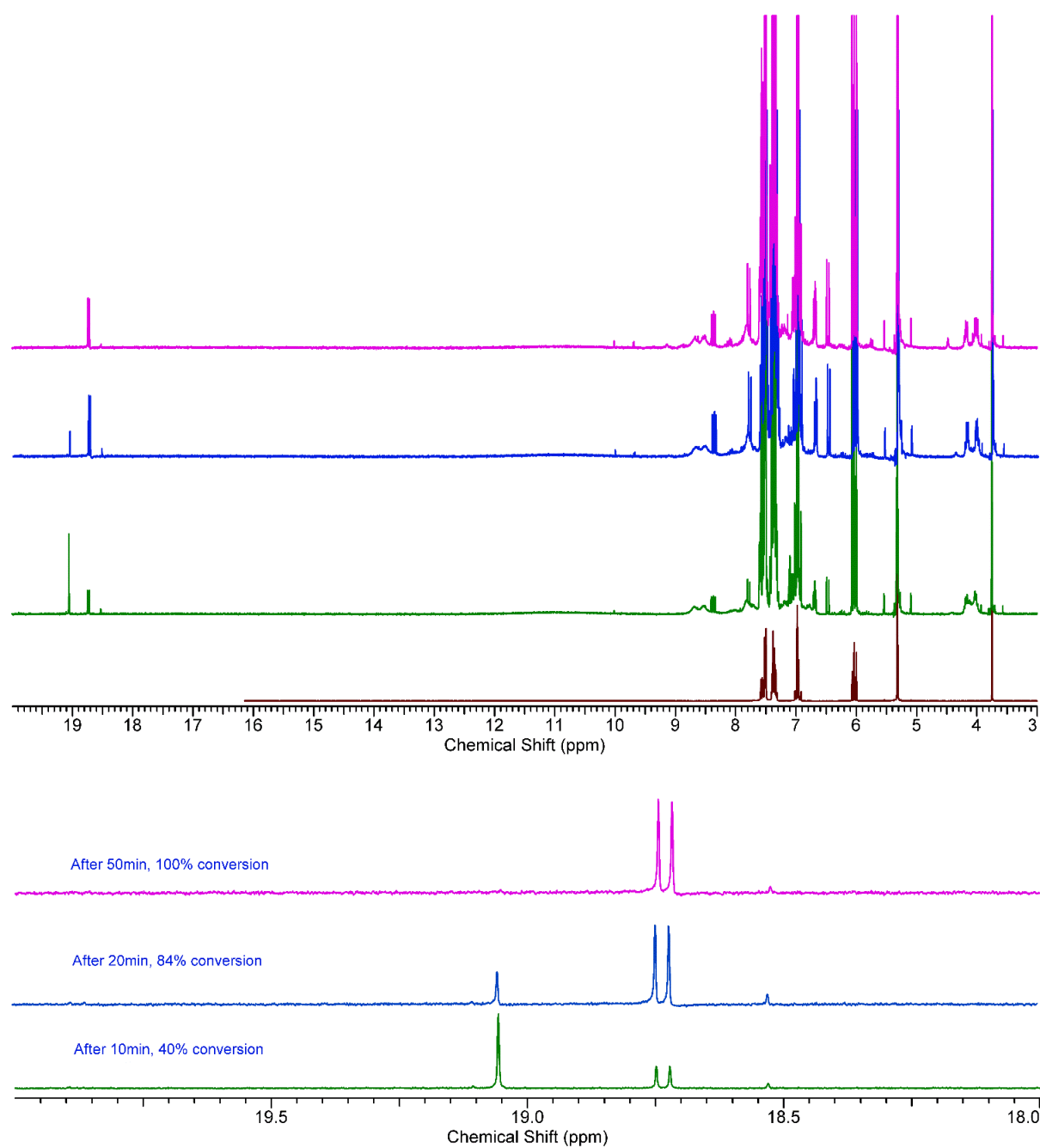


Fig. S25: ¹H NMR (CD₂Cl₂, 400 MHz) of reaction of **CTA15** (5 equiv.) with **G3** (1 equiv.).

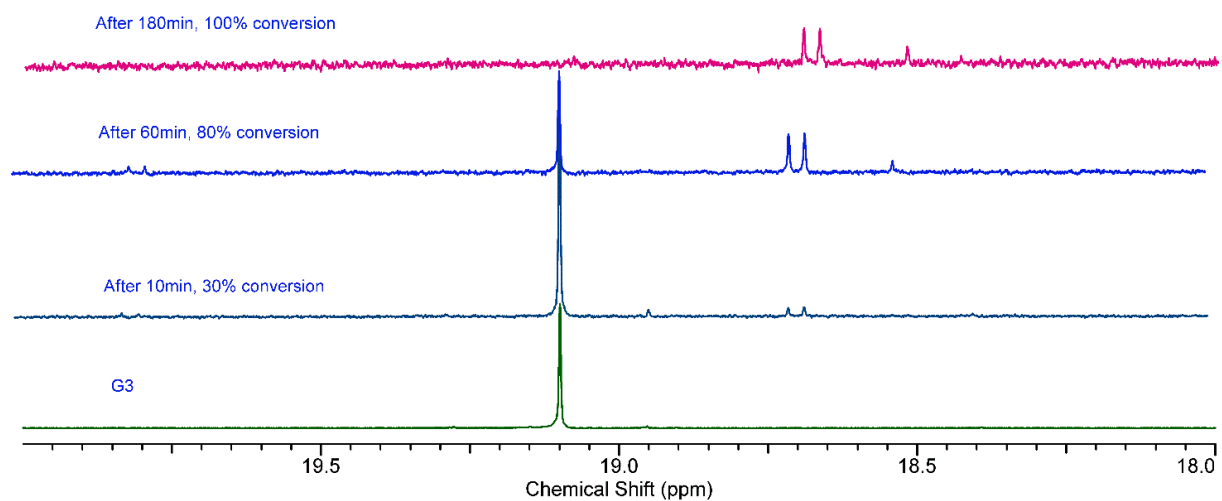


Fig. S26: ¹H NMR (400 MHz) of reaction of **CTA16** (10 equiv.) with **G3** (1 equiv.) in THF-d₈.

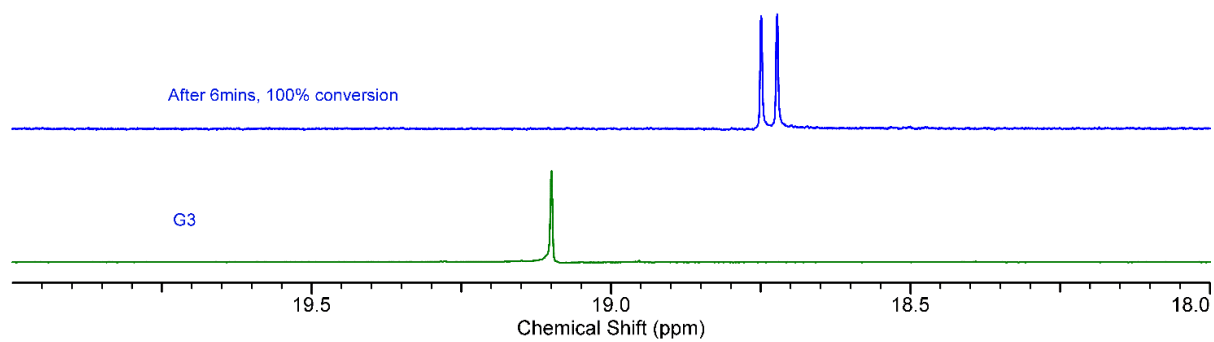


Fig. S27: ¹H NMR (CD₂Cl₂, 400 MHz) of reaction of **CTA17** (10 equiv.) with **G3** (1 equiv.).

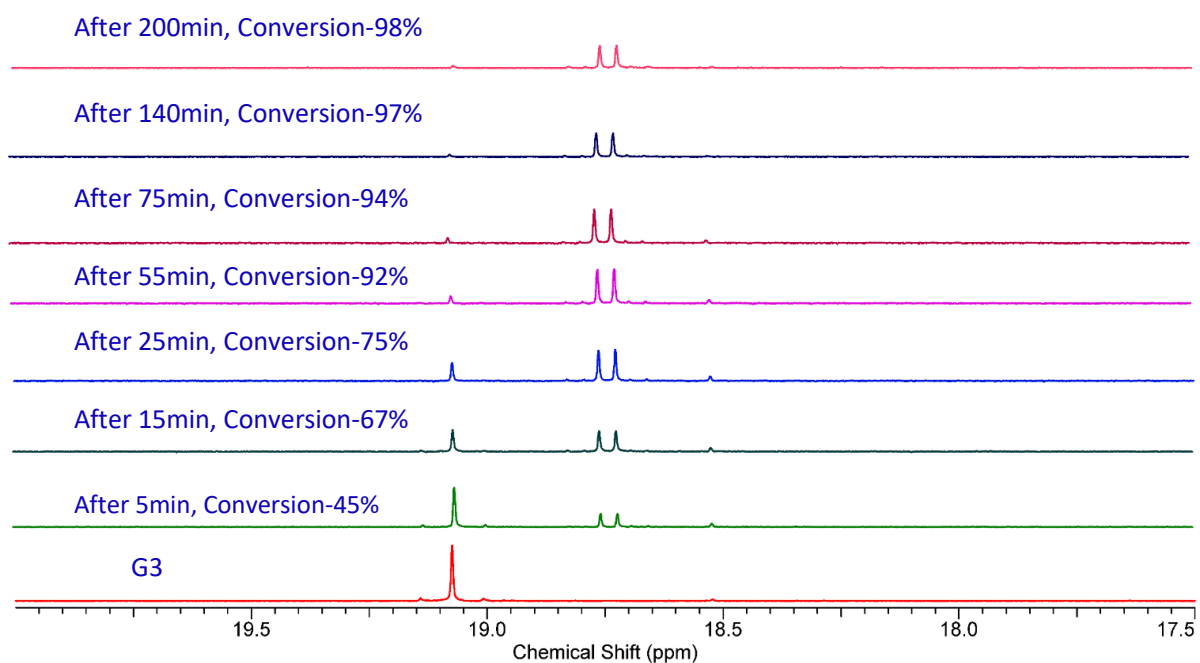
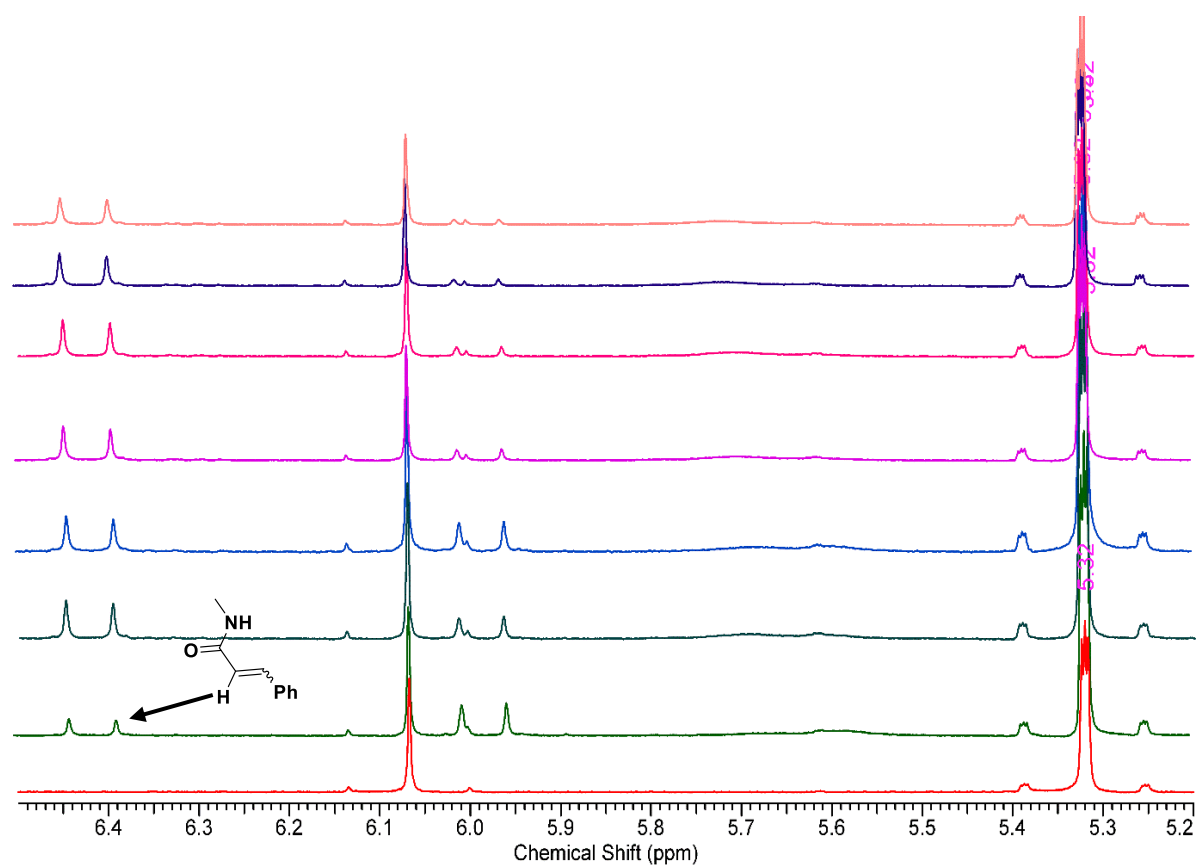


Fig. S28: ^1H NMR (CD_2Cl_2 , 400 MHz) of reaction of **CTA17** (1 equiv.) with **G3** (1 equiv.). The regioselective cross-metathesis reaction produced a cinnamyl amide derivative as a side product upon reaction with **G3**, which could also be observed via ^1H NMR spectroscopy (signal at 6.42 ppm).

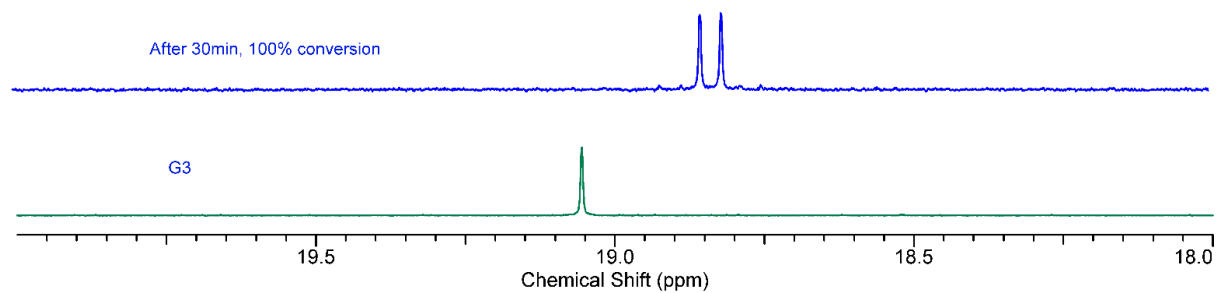


Fig. S29: ¹H NMR (CD₂Cl₂, 400 MHz) of reaction of **CTA19** (5 equiv.) with **G3** (1 equiv.).

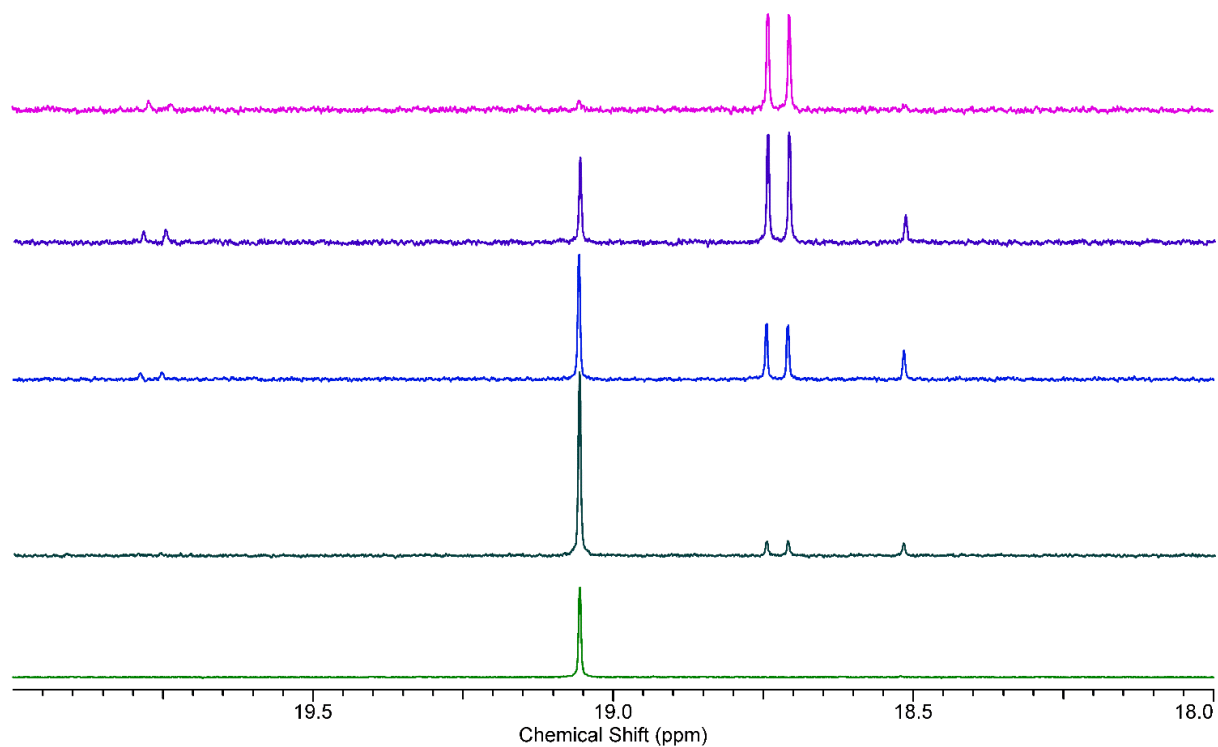


Fig. S30: ¹H NMR (CD₂Cl₂, 400 MHz) of reaction of **CTA20** (5 equiv.) with **G3** (1 equiv.).

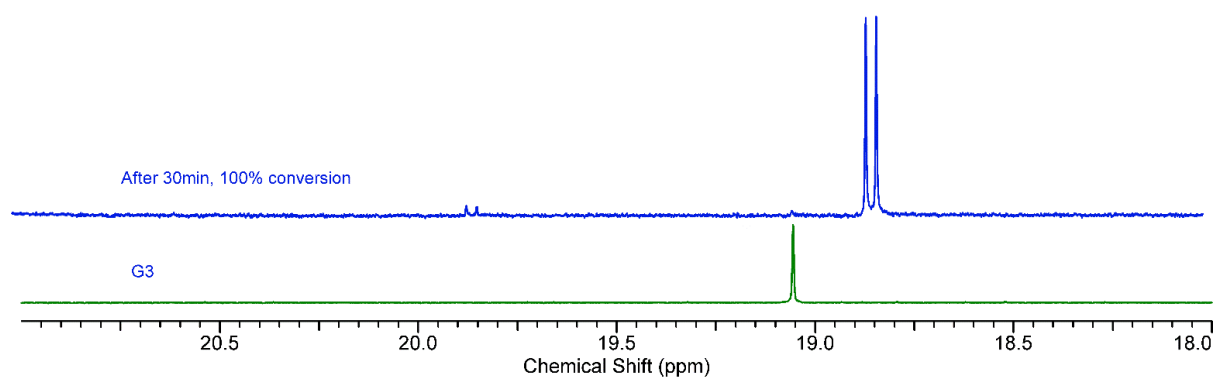


Fig. S31: ¹H NMR (CD₂Cl₂, 400 MHz) of reaction of **CTA21** (20 equiv.) with **G3** (1 equiv.).

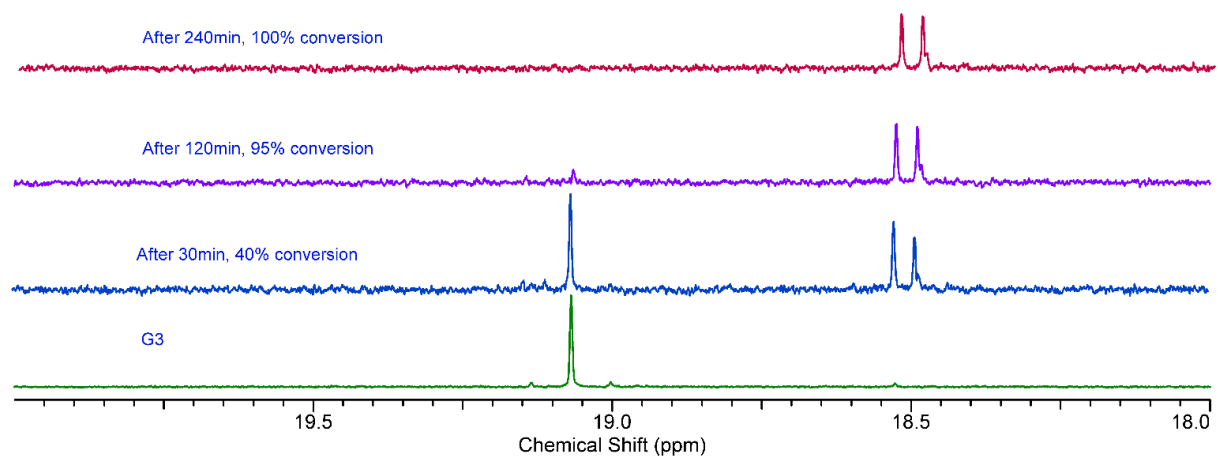


Fig. S32: ¹H NMR (CD₂Cl₂, 400 MHz) of reaction of **CTA22** (5 equiv.) with **G3** (1 equiv.).

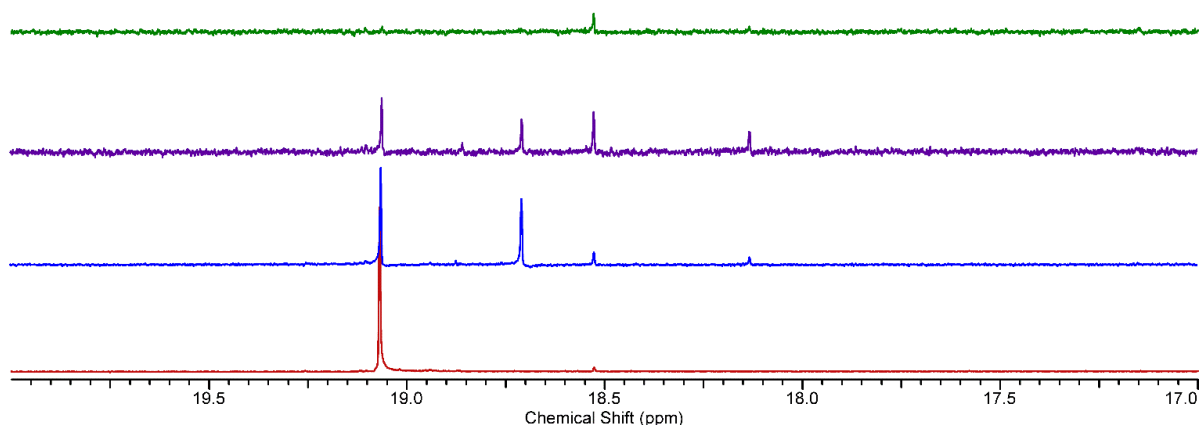


Fig. S33: ^1H NMR (CD_2Cl_2 , 400 MHz) of reaction of **CTA23** (2 equiv.) with **G3** (1 equiv.) in over 180 mins.

The reaction of CTA5 with G3:



In an NMR tube, **G3** (1 equiv., 0.0034mmol, 3 mg) and 1,3,5 trimethoxybenzene (as an internal standard) were dissolved in 0.5mL dichloromethane- d_2 (DCM-d_2), and ^1H NMR was measured. **CTA5** (2 equiv., 0.0068mmol, 1.56 mg) in 0.2mL DCM-d_2 was added, and ^1H NMR was measured immediately.

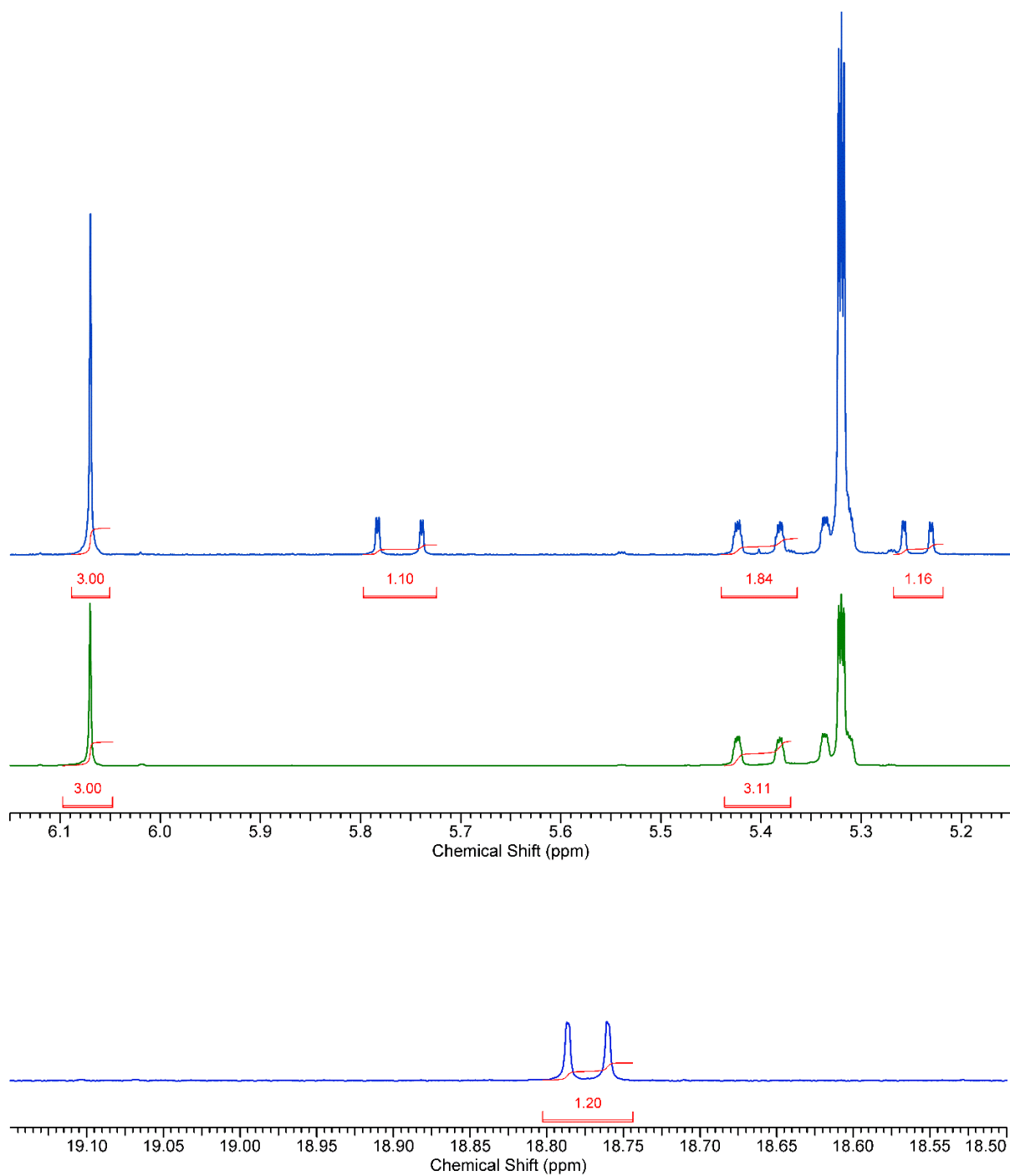


Fig. S34: ¹H NMR (CD₂Cl₂, 400 MHz) of reaction of **CTA5** (2 equiv.) with **G3** (1 equiv.). The green line in the top spectrum shows only **CTA5**, and the blue spectrum is after adding **G3** to it. The formation of styrene was clearly observed.

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.

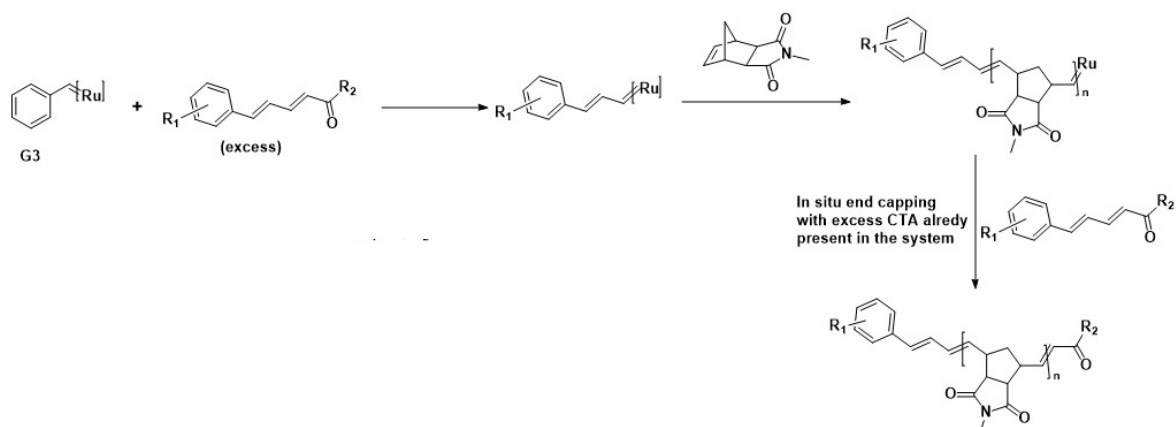


Fig. S35: Mechanism of one-pot heterotelechelic polymer synthesis.

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_2Cl_2) in an NMR tube and to it **CTA17** (5 equiv., 0.023 mmol, 4.3 mg) in 0.2 mL CD_2Cl_2 was quickly added. 1H NMR was measured over time. After 20 mins, **M1** (20 equiv., 0.09 mmol, 16 mg) dissolved in 0.2 mL CD_2Cl_2 was added, and 1H NMR was measured over time. After 80 mins, the CD_2Cl_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.

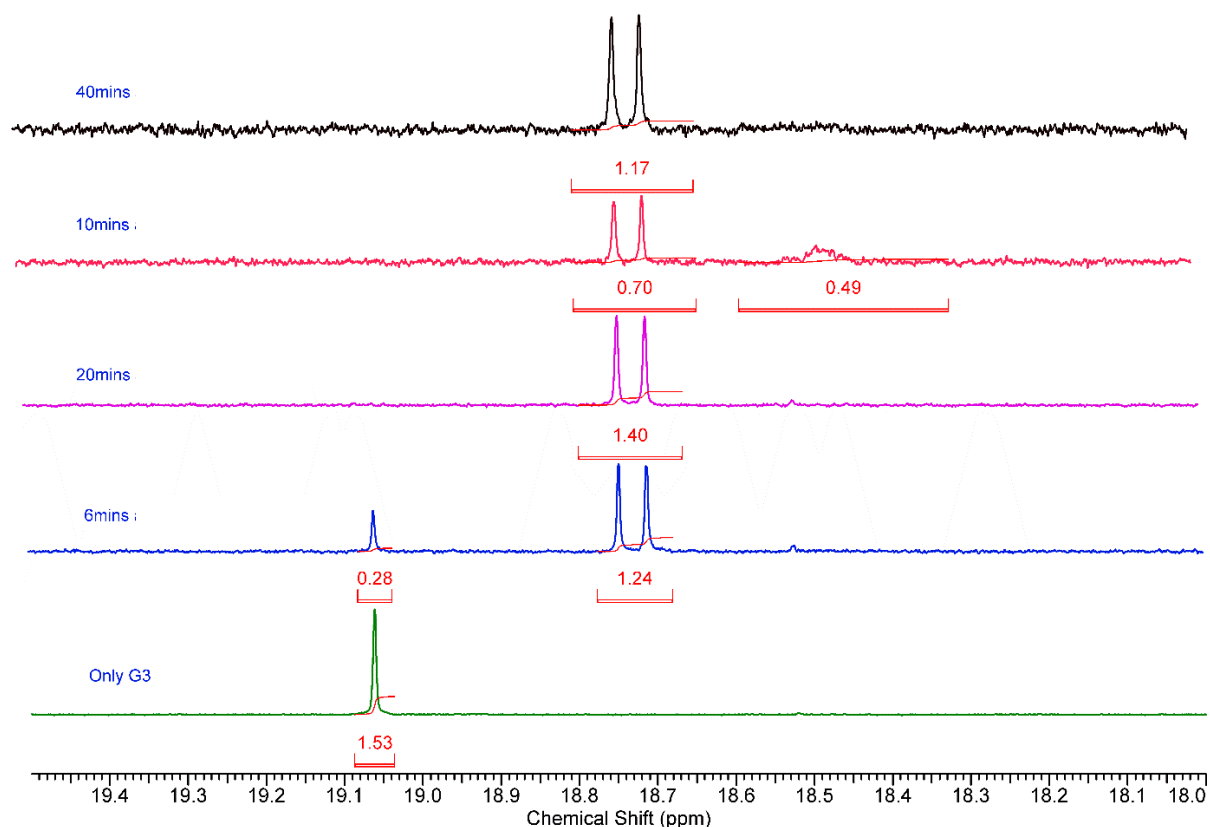


Fig. S36: 1H NMR (CD_2Cl_2 , 400 MHz) of polymerization reaction of **M1** using **CTA17**. Pre-functionalization of **G3** was achieved fully within 20 mins using only 5 equiv. of **CTA17** (spectrum in purple). The addition of monomer (**M1**) immediately formed polymer followed by chain transfer with 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 ^1H NMR spectroscopy. Then, the prerequisite amount of monomer (**M1** or **M3**) was dissolved in CD_2Cl_2 and added quickly to the same NMR tube. Complete monomer consumption was observed within 10 to 15 mins via ^1H 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**, $M_{n, \text{SEC}(\text{CHCl}_3)} = 6.3 \text{ kDa}$, $\text{Đ} = 1.22$) 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-

Entry	CTA	Monomer (M)	G3: CTA:M	M _n (Max, M/G3) (kDa)	M _n (SEC, CHCl ₃) kDa	Đ
P33	CTA15	M1	1:70:70	12.4	11	1.19
P34	CTA15	M1	1:70:35	6.2	5.3	1.37
P35	CTA15	M3	1:20:60	10.6	55	1.17
P36	CTA15	M1	1:40:200	36	30	2.0
P37	CTA17	M1	1:5:20	3.7	5.5	1.23
P38	CTA18	M1	1:70:35	6.2	7.8	1.26
P39	CTA19	M1	1:5:35	6.2	8.2	1.24
P40	CTA19	M1	1:25:50	9	10	1.21
P41	CTA19	M1	1:70:70	12.4	13	1.20
P42	CTA19	M1	1:70:35	6.2	6.8	1.21
P43	CTA20	M1	1:70:20	3.5	6.3	1.22

P33:

^1H NMR (CDCl_3 , 400 MHz) δ 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) δ 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.

^1H NMR (CDCl_3 , 400 MHz) δ 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, 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) δ 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.

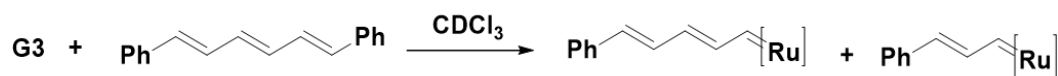
^1H NMR (CDCl_3 , 400 MHz) δ ppm: 0.04 - 0.10, 1.12 - 1.40, 1.55 - 1.83, 2.00 - 2.22, 2.24 - 2.31, 2.57, 2.67 - 2.88, 2.89 - 3.15, 3.19 - 3.40, 5.44 - 5.65, 5.65 - 5.84, 6.21 - 6.41, 7.26 - 7.36. ^{13}C NMR (CDCl_3 , 101 MHz) δ 15.2, 24.7, 24.8, 24.9, 40.8, 41.2, 41.4, 41.9, 42.4, 45.6, 45.6, 46.0, 46.2, 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.

^1H NMR (300 MHz, CDCl_3) δ 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) δ 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.

¹H NMR reaction of (1E,3E,5E)-1,6-diphenylhexa-1,3,5-triene (CTA26) with G3:



G3 (1 equiv., 0.0068 mmol, 6 mg) was dissolved in 0.5 mL dichloromethane-d₂ (CD₂Cl₂) in an NMR tube, and ¹H 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 CD₂Cl₂ was added and ¹H NMR was measured over time. As shown below, it took 150 mins to convert all the G3-benzylidene to a mixture of doublets.

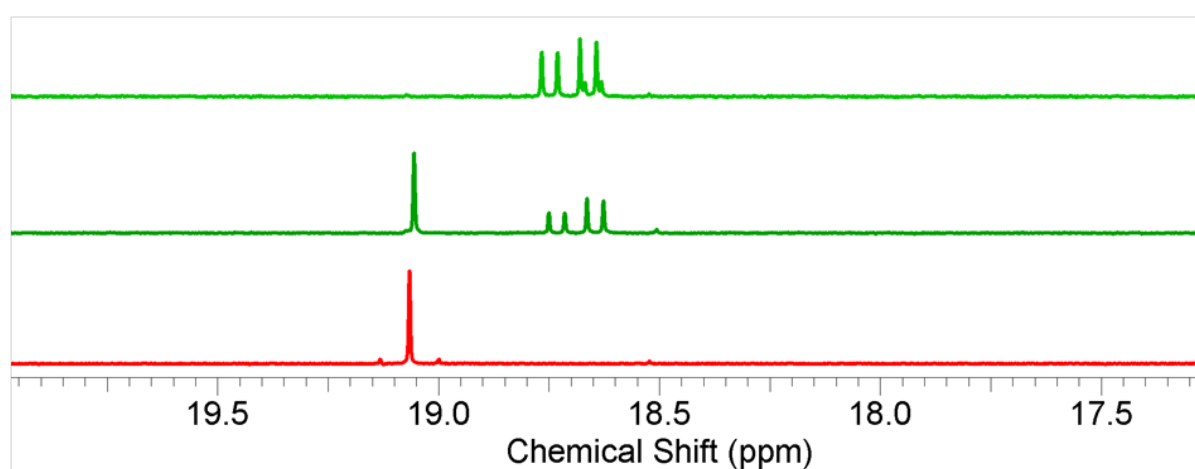
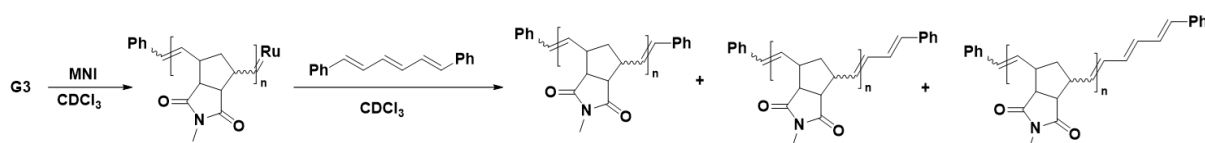


Fig. S37: ¹H NMR (CD₂Cl₂, 300 MHz) of reaction of **CTA26** (10 equiv.) with **G3** (1 equiv.).

End capping experiment with CTA26:



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, **M1** (20 equiv., 0.136 mmol, 24 mg) in 0.2 mL CDCl_3 was quickly added. ¹H NMR was measured. Then, **CTA26** (10 equiv., 0.068 mmol, 16 mg) dissolved in 0.5 mL CDCl_3 was added and ¹H 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 (**P44**) was obtained as a yellow solid in quantitative yield.

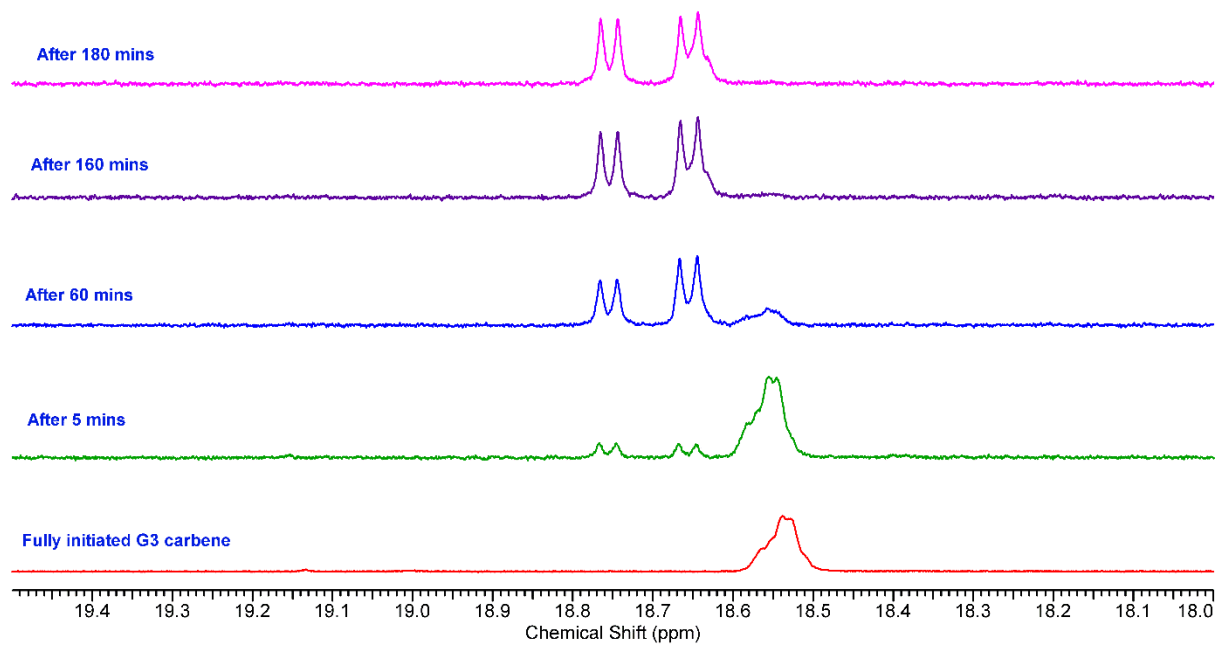
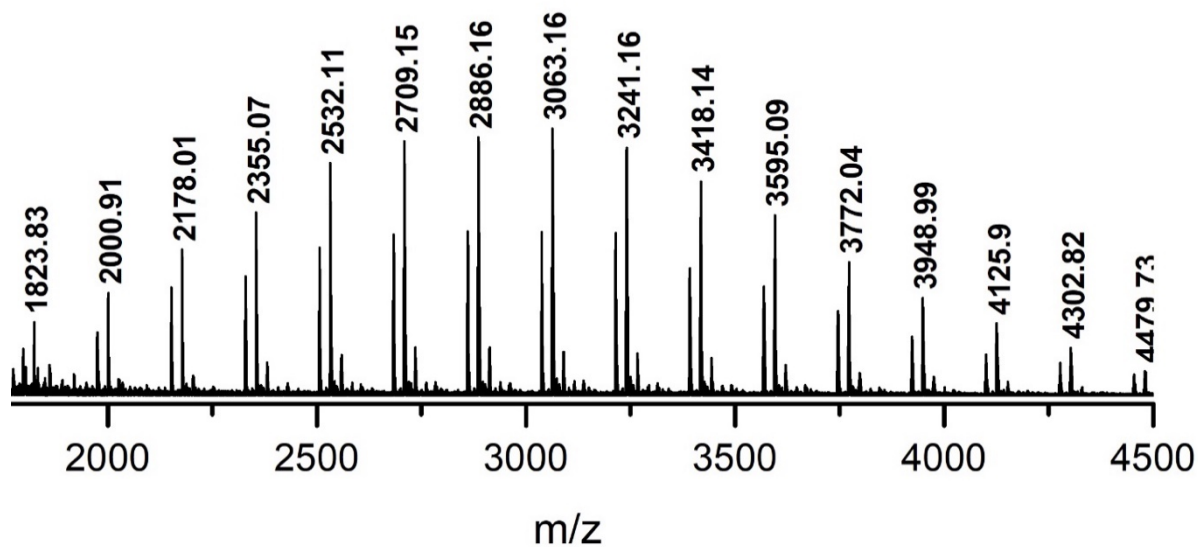


Fig. S38: ¹H NMR spectrum (CD₂Cl₂, 400 MHz) of end capping reaction with CTA26.



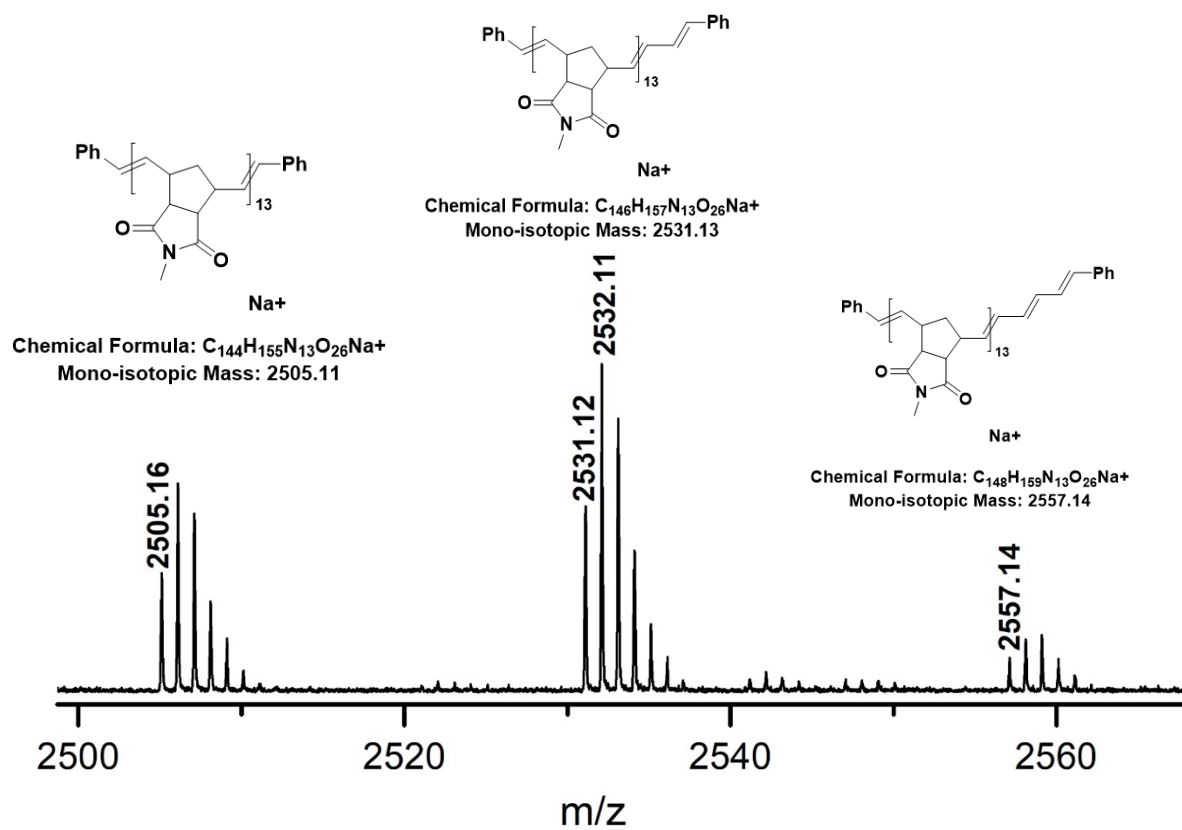
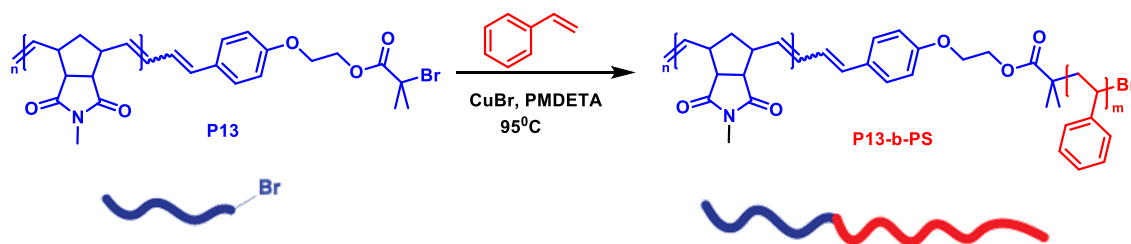


Fig. S39: MALDI-ToF mass spectrum (DCTB, AgTFA) of P44.

Synthesis of Block co-polymers:

ROMP-ATRP block copolymer-



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 μ L 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 μ L) stock solution in DMF. The resulting mixture was stirred at 90°C for 19h. The reaction mixture was quenched by removing the heating 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.

^1H NMR (CDCl_3 , 400 MHz) δ 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.

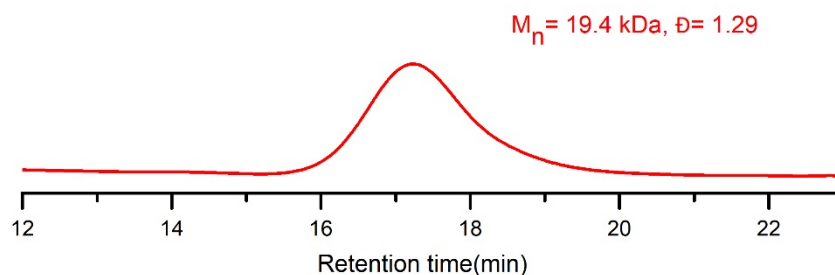
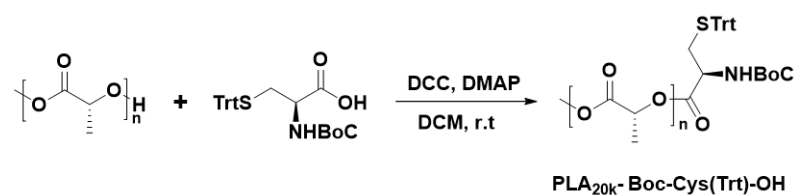


Fig. S40: SEC (CHCl_3) trace of **P13-b-PS**.

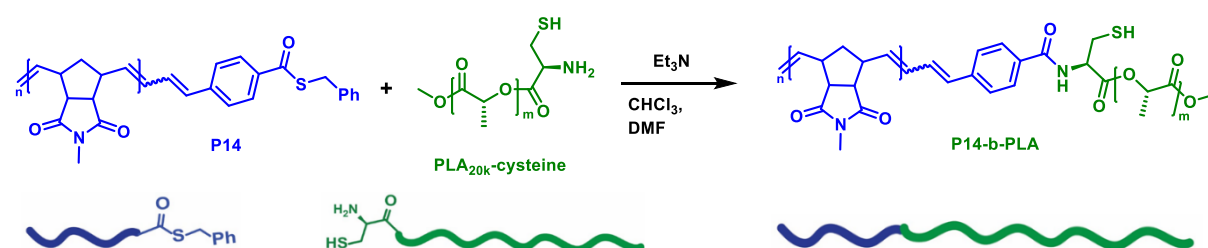
Block copolymer by Native Chemical Ligation (NCL)-



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. ¹H 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**).

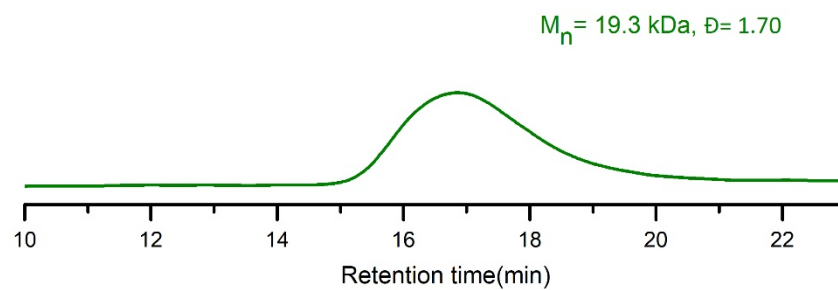
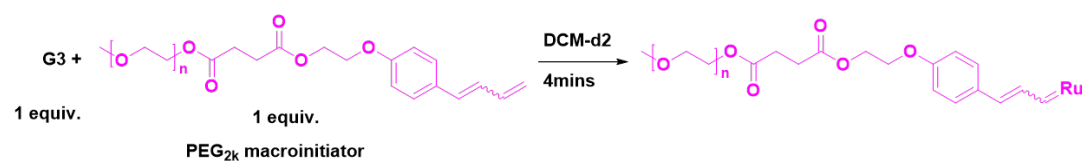


Fig. S41: SEC (CHCl_3) trace of **P14-b-PLA**.

^1H NMR Reaction of PEG_{2k} macroinitiator with G3:



G3 and **PEG_{2k} macroinitiator** stock solution was prepared in DCM-d₂. Then, in an NMR tube, 1 equivalent of **G3** and 1 equivalent of **PEG_{2k} macroinitiator** were mixed. ^1H NMR was measured immediately, which took around 4 to 5 mins. The spectrum is shown below (top spectrum, the blue one). ^1H NMR spectrum of **PEG_{2k} macroinitiator** was measured separately in CDCl₃ 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**.

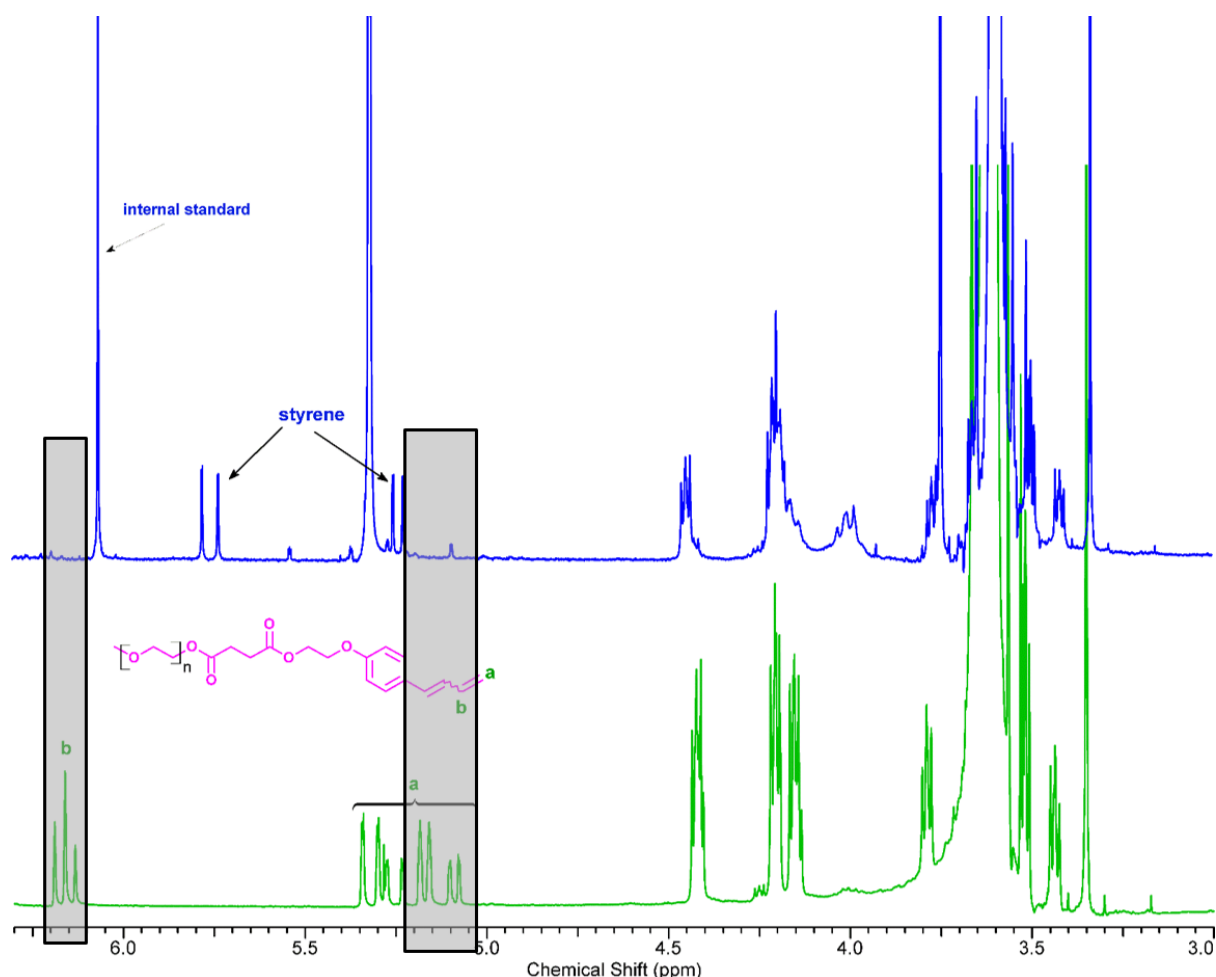
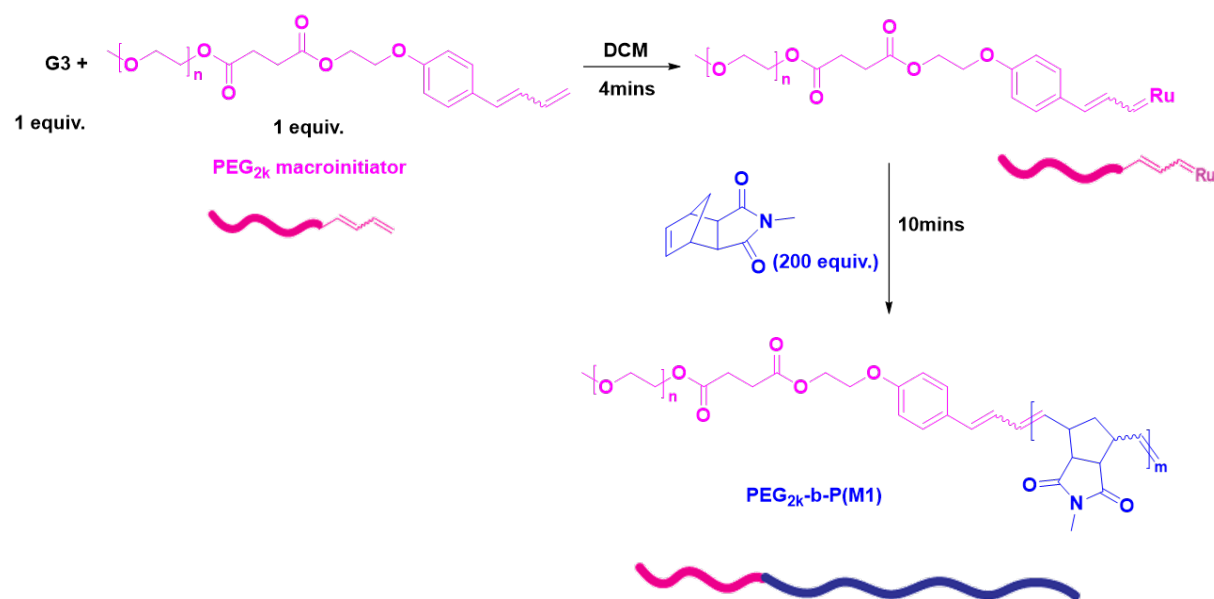


Fig. S42: Stacked ^1H NMR (400 MHz) spectrum showing pre-functionalization of **G3** using **PEG_{2k} macroinitiator**.

PEG-ROMP block copolymer-



G3 and **PEG_{2k} 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_{2k} 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 ¹H 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_{2k}-b-P(M1)**) was obtained as a diblock copolymer.

¹H NMR (CDCl₃, 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. ¹³C NMR (CDCl₃, 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.

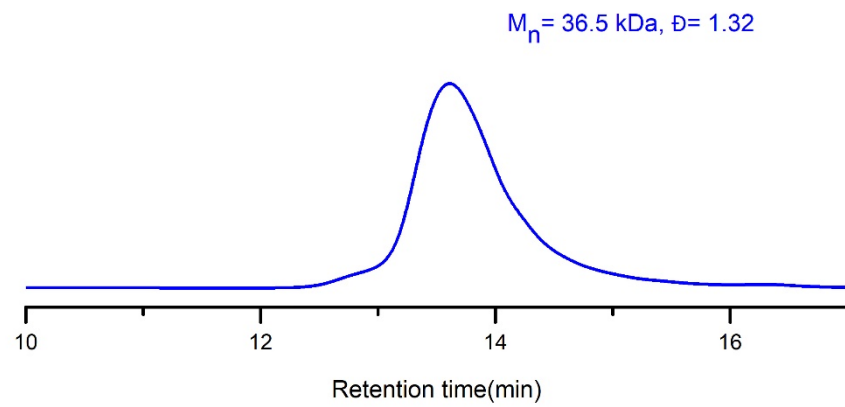


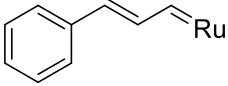
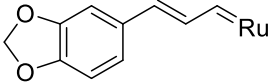
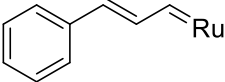
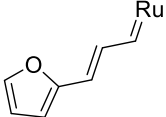
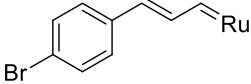
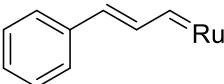
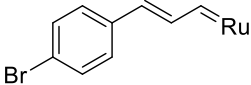
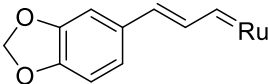
Fig. S43: SEC (DMF) trace of PEG_{2k}-b-P(M1).

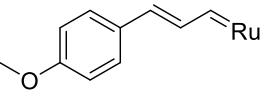
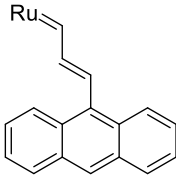
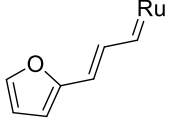
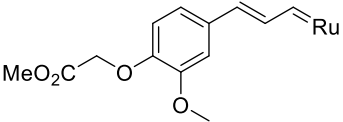
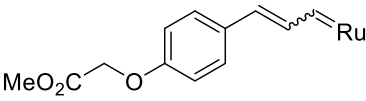
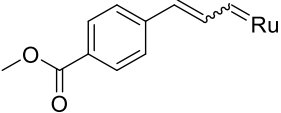
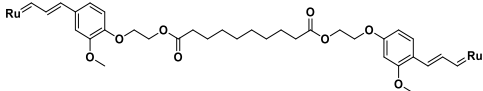
Table S4: Stability of Chain Transfer Agents-

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

CTA	Storage temperature	Time stable up to
CTA1-10, CTA23-25	-20°C	>8 months
CTA11,12	-20°C	2 months
CTA13	room temperature	2-3 hours
CTA14	room temperature	60 minutes
CTA13,14	-20°C	24-48 hours
CTA15,17,26	room temperature	>1 year
CTA18,19	-20°C	>10 months
PEG_{2k} macroinitiator	-20°C	2-4 months

Table S5: Chemical shift data

CTA	Solvent	Structure	Chemical Shift(ppm)
CTA15	CD ₂ Cl ₂		18.73
CTA16	C ₄ D ₈ O (THF-D8)		18.68
CTA17	CD ₂ Cl ₂		18.73
CTA18	CD ₂ Cl ₂		18.55
CTA19	CD ₂ Cl ₂		18.82
CTA20	CD ₂ Cl ₂		18.73
CTA21	CD ₂ Cl ₂		18.83
CTA22	CD ₂ Cl ₂		18.51

CTA2	CD ₂ Cl ₂		18.45
CTA5	CD ₂ Cl ₂		18.77
CTA4	CD ₂ Cl ₂		18.56
CTA1	CD ₂ Cl ₂		18.56
CTA6	CD ₂ Cl ₂		18.54, 18.64, 18.72 & 19.29
CTA8	CD ₂ Cl ₂		18.53-18.63, 19.02-19.06, 19.57-19.61
CTA11	CD ₂ Cl ₂		18.55

NMR Spectra of CTAs and Monomer:

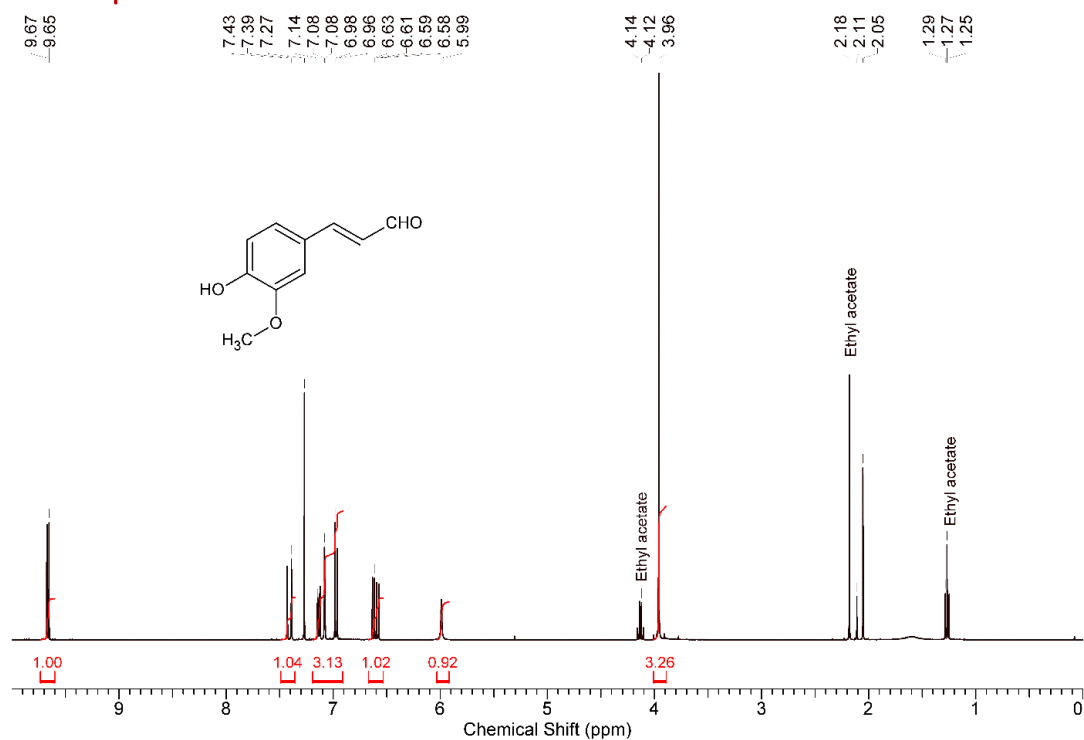


Fig. S44: ¹H NMR (CDCl₃, 400 MHz) spectrum of I1.

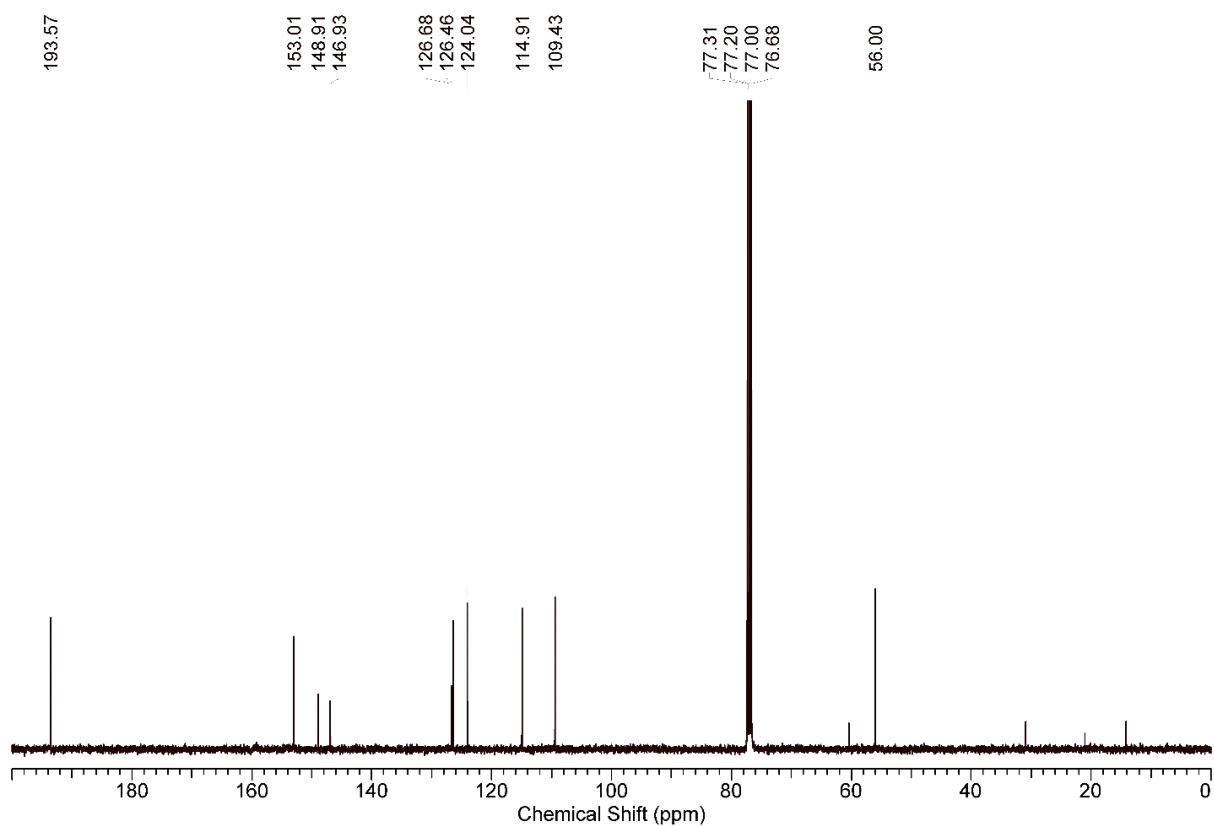


Fig. S45: ¹³C NMR (CDCl₃, 101 MHz) spectrum of I1.

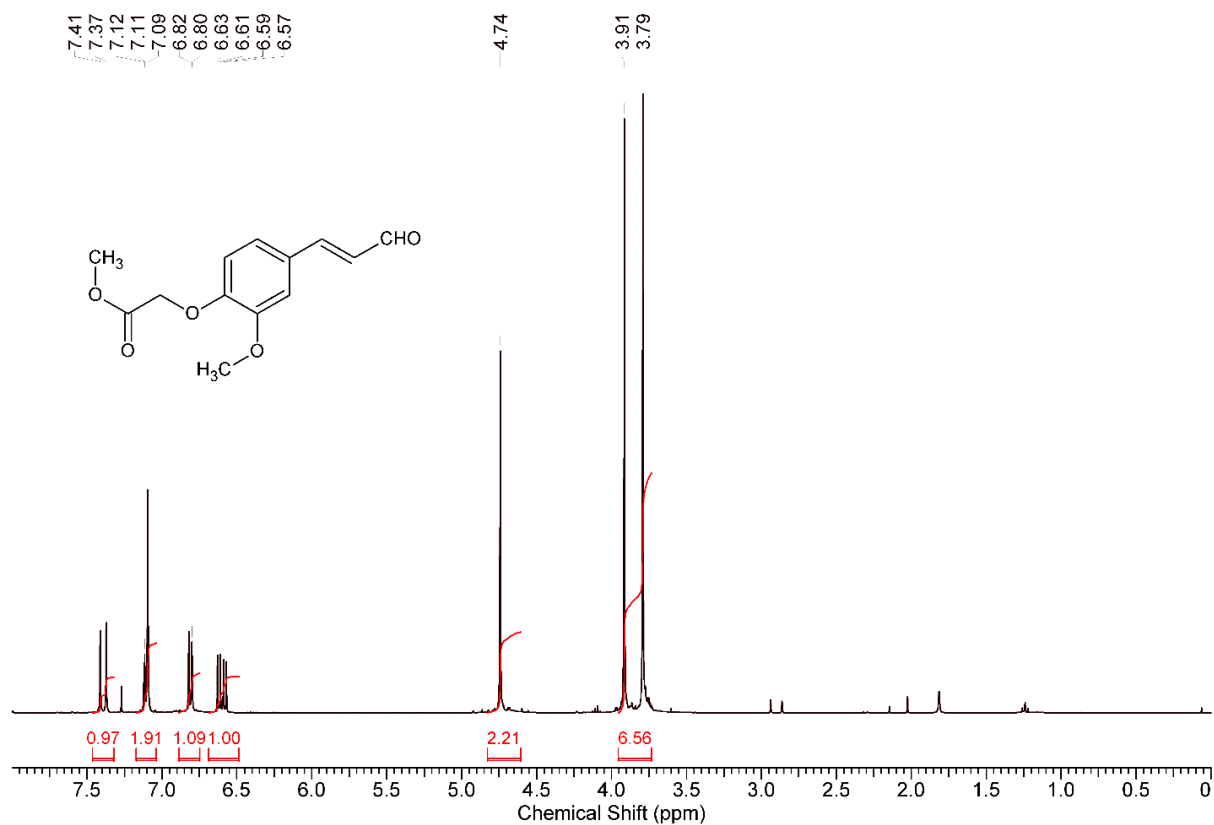


Fig. S46: ¹H NMR (CDCl₃, 400 MHz) spectrum of **12**.

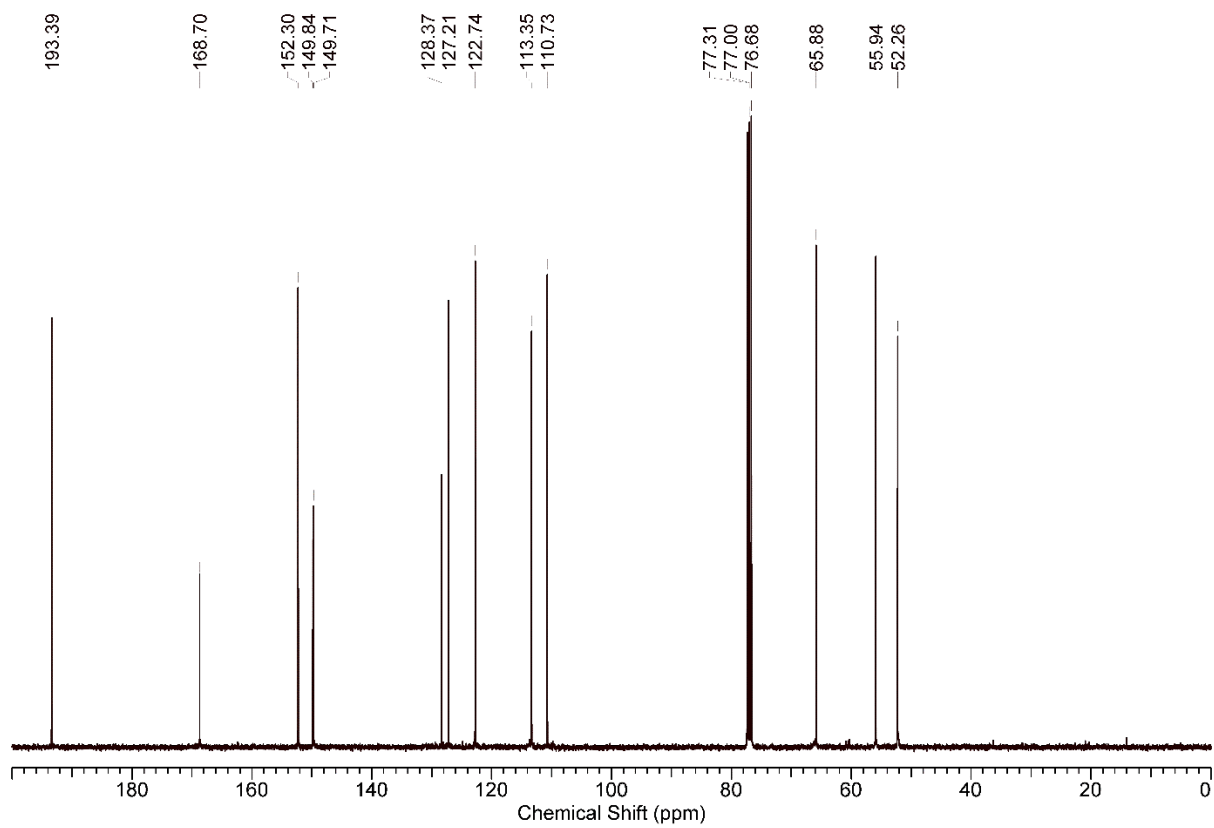


Fig. S47: ¹³C NMR (CDCl₃, 101 MHz) spectrum of **12**.

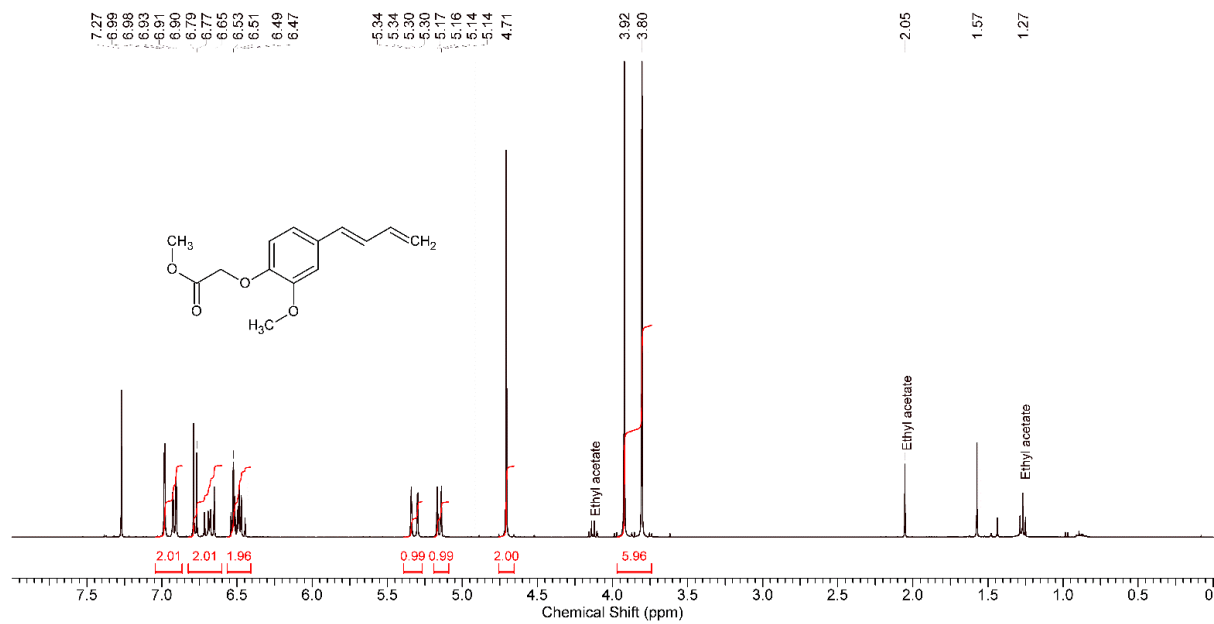


Fig. S48: ^1H NMR (CDCl_3 , 400 MHz) spectrum of **CTA1**.

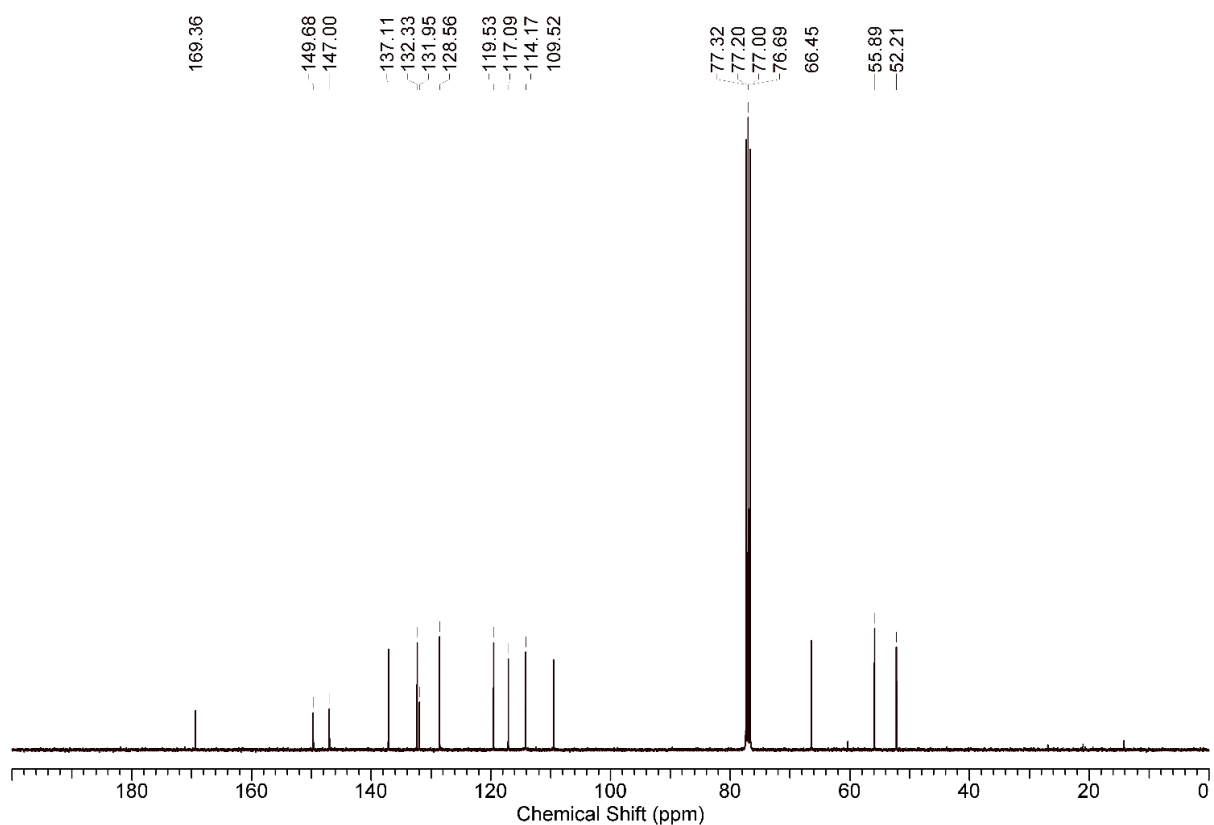


Fig. S49: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **CTA1**.

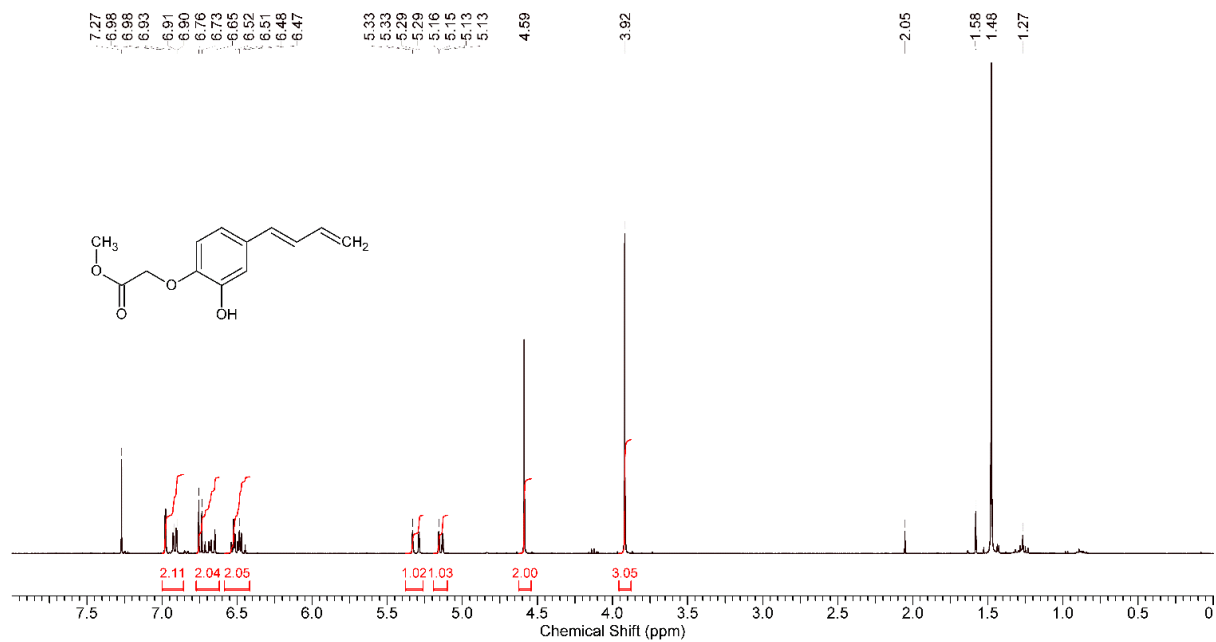


Fig. S50: ^1H NMR (CDCl_3 , 400 MHz) spectrum of **13**.

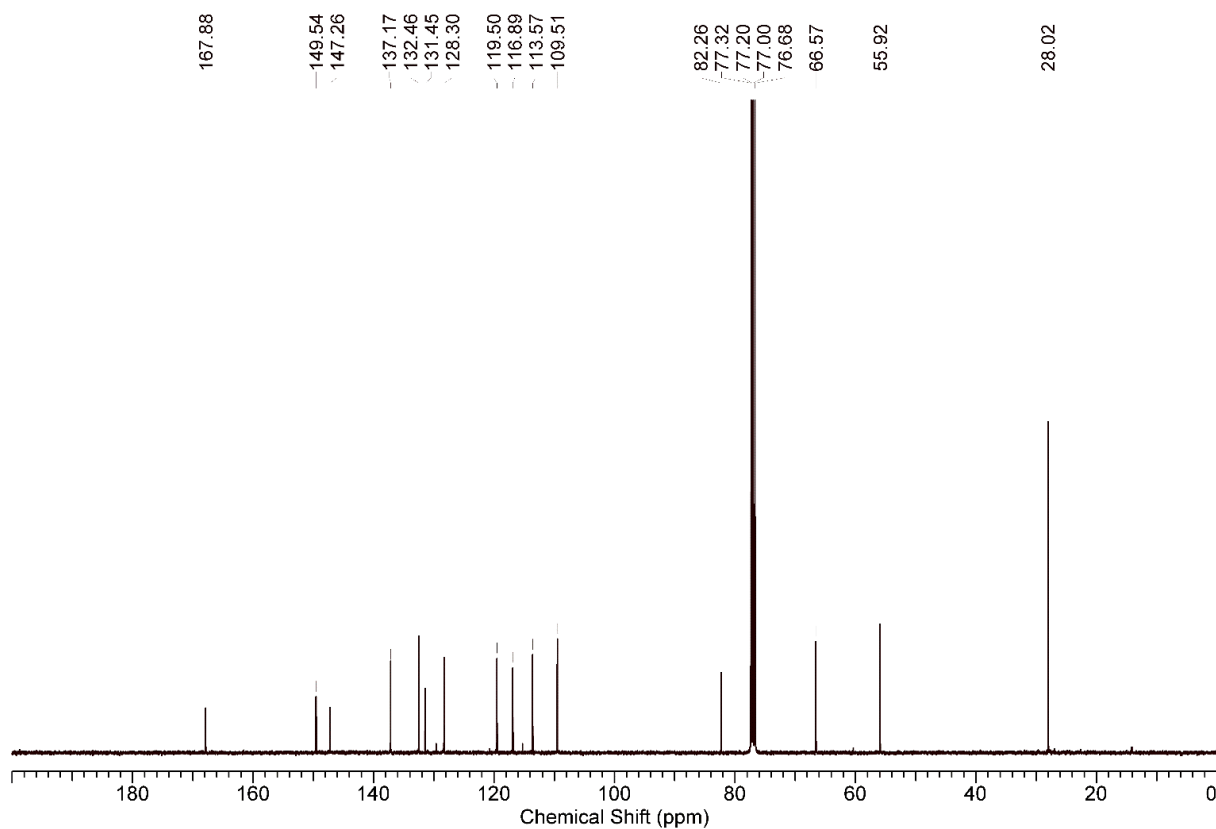


Fig. S51: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **13**.

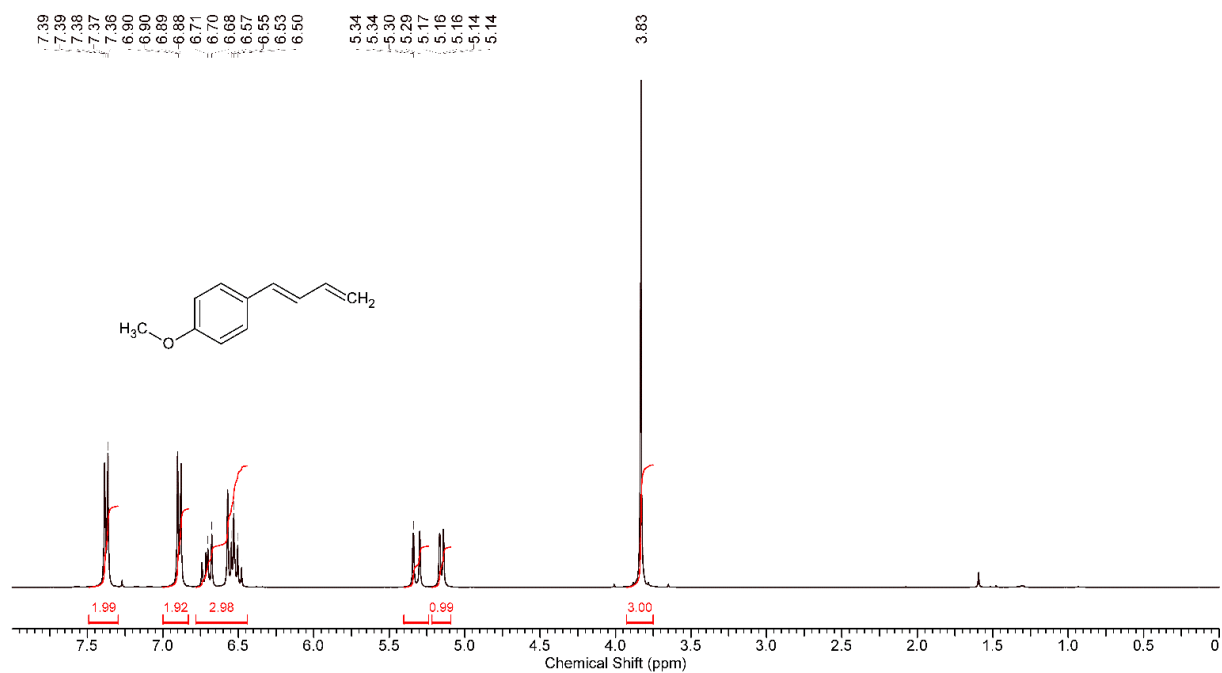


Fig. S52: ¹H NMR (CDCl₃, 400 MHz) spectrum of **CTA2**.

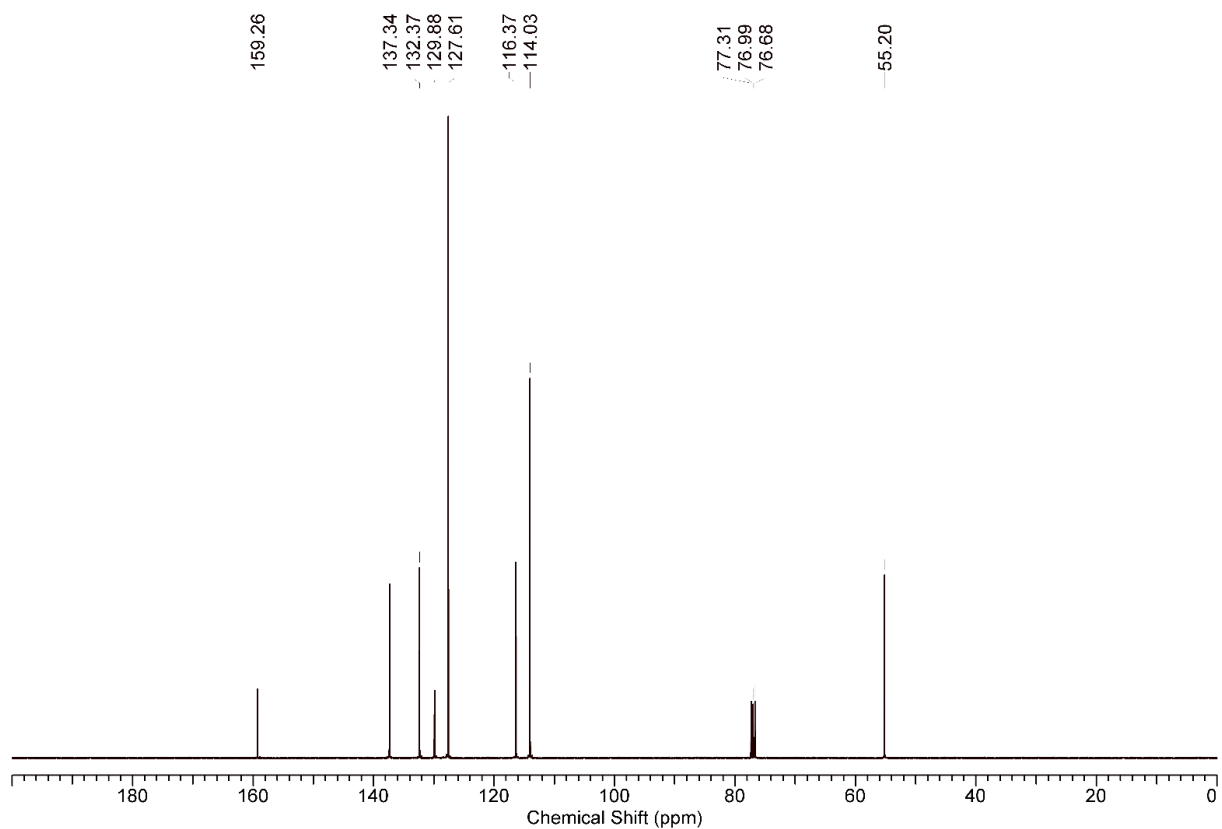


Fig. S53: ¹³C NMR (CDCl₃, 101 MHz) spectrum of **CTA2**.

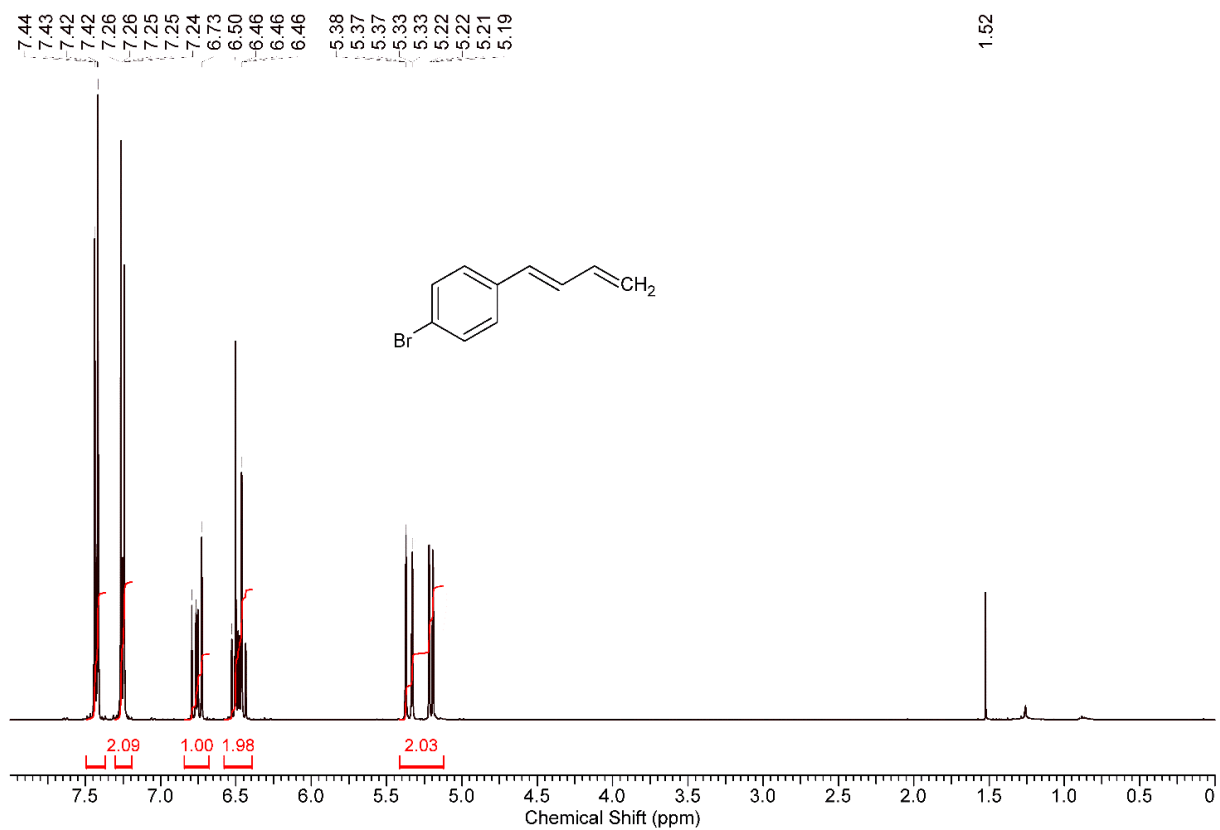


Fig. S54: ^1H NMR (CDCl_3 , 400 MHz) spectrum of CTa3.

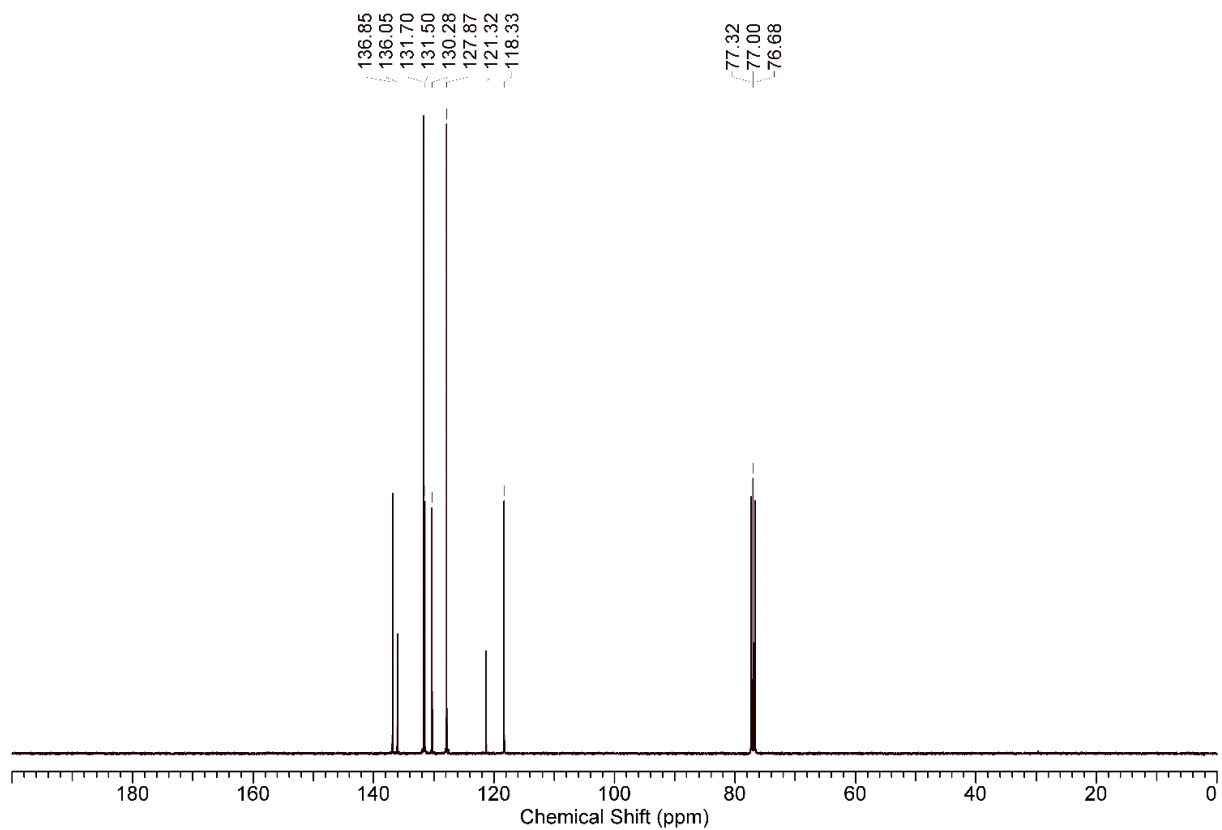


Fig. S55: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of CTa3.

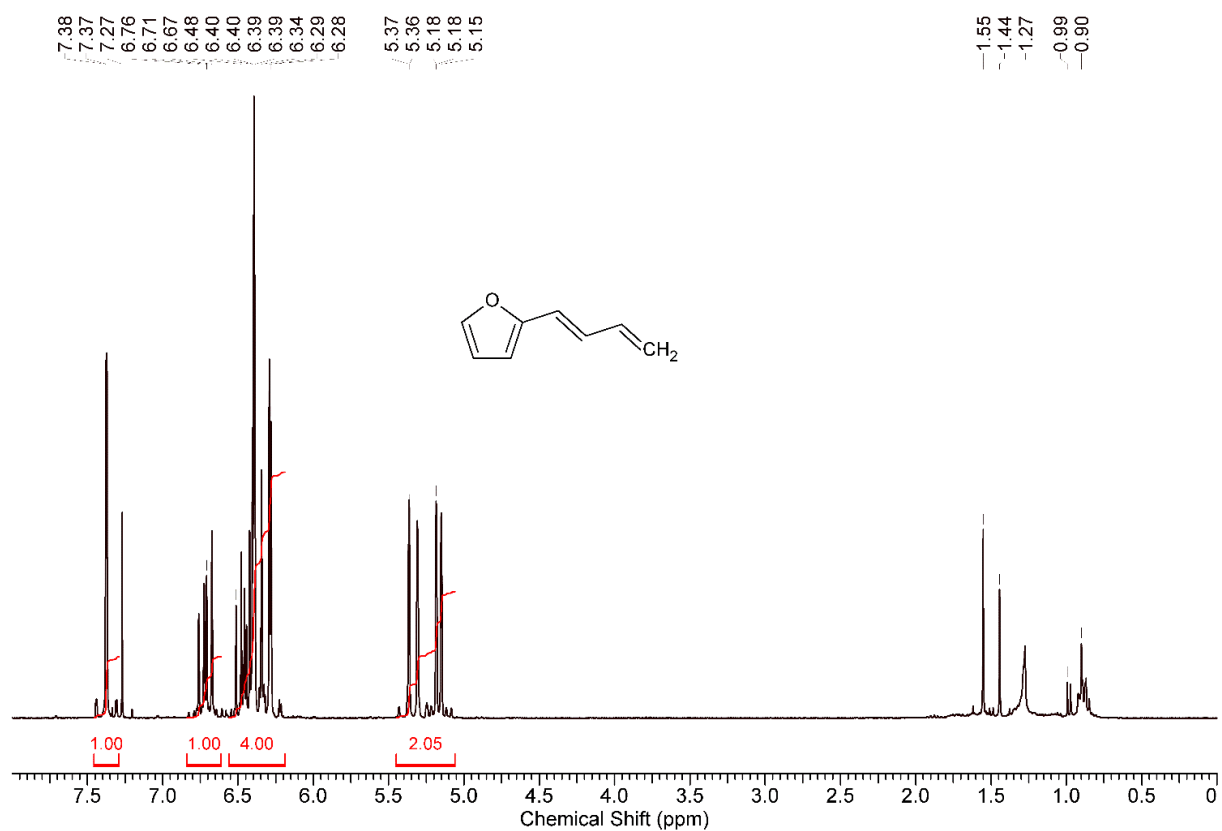


Fig. S56: ^1H NMR (CDCl_3 , 400 MHz) spectrum of CTA4.

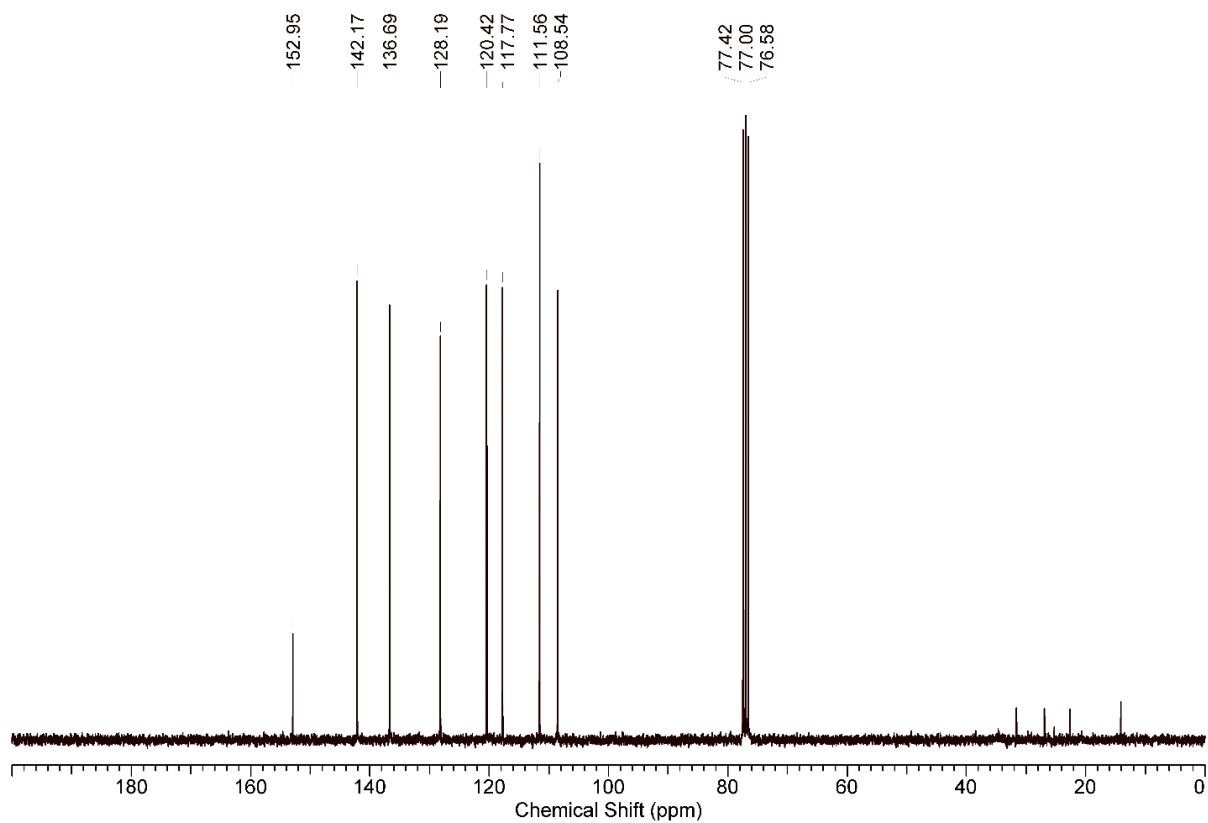


Fig. S57: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of CTA4.

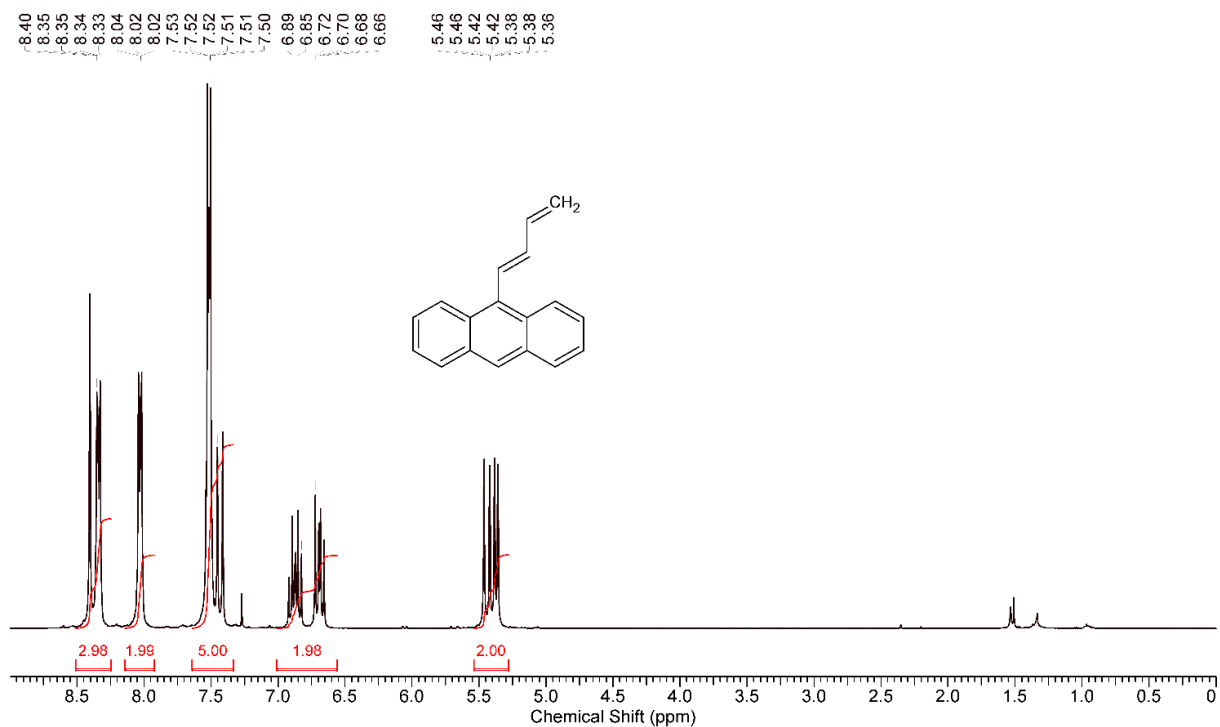


Fig. S58: ^1H NMR (CDCl_3 , 400 MHz) spectrum of CTA5.

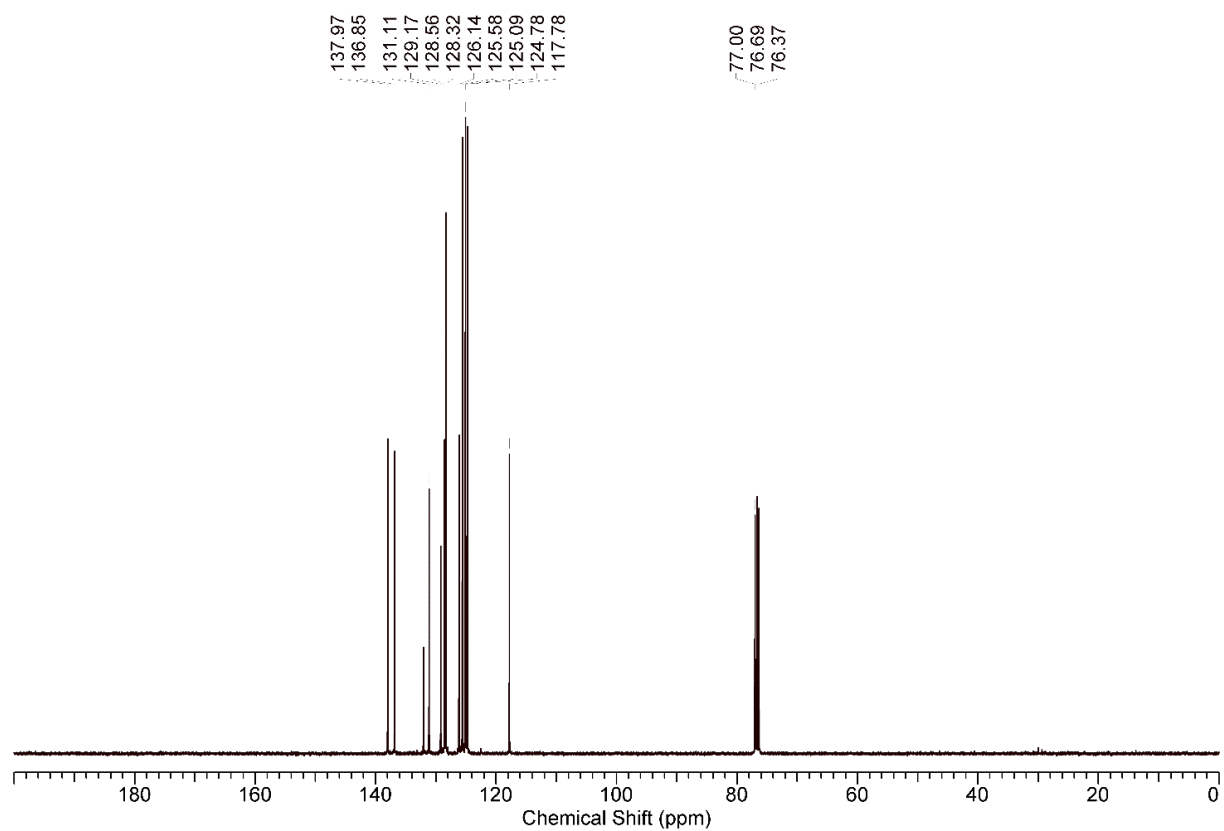


Fig. S59: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of CTA5.

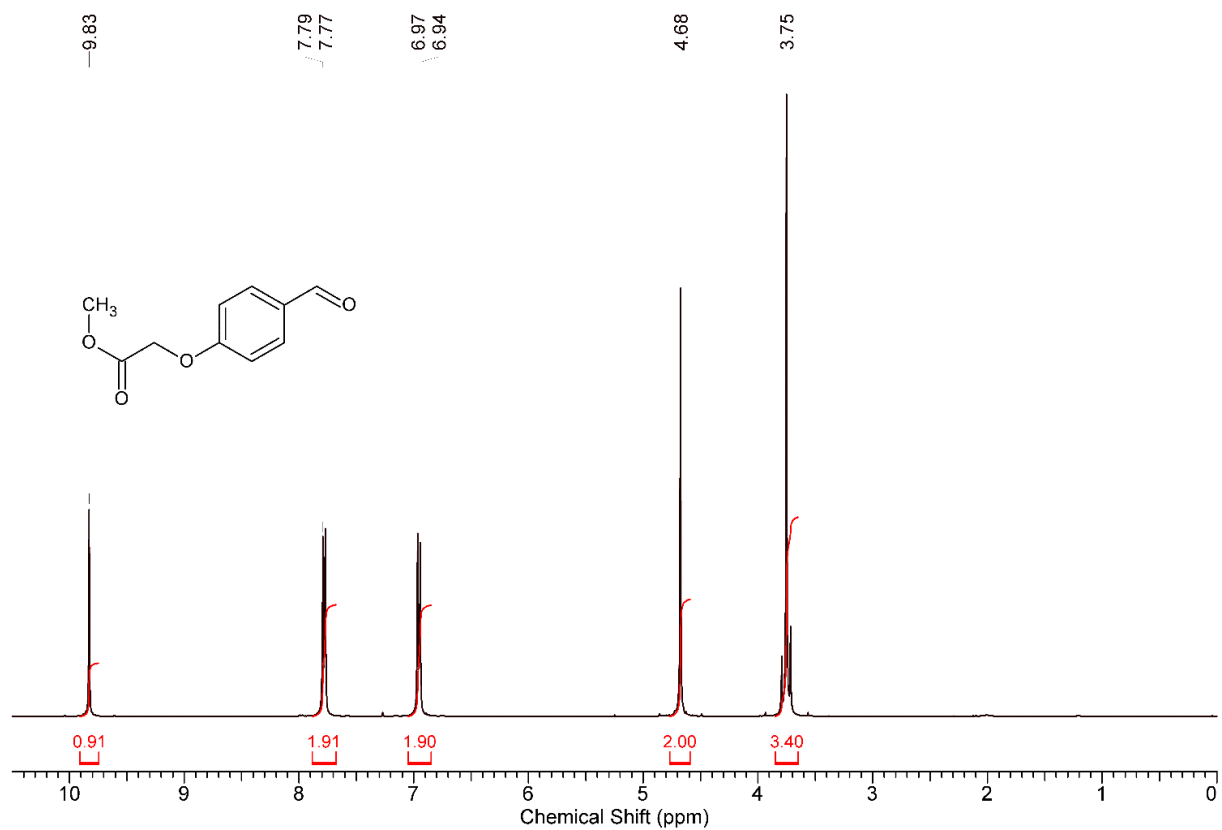


Fig. S60: ^1H NMR (CDCl_3 , 400 MHz) spectrum of **14**.

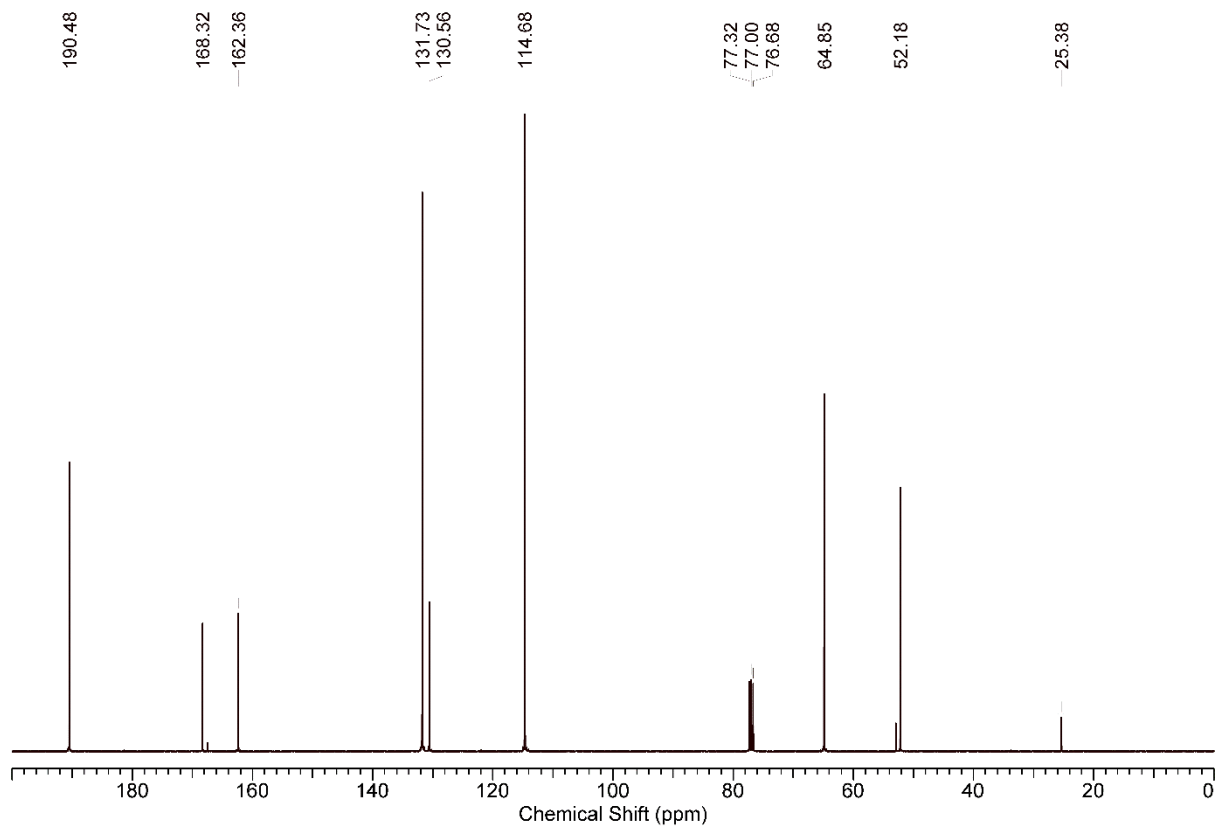


Fig. S61: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **14**.

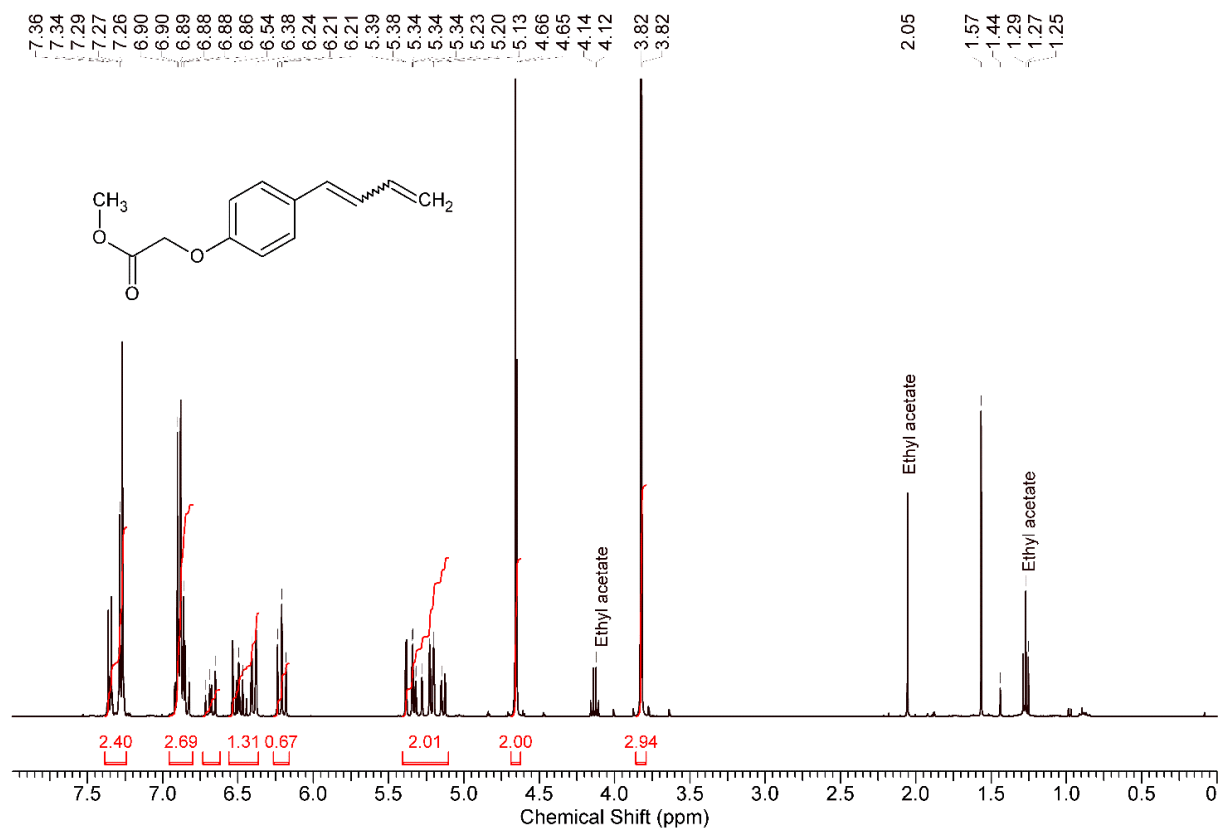


Fig. S62: ^1H NMR (CDCl_3 , 400 MHz) spectrum of CTA6.

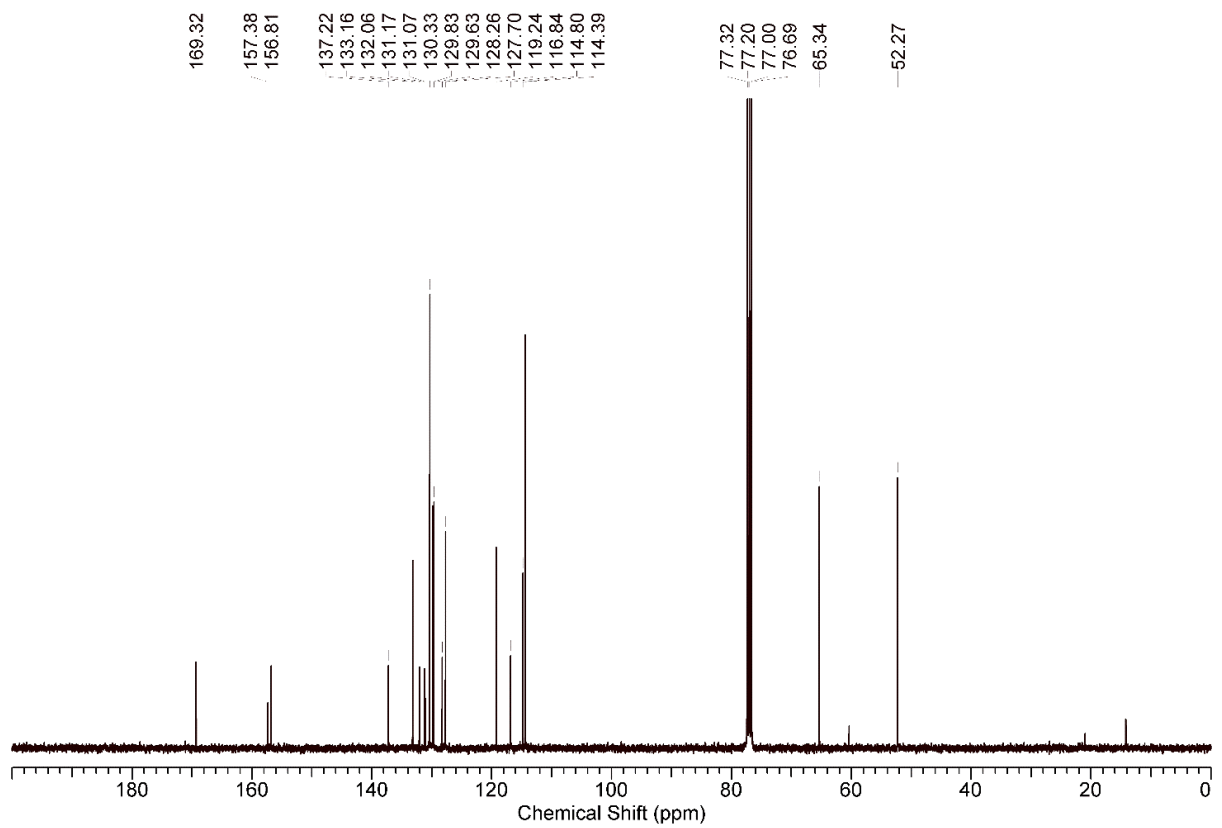


Fig. S63: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of CTA6.

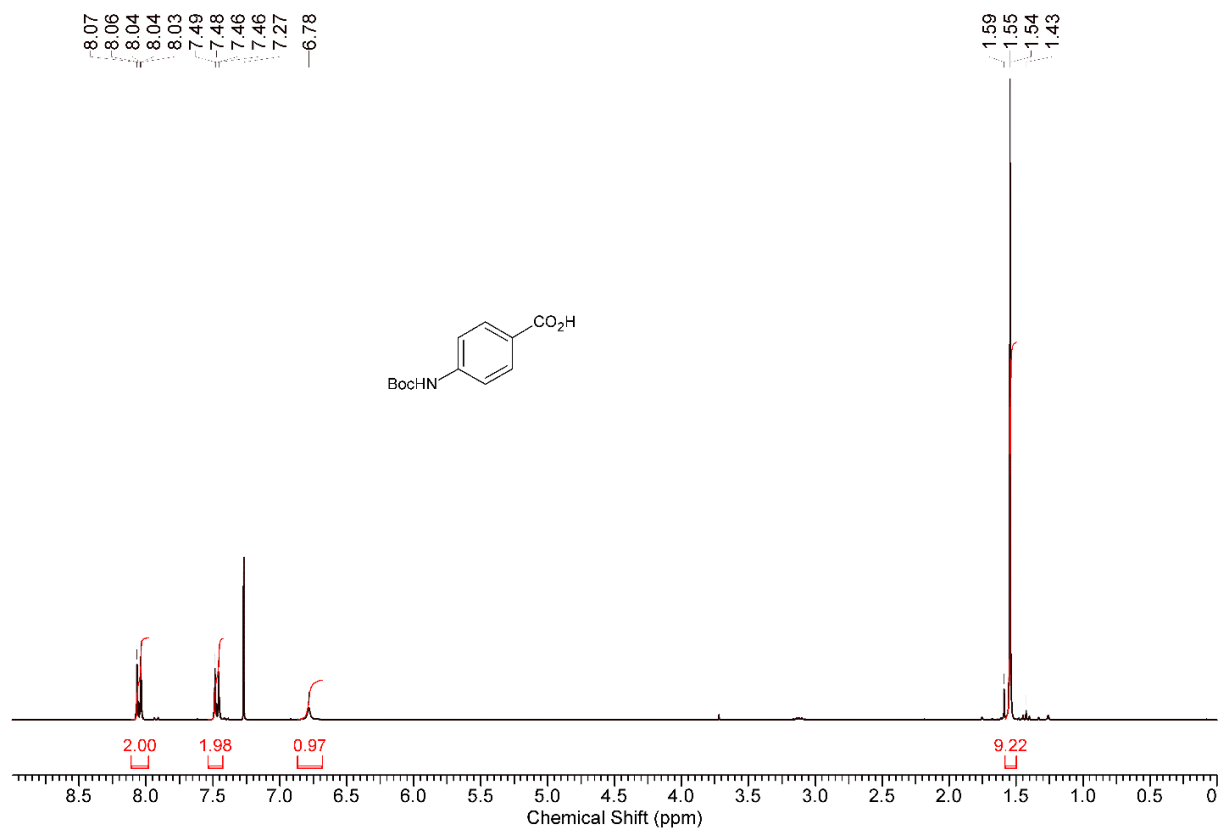


Fig. S64: ¹H NMR (CDCl₃, 400 MHz) spectrum of **15**.

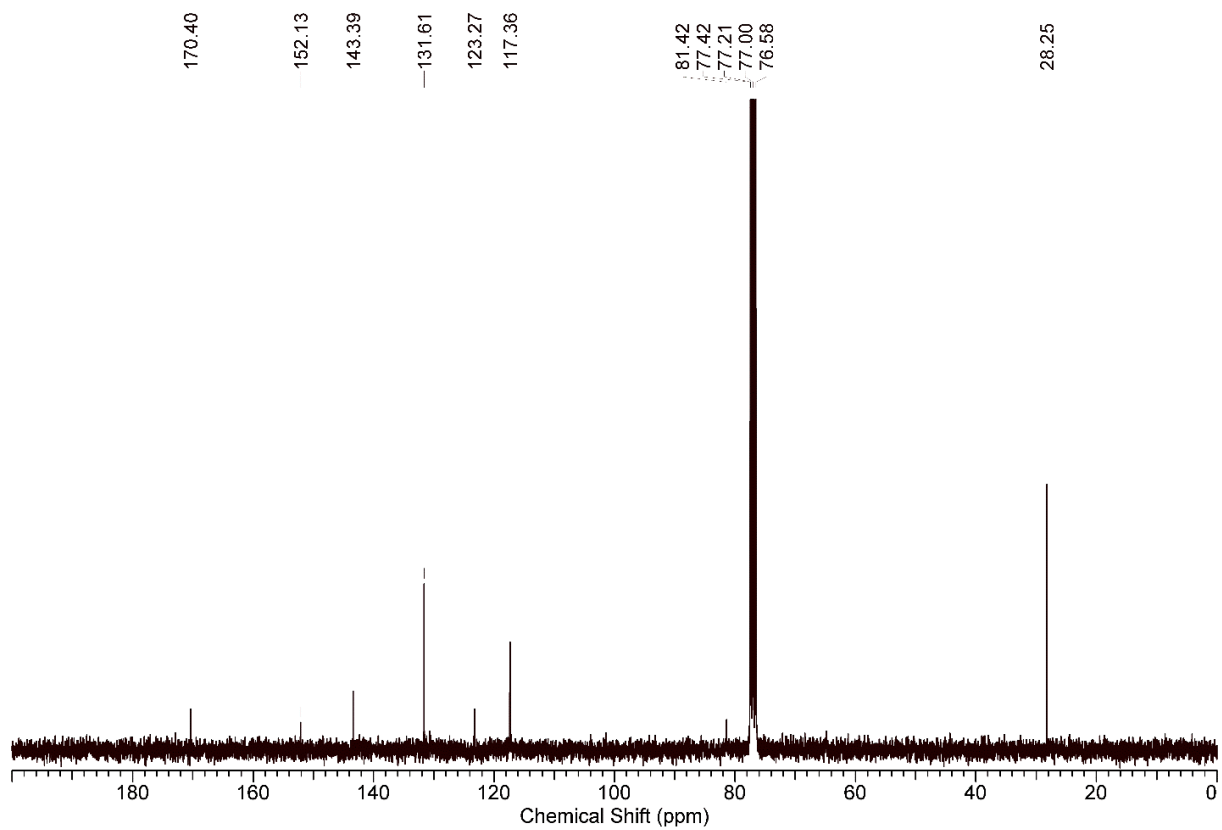


Fig. S65: ¹³C NMR (CDCl₃, 101 MHz) spectrum of **15**.

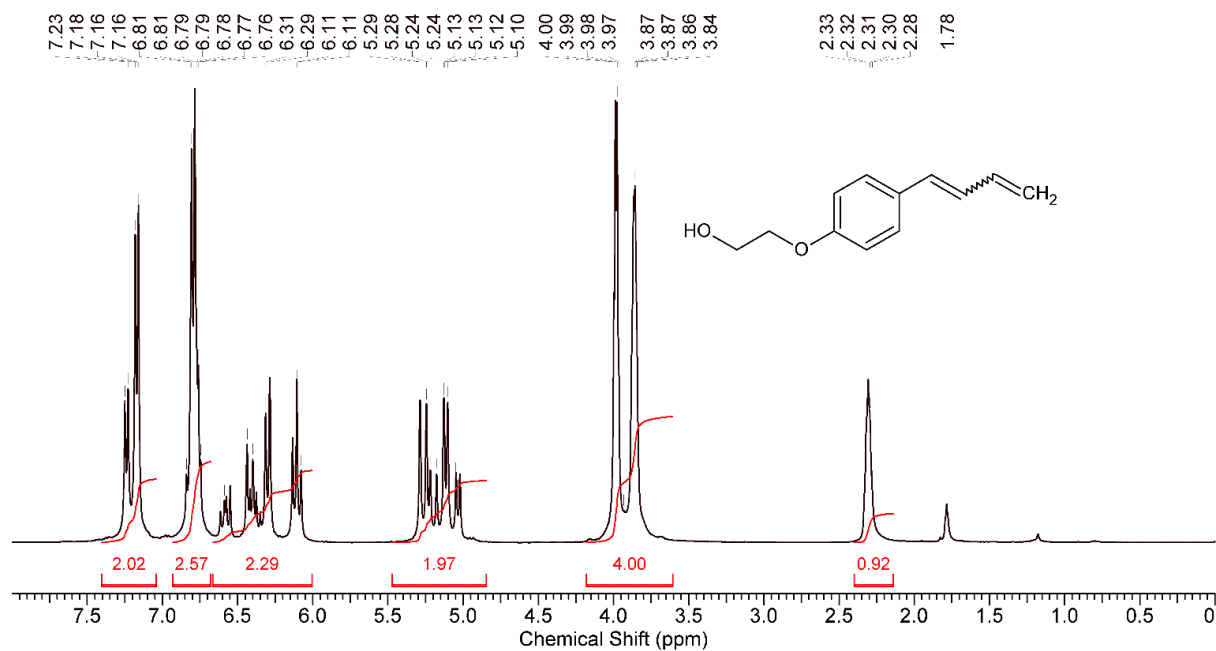


Fig. S66: ^1H NMR (CDCl_3 , 400 MHz) spectrum of **16**.

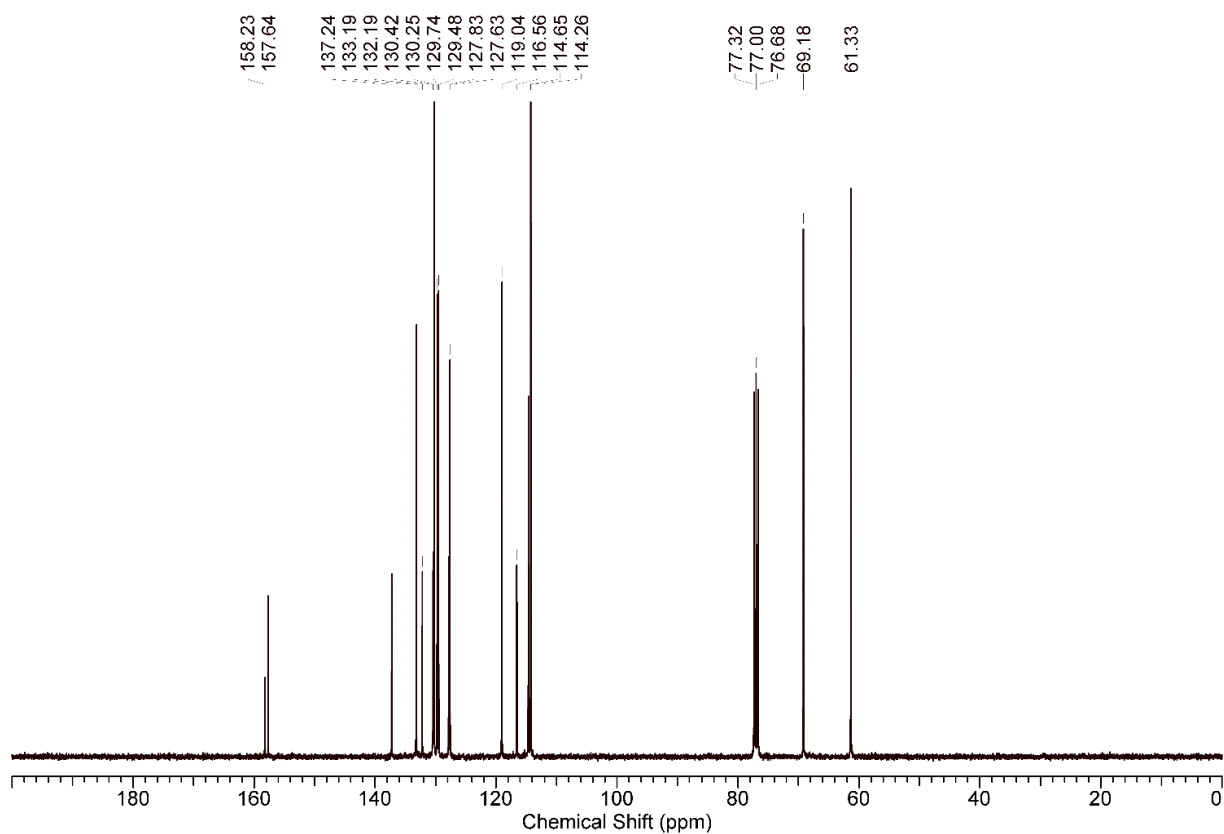


Fig. S67: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **16**.

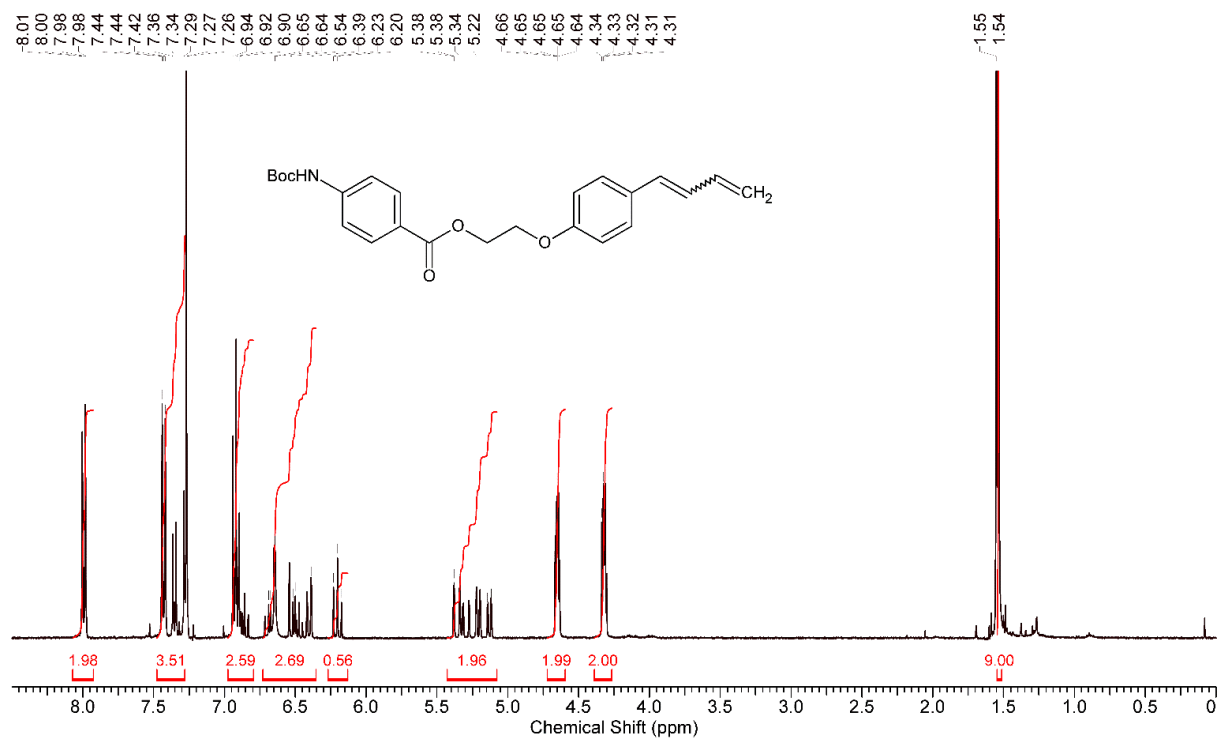


Fig. S68: ^1H NMR (CDCl_3 , 400 MHz) spectrum of CTA7.

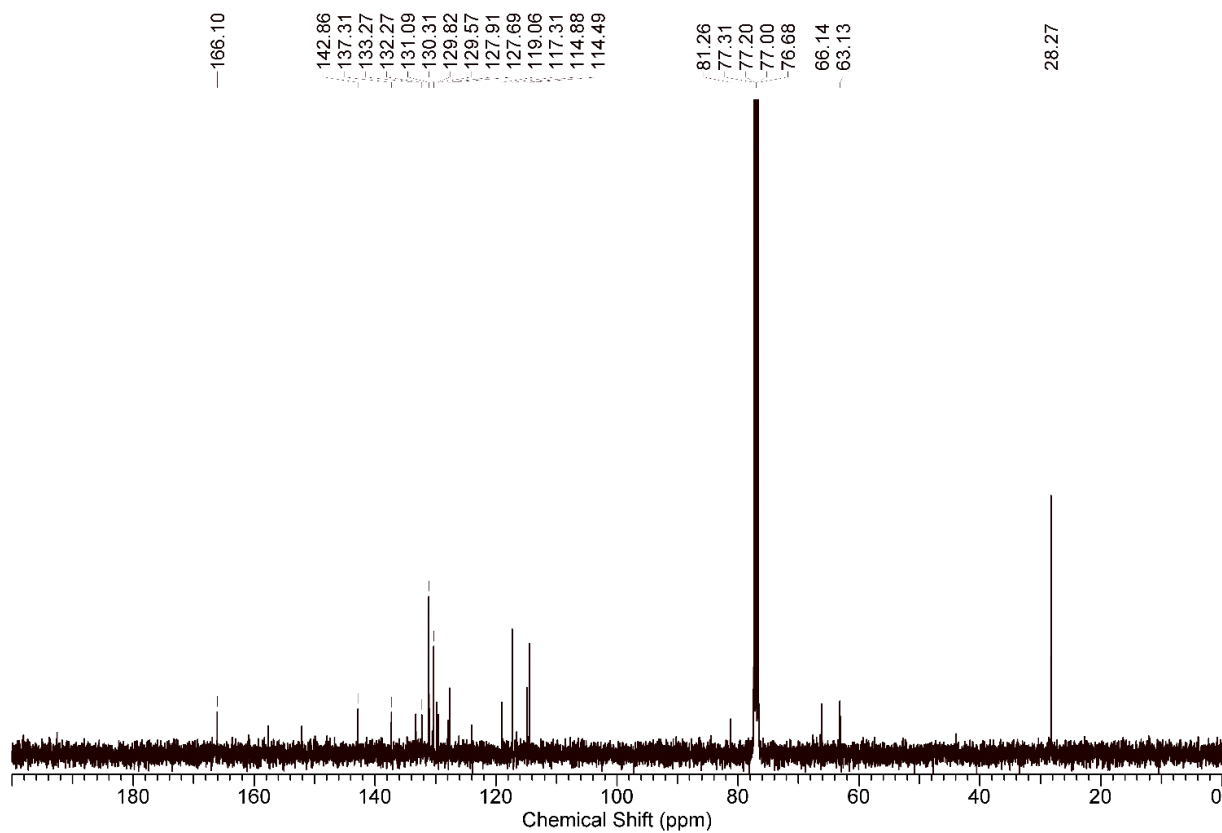


Fig. S69: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of CTA7.

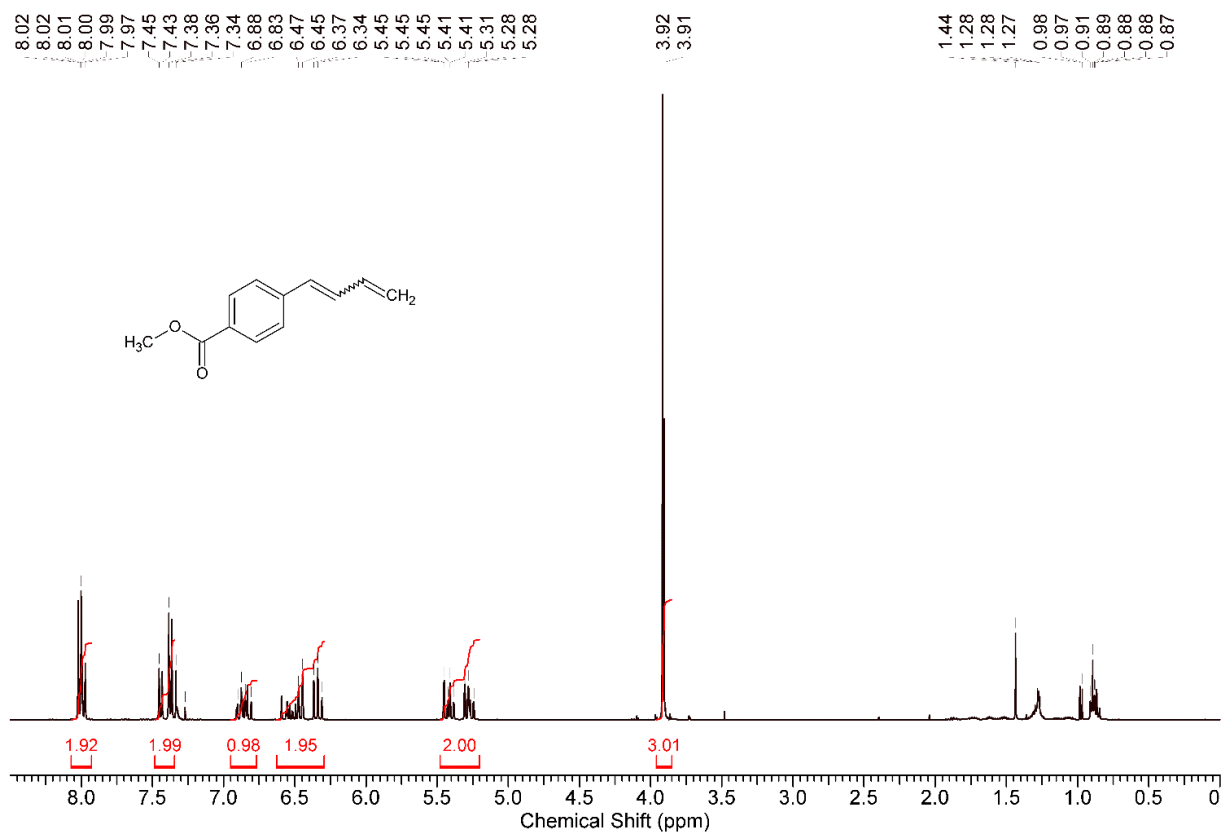


Fig. S70: ¹H NMR (CDCl₃, 400 MHz) spectrum of CTA8.

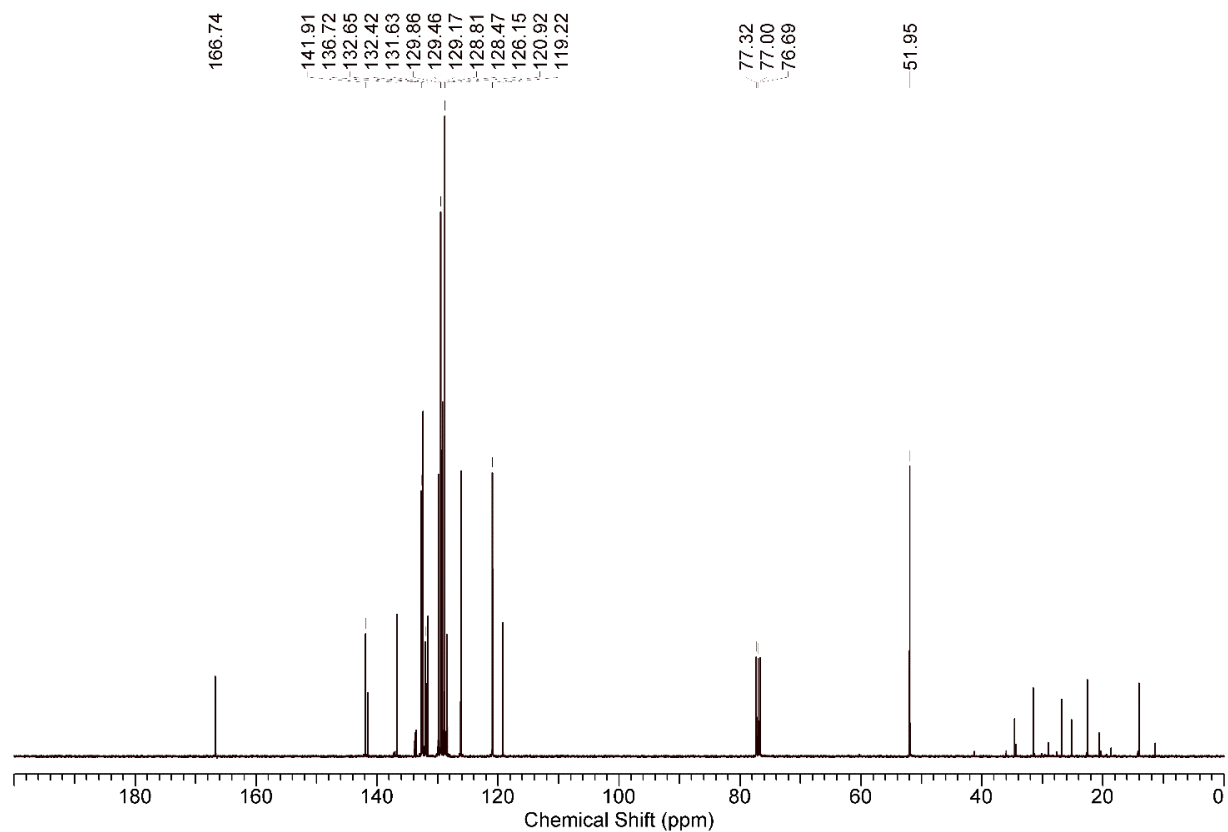


Fig. S71: ¹³C NMR (CDCl₃, 101 MHz) spectrum of CTA8.

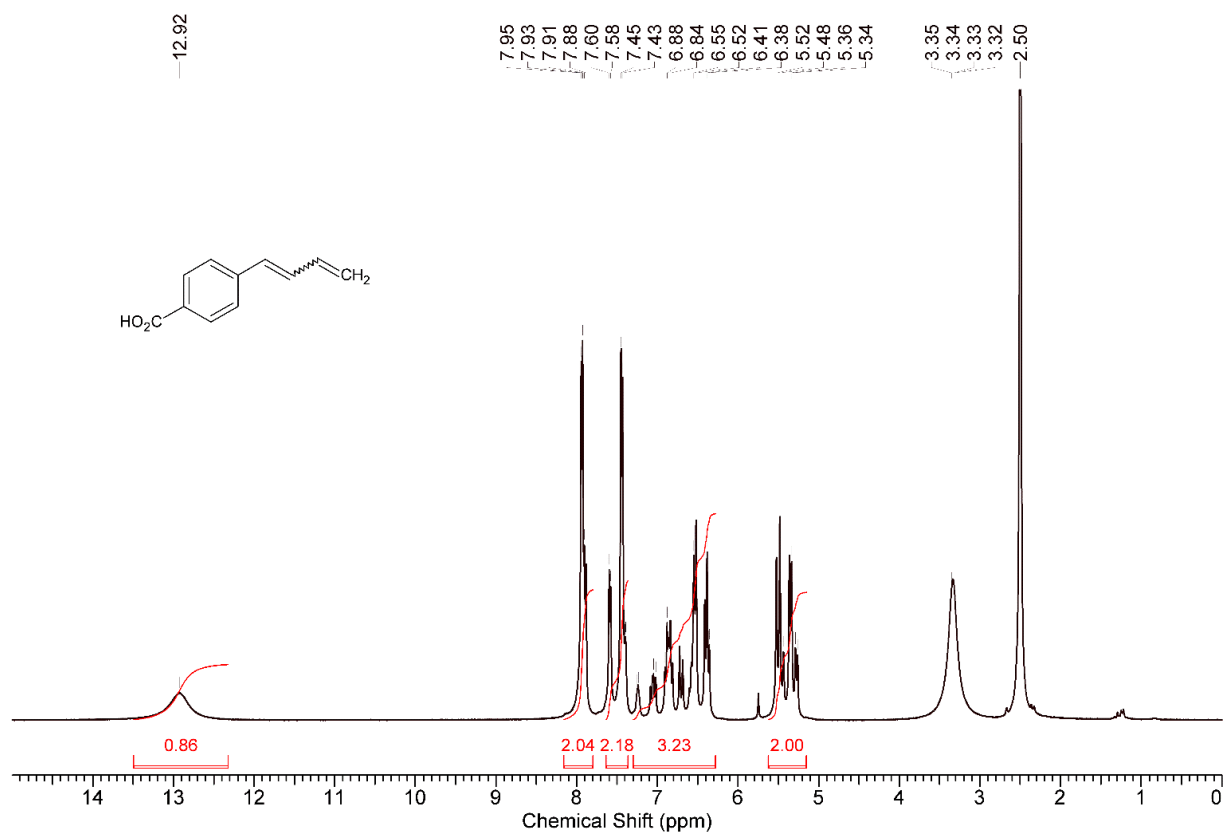


Fig. S72: ¹H NMR (Dimethylsulfoxide-d₆, 400 MHz) spectrum of **17**.

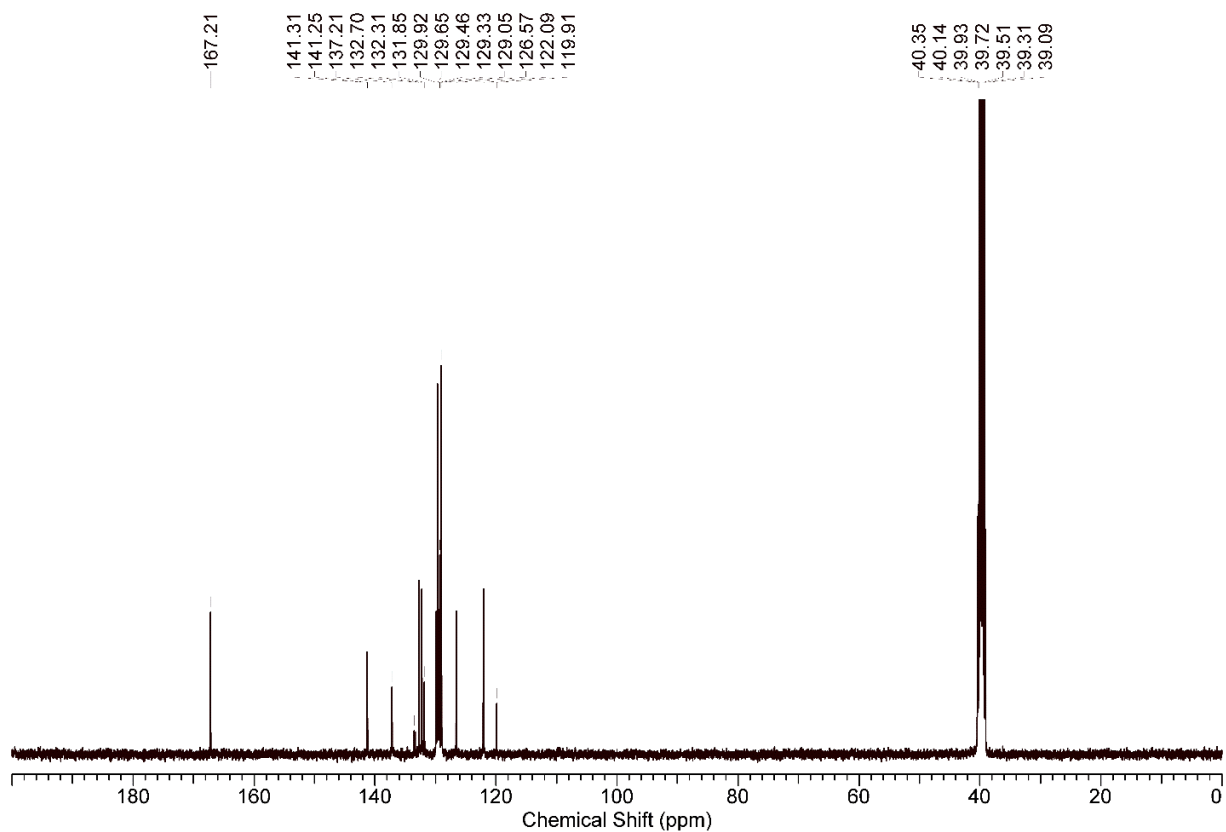


Fig. S73: ¹³C NMR (Dimethylsulfoxide-d₆, 101 MHz) spectrum of **17**.

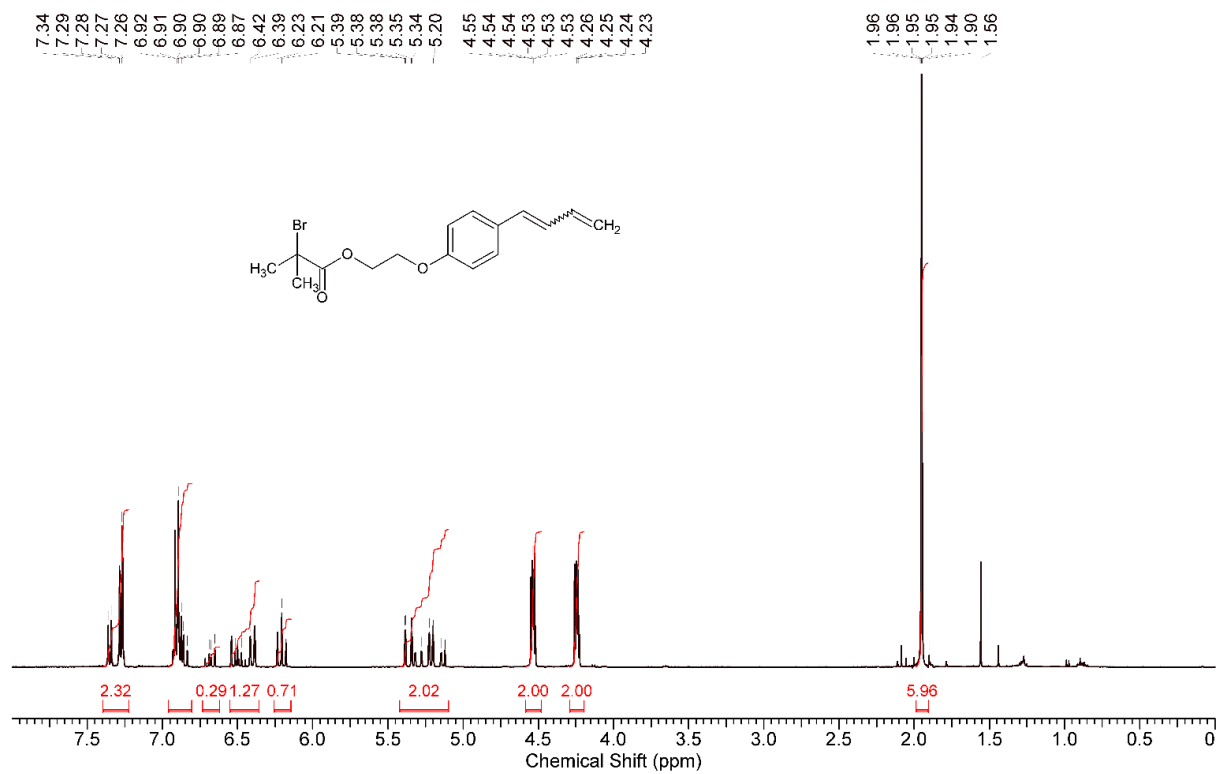


Fig. S74: ^1H NMR (CDCl_3 , 400 MHz) spectrum of CTA9.

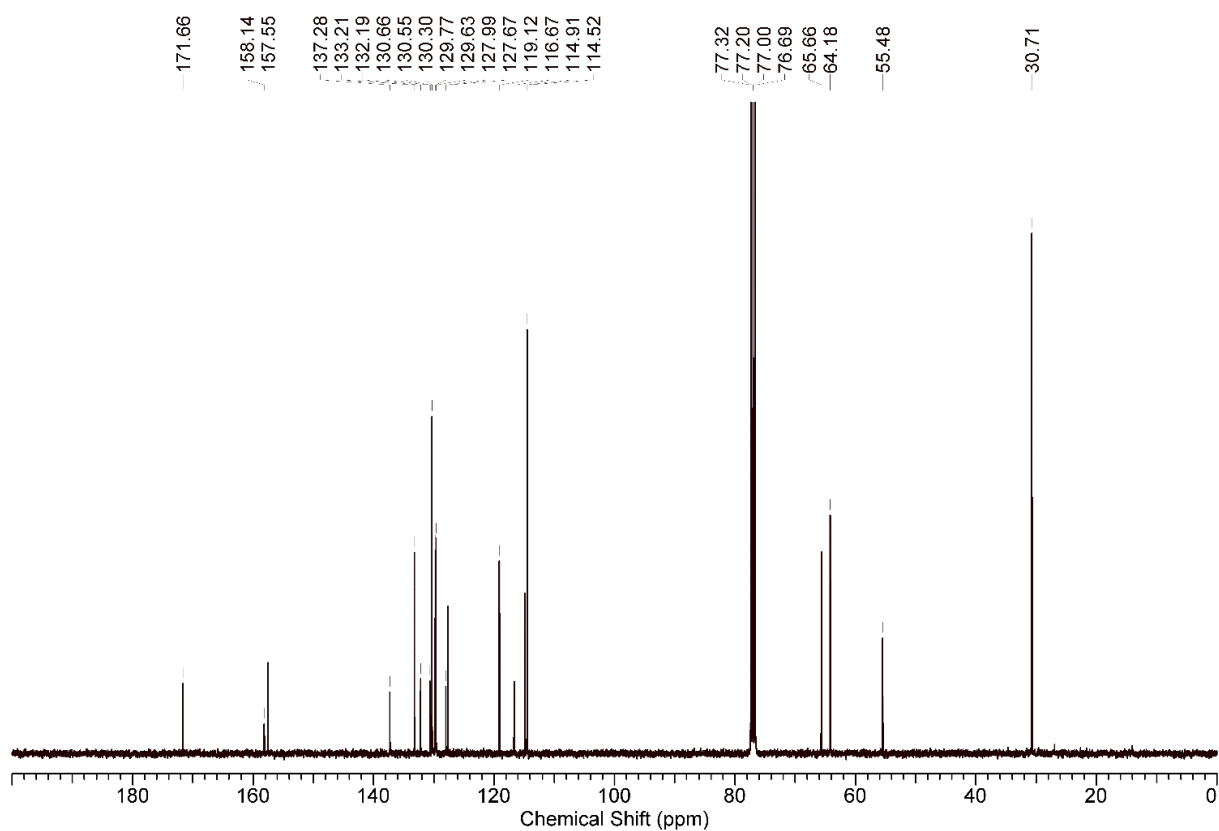


Fig. S75: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of CTA9.

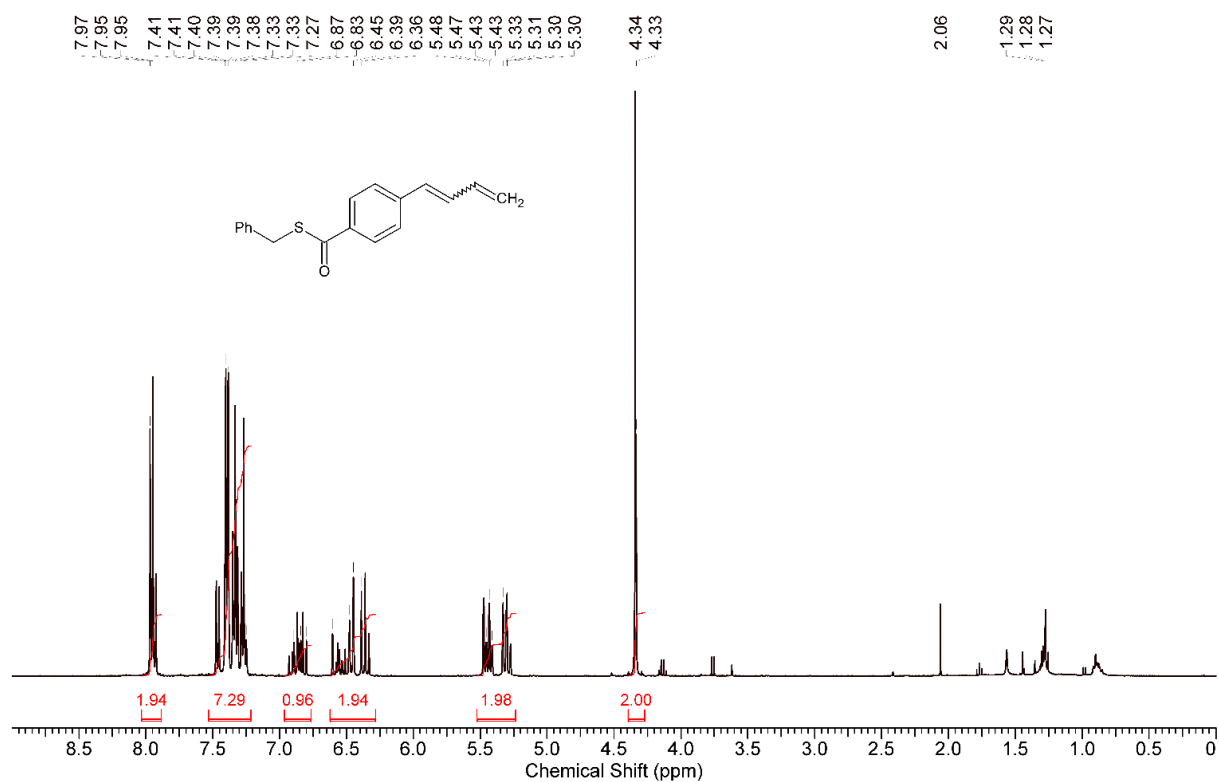


Fig. S76: ^1H NMR (CDCl_3 , 400 MHz) spectrum of CTA10.

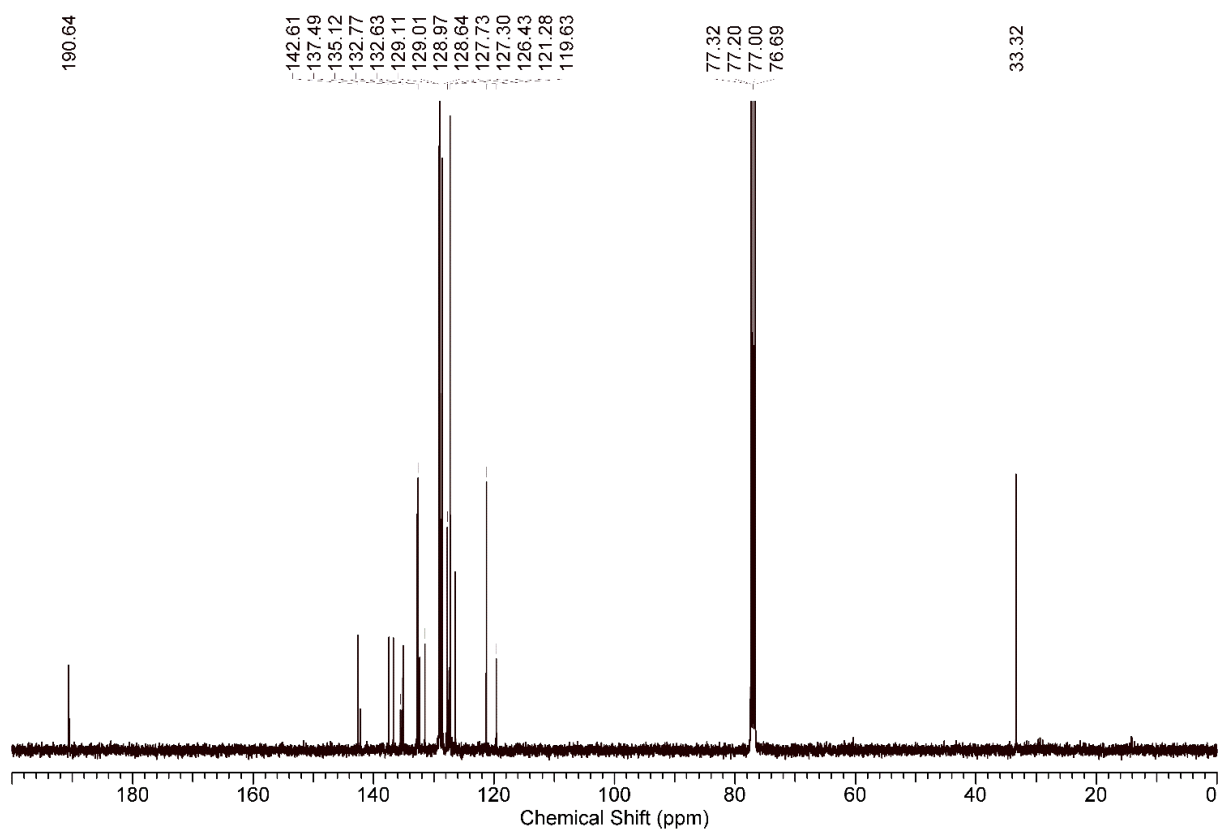


Fig. S77: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of CTA10.

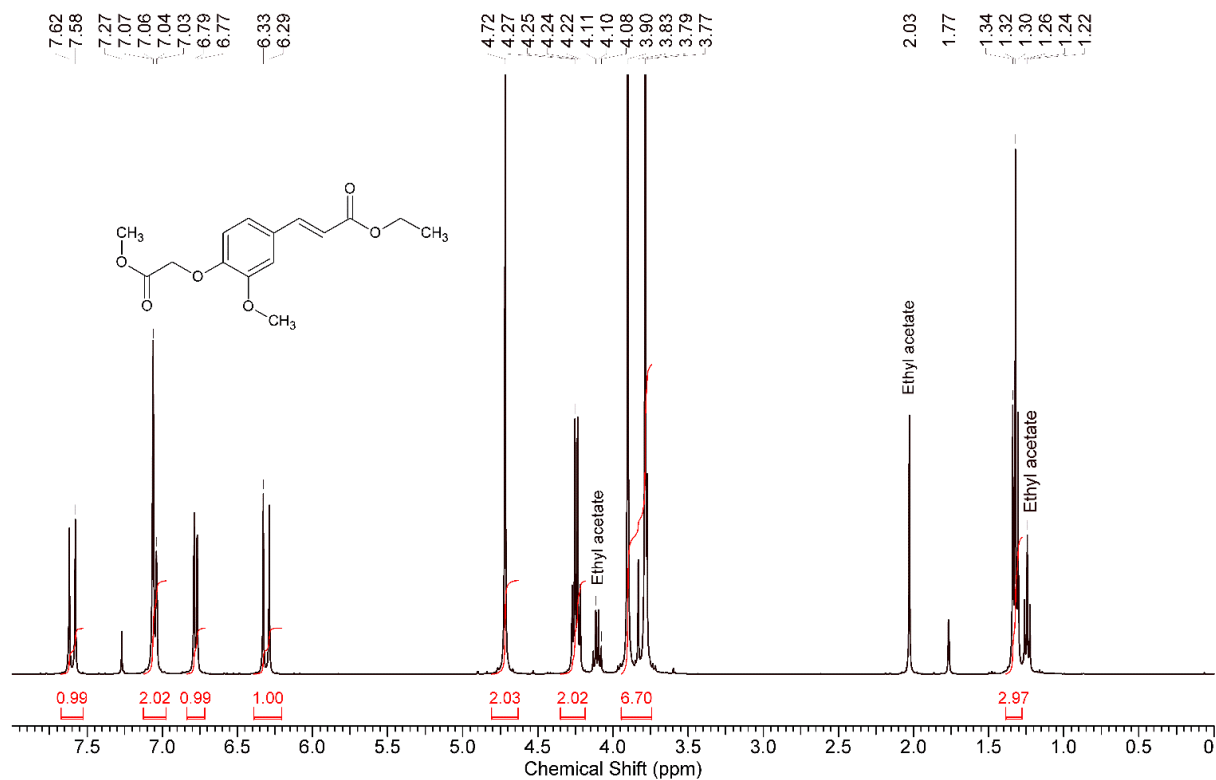


Fig. S78: ^1H NMR (CDCl_3 , 400 MHz) spectrum of I8.

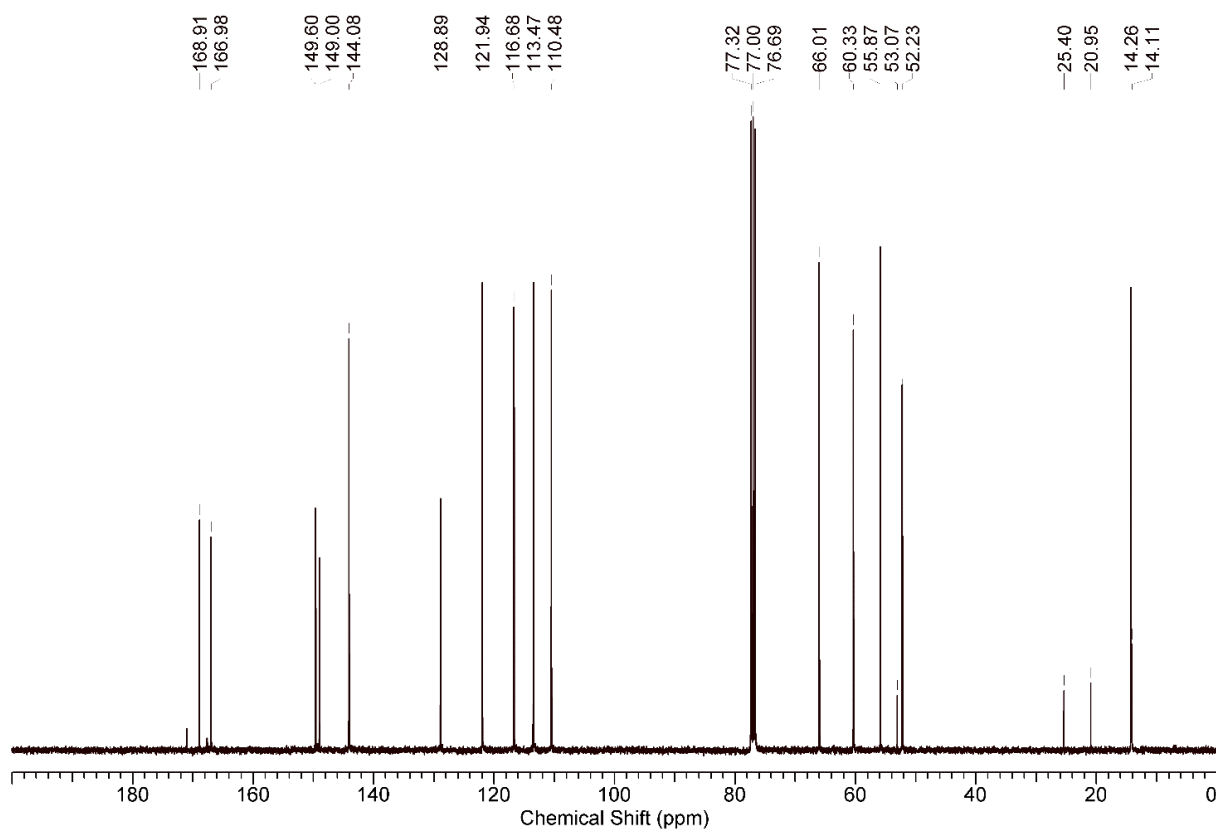


Fig. S79: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of I8.

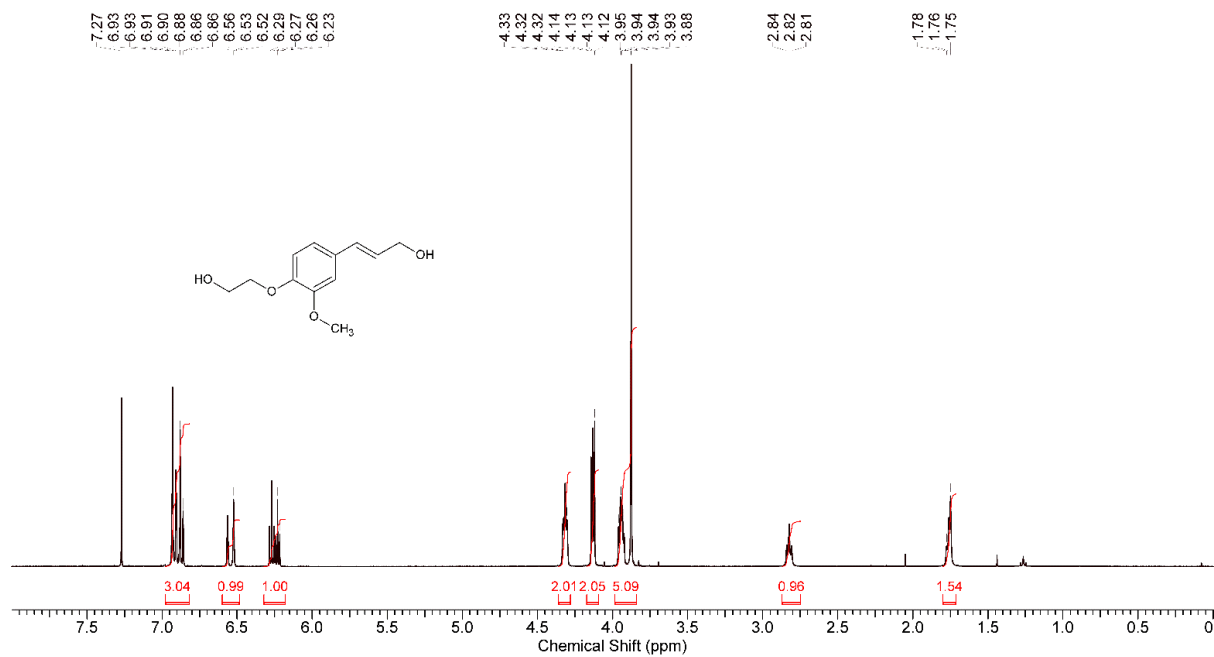


Fig. S80: ¹H NMR (CDCl₃, 400 MHz) spectrum of 19.

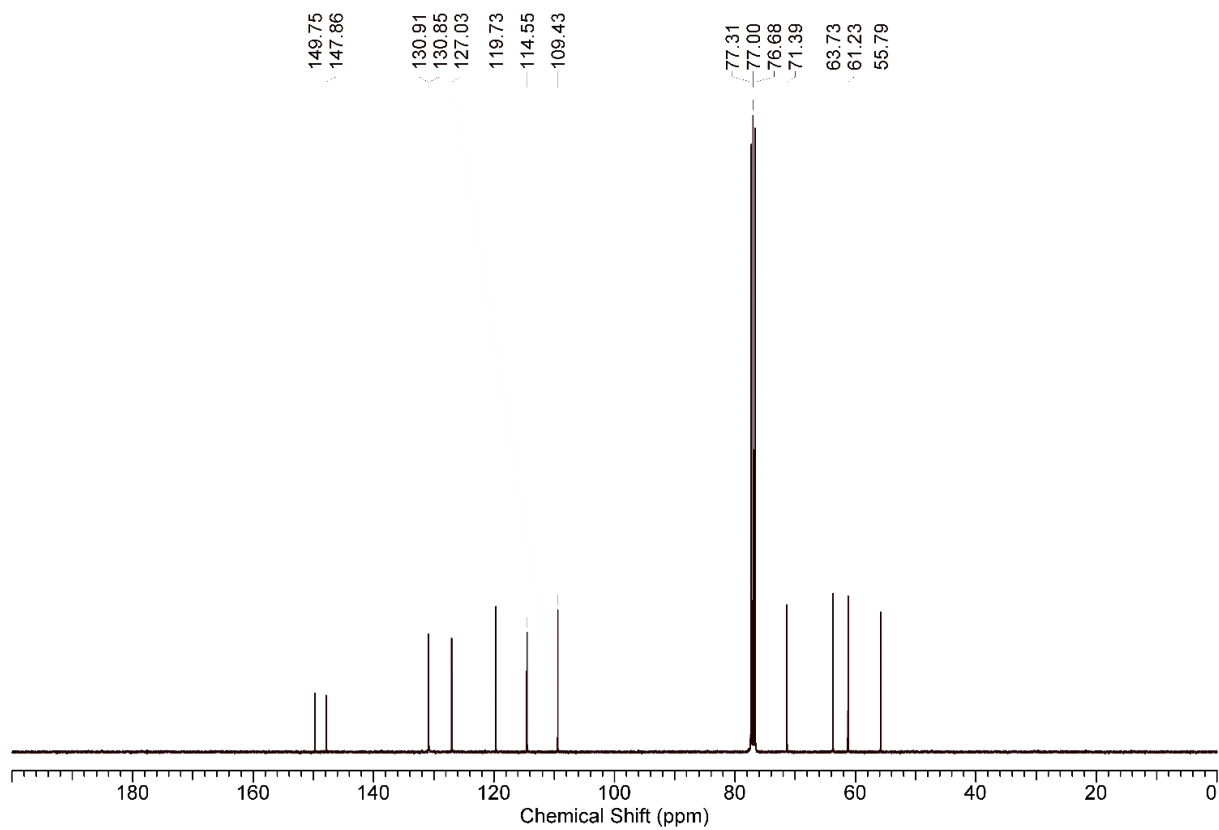


Fig. S81: ¹³C NMR (CDCl₃, 101 MHz) spectrum of 19.

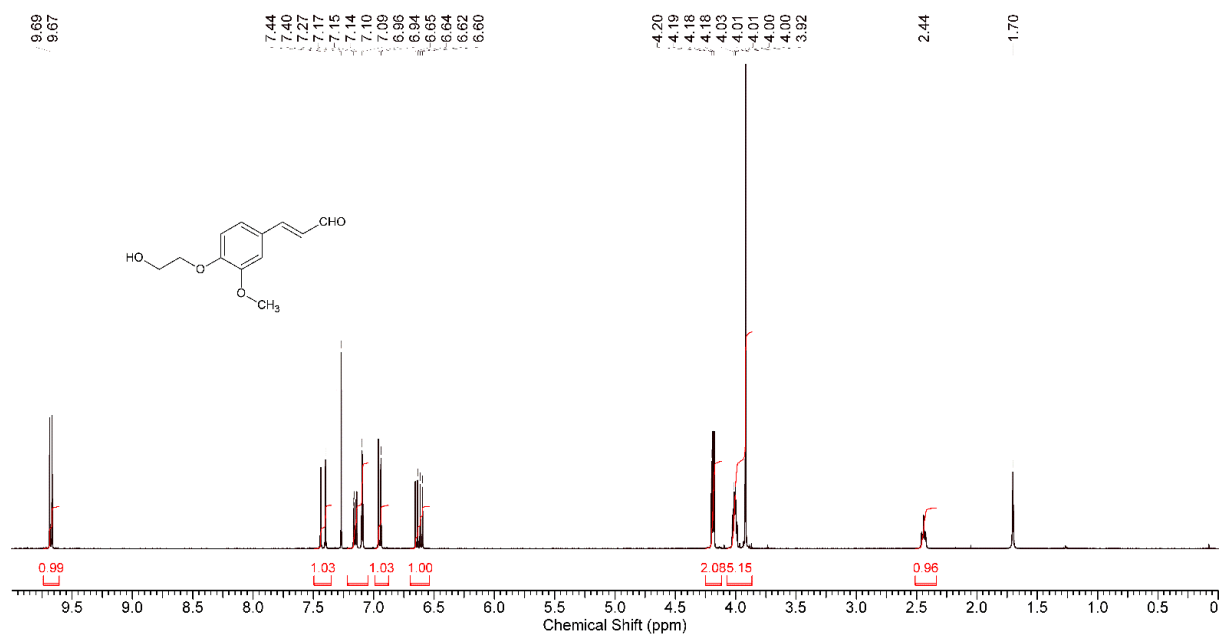


Fig. S82: ¹H NMR (CDCl₃, 400 MHz) spectrum of I10.

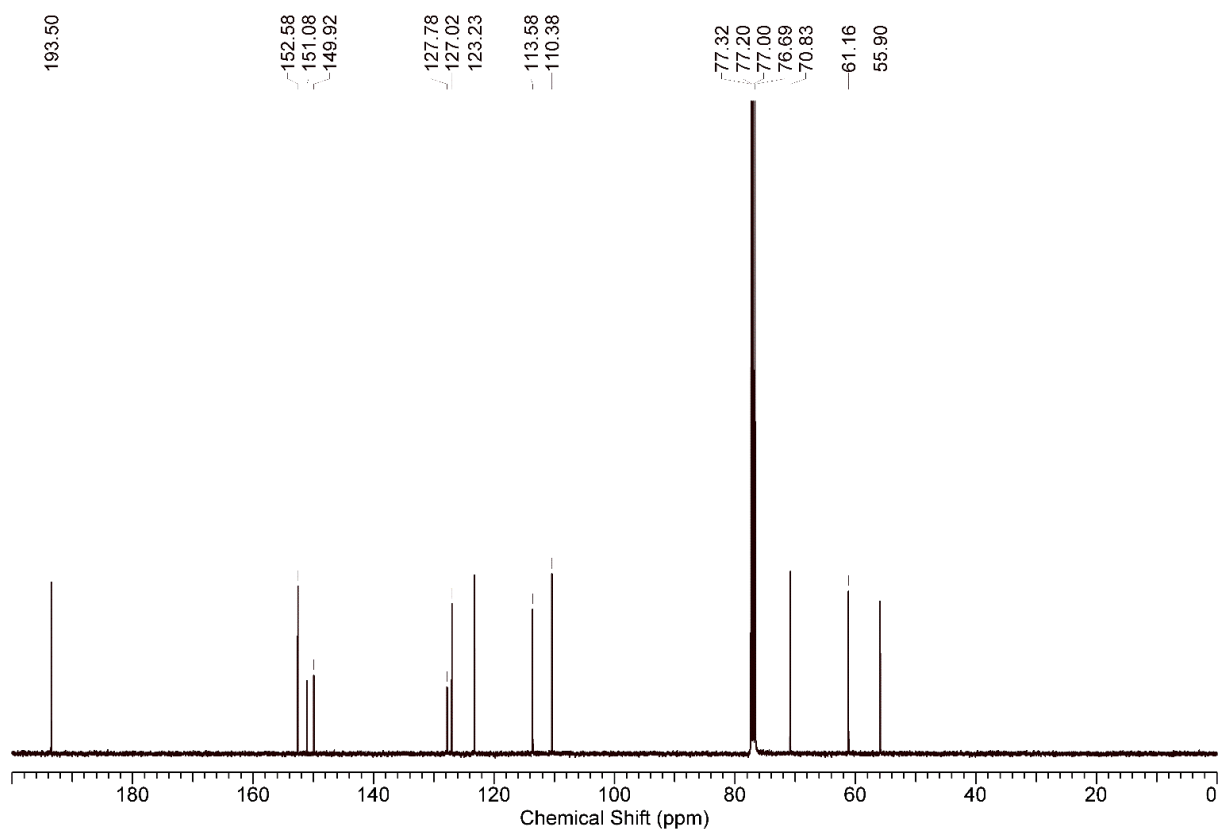


Fig. S83: ¹³C NMR (CDCl₃, 101 MHz) spectrum of I10.

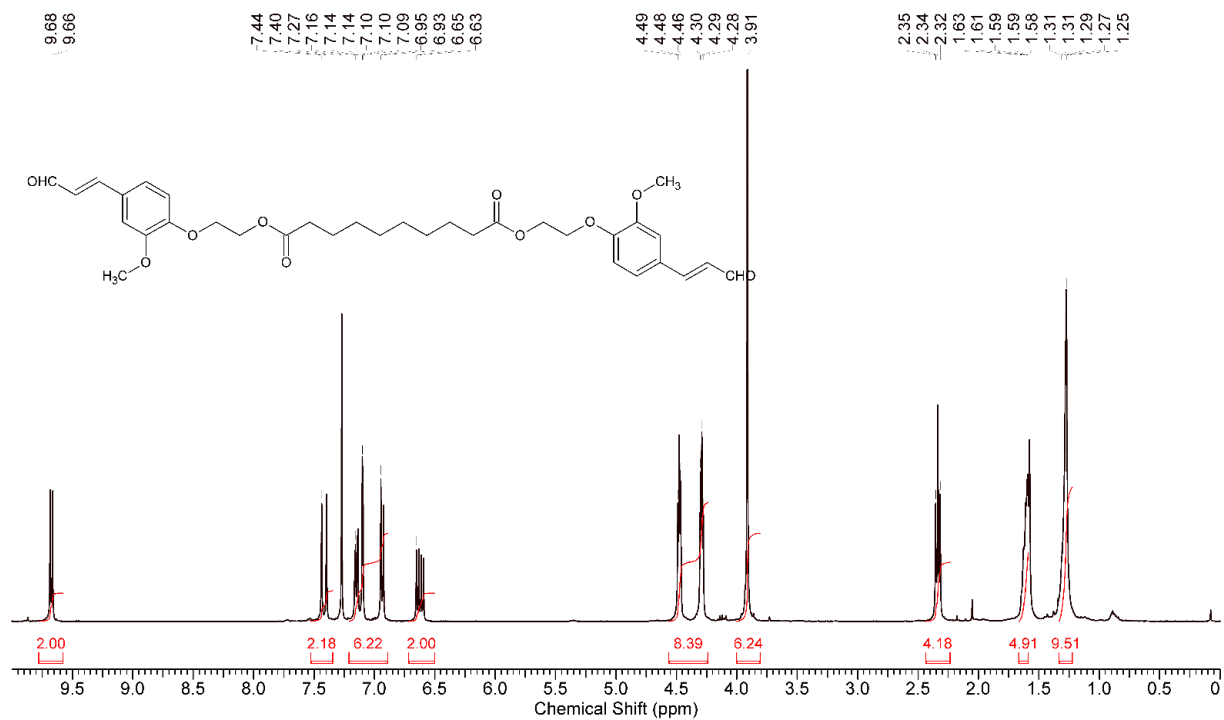


Fig. S84: ¹H NMR (CDCl₃, 400 MHz) spectrum of **I11**.

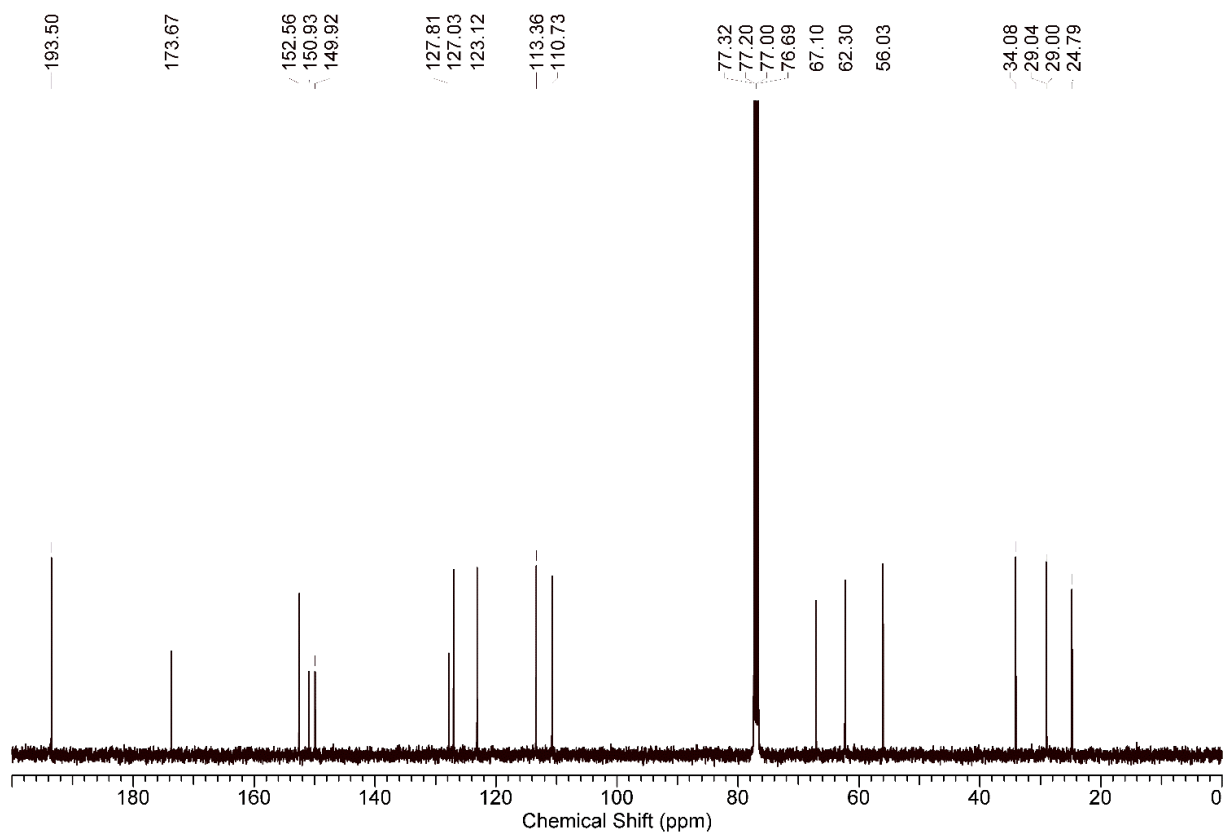


Fig. S85: ¹³C NMR (CDCl₃, 101 MHz) spectrum of **I11**.

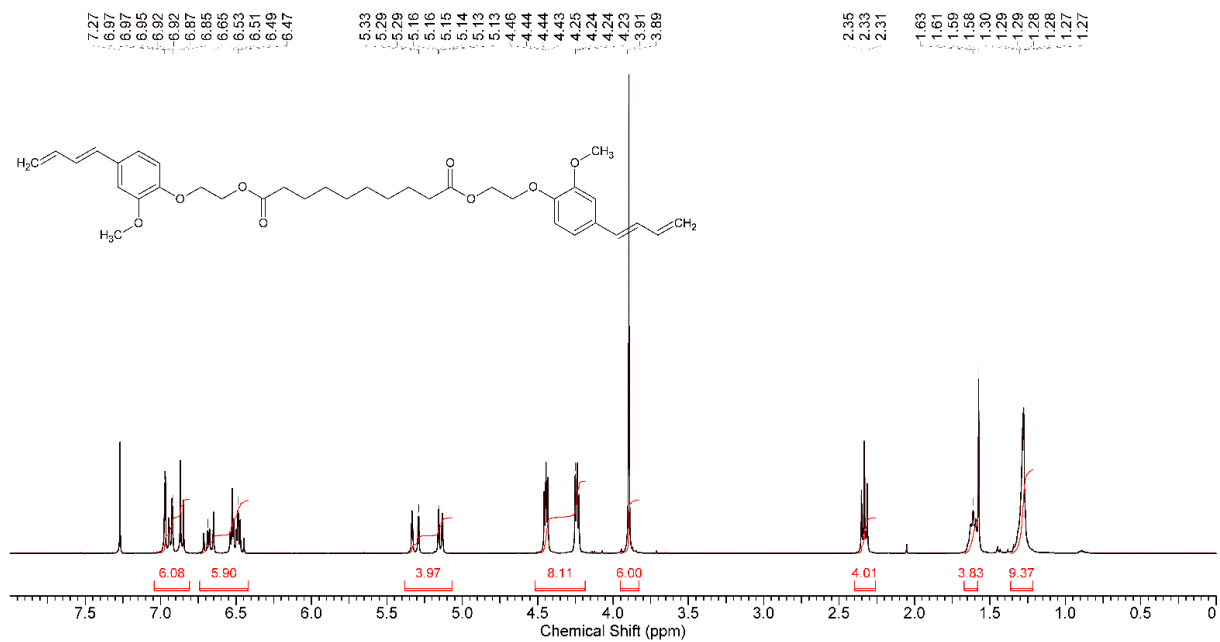


Fig. S86: ¹H NMR (CDCl₃, 400 MHz) spectrum of CTA11.

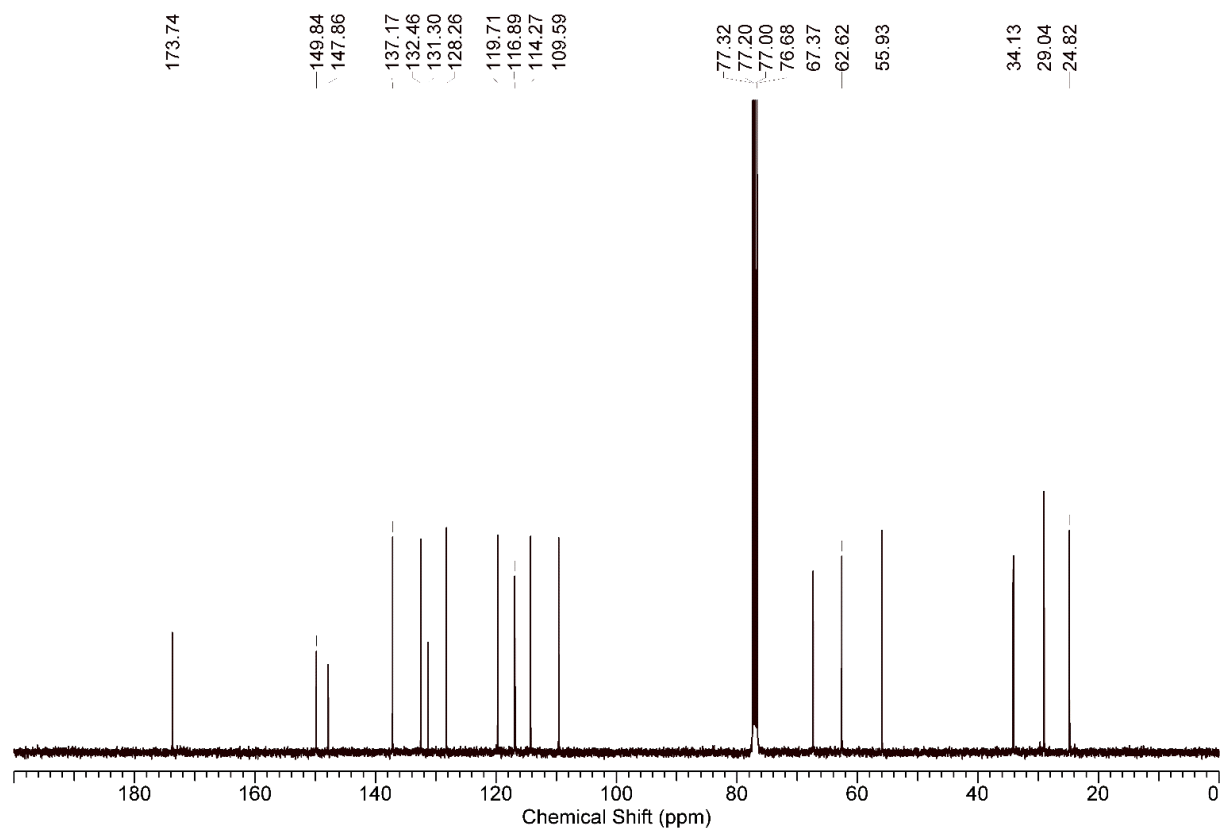


Fig. S87: ¹³C NMR (CDCl₃, 101 MHz) spectrum of CTA11.

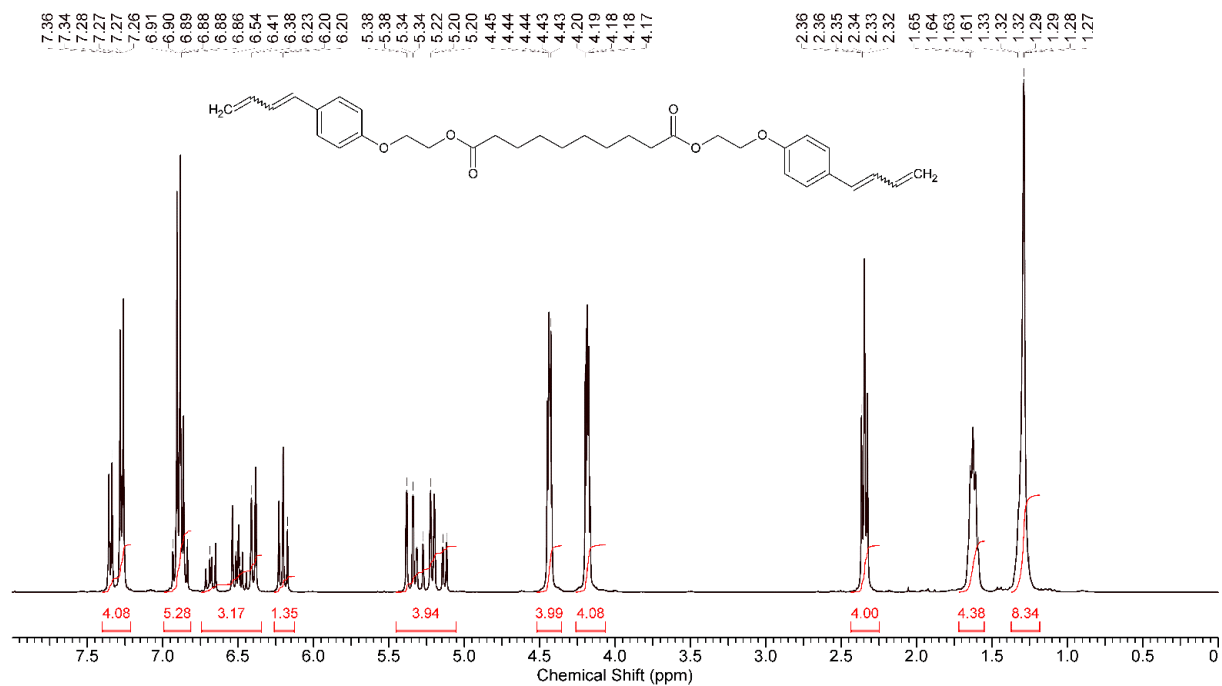


Fig. S88: ^1H NMR (CDCl_3 , 400 MHz) spectrum of CTA12.

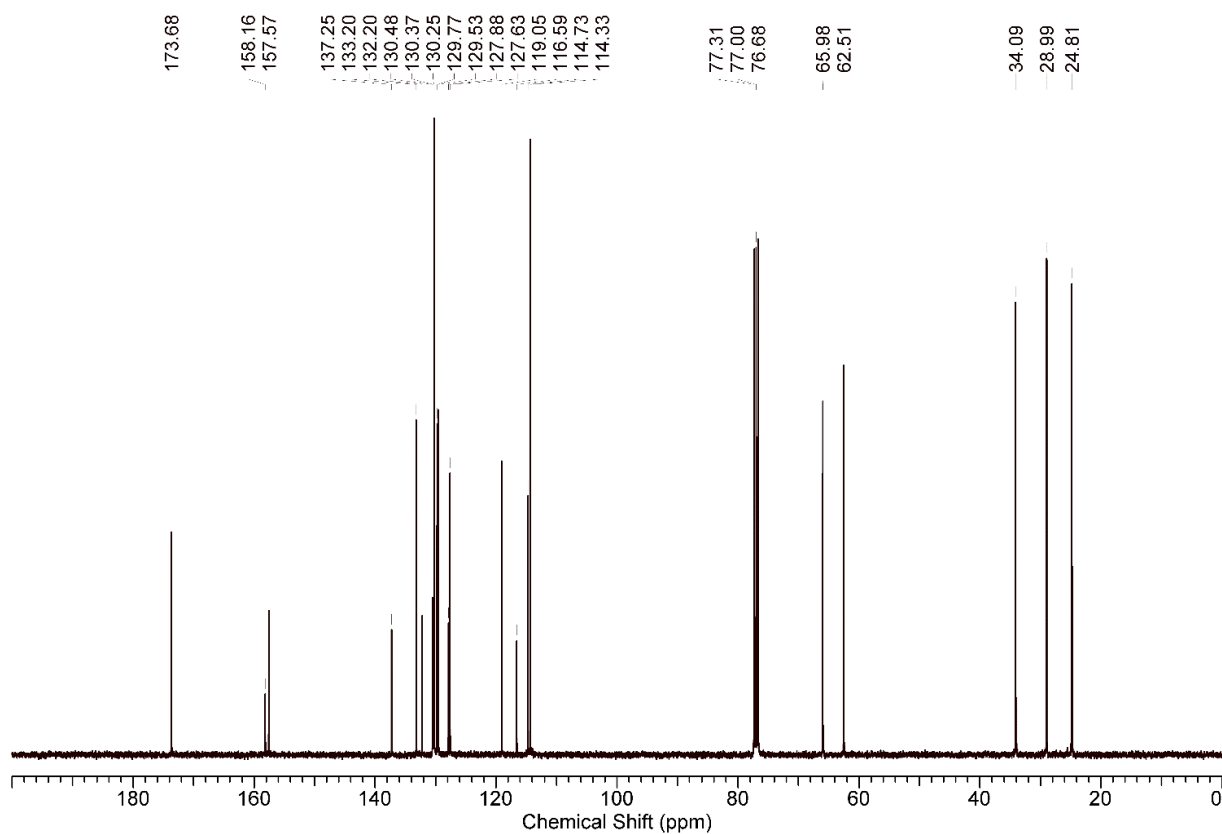


Fig. S89: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of CTA12.

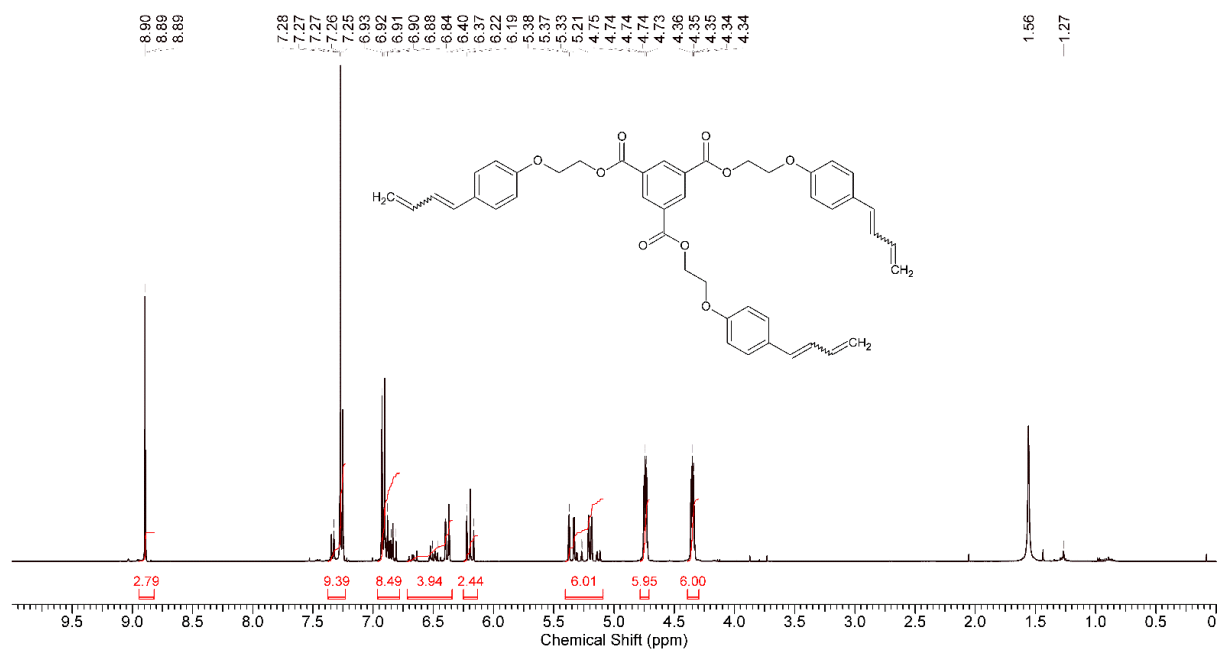


Fig. S90: ^1H NMR (CDCl_3 , 400 MHz) spectrum of CTA13.

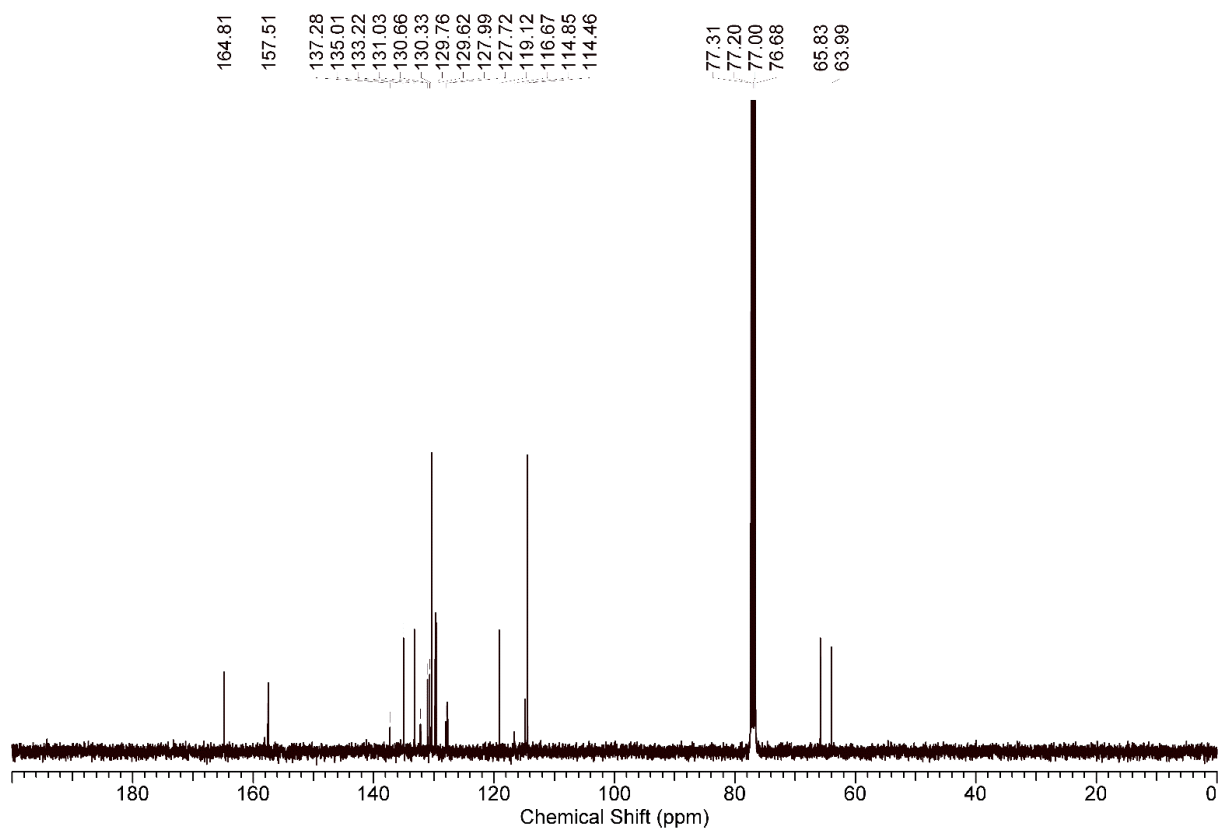


Fig. S91: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of CTA13.

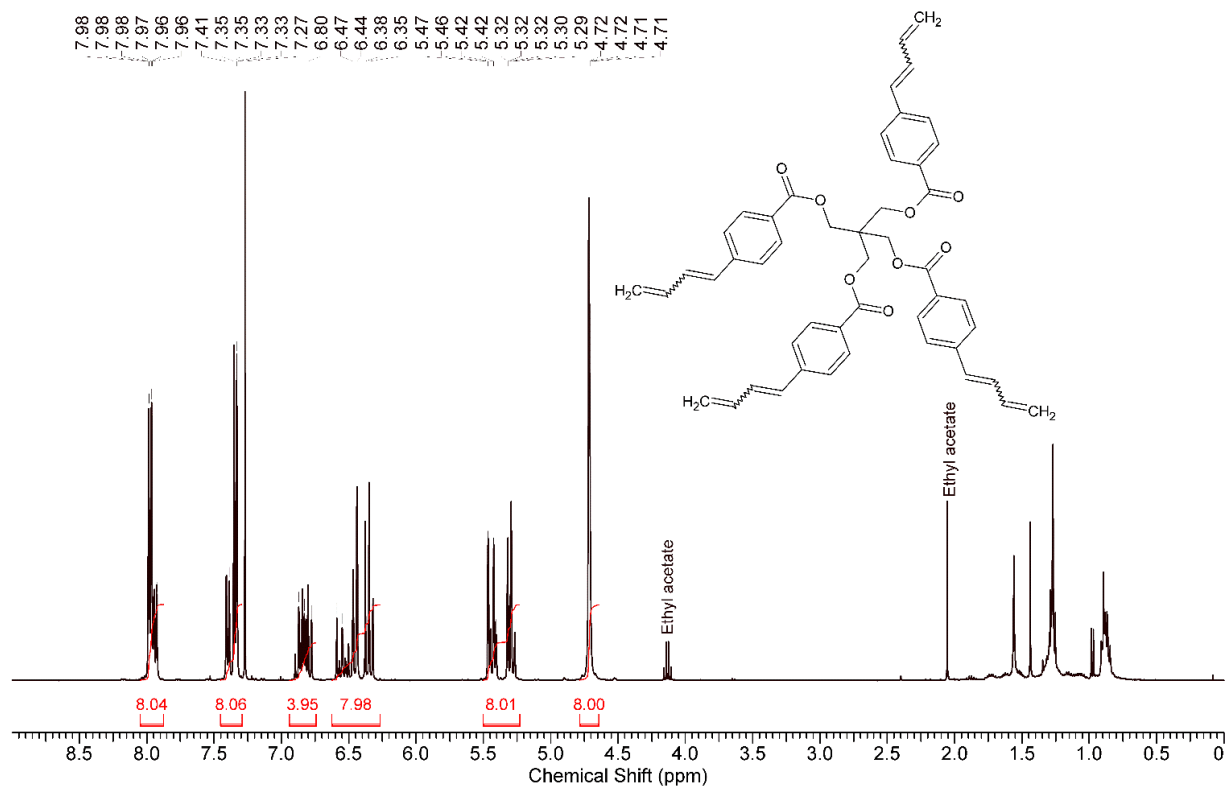


Fig. S92: ^1H NMR (CDCl_3 , 400 MHz) spectrum of **CTA14**.

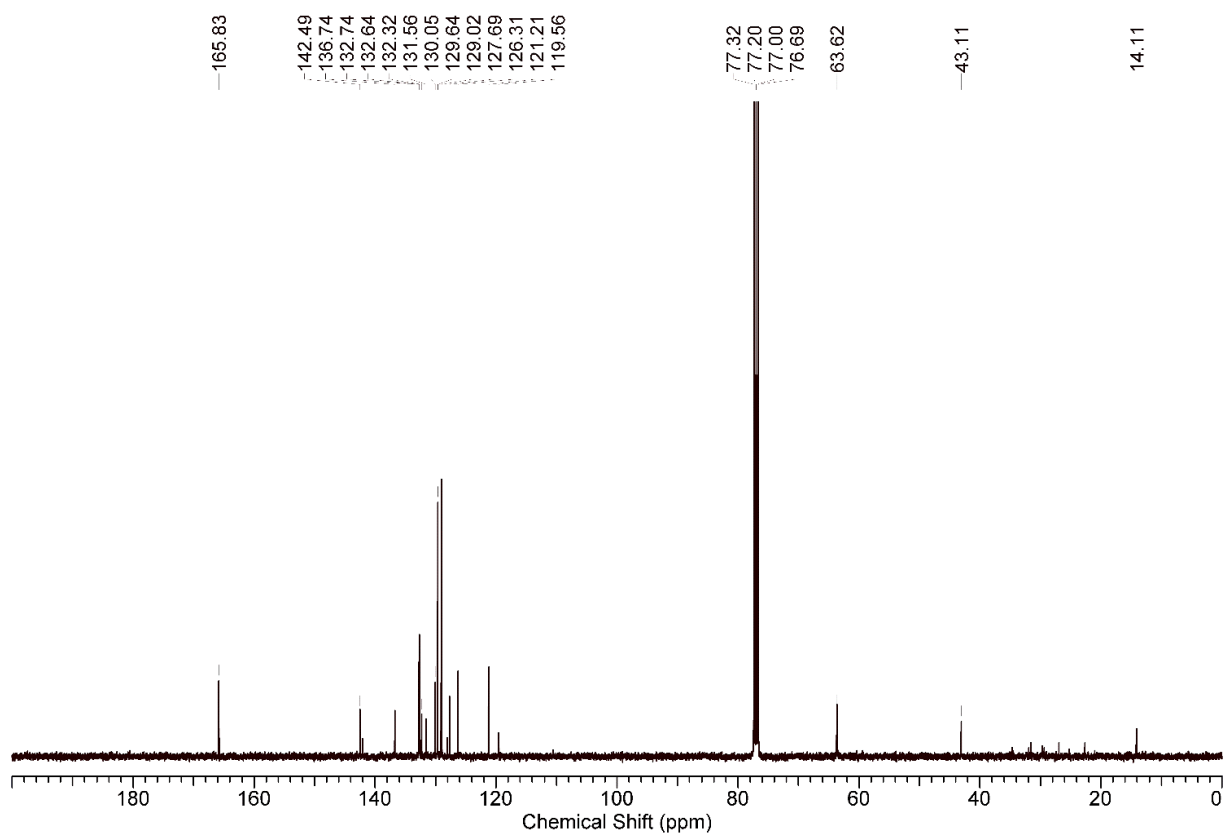


Fig. S93: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **CTA14**.

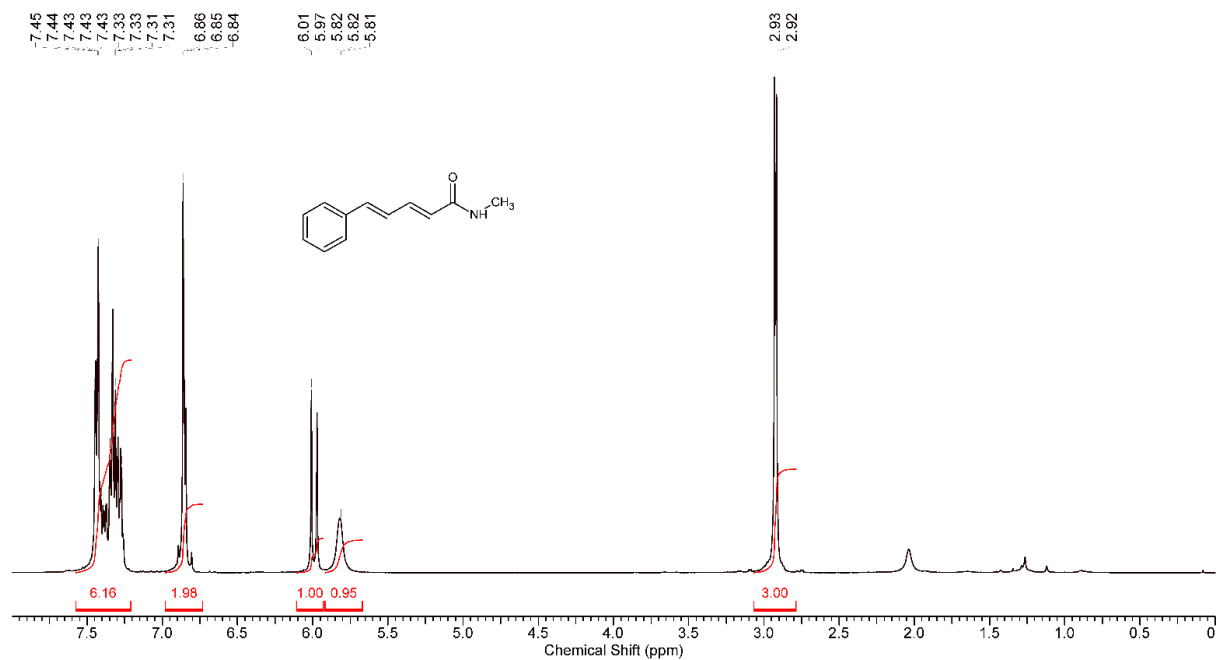


Fig. S94: ^1H NMR (CDCl_3 , 400 MHz) spectrum of CTA17.

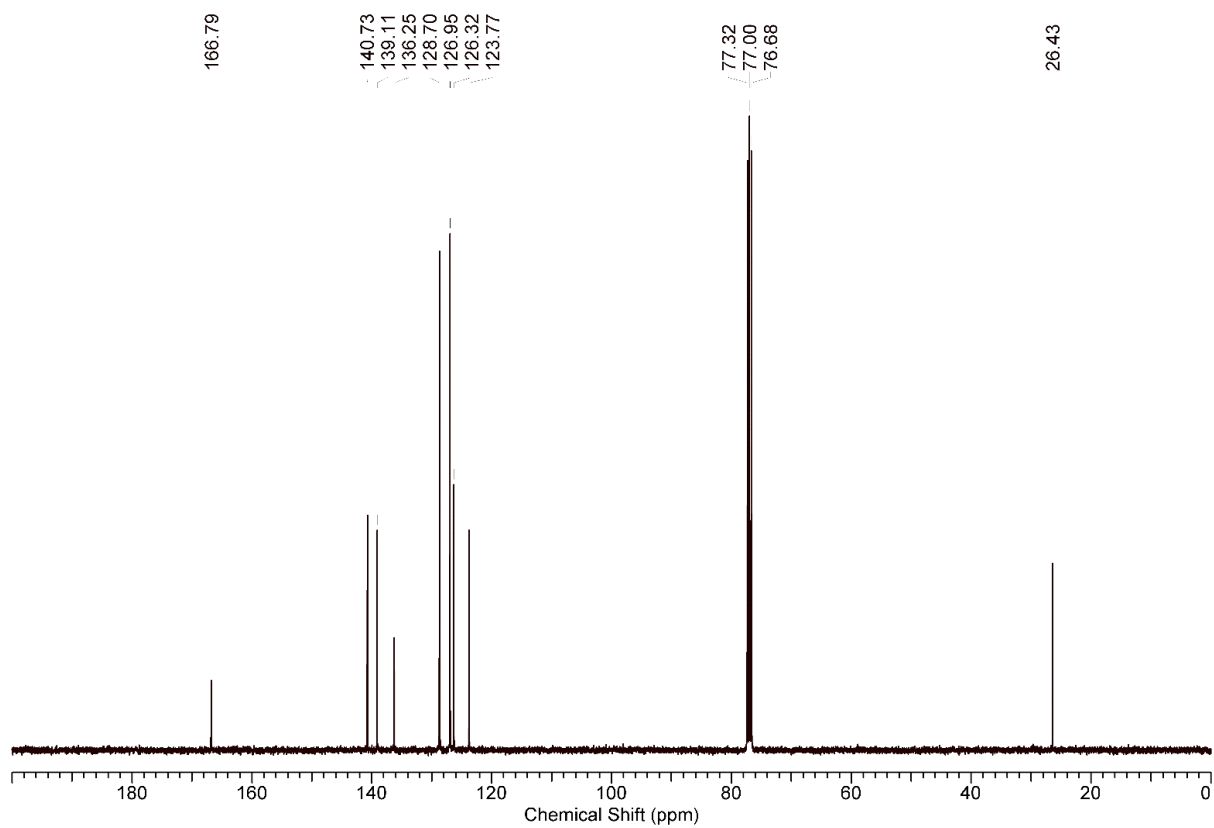


Fig. S95: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of CTA17.

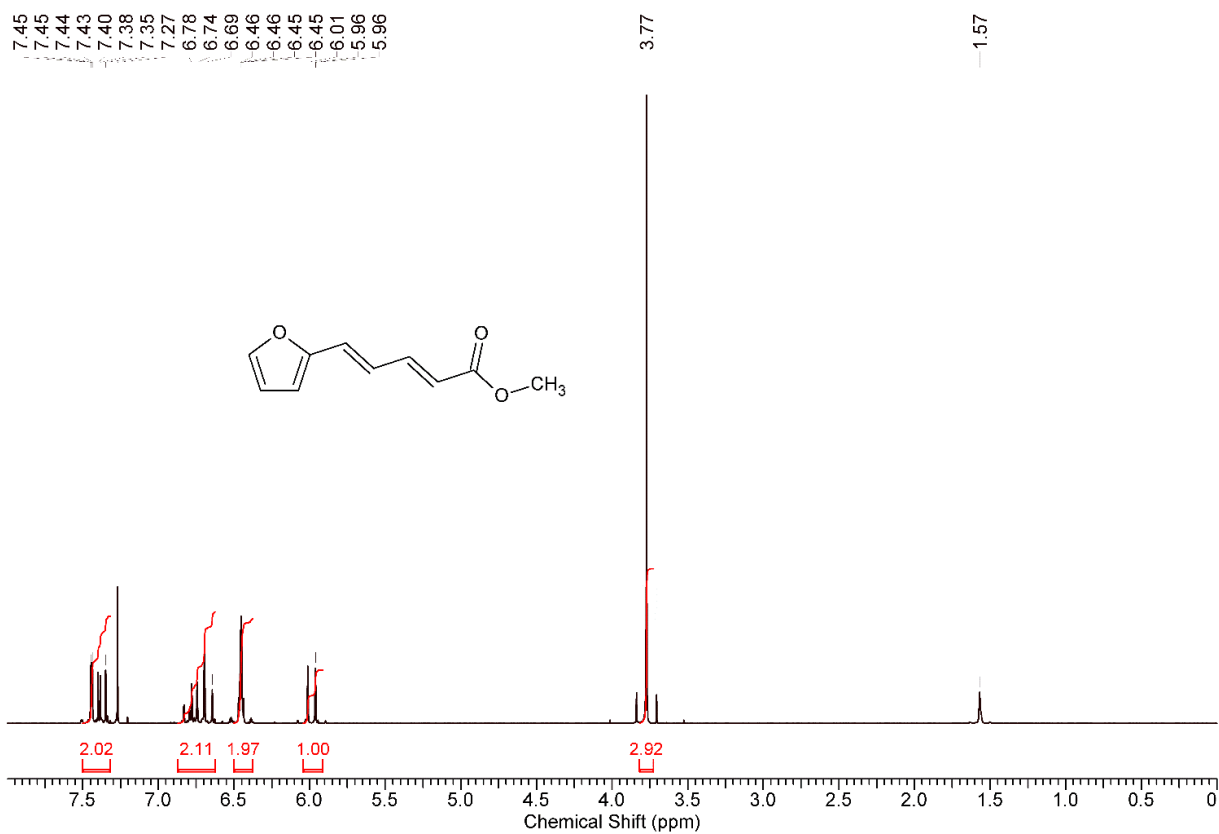


Fig. S96: ¹H NMR (CDCl₃, 400 MHz) spectrum of **I12**.

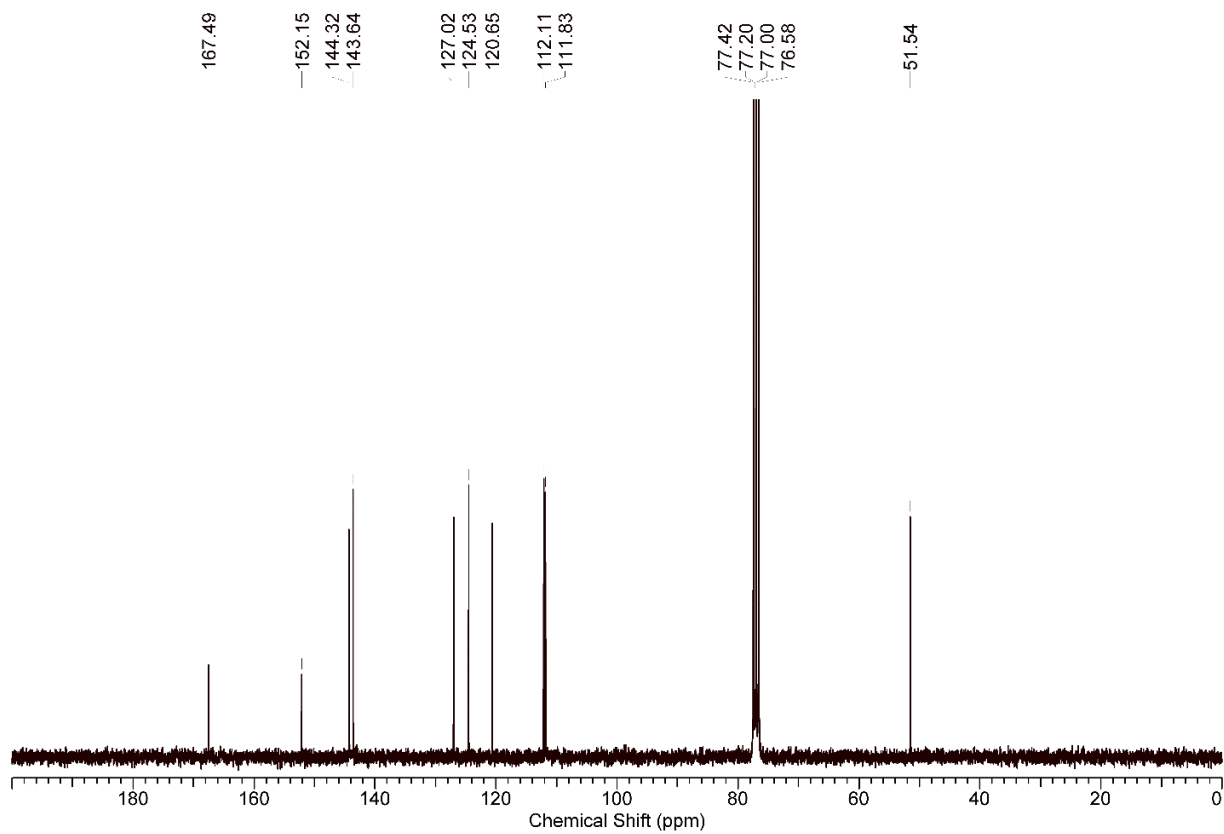


Fig. S97: ¹³C NMR (CDCl₃, 101 MHz) spectrum of **I12**.

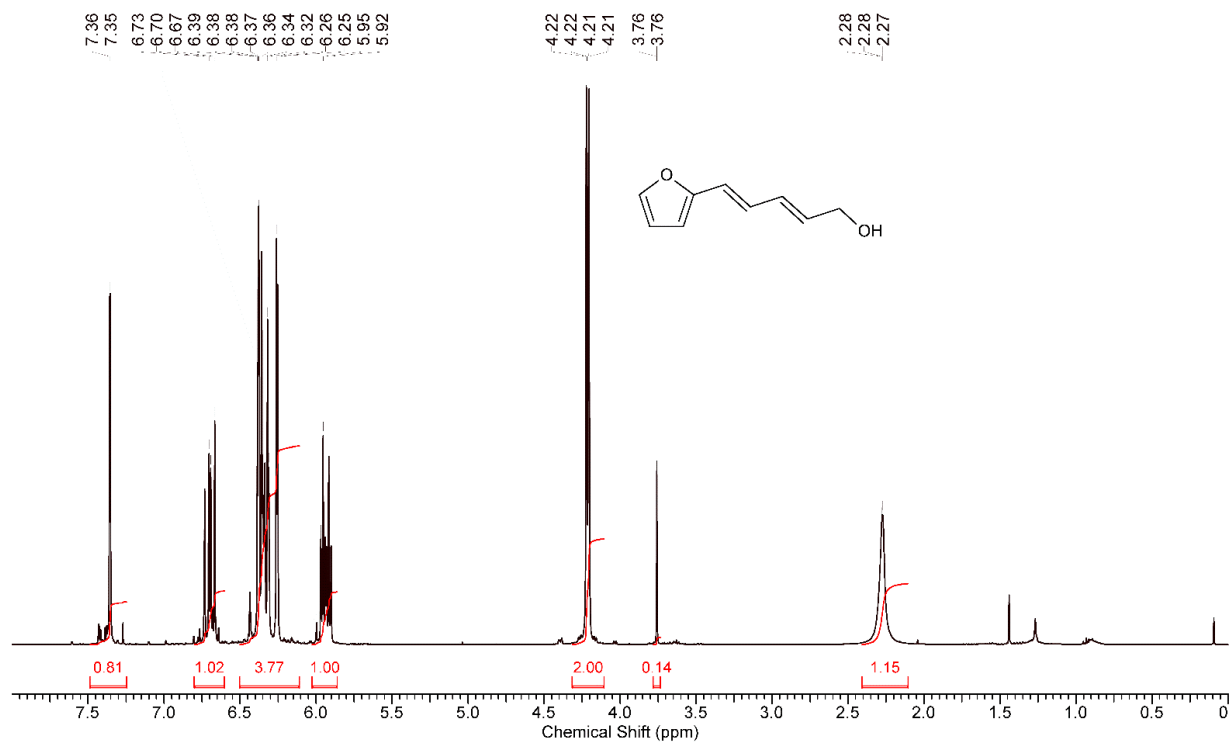


Fig. S98: ^1H NMR (CDCl_3 , 400 MHz) spectrum of **I13**. The peak at 3.76 corresponds to 4.5% unreacted methyl ester (starting material).

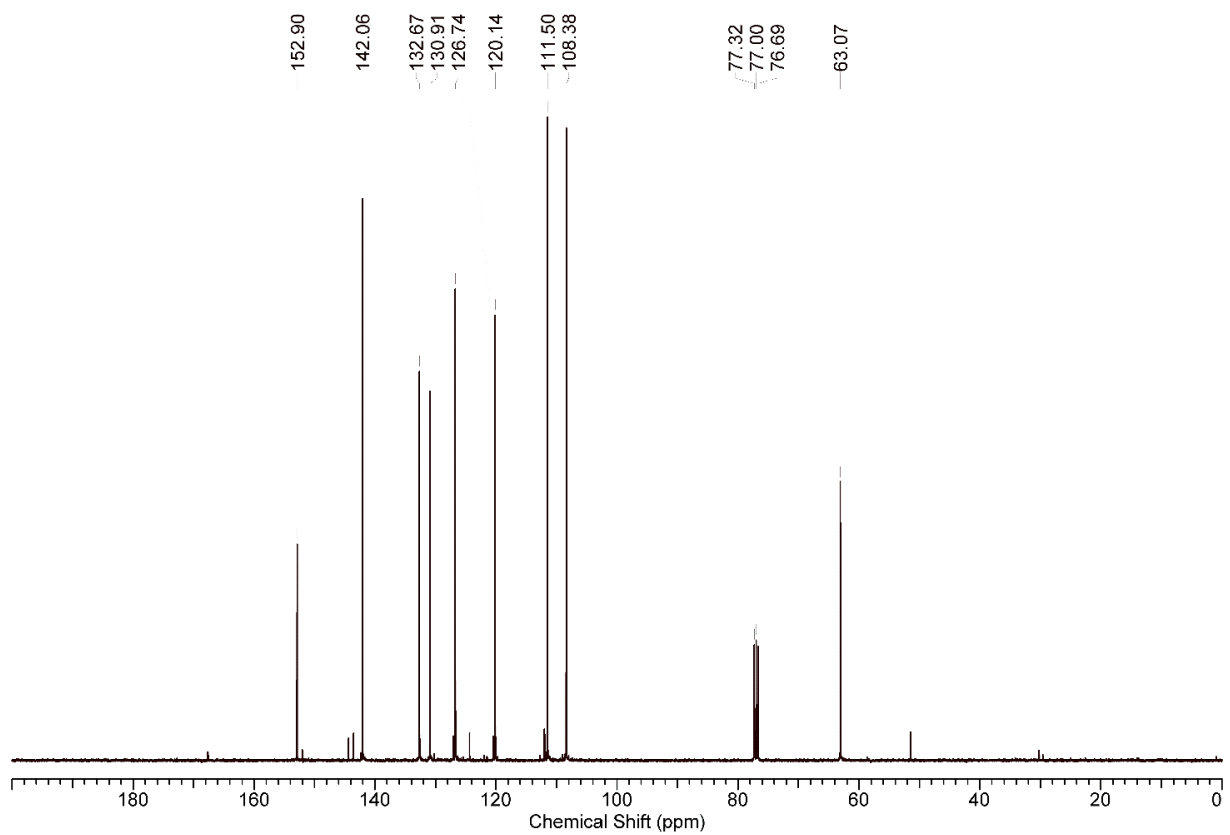


Fig. S99: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **I13**.

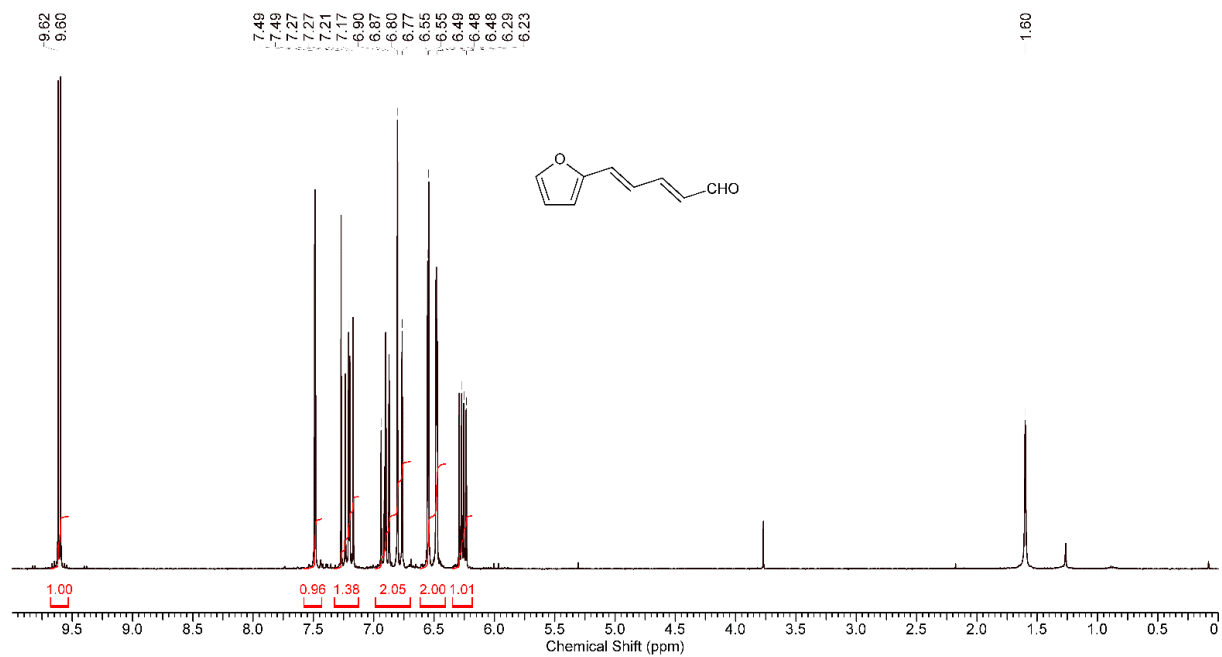


Fig. S100: ^1H NMR (CDCl_3 , 400 MHz) spectrum of CTA18.

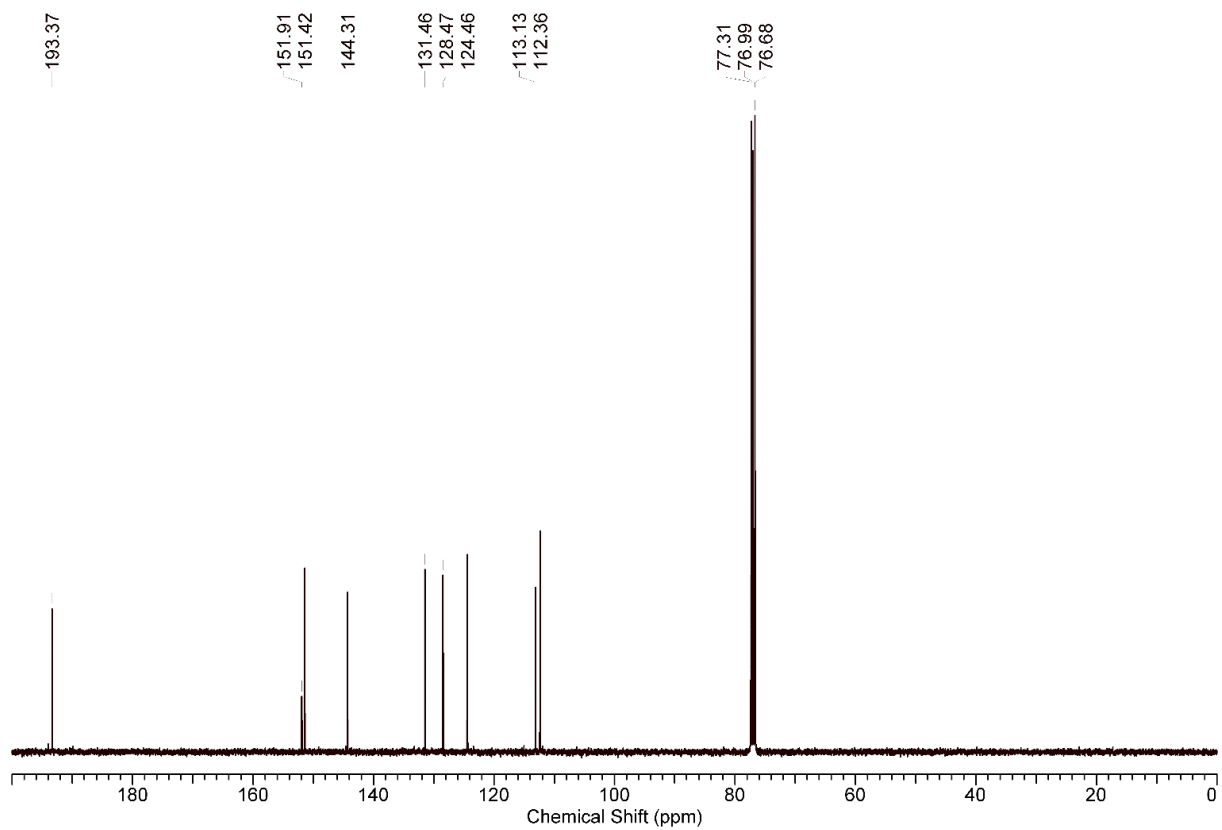


Fig. S101: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of CTA18.

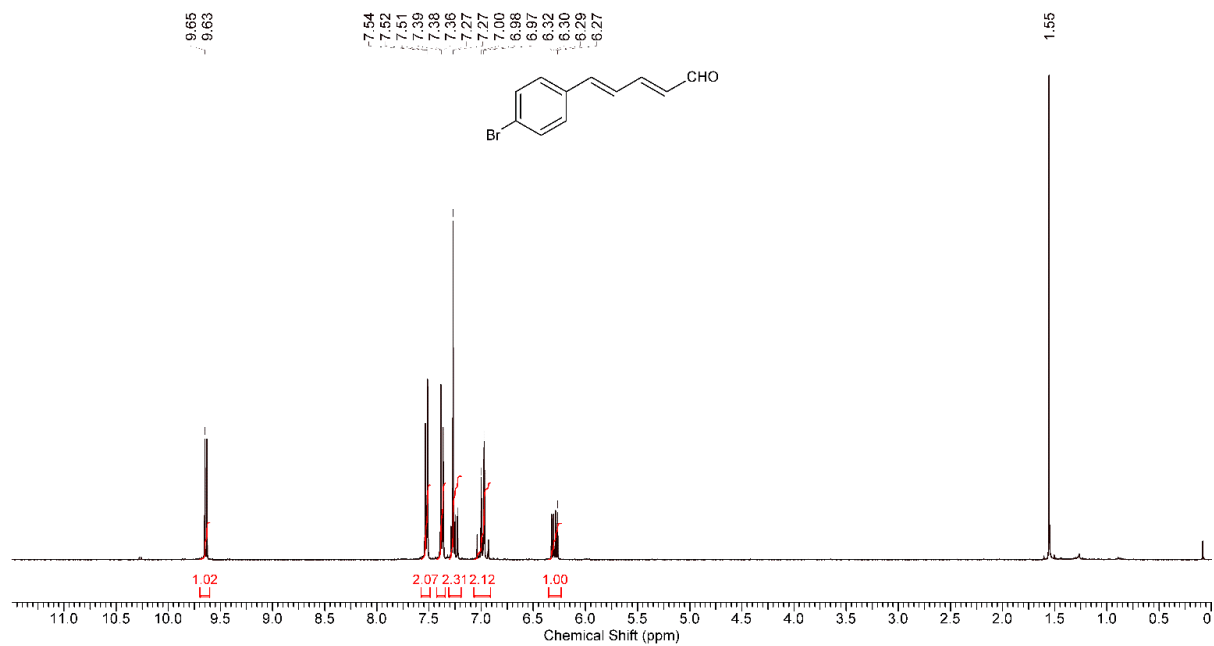


Fig. S102: ^1H NMR (CDCl_3 , 400 MHz) spectrum of **CTA19** (Predominantly trans).

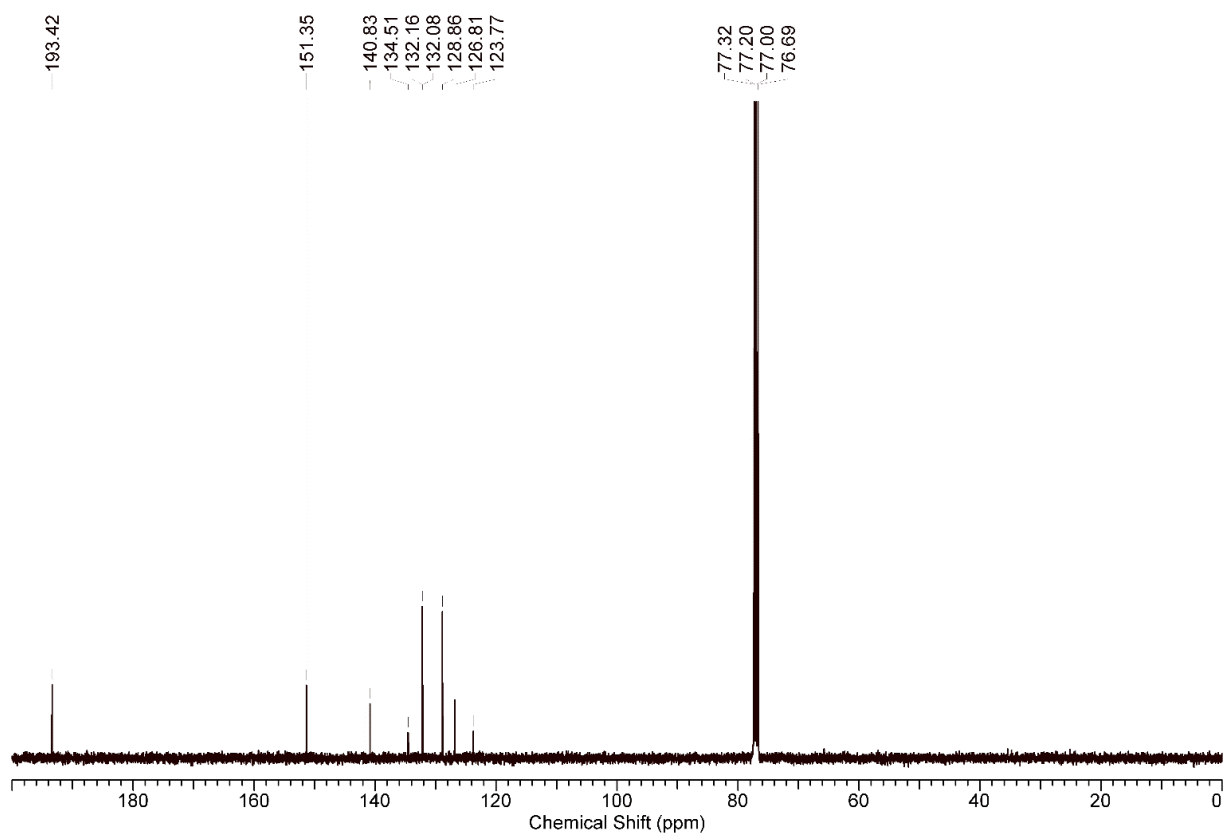


Fig. S103: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **CTA19** (Predominantly trans).

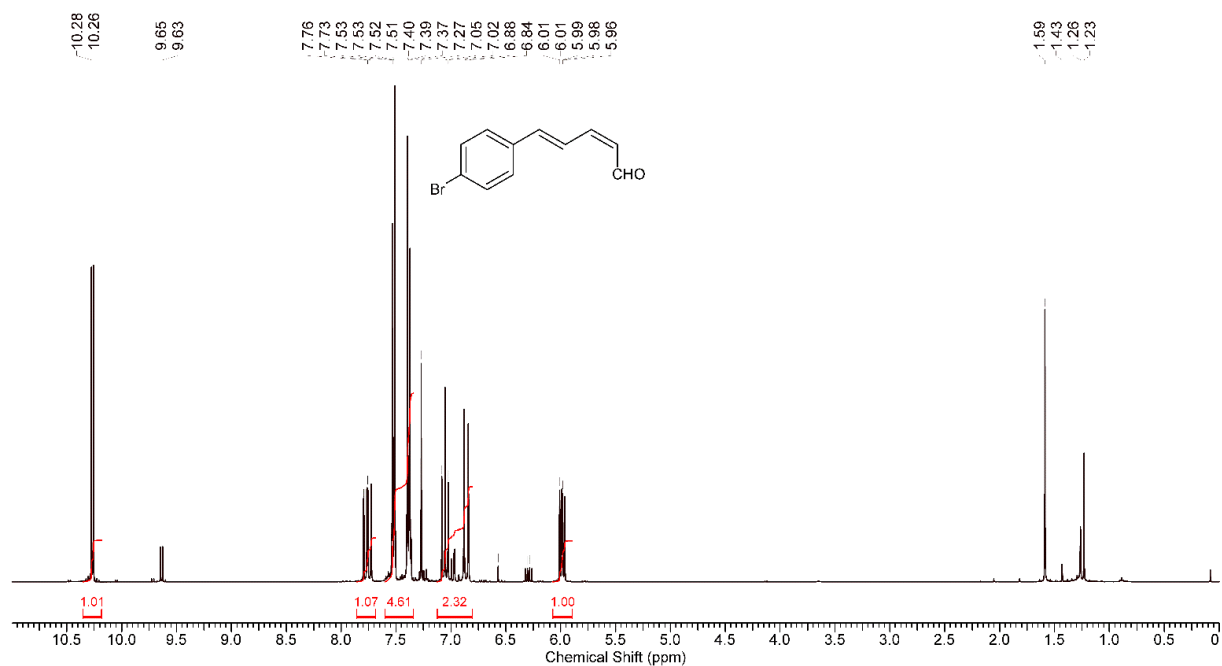


Fig. S104: ^1H NMR (CDCl_3 , 400 MHz) spectrum of **CTA19** (Predominantly cis).

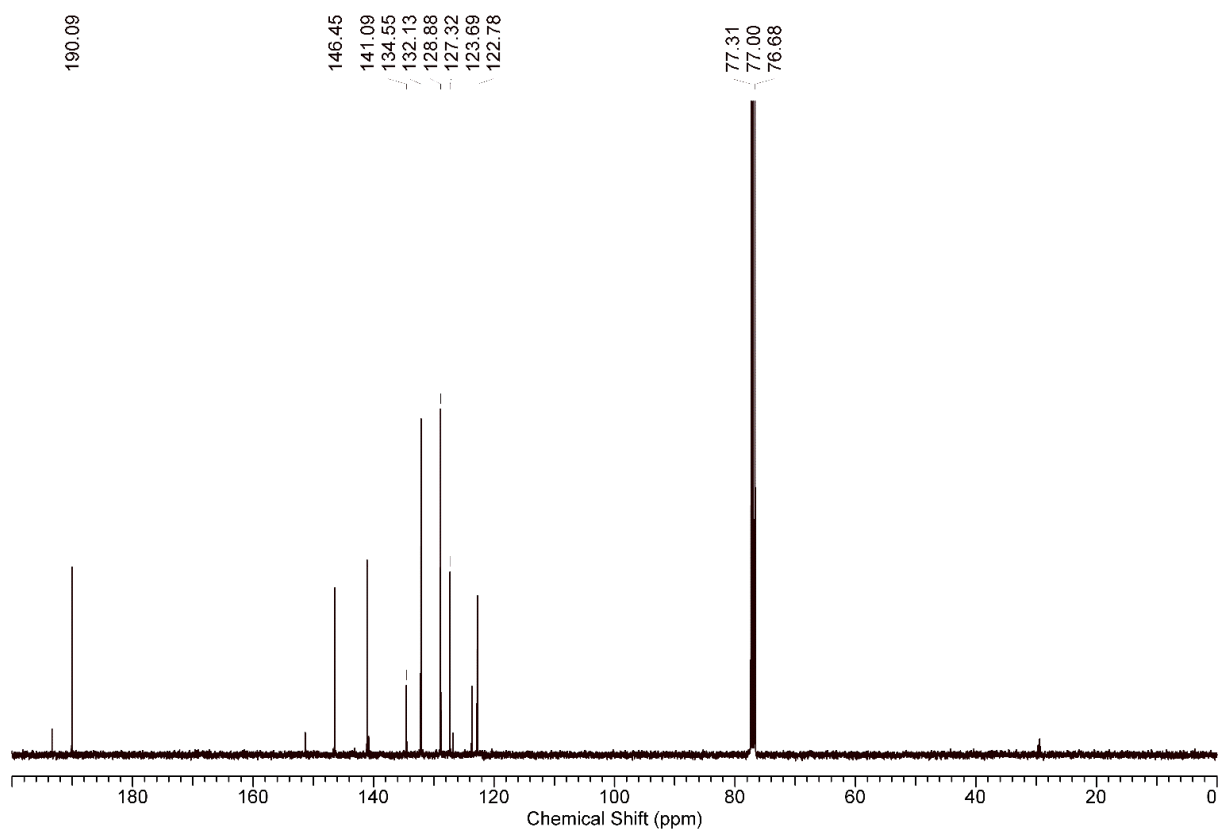


Fig. S105: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **CTA19** (Predominantly cis).

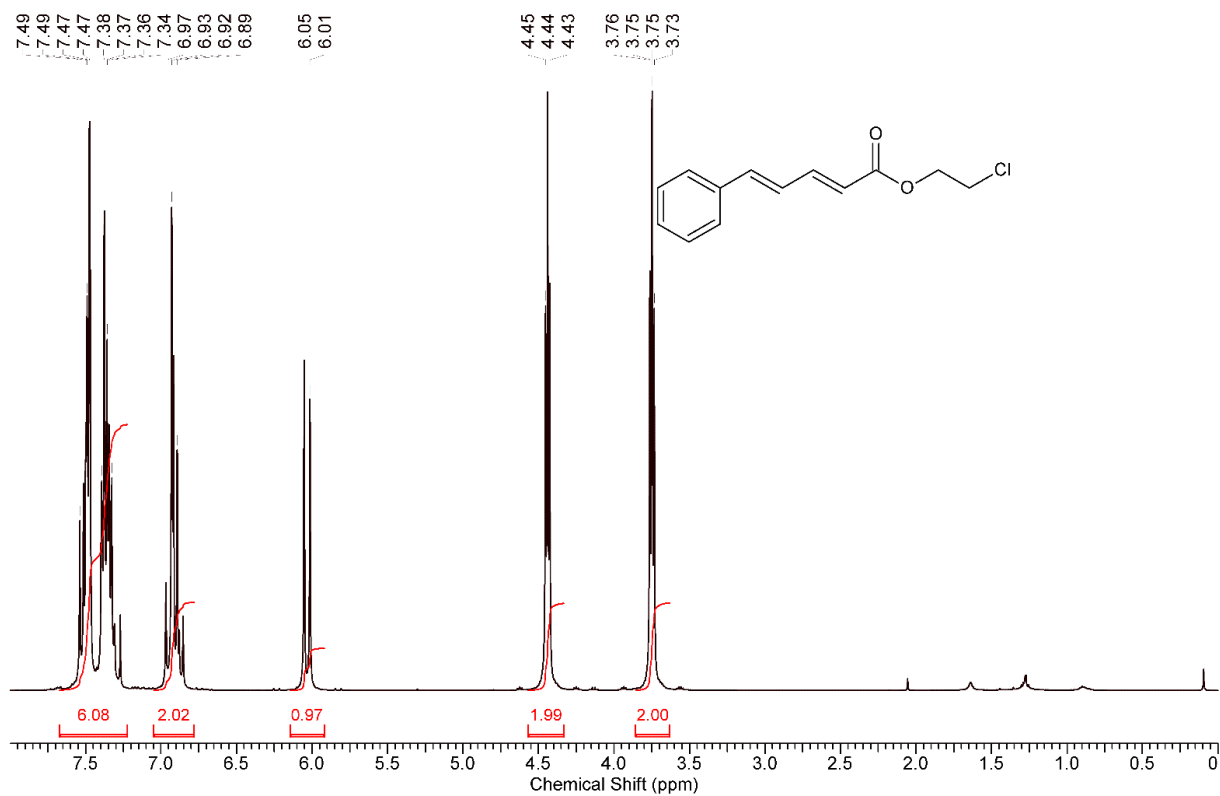


Fig. S106: ^1H NMR (CDCl_3 , 400 MHz) spectrum of CTA20.

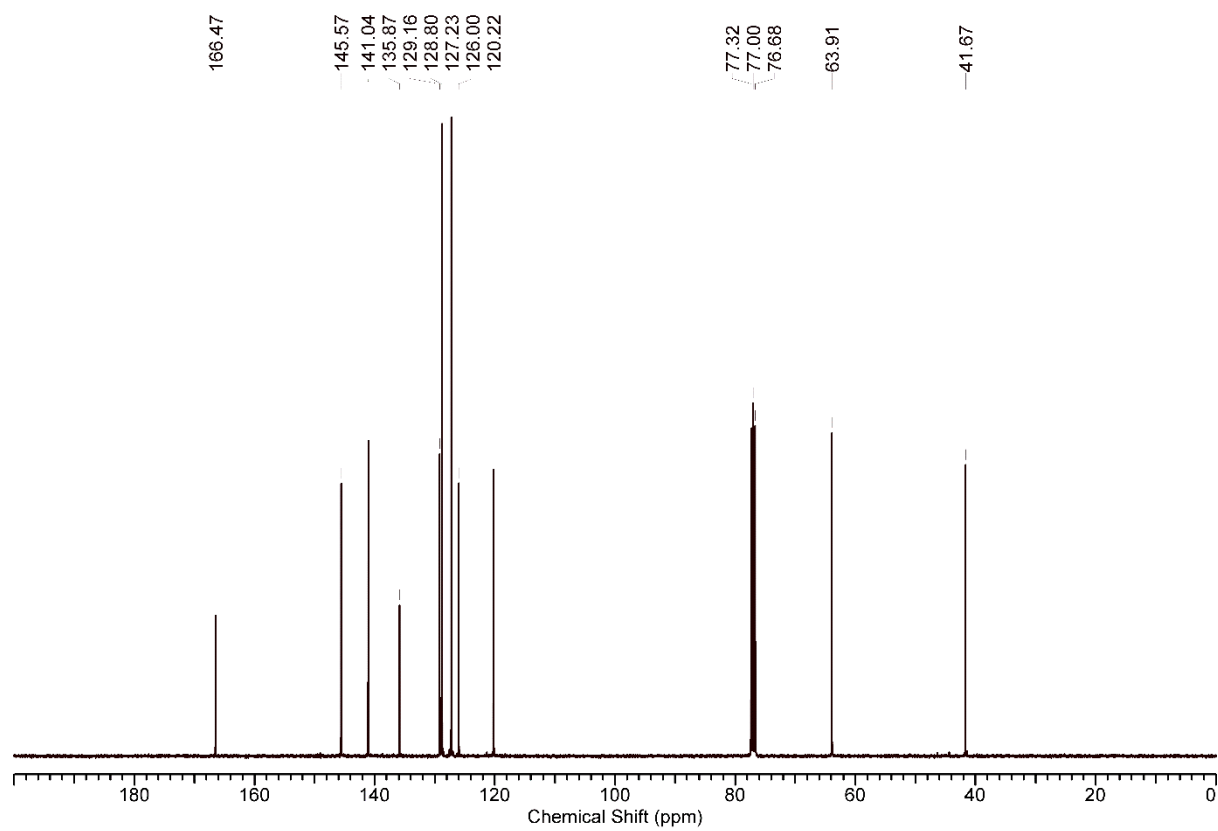


Fig. S107: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of CTA20.

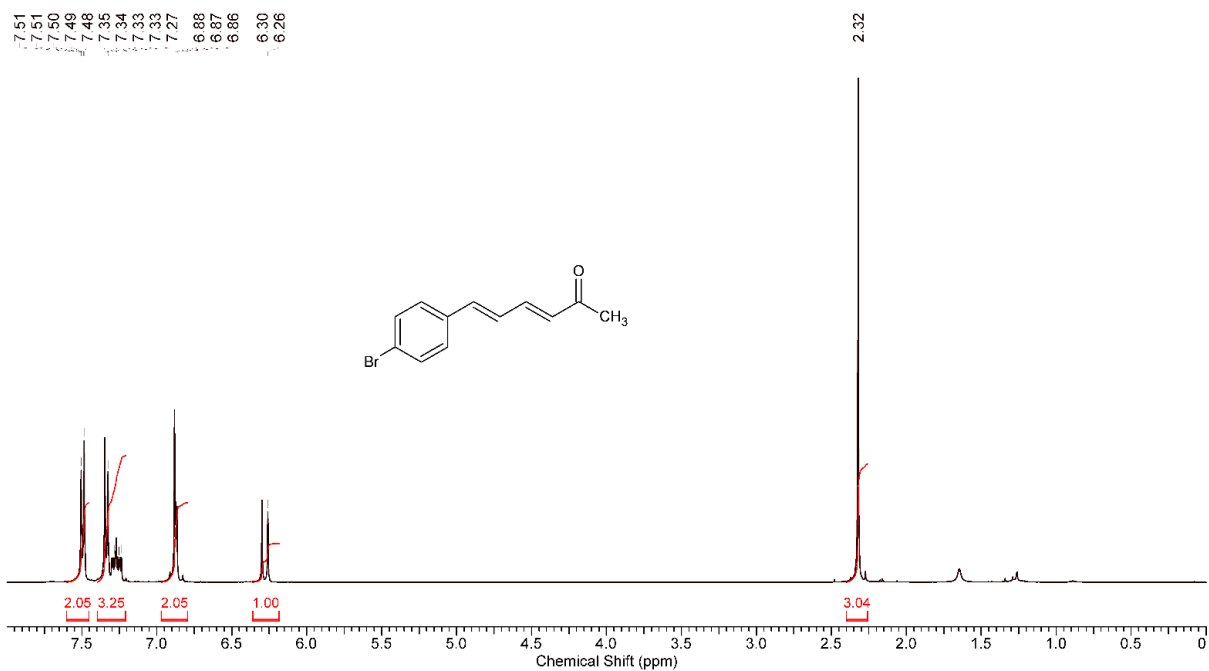


Fig. S108: ¹H NMR (CDCl₃, 400 MHz) spectrum of CTA21.

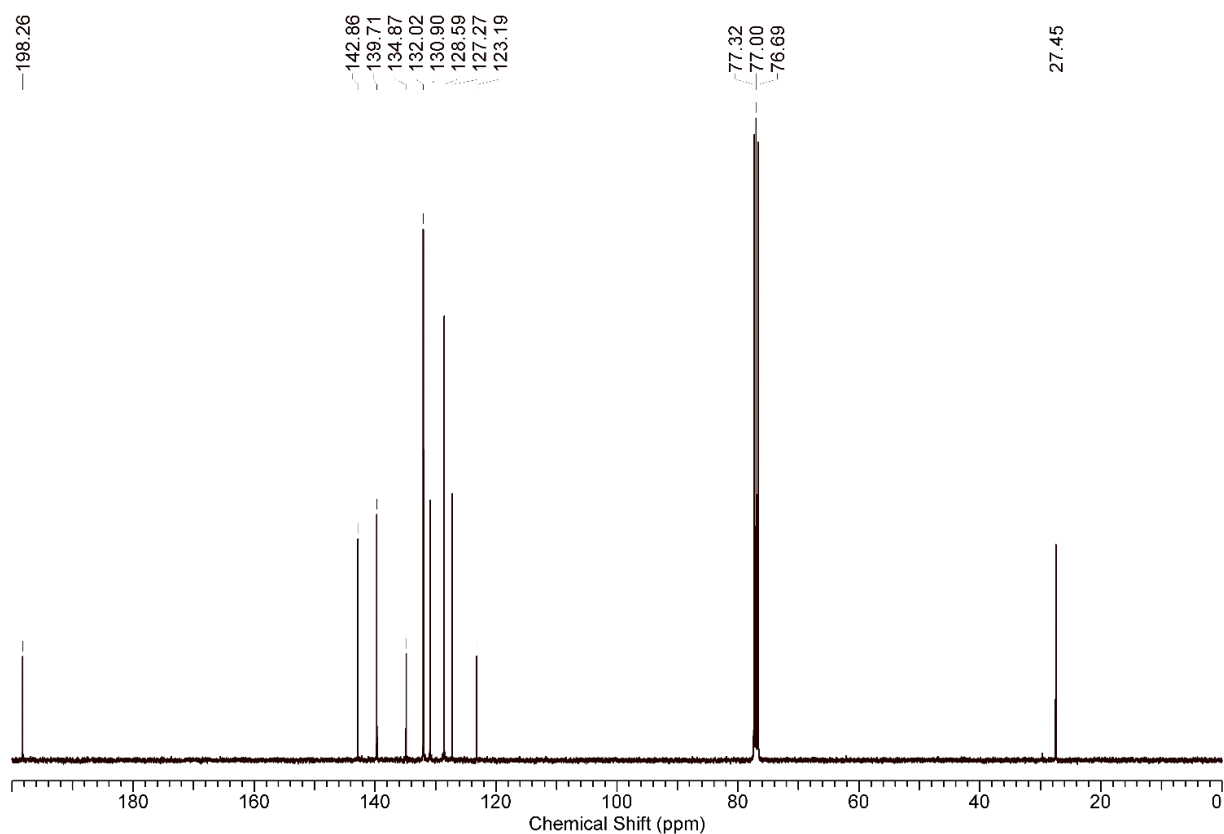


Fig. S109: ¹³C NMR (CDCl₃, 101 MHz) spectrum of CTA21.

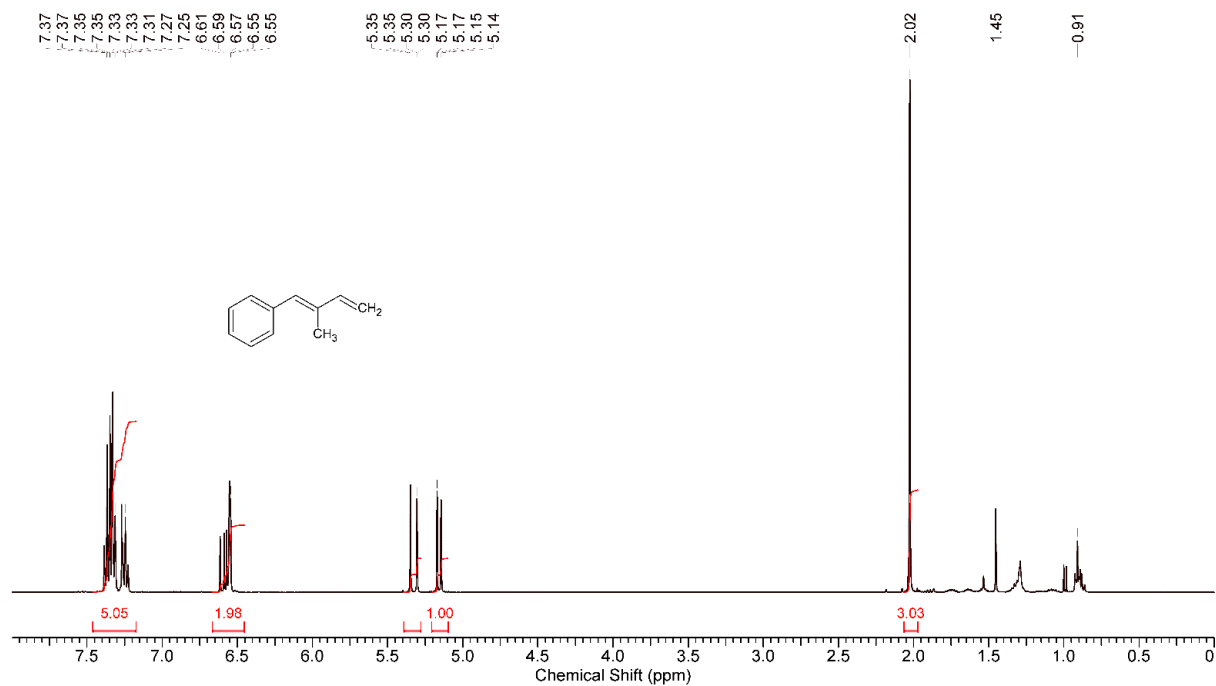


Fig. S110: ¹H NMR (CDCl₃, 400 MHz) spectrum of CTA23.

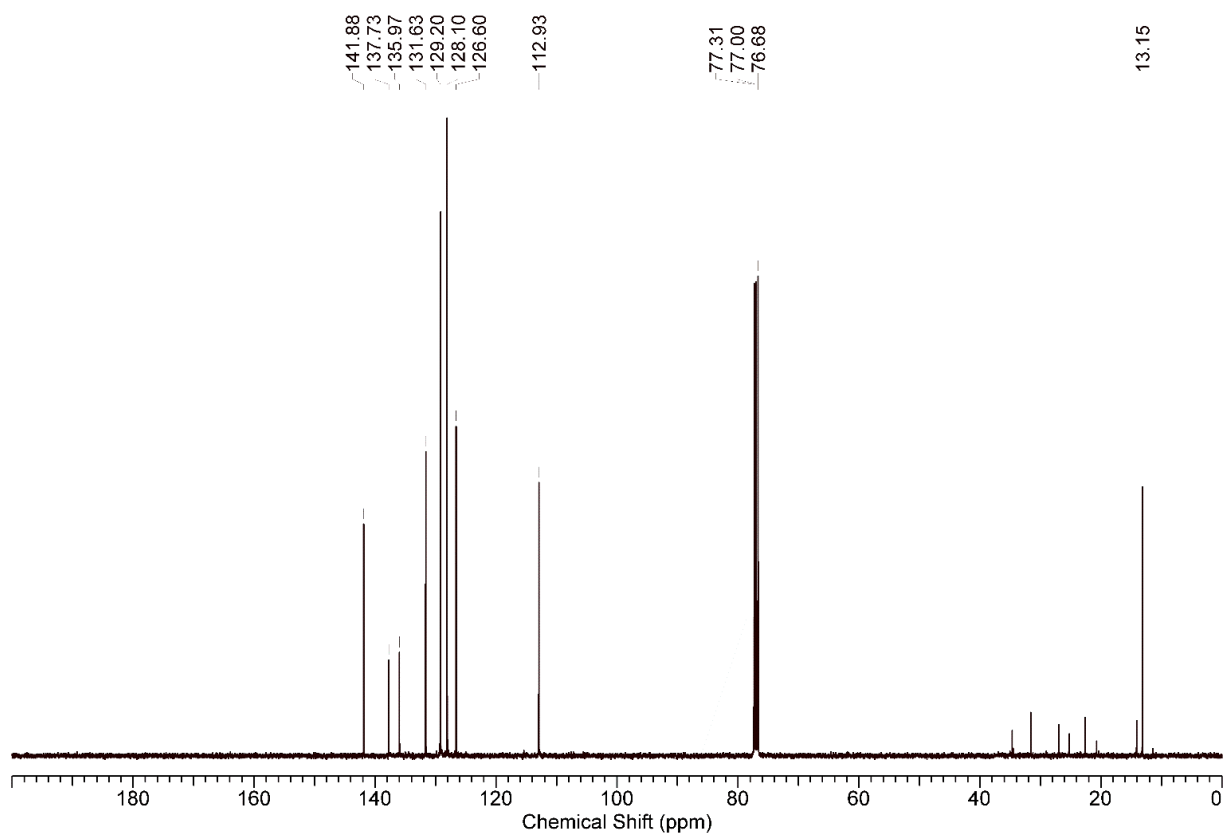


Fig. S111: ¹³C NMR (CDCl₃, 101 MHz) spectrum of CTA23.

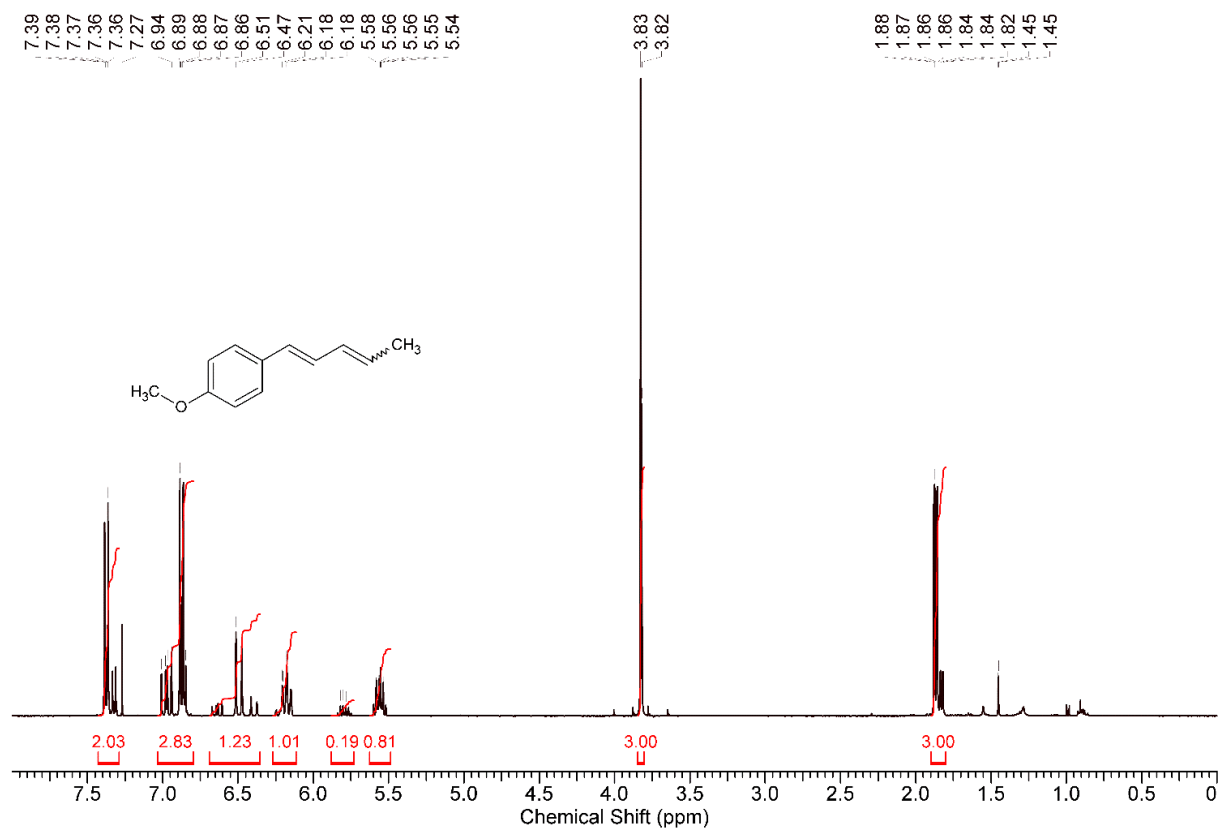


Fig. S112: ¹H NMR (CDCl₃, 400 MHz) spectrum of CTA24.

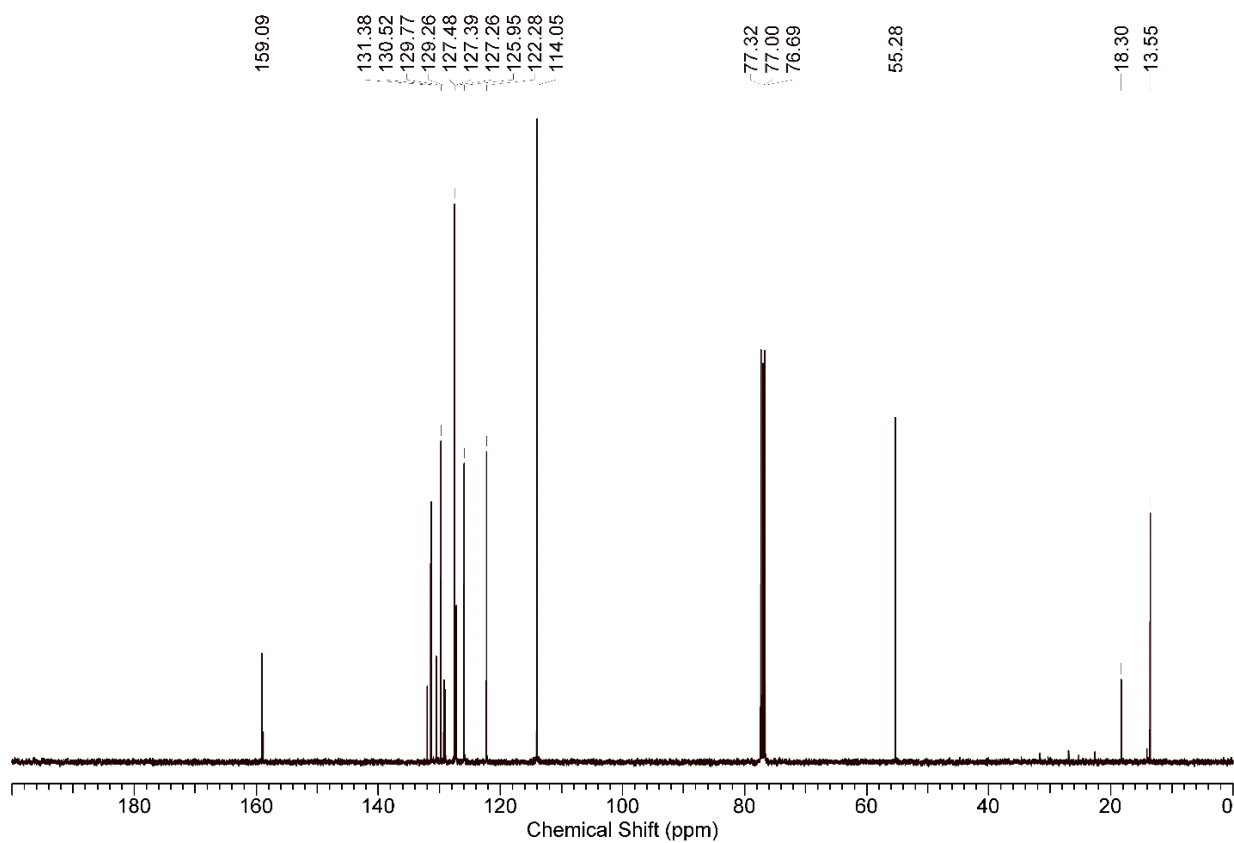


Fig. S113: ¹³C NMR (CDCl₃, 101 MHz) spectrum of CTA24.

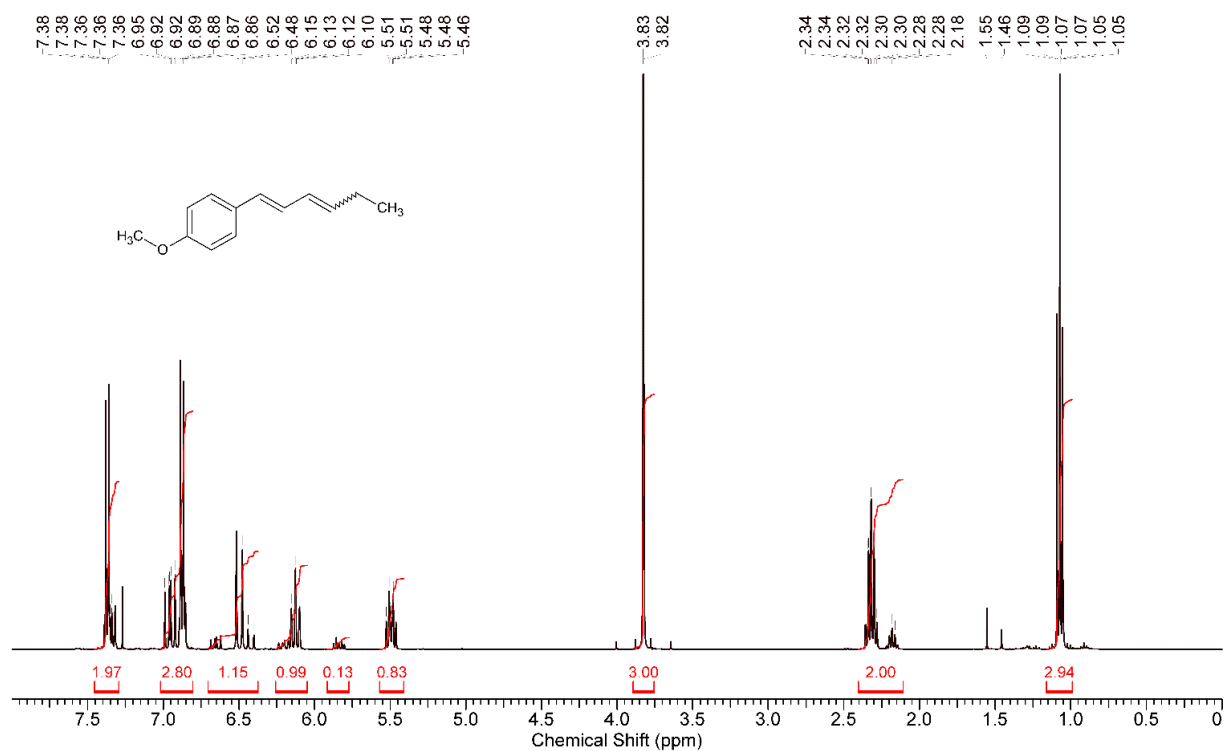


Fig. S114: ^1H NMR (CDCl_3 , 400 MHz) spectrum of CTA25.

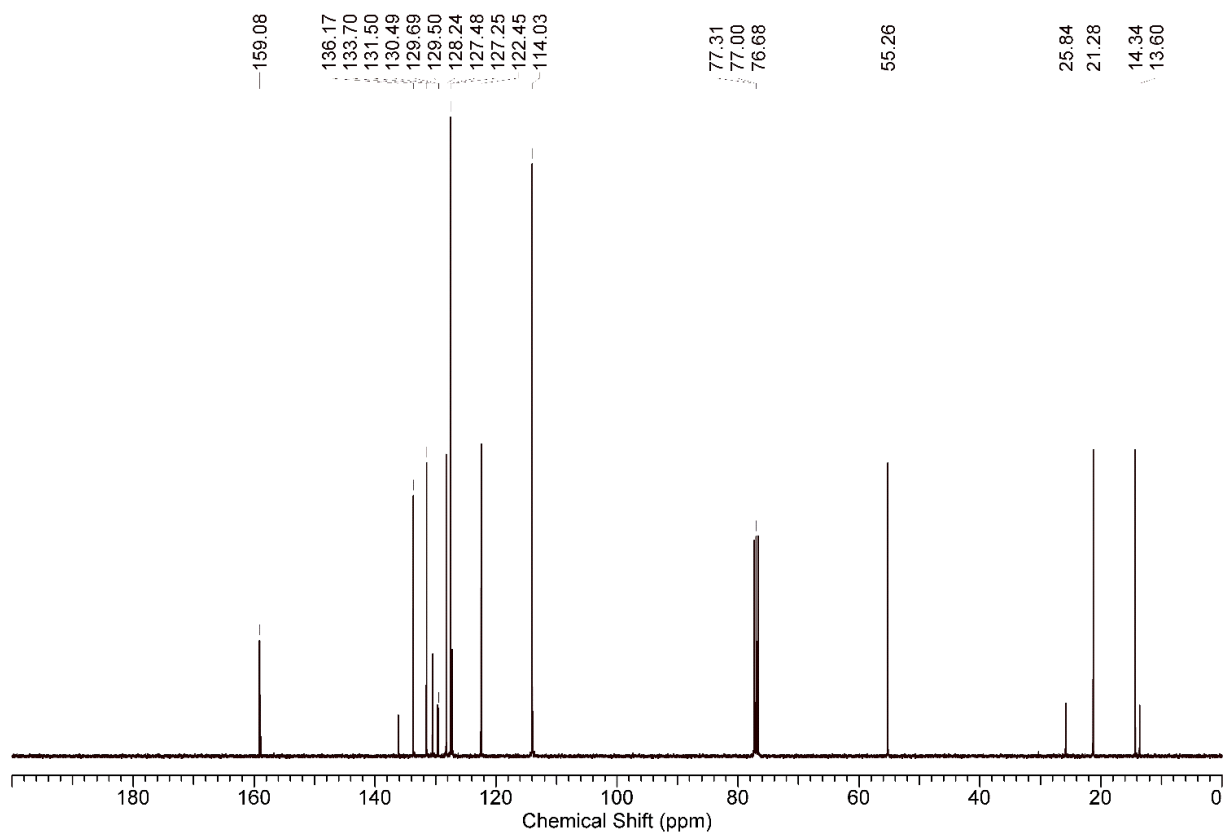


Fig. S115: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of CTA25.

NMR Spectra of polymers:

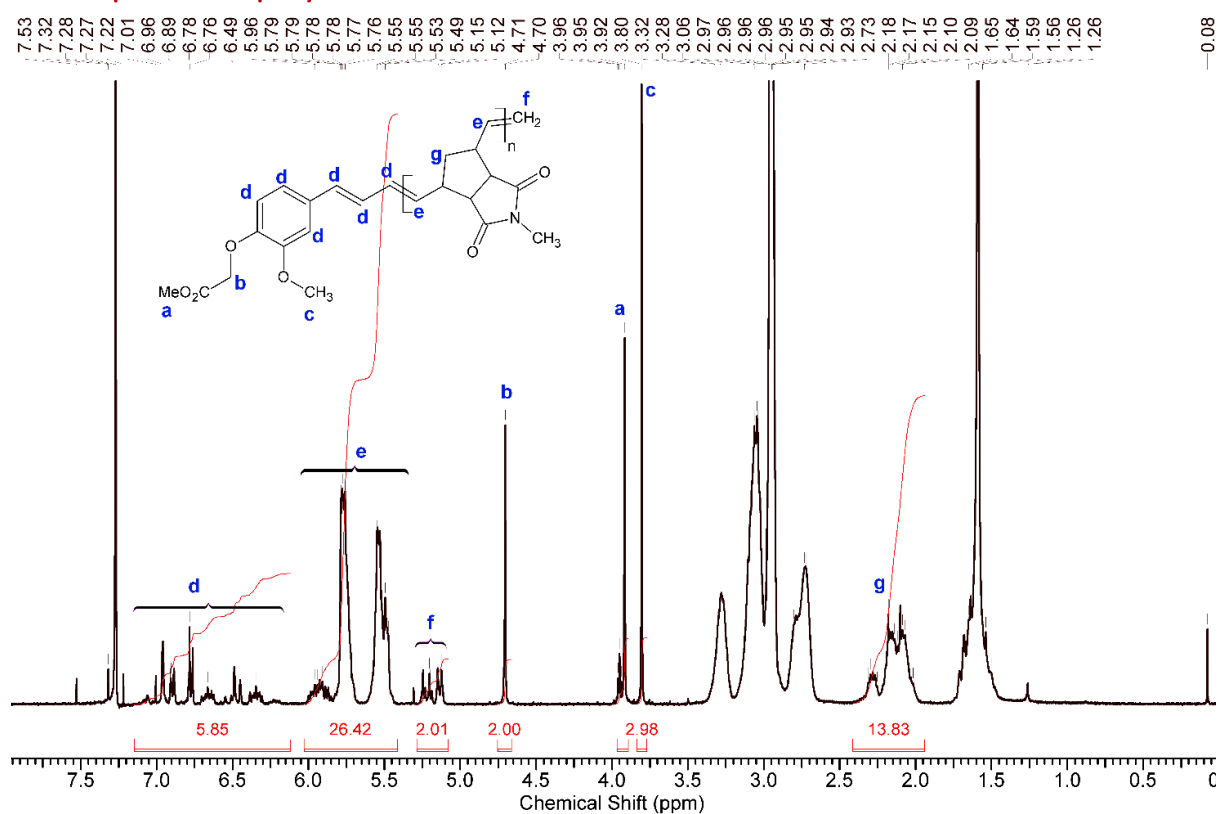


Fig. S118: ^1H NMR (CDCl_3 , 400 MHz) spectrum of P2.

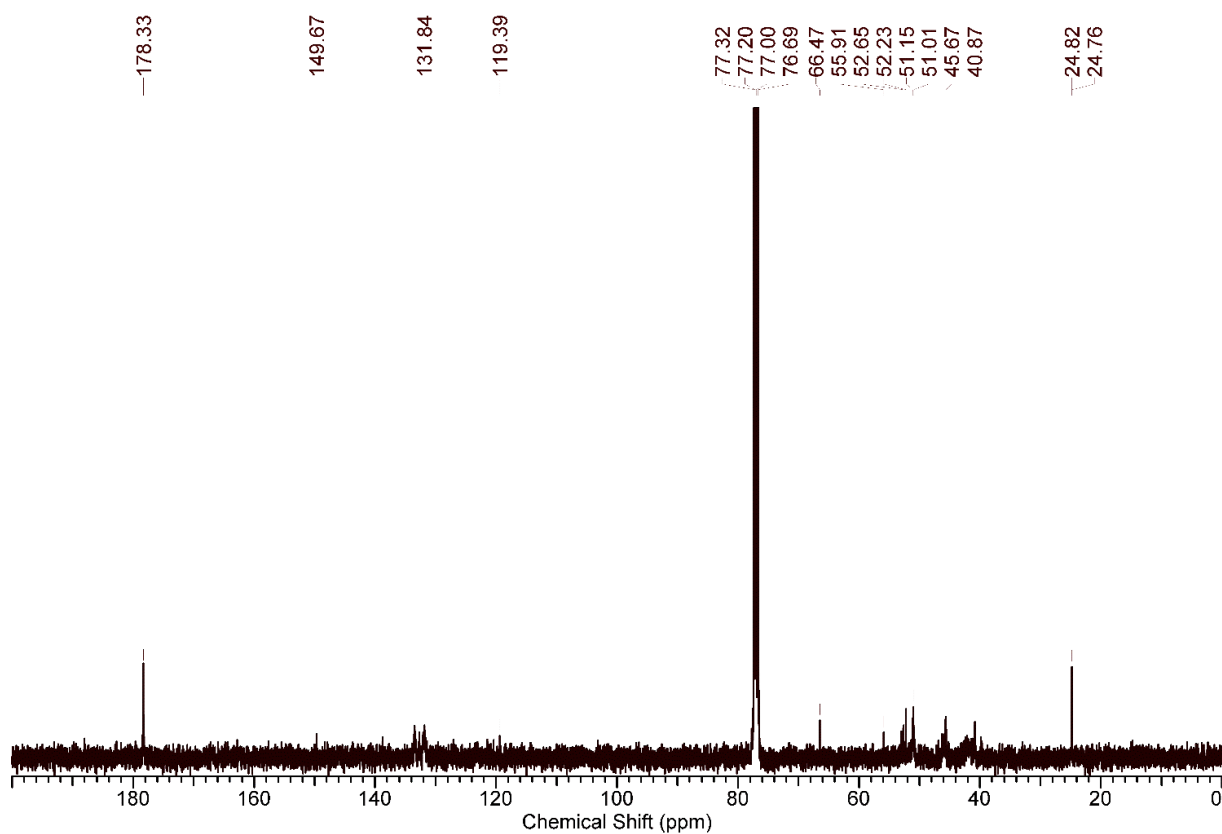


Fig. S119: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of P2.

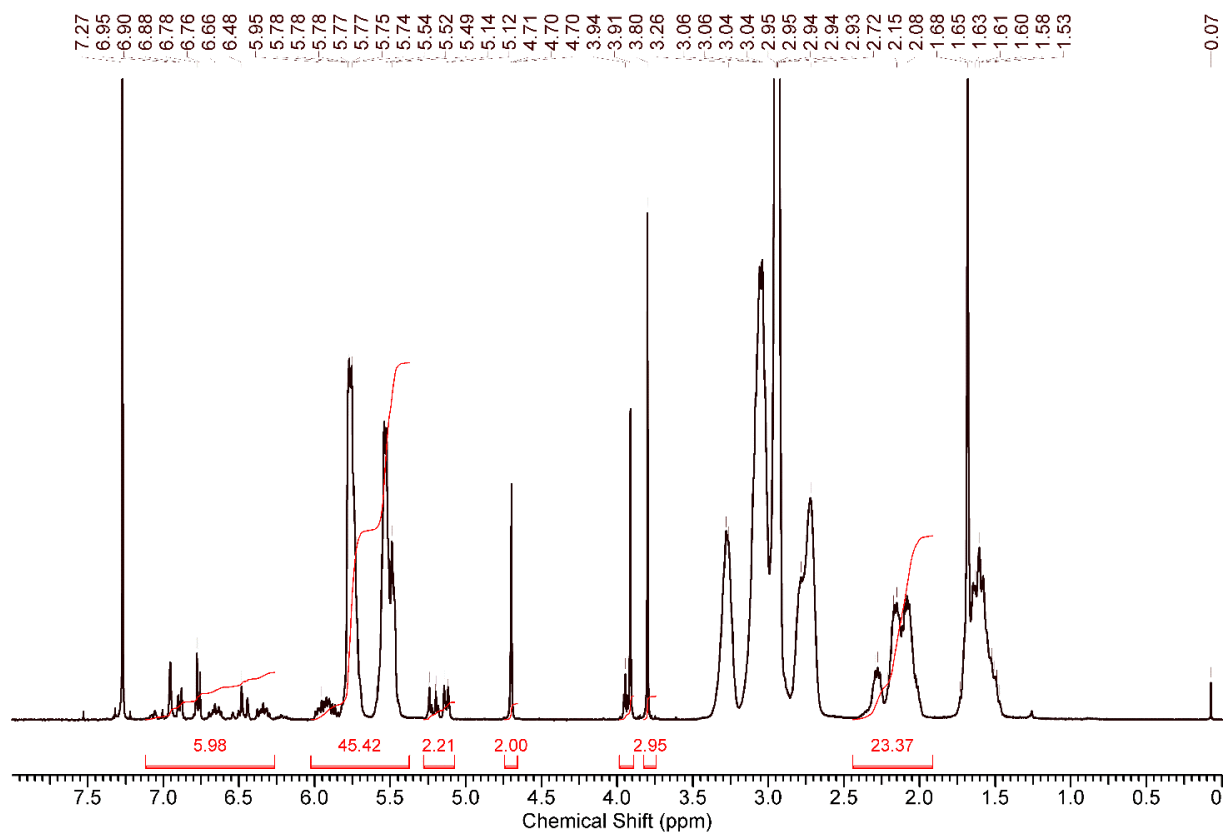


Fig. S120: ^1H NMR (CDCl_3 , 400 MHz) spectrum of **P3**.

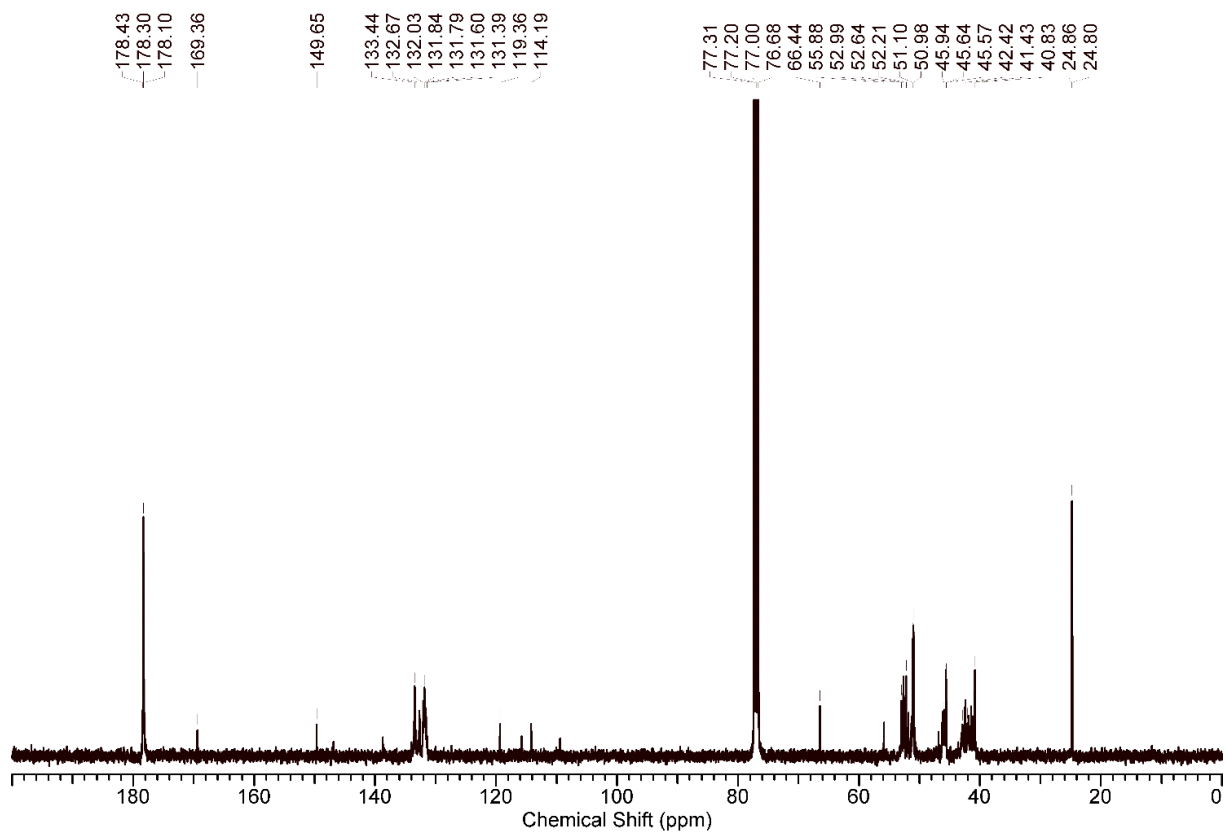


Fig. S121: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **P3**.

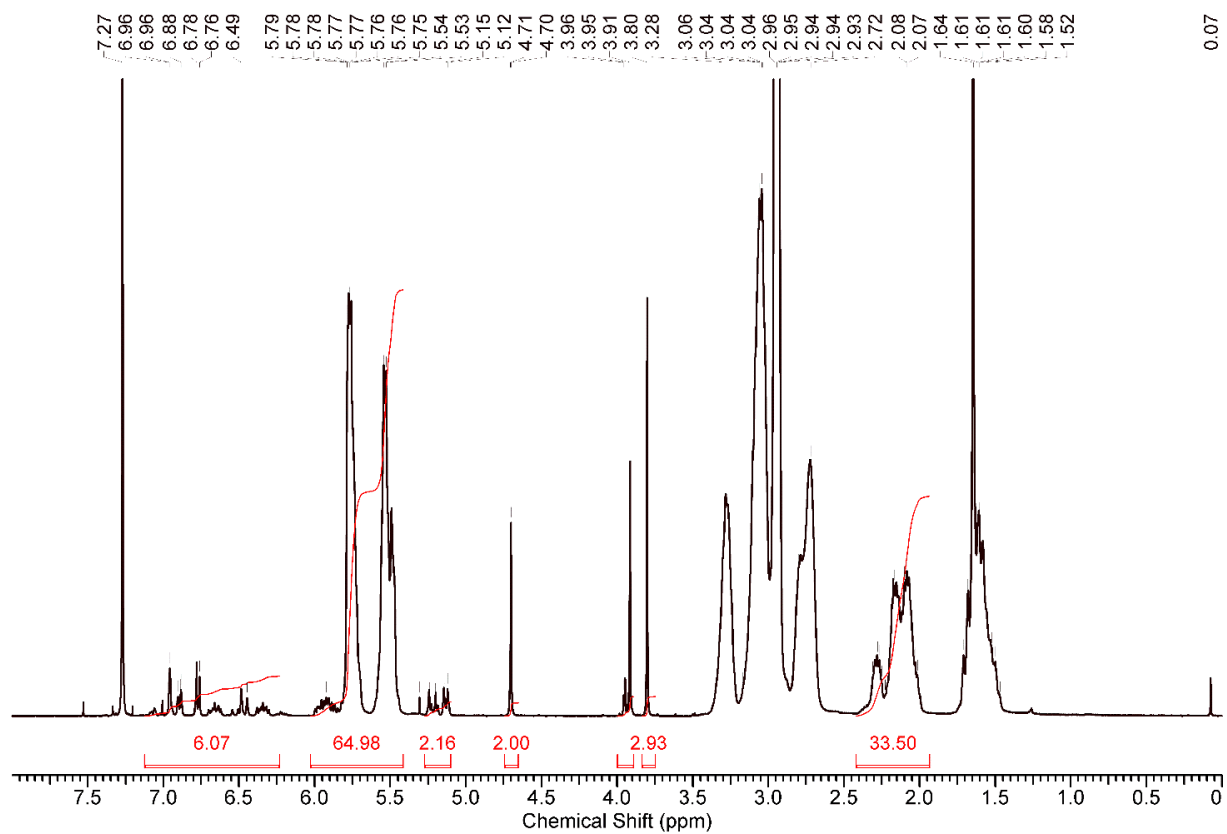


Fig. S122: ^1H NMR (CDCl_3 , 400 MHz) spectrum of **P4**.

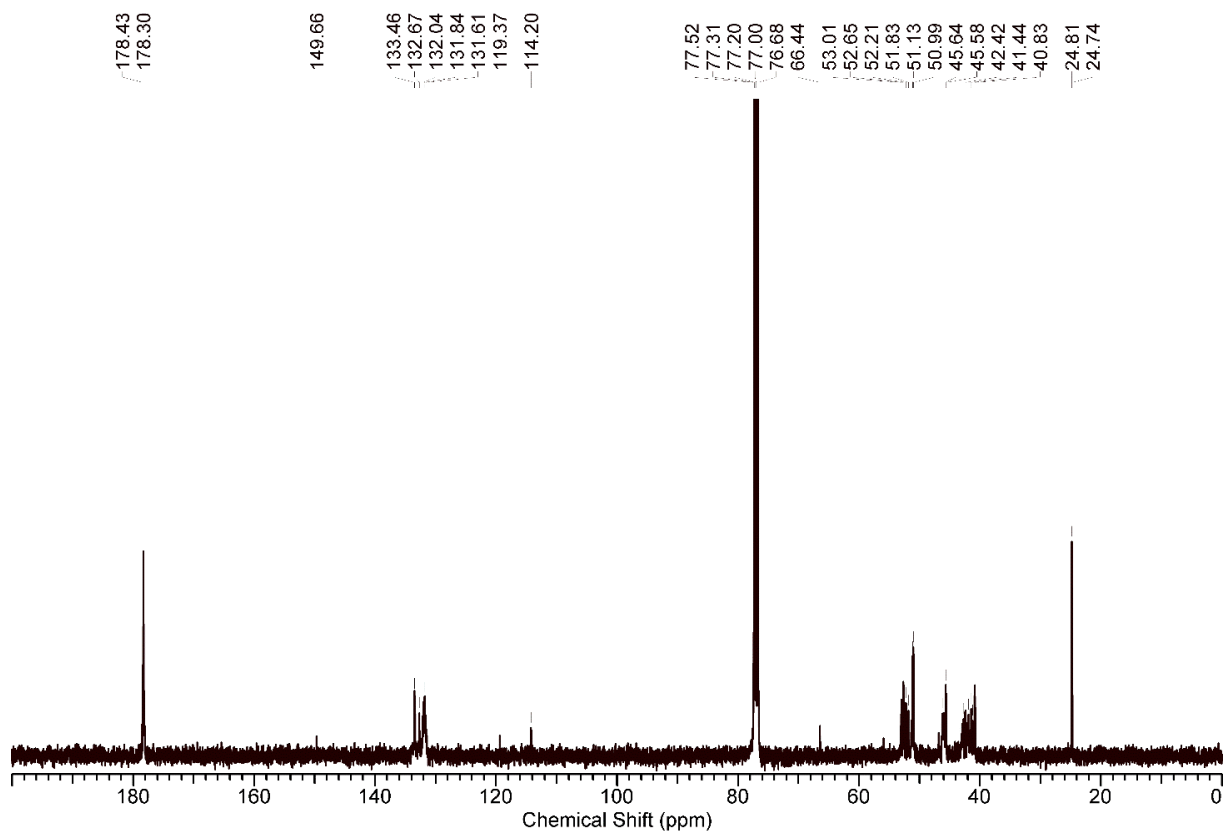


Fig. S123: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **P4**.

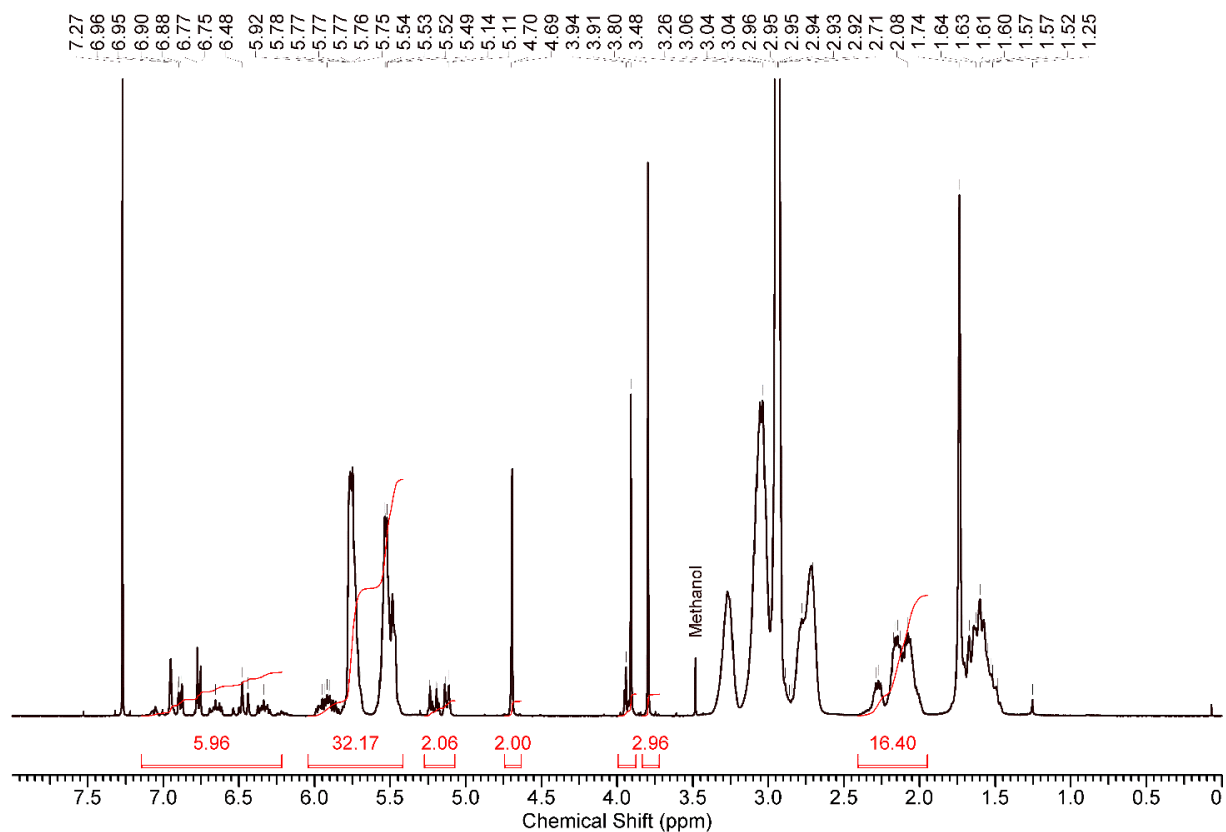


Fig. S124: ^1H NMR (CDCl_3 , 400 MHz) spectrum of **P5**.

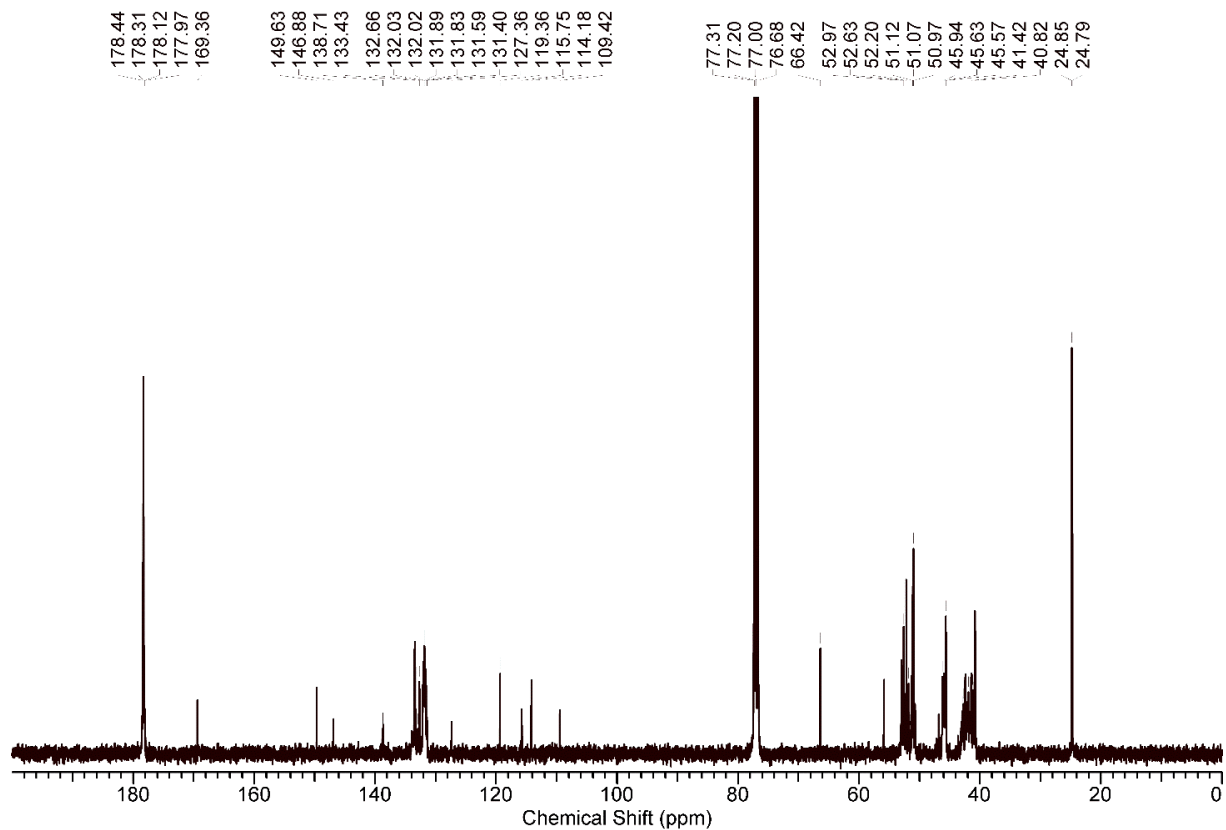


Fig. S125: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **P5**.

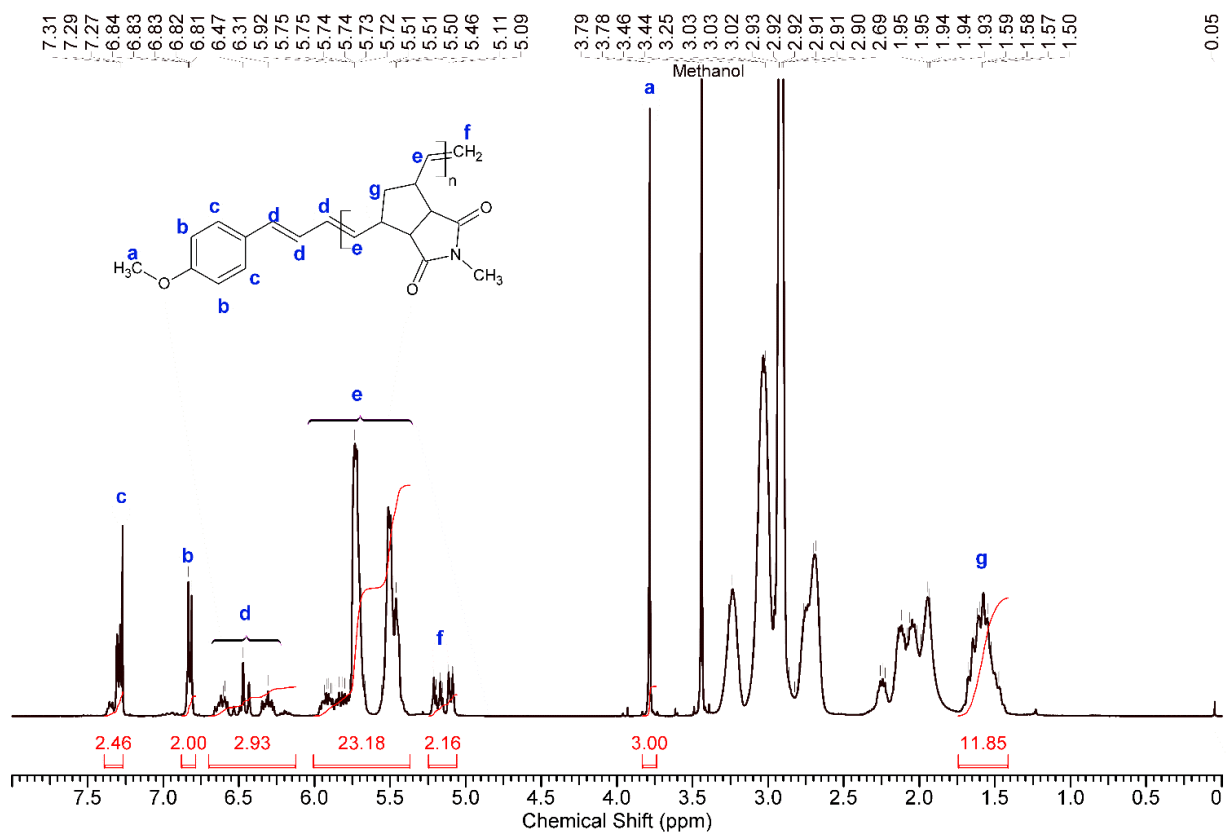


Fig. S126: ^1H NMR (CDCl_3 , 400 MHz) spectrum of P6.

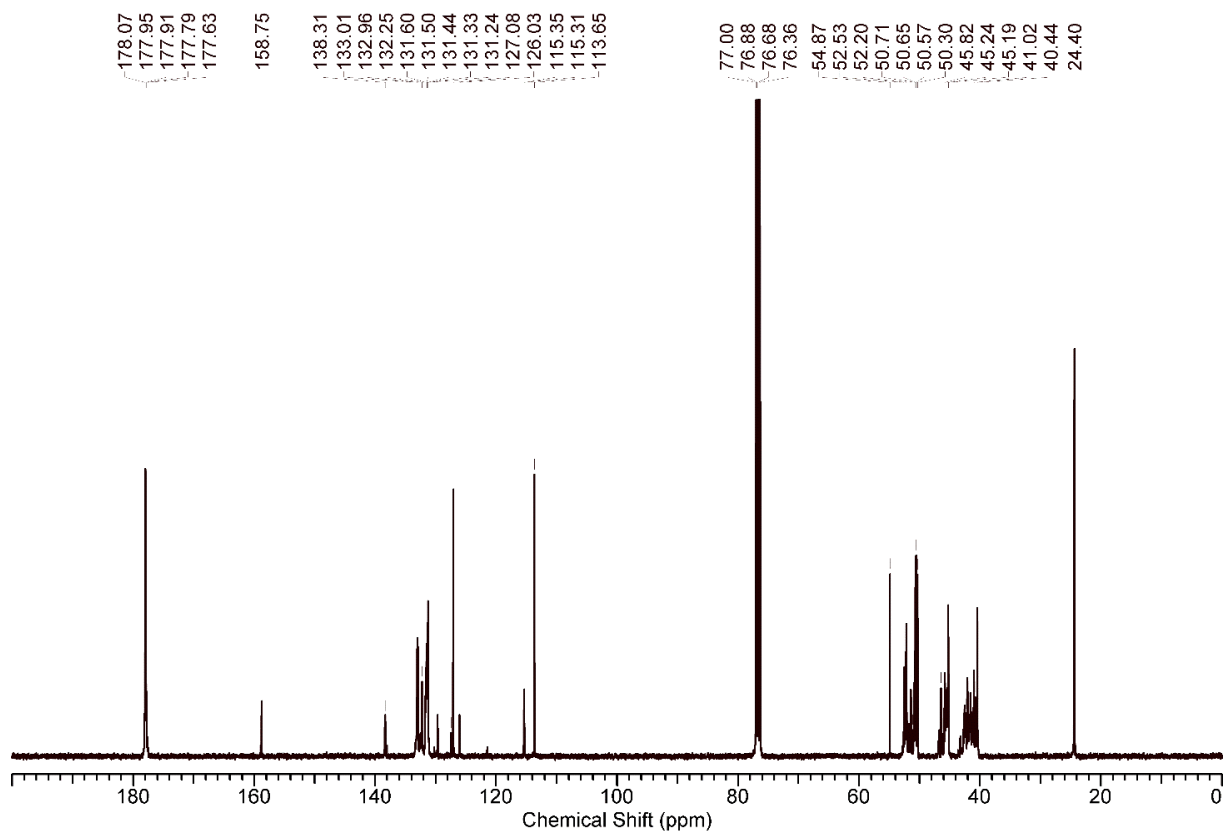


Fig. S127: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of P6.

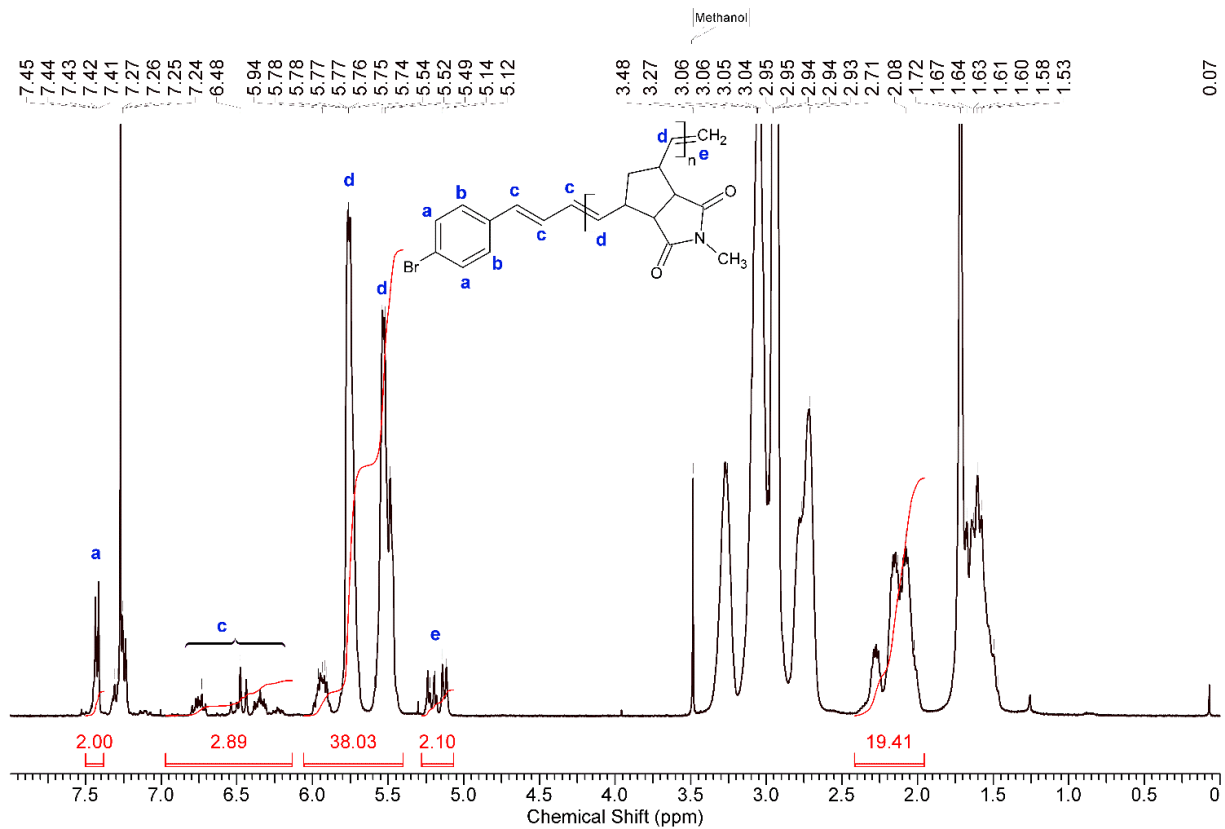


Fig. S128: ^1H NMR (CDCl_3 , 400 MHz) spectrum of P7.

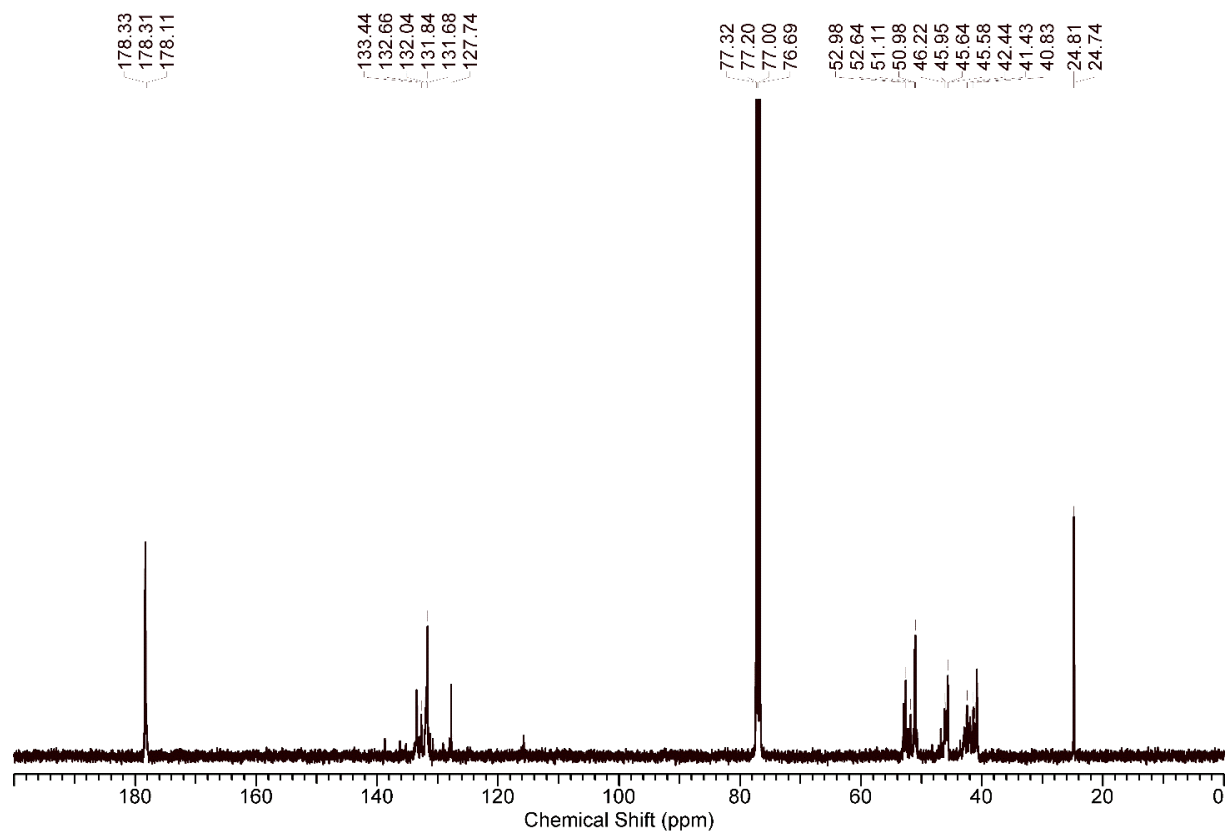


Fig. S129: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of P7.

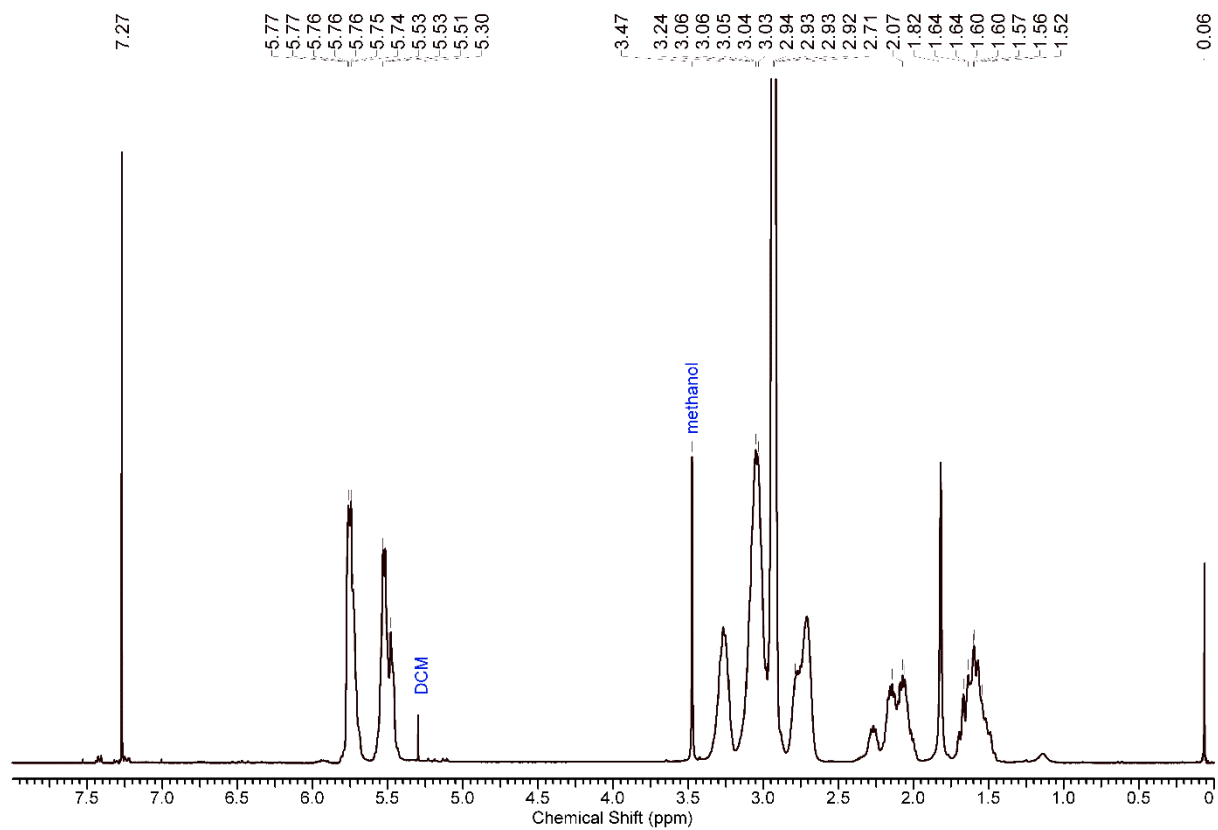


Fig. S130: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **P8**.

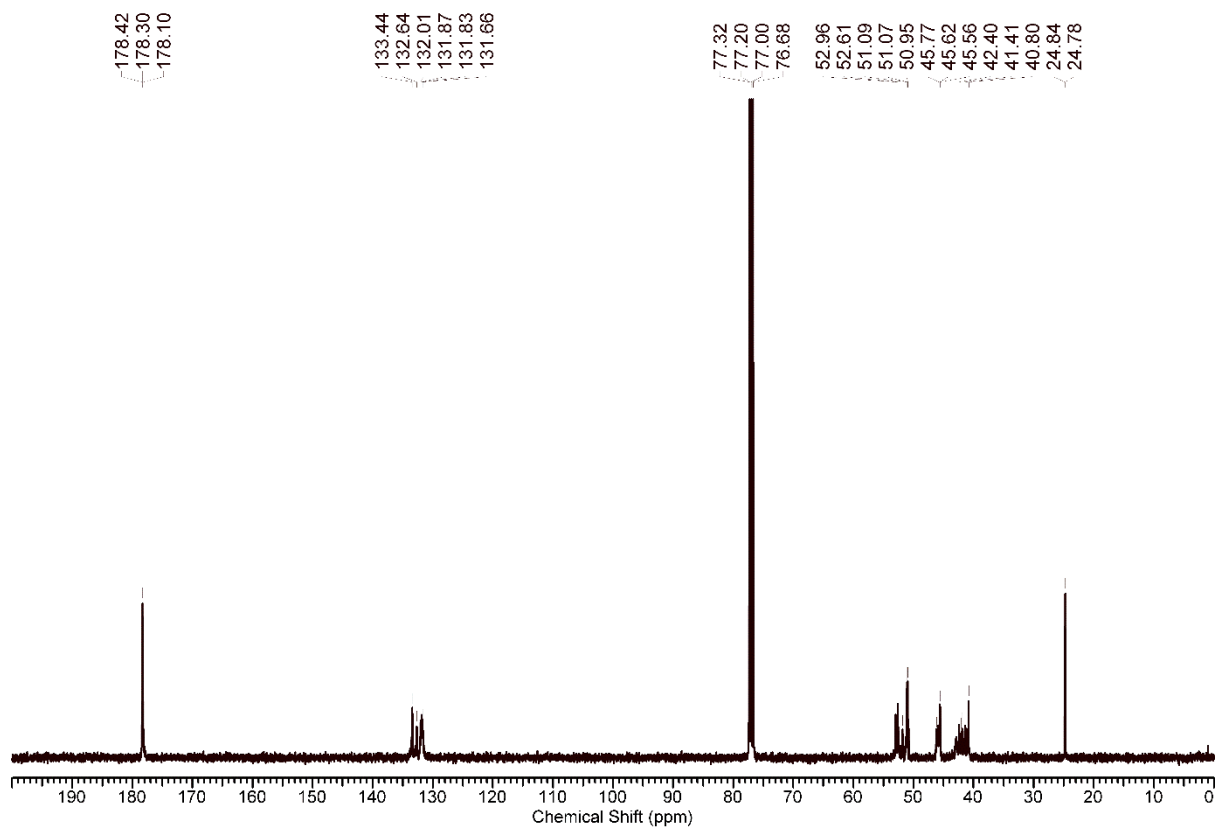


Fig. S131: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **P8**.

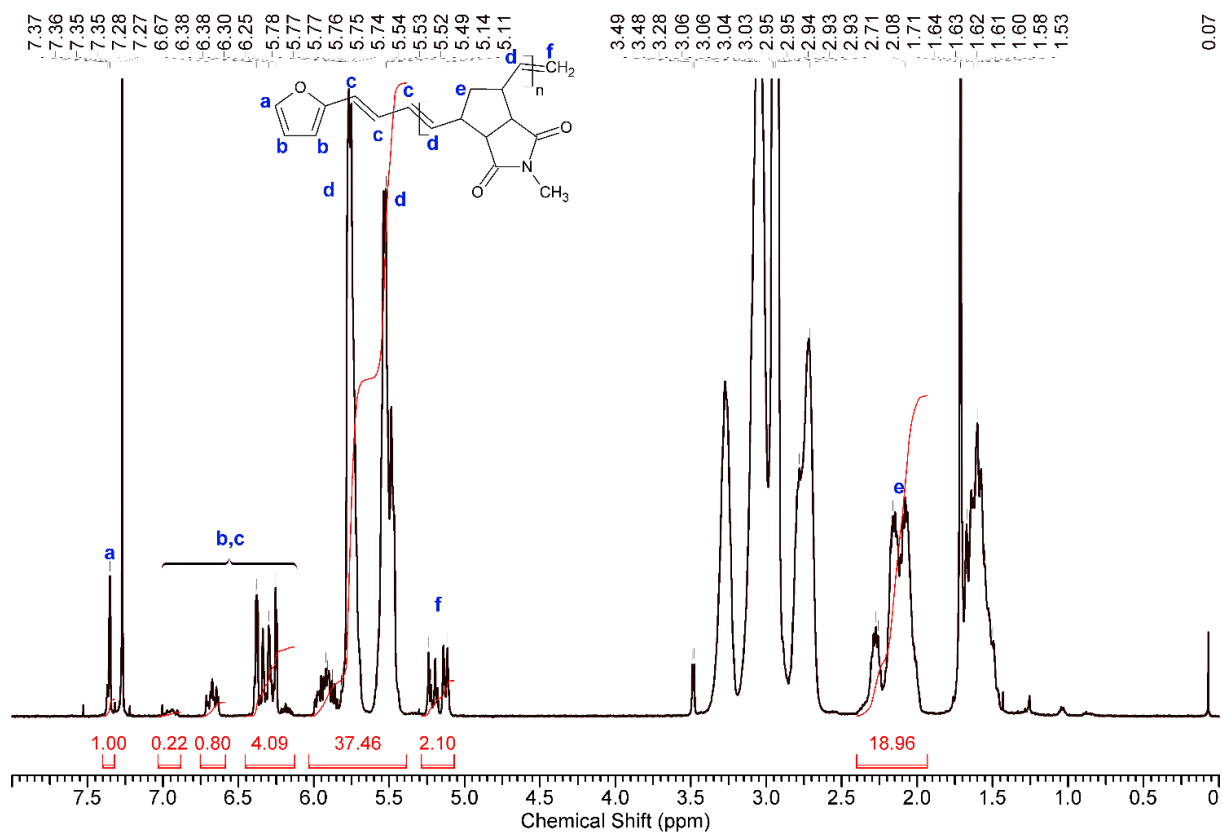


Fig. S132: ^1H NMR (CDCl_3 , 400 MHz) spectrum of P9.

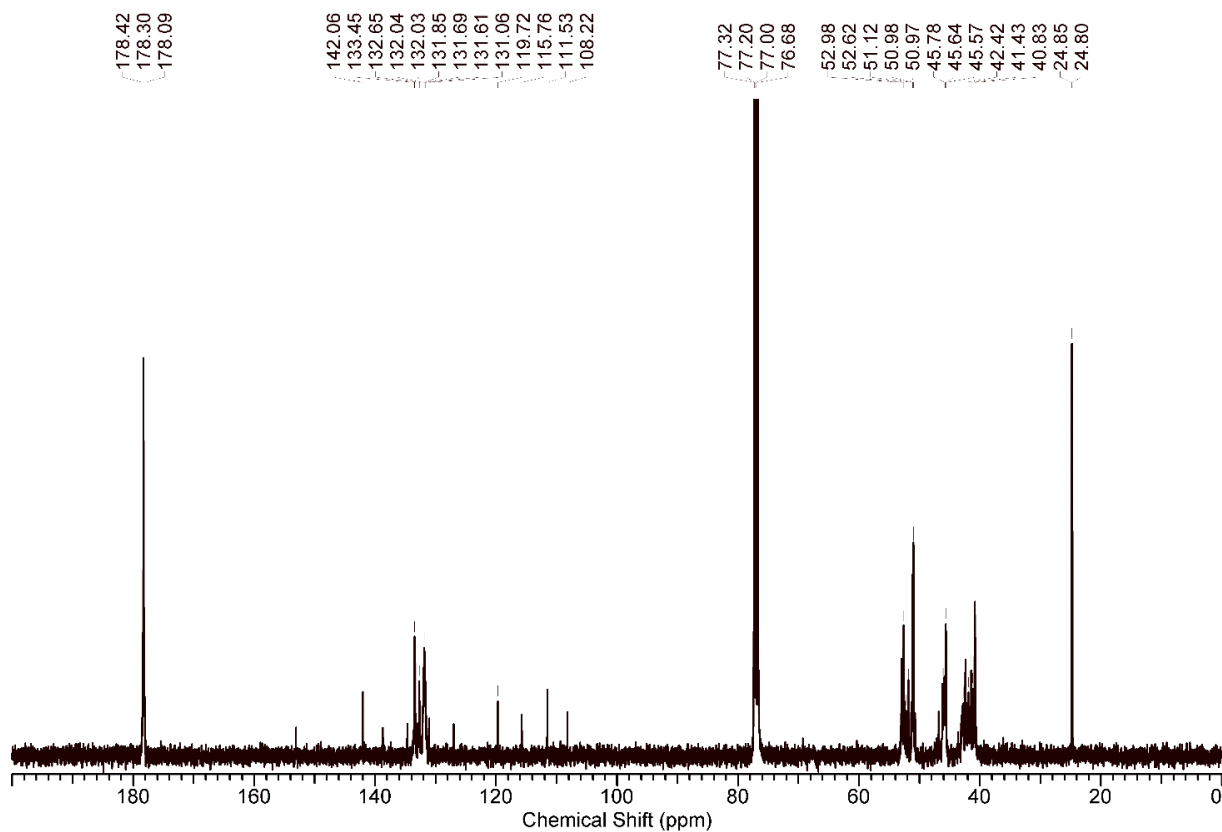


Fig. S133: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of P9.

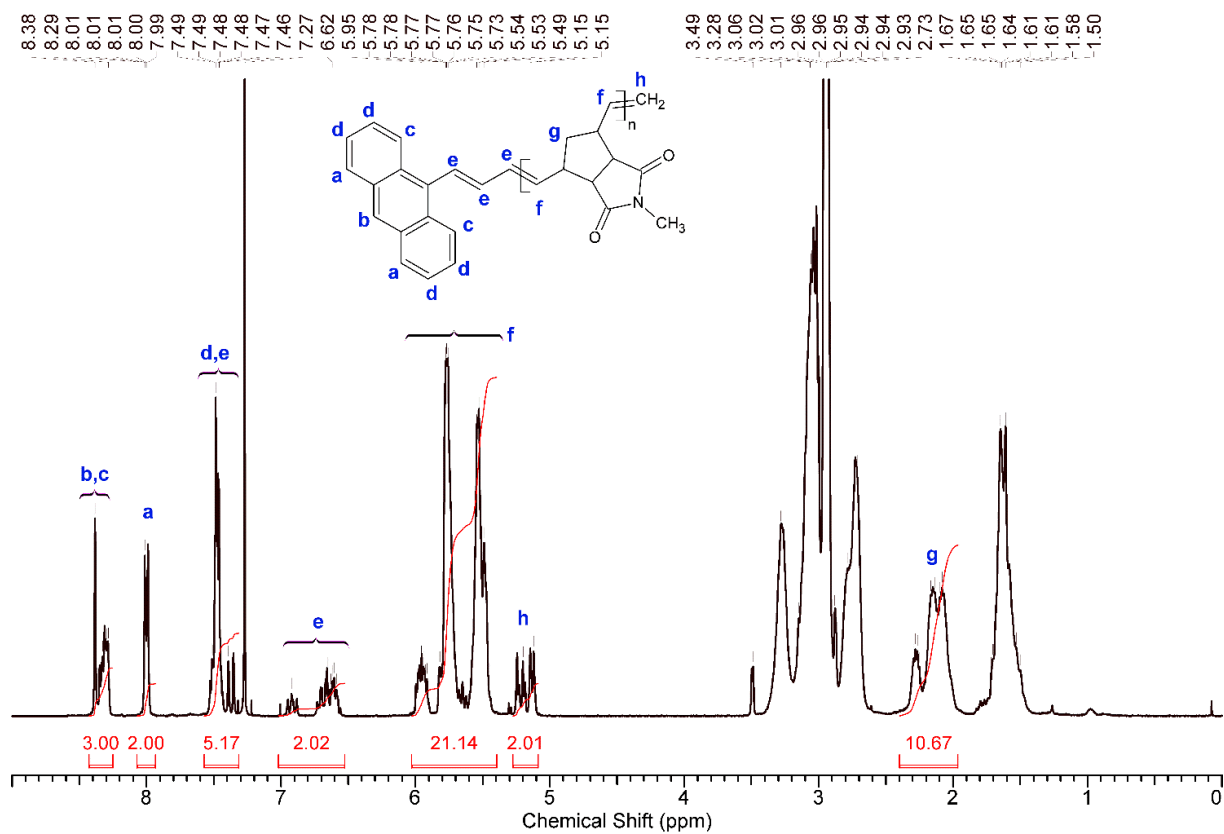


Fig. S134: ¹H NMR (CDCl₃, 400 MHz) spectrum of P10.

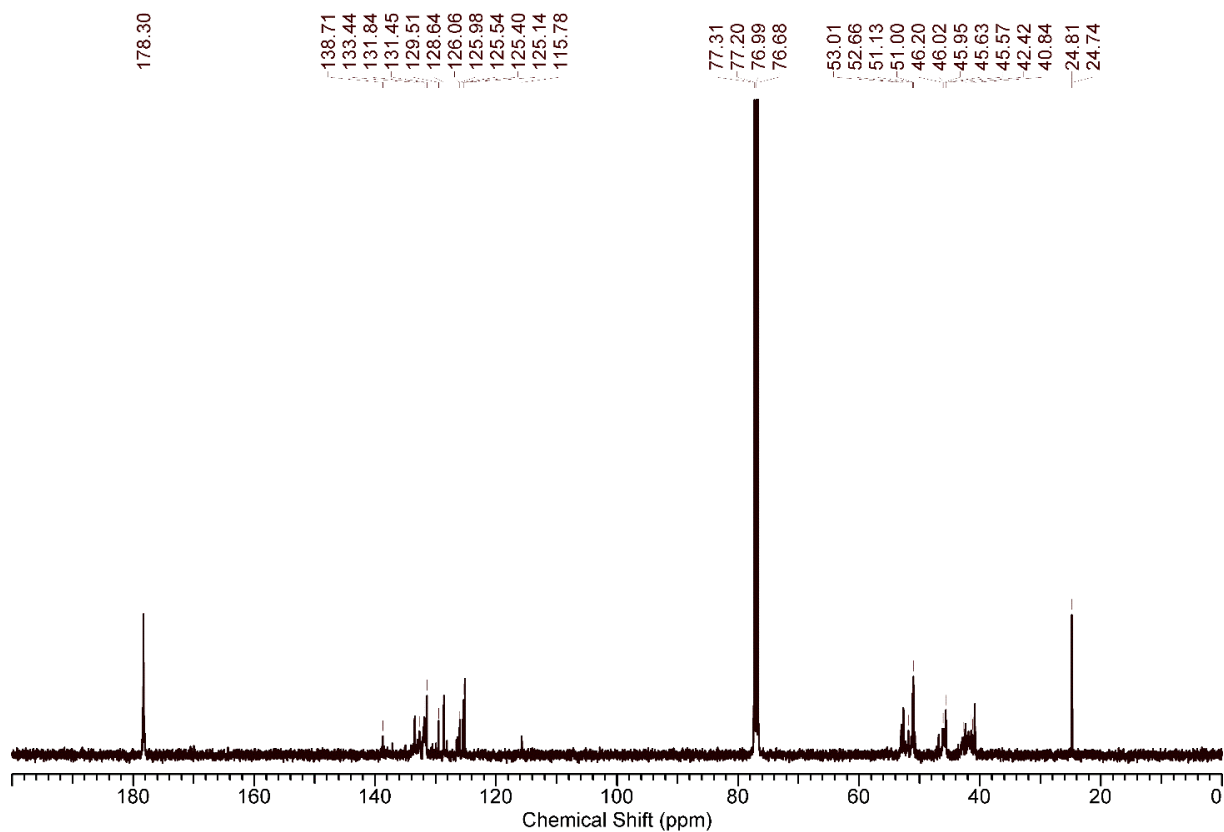


Fig. S135: ¹³C NMR (CDCl₃, 101 MHz) spectrum of P10.

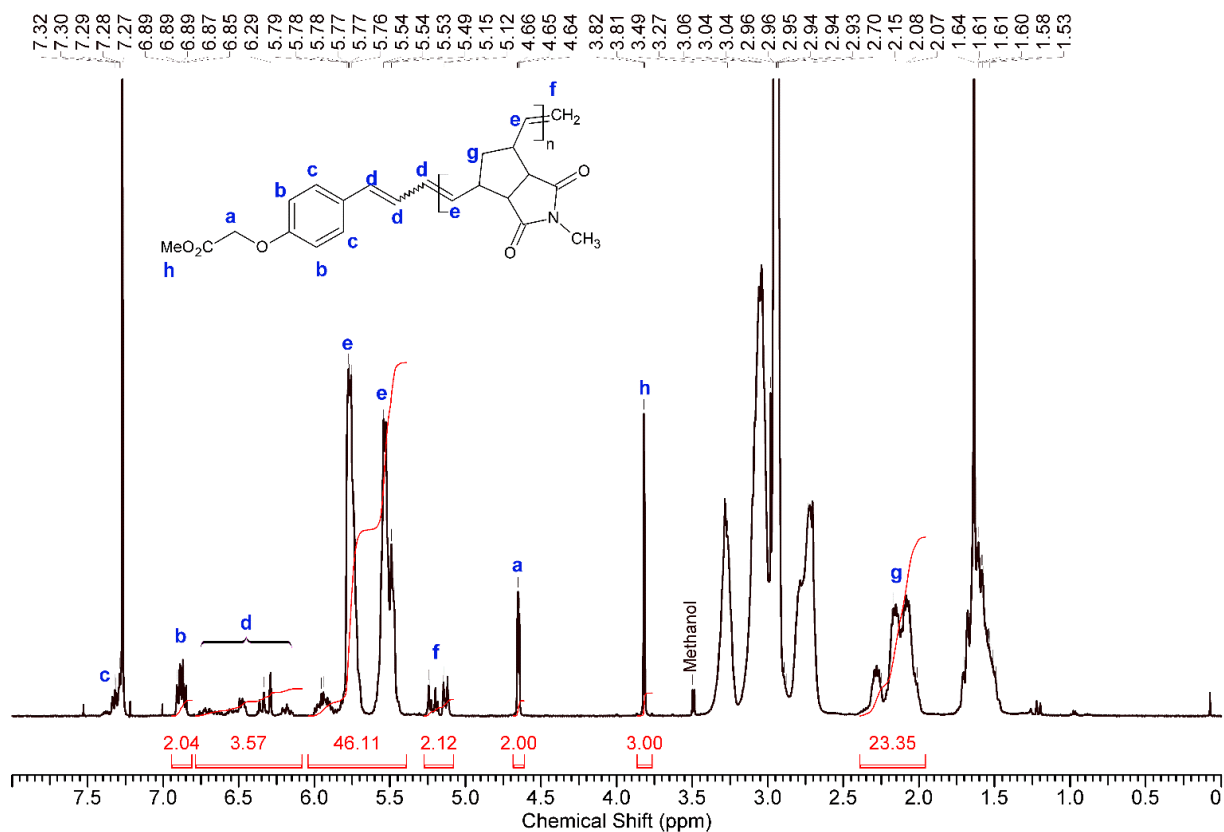


Fig. S136: ^1H NMR (CDCl_3 , 400 MHz) spectrum of **P11**.

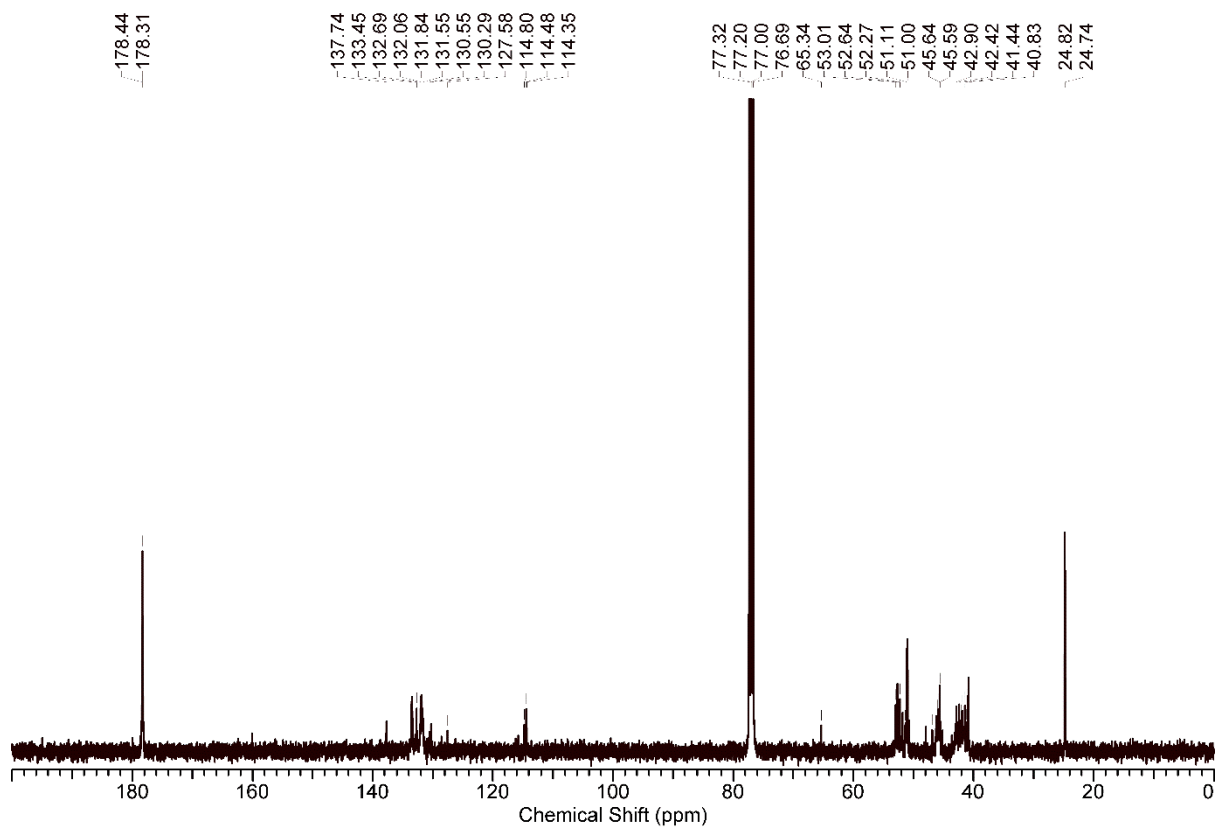


Fig. S137: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **P11**.

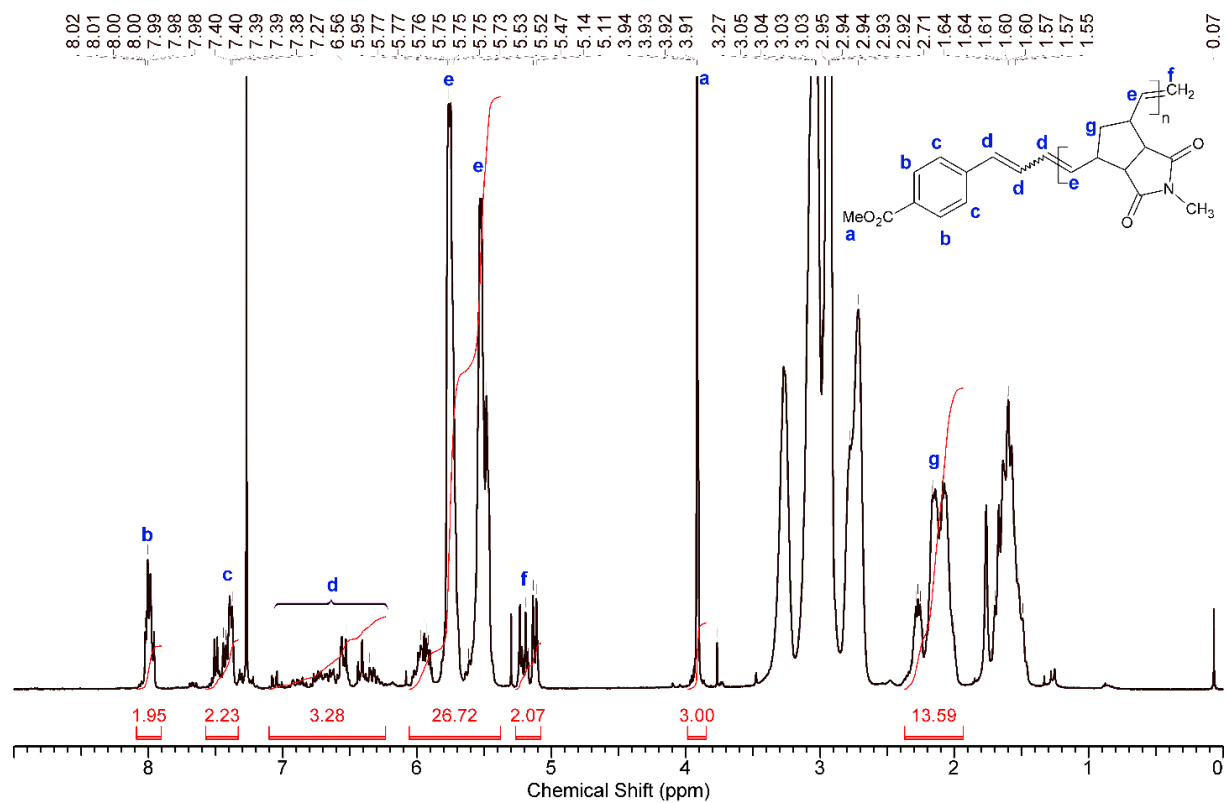


Fig. S138: ^1H NMR (CDCl_3 , 400 MHz) spectrum of **P12**.

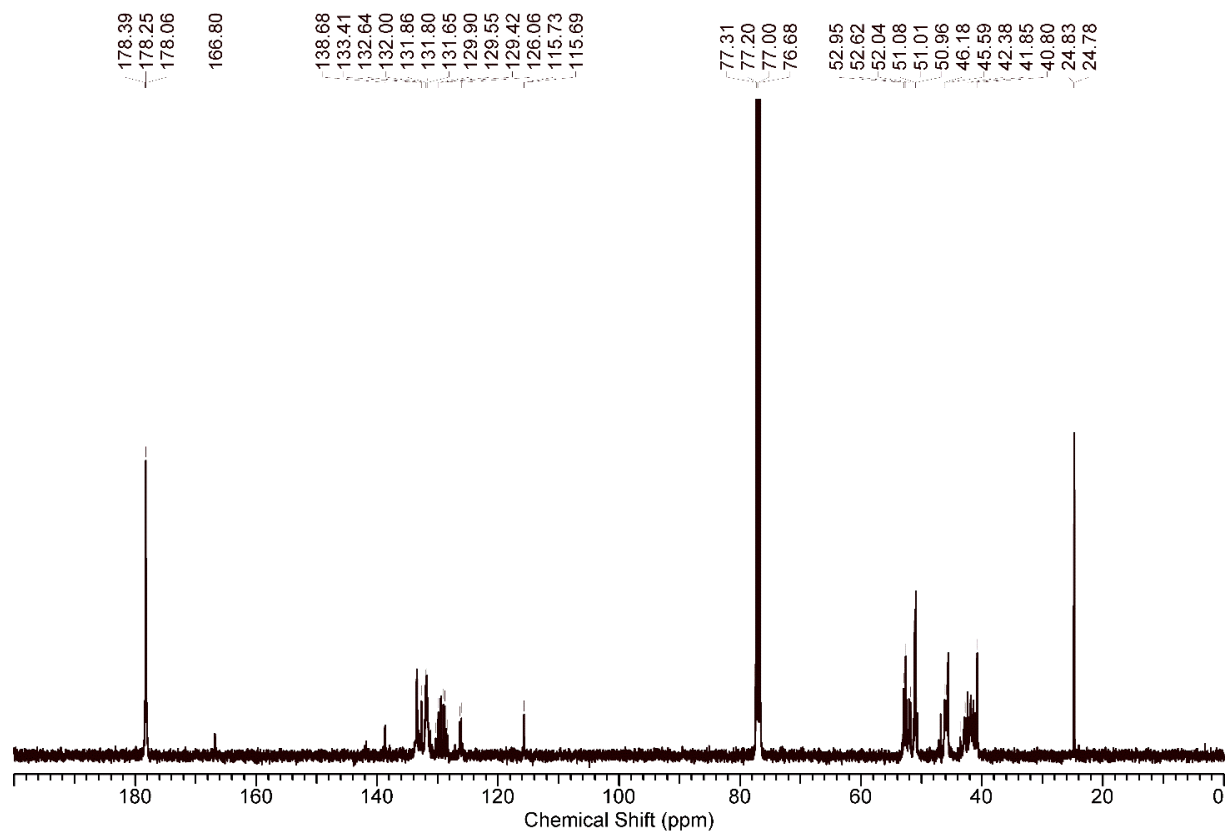


Fig. S139: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **P12**.

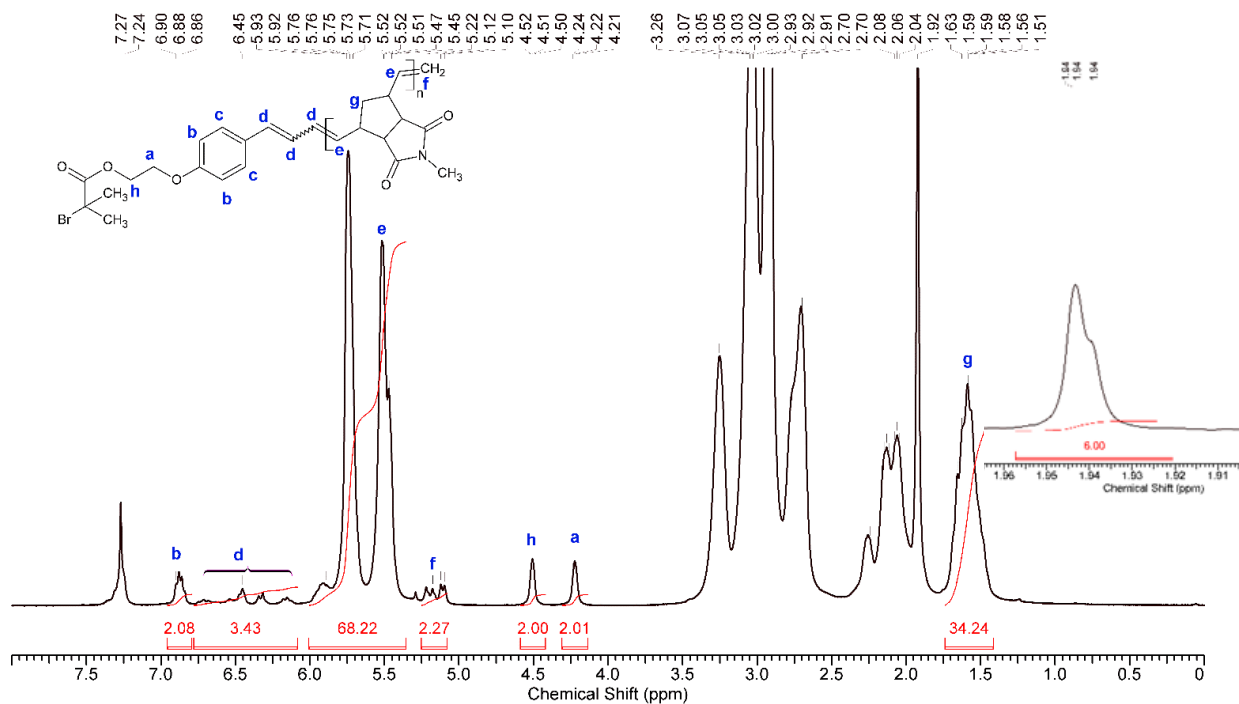


Fig. S140: ¹H NMR (CDCl₃, 400 MHz) spectrum of P13.

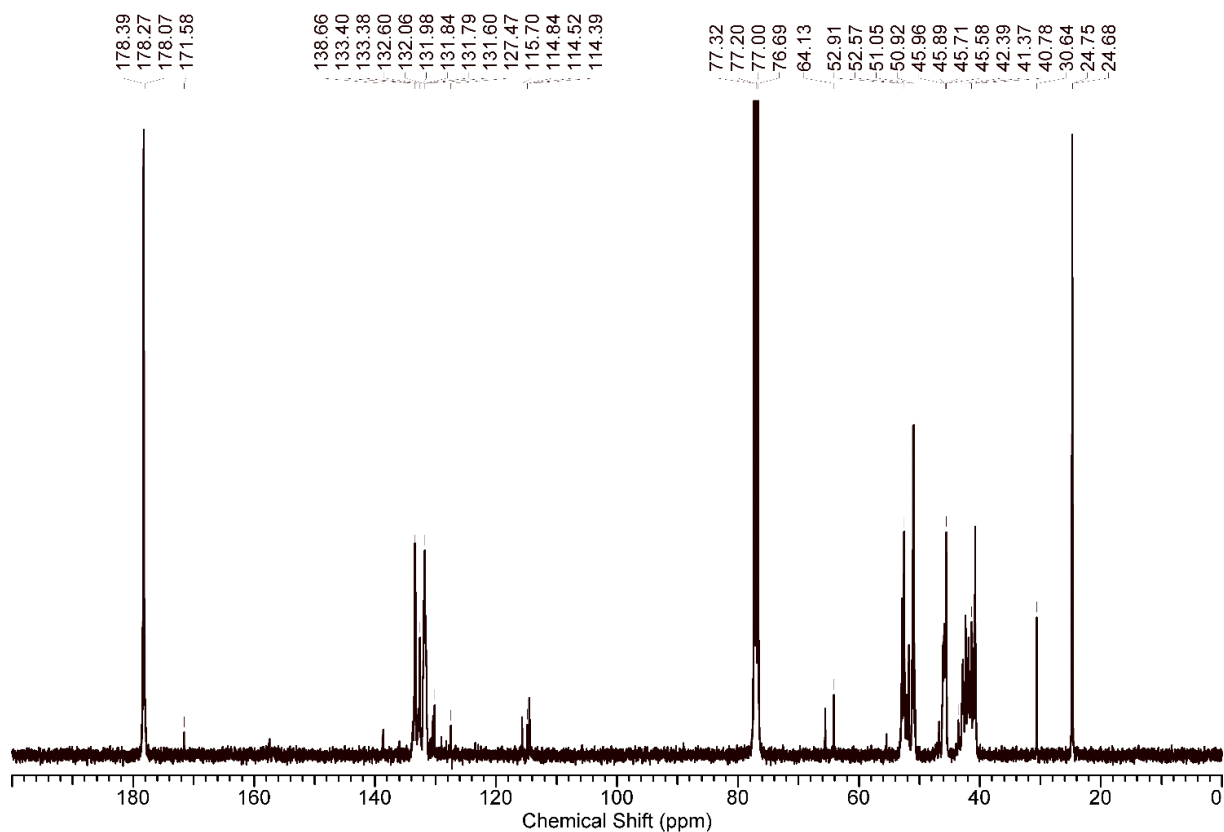


Fig. S141: ¹³C NMR (CDCl₃, 101 MHz) spectrum of P13.

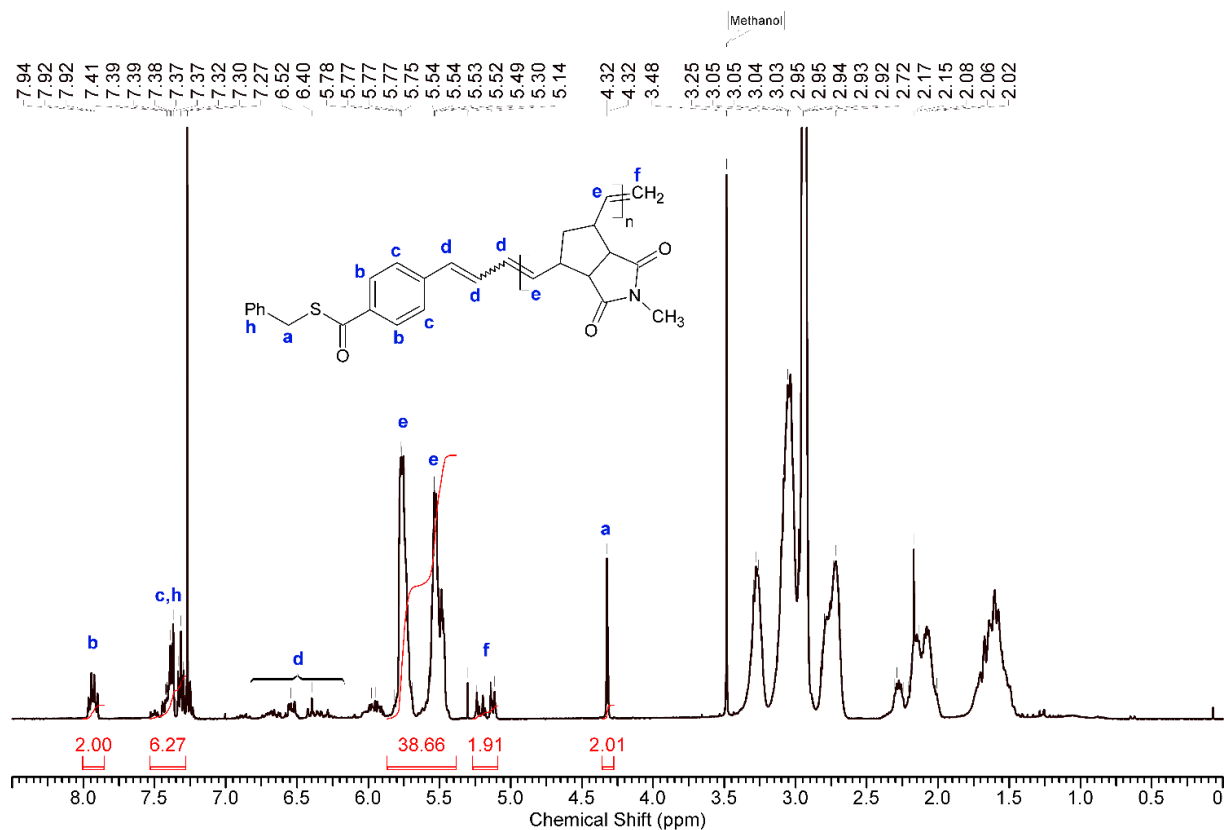


Fig. S142: ^1H NMR (CDCl_3 , 400 MHz) spectrum of **P14**.

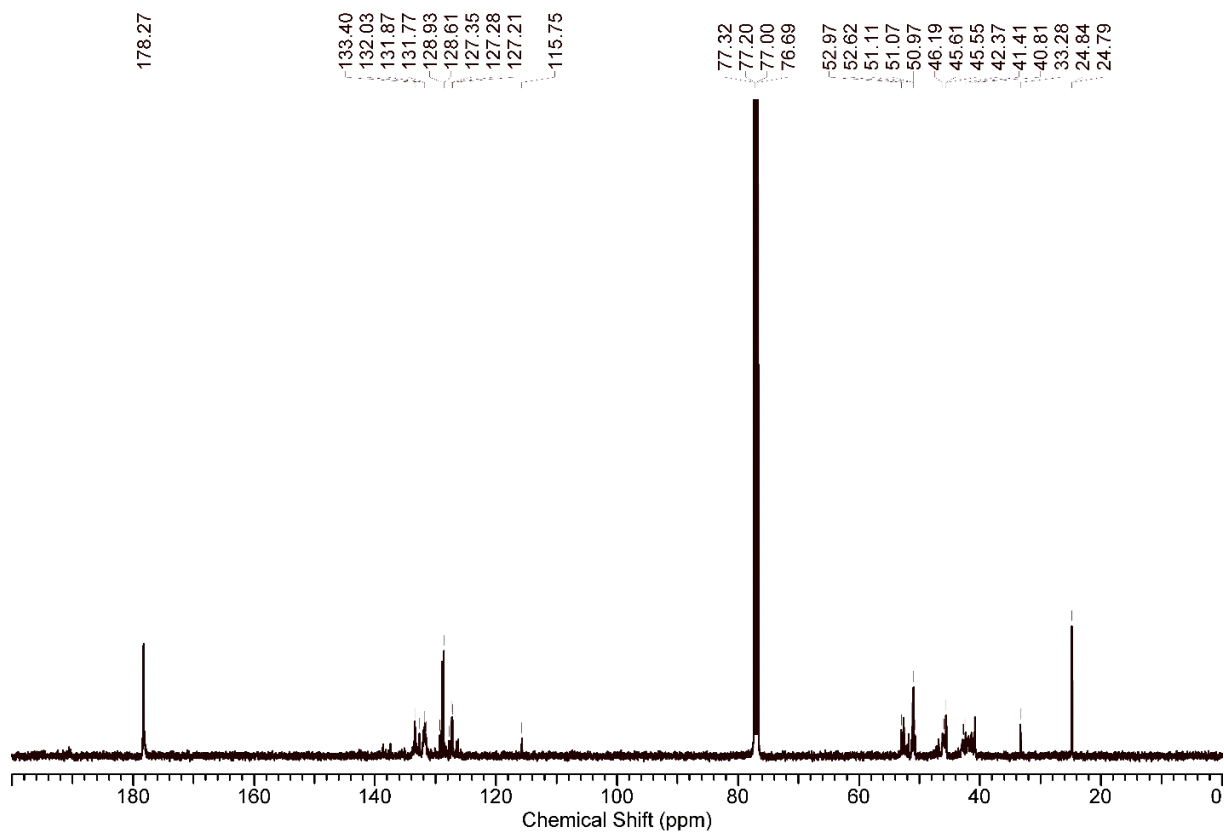


Fig. S143: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **P14**.

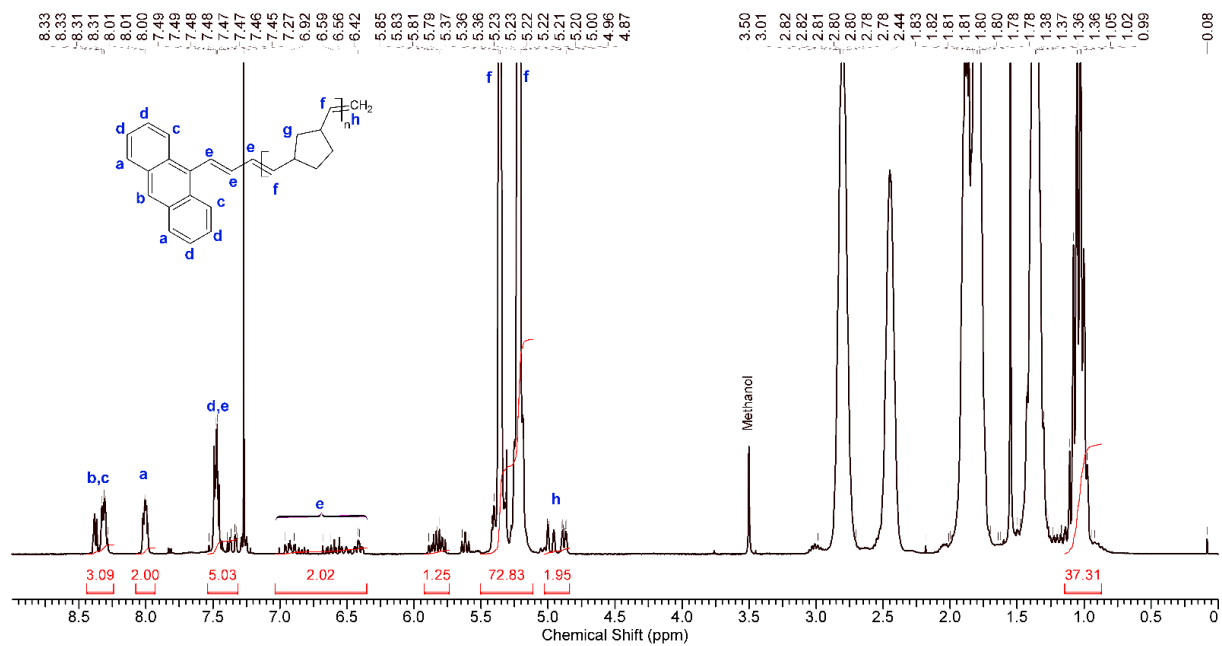


Fig. S146: ¹H NMR (CDCl₃, 400 MHz) spectrum of P16.

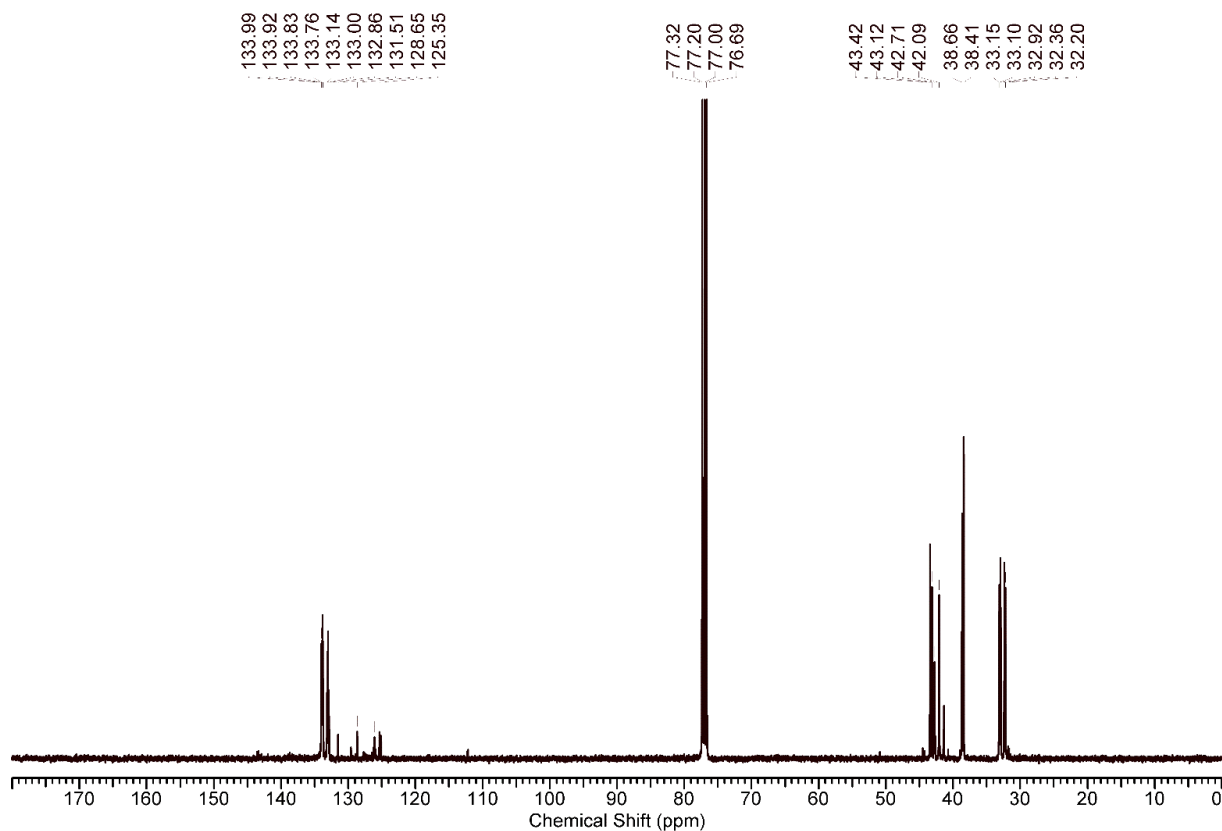


Fig. S147: ¹³C NMR (CDCl₃, 101 MHz) spectrum of P16.

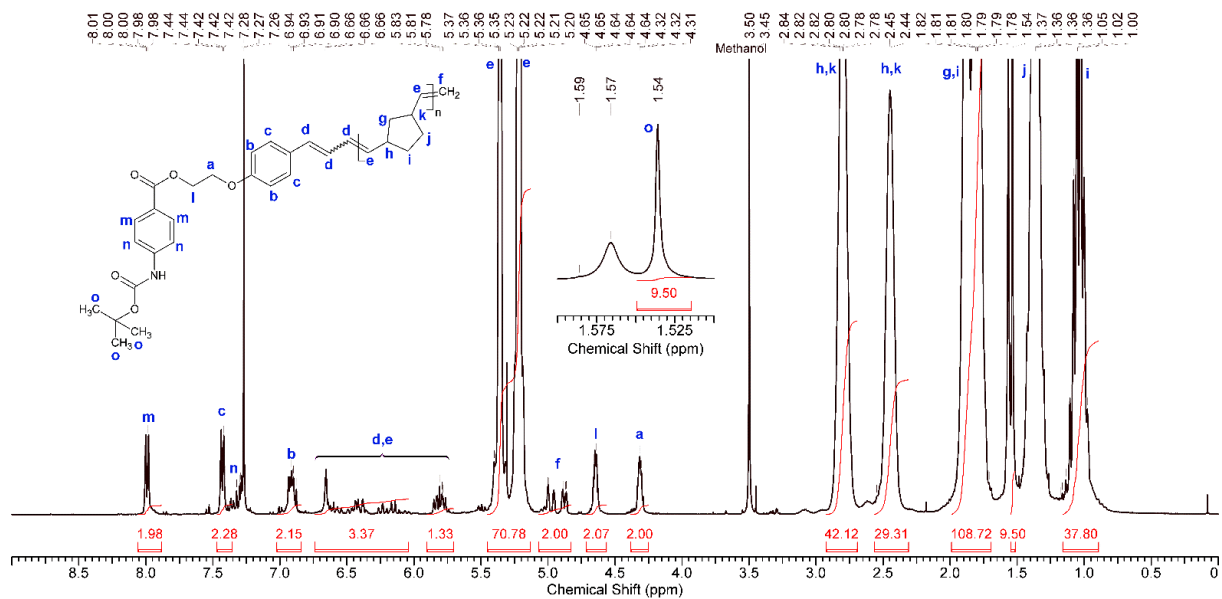


Fig. S148: ^1H NMR (CDCl_3 , 400 MHz) spectrum of P17.

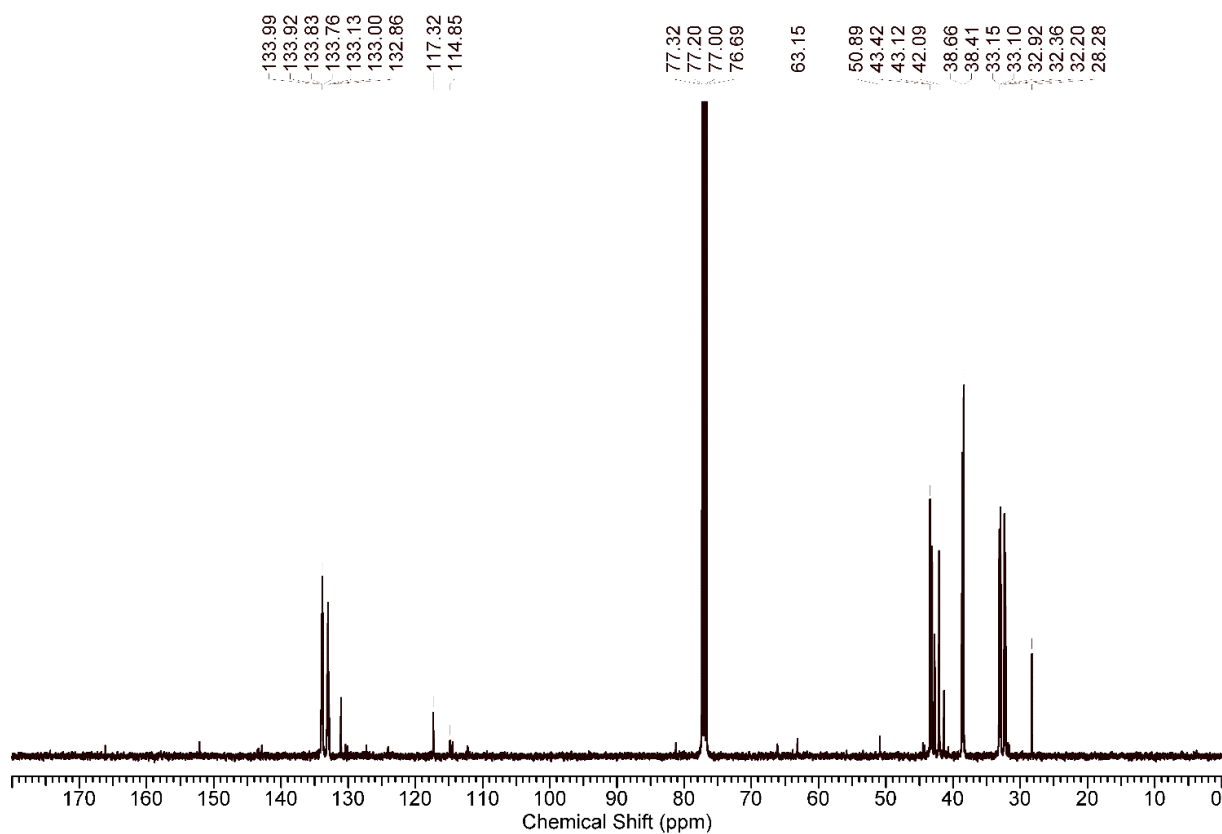


Fig. S149: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of P17.

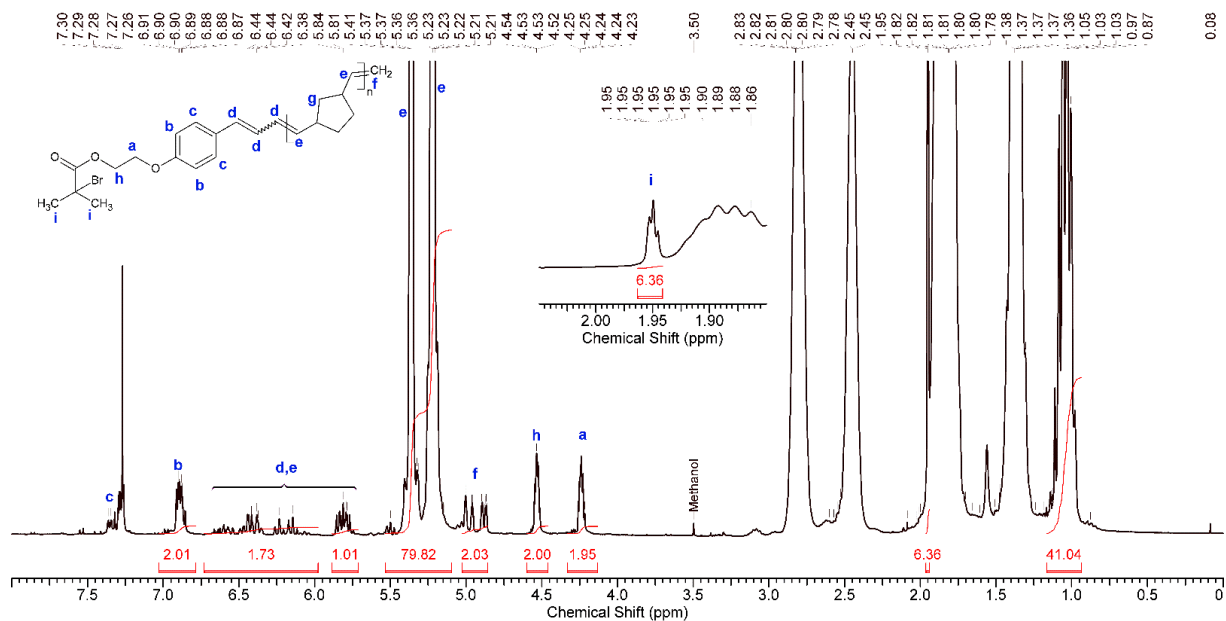


Fig. S150: ^1H NMR (CDCl_3 , 400 MHz) spectrum of **P18**.

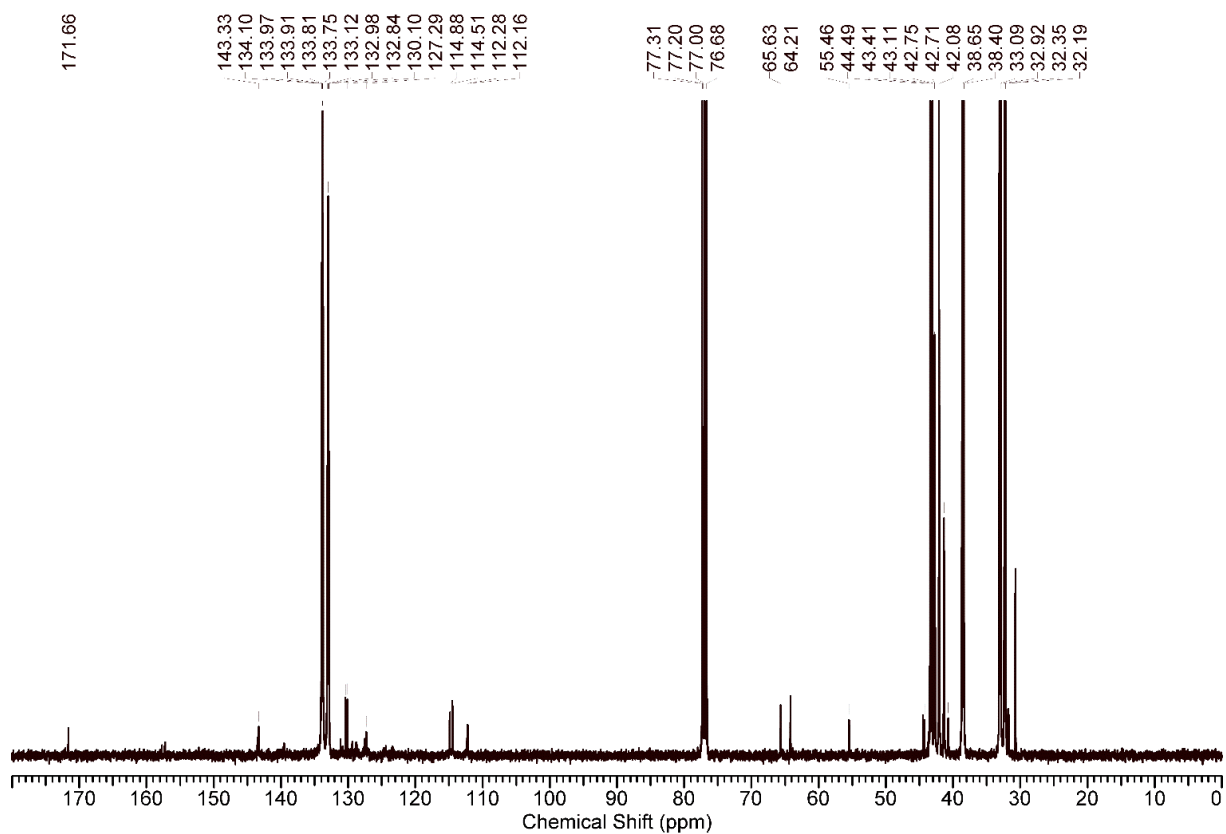


Fig. S151: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **P18**.

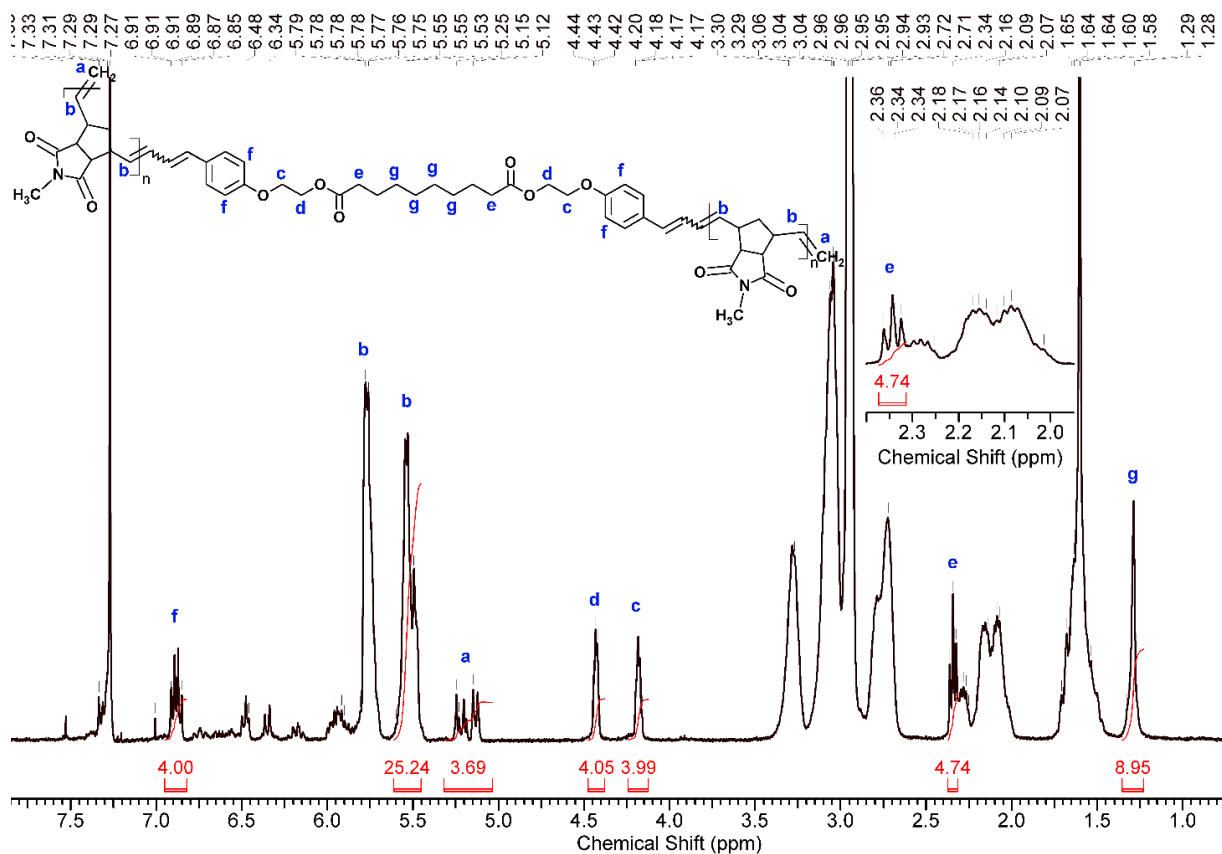


Fig. S152: ^1H NMR (CDCl_3 , 400 MHz) spectrum of P20.

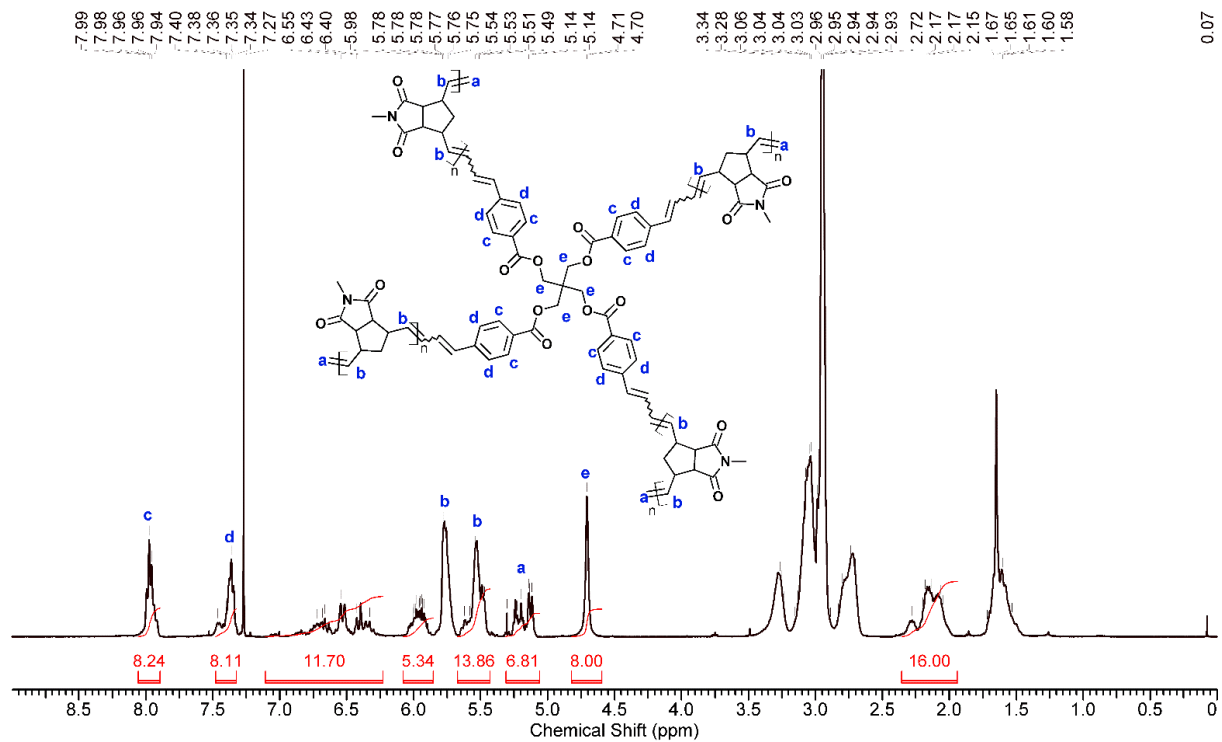


Fig. S153: ^1H NMR (CDCl_3 , 400 MHz) spectrum of P22.

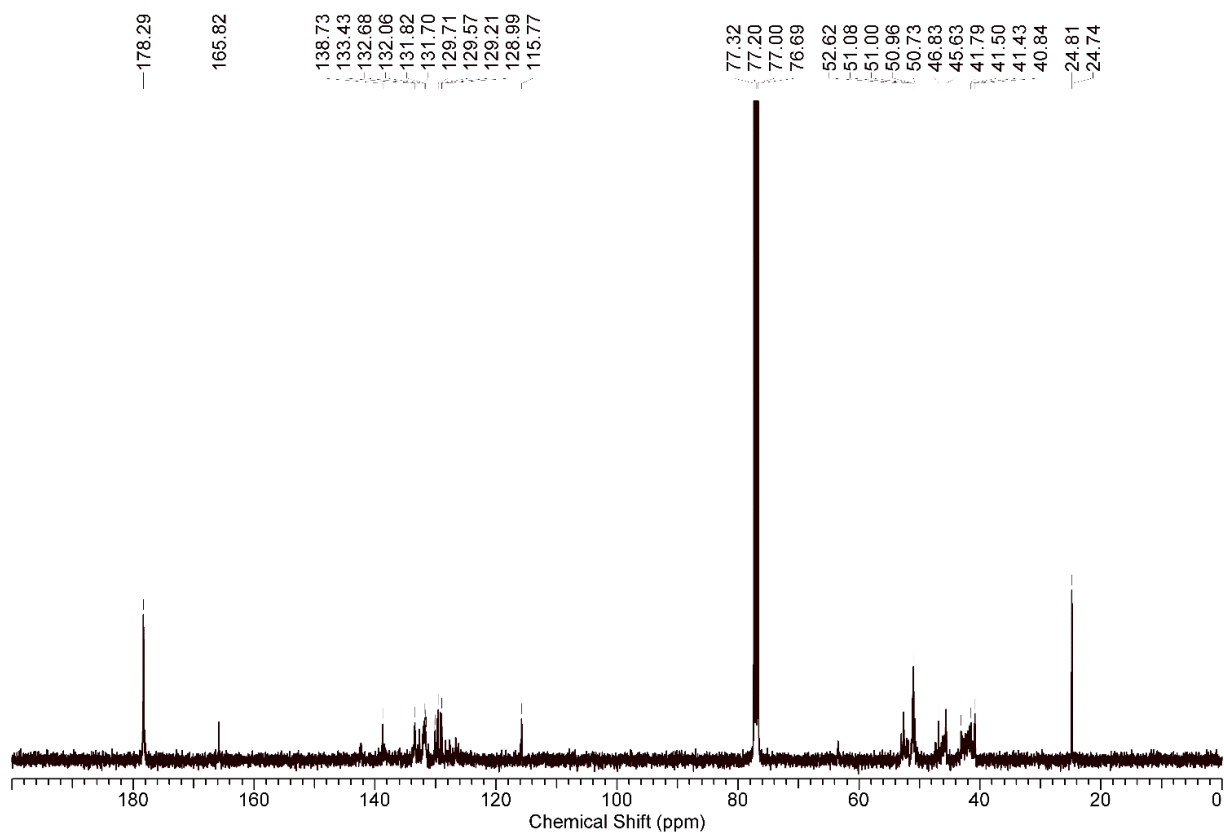


Fig. S154: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of **P22**.

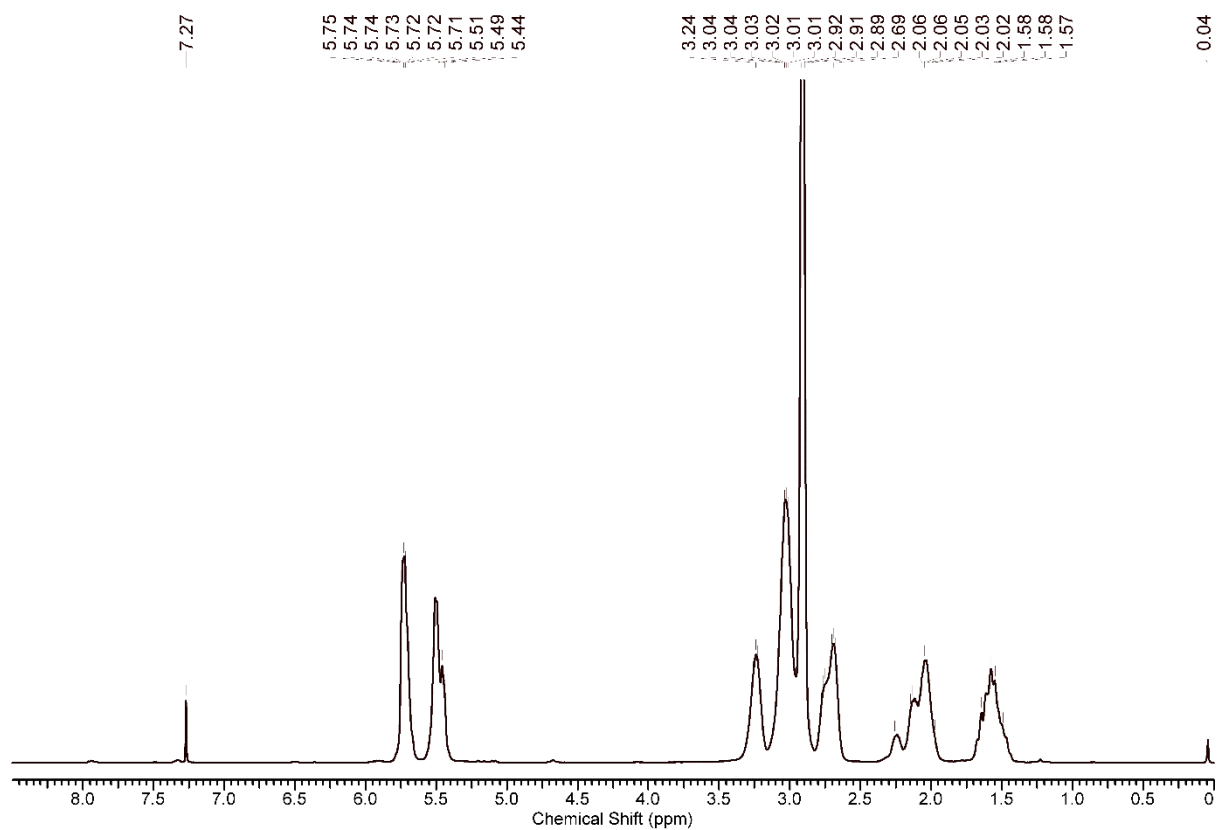


Fig. S155: ^1H NMR (CDCl_3 , 400 MHz) spectrum of **P22**.

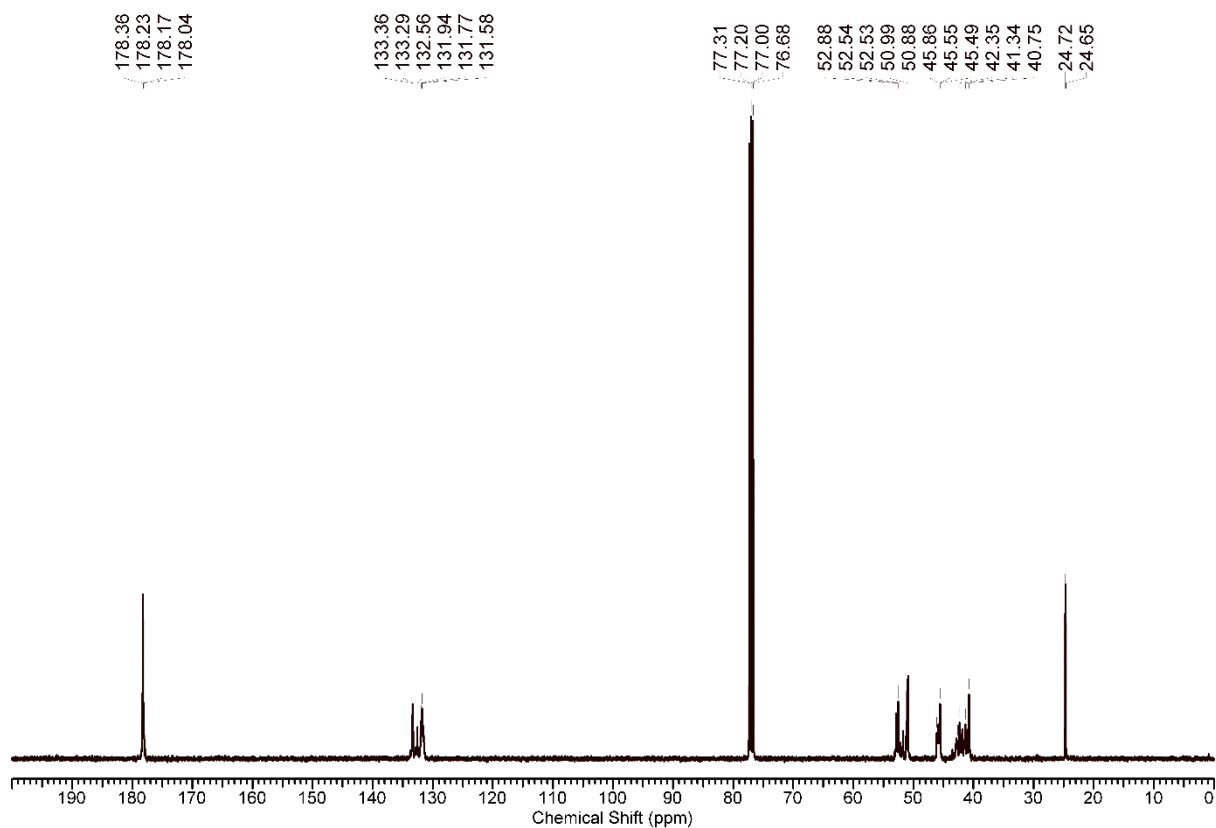


Fig. S156: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of P23.

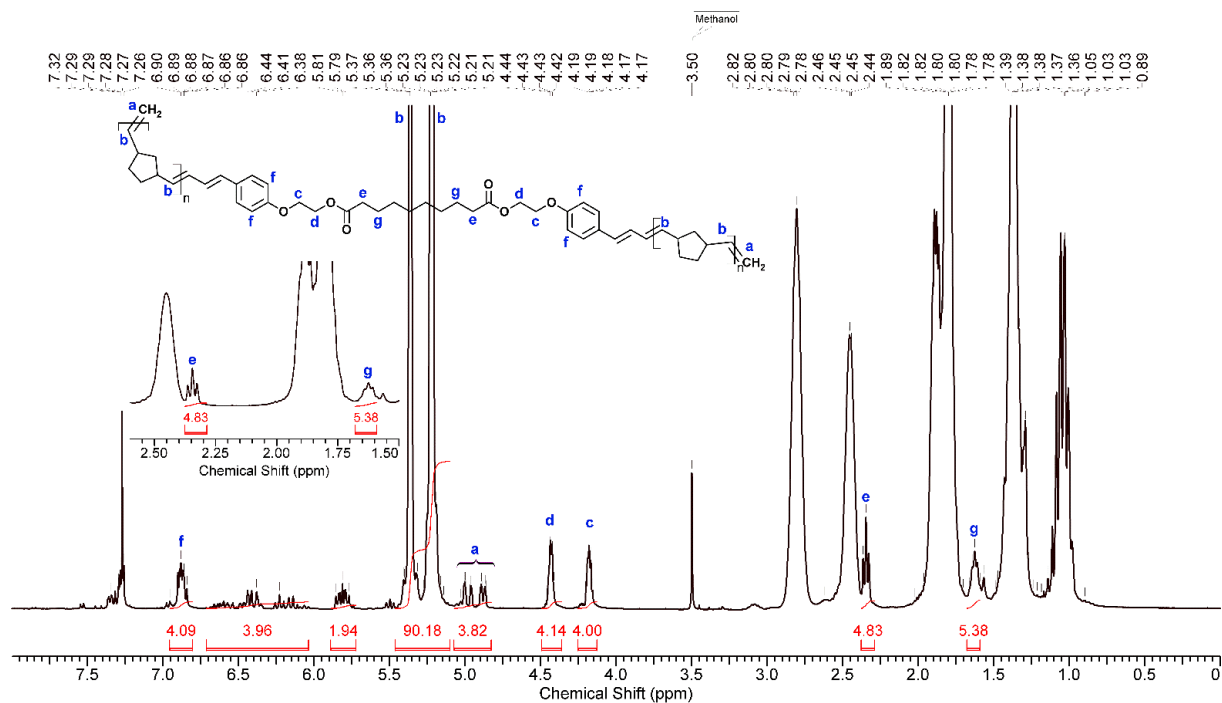


Fig. S157: ^1H NMR (CDCl_3 , 400 MHz) spectrum of P24.

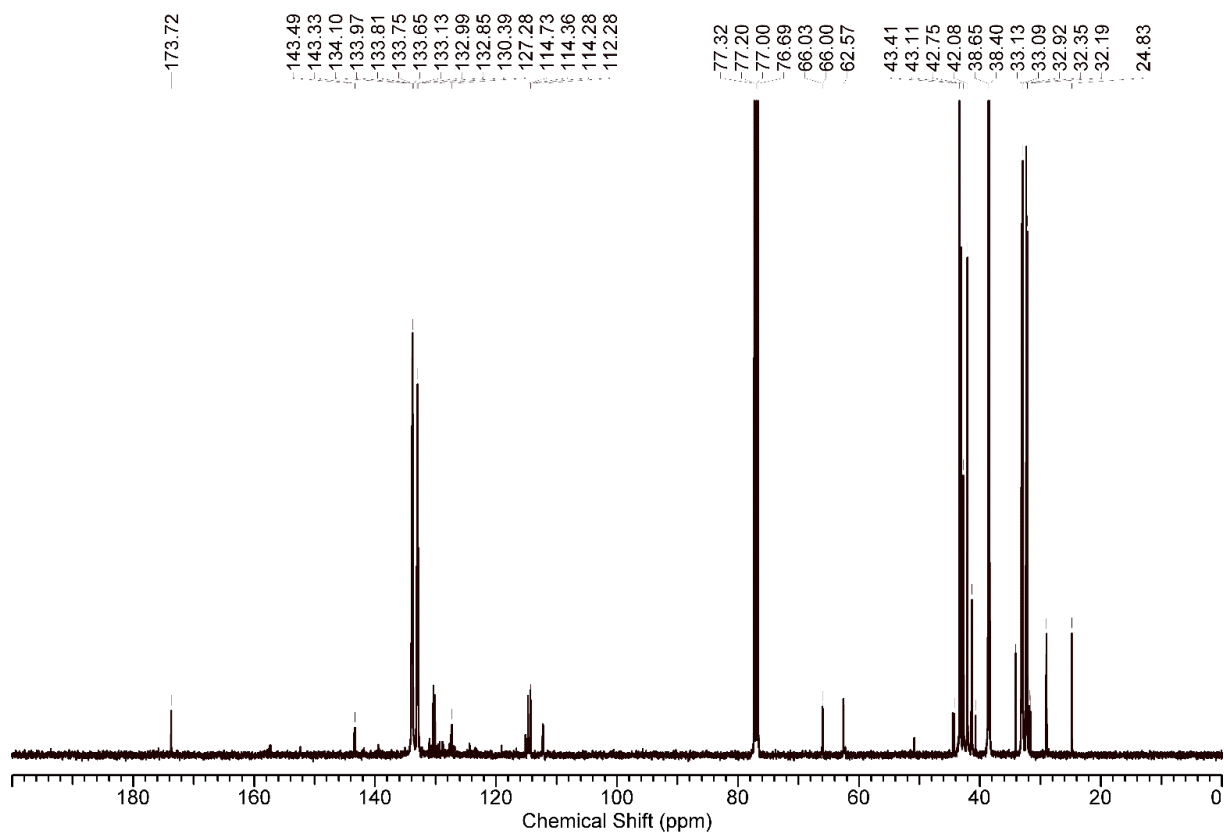


Fig. S158: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of P24.

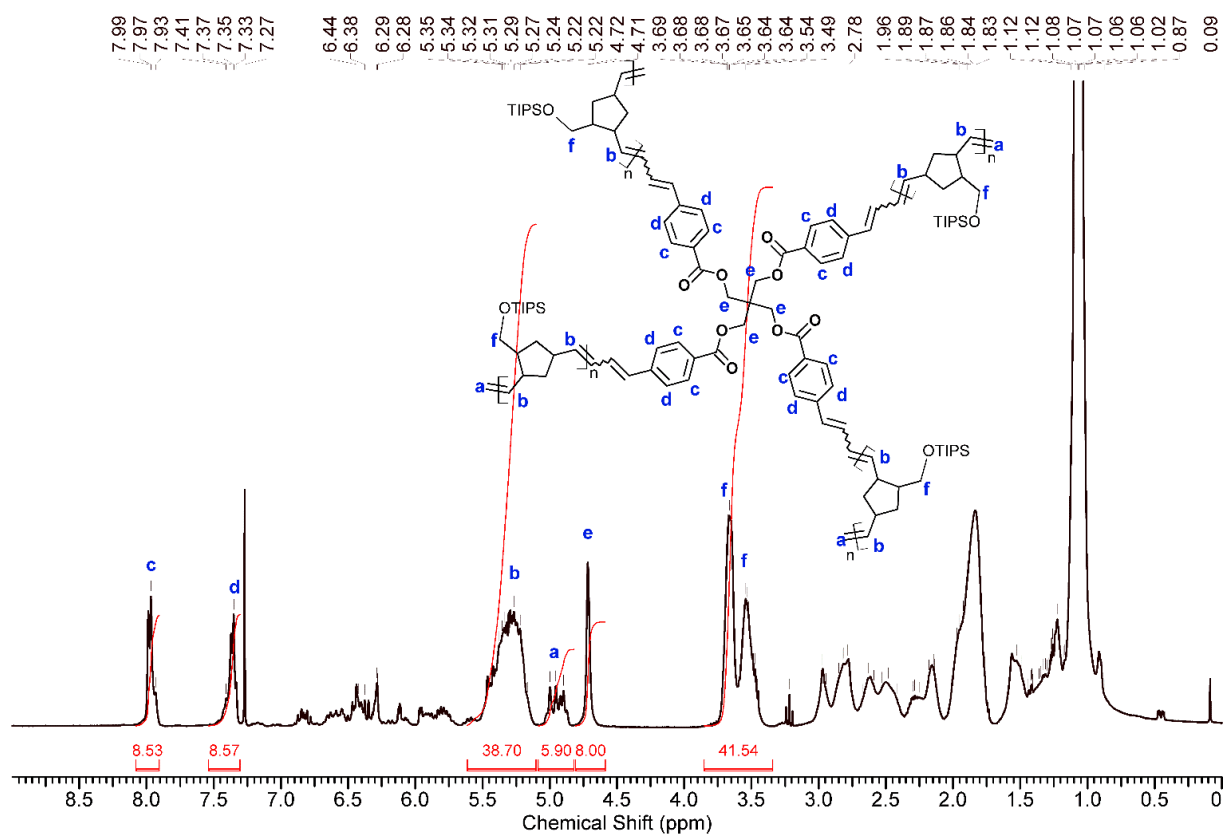


Fig. S159: ^1H NMR (CDCl_3 , 400 MHz) spectrum of P25.

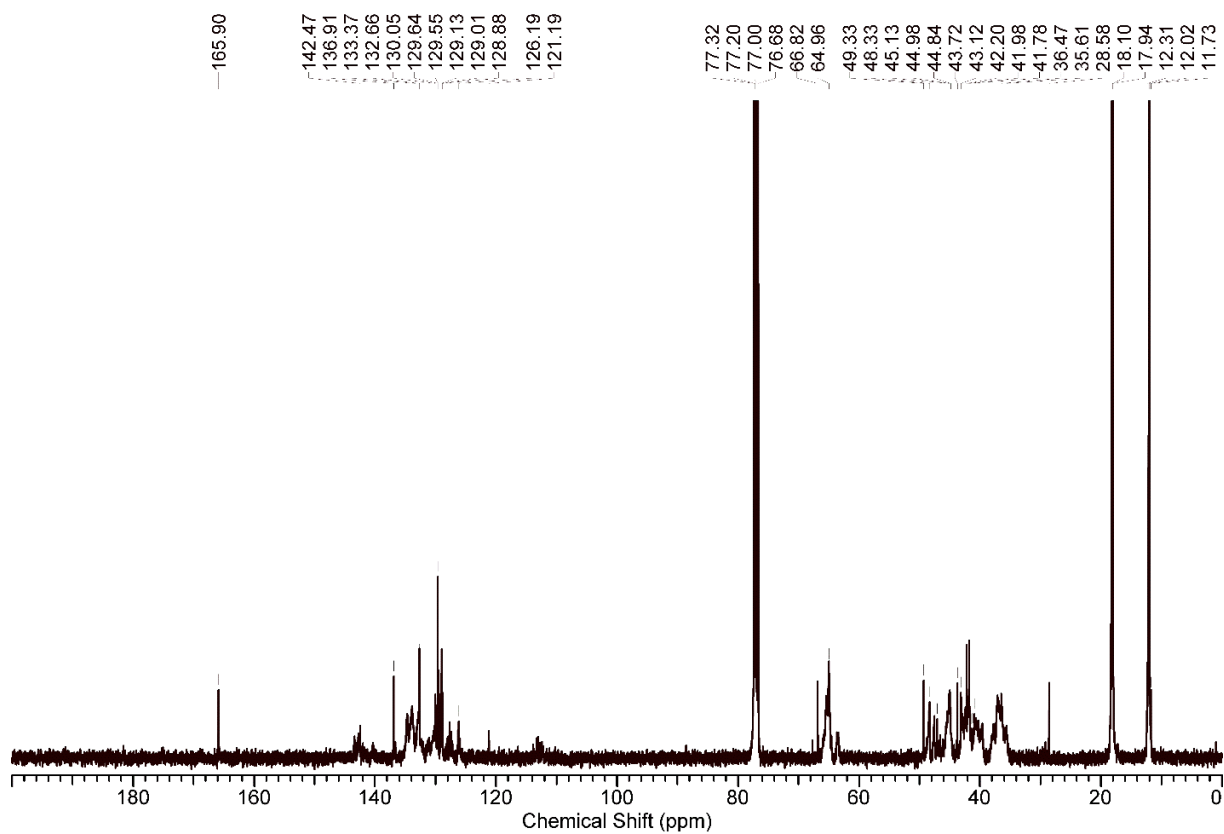


Fig. S160: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of P25.

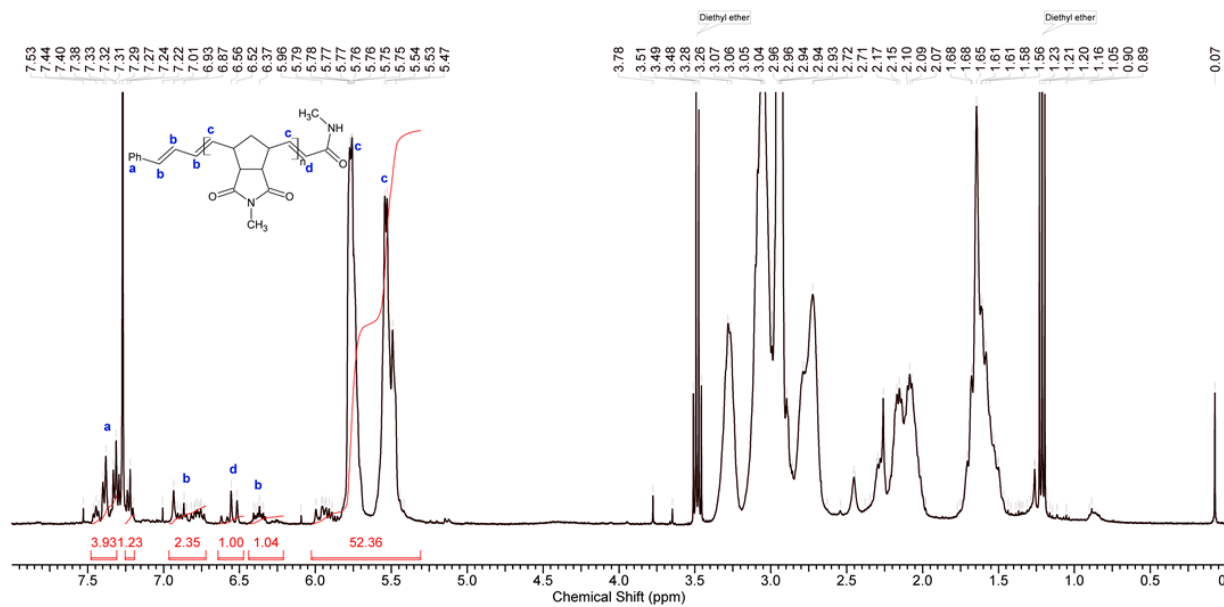


Fig. S161: ^1H NMR (CDCl_3 , 400 MHz) spectrum of P37.

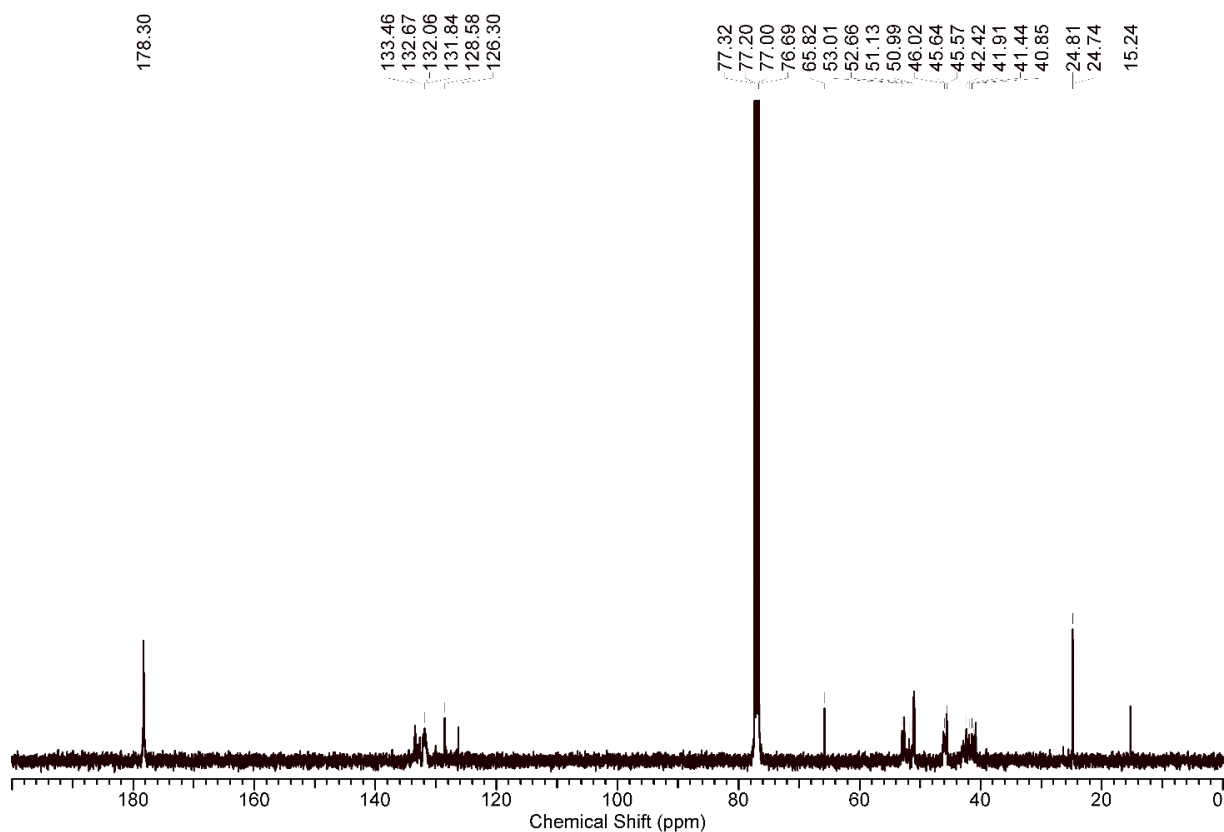


Fig. S162: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of P37.

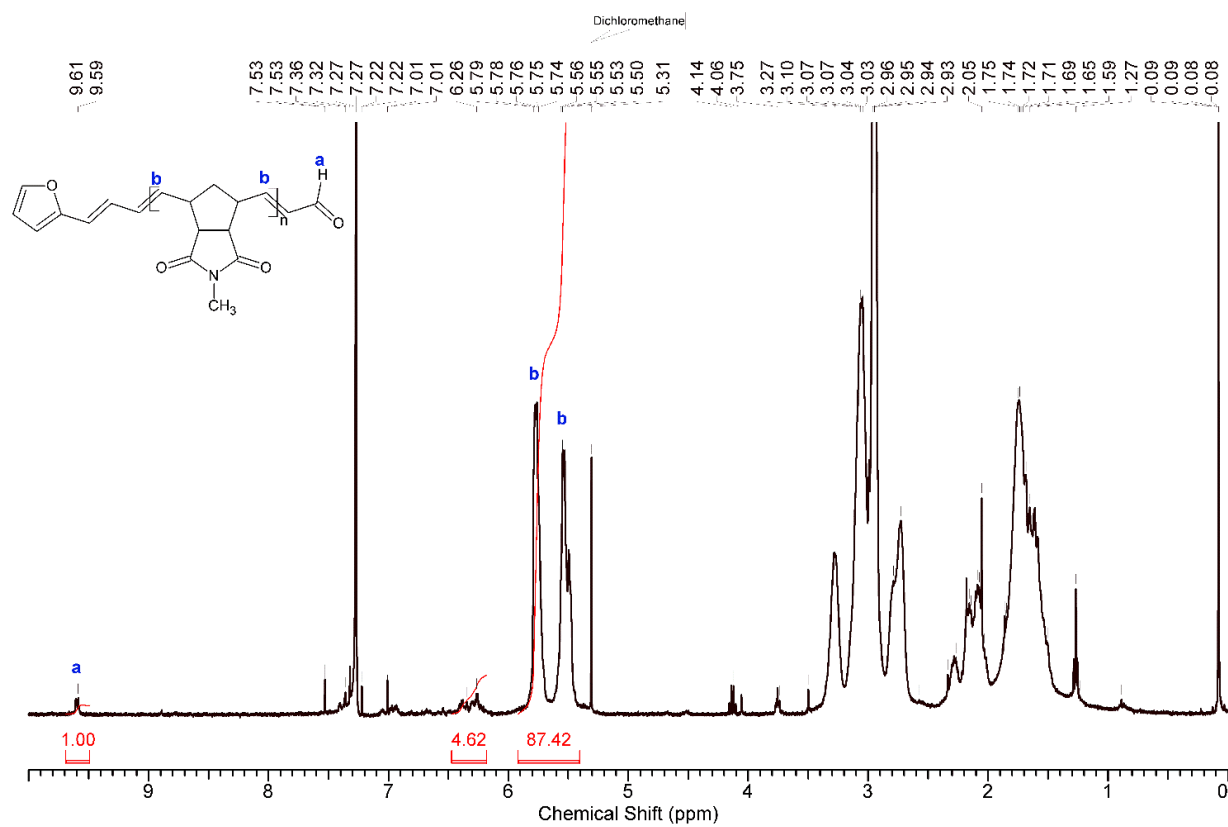
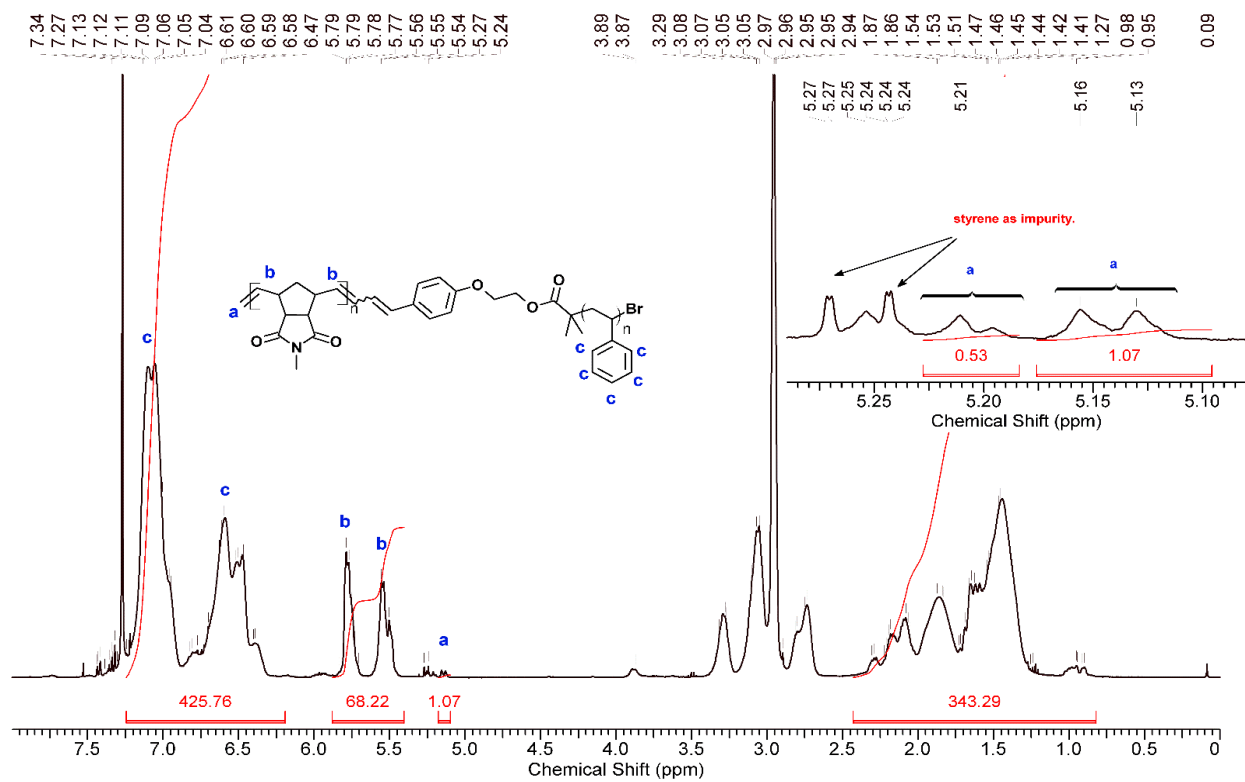
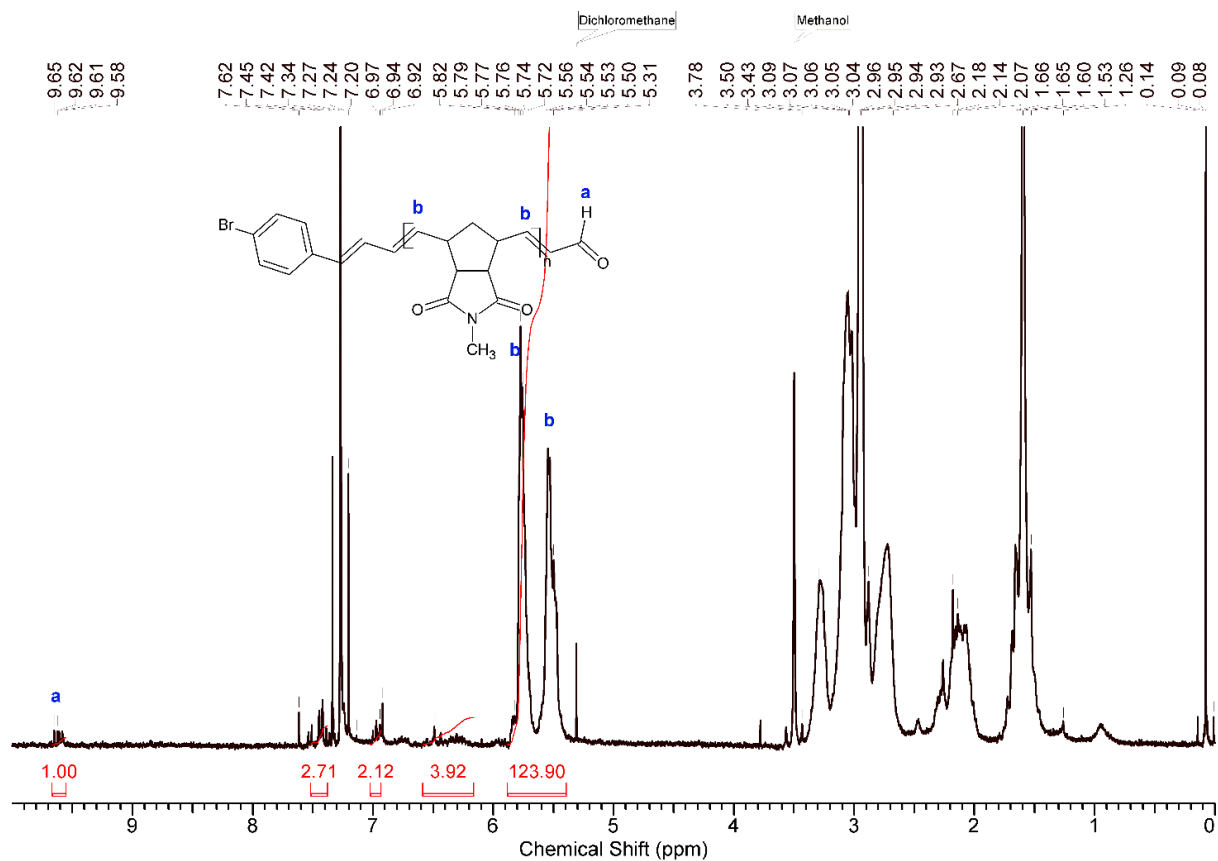


Fig. S163: ^1H NMR (CDCl_3 , 400 MHz) spectrum of P38.



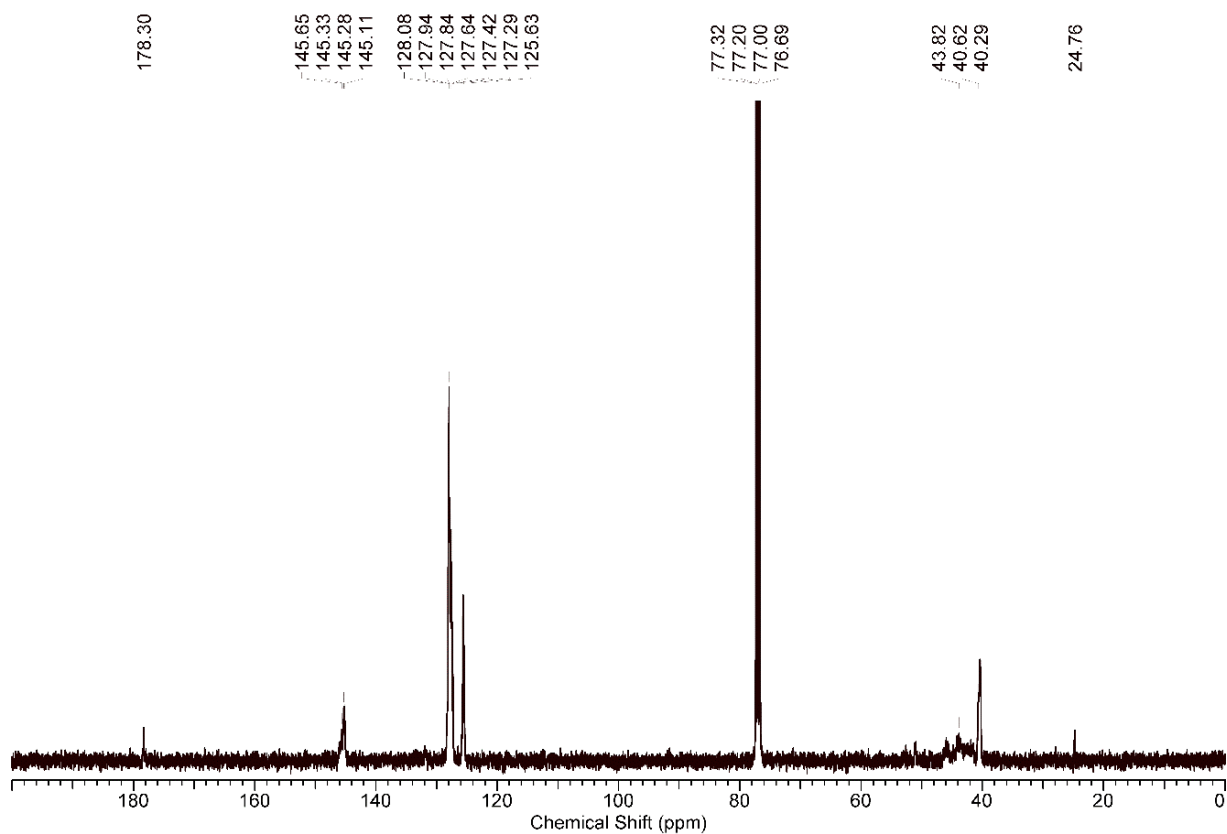


Fig. S166: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of P13-b-PS.

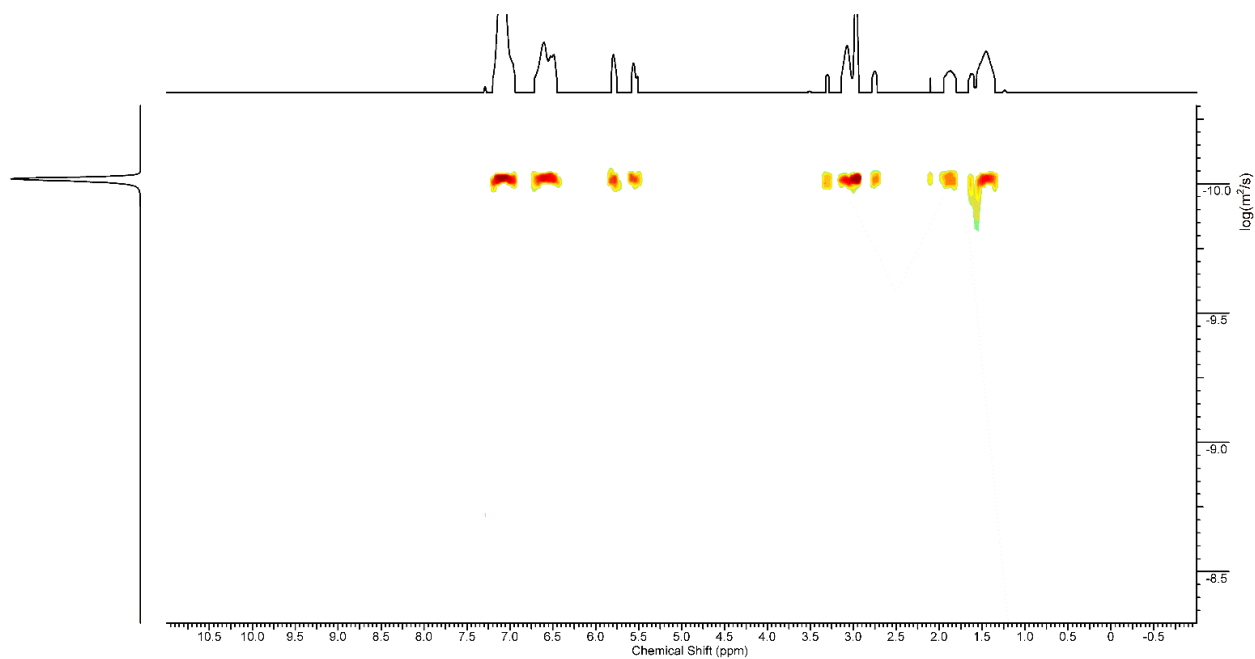


Fig. S167: DOSY ^1H NMR (CDCl_3 , 400 MHz) spectrum of P13-b-PS.

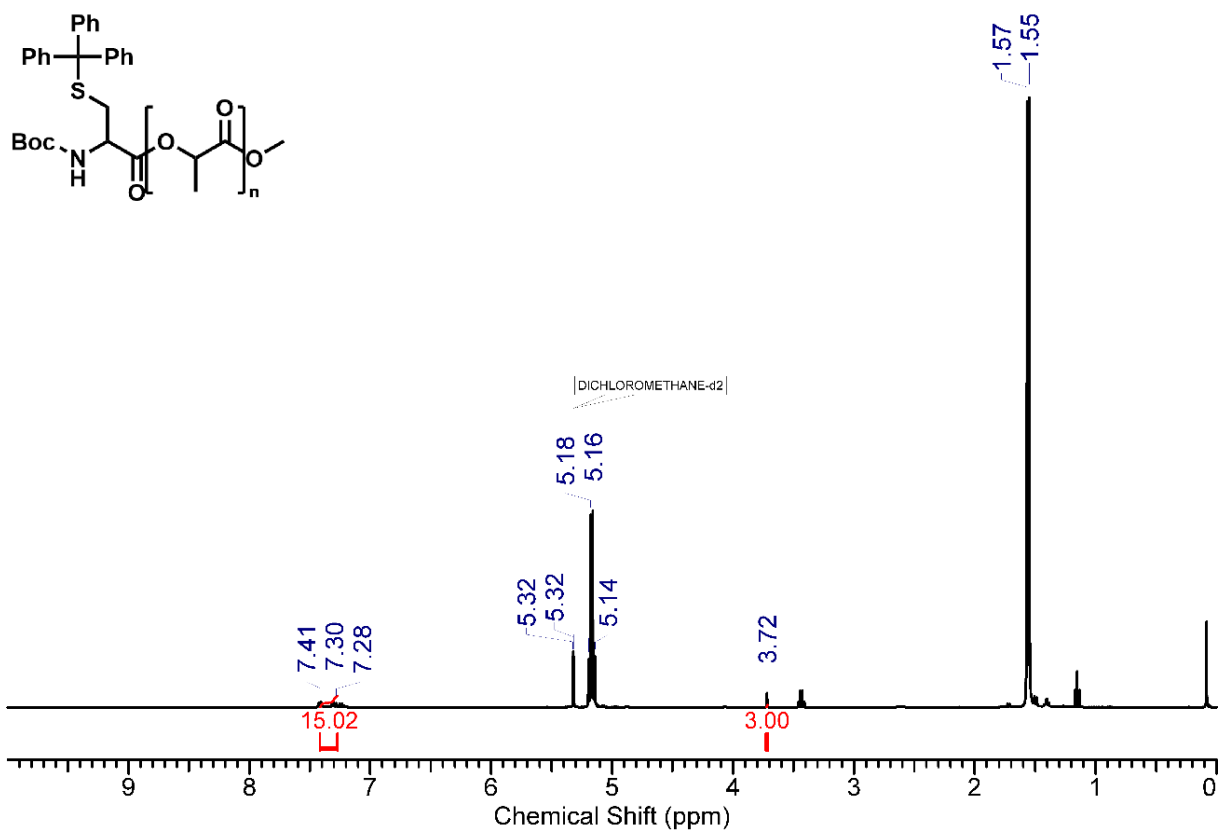


Fig. S168: ^1H NMR (CD_2Cl_2 , 400 MHz) spectrum of $\text{PLA}_{20k}\text{-Boc-Cys(Trt)-OH}$.

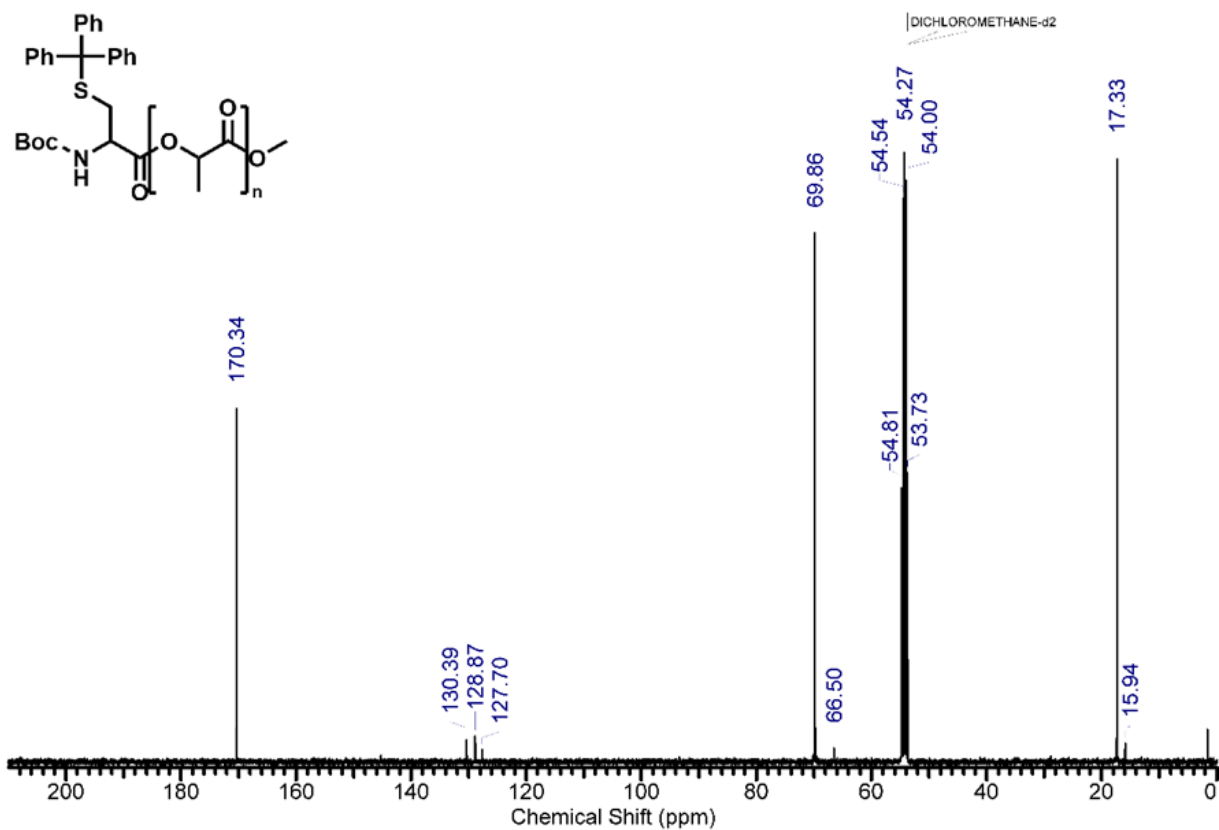


Fig. S169: ^{13}C NMR (CD_2Cl_2 , 101 MHz) spectrum of $\text{PLA}_{20k}\text{-Boc-Cys(Trt)-OH}$.

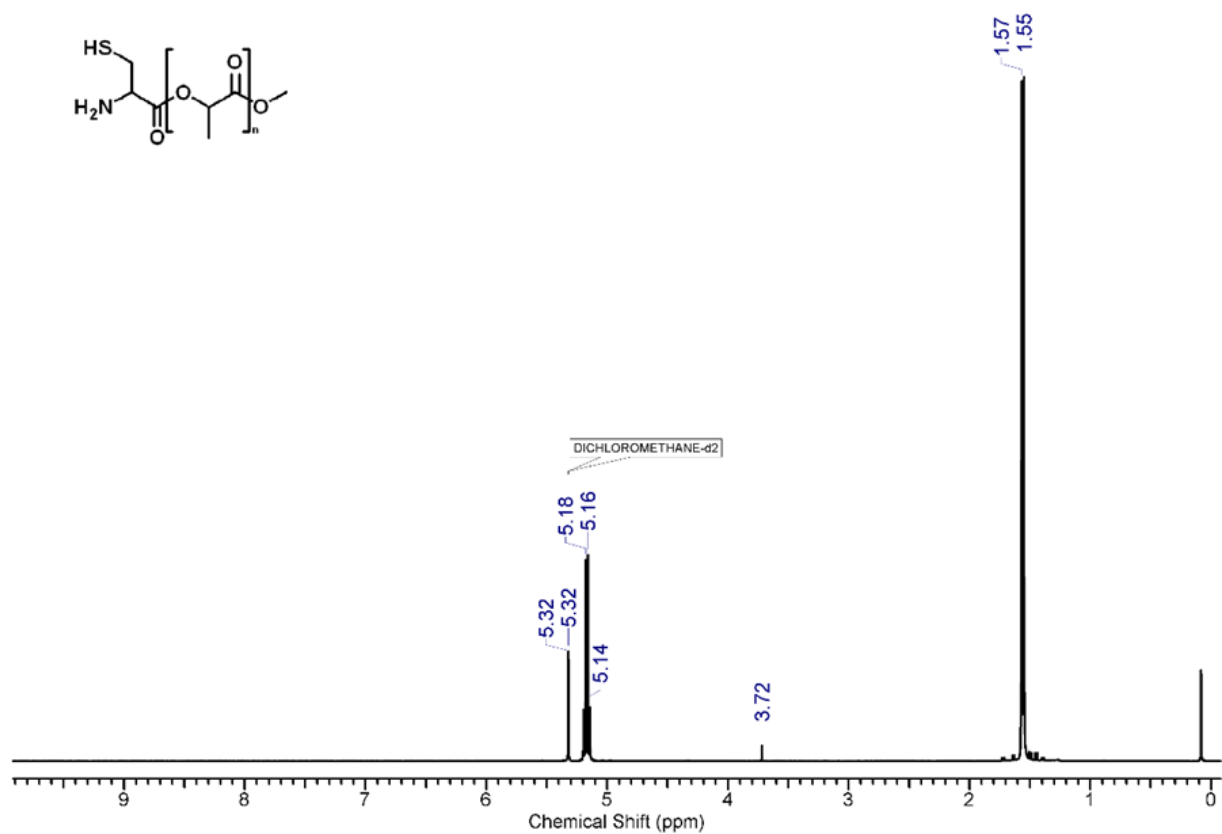


Fig. S170: ¹H NMR (CD₂Cl₂, 400 MHz) spectrum of PLA_{20k}-cysteine.

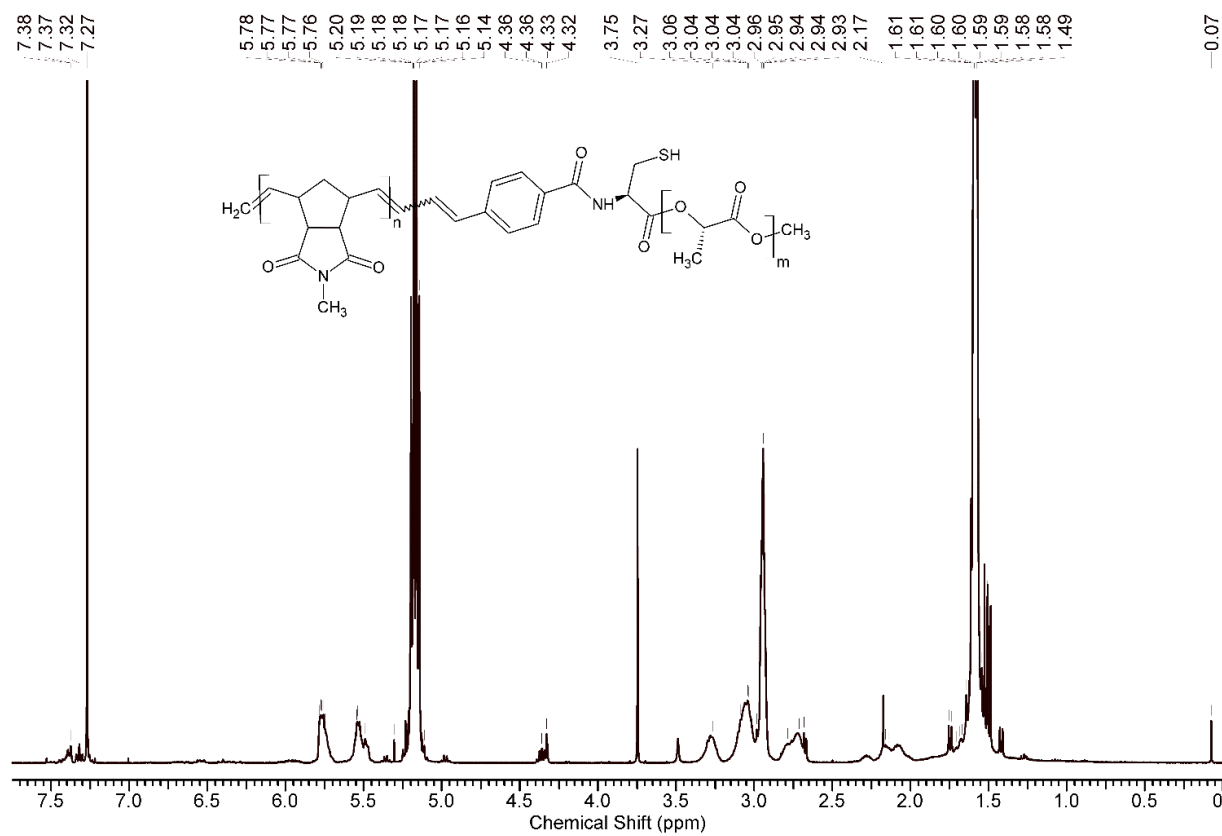


Fig. S171: ¹H NMR (CD₂Cl₂, 400 MHz) spectrum of P14-b-PLA.

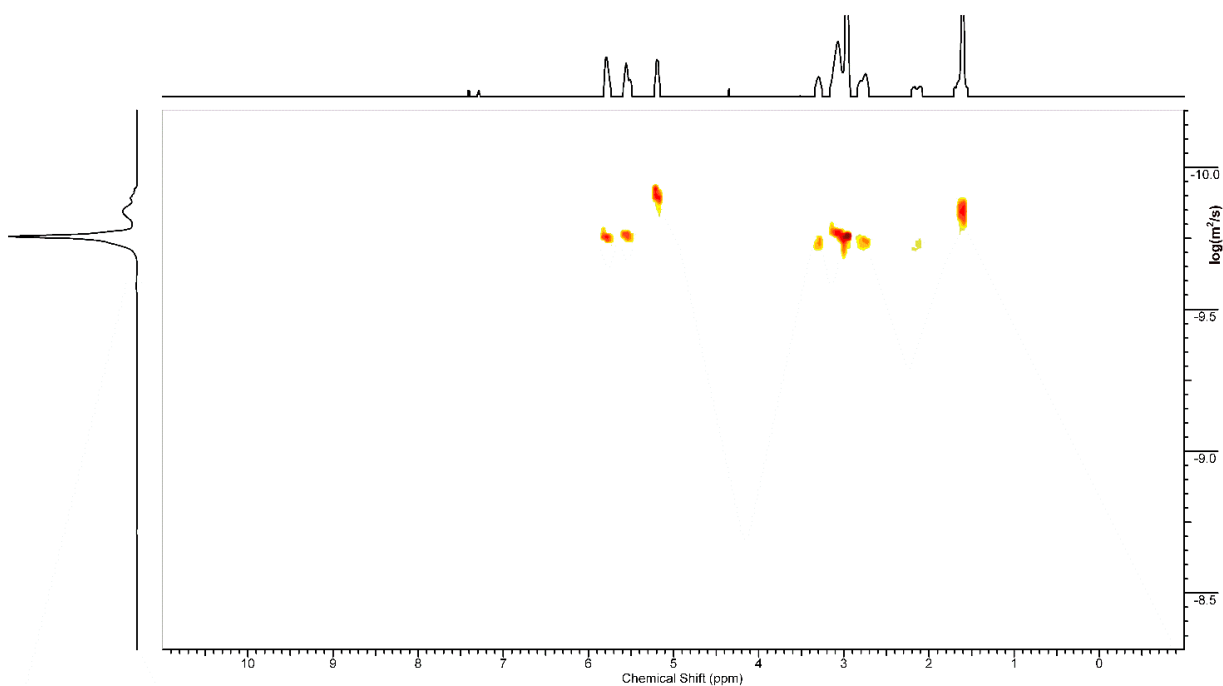


Fig. S172: DOSY ^1H NMR (CDCl_3 , 400 MHz) spectrum of a mixture of P14 and PLA_{20k}-Boc-Cys (Trt)-OH before coupling.

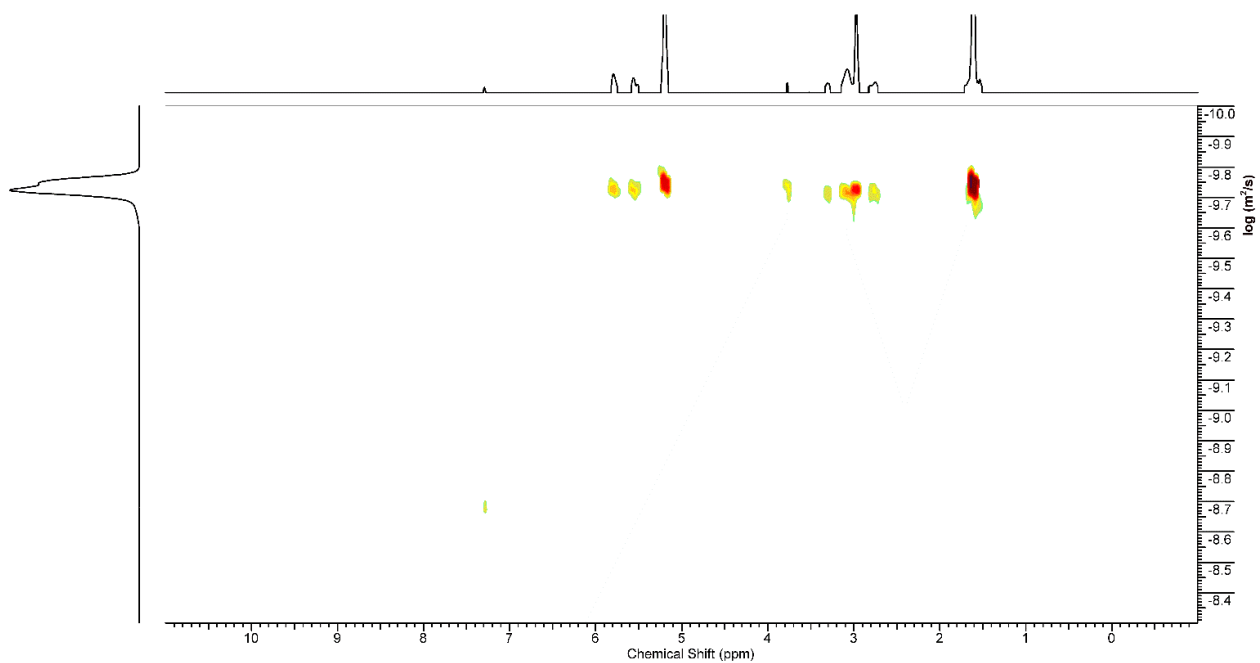


Fig. S173: DOSY ^1H NMR (CDCl_3 , 400 MHz) spectrum of P14-b-PLA.

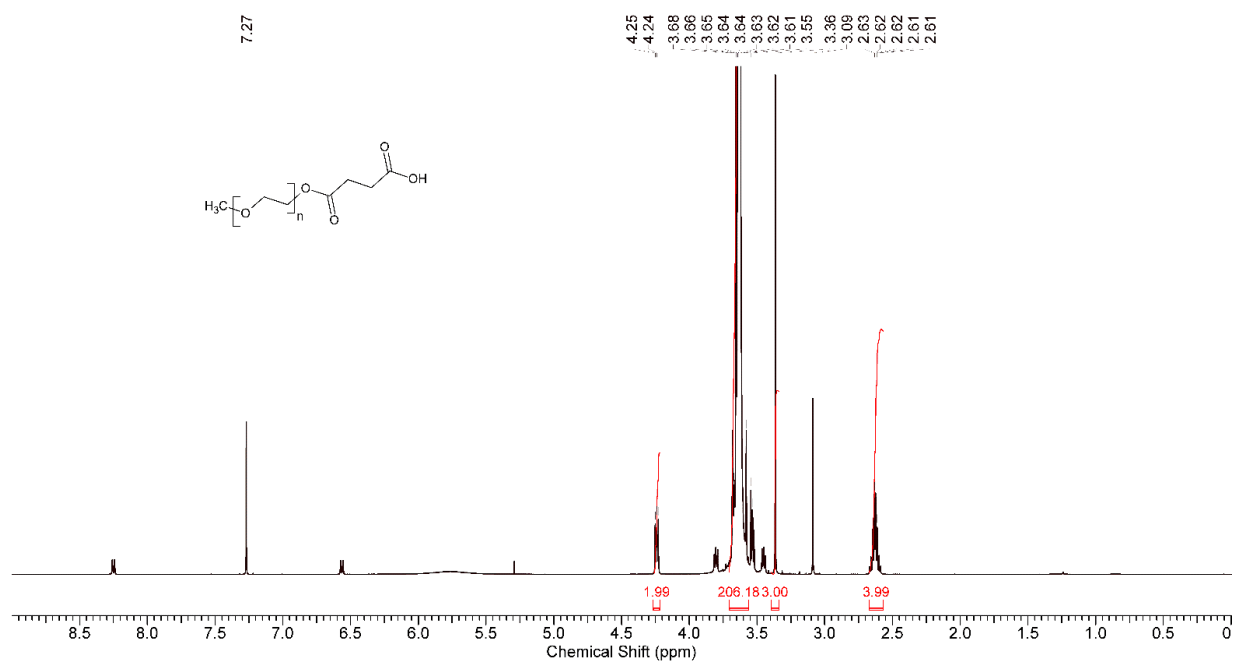


Fig. S174: ¹H NMR (CDCl₃, 400 MHz) spectrum of MeOPEG_{2k} acid. DMAP as an impurity (peaks at around 3, 6.6, and 8.25 ppm).

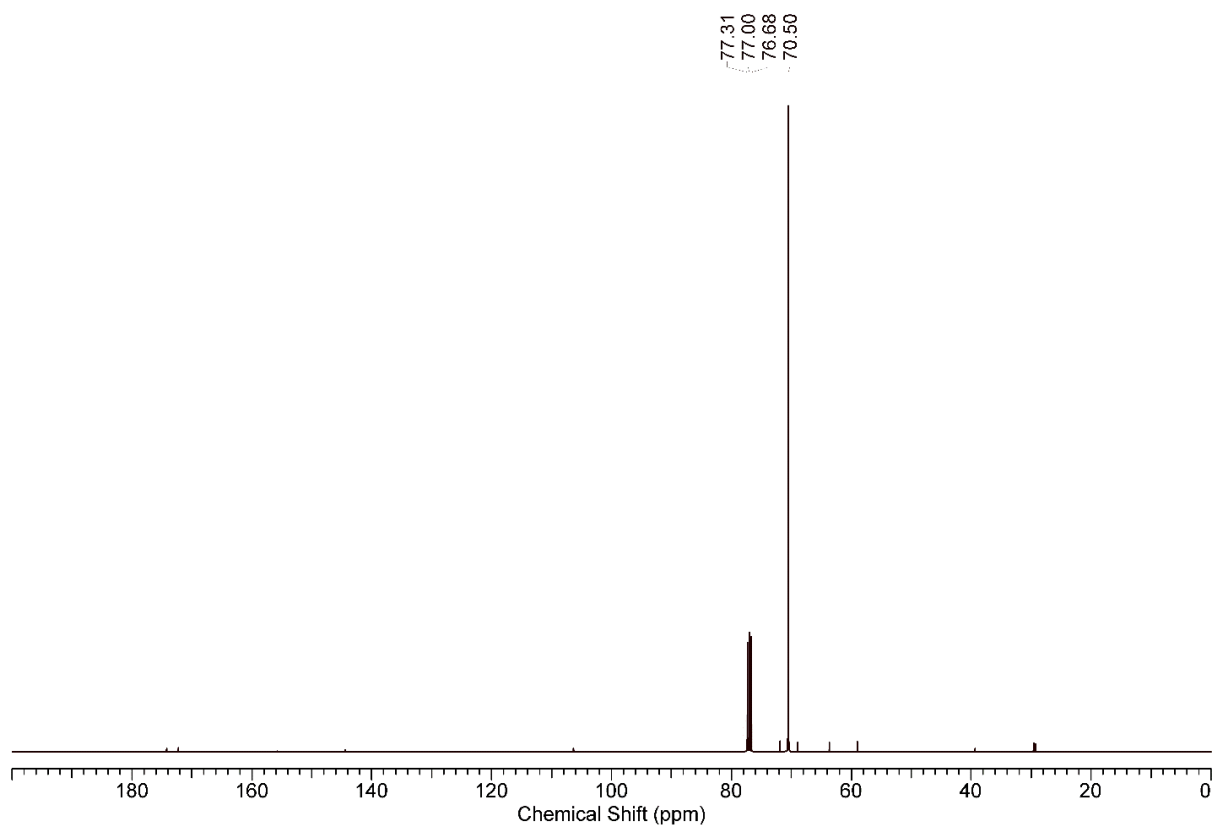


Fig. S175: ¹³C NMR (CDCl₃, 101 MHz) spectrum of MeOPEG_{2k} acid.

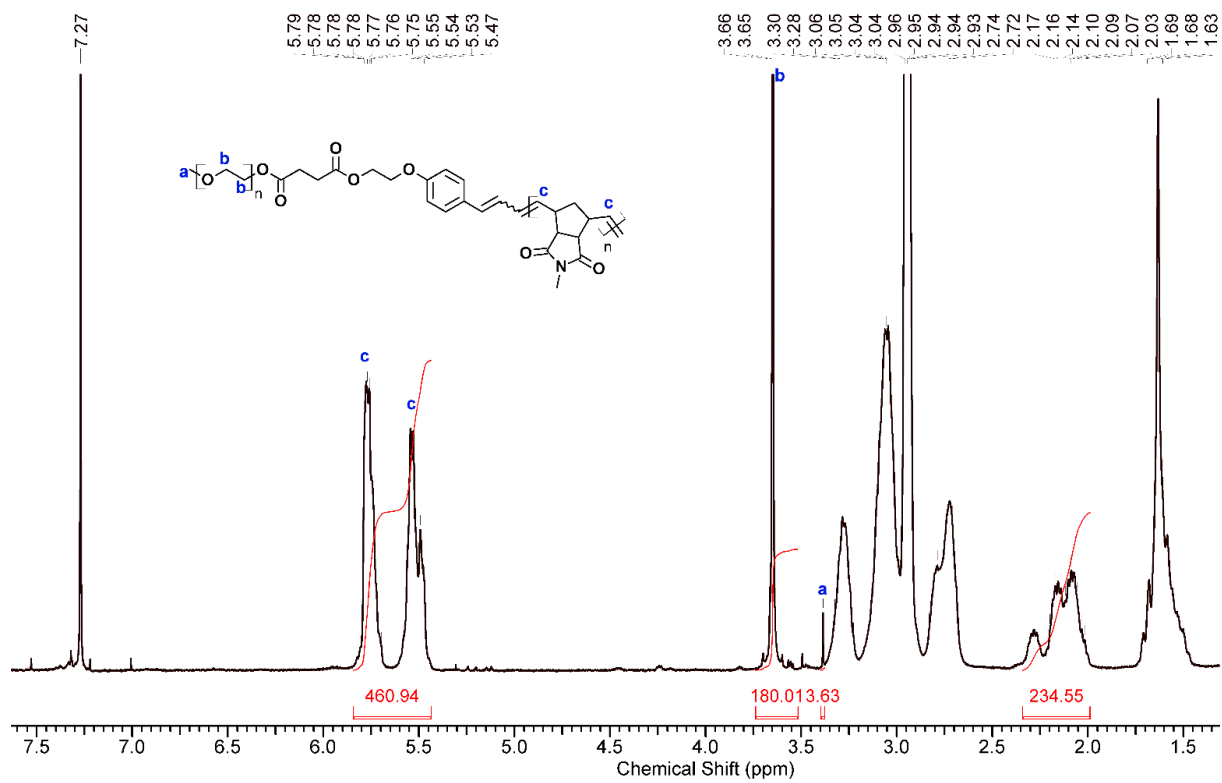


Fig. S178: ^1H NMR (CDCl_3 , 400 MHz) spectrum of $\text{PEG}_{2k}\text{-b-P}$ (M1).

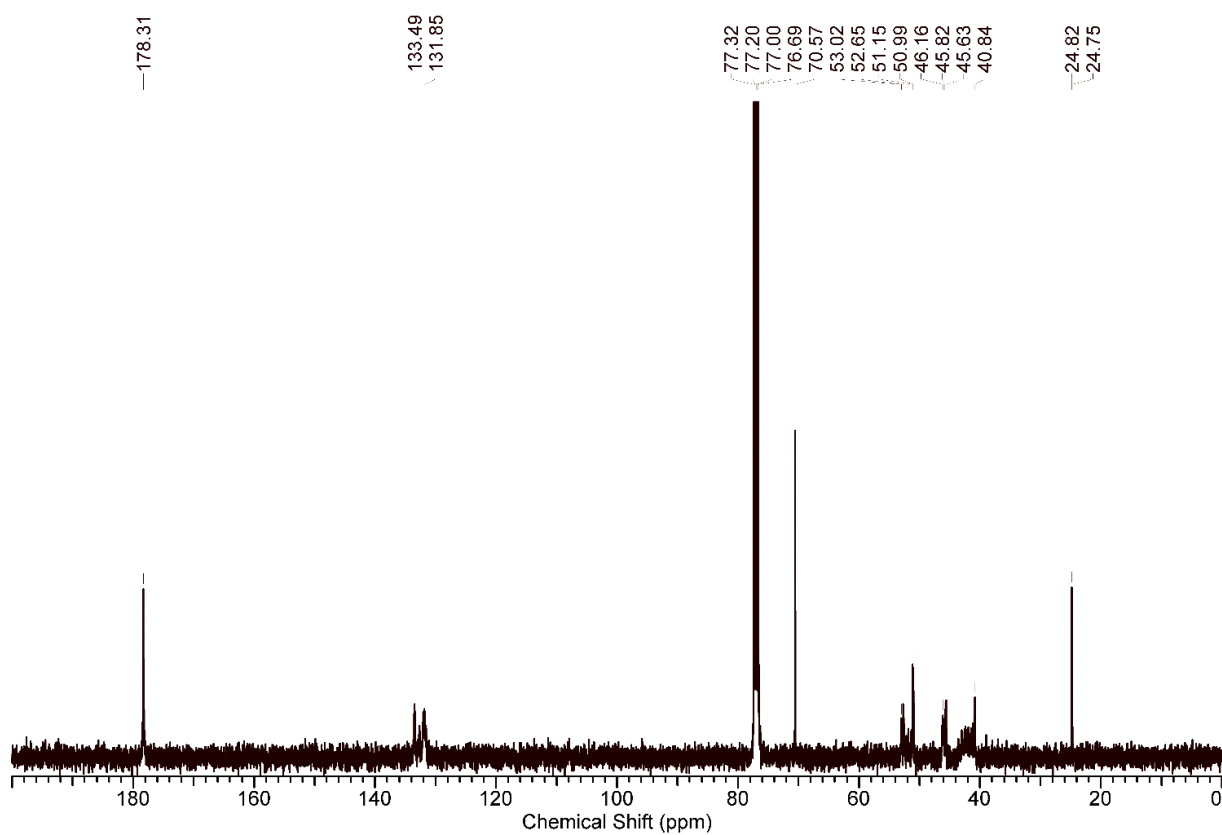


Fig. S179: ^{13}C NMR (CDCl_3 , 101 MHz) spectrum of $\text{PEG}_{2k}\text{-b-P}$ (M1).

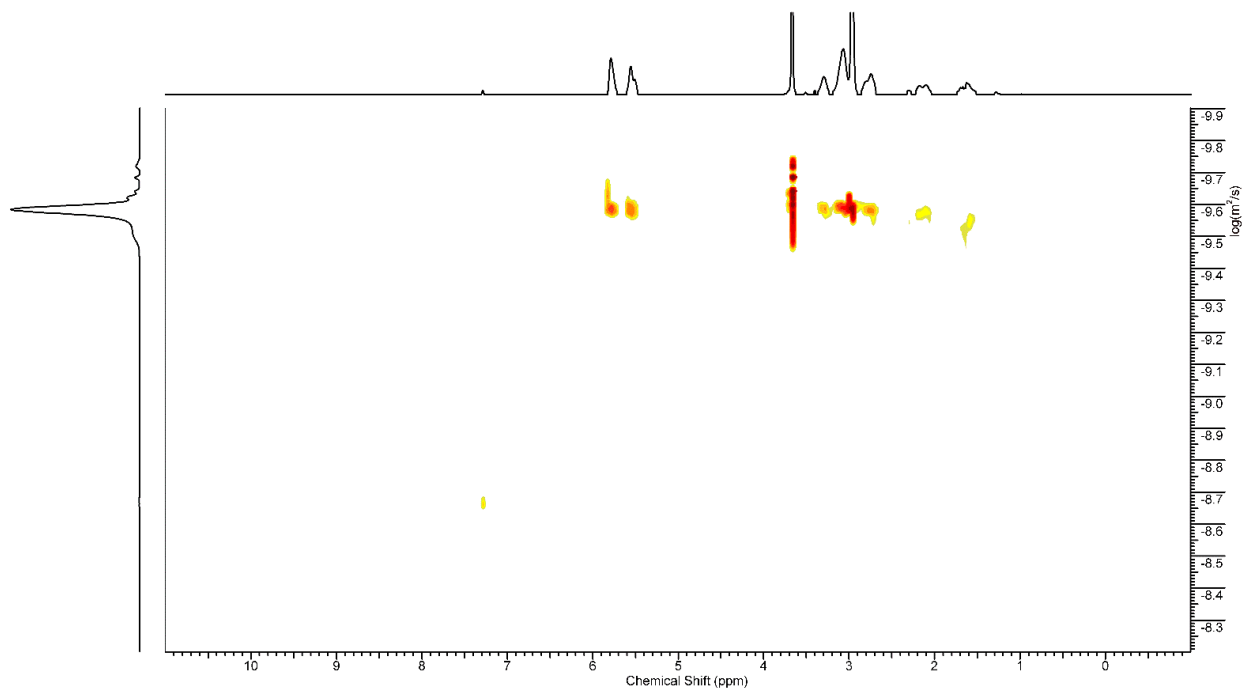
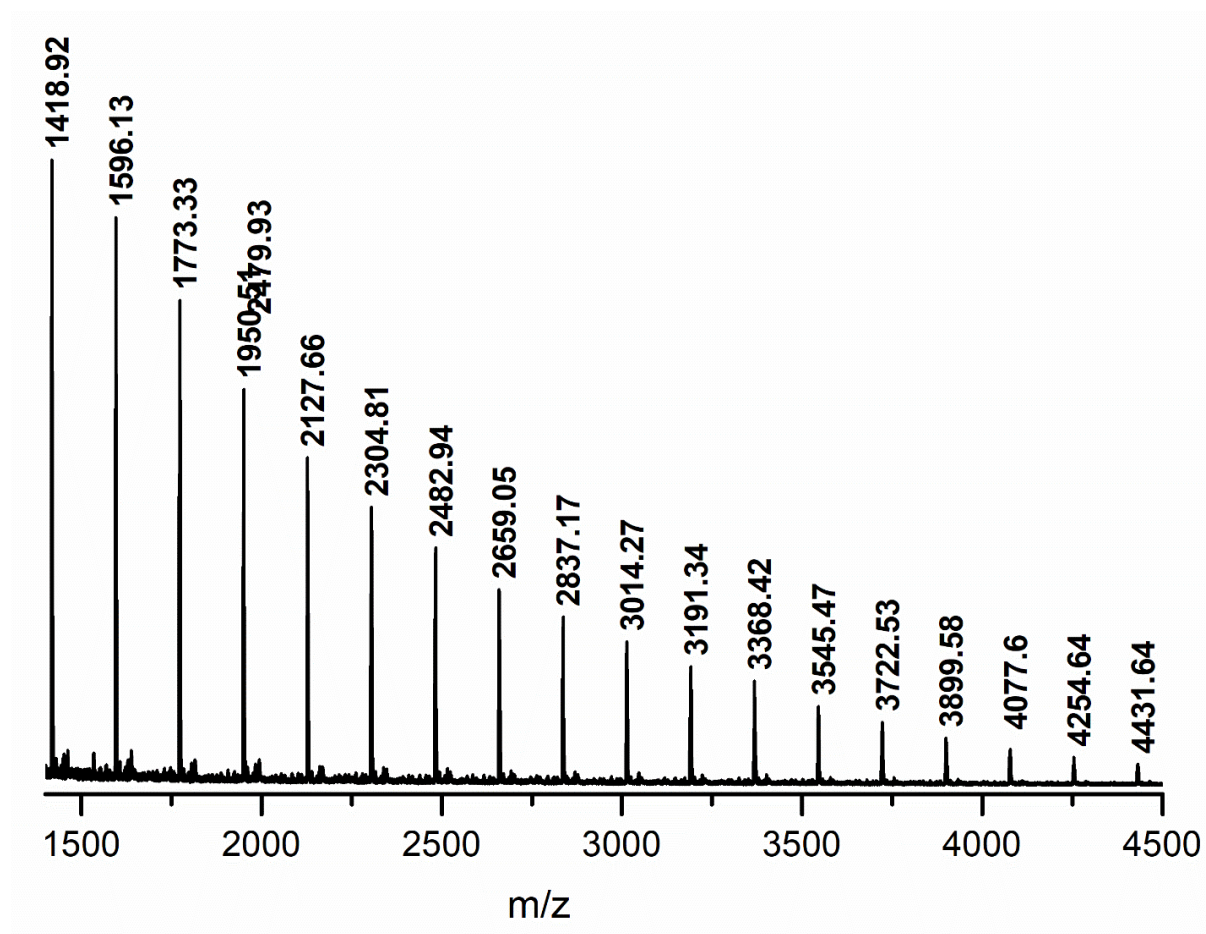


Fig. S180: DOSY ¹H NMR (CDCl₃, 400 MHz) spectrum of PEG_{2k}-b-p (M1).

MALDI-ToF mass spectra of Polymers:

Sample preparation: A stock solution of a DCTB matrix of 20 mg/mL concentration in CHCl_3 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 CHCl_3 . 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 CSl_3 or using poly (styrene) standards.



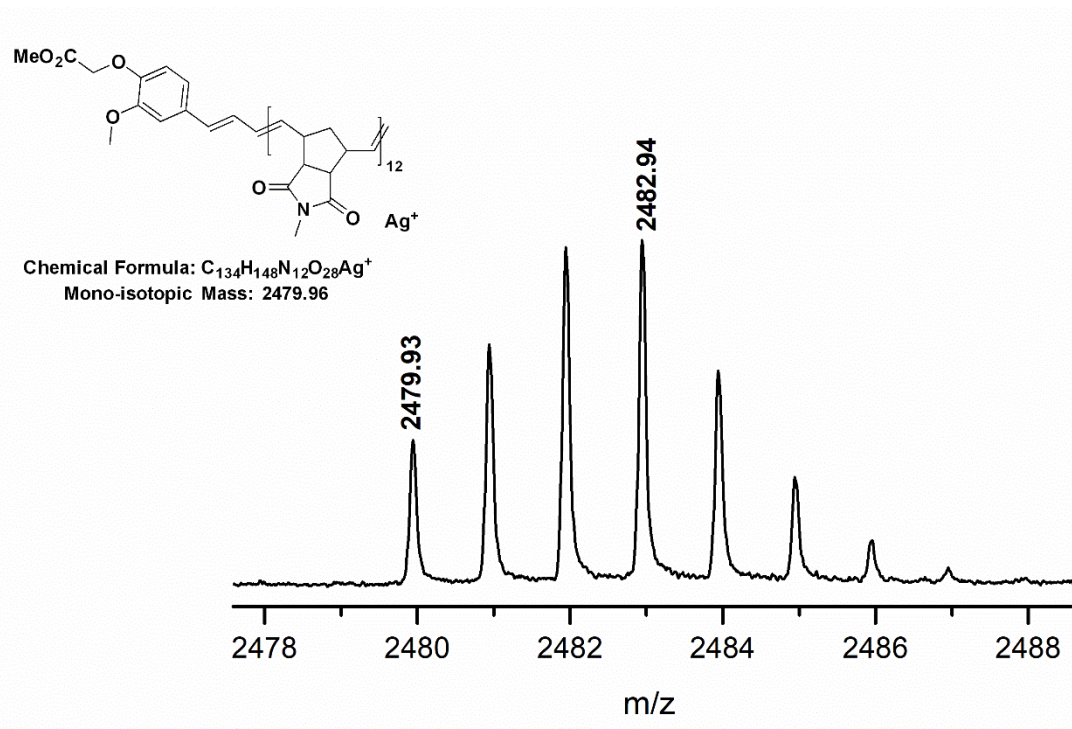
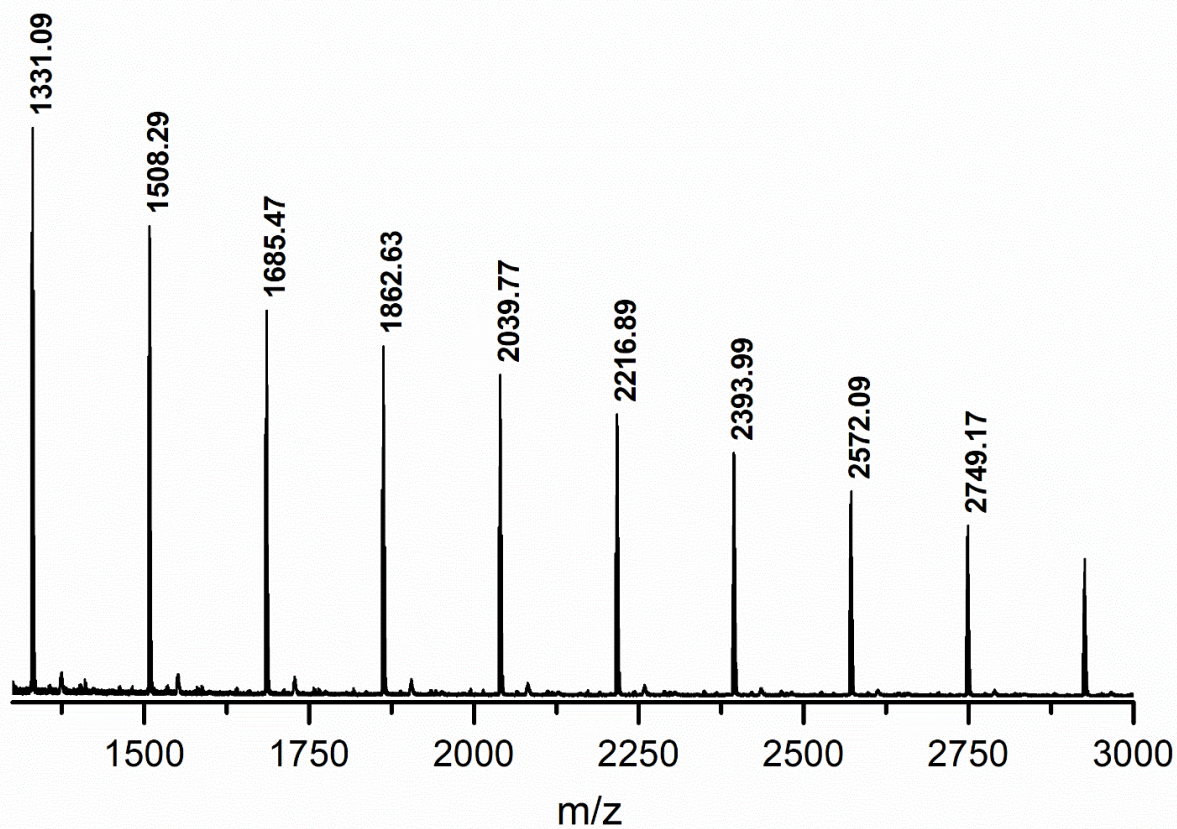
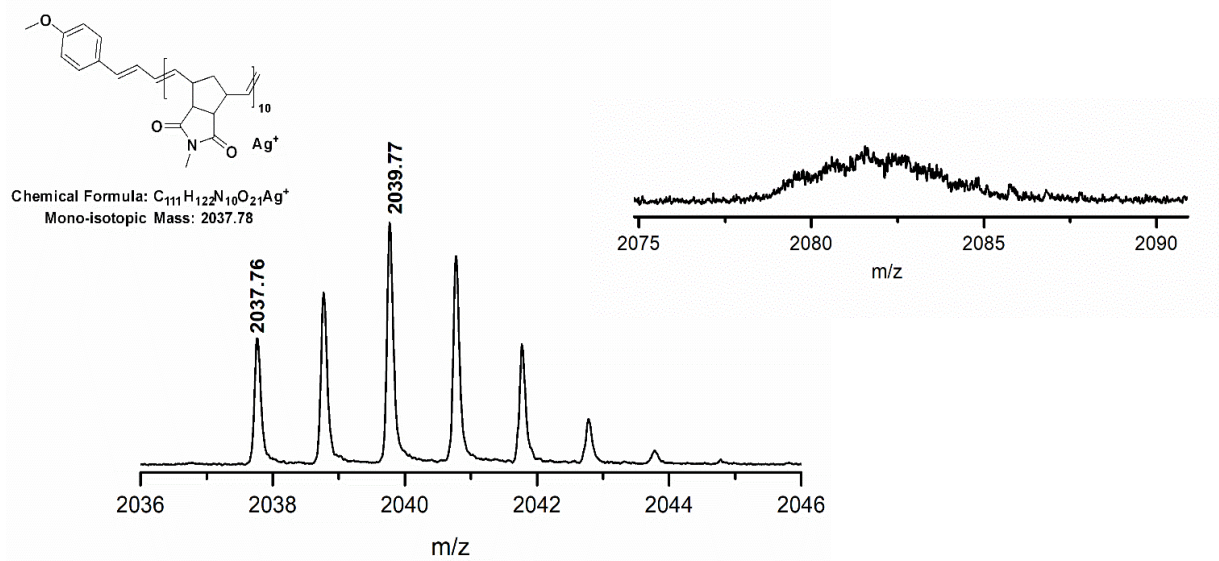


Fig. S181: MALDI-ToF mass spectrum (DCTB, AgTFA) of P4.





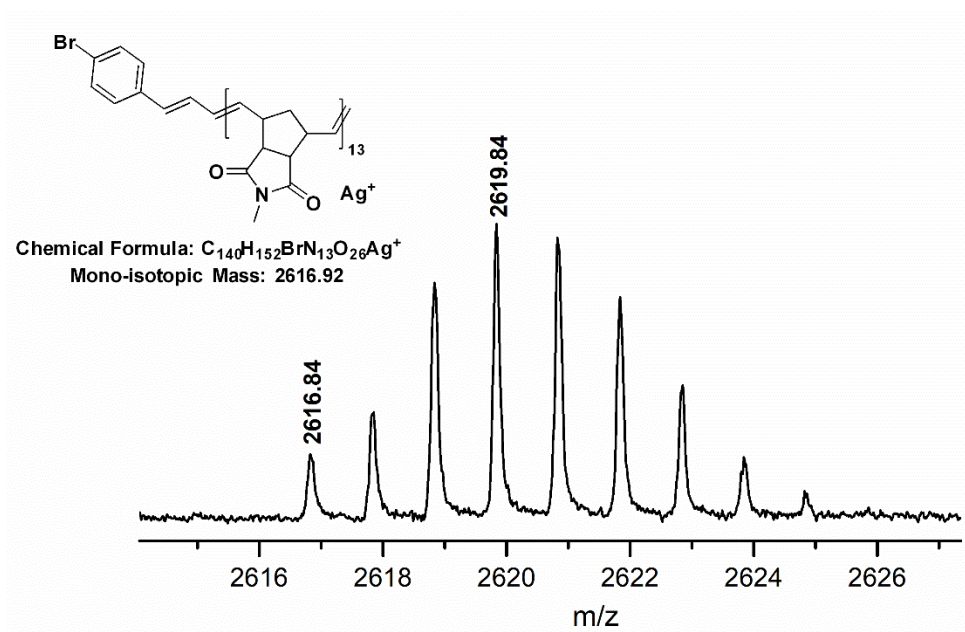
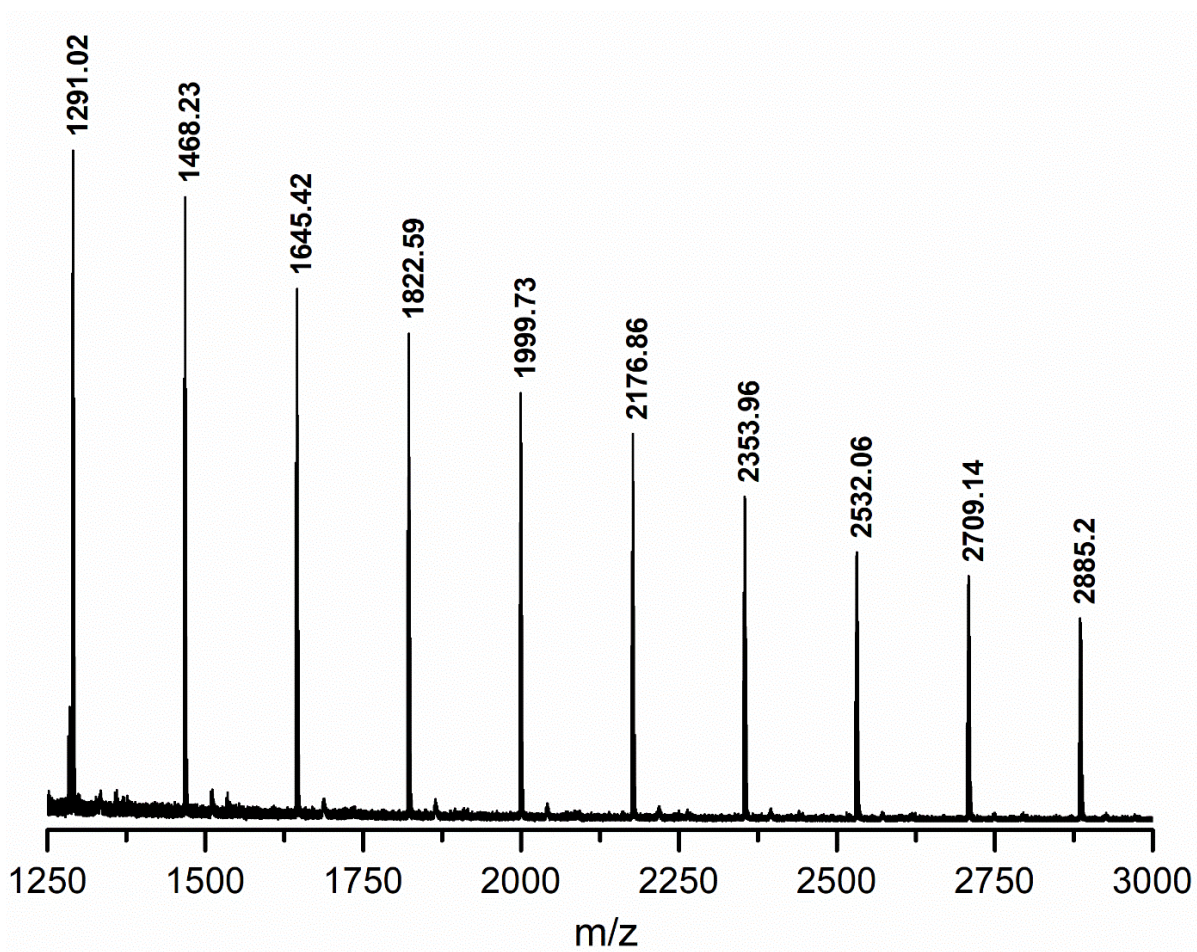


Fig. S183: MALDI-ToF mass spectrum (DCTB, AgTFA) of P7.



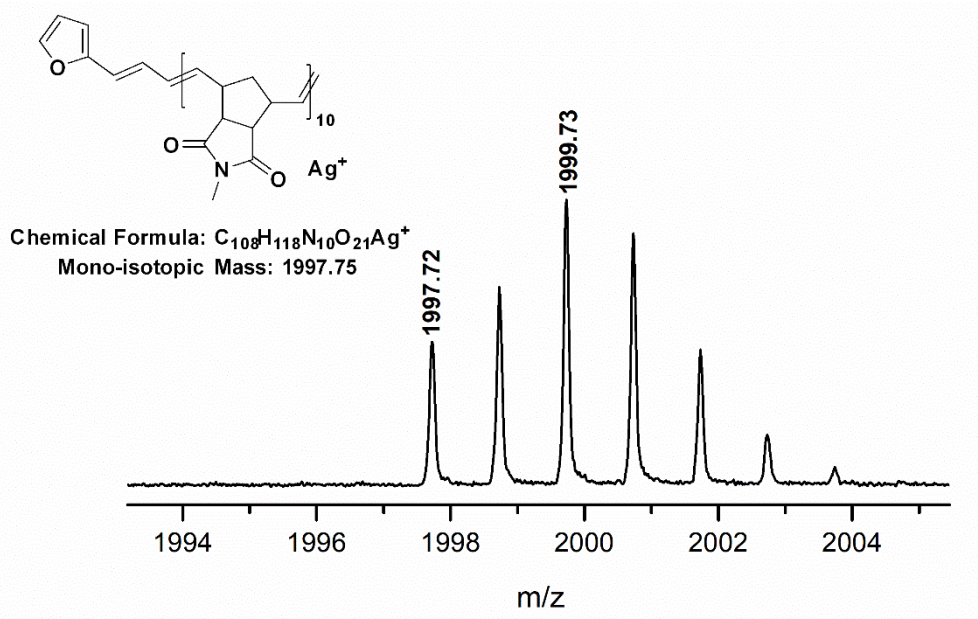
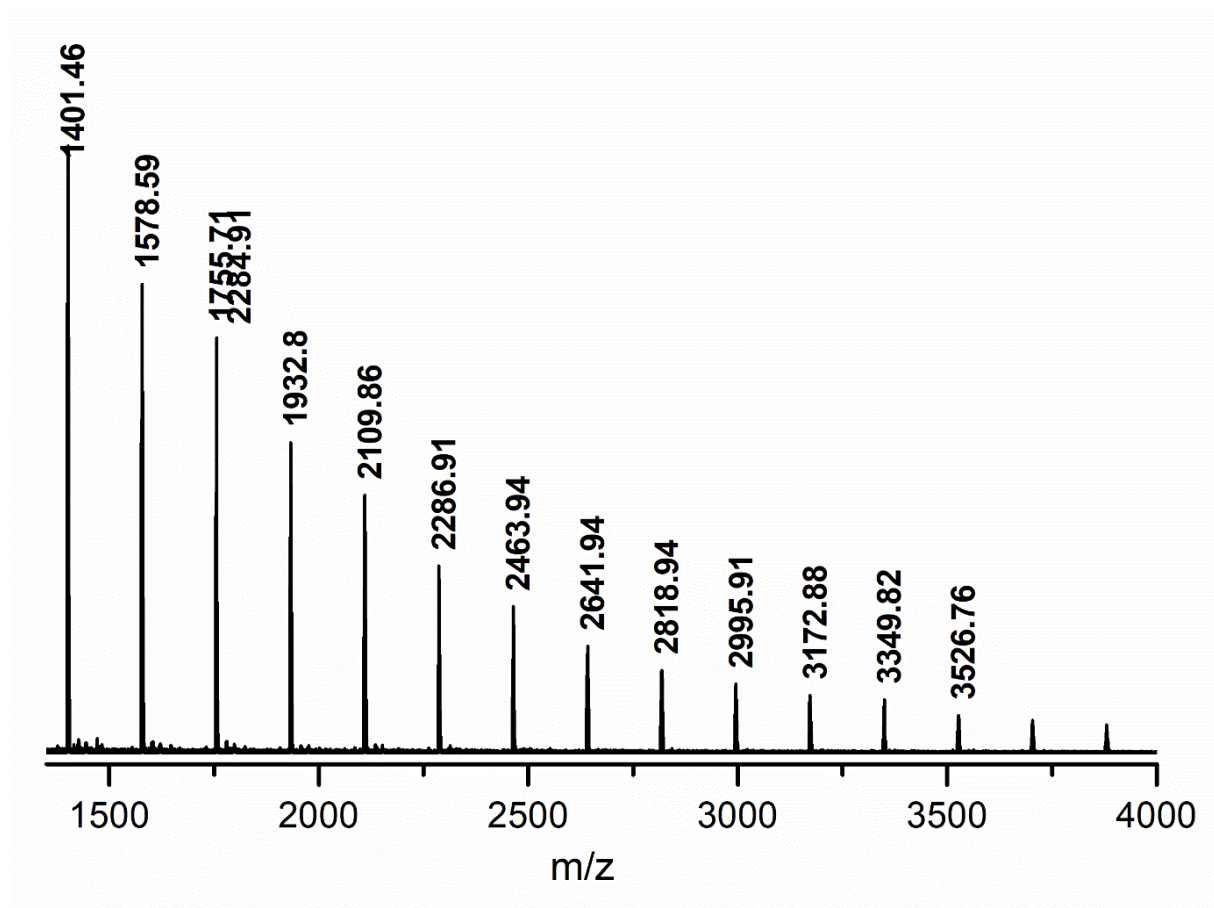


Fig. S184: MALDI-ToF mass spectrum (DCTB, AgTFA) of P9.



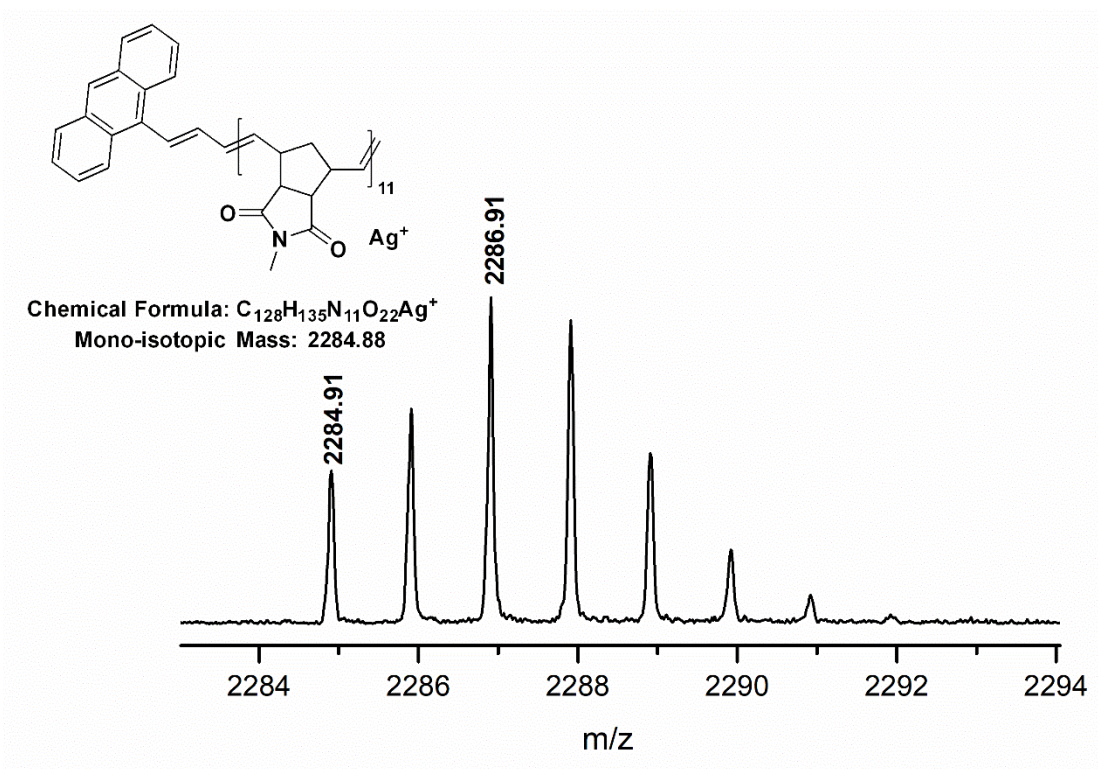
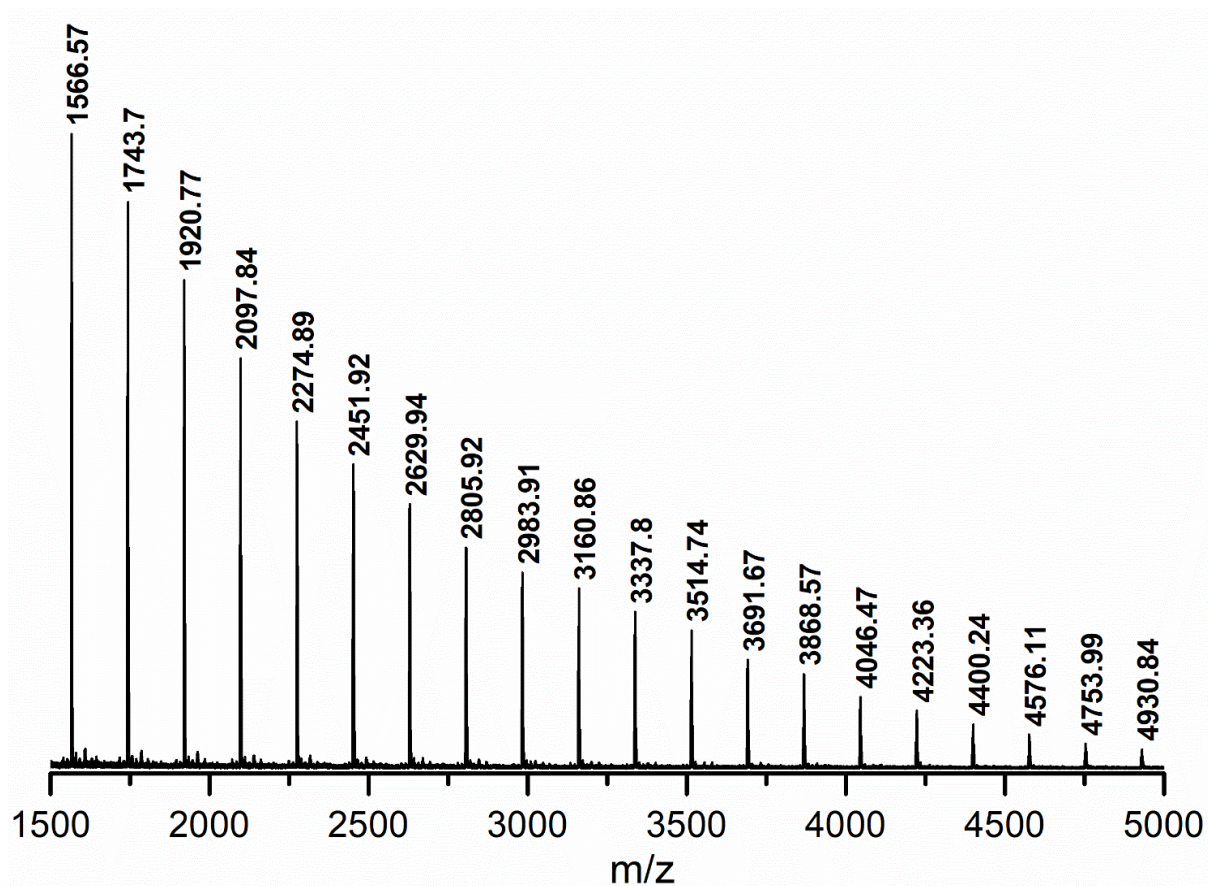


Fig. S185: MALDI-ToF mass spectrum (DCTB, AgTFA) of P10.



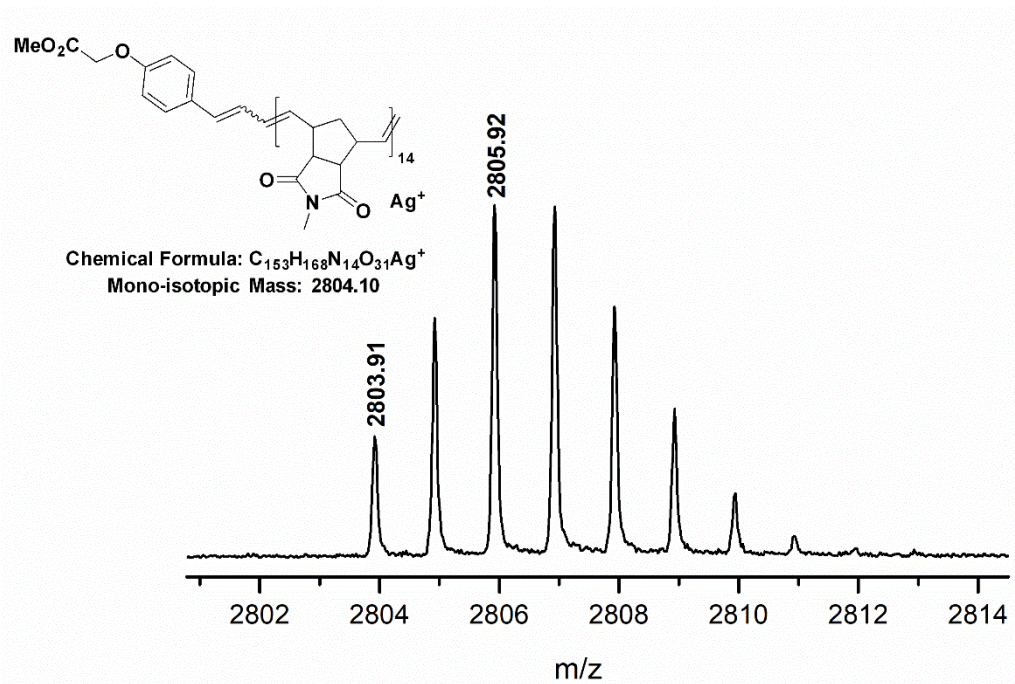
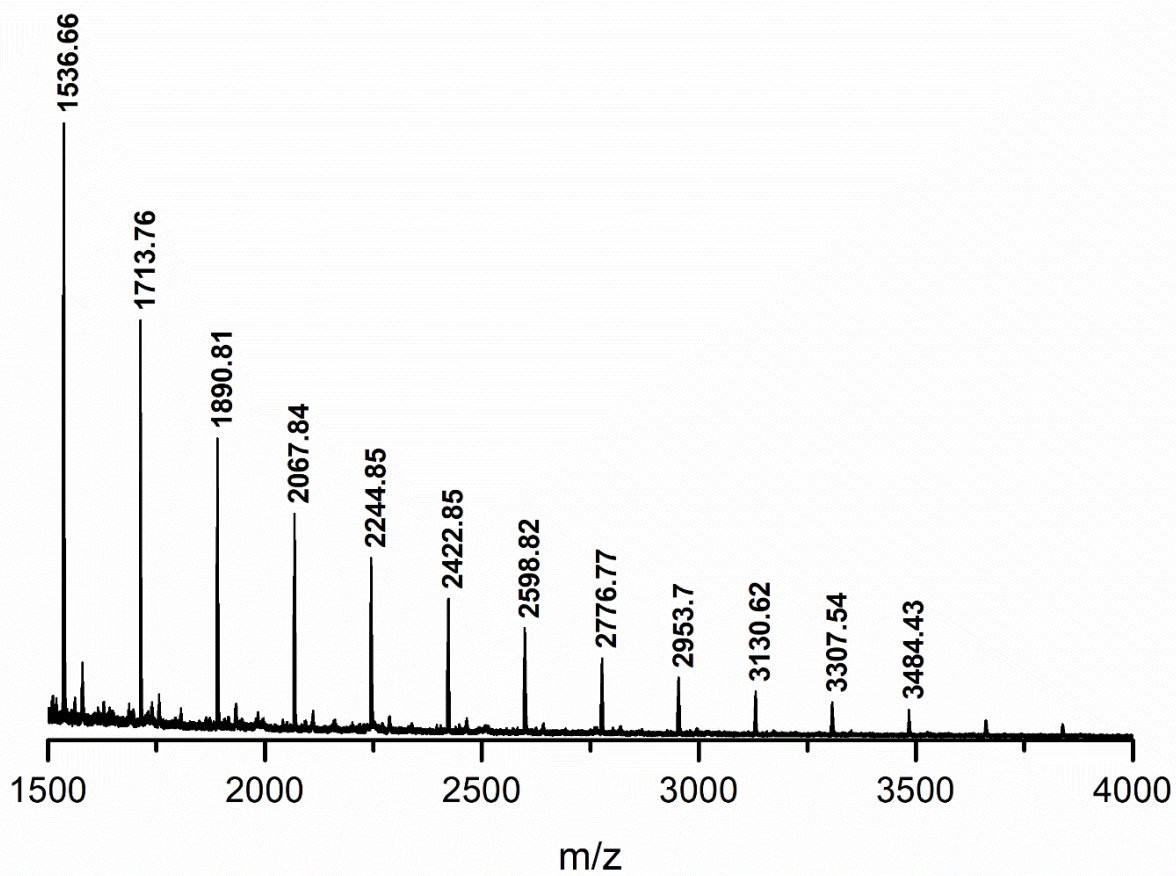


Fig. S186: MALDI-ToF mass spectrum (DCTB, AgTFA) of P11.



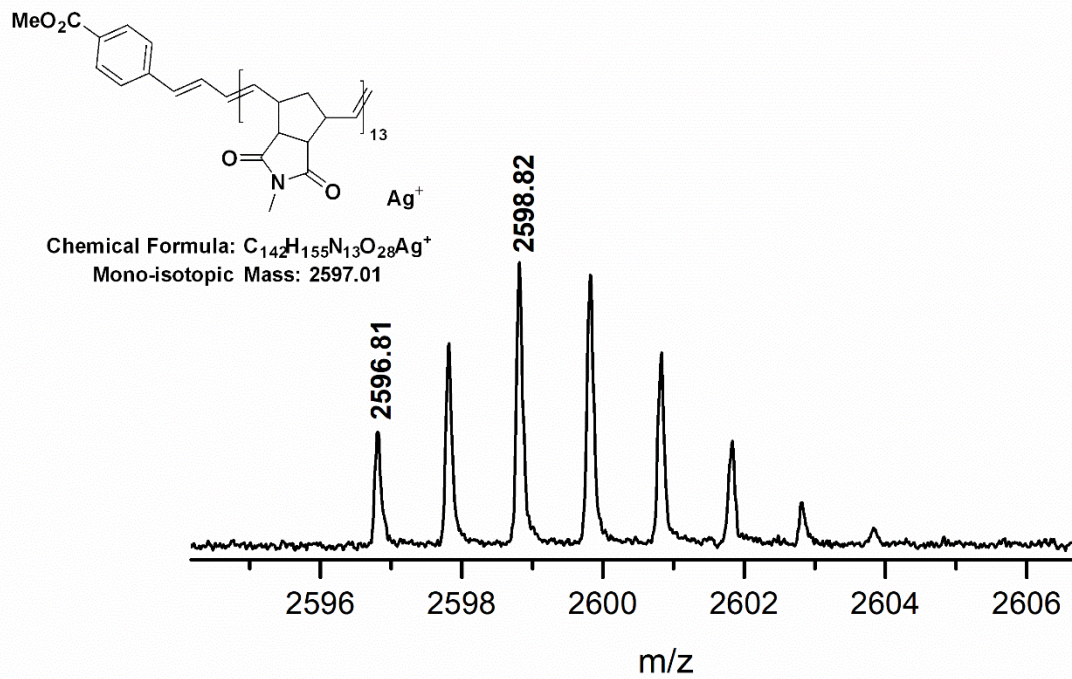
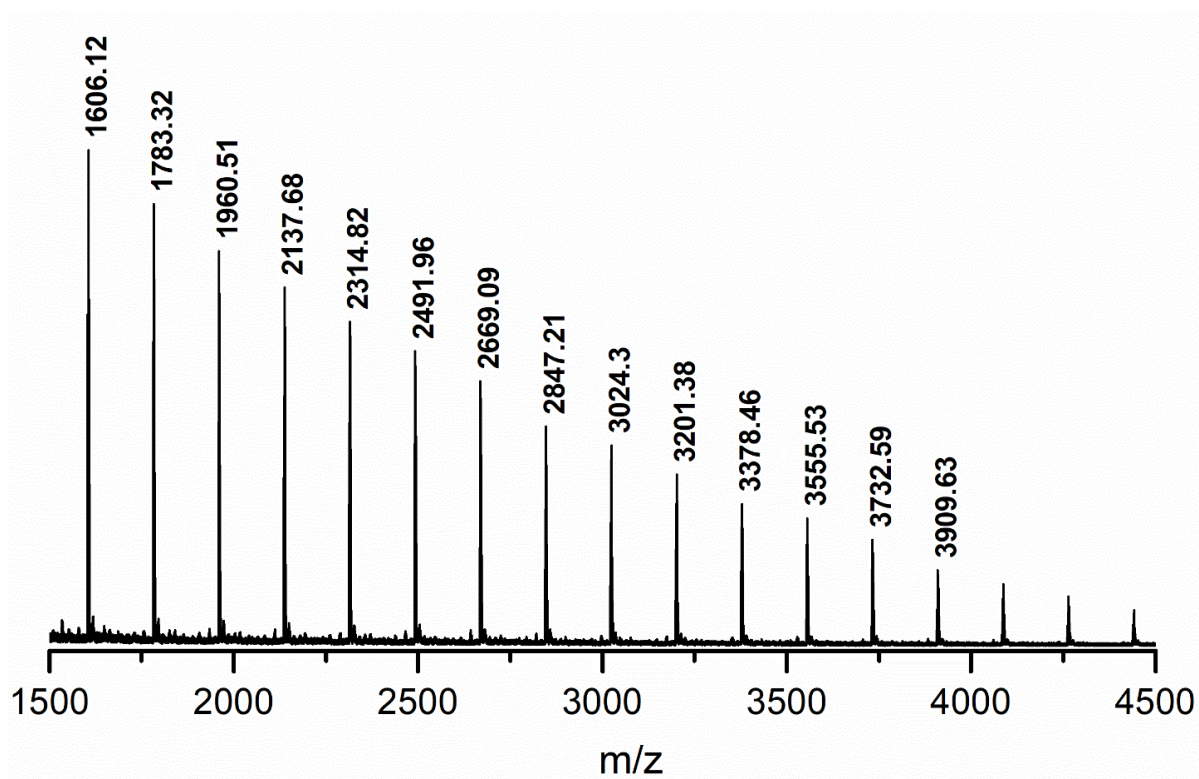


Fig. S187: MALDI-ToF mass spectrum (DCTB, AgTFA) of P12.



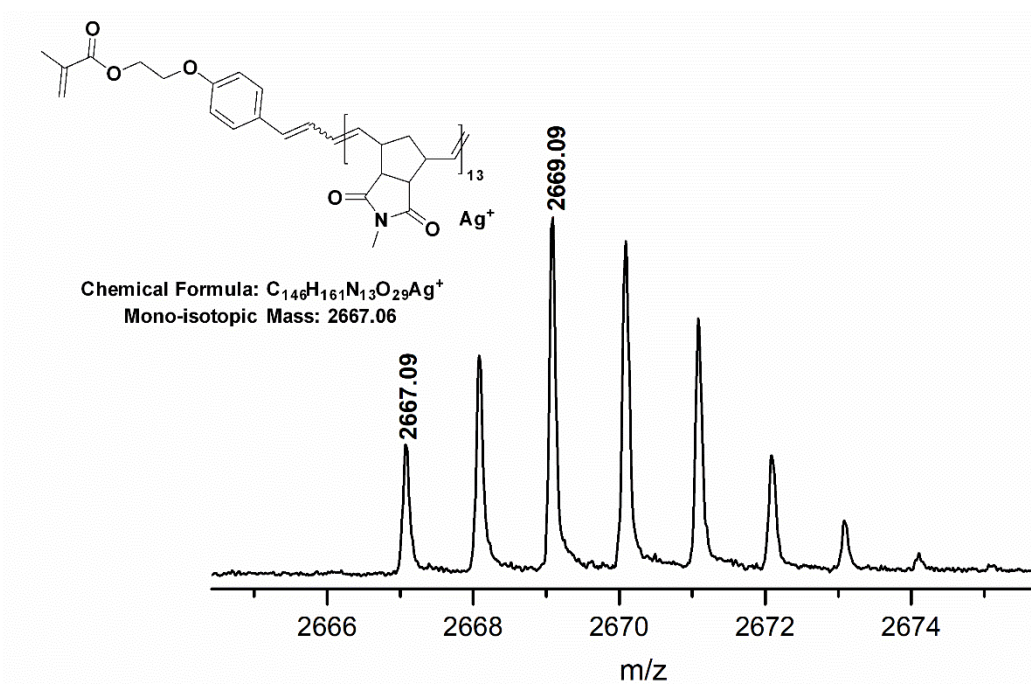
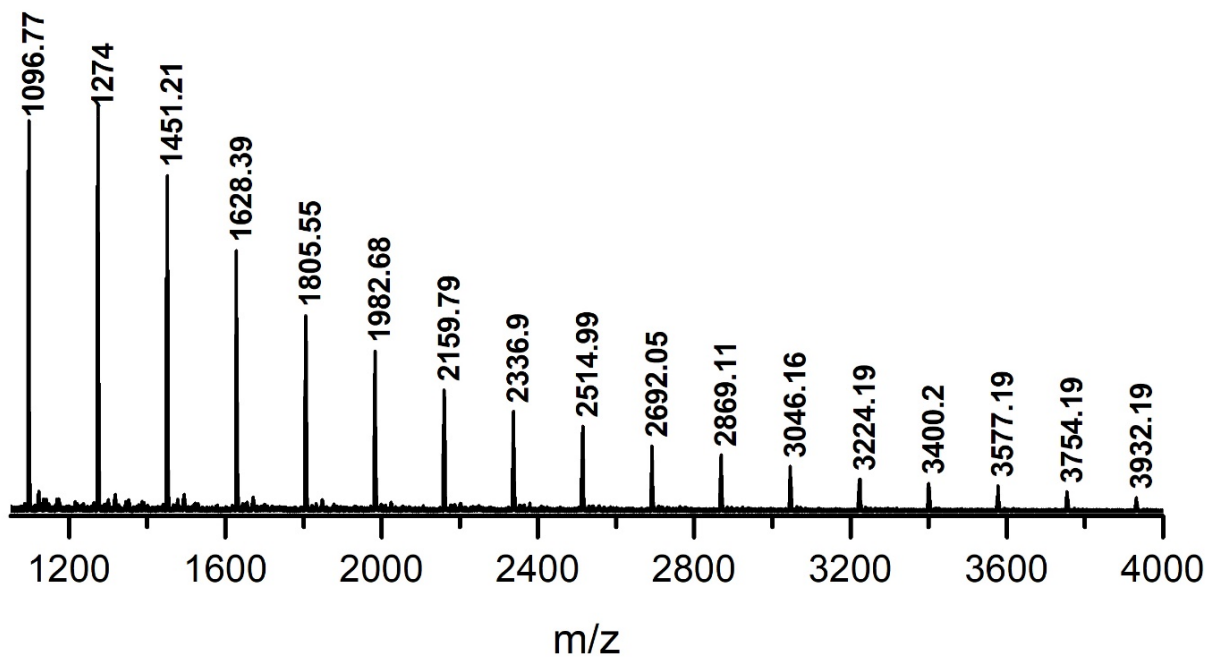


Fig. S188: MALDI-ToF mass spectrum (DCTB, AgTFA) of **P13**. Elimination of HBr in high laser energy of MALDI machine, presumably, generates the above structure.



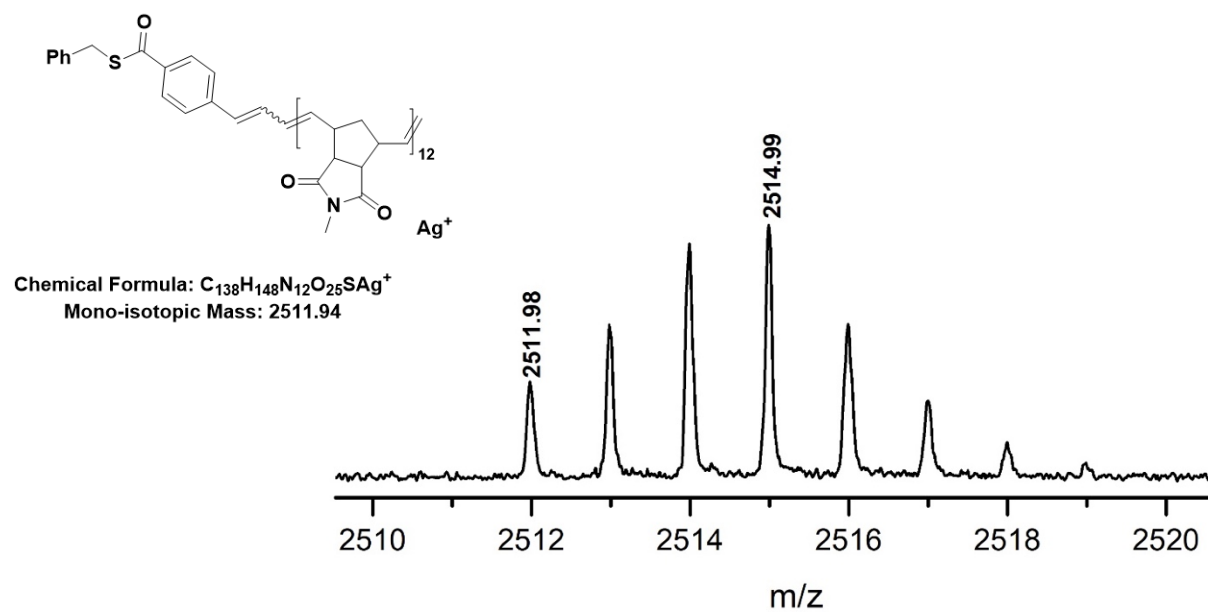
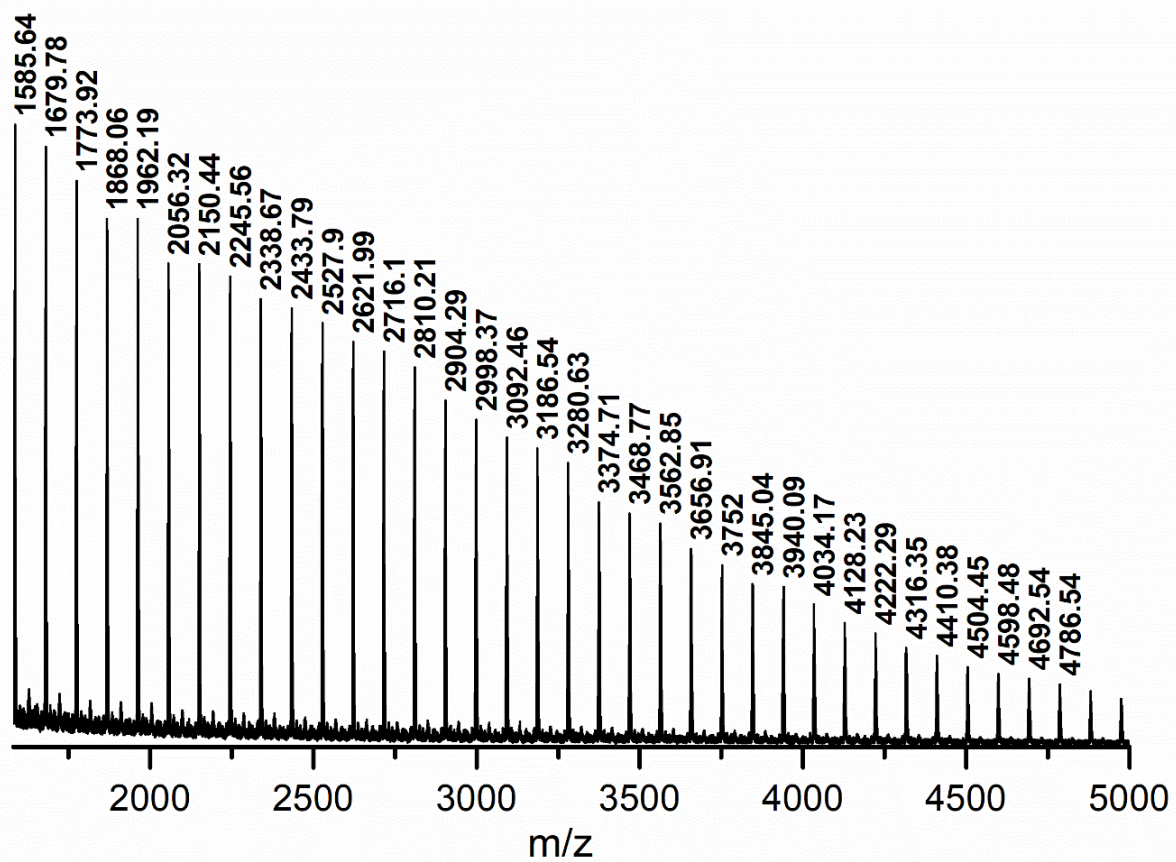


Fig. S189: MALDI-ToF mass spectrum (DCTB, AgTFA) of P14.



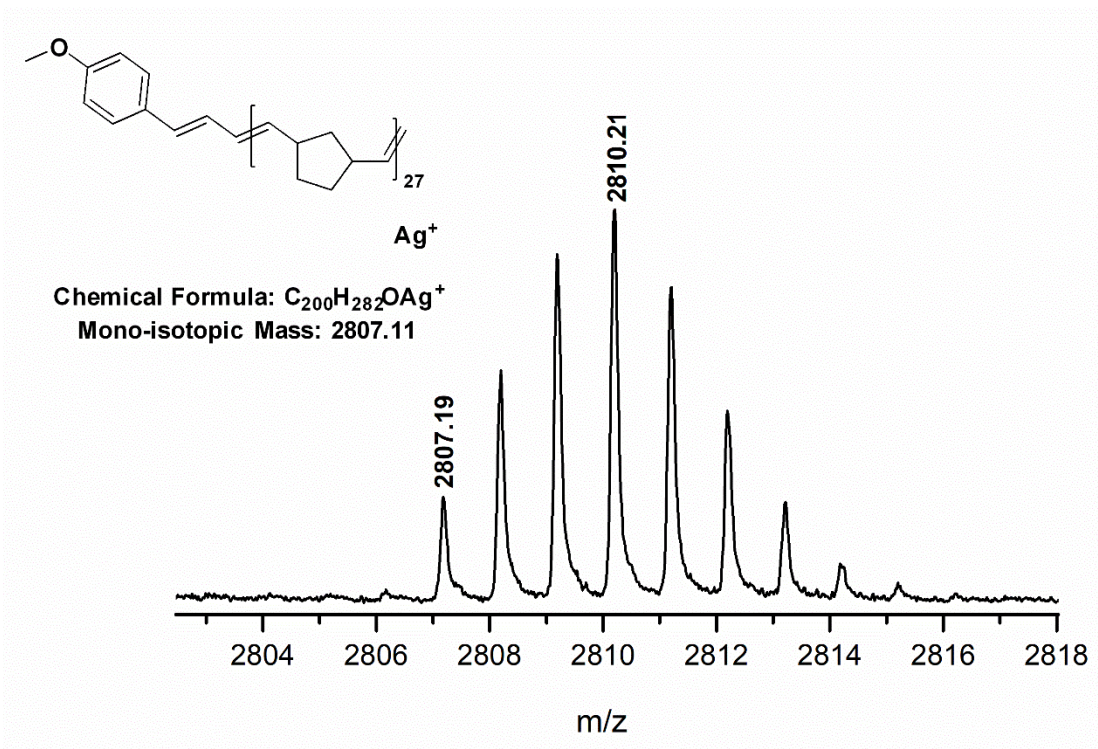
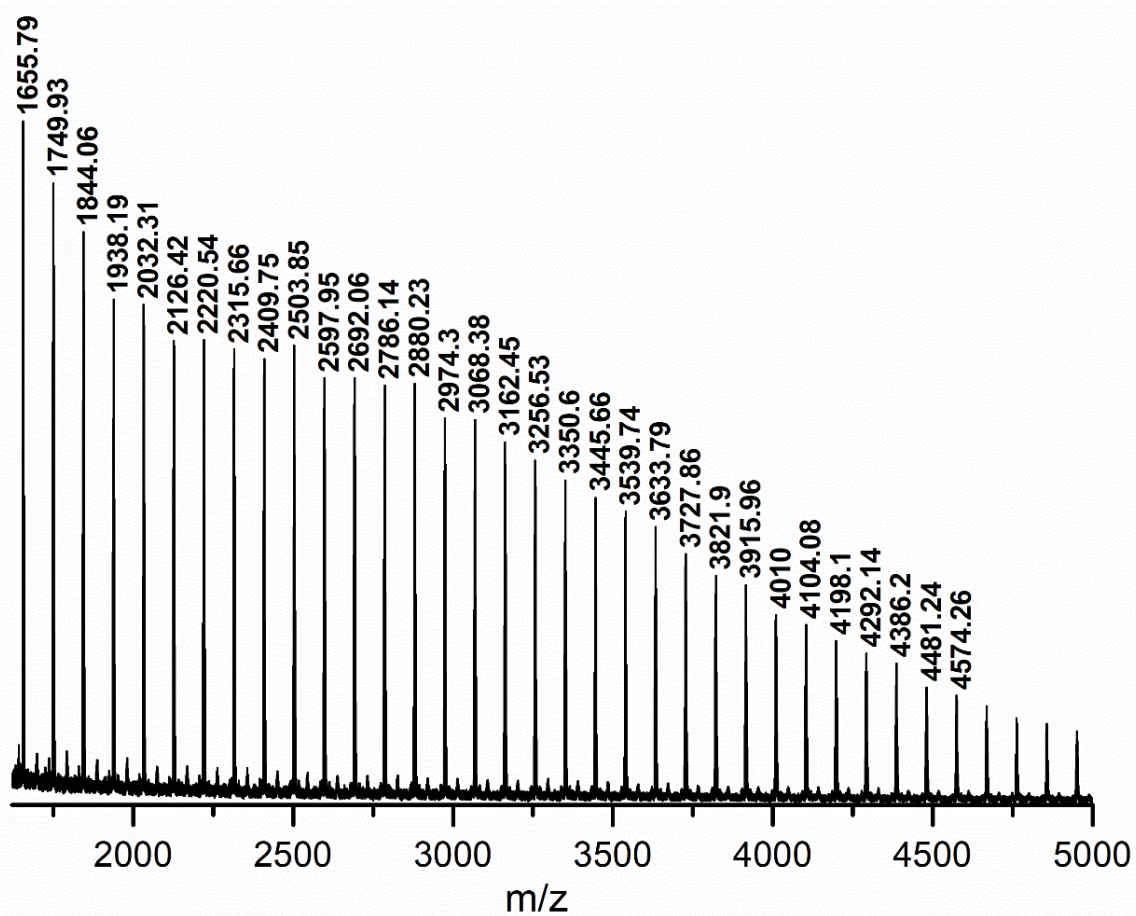


Fig. S190: MALDI-ToF mass spectrum (DCTB, AgTFA) of P15.



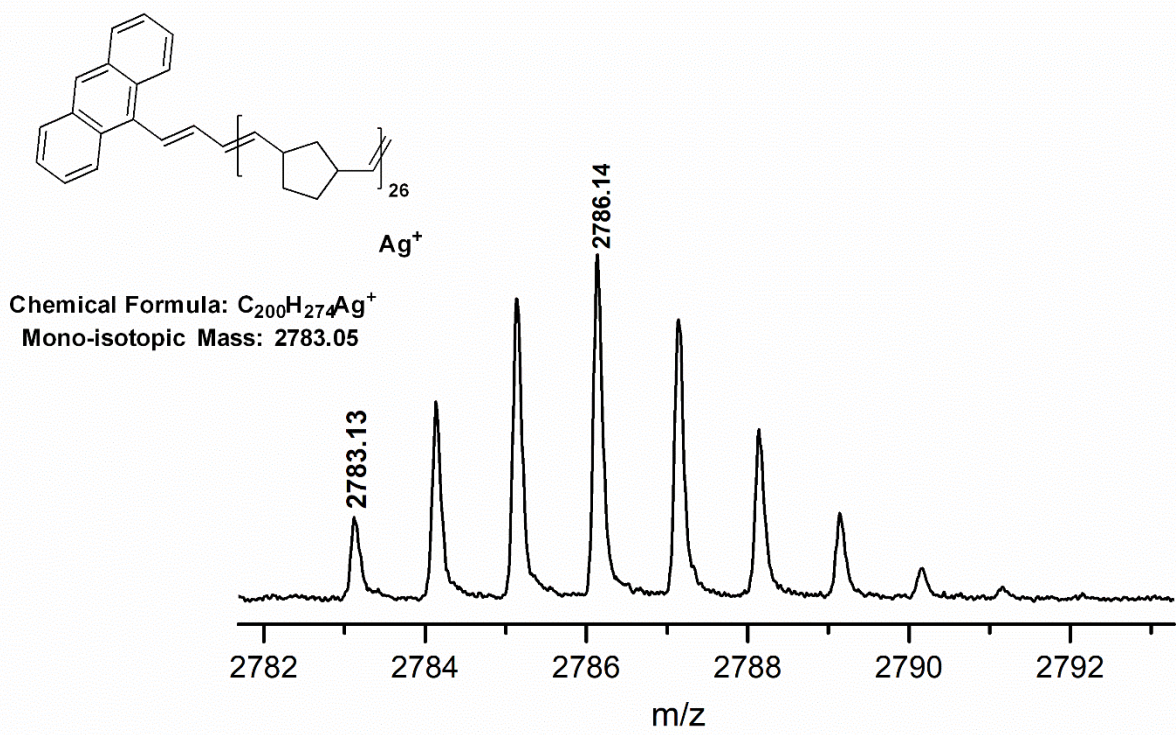
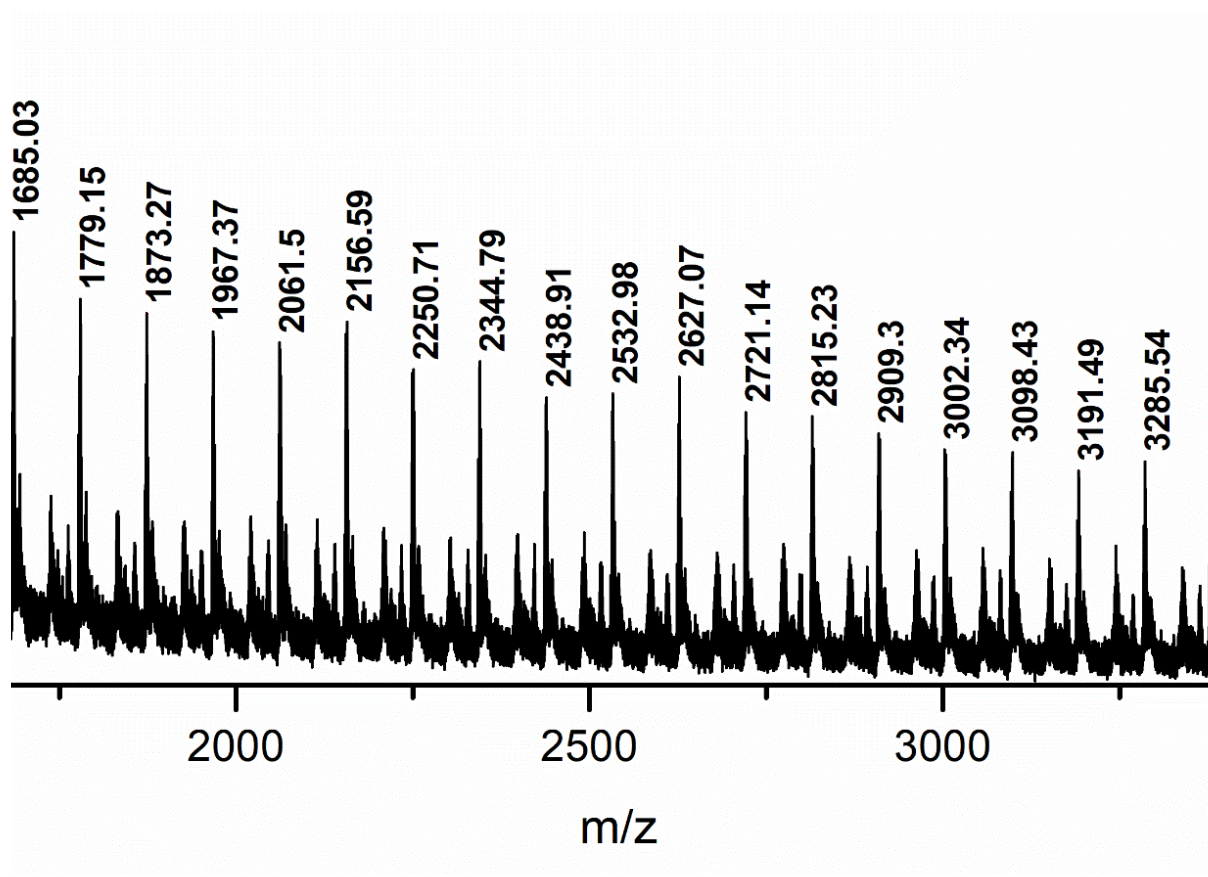


Fig. S191: MALDI-ToF mass spectrum (DCTB, AgTFA) of P16.



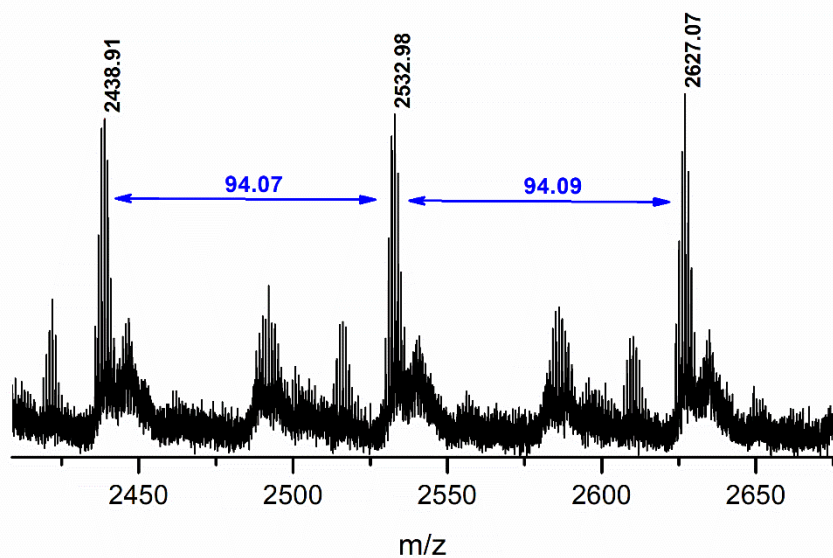
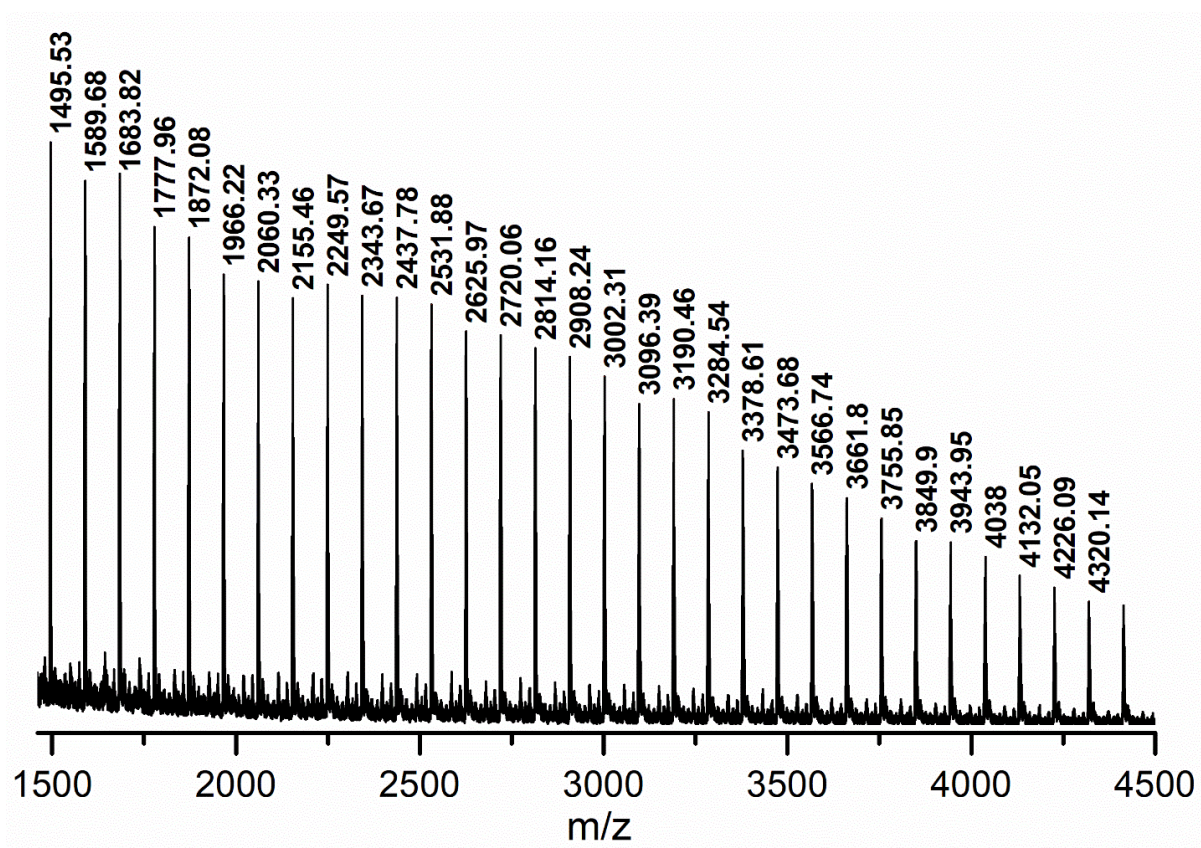


Fig. S192: MALDI-ToF mass spectrum (DCTB, AgTFA) of **P17** showing the difference in repeating unit of mass 94 (mass of norbornene) as isotopically resolved end group analysis was not possible (arguably, due to the presence of amineBoc group) due to unidentified degradation under MALDI-ToF high energy laser condition.



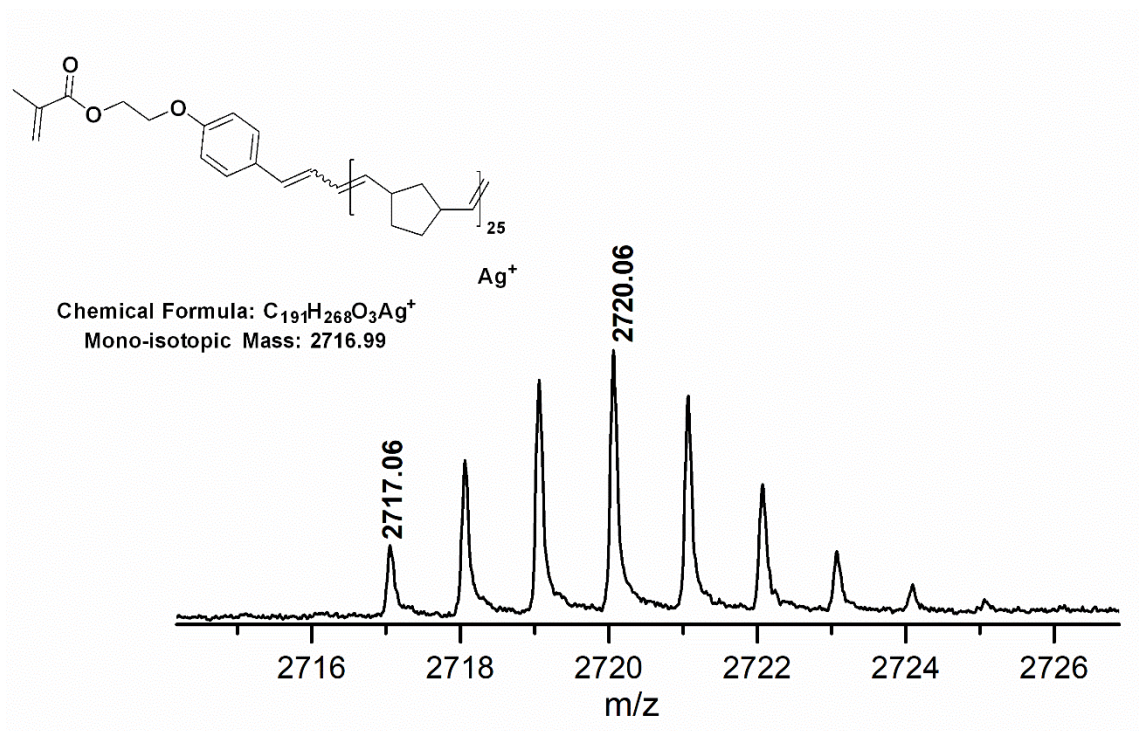
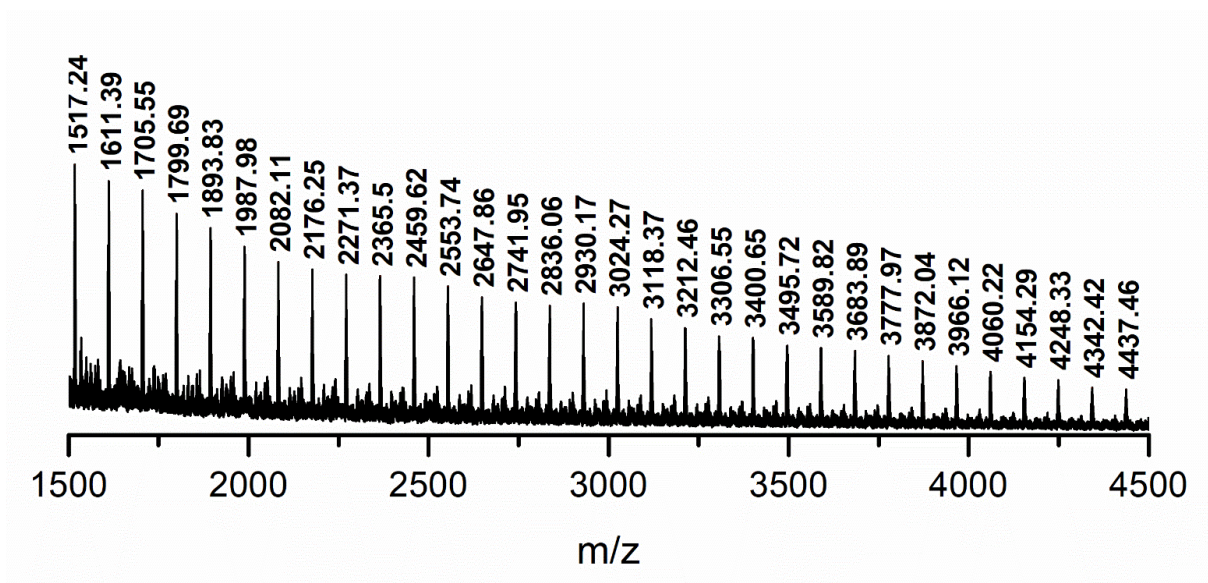


Fig. S193: MALDI-ToF mass spectrum (DCTB, AgTFA) of P18.



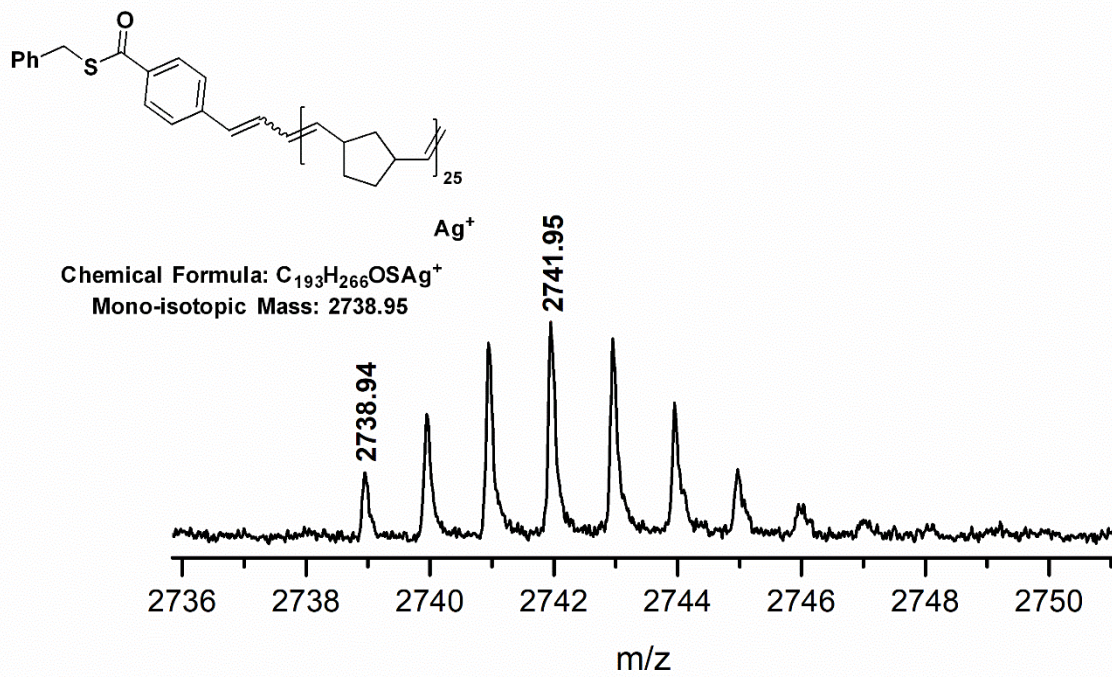
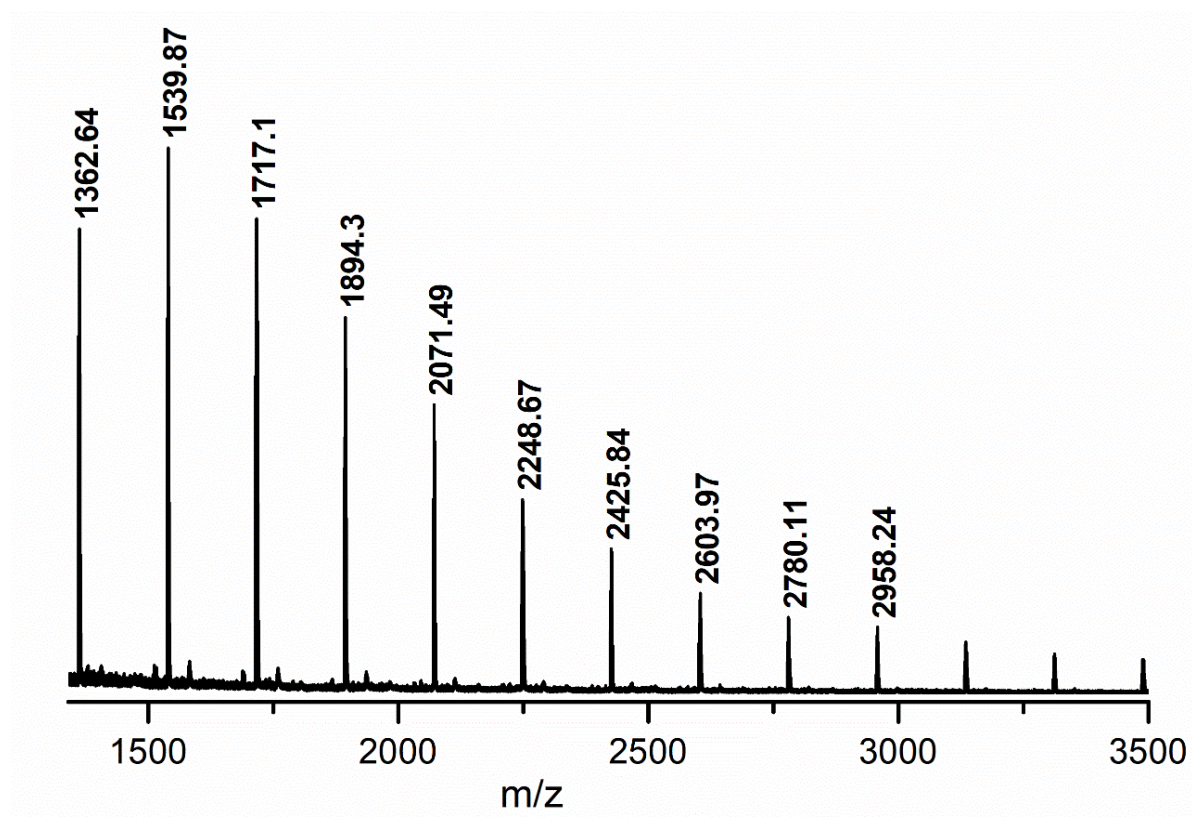


Fig. S194: MALDI-ToF mass spectrum (DCTB, AgTFA) of P19.



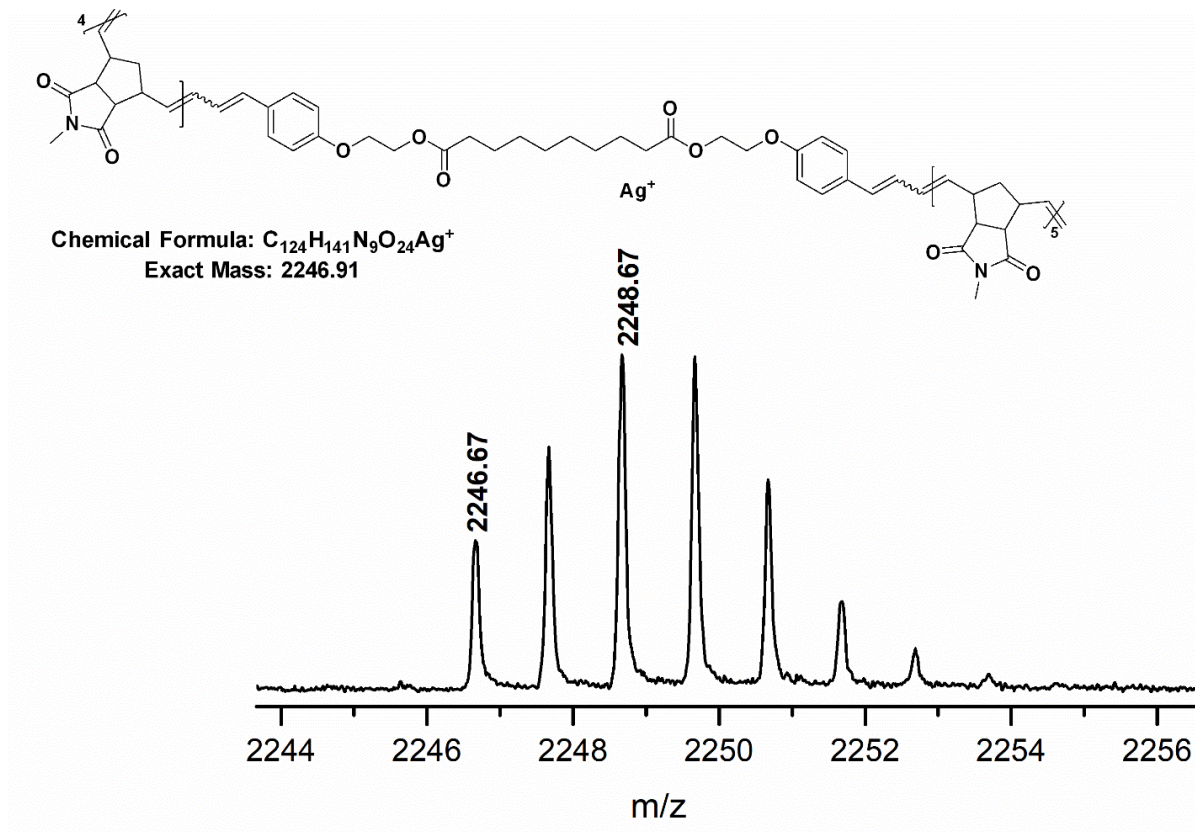
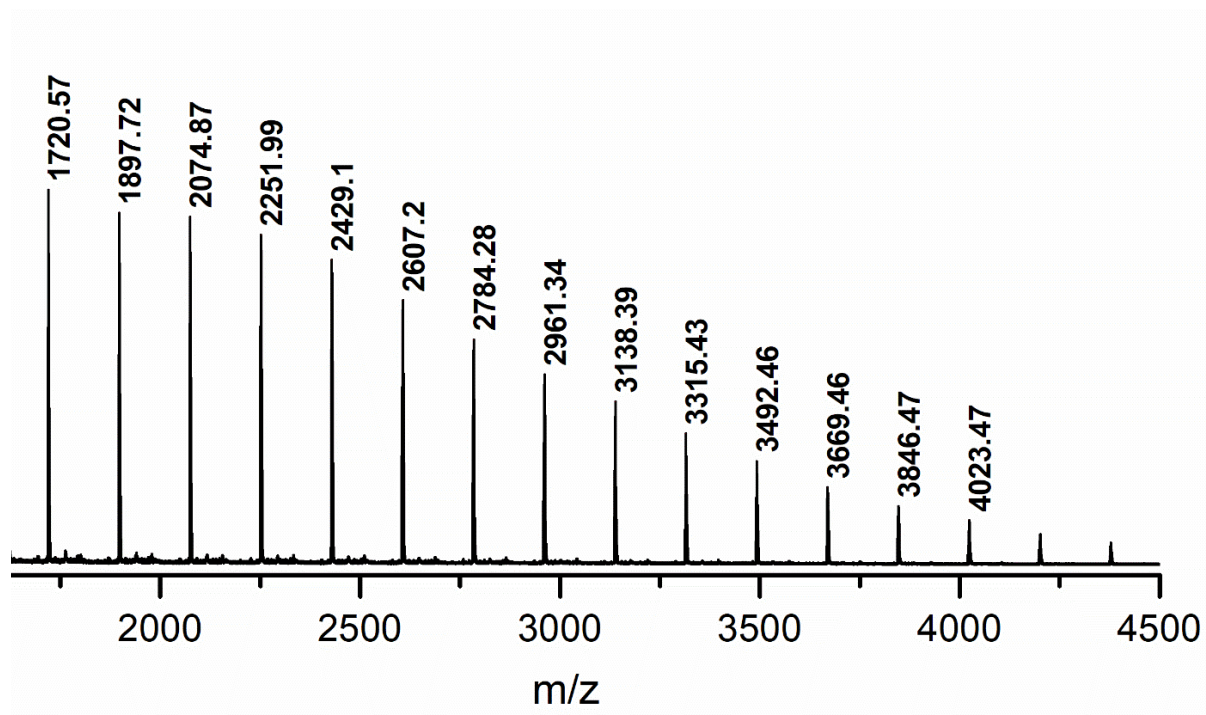


Fig. S195: MALDI-ToF mass spectrum (DCTB, AgTFA) of P20.



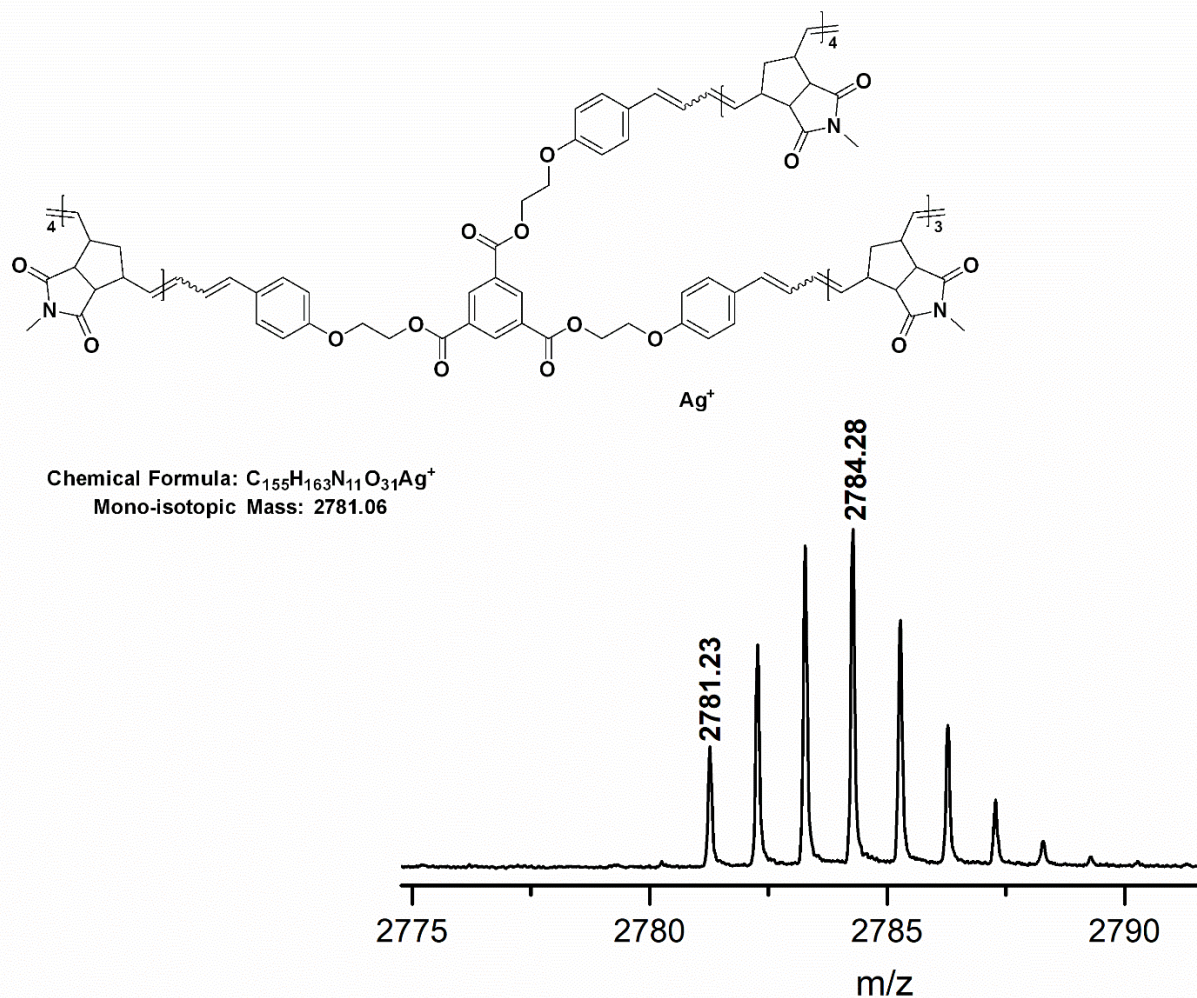
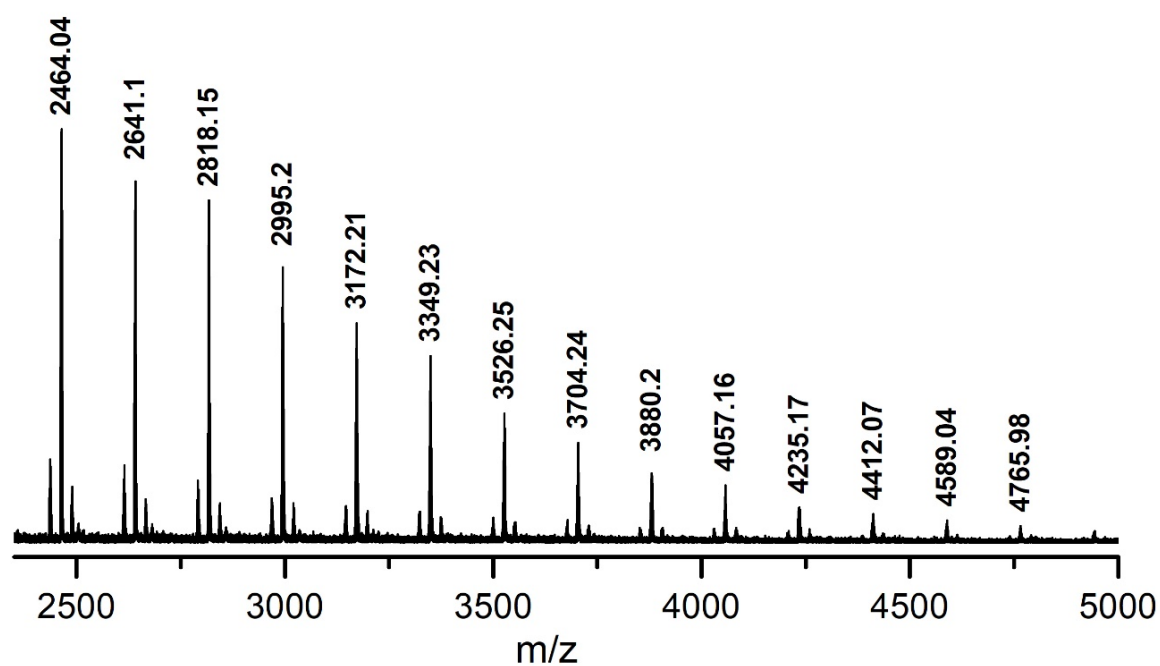


Fig. S196: MALDI-ToF mass spectrum (DCTB, AgTFA) of P21.



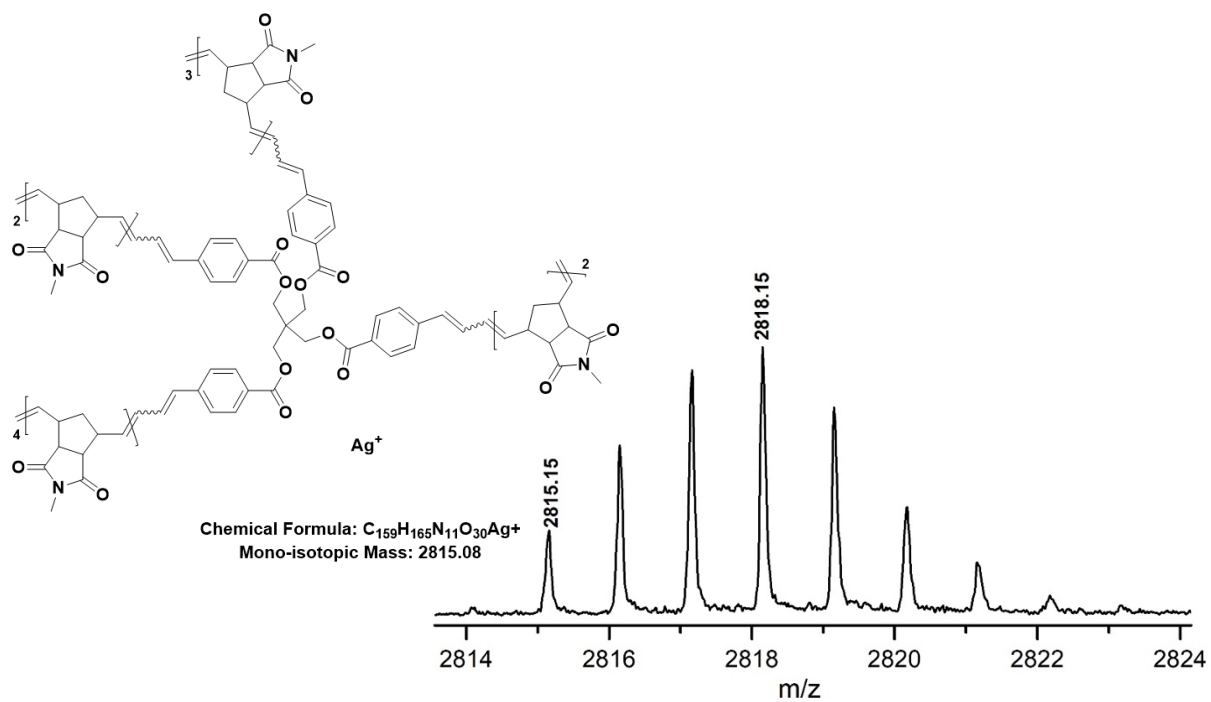
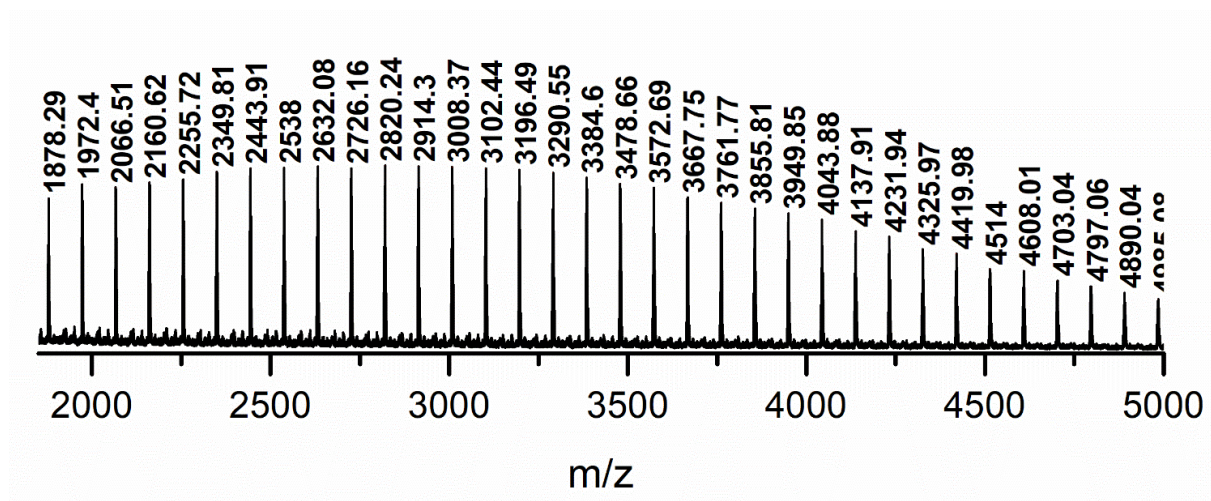


Fig. S197: MALDI-ToF mass spectrum (DCTB, AgTFA) of P22.



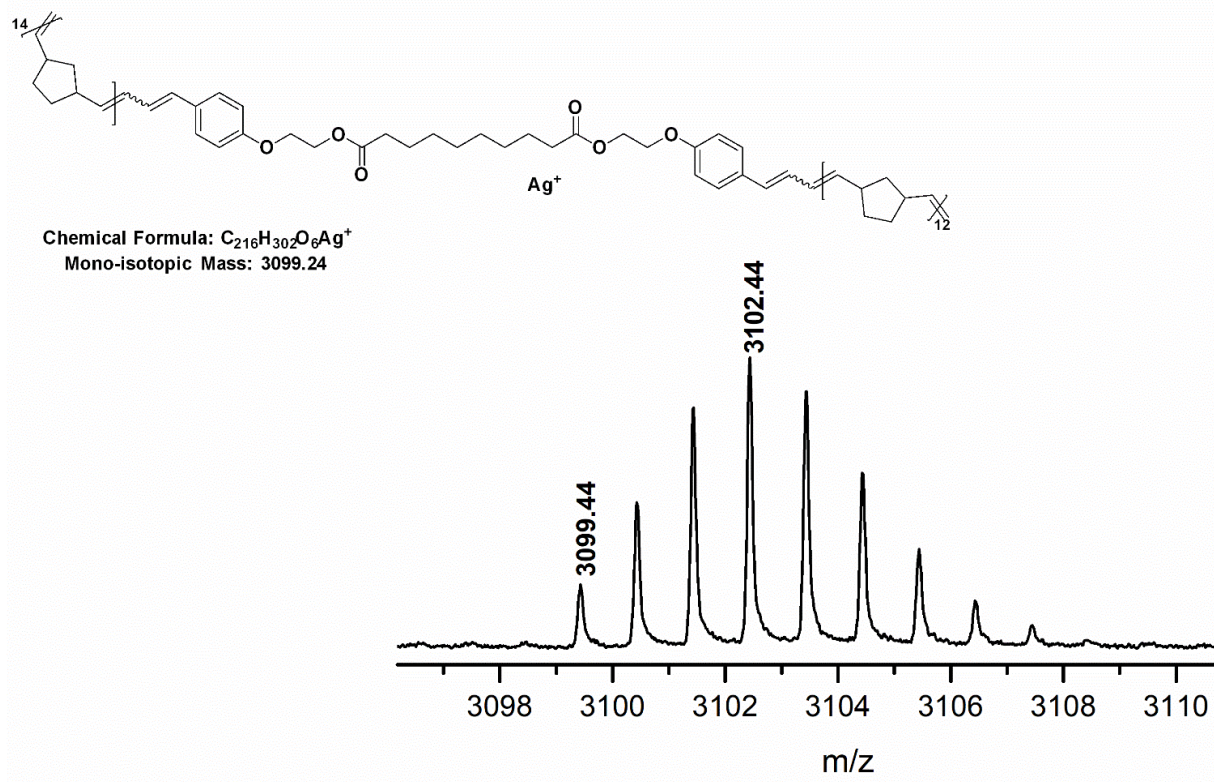
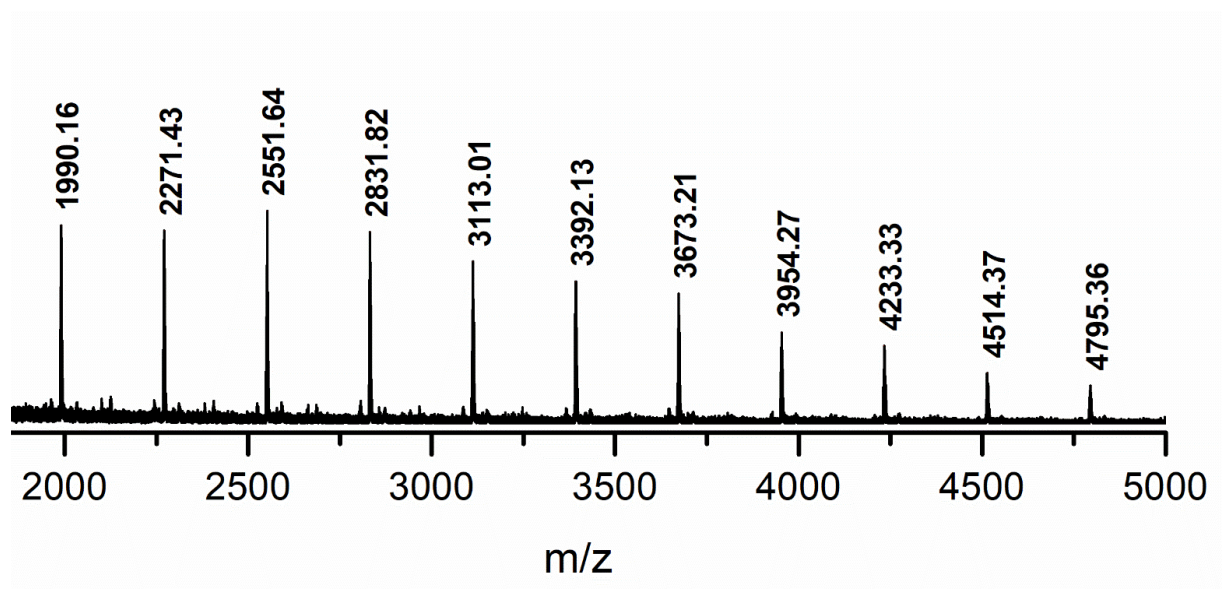


Fig. S198: MALDI-ToF mass spectrum (DCTB, AgTFA) of P24.



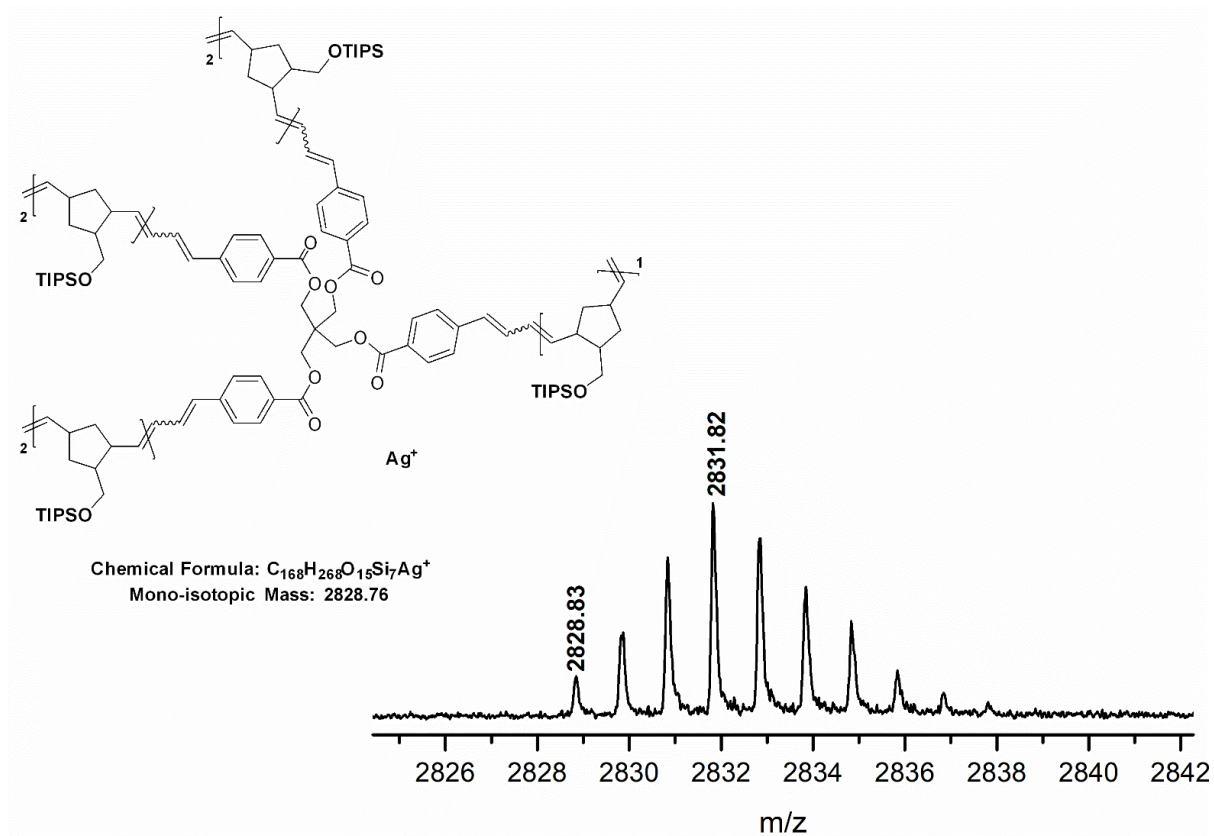
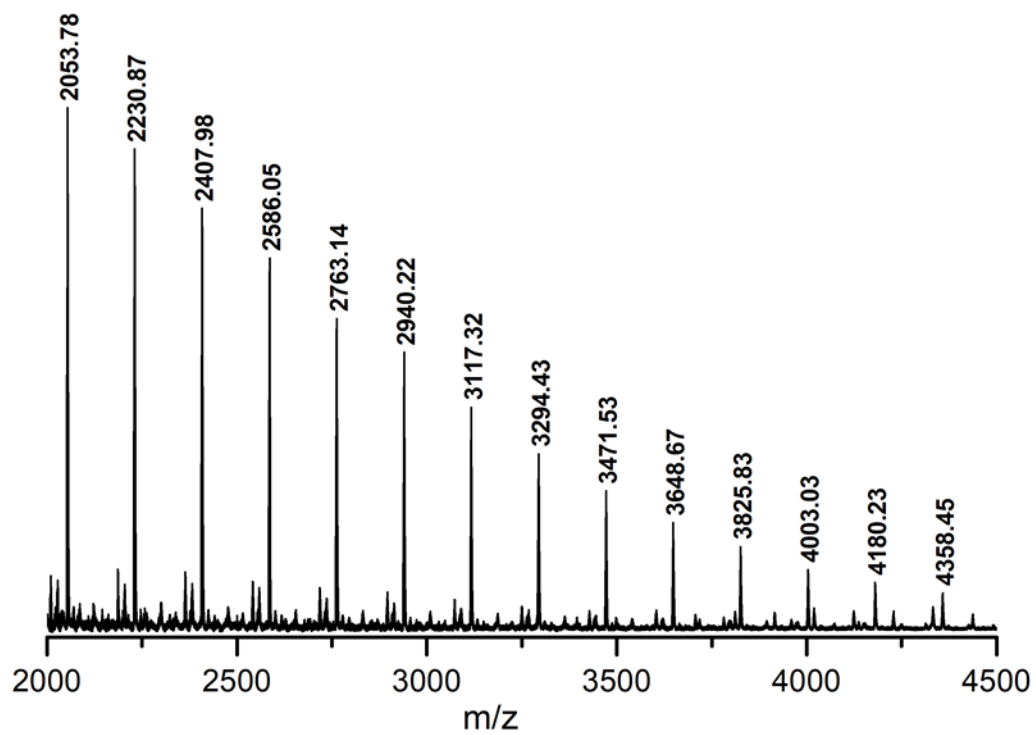


Fig. S199: MALDI-ToF mass spectrum (DCTB, AgTFA) of P25.



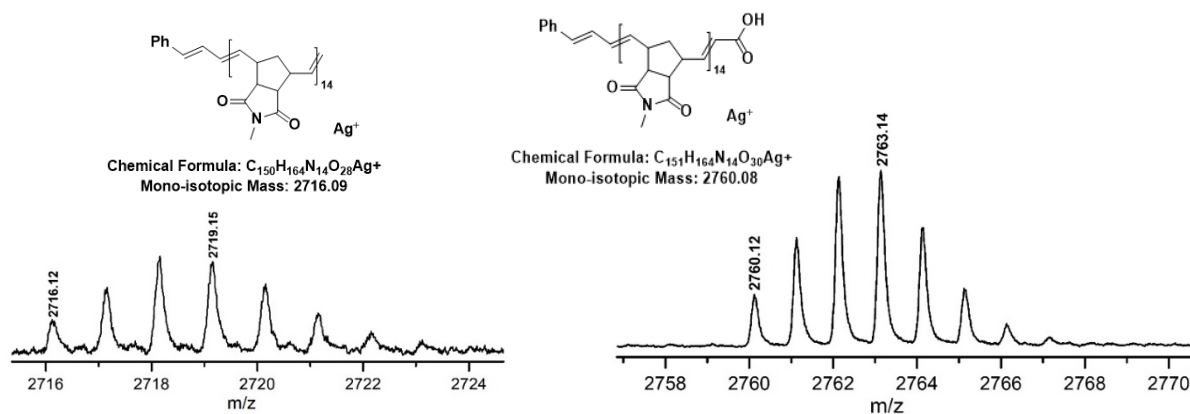


Fig. S200: MALDI-ToF mass spectrum (DCTB, AgTFA) of **P34**. The minor distribution matching with a methylene end group came from the ethyl vinyl ether (which was used to deactivate the ruthenium complex).

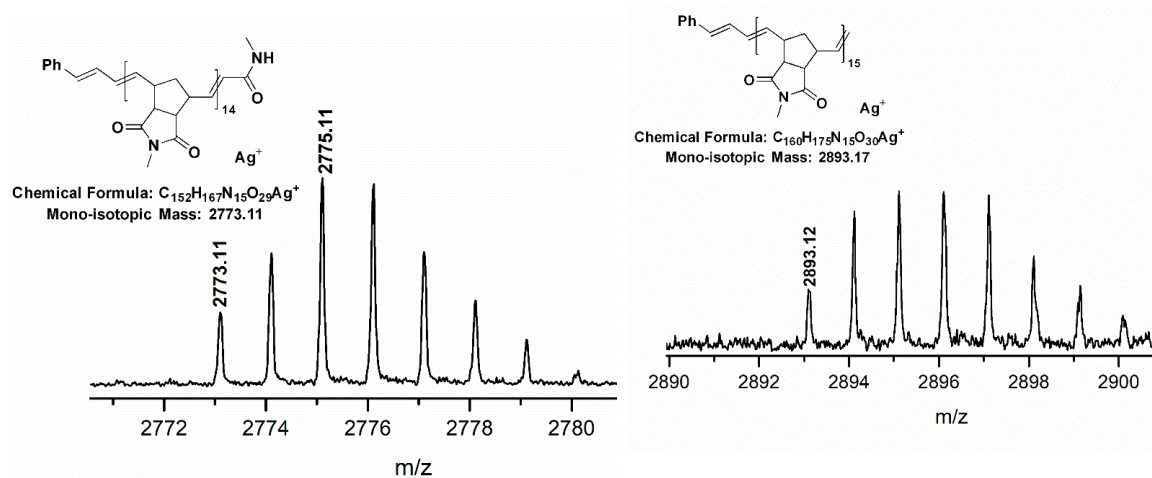
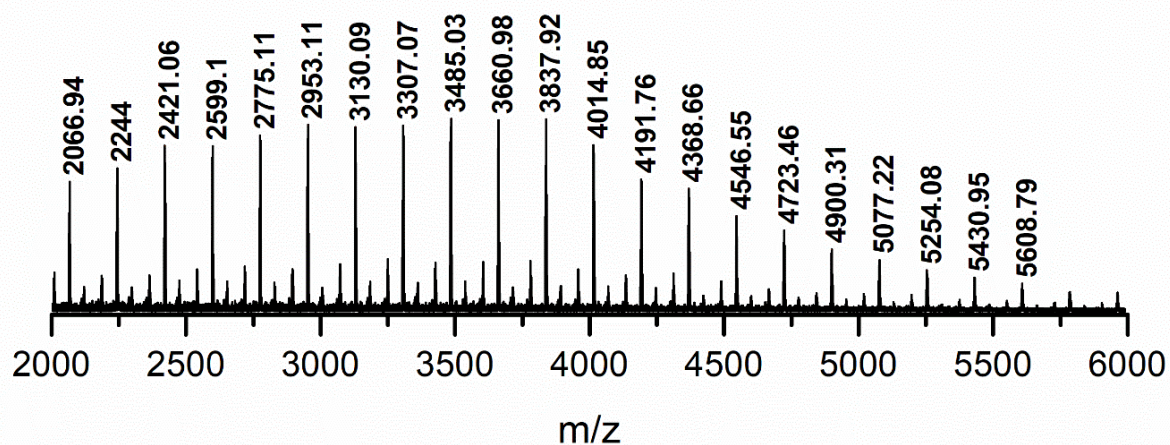


Fig. S201: MALDI-ToF mass spectrum (DCTB, AgTFA) of **P37**.

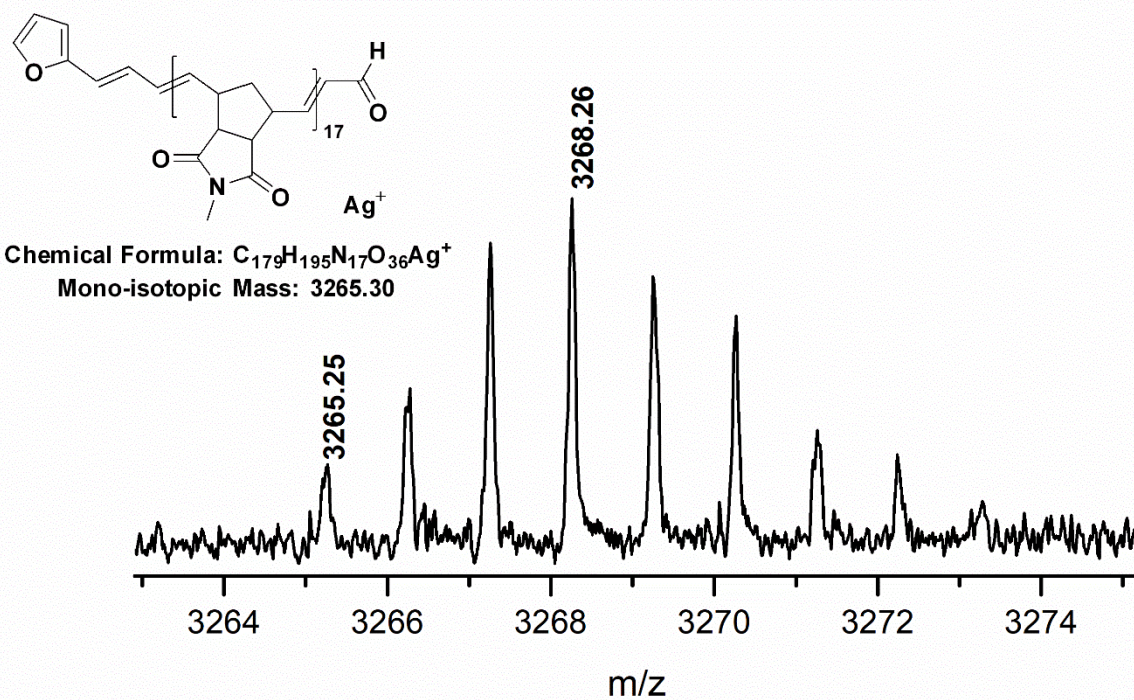
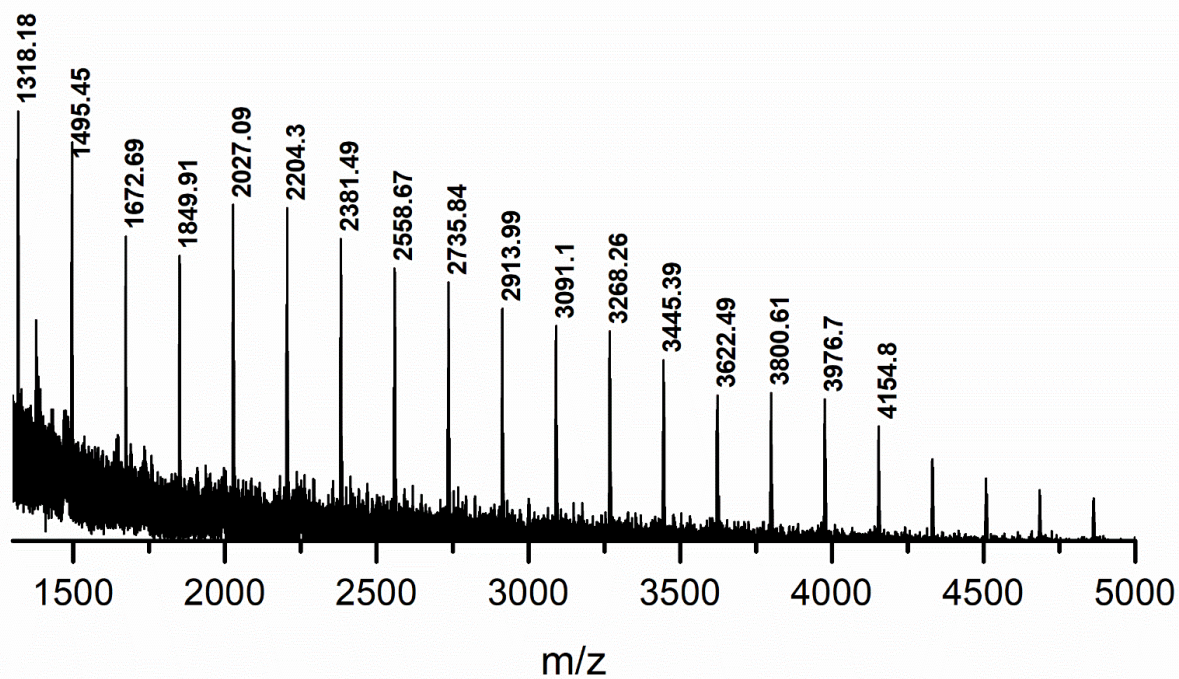


Fig. S202: MALDI-ToF mass spectrum (DCTB, AgTFA) of P38.

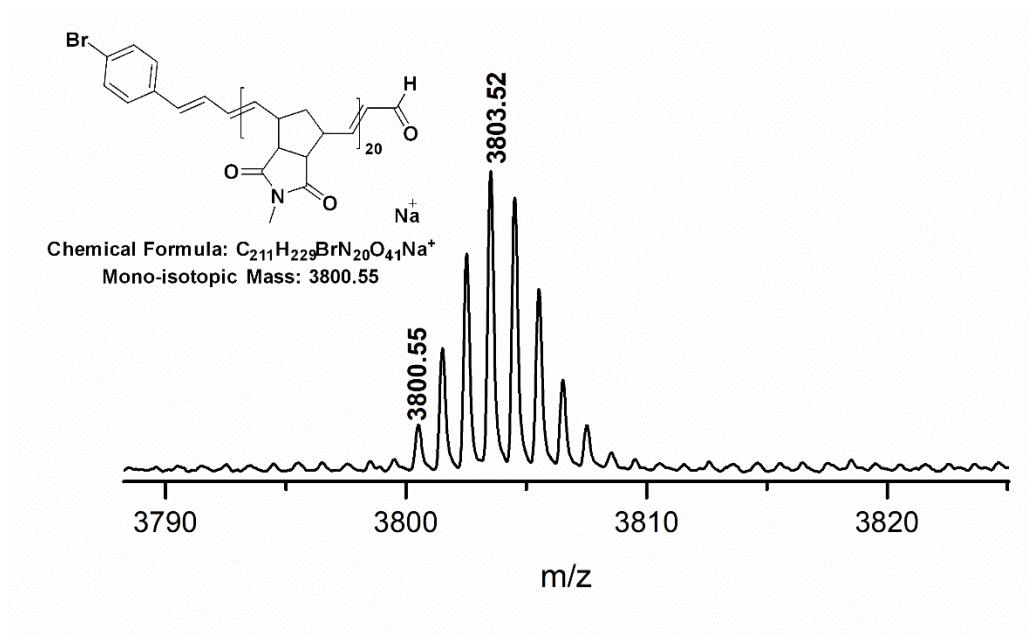
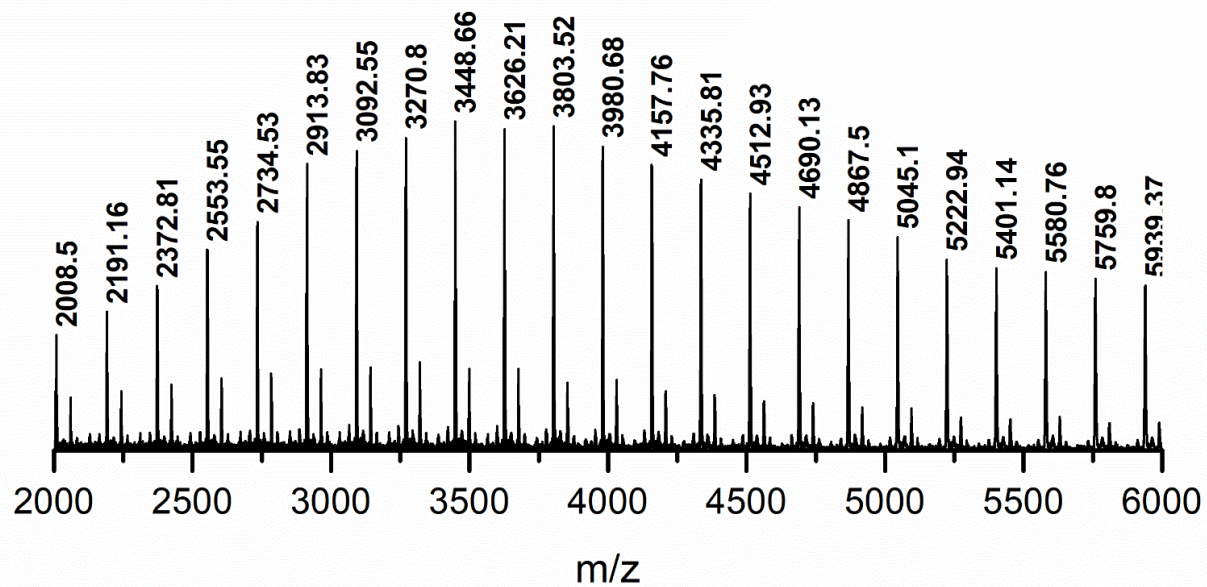


Fig. S203: MALDI-ToF mass spectrum (DCTB, NaTFA) of P39.

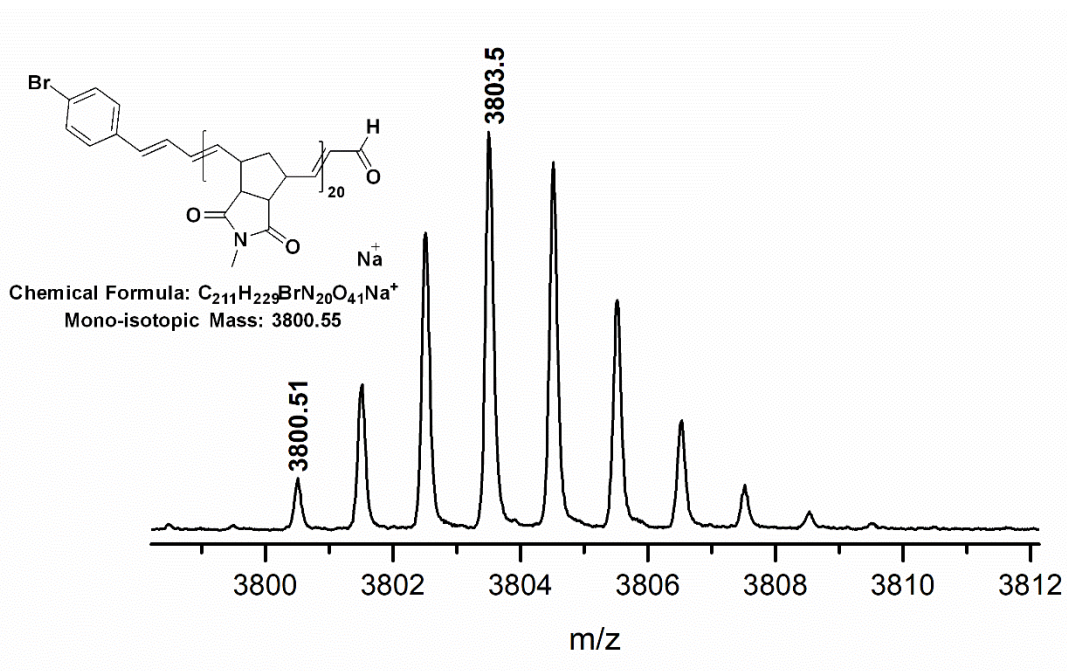
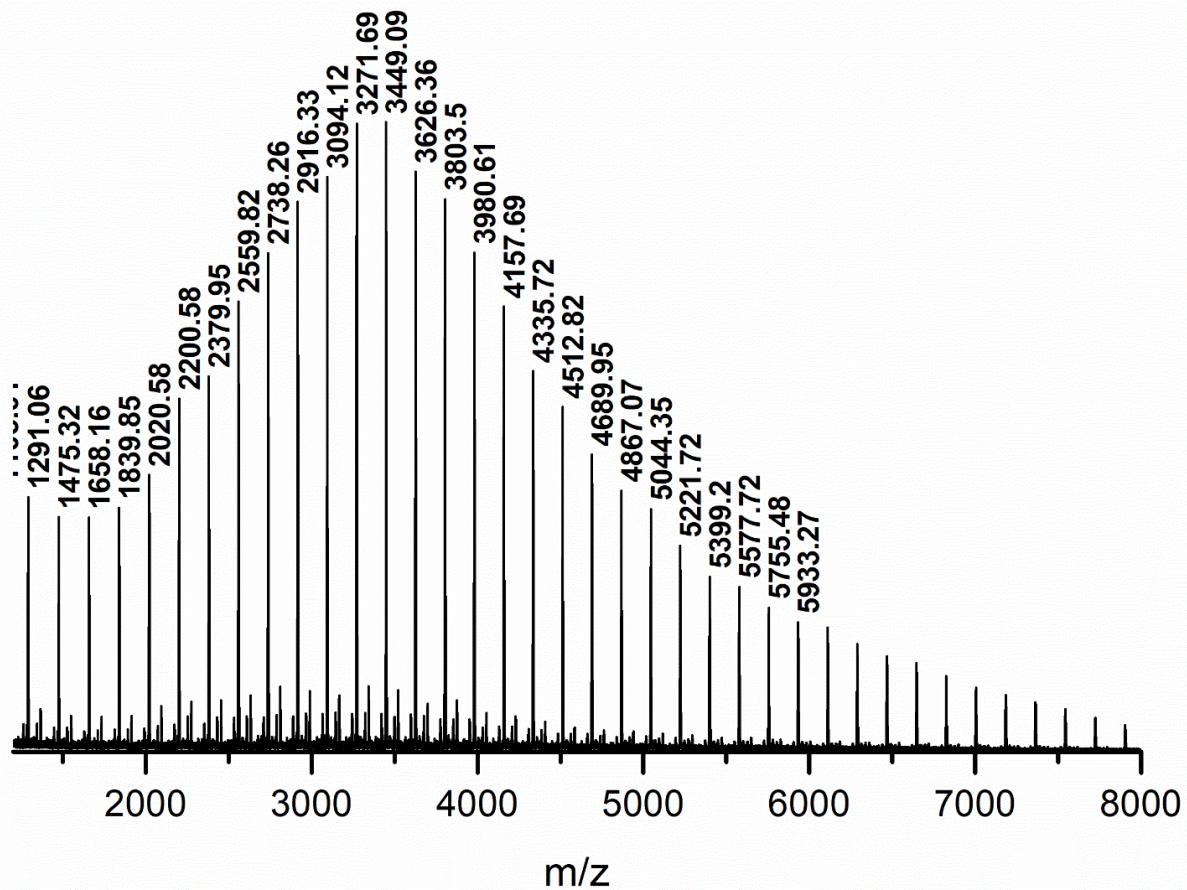


Fig. S204: MALDI-ToF mass spectrum (DCTB, NaTFA) of P42.

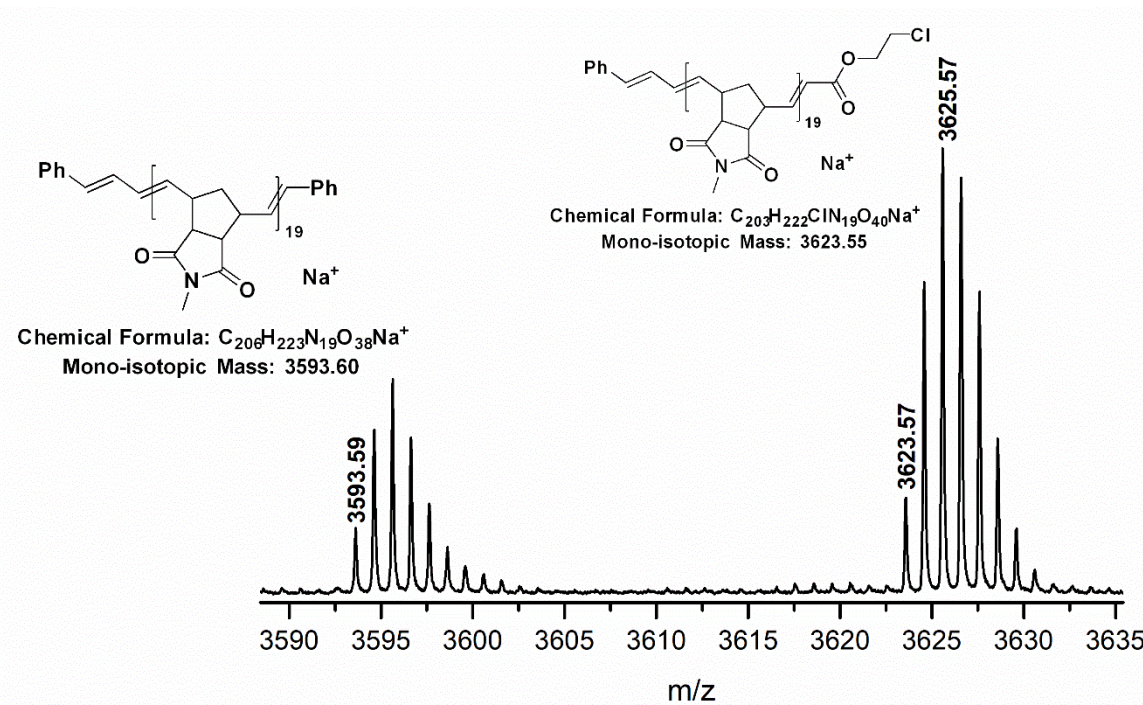
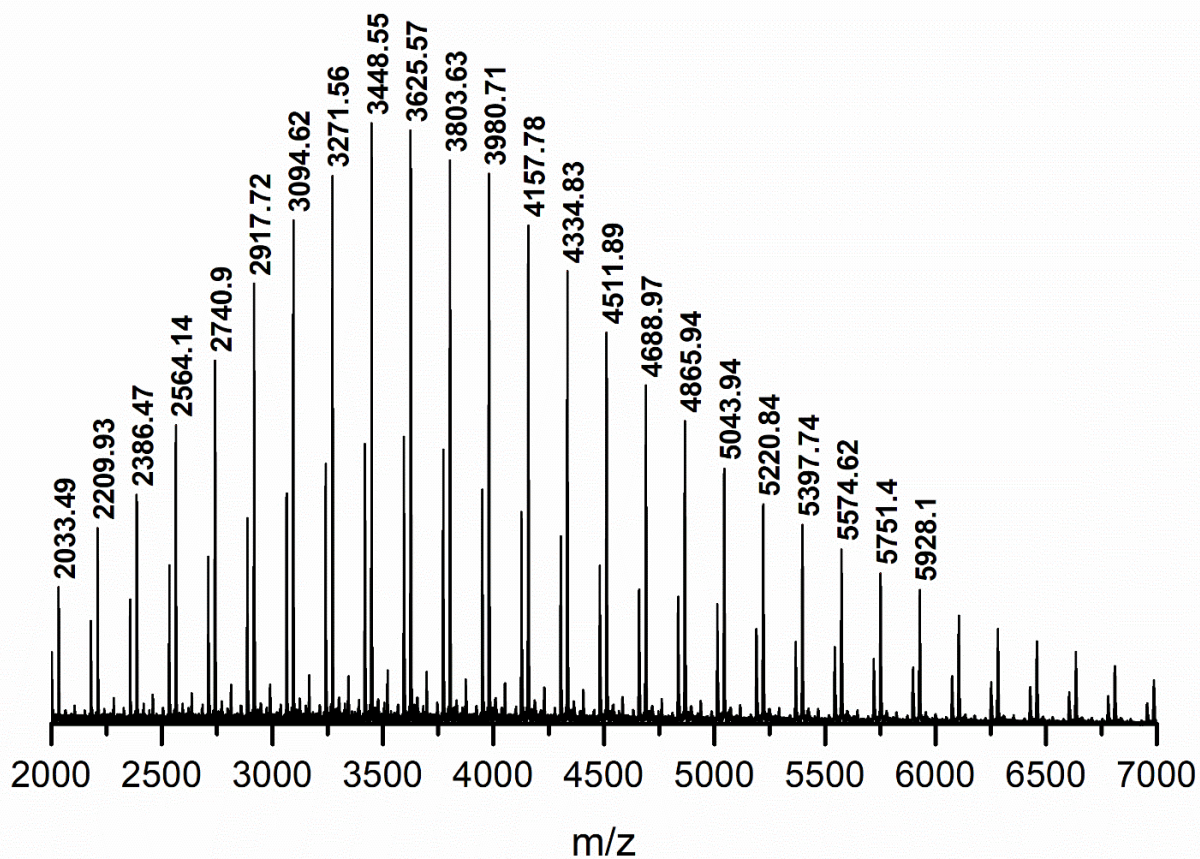
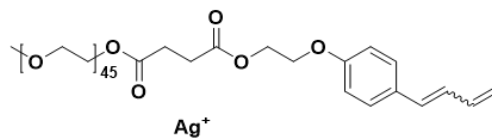
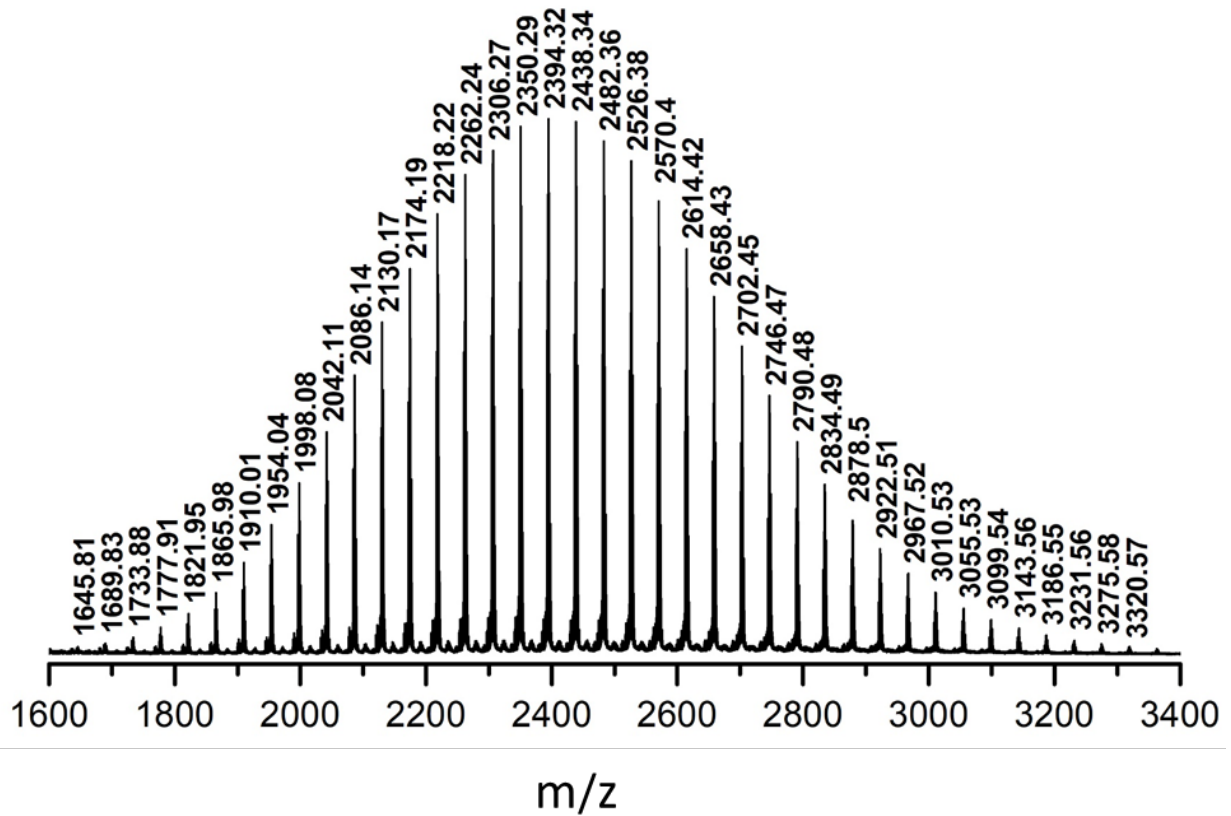


Fig. S205: MALDI-ToF mass spectrum (DCTB, NaTFA) of P43.



Chemical Formula: $\text{C}_{107}\text{H}_{200}\text{O}_{50}\text{Ag}^+$
 Mono-isotopic Mass: 2392.22

Ag^+

Chemical Formula: $\text{C}_{103}\text{H}_{206}\text{O}_{52}\text{Ag}^+$
 Mono-isotopic Mass: 2384.27

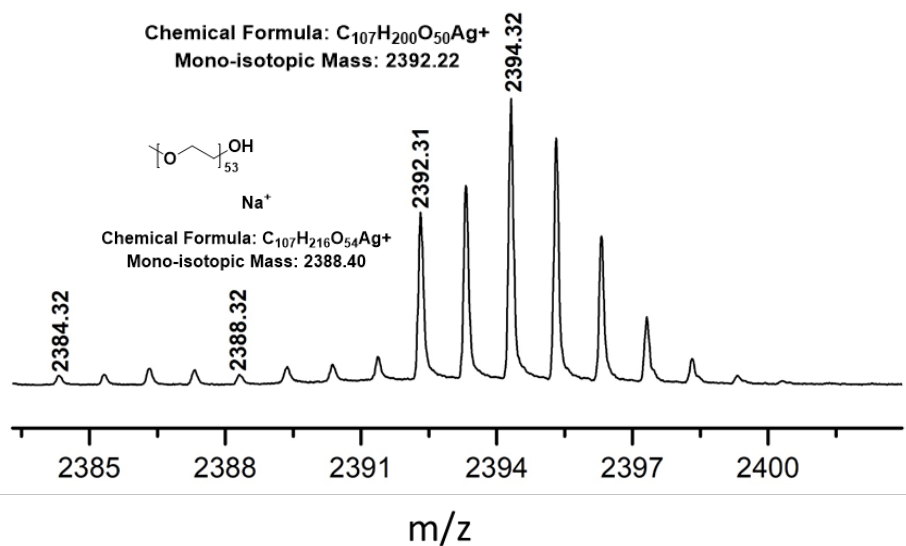


Fig. S207: MALDI-ToF mass spectrum (DCTB, AgTFA) of **PEG_{2k} macroinitiator**. Shallow intensity peaks corresponded to monomethoxy PEG that could come from hydrolysis of PEG_{2k} carboxylic acid during the reaction.

SEC traces of polymers:

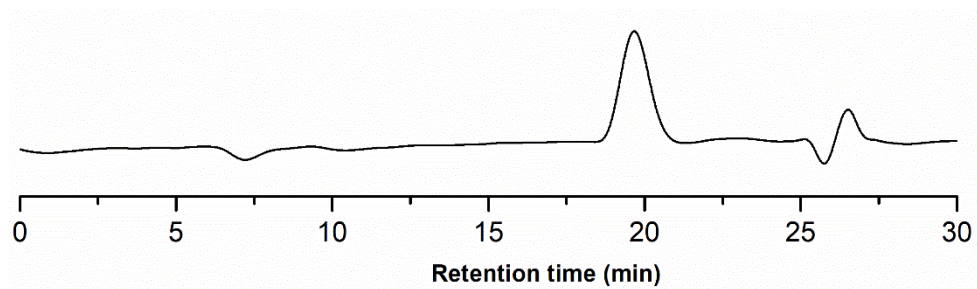


Fig. S208: SEC (CHCl_3) trace for P1.

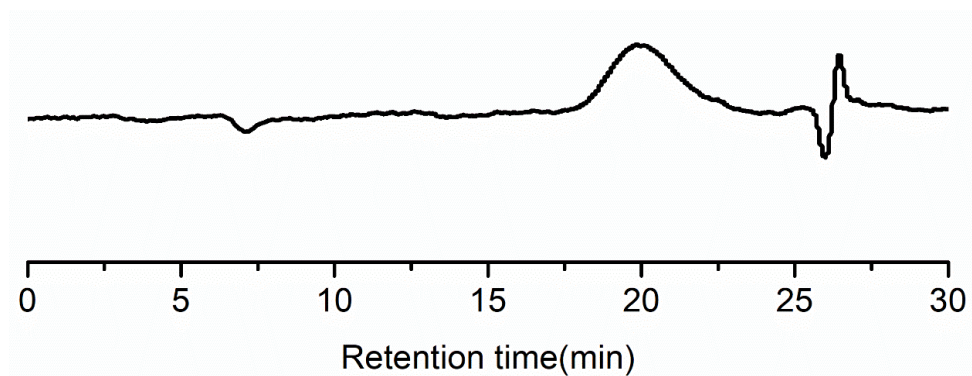


Fig. S209: SEC (CHCl_3) trace for P2.

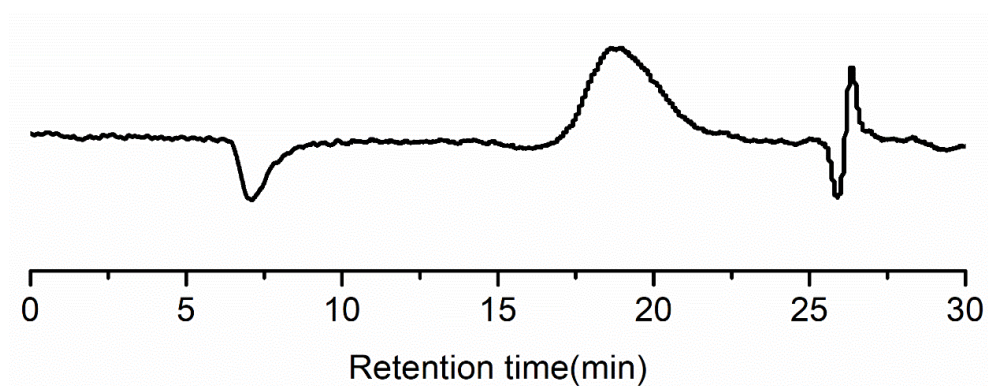


Fig. S210: SEC (CHCl_3) trace for P3.

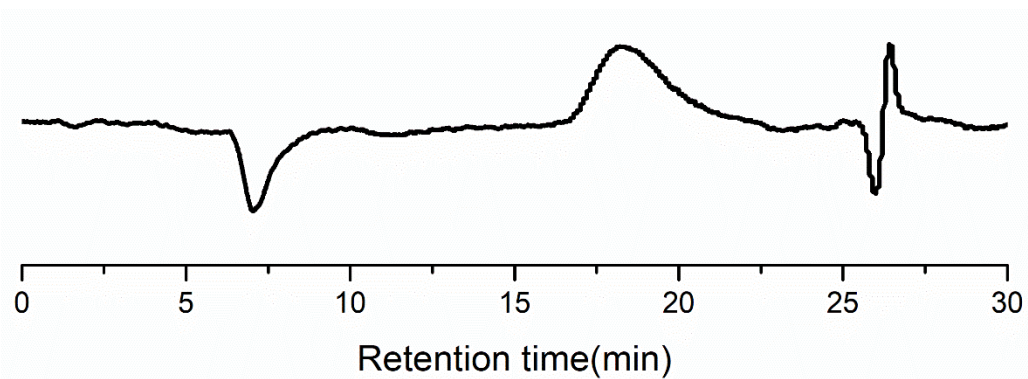


Fig. S211: SEC (CHCl_3) trace for **P4**.

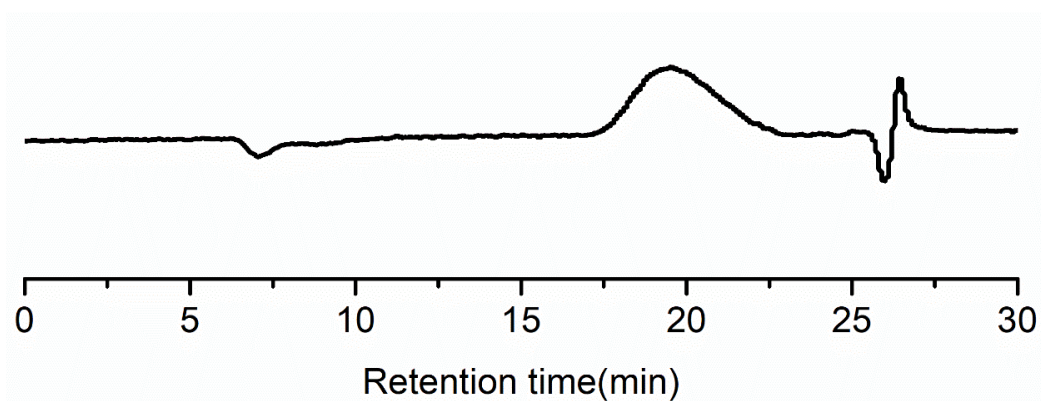


Fig. S212: SEC (CHCl_3) trace for **P5 (crude polymer)**.

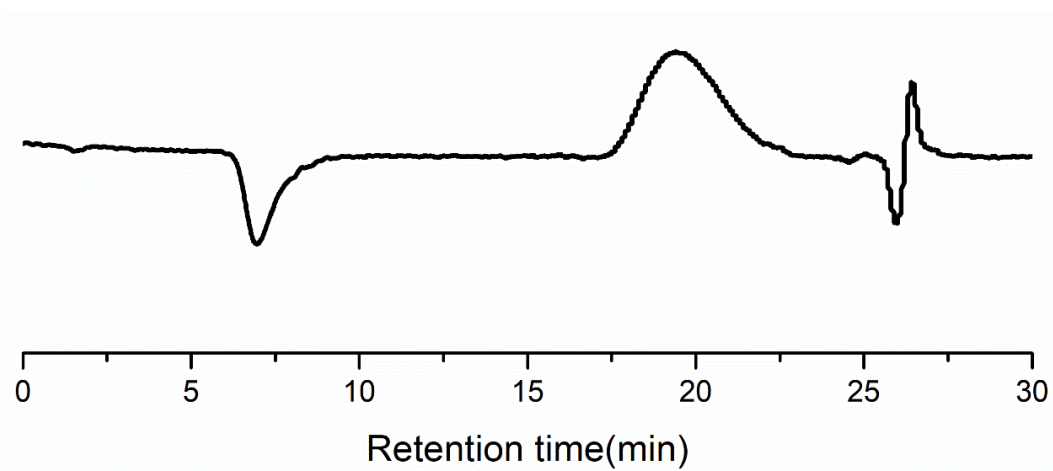


Fig. S213: SEC (CHCl_3) trace for **P5 (precipitated polymer)**.

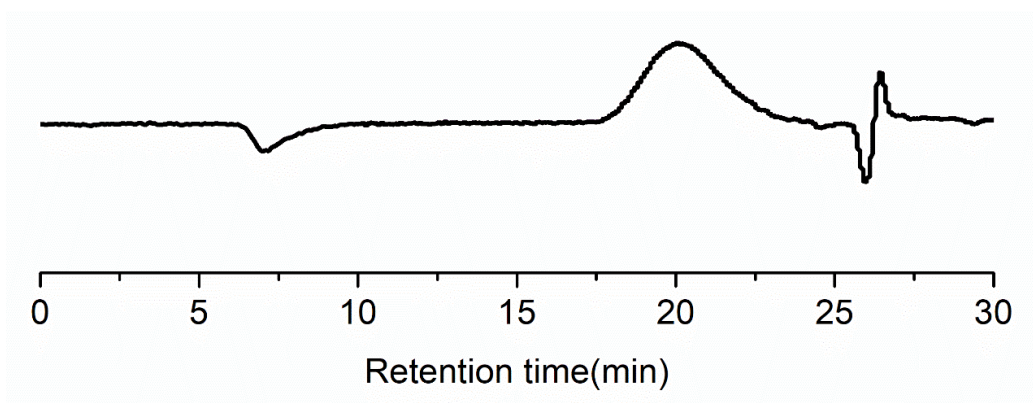


Fig. S214: SEC (CHCl₃) trace for **P6**.

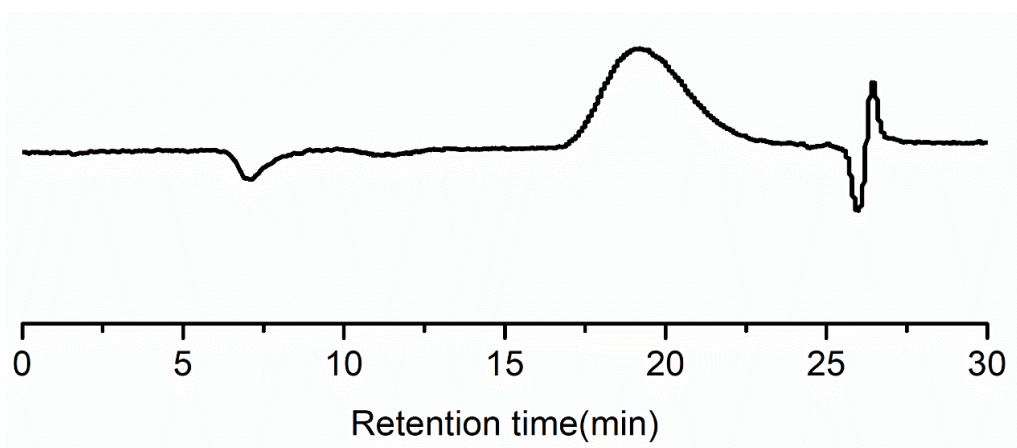


Fig. S215: SEC (CHCl₃) trace for **P7**.

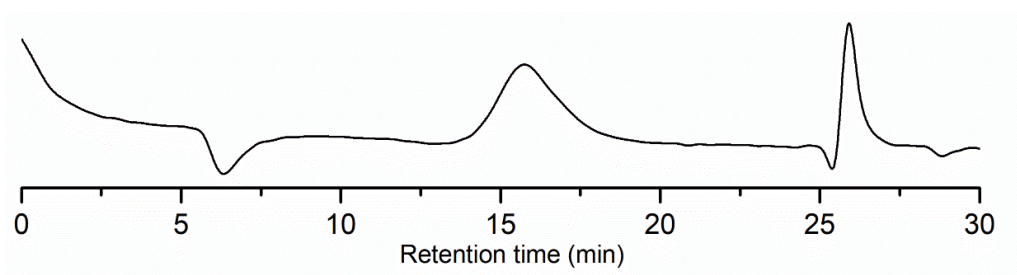


Fig. S216: SEC (CHCl₃) trace for **P8**.

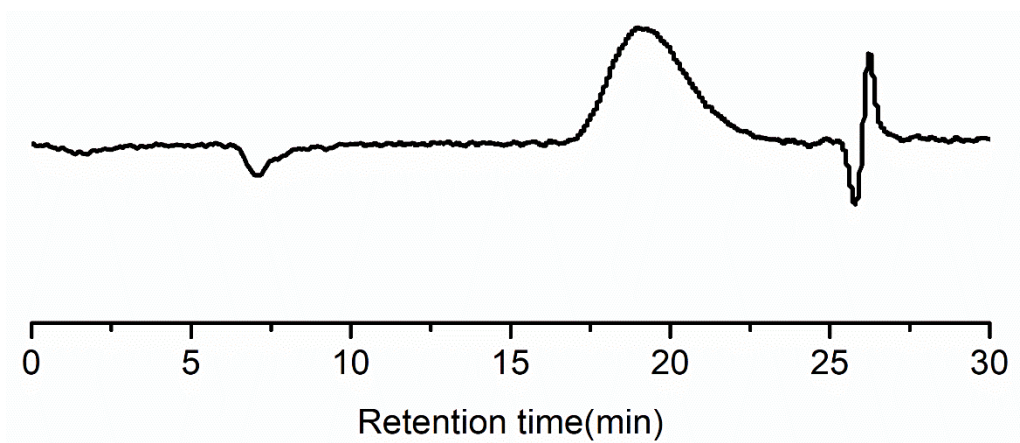


Fig. S217: SEC (CHCl₃) trace for **P9**.

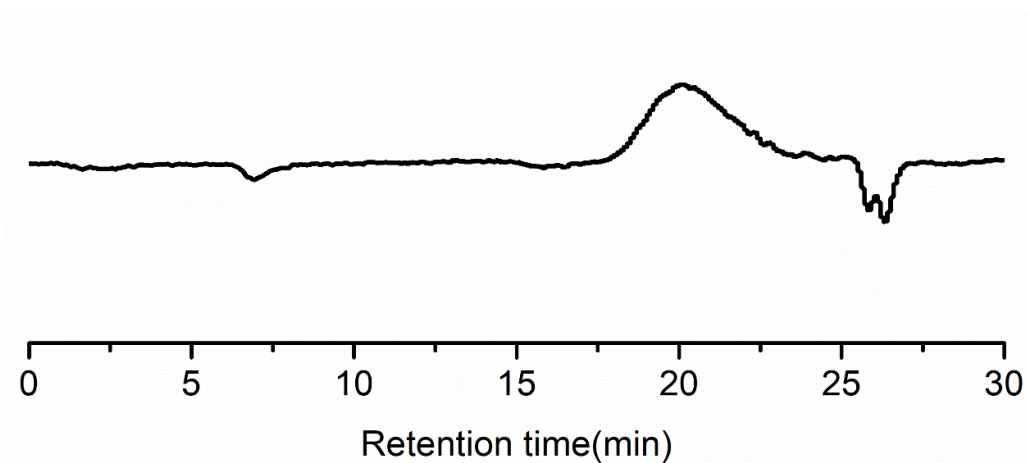


Fig. S218: SEC (CHCl₃) trace for **P10**.

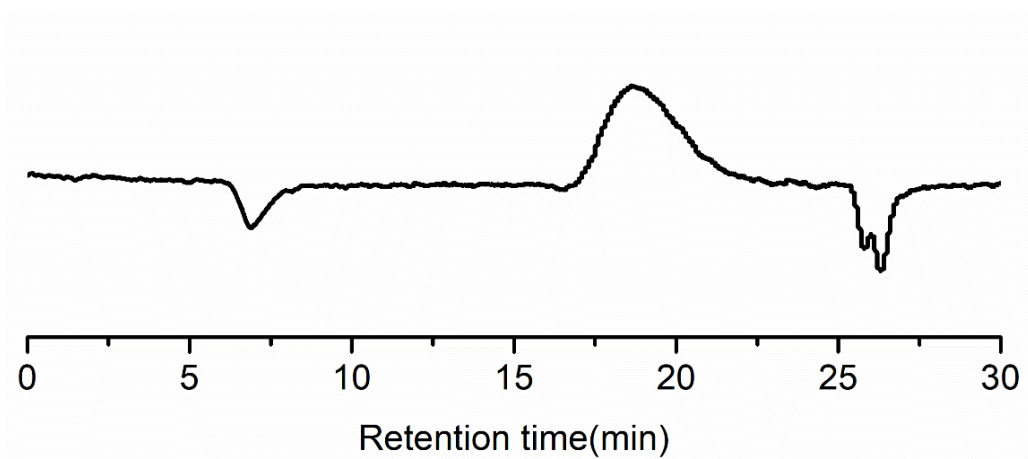


Fig. S219: SEC (CHCl₃) trace for **P11**.

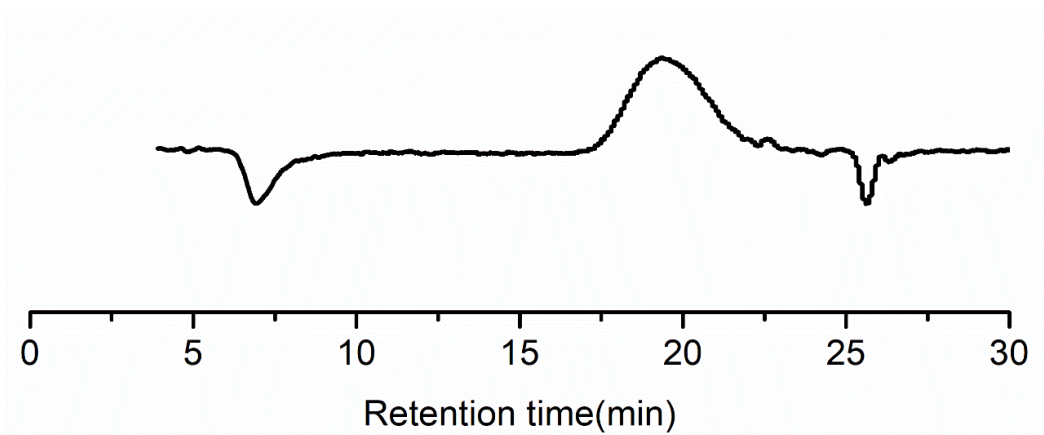


Fig. S220: SEC (CHCl₃) trace for **P12**.

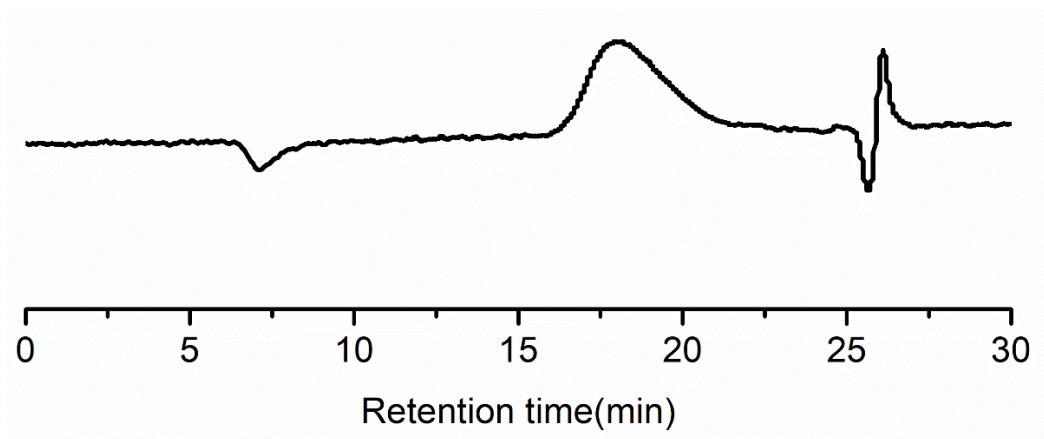


Fig. S221: SEC (CHCl₃) trace for **P13**.

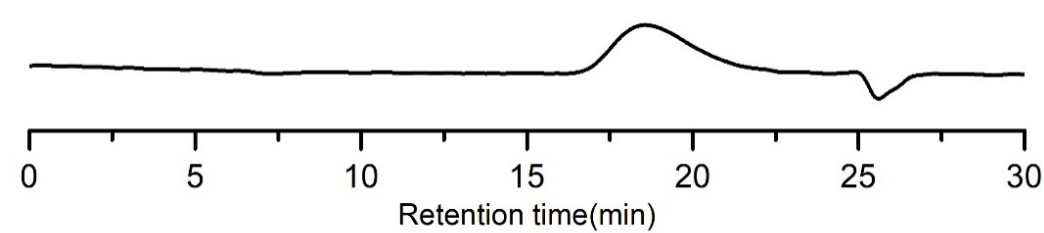


Fig. S222: SEC (CHCl₃) trace for **P14**.

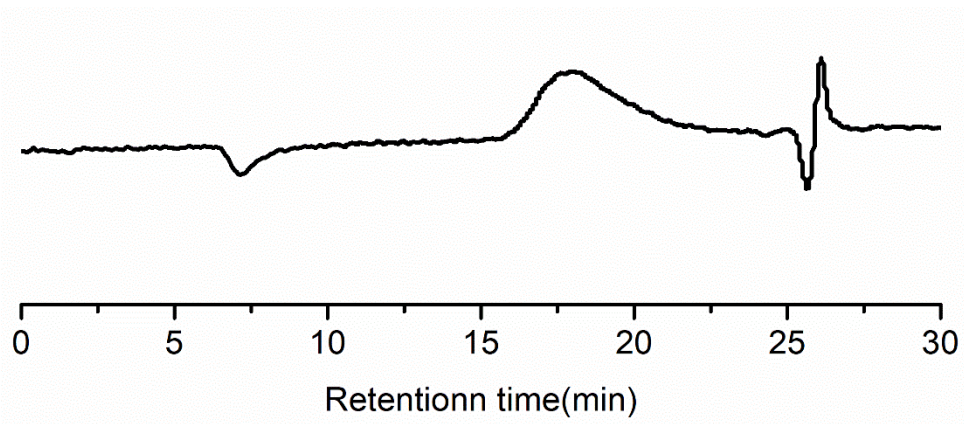


Fig. S223: SEC (CHCl_3) trace for P15.

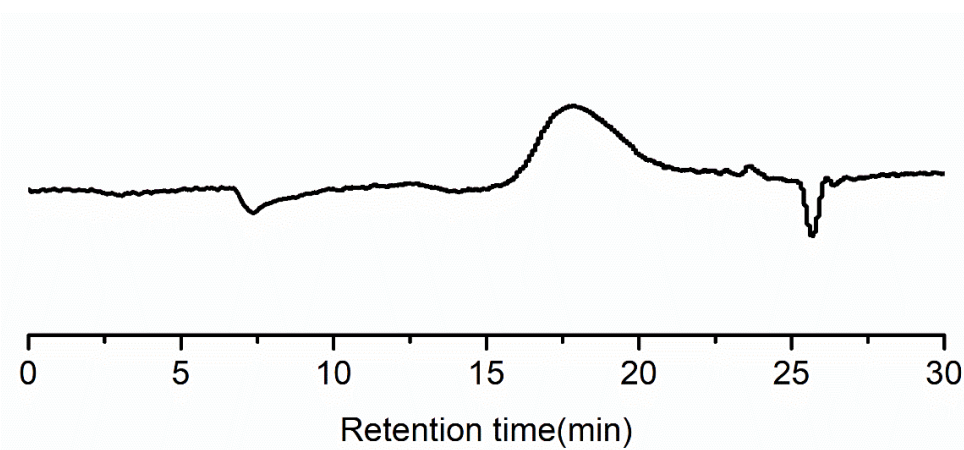


Fig. S224: SEC (CHCl_3) trace for P16.

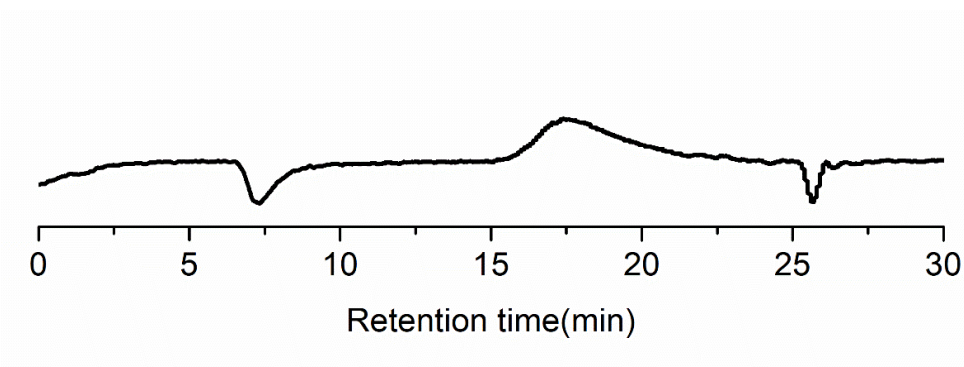


Fig. S225: SEC (CHCl_3) trace for P17.

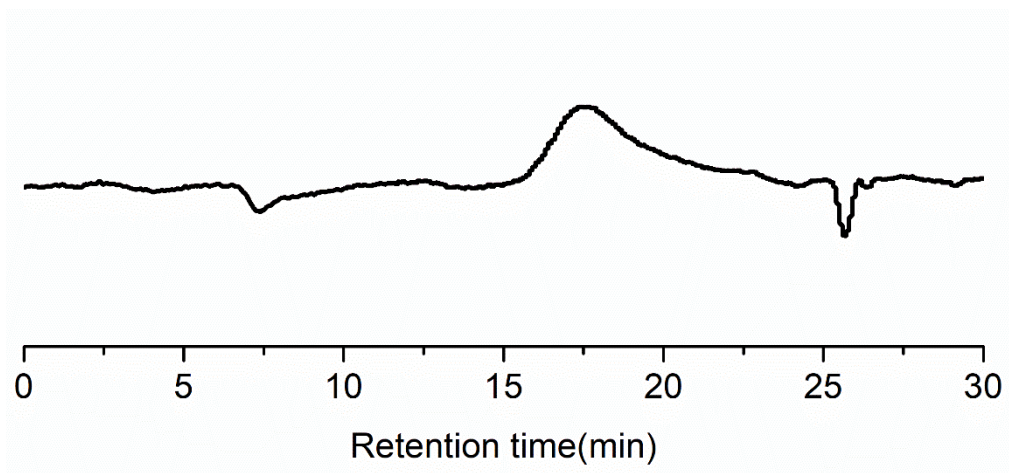


Fig. S226: SEC (CHCl₃) trace for P18.

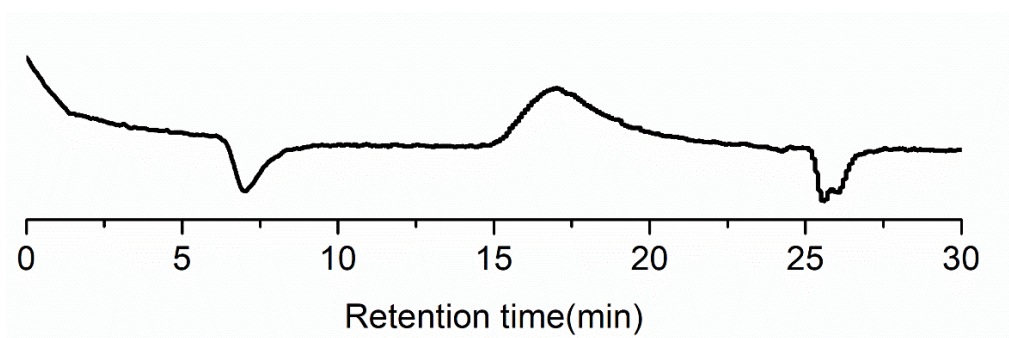


Fig. S227: SEC (CHCl₃) trace for P19.

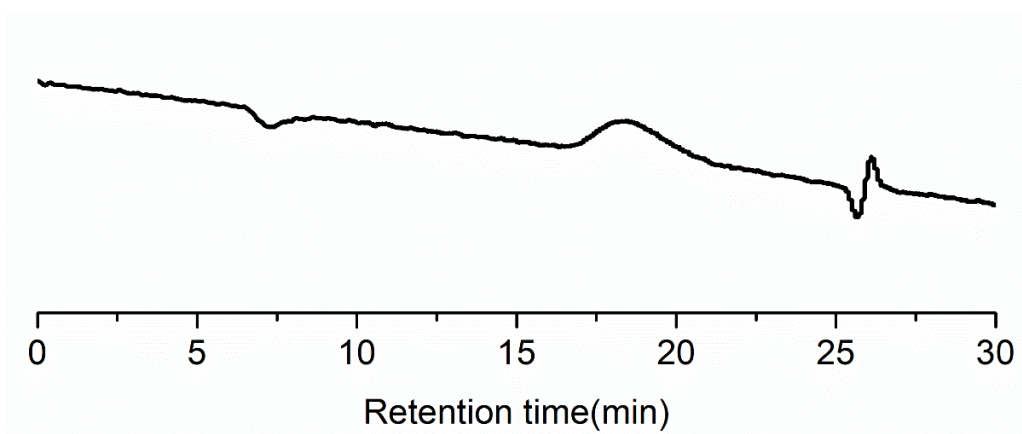


Fig. S228: SEC (CHCl₃) trace for P20.

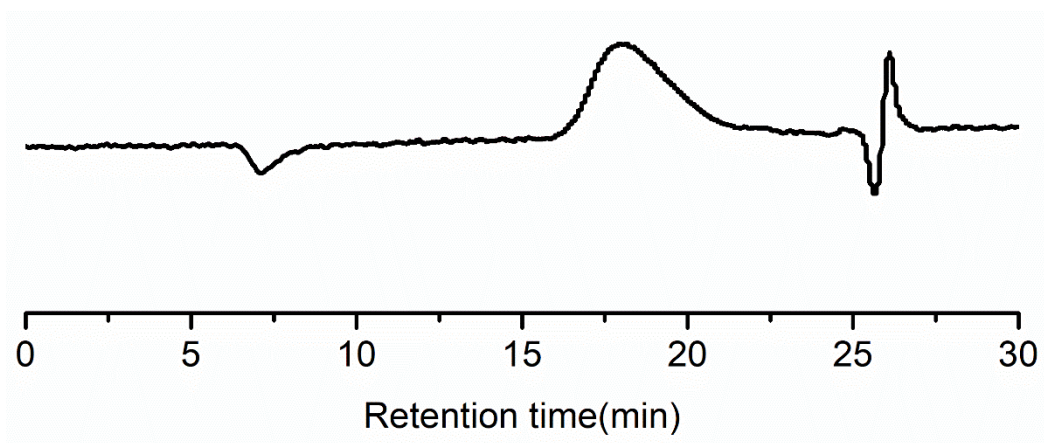


Fig. S229: SEC (CHCl₃) trace for **P21**.

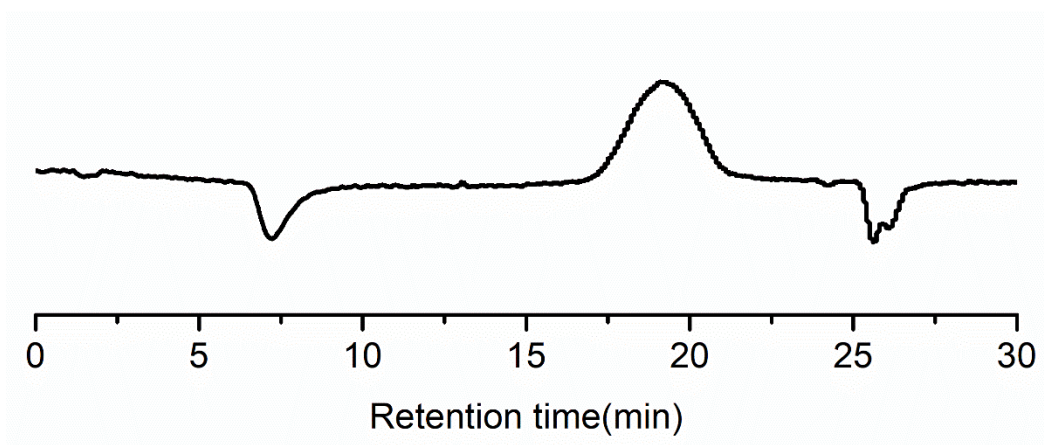


Fig. S230: SEC (CHCl₃) trace for **P22**.

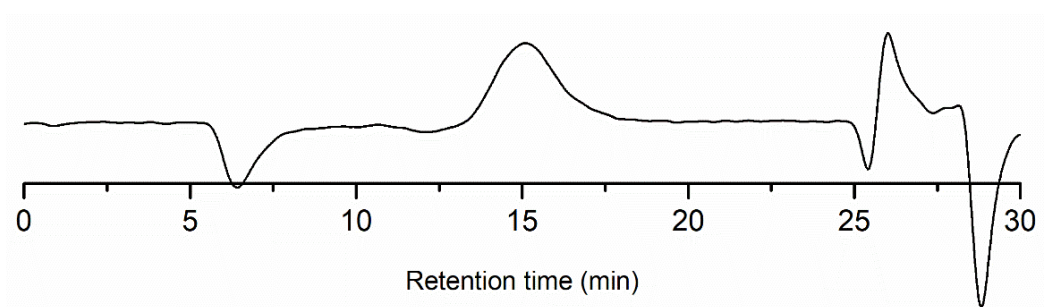


Fig. S231: SEC (CHCl₃) trace for **P23**.

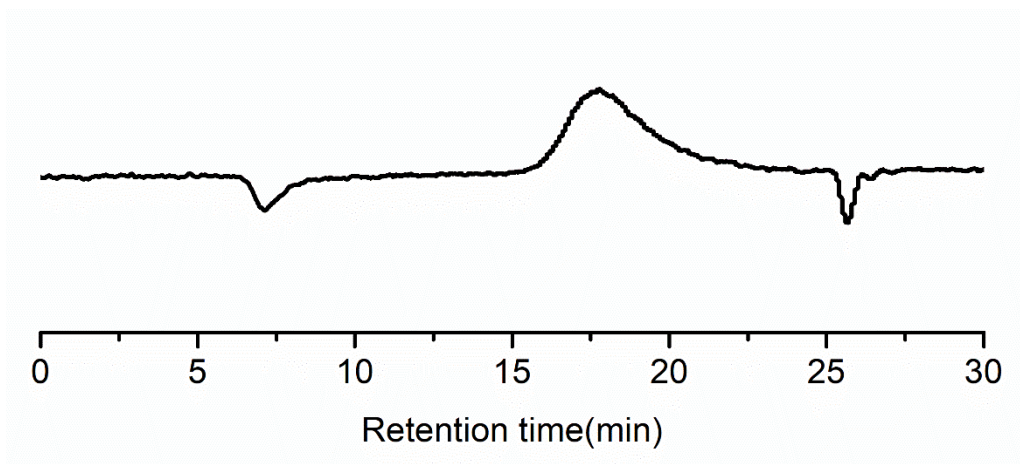


Fig. S232: SEC (CHCl₃) trace for P24.

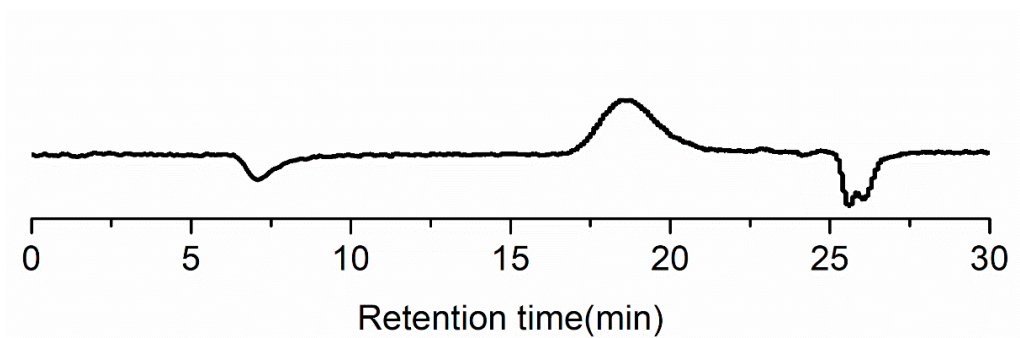


Fig. S233: SEC (CHCl₃) trace for P25.

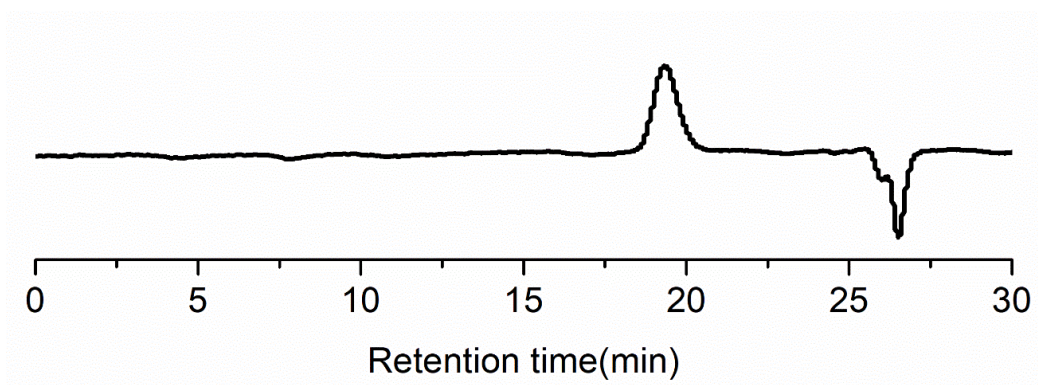


Fig. S234: SEC (CHCl₃) trace for P28.

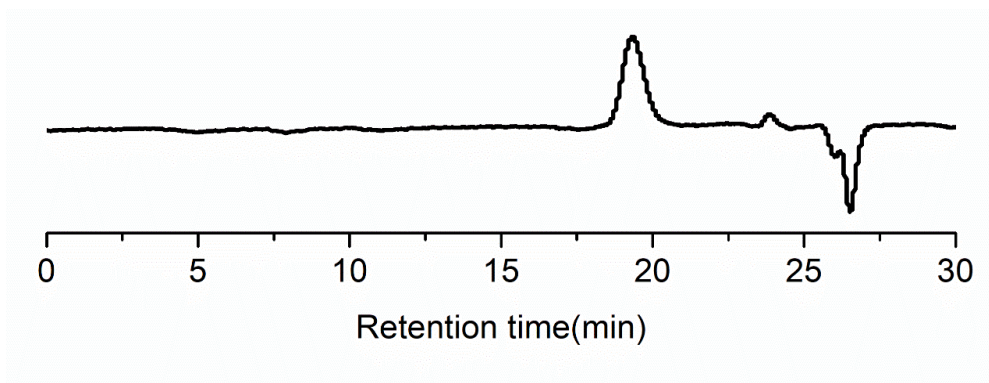


Fig. S235: SEC (CHCl₃) trace for **P30**.

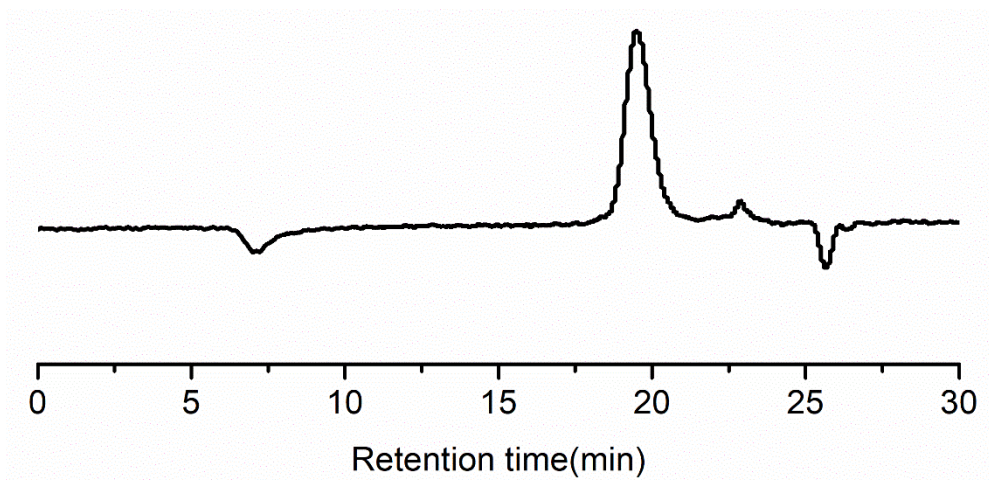


Fig. S236: SEC (CHCl₃) trace for **P31**.

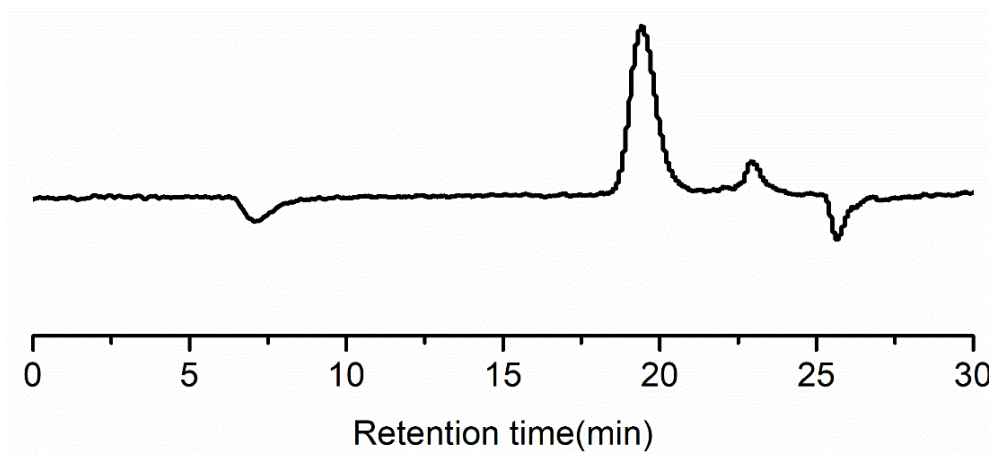


Fig. S237: SEC (CHCl₃) trace for **P32**.

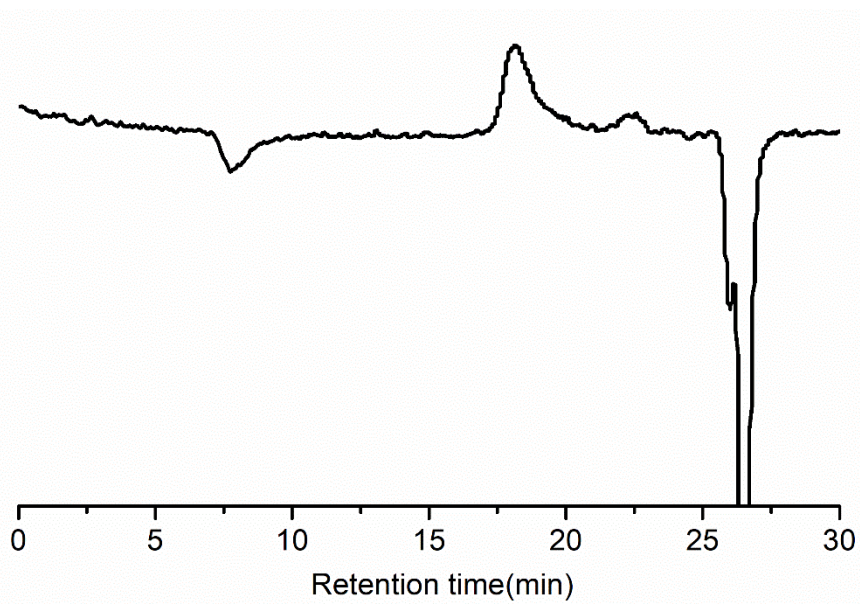


Fig. S238: SEC (CHCl₃) trace for **P33**.

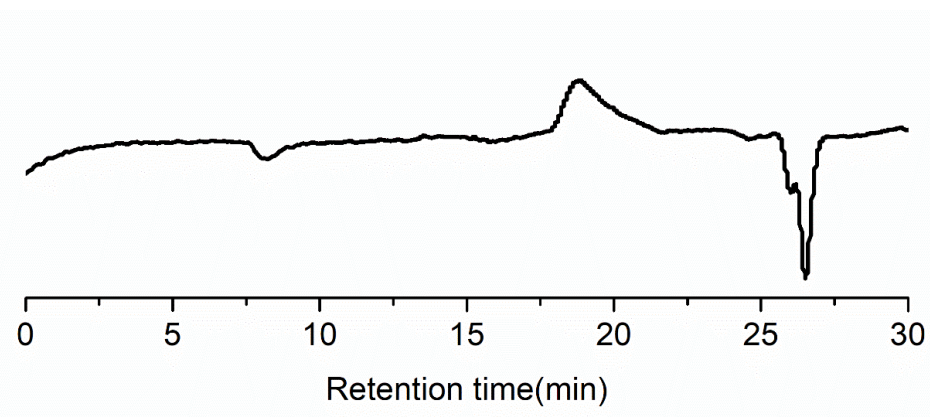


Fig. S239: SEC (CHCl₃) trace for **P34**.

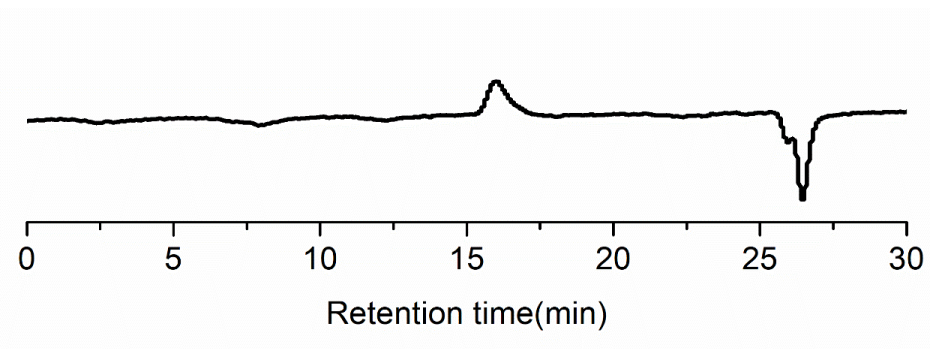


Fig. S240: SEC (CHCl₃) trace for **P35**.

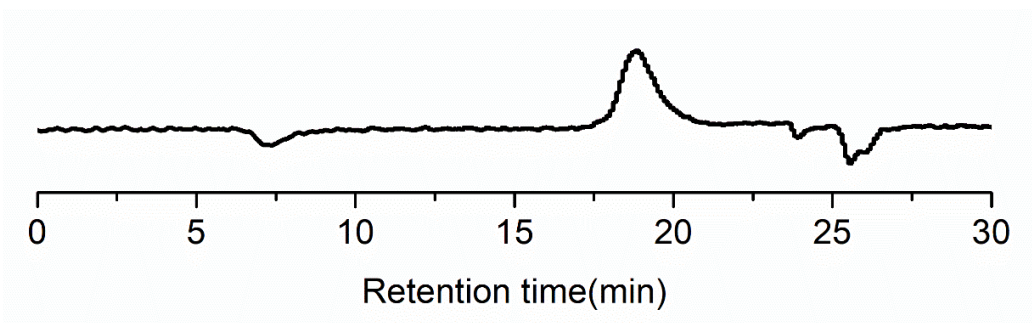


Fig. S241: SEC (CHCl₃) trace for **P37**.

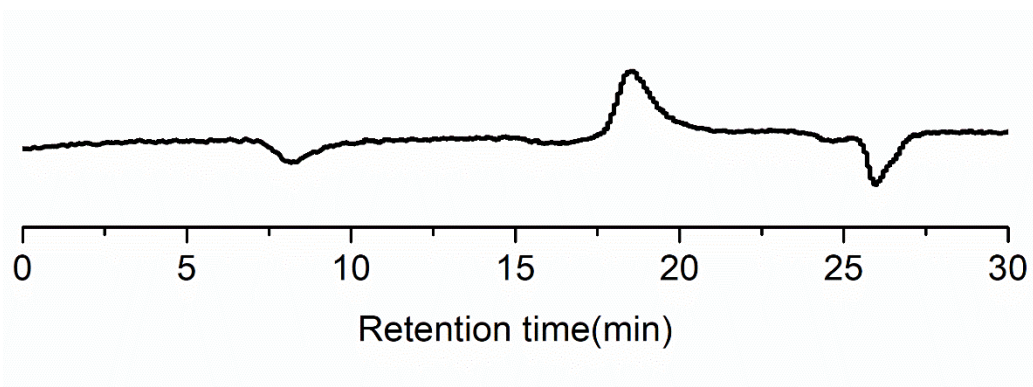


Fig. S242: SEC (CHCl₃) trace for **P38**.

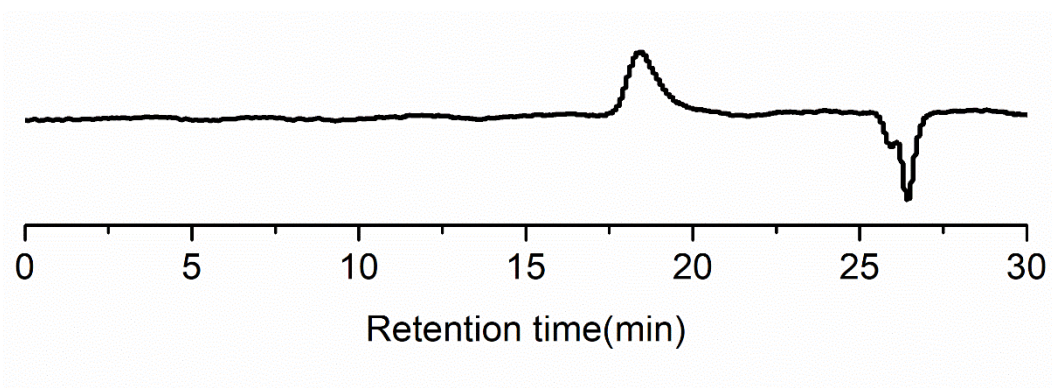


Fig. S243: SEC (CHCl₃) trace for **P39**.

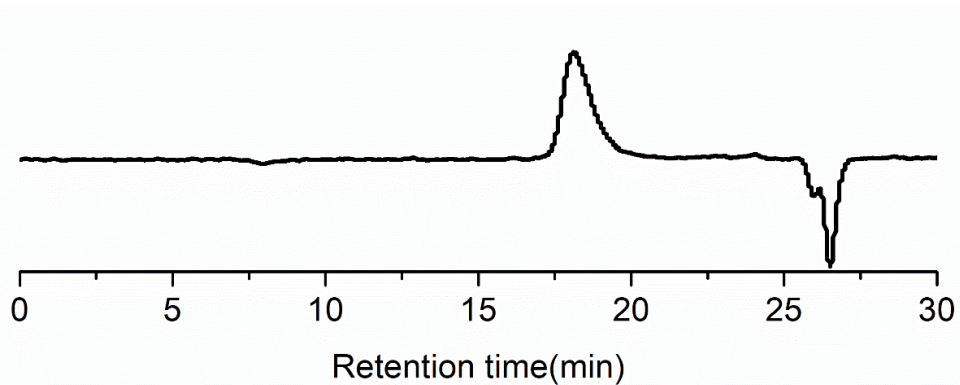


Fig. S244: SEC (CHCl₃) trace for **P40**.

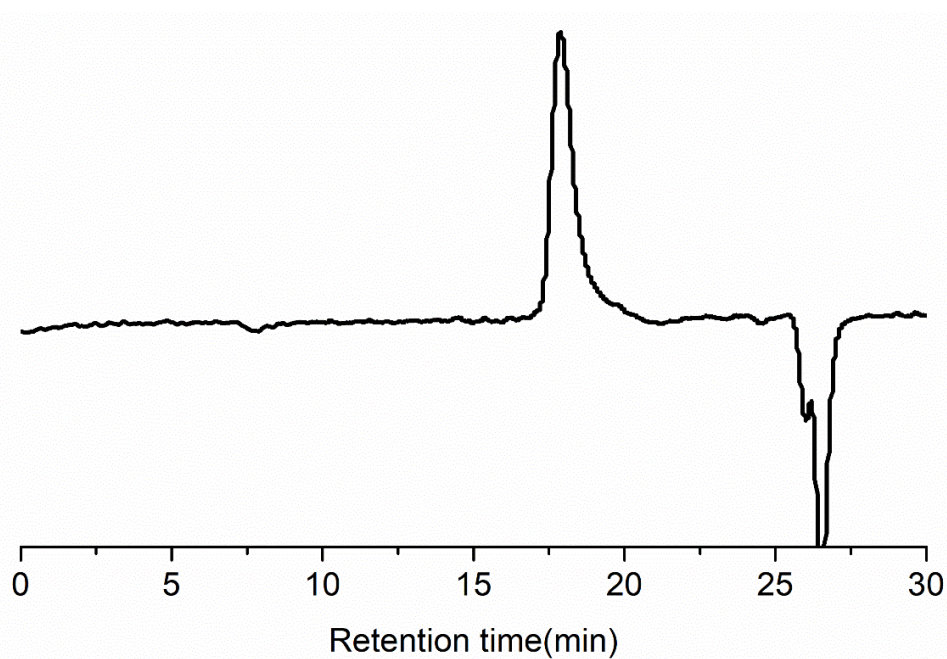


Fig. S245: SEC (CHCl₃) trace for **P41**.

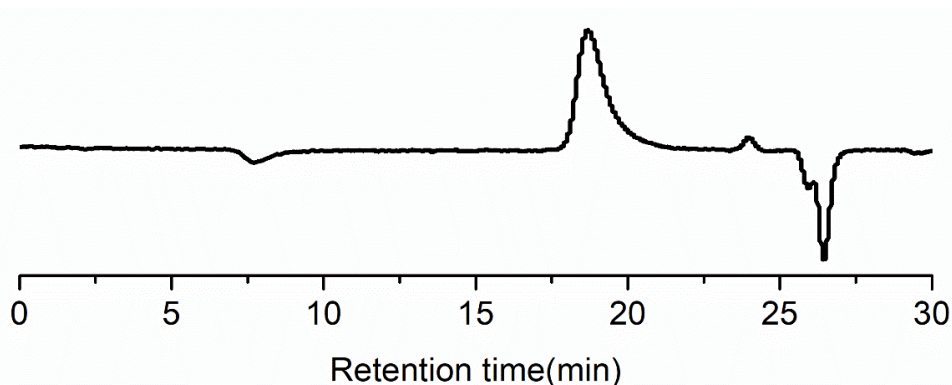


Fig. S246: SEC (CHCl₃) trace for **P42**.

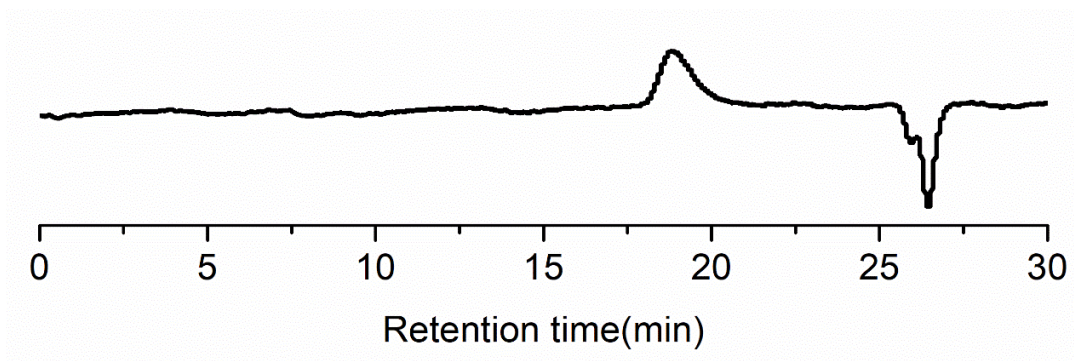


Fig. S247: SEC (CHCl₃) trace for **P43**.

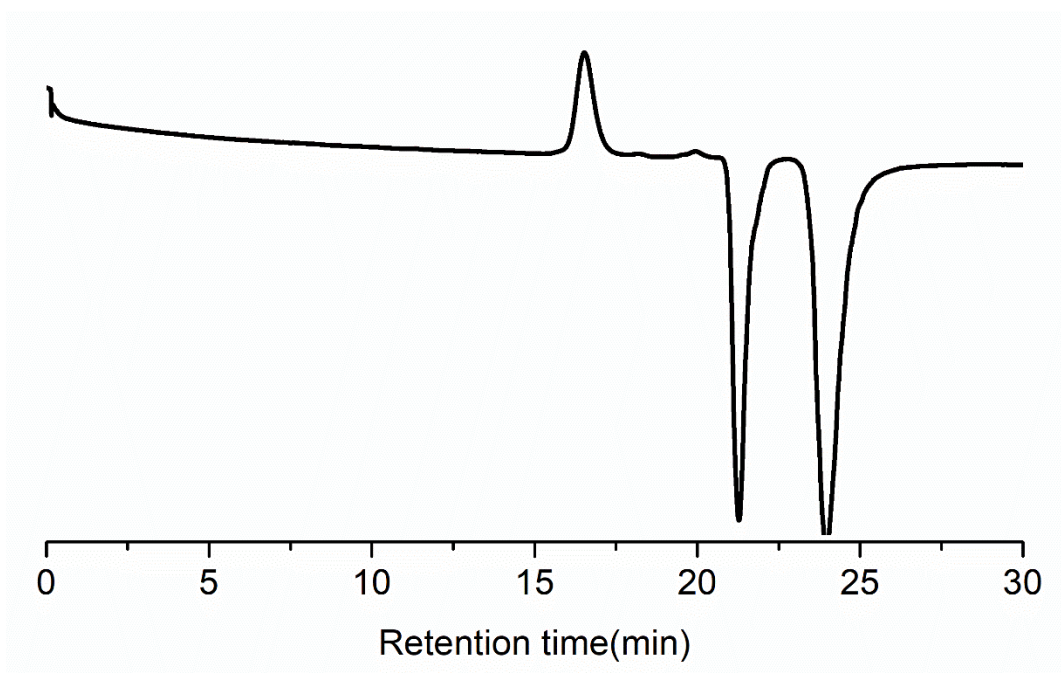


Fig. S248: SEC (DMF) trace for **PEG_{2k} macroinitiator**.

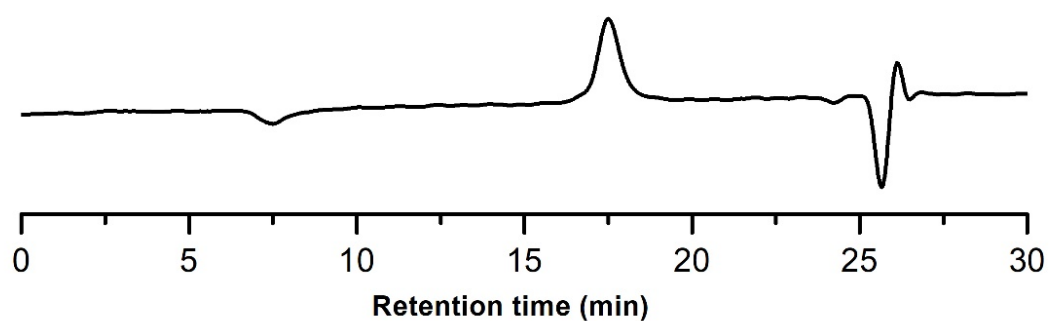


Fig. S249: SEC (CHCl₃) trace for **PLA_{20k}- Boc-Cys (Trt)-OH**.

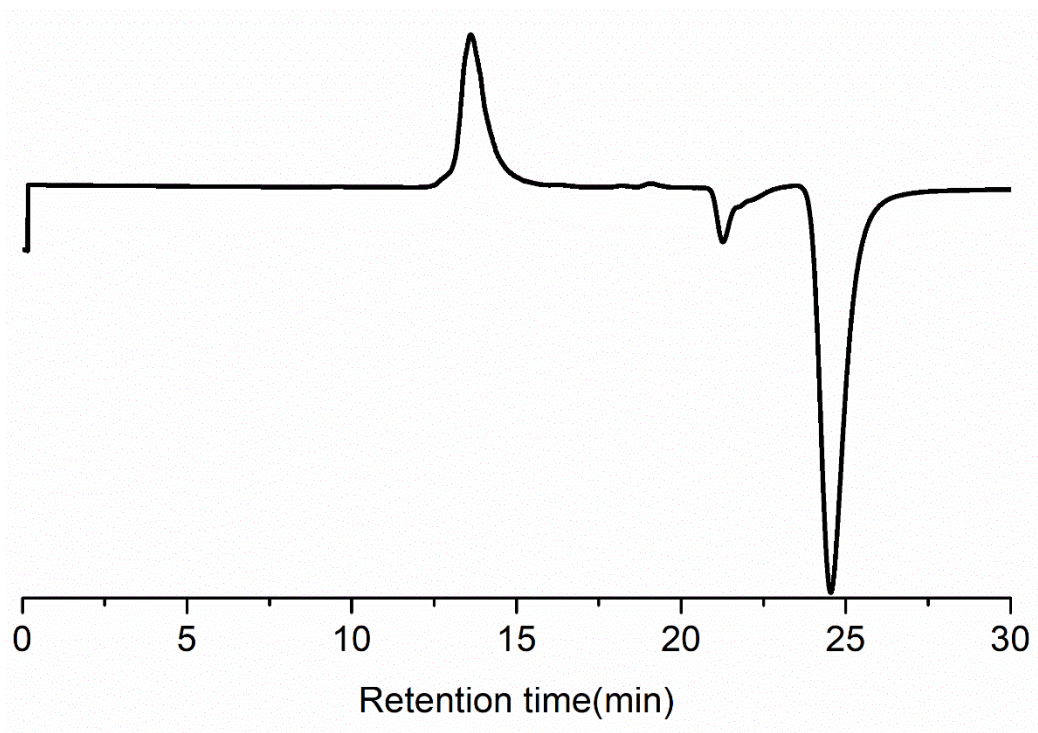


Fig. S250: SEC (DMF) trace for **PEG_{2k}-b-P(M1)**.

High-Resolution Mass Spectrometric Data:

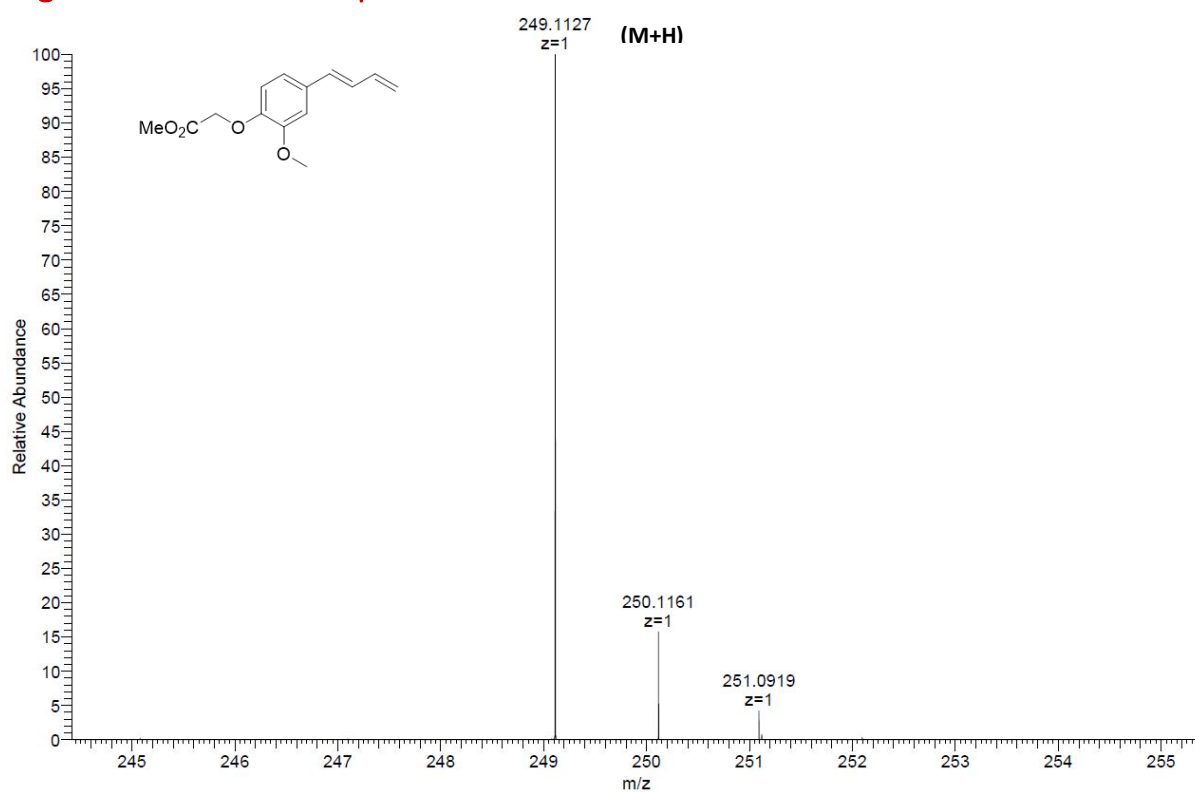


Fig. S251: HR-MS spectrum of CTA1.

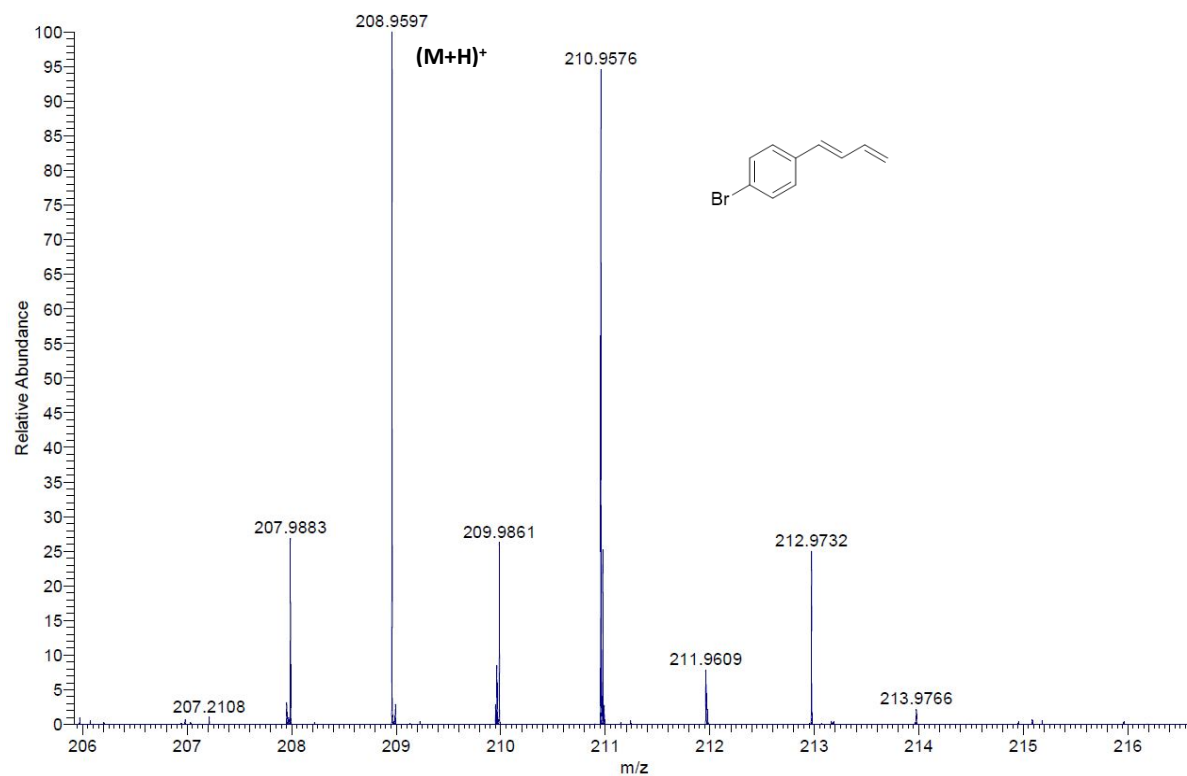


Fig. S252: HR-MS spectrum of CTA3.

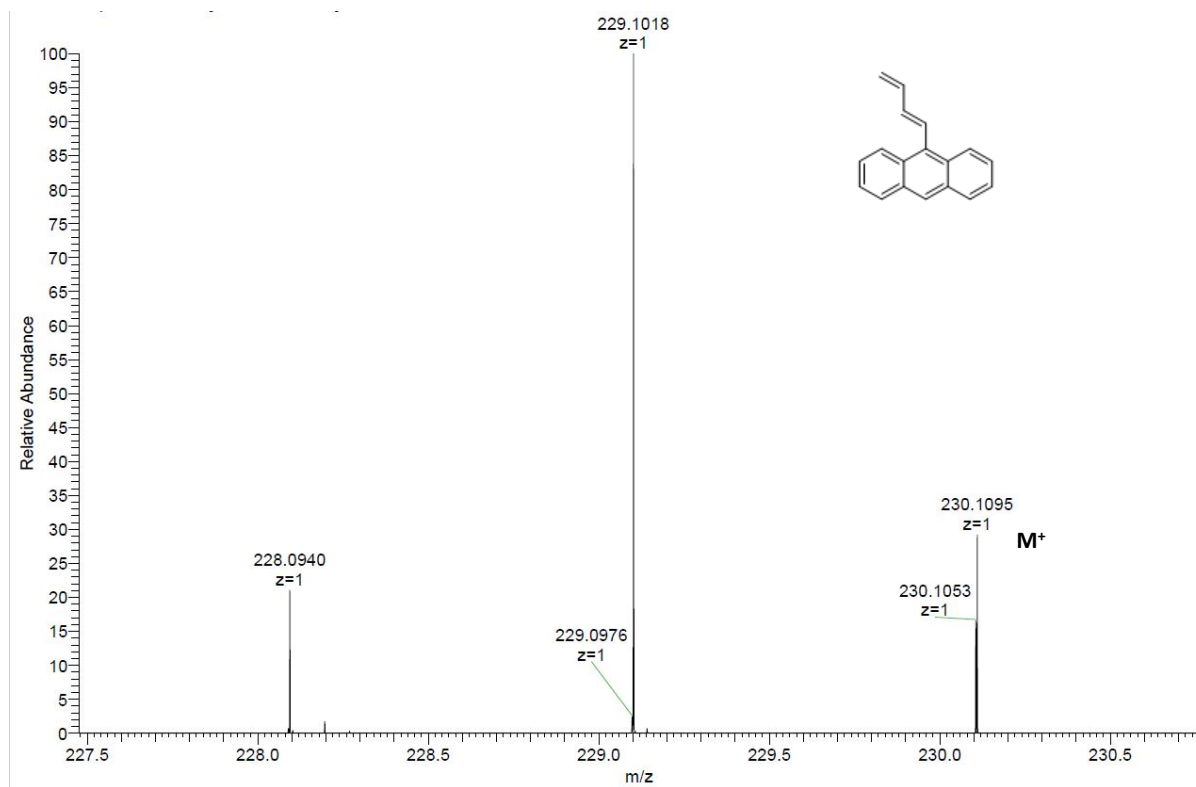


Fig. S253: HR-MS spectrum of CTA5.

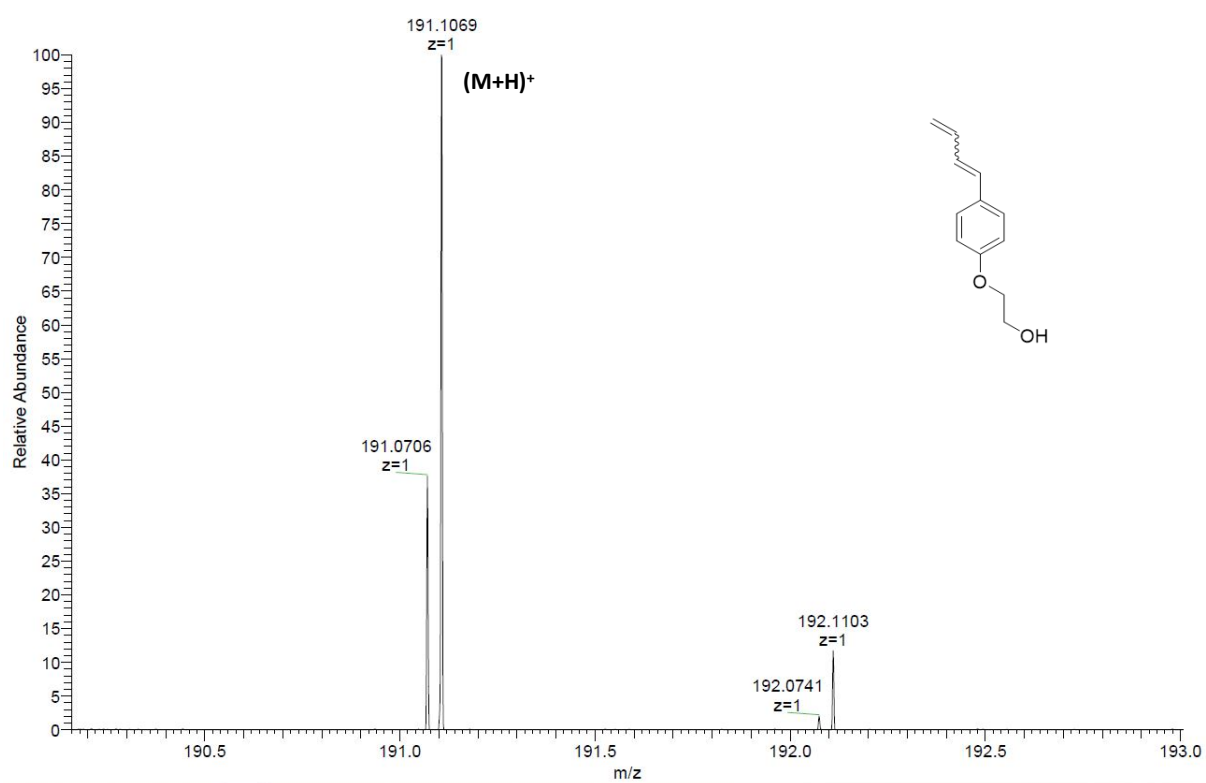


Fig. S254: HR-MS spectrum of I6.

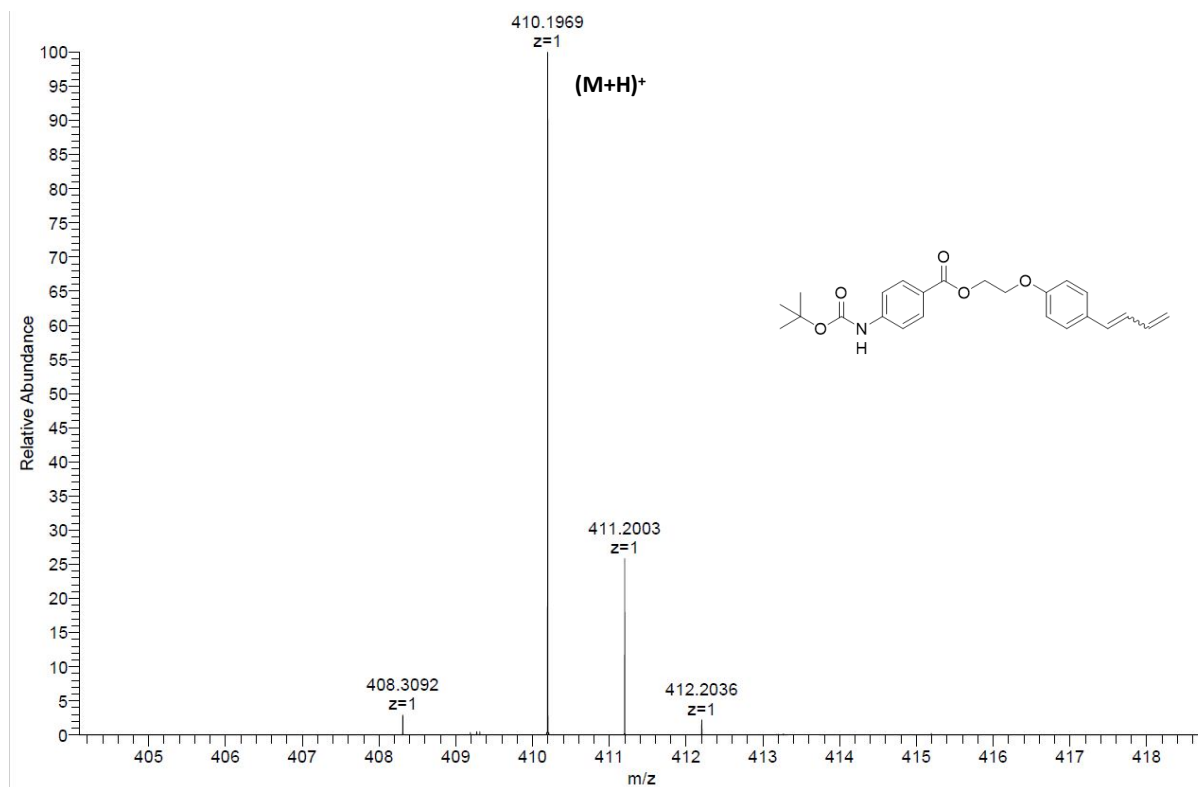


Fig. S255: HR-MS spectrum of CTA7.

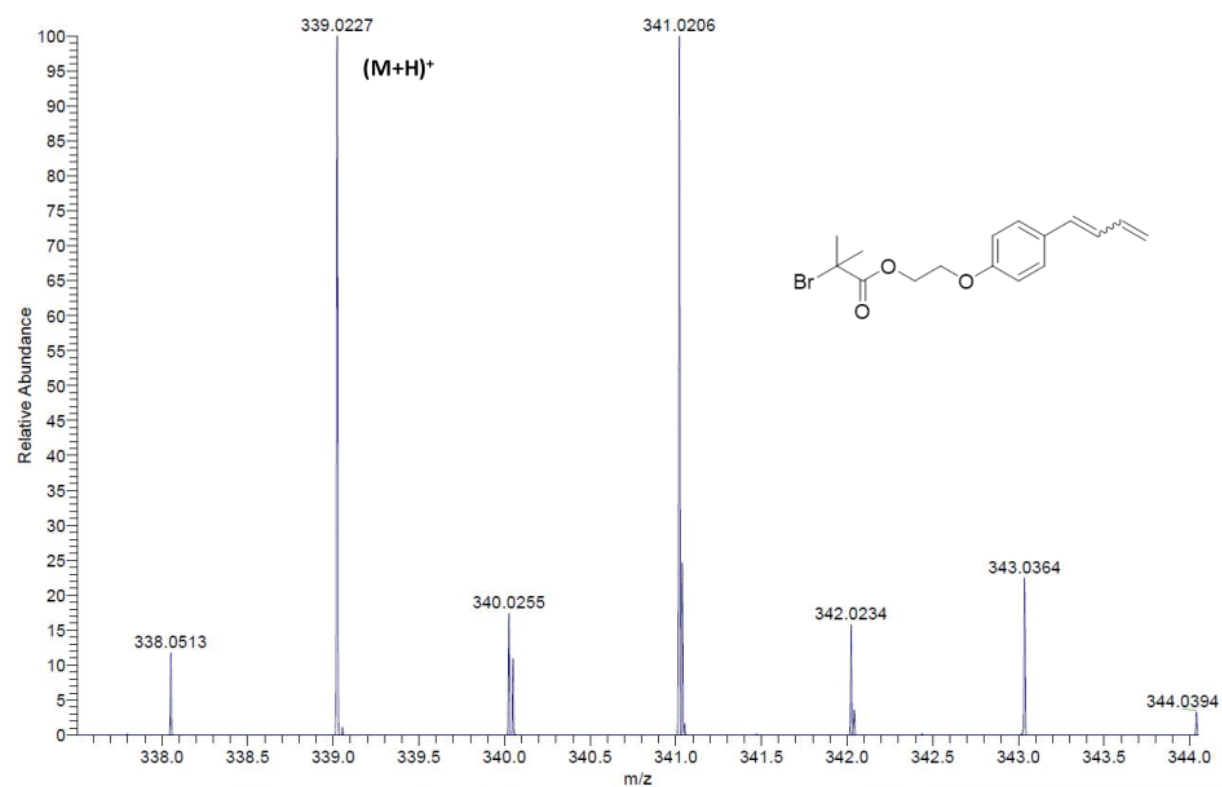


Fig. S256: HR-MS spectrum of CTA9.

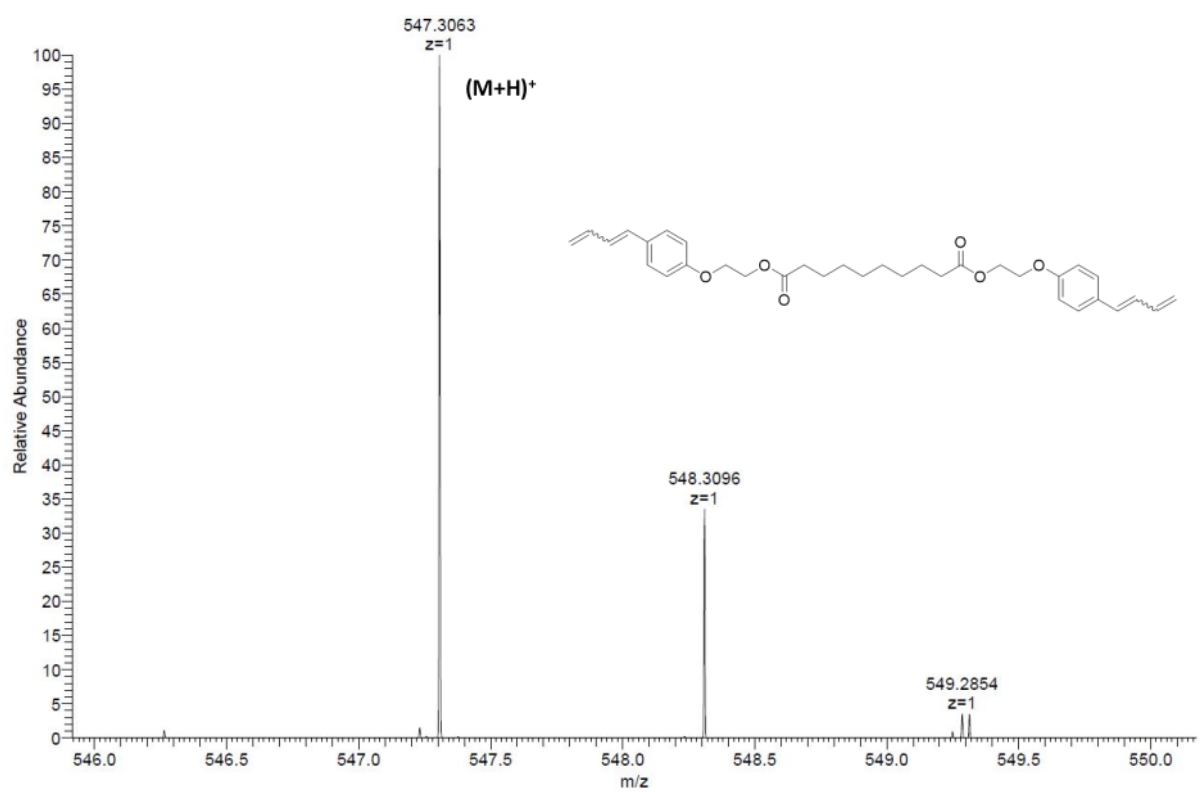
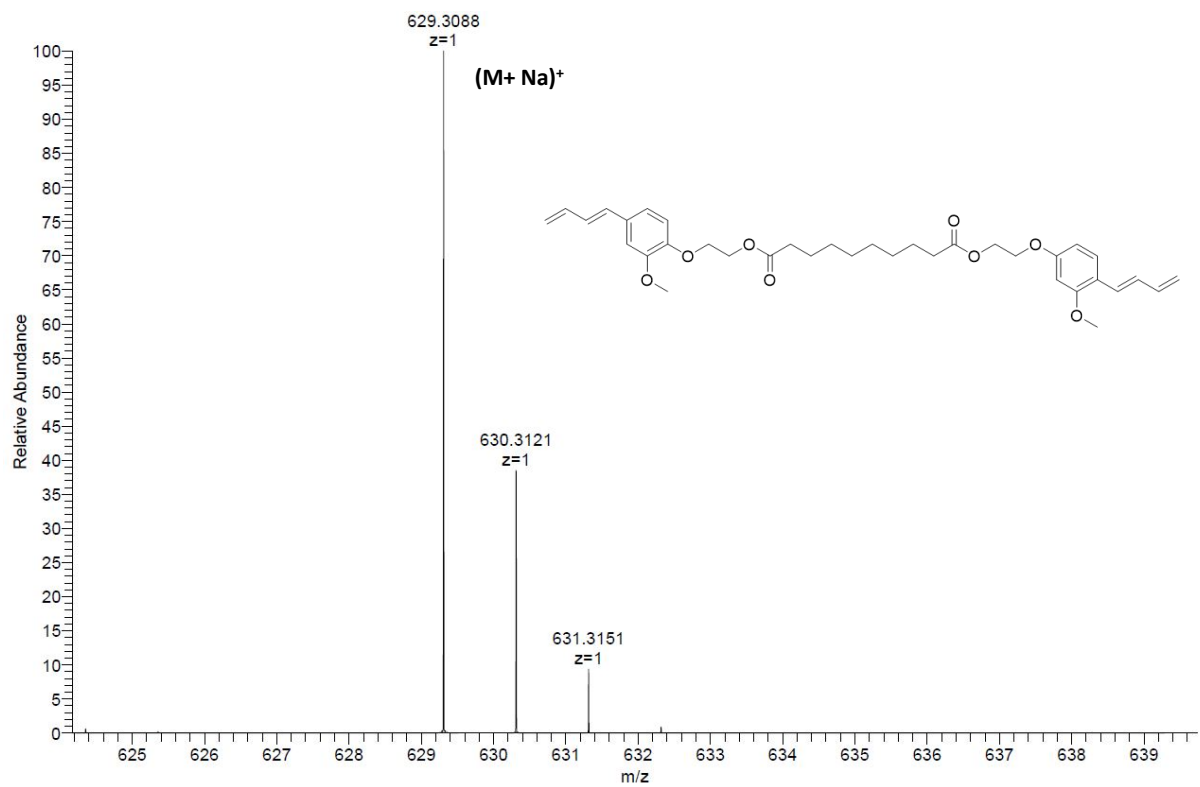


Fig. S257: HR-MS spectrum of CTA11.

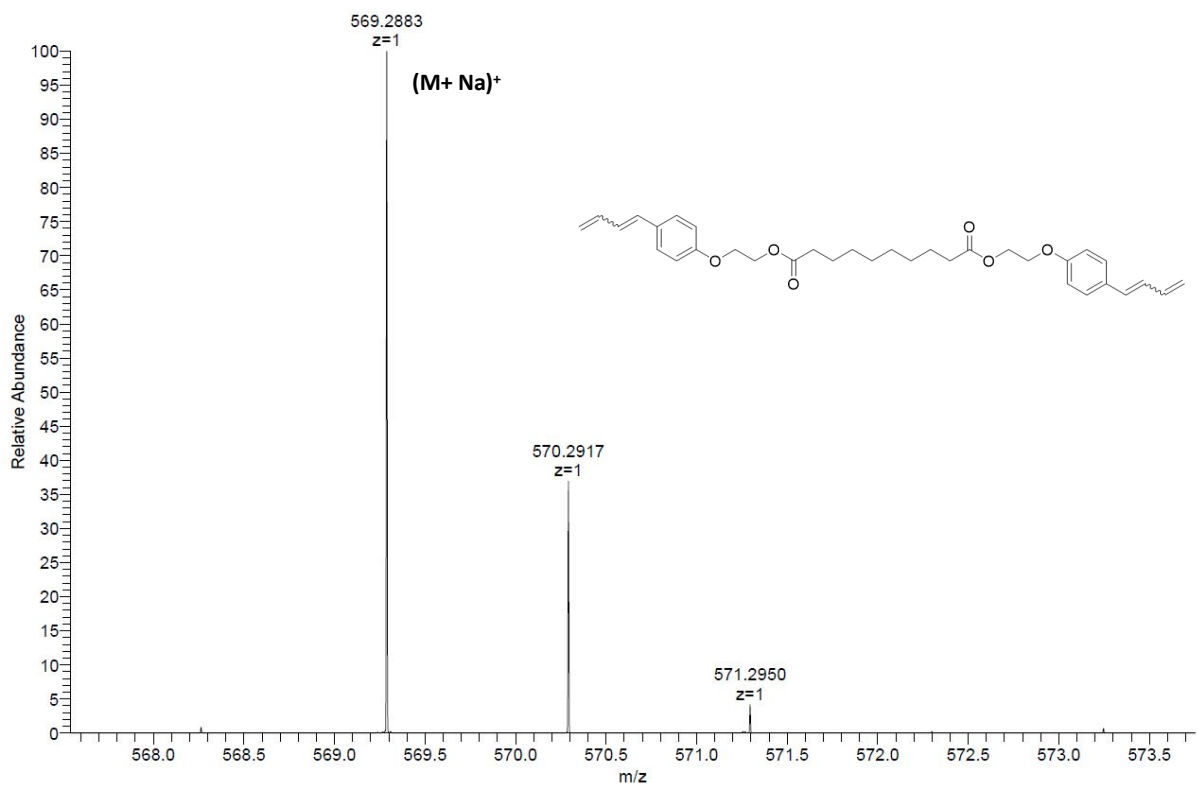


Fig. S258: HR-MS spectrum of CTA12.

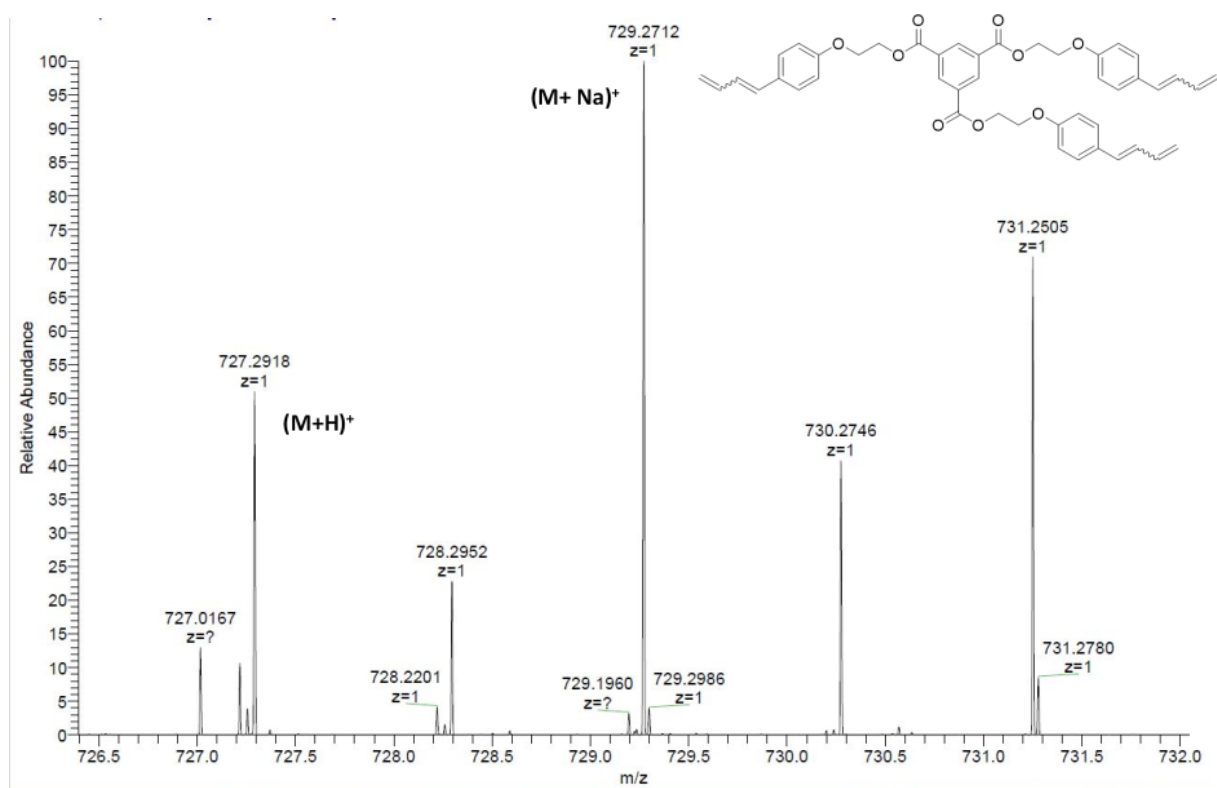


Fig. S259: HR-MS spectrum of CTA13.

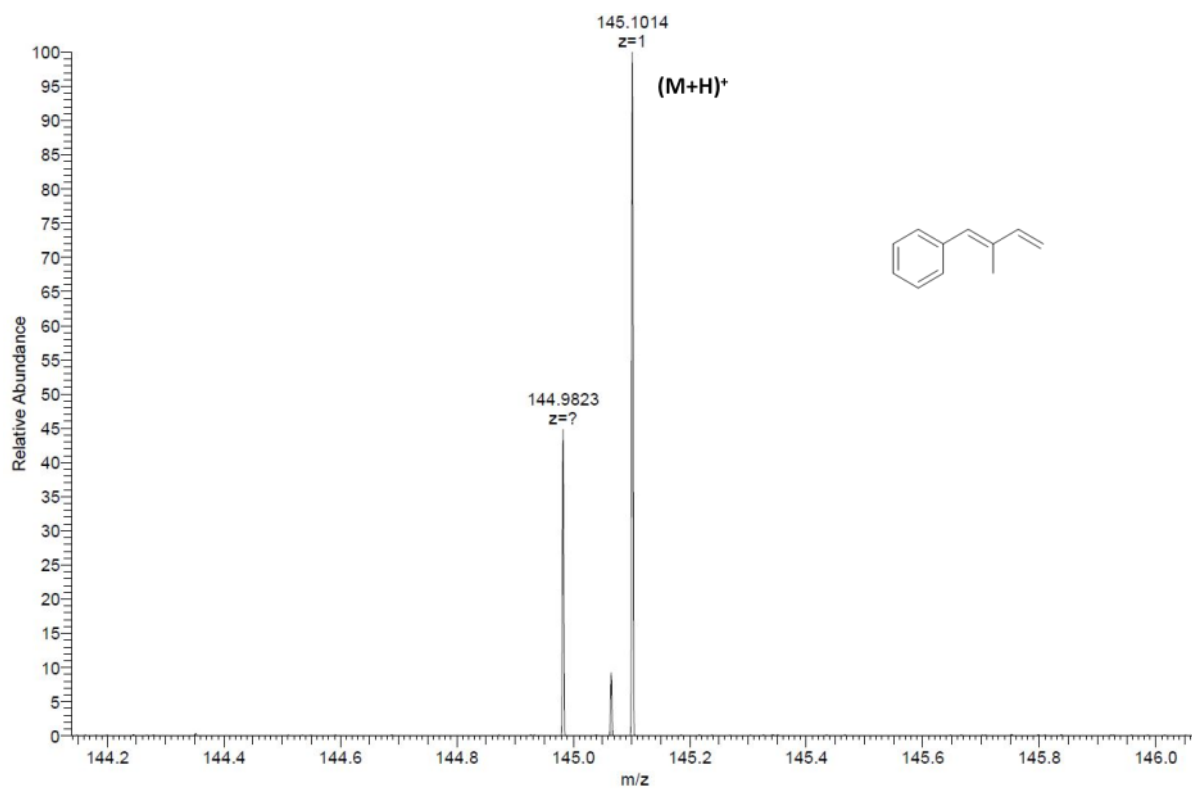


Fig. S260: HR-MS spectrum of CTA23.

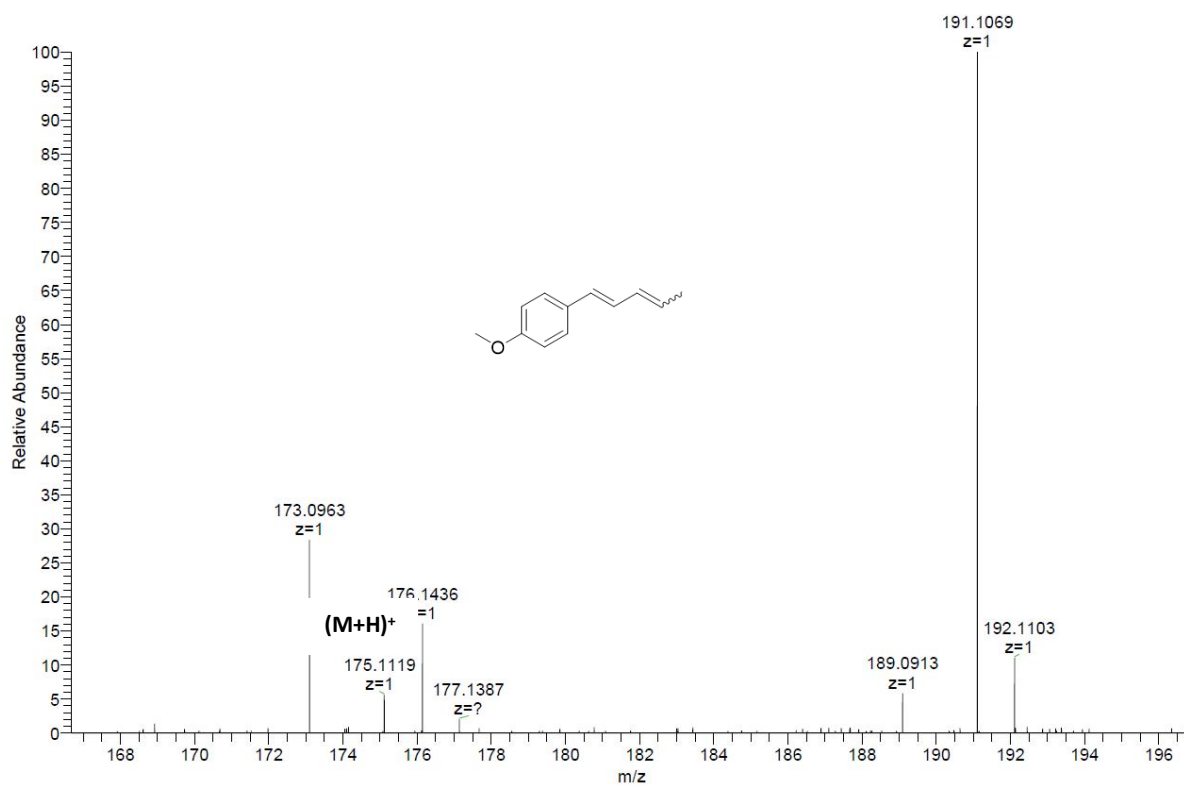


Fig. S261: HR-MS spectrum of CTA24.

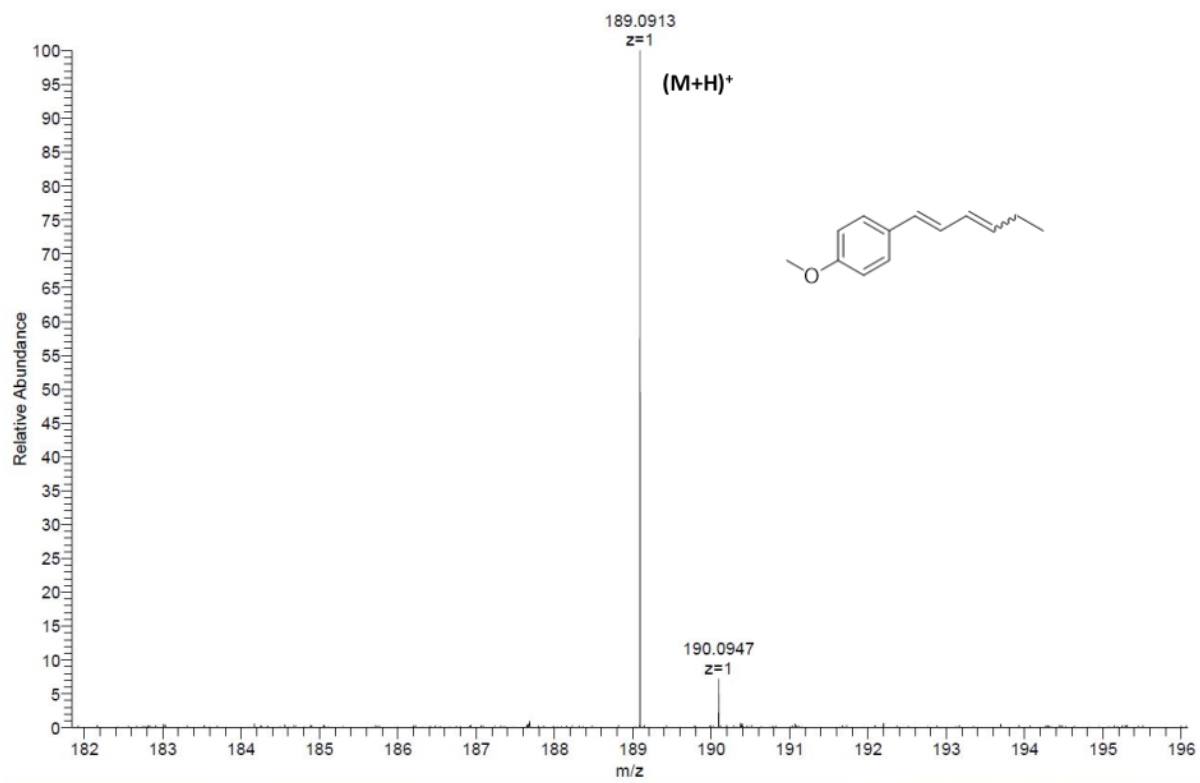
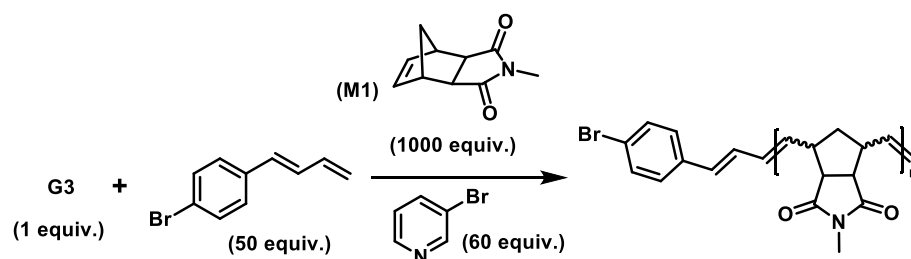


Fig. S262: HR-MS spectrum of CTA25.

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.

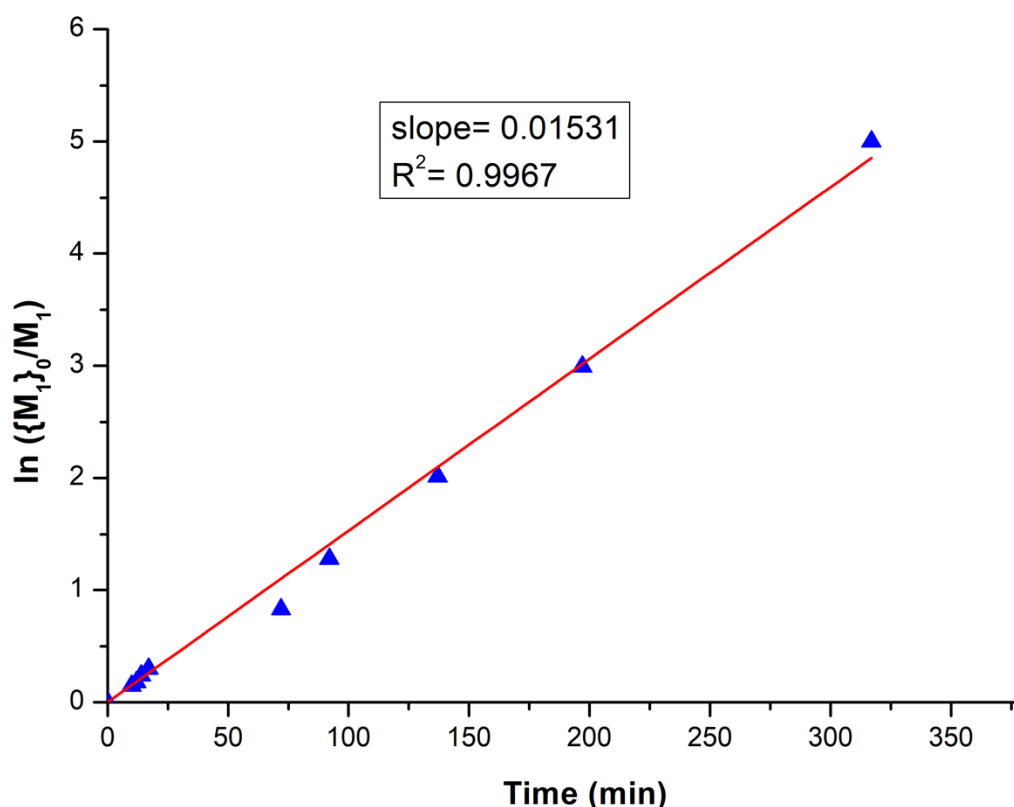


Fig. S263: Plot of $\ln(\{M_1\}_0/M_1)$ against time.

Here, $\{M_1\}_0$ correspond to the initial concentration of monomer (**M1**) 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, $k_{M1} = 0.01531 \text{ min}^{-1}$.

Similarly, rate constant for CTA consumption (k_{CTA}) was also determined utilizing the same reaction conditions as follows-

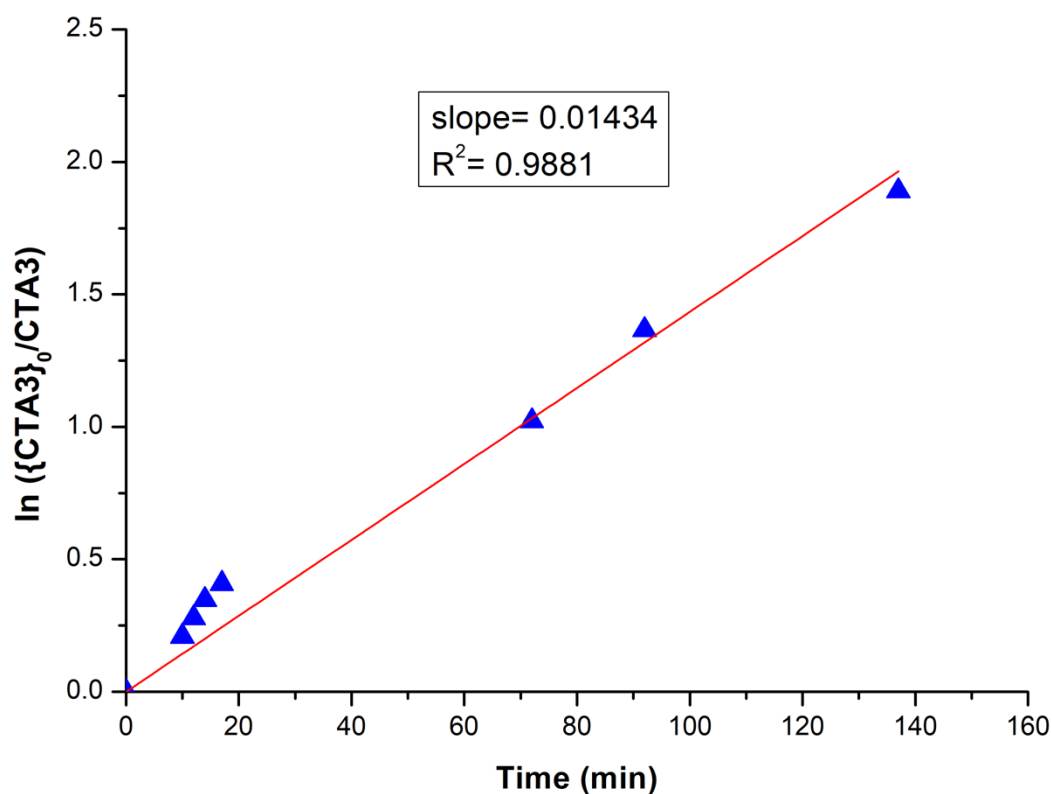


Fig. S264: Plot of $\ln(\{CTA3\}_0/CTA3)$ against time.

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.

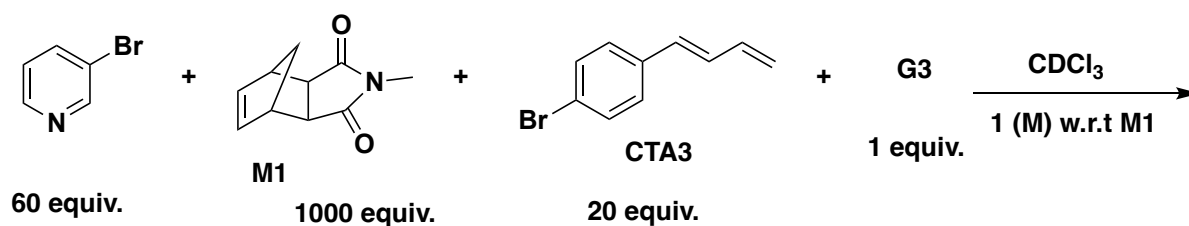
Additionally, the measured linear relation between $\ln([S_0]/[S_t])$ (S = substrate) and time confirmed the first-order dependence in concentration of both monomer (**M1**) and CTA (**CTA3**) as expected for a chain-growth process.

CTA concentration effects on kinetically controlled ROMP:

To understand how concentration of chain transfer agents influence kinetics the following ^1H 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 ^1H NMR were measured. Then, **G3** (1 equiv., 0.0011 mmol, 1 mg) dissolved in 0.2 mL was added quickly, and ^1H NMR was measured overtime.



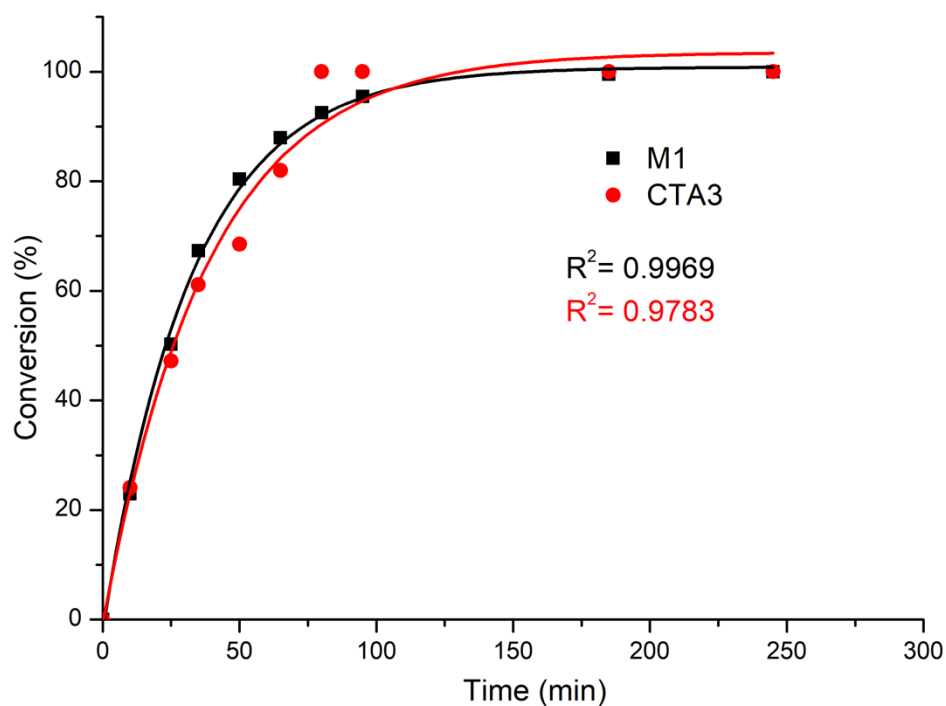
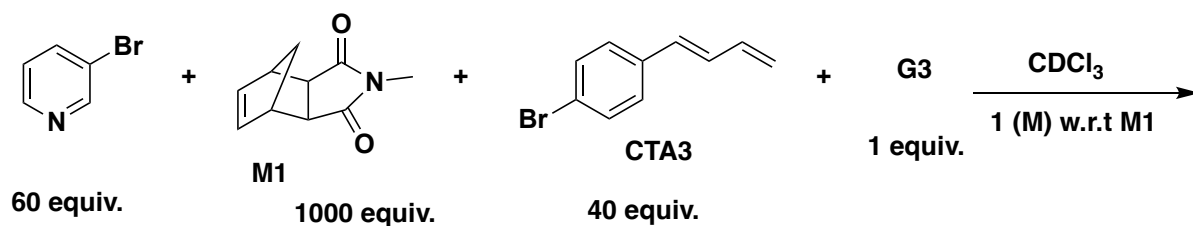


Fig. S266: A plot of monomer (**M1**, 1000 equiv.) and **CTA3** (20 equiv.) conversion vs. time determined by ^1H NMR spectroscopy (CDCl_3 , 300 MHz) showing both monomer and CTA were consumed at a similar rate during the polymerization, thus, suggesting a kinetically controlled mechanism.



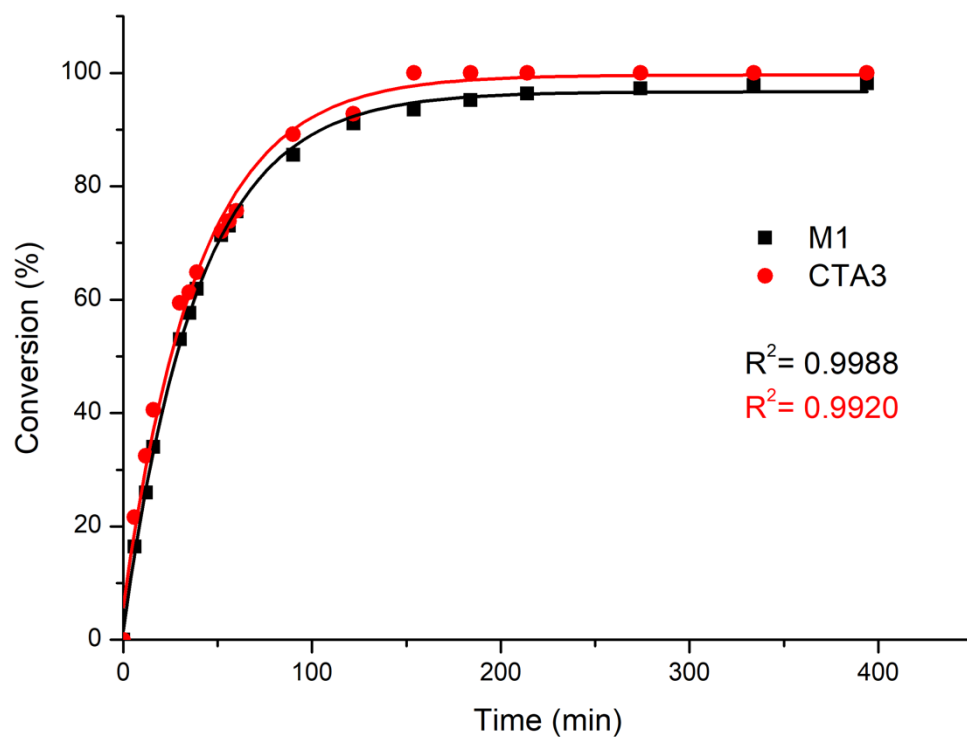
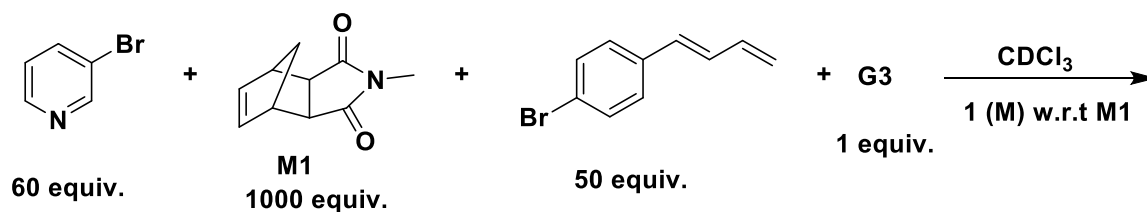


Fig. S268: A plot of monomer (**M1**, 1000 equiv.) and **CTA3** (40 equiv.) conversion vs. time determined by ^1H NMR spectroscopy (CDCl_3 , 300 MHz) showing both monomer and CTA were consumed at a similar rate during the polymerization, thus, suggesting a kinetically controlled mechanism.



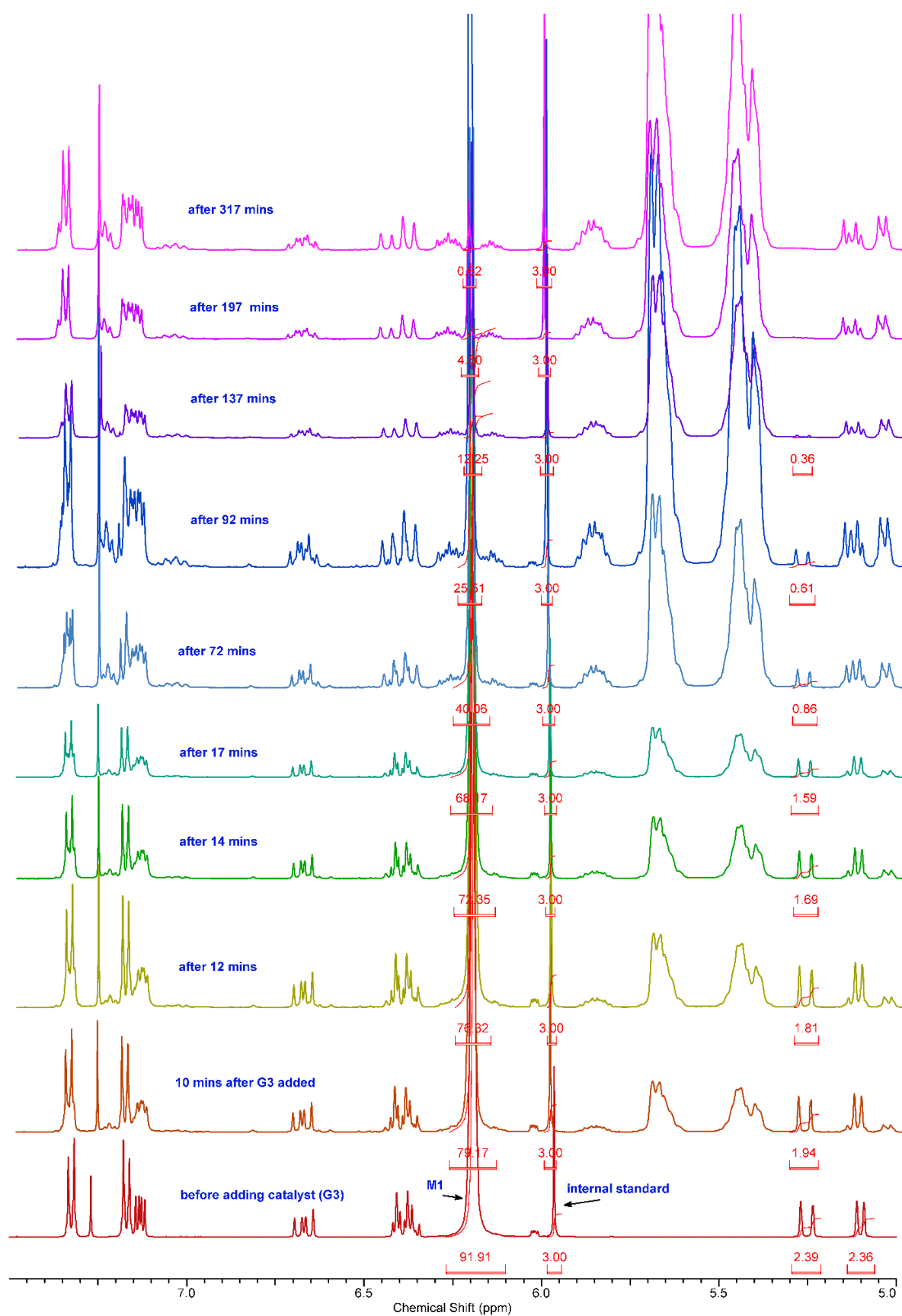


Fig. S269: ¹H NMR (CDCl₃, 300 MHz) of reaction of **CTA3** (50 equiv.), 3 bromopyridine (60 equiv.) and **M1** (1000 equiv.) with **G3** (2.1 equiv.) in CDCl₃.

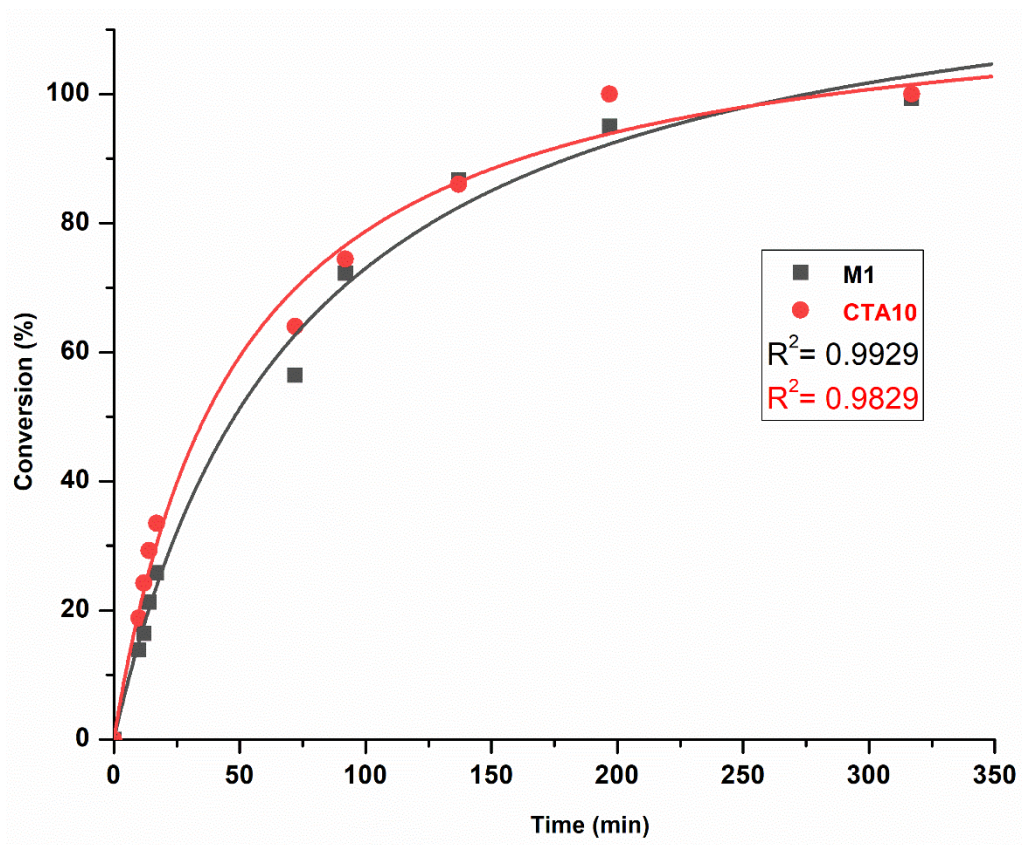


Fig. S270: A plot of monomer (**M1**, 1000 equiv.) and **CTA3** (50 equiv.) conversion vs. time determined by ^1H NMR spectroscopy (CDCl_3 , 300 MHz) showing both monomer and CTA were consumed at a similar rate during the polymerization, thus, suggesting a kinetically controlled mechanism.

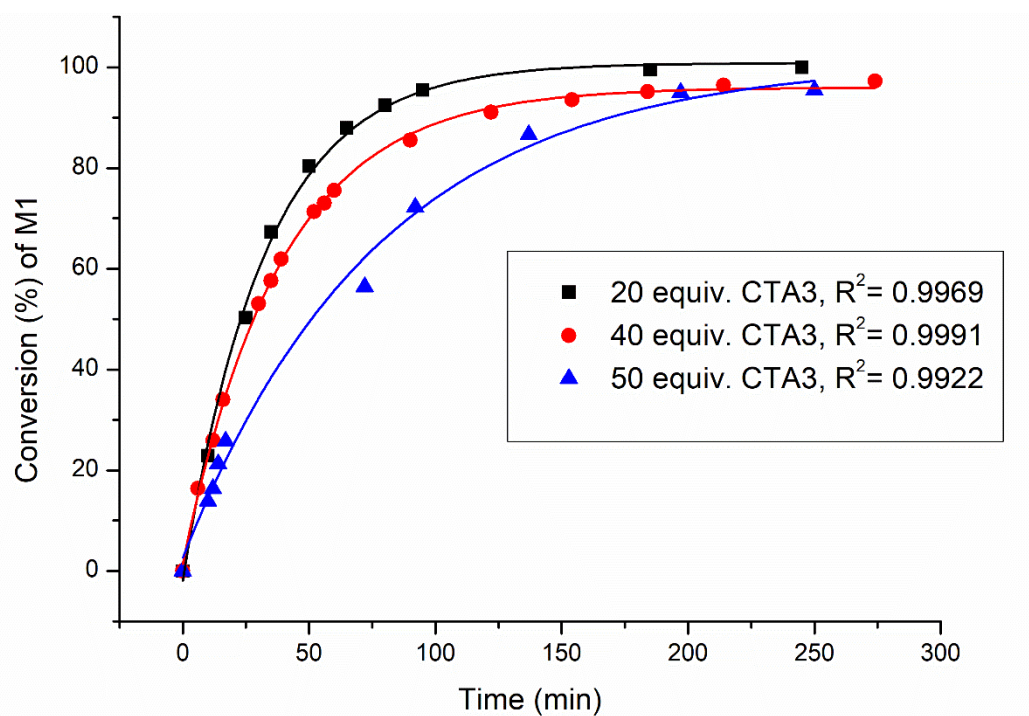


Fig. S271: A plot of monomer (**M1**, 1000 equiv.) conversion vs. time at different concentration of **CTA3** (20 equiv. /40 equiv. /50 equiv.) determined by ^1H NMR spectroscopy (CDCl_3 , 300 MHz) showing rate of consumption of **M1** decreased with the increase in the concentration of **CTA3**.

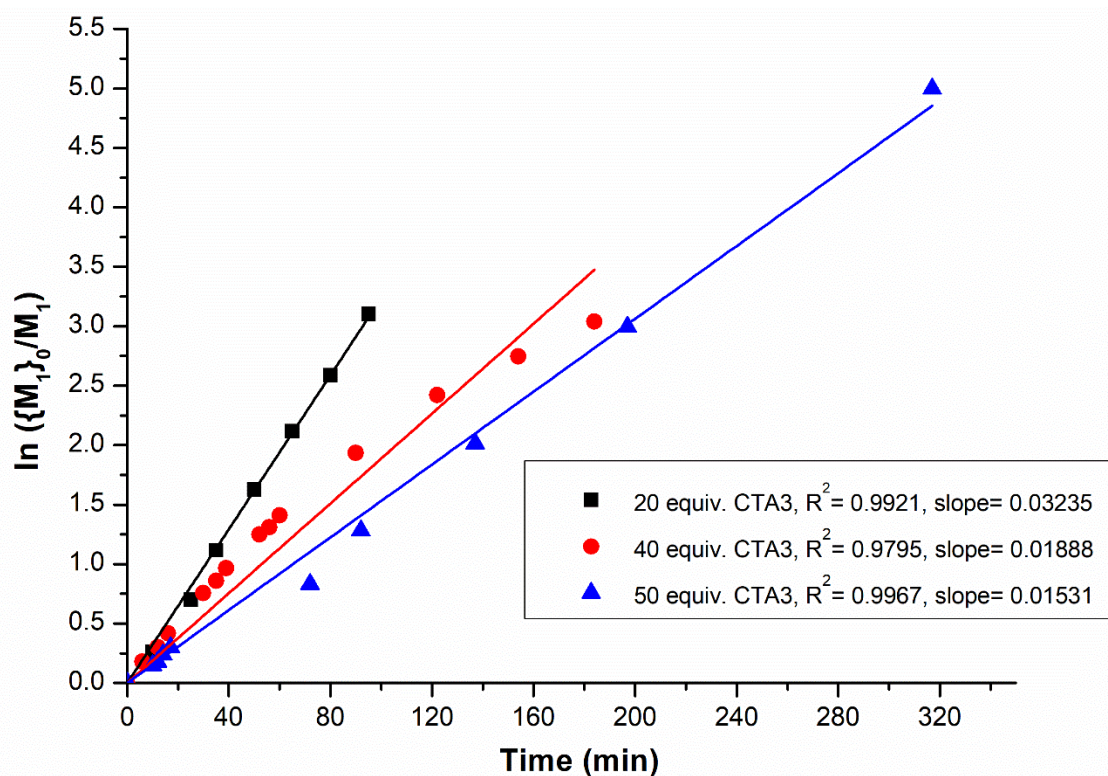


Fig. S272: Plot of $\ln(\{M_1\}_0/M_1)$ against time at different **CTA3** concentration.

Table S6: Data for the determination of k_{M1} for different CTA3 concentration in $CDCl_3$:

Degree of polymerization (DP)	G3:CTA3:M1 ^a	Concentration of CTA3 (mmol/L)	R ² value	k_{M1} (1/min)
50	1:20:1000	20.00	0.9921	0.03235
25	1:40:1000	40.01	0.9795	0.01888
20	1:50:1000	50.02	0.9967	0.01531

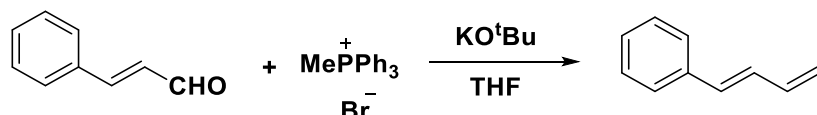
a: 60 equiv. of 3 bromopyridine was used to decrease the overall rate of the polymerization.

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-



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).

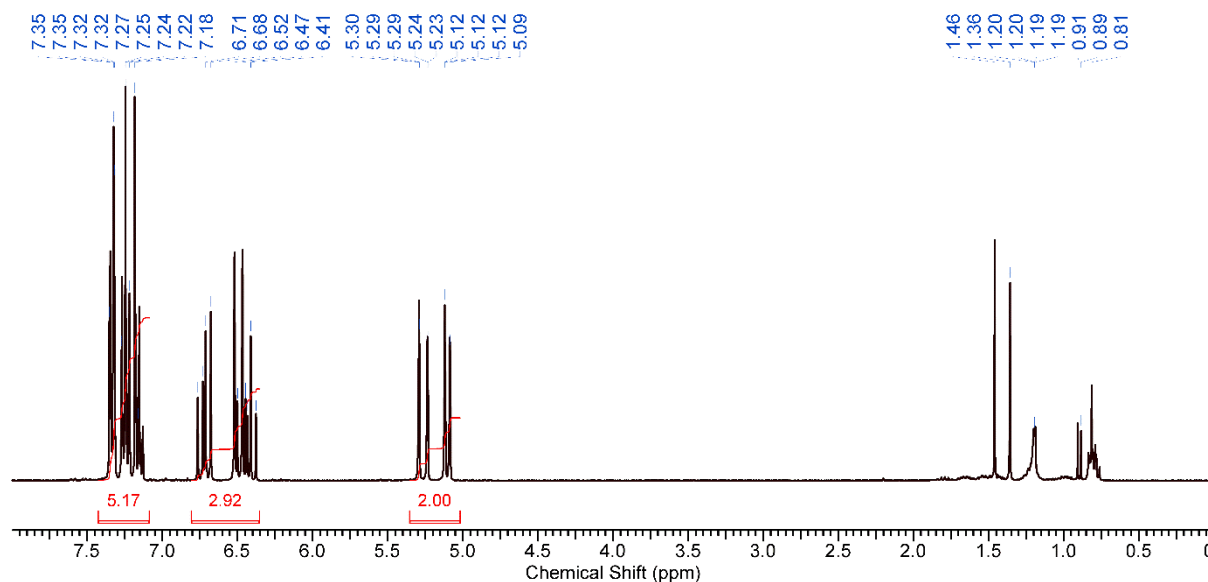


Fig. S273: ¹H NMR (CDCl₃, 300 MHz) spectrum of **CTA27**. The peaks in the aliphatic region (0.7-1.4 ppm) is from grease as the eluent for column chromatography was pure hexanes.

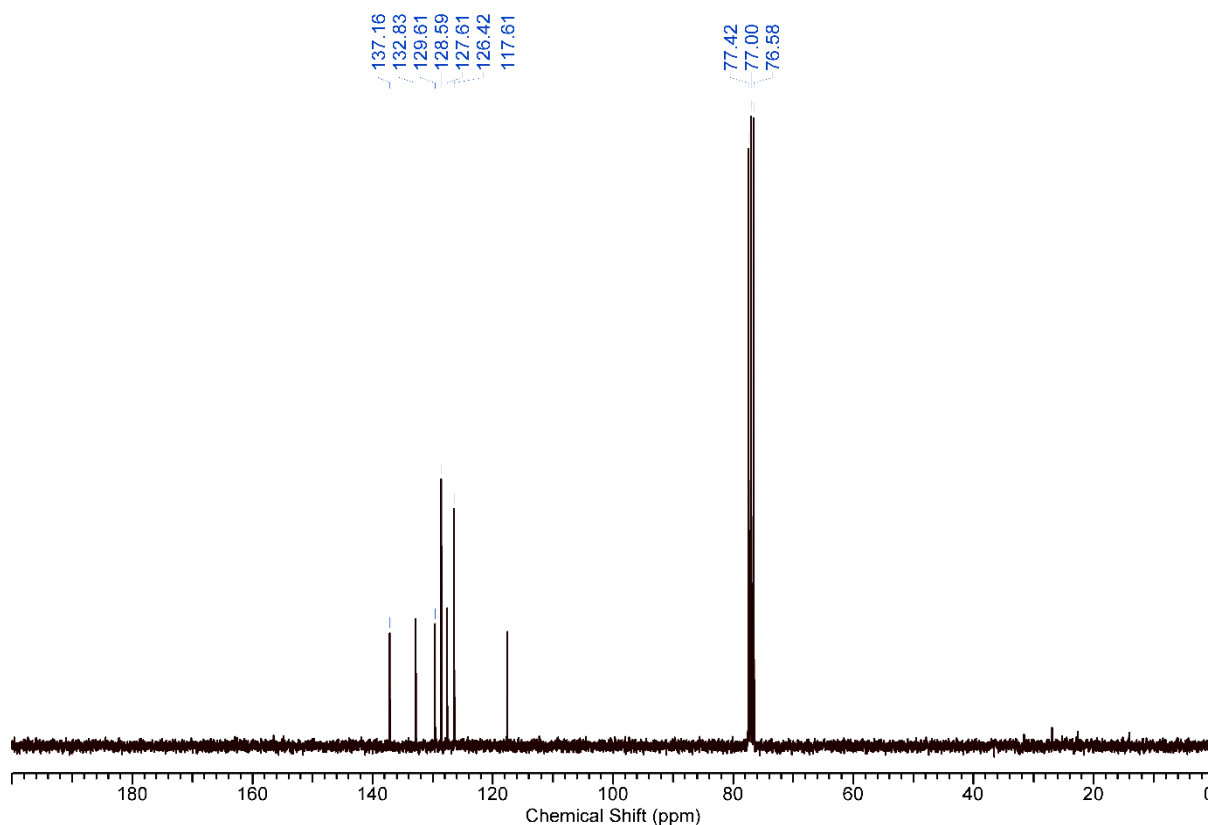
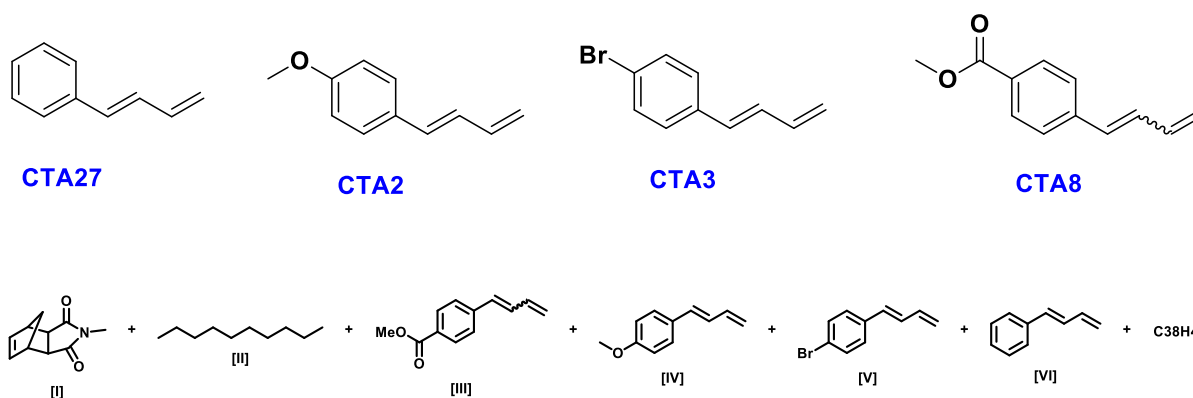


Fig. S274: ^{13}C NMR (CDCl_3 , 300 MHz) spectrum of **CTA27**.

CTAs considered for Hammett studies:



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.



R= H, CTA27
 = OMe, CTA2
 = Br, CTA3
 = CO₂Me, CTA8

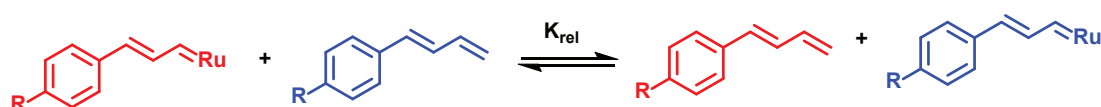


Table S7: Data analysis for Hammett plot

Entry	GC-MS peak	Initial area (A_0)	Final area (A)	$\ln(A/A_0)$	$\ln(A/A_0)/\ln(A_H/A_{H0}) = K_{rel}$	$\log K_{rel}$	σ_{para}^3
CTA27 (H)	7.88	4813862	3213345	-0.404187	1	0	0.00
CTA2 (OMe)	10.47	7091024	3820190	-0.618529	1.53030	0.42546	-0.27
CTA3 (Br)	10.66	5131951	3607275	-0.352533	0.87220	-0.05938	0.23
CTA8 (CO ₂ Me)	11.55/12.01	6032684	4648163	-0.260719	0.64504	-0.19041	0.44

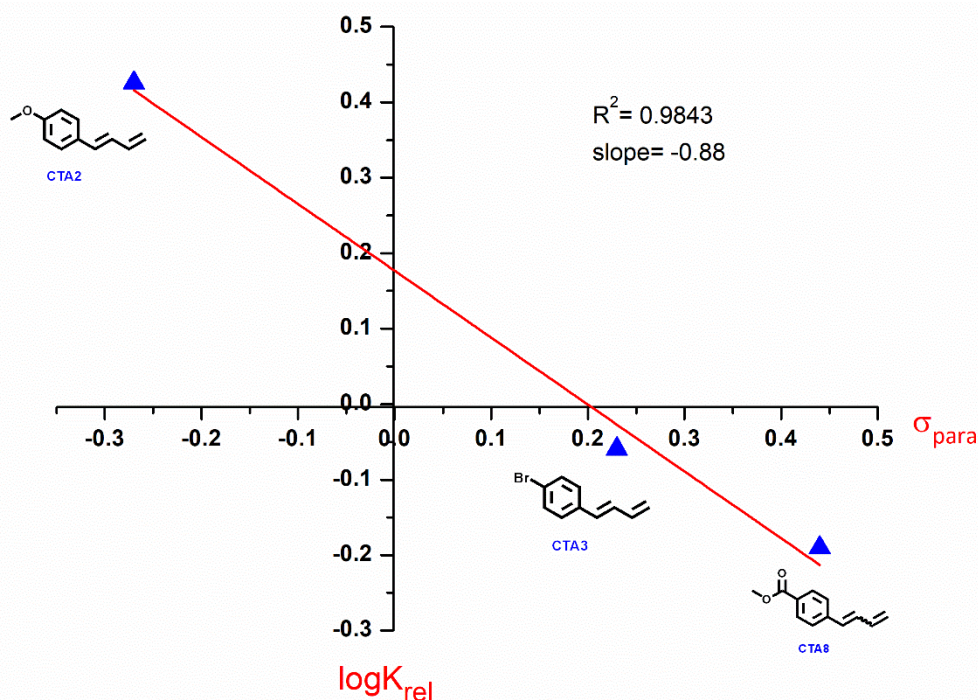


Fig. S275: Hammett plot ($\log K_{rel}$ vs σ_{para}) for differently para-substituted CTAs differing in electron donation capabilities.

From the slope, the reaction constant (ρ) 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:

Entry	CTA	Monomer (M)	G3:CTA: Monomer ratio	M_n (Non-catalytic, M/G3) (kDa)	M_n (Catalytic, M/CTA) kDa	M_n (SEC, CHCl_3) kDa	\bar{D}	Polymer Yield (%)
P45	CTA2	M1	1:20:10000	1770	88.5	83.0	1.65	92
P46	CTA2	M1	1:20:20000	3540	177	165.0	1.68	92

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 ^1H NMR spectroscopy from the polymerization mixture given below-

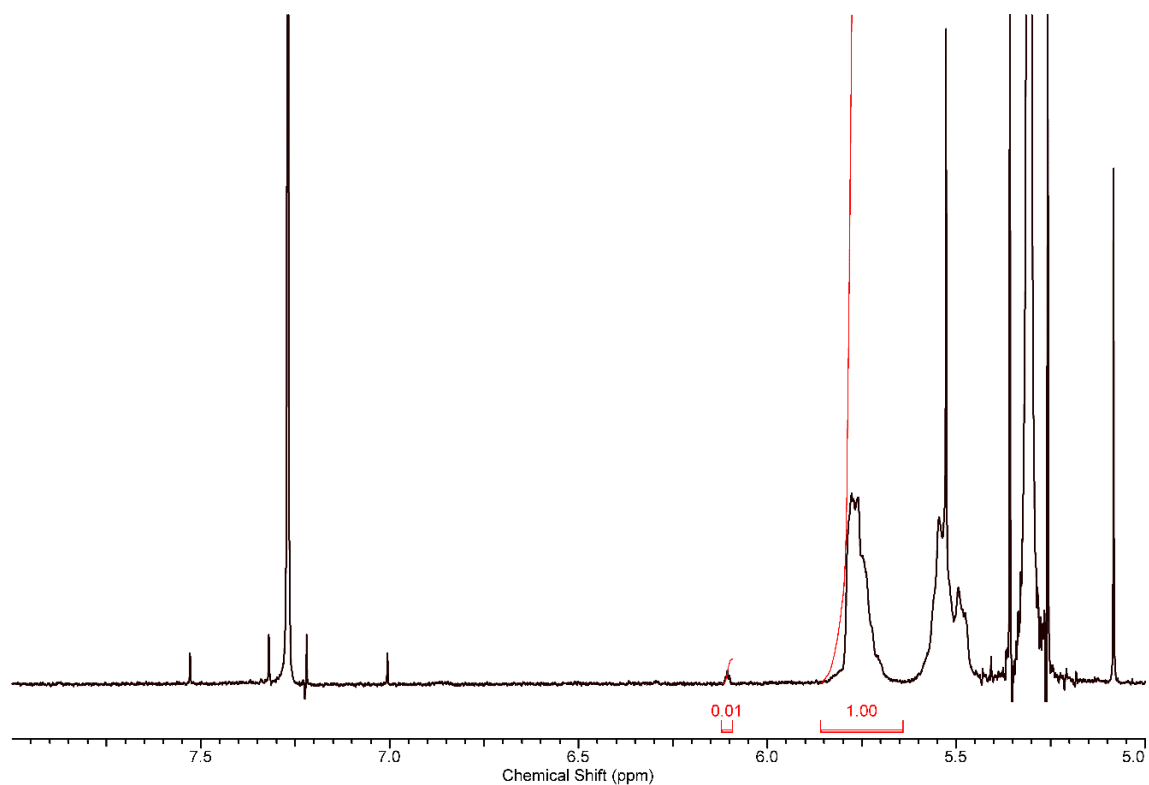


Fig. S276: Crude ^1H NMR (CDCl_3 , 400 MHz) spectra of polymerization mixture of **P45** showing olefinic region. Absence of any peak at 6.26 ppm confirmed full consumption of **M1**.

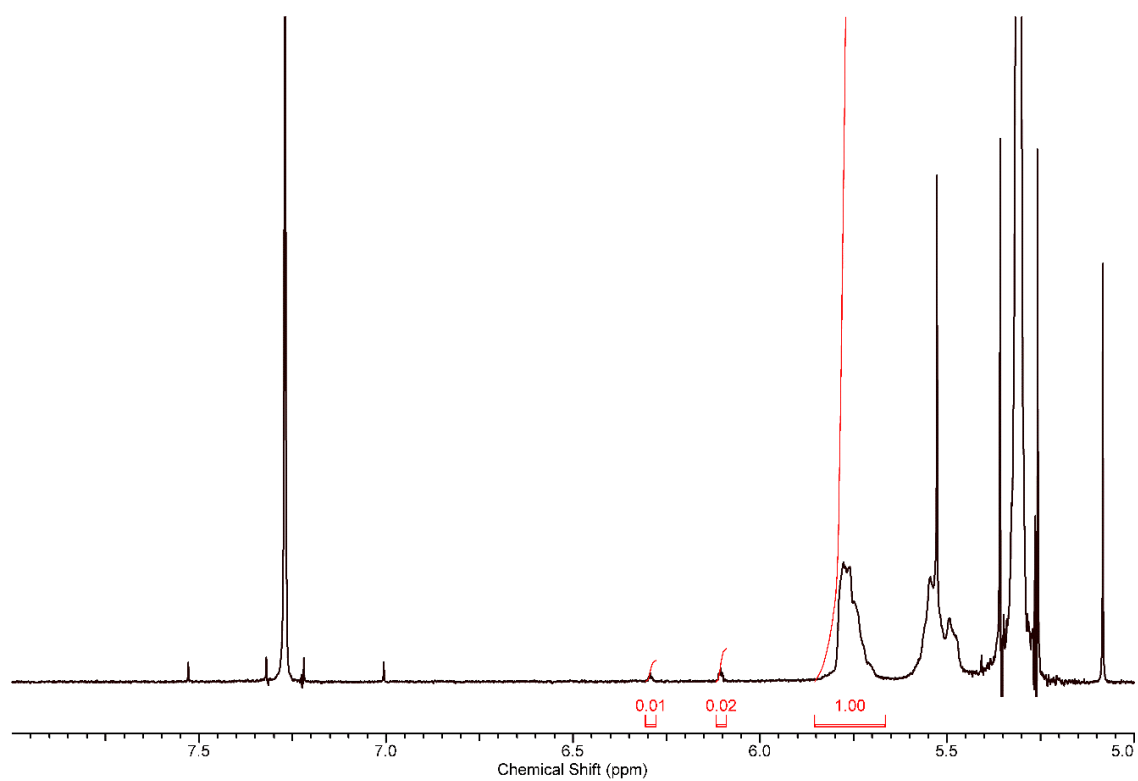


Fig. S277: Crude ¹H NMR (CDCl₃, 400 MHz) spectra of polymerization mixture of **P46** showing olefinic region.

SEC traces of P45 and P46:

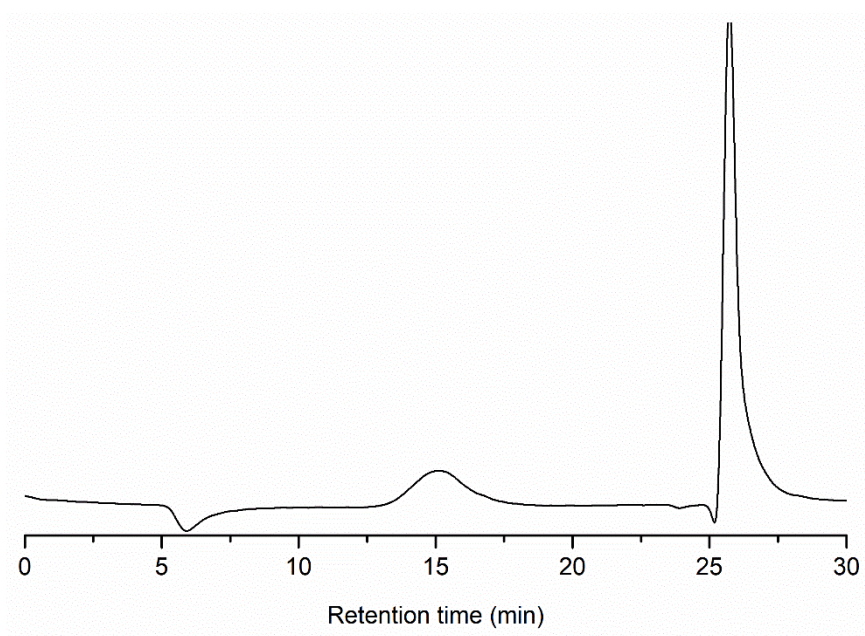


Fig. S278: SEC (CHCl₃) trace for **P45**.

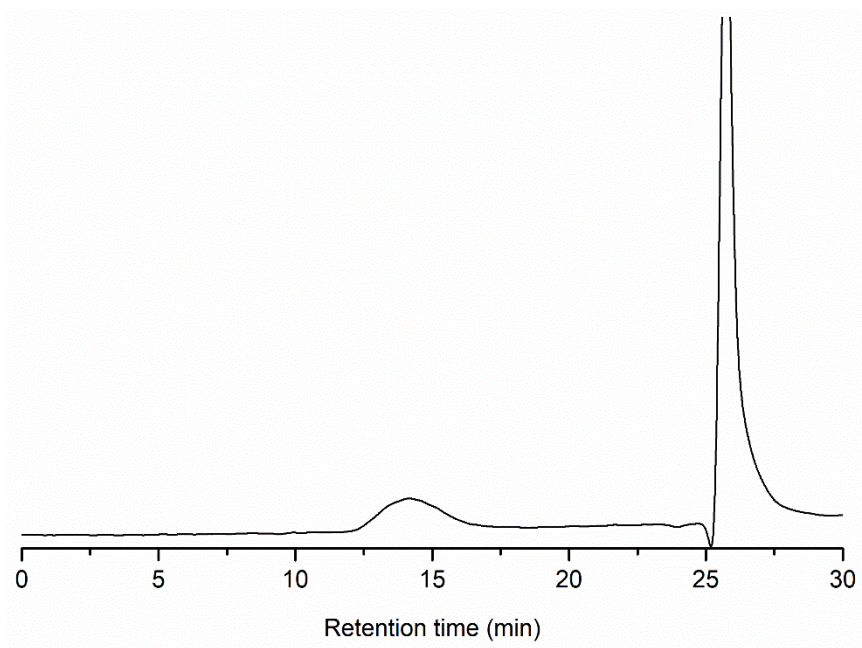


Fig. S279: SEC (CHCl₃) trace for **P46**.

Polymer pictures:

a)



b)

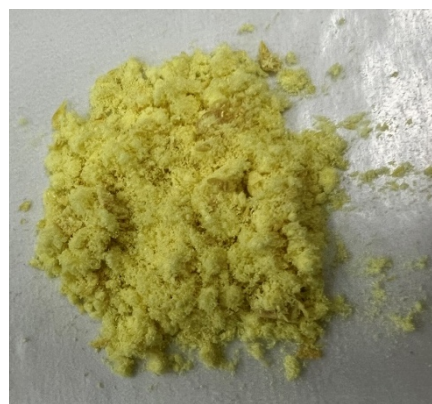


Fig. S280: a) Image of **P15**, b) Image of **P16**.

References

1. J. A. Love, J. P. Morgan, T. M. Trnka and R. H. Grubbs, *Angew. Chemie - Int. Ed.*, 2002, **114**, 4035–4037.
2. P. Liu, M. Yasir and A. F. M. Kilbinger, *Angewandte Chemie International Edition*, 2019, **58**, 15278–15282.
3. C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165–195.