Supporting Information for:

Synthesis of Optically Active Star Polymers Consisting of Helical Poly(phenylacetylene) Chains by the Living Polymerization of Phenylacetylenes and Their Chiroptical Properties

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1. Materials

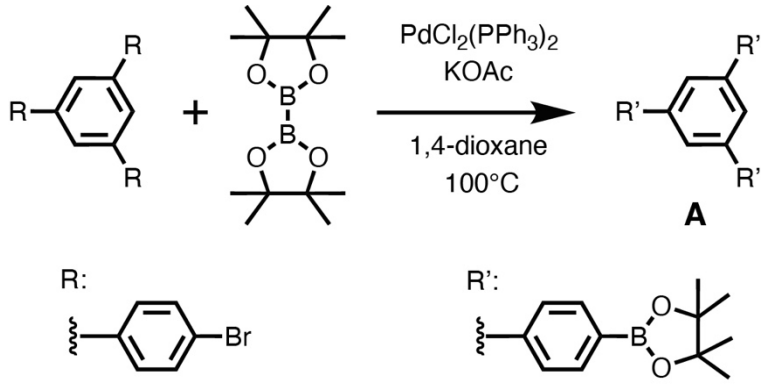
Bis(pinacolato)diboron and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) were purchased from Oakwood Chemical (South Carolina, USA). Triphenylphosphine, potassium acetate (KOAc), and potassium hydroxide (KOH) were purchased from FUJIFILM Wako Pure Chemical (Osaka, Japan). Dimethylaminopyridine (DMAP), 1,3,5-Tri(bromophenyl)benzene, bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$), diphenylacetylene, ethynylbenzene, L-alanine, D-alanine, and *n*-decanol were obtained from Tokyo Chemical Industry (TCI, Tokyo, Japan). (Bicyclo[2.2.1]hepta-2,5-diene)chlororhodium(I) dimer ($[Rh(nbd)Cl]_2$) was obtained from Sigma-Aldrich (St. Louis, MO, USA). Anhydrous tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) were purchased from Kanto Kagaku (Tokyo, Japan), and these solvents were stocked under N_2 atmosphere. Other solvents were purchased from commercial sources and were used without any purification. Ethyl 4-ethynylbenzoate (**2**)[S1] and optically active phenylacetylene monomers (**3***S* and **3***R*)[S2] were synthesized according to the previous paper.

2. Instruments

NMR spectra were taken on a JNM-ECA 500 (JEOL, Tokyo, Japan) (500 MHz for ^{1}H and 125 MHz for ^{13}C) spectrometer in $CDCl_3$ using TMS as the internal standard. IR spectra were measured with a JASCO (Hachioji, Japan) Fourier Transform IR-460 spectrometer. Preparative size exclusion chromatography (SEC) was performed with a LaboACE LC-7080 liquid chromatography system (Japan Analytical Industry (JAI), Tokyo, Japan) using a JAIGEL-2HR (JAI) at room temperature using $CHCl_3$ as the eluent at a flow rate of 10.0 mL/min. The SEC measurements were performed with a JASCO PU-4580 liquid chromatograph equipped with a UV-vis (JASCO MD-4010) detector at 40 °C (controlled by a JASCO CO-4060) using a Shodex (Tokyo, Japan) KF-805L (30 cm) column or three Tosoh (Tokyo, Japan) TSKgel ($G4000H_{XL}$ (30 cm) + $G3000H_{XL}$ (30 cm) + $G3000H_{XL}$ (30 cm)) columns connected in series. THF was used as the eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curves were obtained with polystyrene standards (Tosoh). The absolute weight-average molecular weight (M_w) was measured by SEC fitted with a multiangle light scattering instrument (MALS; Wyatt Technology Corporation DAWN HELEOS I, wavelength 658 nm). The SEC measurement was carried out at 25 °C using THF as an eluent and flow rate of 1.0 $cm^3\ min^{-1}$ with a JASCO DG-2080-53 degasser, an 1100 Series isocratic pump (Agilent), a JASCO CO-2060 Plus column oven, an RI-8020 (Tosoh), and three Shodex KF806L columns. The differential refractive index increase (dn/dc) value was measured in THF at 25 °C using a differential refractometer (Otsuka Electronics, DRM-3000, wavelength 632.8 nm), and it was determined to be $0.158_5\ g^{-1}\ cm^3$. Absorption and circular dichroism (CD) spectra were recorded in a 1.0 cm quartz cell on a JASCO V-650 spectrophotometer and a JASCO J-750 spectropolarimeter equipped with a JASCO PTC-348WI apparatus for temperature control, respectively. The general concentration of polymers was 0.05 mg/mL and calculated based on the monomer units. Elemental analyses were performed by the Research Institute for Instrumental Analysis of Advanced Science Research Center, Kanazawa University, Kanazawa, Japan. Mass spectra were recorded on Bruker Daltonics 9.4T FT-ICR MS SolariX equipped with MALDI source. Differential scanning calorimetry (DSC) measurement was performed on a DSC 250 (TA Instruments, Inc., New Castle, US) from –10 °C to 200 °C by a heating rate of 10 °C/min under nitrogen. Atomic force microscopy (AFM) measurements were performed using a Cypher AFM system (Oxford Instruments-Asylum Research, CA, USA) in air at ambient temperature with standard silicon cantilevers (160AC-NG: MikroMasch operated by NanoAndMore Japan, Saitama, Japan) in the amplitude modulation AFM (AM-AFM).

3. Synthesis

Trifunctional initiator **A** was prepared according to Scheme S1.[S3]

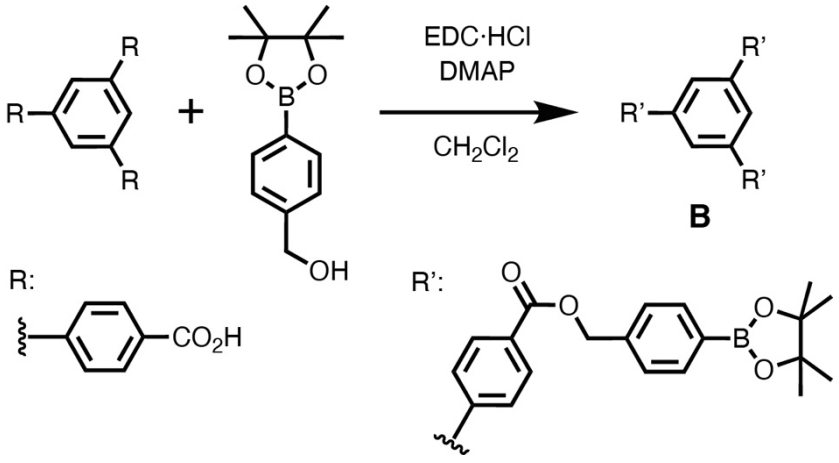


Scheme S1. Synthesis of initiator **A**.

Synthesis of A. Under N_2 atmosphere, 1,3,5-tri(4-bromophenyl)benzene (2.05 g, 3.77 mmol), bis(pinacolato)diboron (4.24 g, 16.6 mmol), KOAc (1.67 mg, 16.6 mmol), and $Pd(PPh_3)_2Cl_2$ (0.15 g, 0.22 mmol) were dissolved in 1,4-dioxane (37 mL). The reaction mixture was refluxed for 19 h and then cooled to room temperature. After filtration, the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: *n*-hexane/ethyl acetate, 10/1 then 2/1, v/v) and then by recycling preparative SEC using chloroform as the eluent to give **A** as a white solid (1.68 g, 66.7% yield).

^{1}H NMR ($CDCl_3$, 500 MHz, 25°C): δ 7.93 (d, J = 8.0 Hz, 6H), 7.82 (s, 3H), 7.71 (d, J = 8.0 Hz, 6H), 1.37 (s, 36H). ^{13}C NMR ($CDCl_3$, 125 MHz, 25°C): δ 143.84, 142.39, 135.49, 126.83, 125.70, 84.01, 25.02 (Note: *C*-B was not detected).

Hydrolyzable trifunctional initiator **B** was prepared according to Scheme S2.



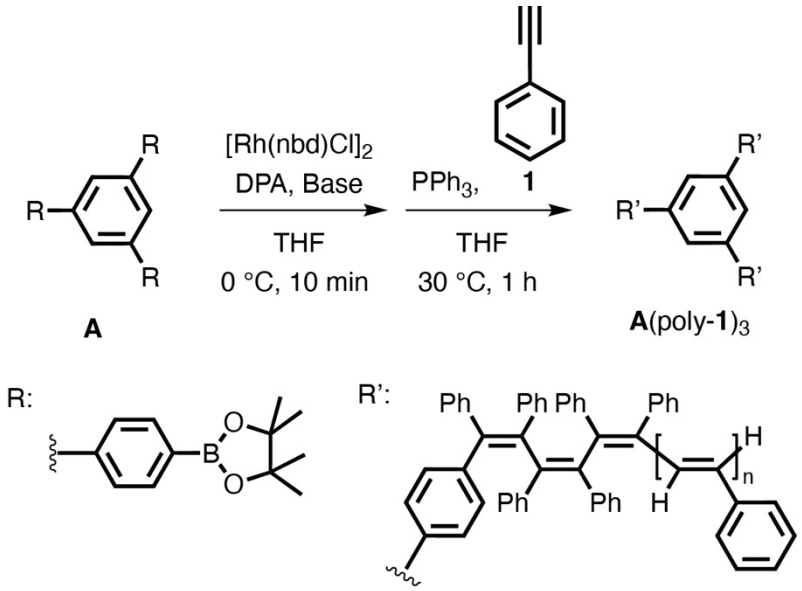
Scheme S2. Synthesis of initiator **B**.

Synthesis of B. Under N_2 atmosphere, 1,3,5-tris(4-carboxyphenyl)benzene (402.95 mg, 0.92 mmol, 1.0 eq.), DMAP (35.21 mg, 0.29mmol, 0.3 eq.), and 4-(hydroxymethyl)phenylboronic acid pinacol ester (753.59 mg, 3.22 mmol, 3.5 eq.) were dissolved in CH_2Cl_2 (9 mL), and then EDC·HCl (626.06 mg, 3.27 mmol, 3.6 eq.) was added. After stirring at 0 °C for 14 h, EDC·HCl (229.74, 1.20 mmol) and 4-(hydroxymethyl)phenylboronic acid pinacol ester (160.39 mg, 0.69 mmol) were added into the reaction mixture again. After stirring at room temperature for another 15 h, the reaction was quenched by the addition of 1N HCl. The solution was extracted with ethyl acetate/*n*-hexane (3/1, v/v) mixture. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, and then dried over anhydrous sodium sulfate. After filtration, the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography using *n*-hexane/ethyl acetate (4/1, v/v) as the eluent and then by recycling preparative SEC using chloroform as the eluent to give **B** as a white solid (146.72 mg, 14.7% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.19 (d, J = 8.0 Hz, 6H), 7.85 (d with s overlapping, 9H), 7.76 (d, J = 8.5 Hz, 6H), 7.47 (d, J = 8.5 Hz, 6H), 5.41 (s, 6H), 1.35 (s, 36H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.30, 145.27, 141.76, 139.13, 135.23, 130.56, 129.52, 127.48, 126.24, 84.04, 66.86, 25.00 (Note: *C*-B was not detected). Elemental analysis: Anal. Calcd. (%) for $C_{66}H_{69}B_3O_{12}$ + $2H_2O$: C, 70.61; H, 6.55; N, 0.00. Found: C, 70.63; H, 6.47; N, 0.07.

4. Polymerization

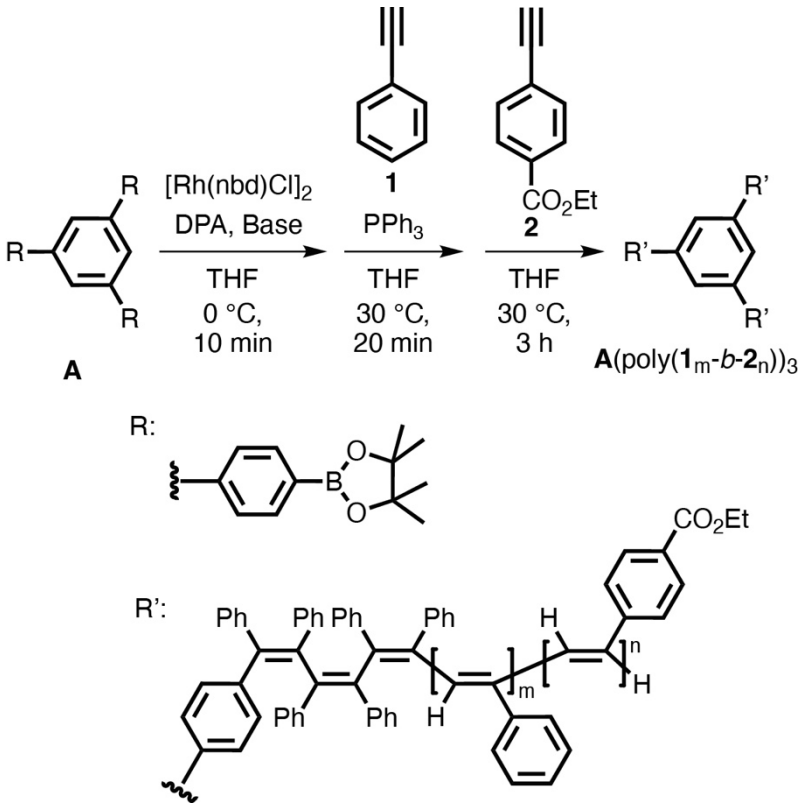
Polymerization of phenylacetylene monomers was performed according to Scheme S3–S7 in a flask under argon atmosphere using a multicomponent Rh-based catalyst system in a similar way as the previously reported procedure[S2] with a slight modification.



Scheme S3. Synthesis of star-shaped polymer **A**(poly-**1**)$_3$ by polymerization of **1** using initiator **A**.

Synthesis of A(poly-1$_{50}$)$_3$. A solution of **A** (6.84 mg, 0.01 mmol), [Rh(nbd)Cl]$_2$ (13.8 mg, 0.03 mmol), and diphenylacetylene (32.1 mg, 0.18 mmol) in THF (0.20 mL) was prepared at 0 °C. To this was added 10% (w/v) KOH aqueous solution (51 μL, 0.09 mmol), and the resultant solution was stirred for 10 min at 0 °C. After PPh_3 (47.4 mg, 0.18mmol) was rapidly added to the solution, an orange solution including active catalyst was obtained. After this catalyst solution was diluted with THF (2.8 mL), phenylacetylene **1** (165 μL, 1.5mmol) was instantaneously added to the catalyst solution at 0 °C. After stirring for 1 h at 30 °C, the polymerization reaction was quenched by the addition of acetic acid (100 μL). The mixture was poured into excess methanol (MeOH) and the formed yellow precipitate was collected by centrifugation, washed with MeOH, and dried under vacuum at room temperature. **A**(poly-**1**$_{50}$)$_3$ was obtained as a yellow powder (158.2 mg, 91.8% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): Signals based on a polymer chain (only main signals): δ 6.95 (d, J = 7.5 Hz, 3H), 6.63 (d, 6.0 Hz, 2H), 5.84 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.01, 139.43, 131.97, 127.92, 127.69, 126.85.



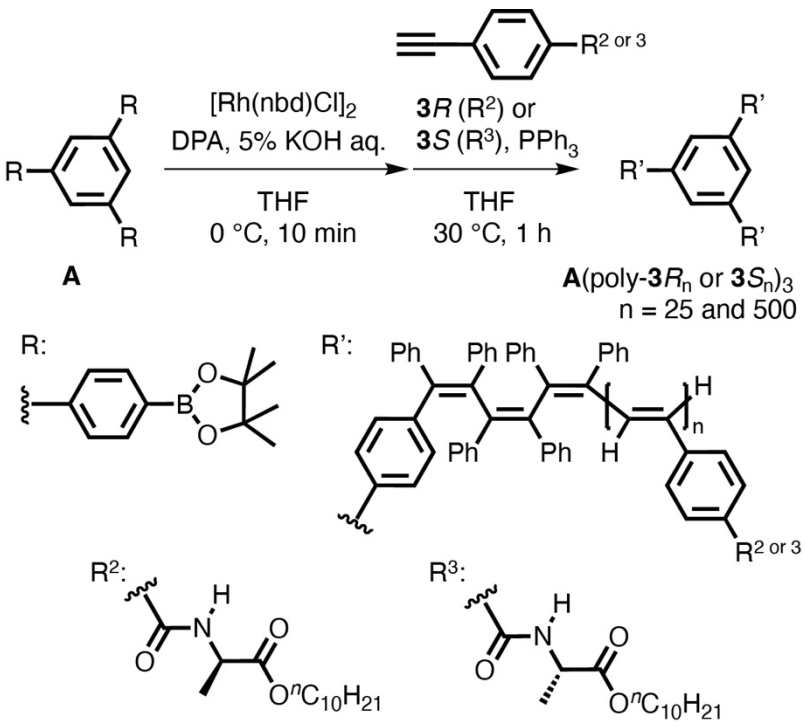
Scheme S4. Synthesis of block-type star-shaped polymer **A**(poly-$\mathbf{1}_m$-*b*-$\mathbf{2}_n$)$_3$ by copolymerization of **1** and **2** using initiator **A**.

Synthesis of A(poly-$\mathbf{1}_{50}$-*b*-$\mathbf{2}_{50}$)$_3$. A solution of **A** (13.7 mg, 0.02 mmol), [Rh(nbd)Cl]$_2$ (27.6 mg, 0.06 mmol), and diphenylacetylene (64.2 mg, 0.36 mmol) in THF (0.80 mL) was prepared at 0 °C. To this was added 10% (w/v) KOH aqueous solution (100 μL, 0.18 mmol) and the resultant solution was stirred for 10 min at 0 °C. After PPh_3 (94.5 mg, 0.36 mmol) was rapidly added to the solution, an orange solution including active catalyst was obtained. After this catalyst solution was diluted with THF (5.2 mL), phenylacetylene **1** (330 μL, 3.0 mmol) was instantaneously added to the catalyst solution at 0 °C and the resultant solution was stirred for 20 min at 30 °C. Ethyl 4-ethynylbenzoate **2** (480 μL, 3.0 mmol) was then quickly added to the mixture. After stirring for 3 h at 30 °C, the polymerization reaction was quenched by the addition of acetic acid (100 μL). The mixture was poured into excess MeOH and the formed yellow precipitate was collected by centrifugation, washed with MeOH, and dried under vacuum. **A**(poly-$\mathbf{1}_{50}$-*b*-$\mathbf{2}_{50}$)$_3$ was obtained as a yellow powder (811.2 mg, 93.5% yield).

^{1}H NMR (500 MHz, $CDCl_3$), Signals based on a polymer chain (only main signals): δ 7.63 (d, J = 7.5 Hz, 2H), 6.94 (d, J = 8.0 Hz, 3H), 6.67 (d, J = 8.0 Hz, 2H), 6.63 (d, J = 6.0 Hz, 2H), 5.84 (s, 1H), 5.80 (s, 1H), 4.29 (q, J = 6.8 Hz, 2H), 1.33 (t, J = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.95, 146.14, 142.98, 139.41, 139.21, 132.46, 131.96, 129.53, 127.89, 127.67, 127.26, 126.83, 61.04, 14.43.

Synthesis of A(poly-1_{250}-*b*-2_{250})$_3$. A catalyst solution was prepared by the same procedure as that described above. The catalyst solution (0.20 mL, 6 μmol) was rapidly added to a THF solution (2.8 mL) of **1** (165 μL, 1.5 mmol) at 0 °C, and the resultant solution was stirred for 20 min at 30 °C. Monomer **2** (240 μL, 1.5 mmol) was then quickly added to the mixture. After stirring for 3h at 30 °C, the polymerization reaction was quenched by the addition of acetic acid (100 μL). The mixture was poured into excess MeOH and the formed yellow precipitate was collected by centrifugation, washed with MeOH, and dried under vacuum. **A**(poly-$\mathbf{1}_{250}$-*b*-$\mathbf{2}_{250}$)$_3$ was obtained as a yellow powder (354.9 mg, 84.8% yield).

^{1}H NMR (500 MHz, $CDCl_3$), Signals based on a polymer chain (only main signals): δ 7.63 (d, J = 7.5 Hz, 2H), 6.94 (d, J = 7.5 Hz, 3H), 6.67 (d, J = 8.0 Hz, 2H), 6.63 (d, J = 7.0 Hz, 2H), 5.85 (s, 1H), 5.80 (s, 1H), 4.29 (q, J = 6.7 Hz, 2H), 1.33 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.95, 146.14, 142.99, 139.42, 139.20, 132.46, 131.96, 129.54, 127.90, 127.67, 127.26, 126.83, 61.04, 14.43.



Scheme S5. Synthesis of **A**(poly-$\mathbf{3}R_n$)$_3$ and **A**(poly-$\mathbf{3}S_n$)$_3$ (n = 25 and 500) by polymerization of **3***R* or **3***S* using initiator **A**.

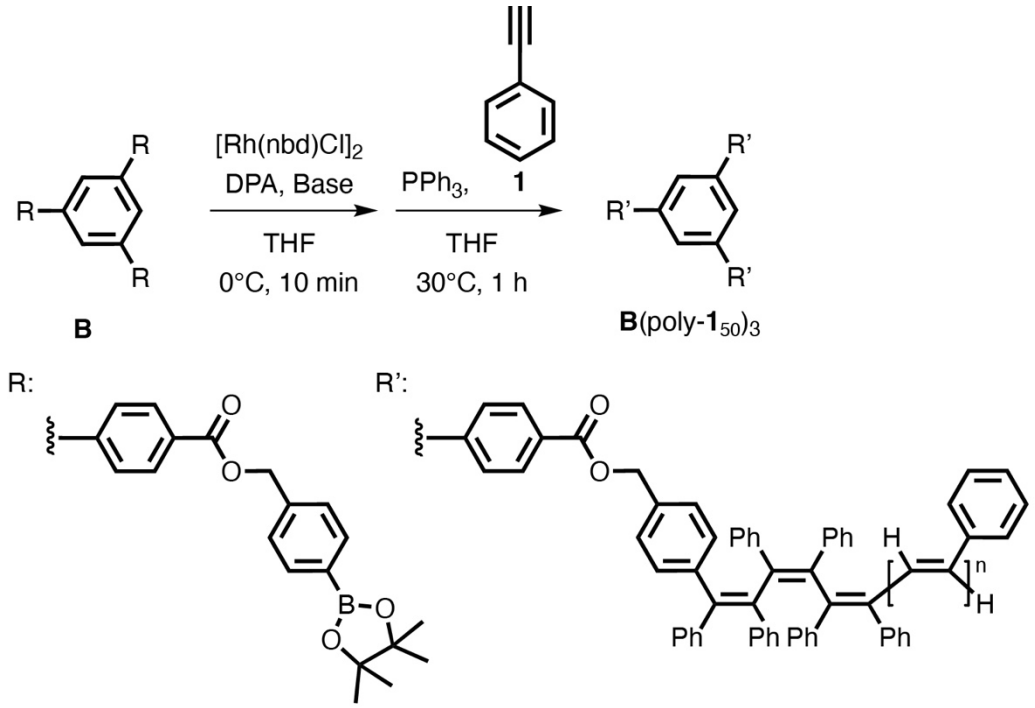
Synthesis of A(poly-$3R_{25}$)$_3$. A catalyst solution was prepared by the same procedure as that described above. The catalyst solution (1.0 mL, 3.3 μmol) was rapidly added to a THF solution (1.5 mL) of chiral monomer **3***R* (89.7 mg, 0.25 mmol) at 0 °C. After stirring for 1 h at 30 °C, the polymerization reaction was quenched by the addition of acetic acid (100 μL). The mixture was poured into excess *n*-hexane and the formed yellow precipitate was collected by centrifugation, washed with MeOH, and

dried under vacuum. **A**(poly-**3***R*$_{25}$)$_3$ was obtained as a yellow powder (91.1 mg, 95.2% yield).
^{1}H NMR (500 MHz, $CDCl_3$), Signals based on a polymer chain (only main signals): δ 5.68-7.69 (br-m, 3H), 4.69 (br, 1H), 4.10 (br, 2H), 1.25-1.61 (br, 19H), 0.87 (br, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.53, 166.43, 132.81, 127.66, 65.57, 48.63, 32.03, 29.72, 29.46, 28.68, 26.02, 22.81, 18.12,14.25 and some signals at downfield region were unclear due to broadening.

Synthesis of A(poly-3*S*$_{25}$)$_3$. In the same way as that for the synthesis of **A**(poly-**3***R*$_{25}$)$_3$, **A**(poly-**3***S*$_{25}$)$_3$, was also obtained as a red solid (86.6 mg, 90.5% yield) by using **3***S* as the monomer.
^{1}H NMR (500 MHz, $CDCl_3$), Signals based on a polymer chain (only main signals): δ 5.89-8.17 (br-m, 6H), 4.70 (br, 1H), 4.10 (br, 2H), 1.25-1.61 (br, 19H), 0.87 (br, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ173.58, 166.51, 132.66, 127.69, 65.53, 48.73 32.02, 29.72, 29.47, 28.68 26.02, 22.81, 18.07, 14.25 and some signals at downfield region were unclear due to broadening.

Synthesis of A(poly-3*R*$_{500}$)$_3$. A catalyst solution was prepared by the same procedure as that described above. The catalyst solution (100 μL, 0.33 μmol) was rapidly added to a THF solution of chiral monomer **3***R* (178.3 mg, 0.5 mmol) at 0 °C. After stirring for 1 h at 30 °C, the polymerization reaction was quenched by the addition of a few drops of acetic acid. The mixture was poured into excess MeOH-water mixture (1/1, v/v) and the formed yellow precipitate was collected by centrifugation and was dried under vacuum. **A**(poly-**3***R*$_{500}$)$_3$ was obtained as a yellow solid (148.2 mg, 82.6% yield).
^{1}H NMR (500 MHz, $CDCl_3$), Signals based on a polymer chain (only main signals): δ 6.24-7.58 (br, 3H), 4.08-4.68 (br, 2H), 0.86-1.61 (br, 22H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.41, 166.84, 132.83, 127.34, 65.54, 48.80, 32.02, 29.68, 29.46, 28.69, 26.00, 22.81, 18.12, 14.25 and some signals at downfield region were unclear due to broadening.

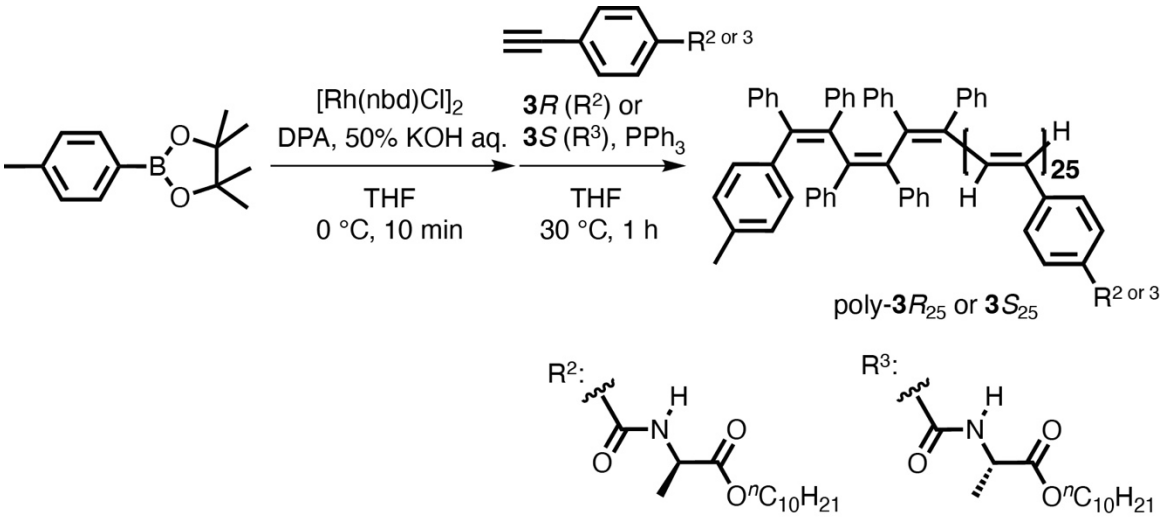
Synthesis of A(poly-3*S*$_{500}$)$_3$. In the same way as that for the synthesis of **A**(poly-**3***R*$_{500}$)$_3$, **A**(poly-**3***S*$_{500}$)$_3$ was obtained as a yellow powder (288.0 mg, 80.3% yield) by using **3***S* as the monomer.
^{1}H NMR (500 MHz, $CDCl_3$), Signals based on a polymer chain (only main signals): δ 6.24-8.26 (br-m, 3H), 3.87-4.69 (br, 2H), 0.85-1.61 (br, 22H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.14, 65.50, 48.53, 32.03, 29.68, 29.45, 26.02, 22.81, 18.07, 14.25 and some signals at downfield region were unclear due to broadening.



Scheme S6. Synthesis of **B**(poly-$\mathbf{1}_{50}$)$_3$ by polymerization of **1** using initiator **B**.

Synthesis of B(poly-$\mathbf{1}_{50}$)$_3$. A solution of **B** (10.8 mg, 0.01 mmol), [Rh(nbd)Cl]$_2$ (13.8 mg, 0.03 mmol), and diphenylacetylene (32.1 mg, 0.18 mmol) in THF (0.20 mL) was prepared at 0 °C. To this was added 10% (w/v) KOH aqueous solution (51 μL, 0.09 mmol) and the resultant solution was stirred for 10 min at 0 °C. After PPh_3 (47.2 mg, 0.18mmol) was rapidly added to the solution, an orange solution including active catalyst was obtained. After this catalyst solution was diluted with THF (2.8 mL), phenylacetylene **1** (165 μL, 1.5mmol) was rapidly added to the catalyst solution at 0 °C. After stirring for 1 h at 30 °C, acetic acid (100 μL) was added to the reaction mixture to quench the polymerization reaction. The mixture was poured into excess MeOH and the formed yellow precipitate was collected by centrifugation, washed with MeOH, and dried under vacuum. **B**(poly-$\mathbf{1}_{50}$)$_3$ was obtained as a yellow powder (162.1 mg, 91.9% yield).

^{1}H NMR (500 MHz, $CDCl_3$), Signals based on a polymer chain (only main signals); δ 6.94 (d, J = 7.5 Hz, 165H), 6.63 (d, J = 6.0 Hz, 96H), 5.84 (s, 49H), Characteristic signals based on a terminal group; 5.04-5.43 (br, 2.0H, -COOC$\underline{H}_2$Ph). ^{13}C NMR ($CDCl_3$, 500 MHz): δ 143.00, 139.42, 131.96, 127.92, 127.69, 126.85.



Scheme S7. Synthesis of linear polymer poly-**3***S*$_{25}$ and poly-**3***R*$_{25}$.

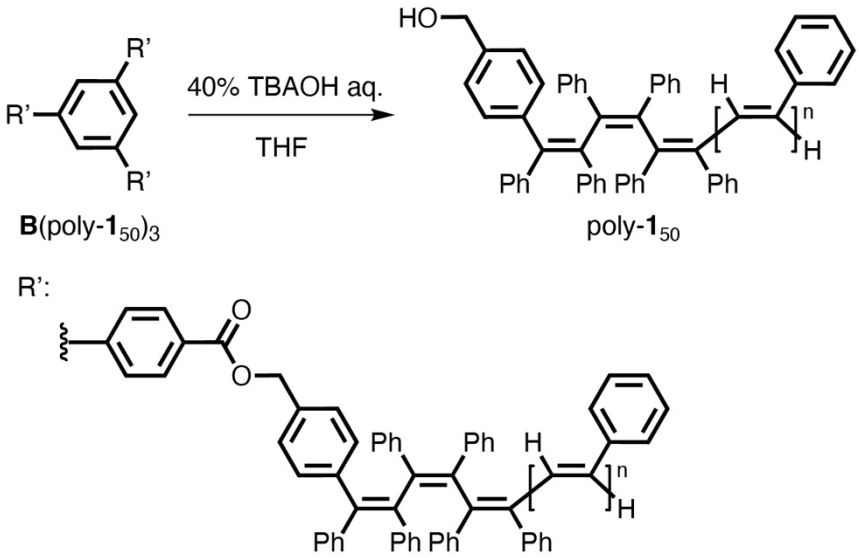
Synthesis of poly-3*S*$_{25}$. A solution of 4-methylphenylboronic acid (8.19 mg, 0.06 mmol), [Rh(nbd)Cl]$_2$ (9.30 mg, 0.02 mmol), and diphenylacetylene (21.3 mg, 0.12 mmol) in THF (0.40 mL) was prepared at 0 °C. To this was added 50% (w/v) KOH aqueous solution (11 μL, 0.10 mmol) and the resultant solution was stirred for 5 min at 0 °C. After PPh_3 (31.4 mg, 0.12mmol) was rapidly added to the solution, an orange solution including active catalyst was obtained. After a THF solution (1.6 mL) of monomer **3*S*** (357.4 mg, 1.0 mmol) was rapidly added to the catalyst solution at 0 °C, the resultant solution was stirred for 1 h at 30 °C. After acetic acid (a few drops) was added to the reaction mixture to quench the reaction, the mixture was poured into excess MeOH. The formed red-brown precipitate was collected by centrifugation, washed with MeOH, and dried under vacuum. Poly-**3***S*$_{25}$ (M_n: 7.2 x 10^3, M_w/M_n: 1.03) was obtained as a red solid (317.2 mg, 84.5% yield).

^{1}H NMR (500 MHz, $CDCl_3$), Signals based on a polymer chain (only main signals): δ 6.87-7.70 (br-m, 6H), 4.71 (br, 1H), 4.12 (br, 2H), 1.26-1.63 (m, 19H), 0.87 (br, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.47, 166.85, 132.77, 127.64, 65.53, 48.71, 32.03, 29.72, 29.47, 28.69, 26.04, 22.82, 18.17, 14.25 and some signals at downfield region were unclear due to broadening.

Synthesis of poly-3*R*$_{25}$. In the same way as that for the synthesis of poly-**3***S*$_{25}$, poly-**3***R*$_{25}$ was also obtained as a red solid (242.8 mg, 79.9% yield) by using **3***R* as the monomer.

^{1}H NMR (500 MHz, $CDCl_3$), Signals based on a polymer chain (only main signals): δ 6.71-7.73 (br-m, 6H), 4.71 (br, 1H), 4.10 (br, 2H), 1.25-1.63 (m, 19H), 0.87 (br, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.40, 166.94, 145.25, 132.71, 127.58, 65.48, 48.66, 31.98, 29.67, 29.42, 28.63, 25.99, 22.77, 18.03, 14.20 and some signals at downfield region were unclear due to broadening.

5. Hydrolysis of B(poly-1_{50})$_3$



Scheme S8. Isolation of the arm poly-$\mathbf{1}_{50}$ chains form **B**(poly-$\mathbf{1}_{50}$)$_3$ upon hydrolysis of the ester groups.

To a THF solution (400 μL) of **B**(poly-$\mathbf{1}_{50}$)$_3$ (30.3 mg, 1.75 x 10^{-3} mmol) was added 40% aqueous TBAOH (5.0 µl, 7.65 x 10^{-3} mmol). After stirring for 4 h at room temperature, the reaction mixture was poured into excess MeOH. The formed precipitate was washed with MeOH and dried under vacuum. Finally, poly-$\mathbf{1}_{50}$ was isolated from the corresponding star-shaped **B**(poly-$\mathbf{1}_{50}$)$_3$ as a yellow powder (22.3 mg, 76.2% yield).

^{1}H NMR (500 MHz, $CDCl_3$), Signals based on a polymer chain (only main signals); δ 6.94 (d, J = 7.5 Hz, 187H), 6.63 (d, J = 7.0 Hz, 100H), 5.84 (s, 49H), Characteristic signals based on a terminal group; 4.23-4.84 (br, 2.0H, -PhC$\underline{H}_2$OH), 3.65-3.87 (br, 1H). ^{13}C NMR ($CDCl_3$, 500 MHz): δ 143.00, 139.43, 131.97, 127.92, 127.69, 126.84.

6. AFM measurements

For identification of single molecules of **A**(poly-$\mathbf{3}R_{500}$)$_3$ (Figures 7 and S4), a very dilute stock solution (0.0005 mg/ml) of **A**(poly-$\mathbf{3}R_{500}$)$_3$ (run 8 in Table 3) was prepared in dry toluene. Samples for the AFM measurements of **A**(poly-$\mathbf{3}R_{500}$)$_3$ were prepared by spin casting 30 μL aliquots of the stock solutions on freshly cleaved mica at room temperature and the sample was dried under vacuum at room temperature for 2 h. The WSXM or Gwyddion image processing software was used for the image analysis.

7. Supporting data

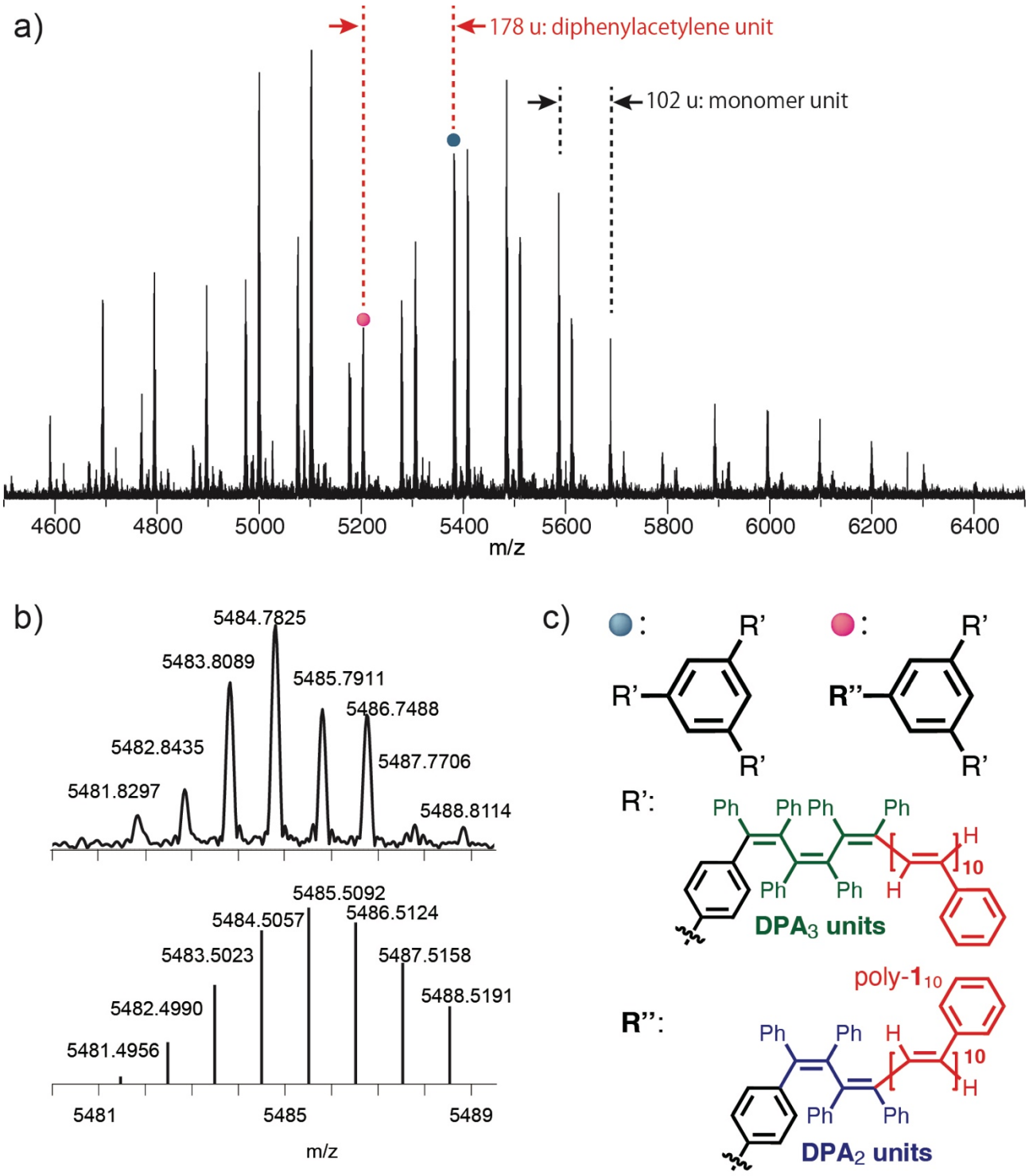


Figure S1. (a) MALDI-TOF-MS spectra of the oligomer of the star-shaped poly(phenylacetylene) (**A**(poly-**1**$_{10}$)$_3$) synthesized under the same condition of run 3 in Table 1 with a different feed ratio ([**1**]/[**A**/3] = 10). (b) Expanded spectra of **A**(poly-**1**$_{10}$)$_3$. (c) Chemical structure of **A**(poly-**1**$_{10}$)$_3$. Two types of poly-**1**$_{10}$ which have 3 DPA units (DPA$_3$) and 2 DPA (DPA$_2$) units are produced.[S4]

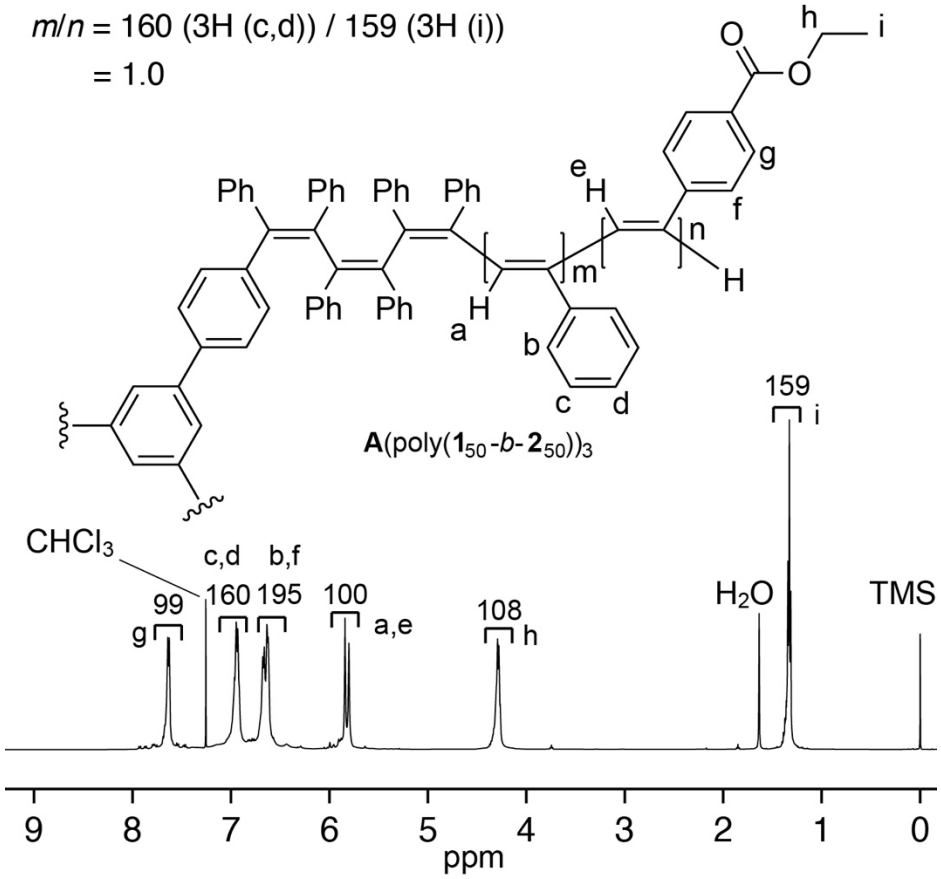


Figure S2. ^{1}H NMR spectrum of **A**(poly(**1**$_{50}$-*b*-**2**$_{50}$))$_3$ (run 4 in Table 2) in $CDCl_3$ at room temperature.

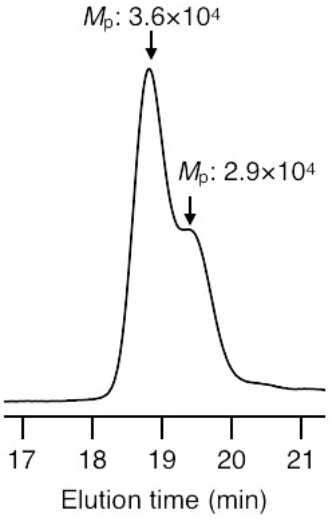
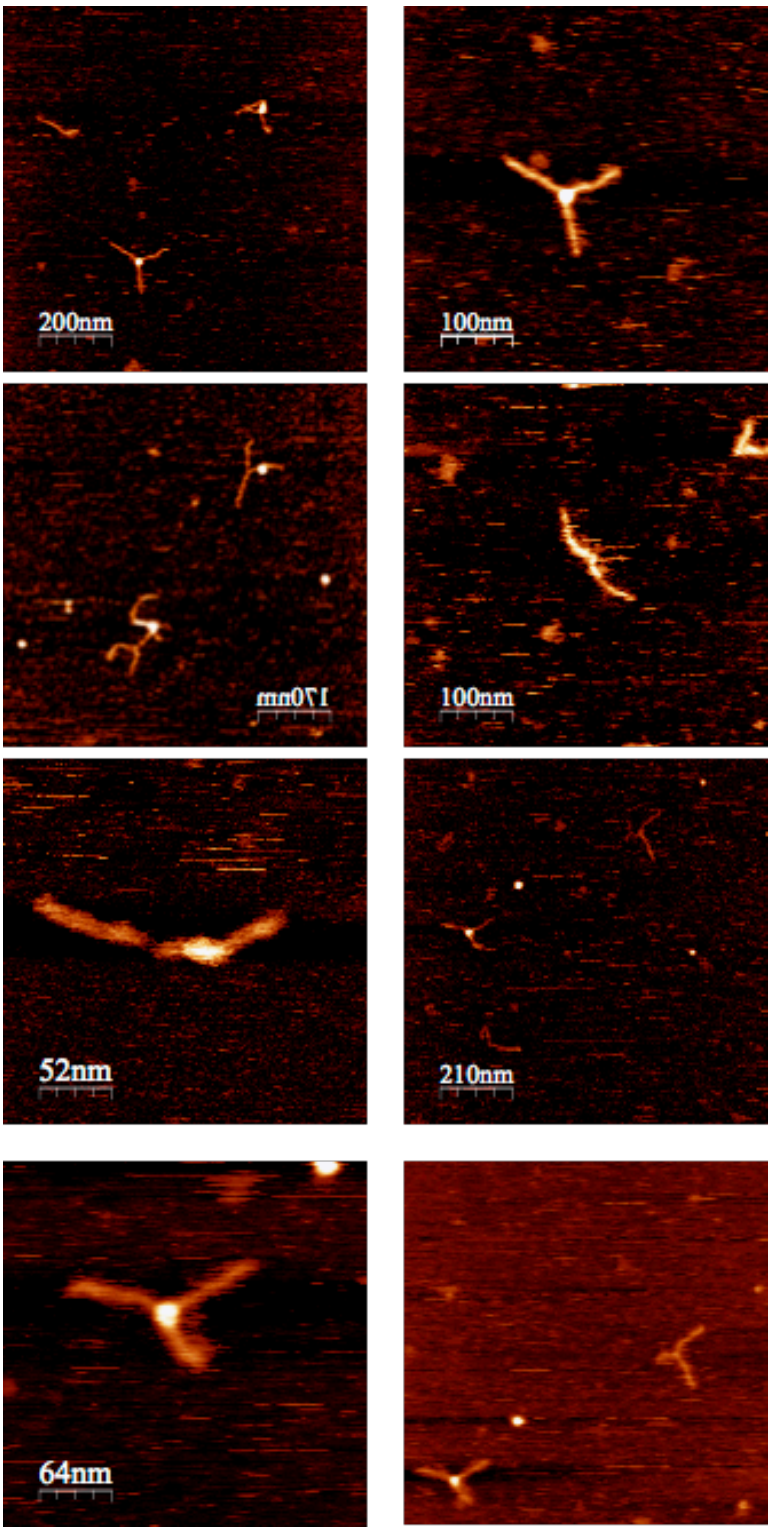
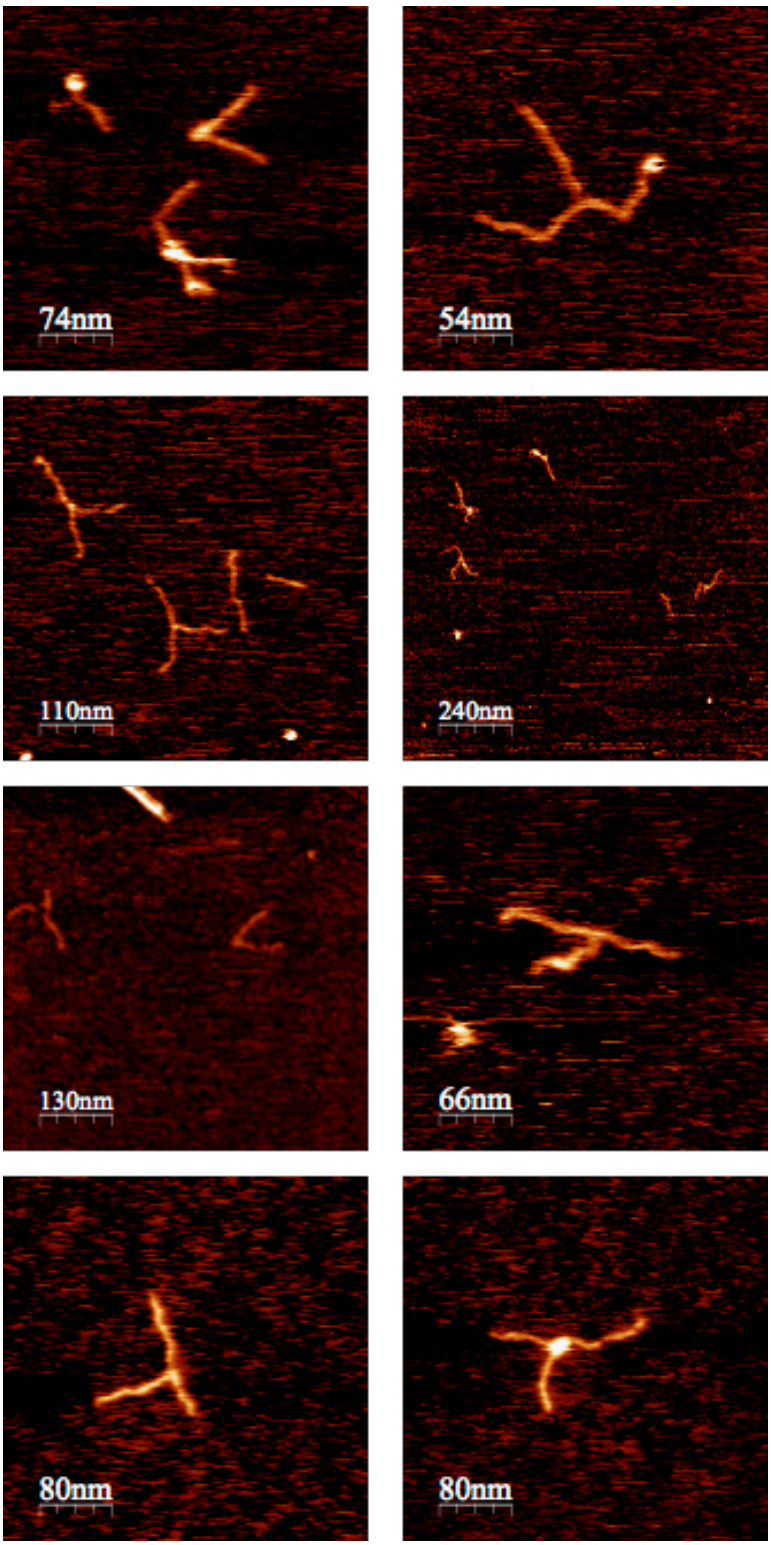


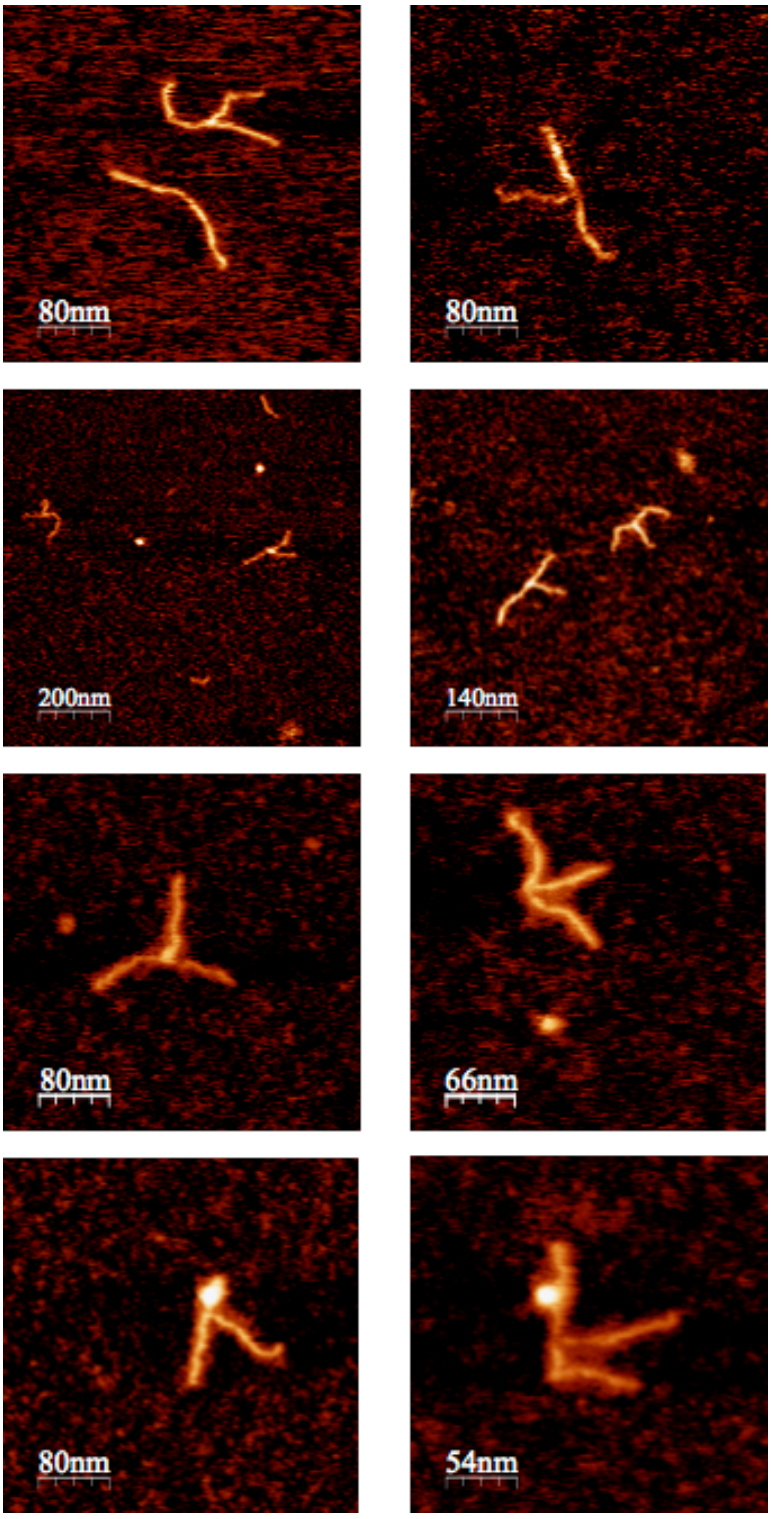
Figure S3. SEC chromatogram of the obtained **A**(poly(**1**$_{50}$-*b*-**2**$_{50}$))$_3$ in the multistage copolymerization of phenylacetylenes (1st stage: **1**, 2nd stage: **2**) with a Rh-based multi-component catalyst system using initiator **A**. The reaction time of 1st stage is 1 h.



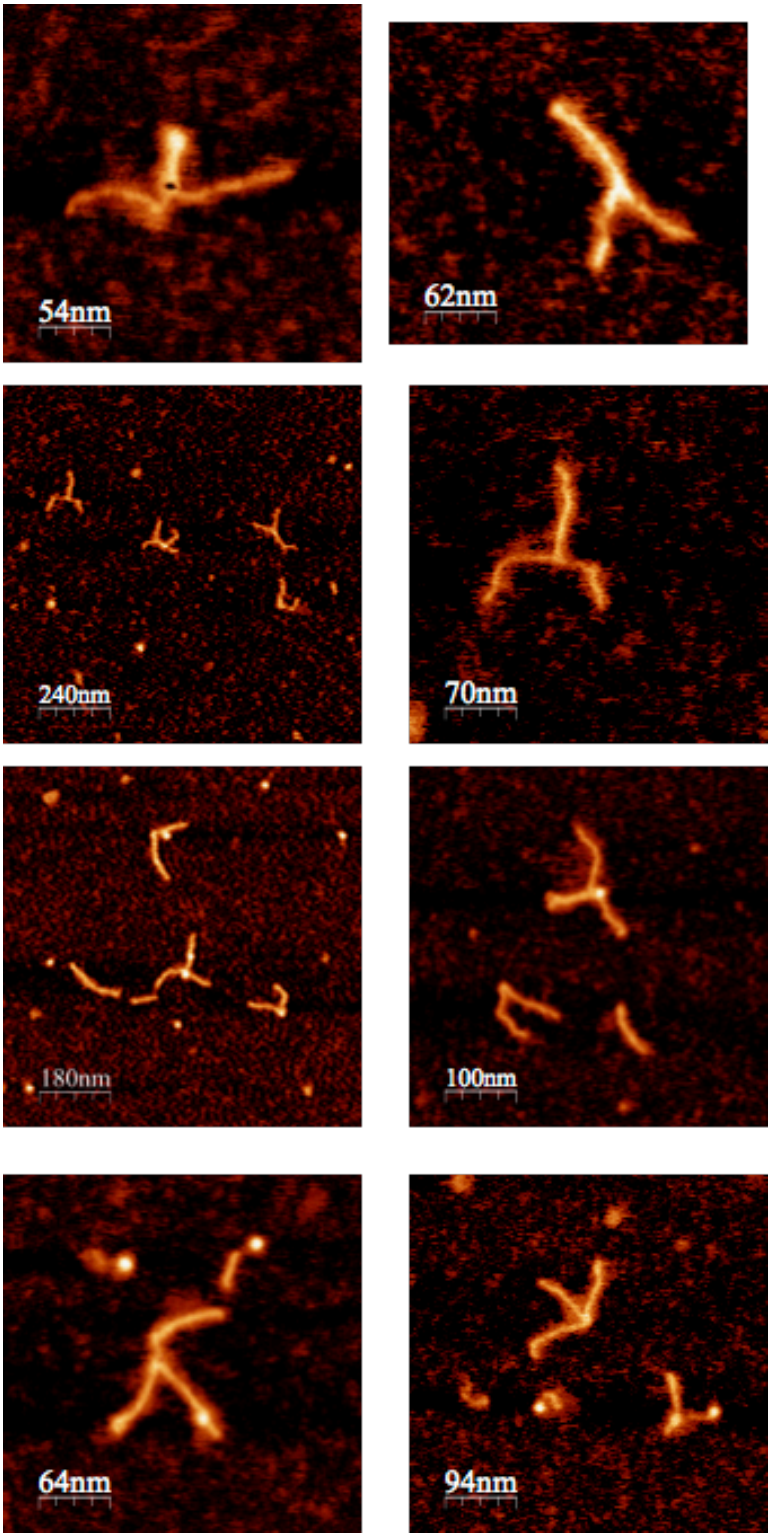
(**Figure S4** to be continued)



(**Figure S4** to be continued)



(**Figure S4** to be continued)



(**Figure S4** to be continued)

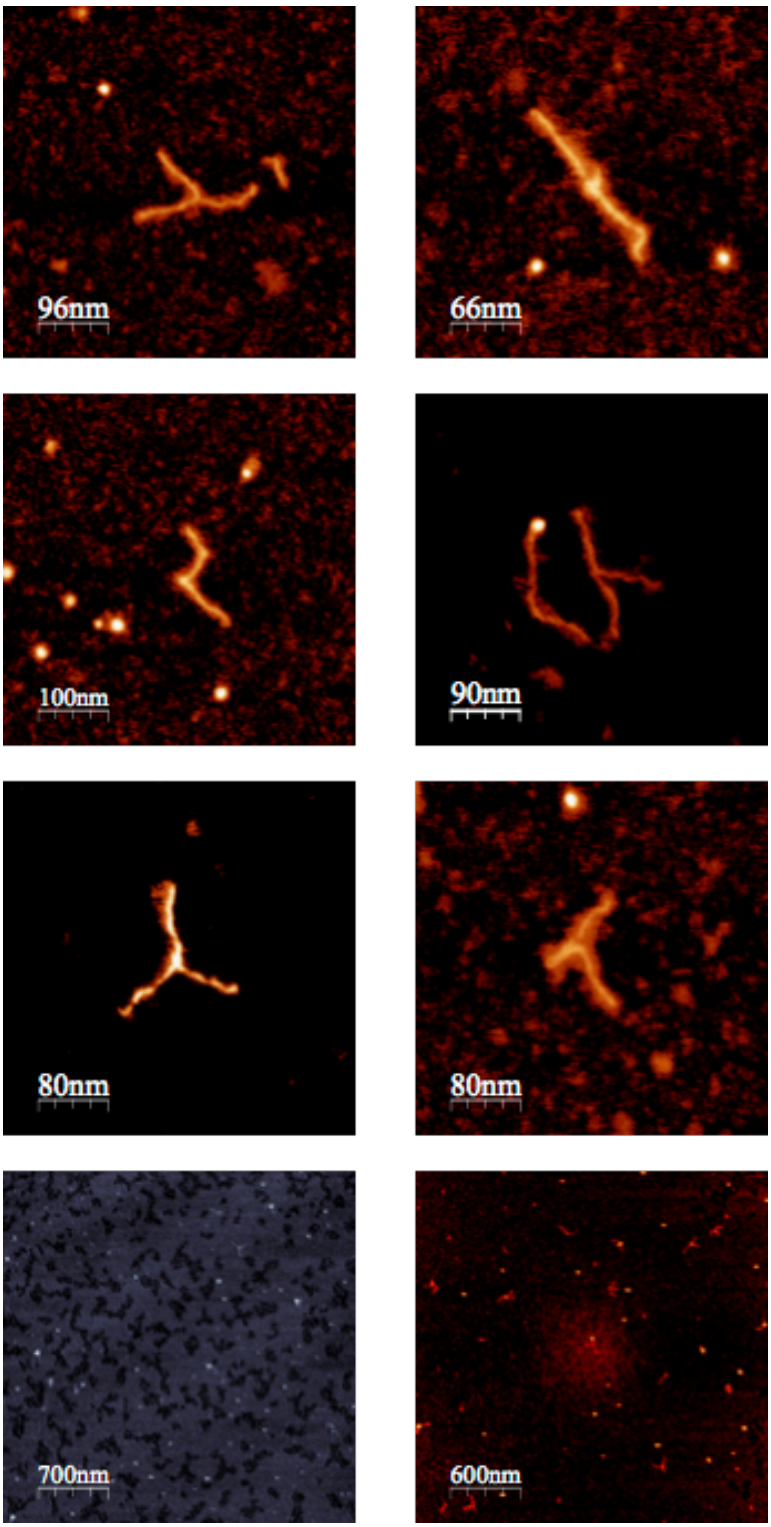


Figure S4. AFM images of star polymer **A**(poly-**3**R_{500})$_3$ on mica.

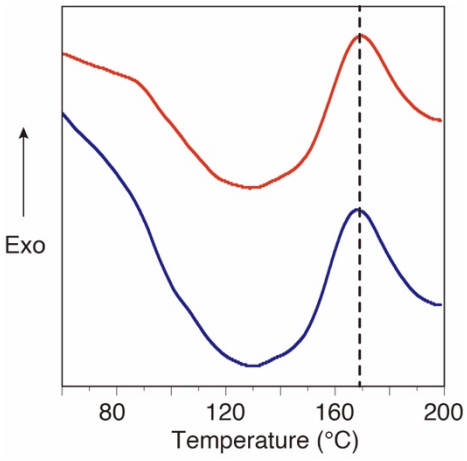


Figure S5. DSC charts of the three-armed chiral polymer (**A**(poly-**3**S_{25})$_3$) (red line) and liner chiral polymer (poly-**3**S_{25}) (blue line).

8. Supporting references

S1) E. Yashima, T. Matsushima and Y. Okamoto, Chirality Assignment of Amines and Amino Alcohols Based on Circular Dichroism Induced by Helix Formation of a Stereoregular Poly((4-carboxyphenyl)acetylene) through Acid－Base Complexation. *J. Am. Chem. Soc.,* **1997**, *119*, 6345-6359. DOI: 10.1021/ja964470y.

S2) K. Okoshi, K. Sakajiri, J. Kumaki and E. Yashima, Well-Defined Lyotropic Liquid Crystalline Properties of Rigid-Rod Helical Polyacetylenes. *Macromolecules.,* **2005**, *38*, 4061-4064. DOI: 10.1021/ma0503312.

S3) Q. Wang, C. Yu, H. Long, Y. Du, Y. Jin and W. Zhang, Solution-Phase Dynamic Assembly of Permanently Interlocked Aryleneethynylene Cages through Alkyne Metathesis. *Angew. Chem. Int. Ed*., **2015**, *54*, 7550-7554. DOI: https://doi.org/10.1002/anie.201501679.

S4) T. Taniguchi, T. Yoshida, K. Echizen, K. Takayama, T. Nishimura and K. Maeda, Facile and Versatile Synthesis of End-Functionalized Poly(phenylacetylene)s: A Multicomponent Catalytic System for Well-Controlled Living Polymerization of Phenylacetylenes. *Angew. Chem. Int. Ed.*, **2020**, *59*, 8670-8680. DOI: 10.1002/anie.202000361

9. NMR spectral data

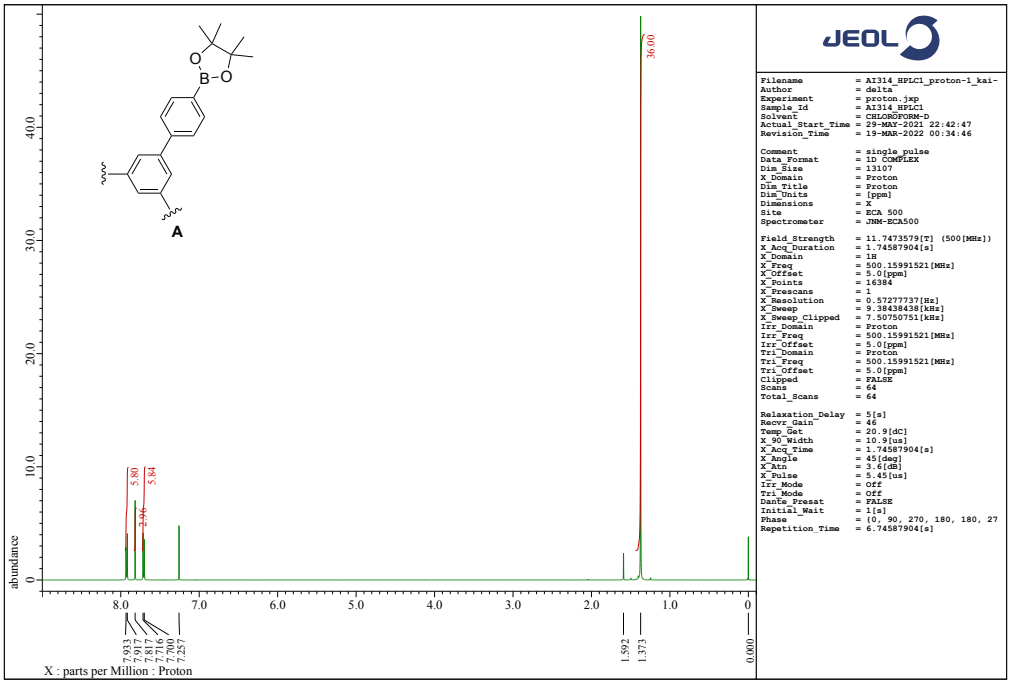


Figure S6. ^{1}H NMR (500 MHz, $CDCl_3$, 21 °C) spectrum of **A**.

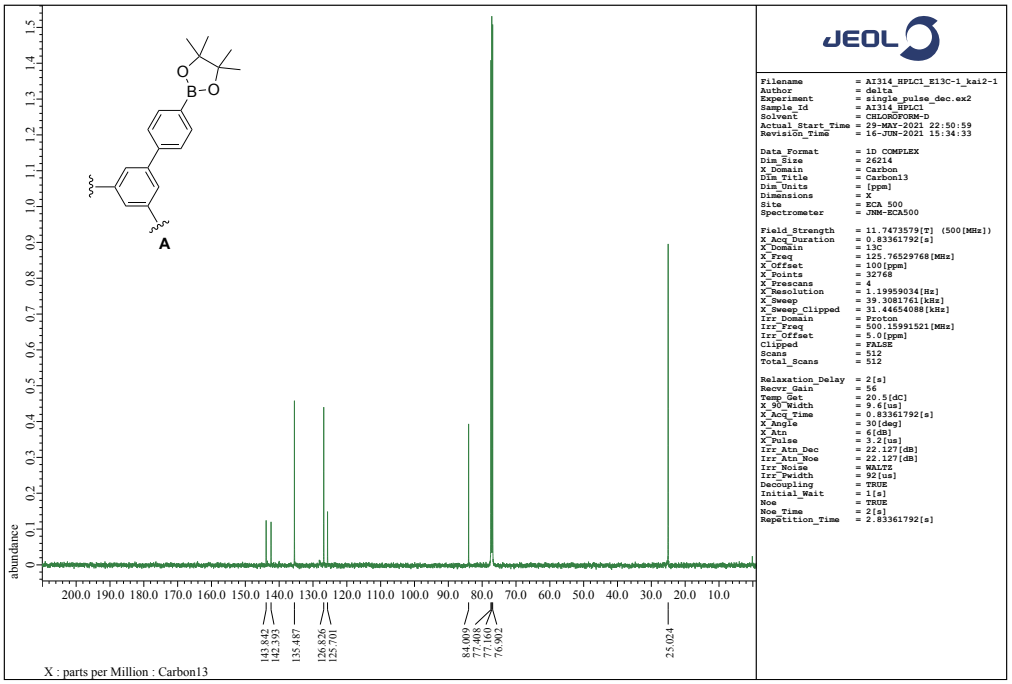


Figure S7. ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C) spectrum of **A**.

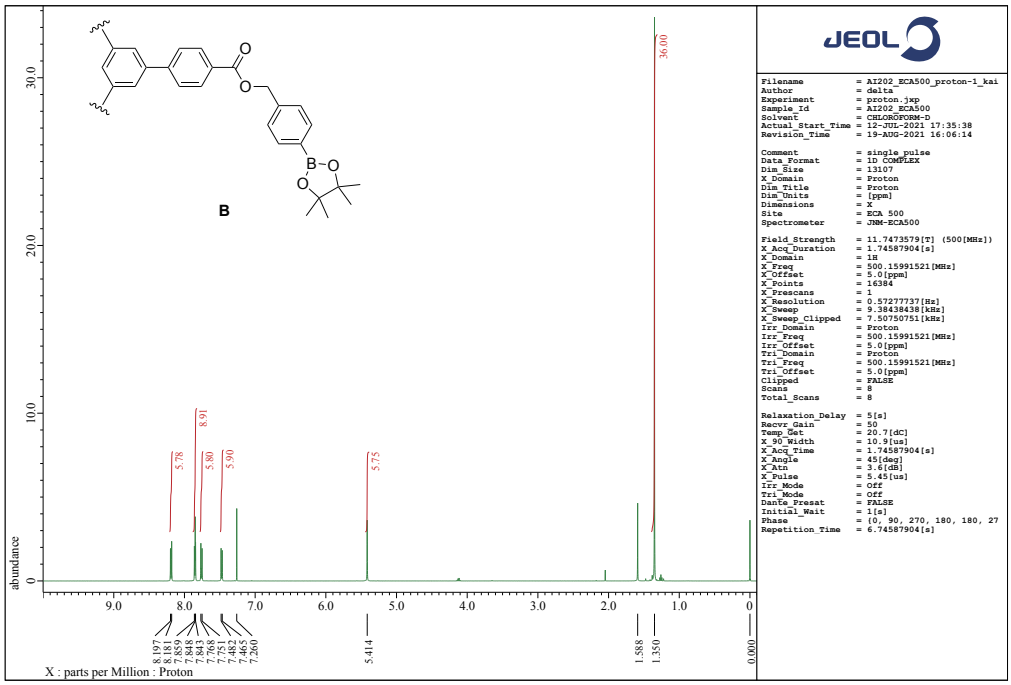


Figure S8. ^{1}H NMR (500 MHz, $CDCl_3$, 21 °C) spectrum of **B**.

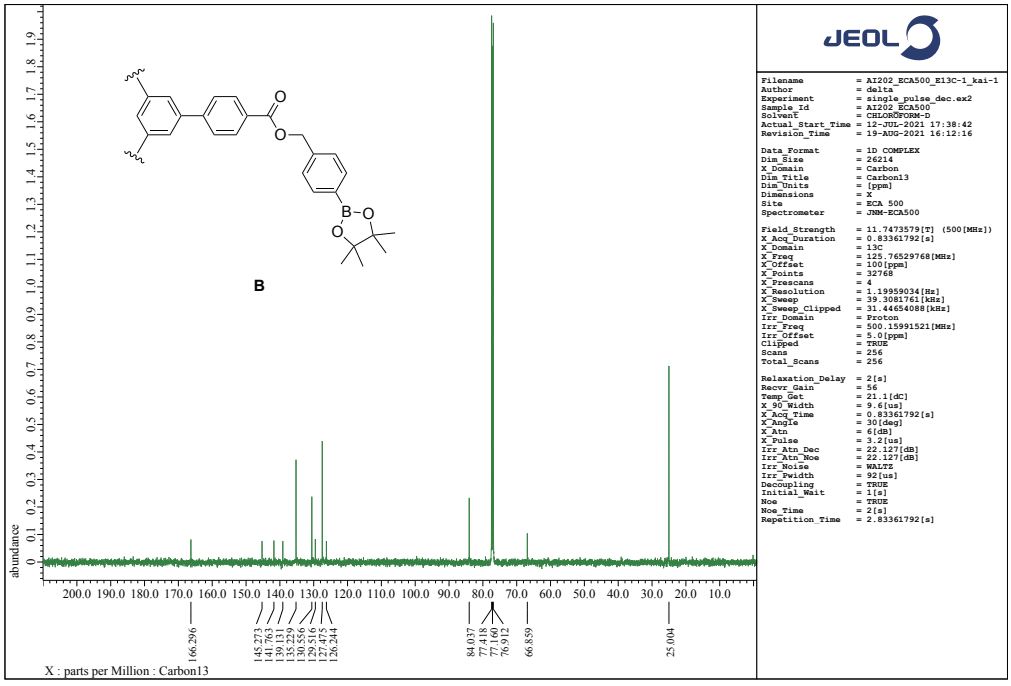


Figure S9. ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C) spectrum of **B**.

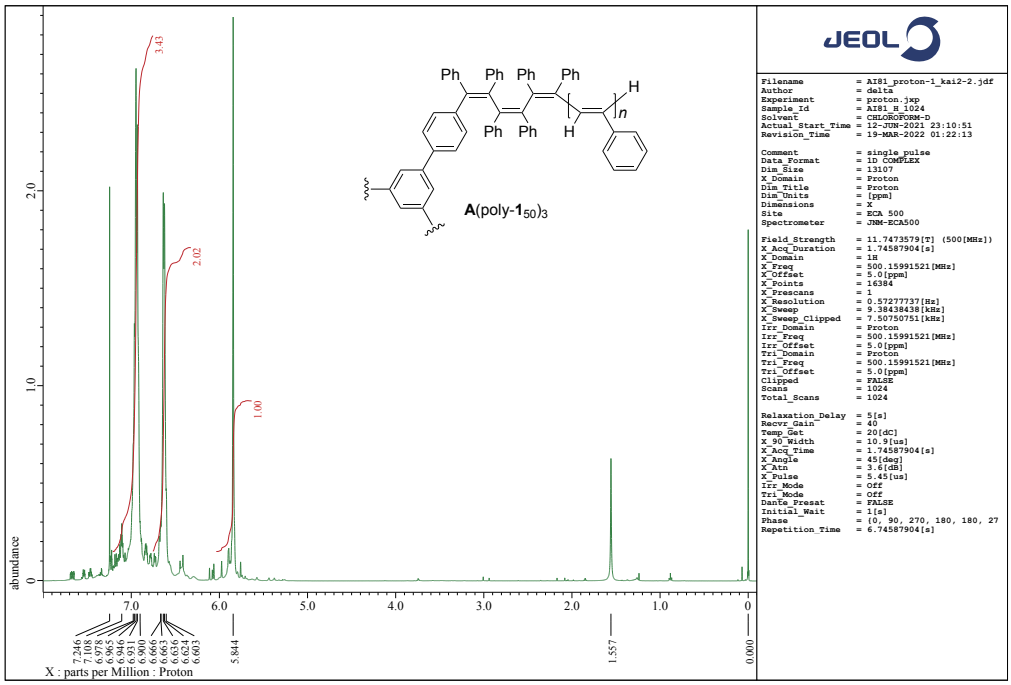


Figure S10. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) spectrum of **A**(poly-**1**$_{50}$)$_3$.

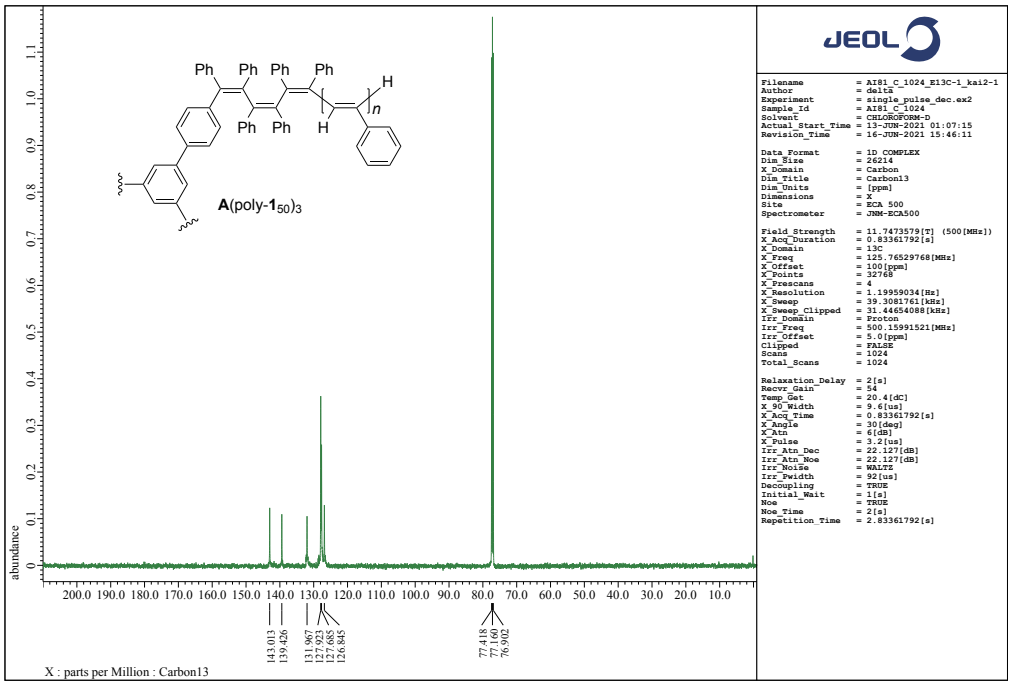


Figure S11. ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) spectrum of **A**(poly-**1**$_{50}$)$_3$.

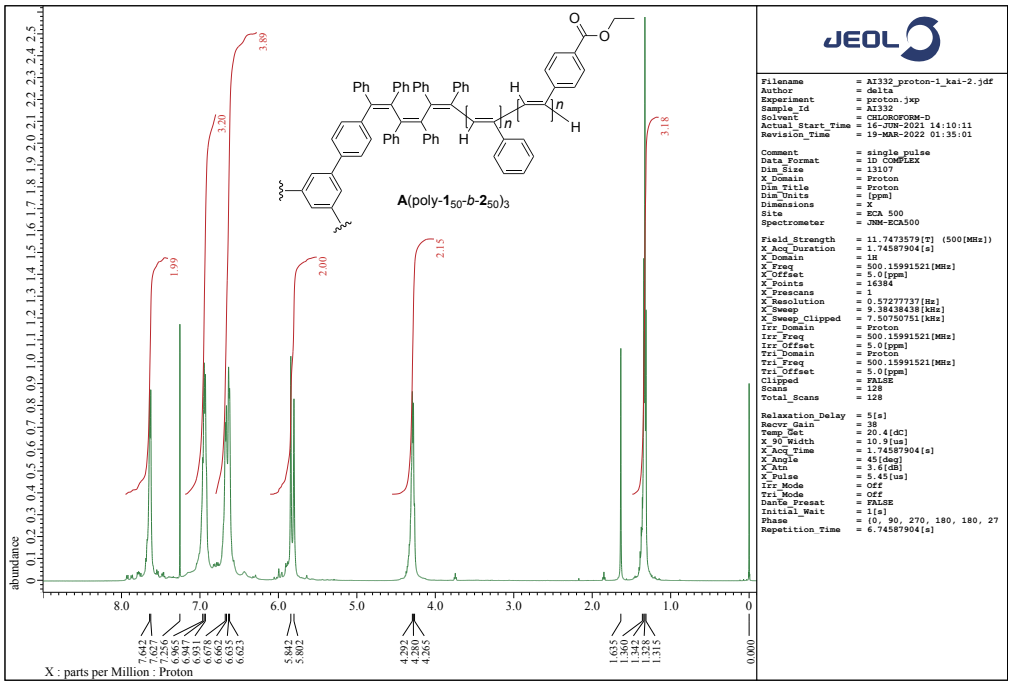


Figure S12. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) spectrum of **A**(poly(**1**$_{50}$-*b*-**2**$_{50}$))$_3$.

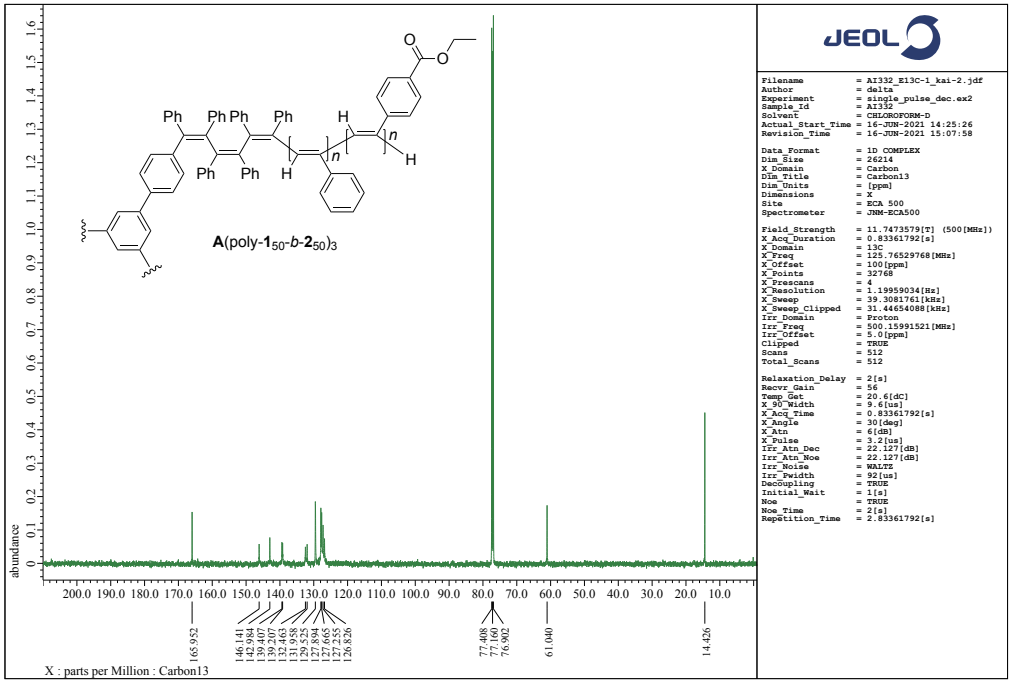


Figure S13. ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C) spectrum of **A**(poly(**1**$_{50}$-*b*-**2**$_{50}$))$_3$.

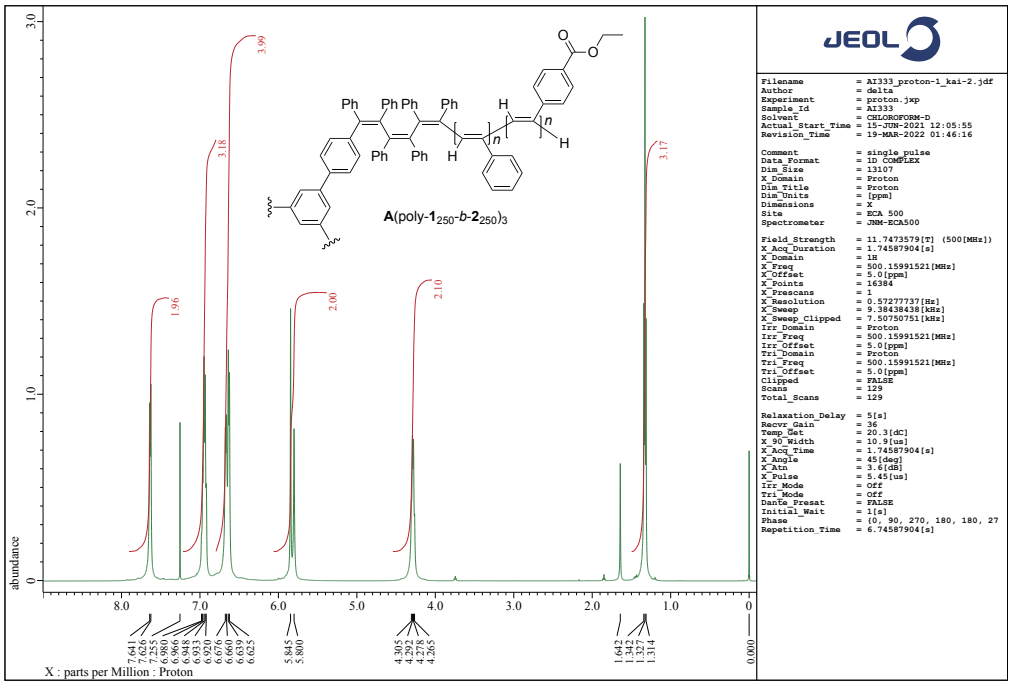


Figure S14. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) spectrum of **A**(poly(**1**$_{250}$-*b*-**2**$_{250}$))$_3$.

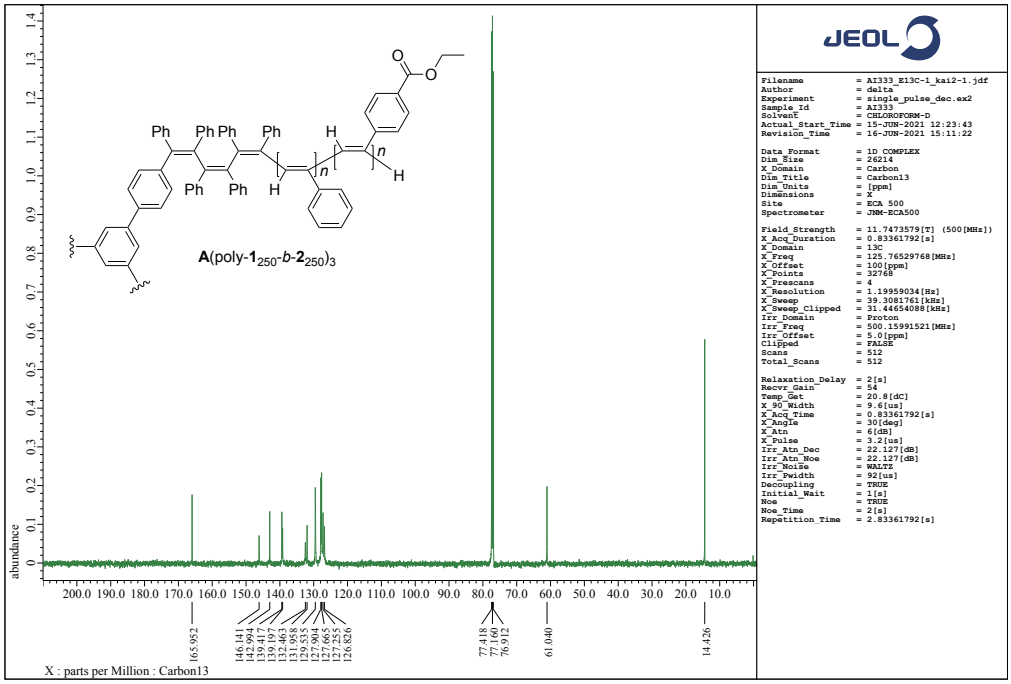


Figure S15. ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C) spectrum of **A**(poly(**1**$_{250}$-*b*-**2**$_{250}$))$_3$.

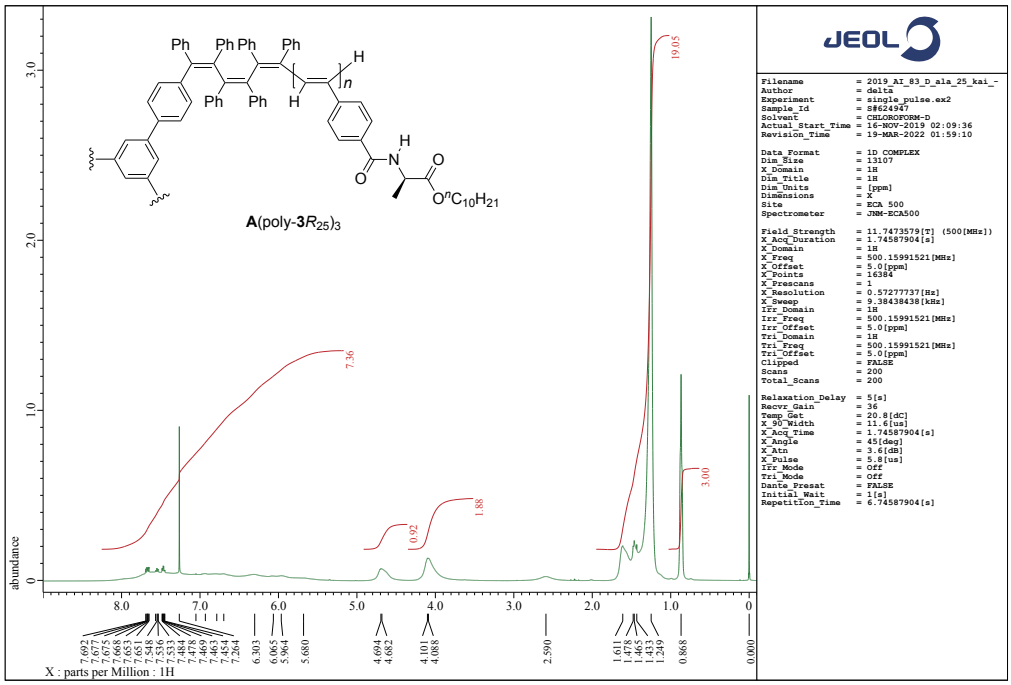


Figure S16. ^{1}H NMR (500 MHz, $CDCl_3$, 21 °C) spectrum of **A**(poly-**3**R_{25})$_3$.

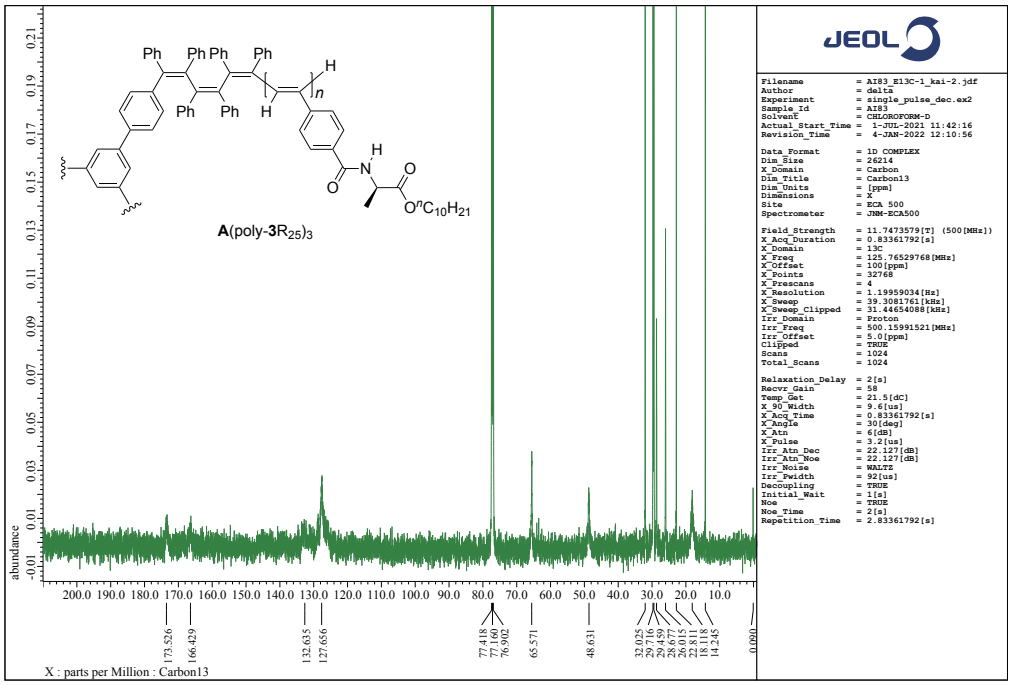


Figure S17. ^{13}C NMR (125 MHz, $CDCl_3$, 22 °C) spectrum of **A**(poly-**3**R_{25})$_3$.

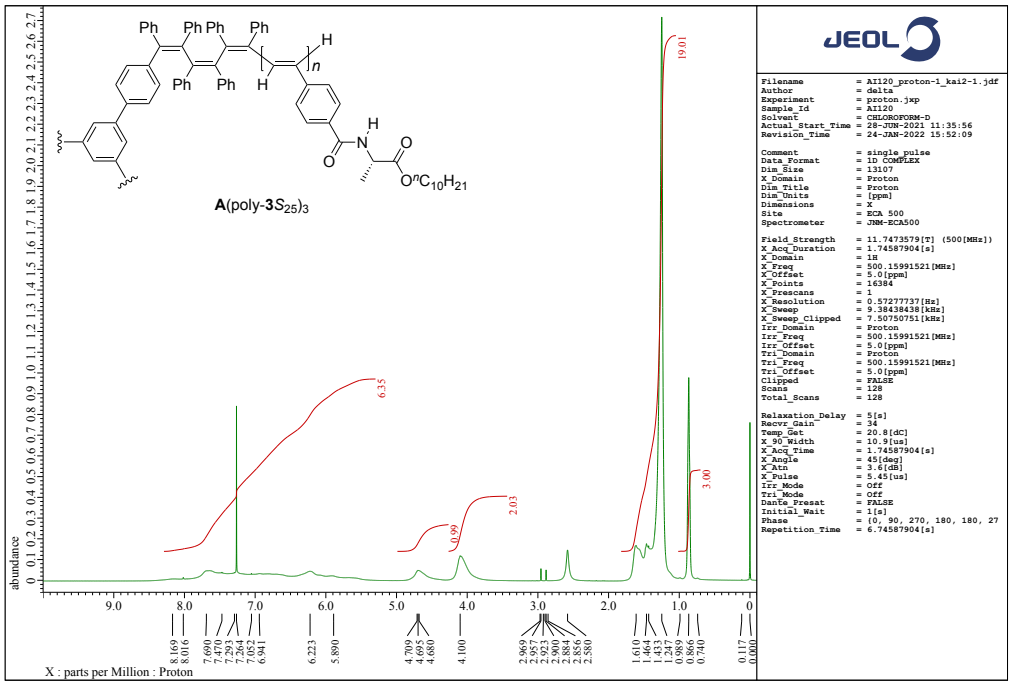


Figure S18. ^{1}H NMR (500 MHz, $CDCl_3$, 21 °C) spectrum of **A**(poly-**3**S_{25})$_3$.

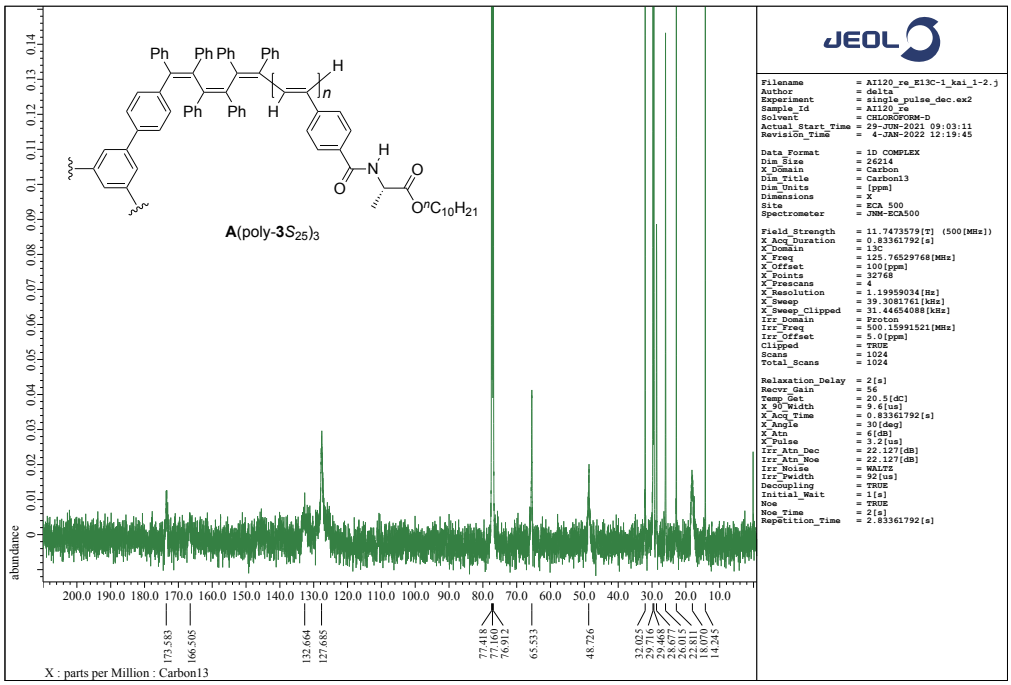


Figure S19. ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C) spectrum of **A**(poly-**3**S_{25})$_3$.

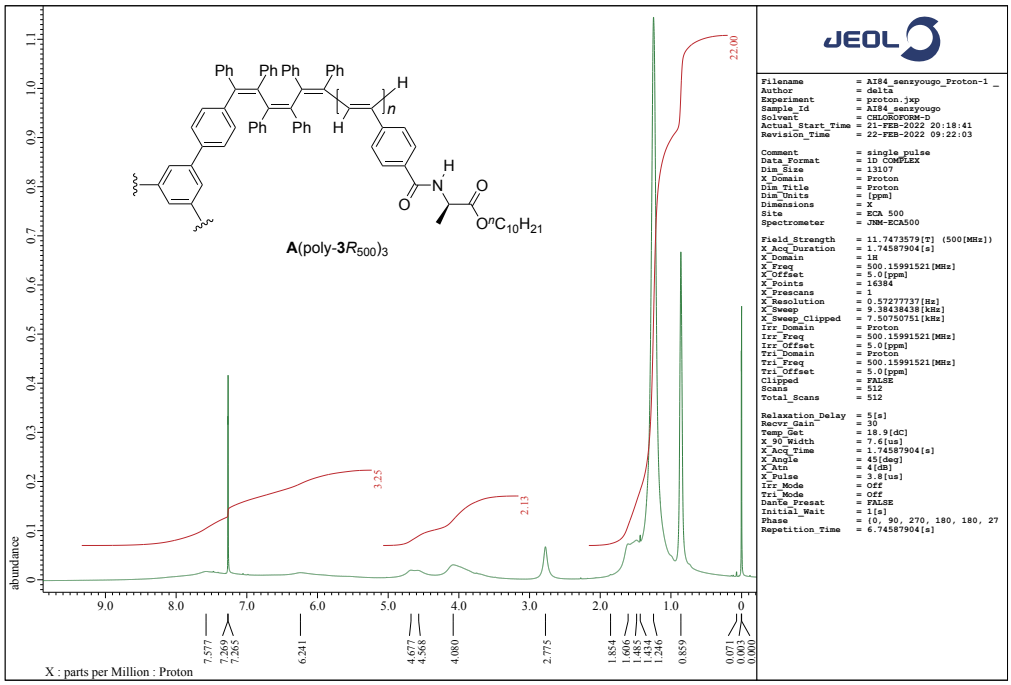


Figure S20. ^{1}H NMR (500 MHz, $CDCl_3$, 19 °C) spectrum of **A**(poly-**3**R_{500})$_3$.

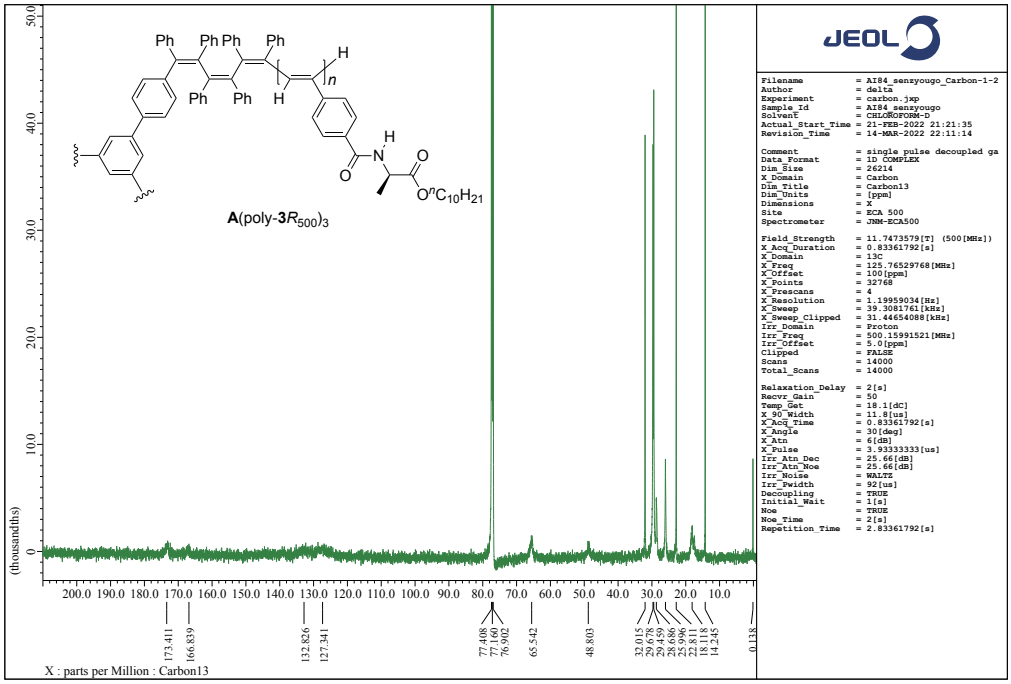


Figure S21. ^{13}C NMR (125 MHz, $CDCl_3$, 18 °C) spectrum of **A**(poly-**3**R_{500})$_3$.

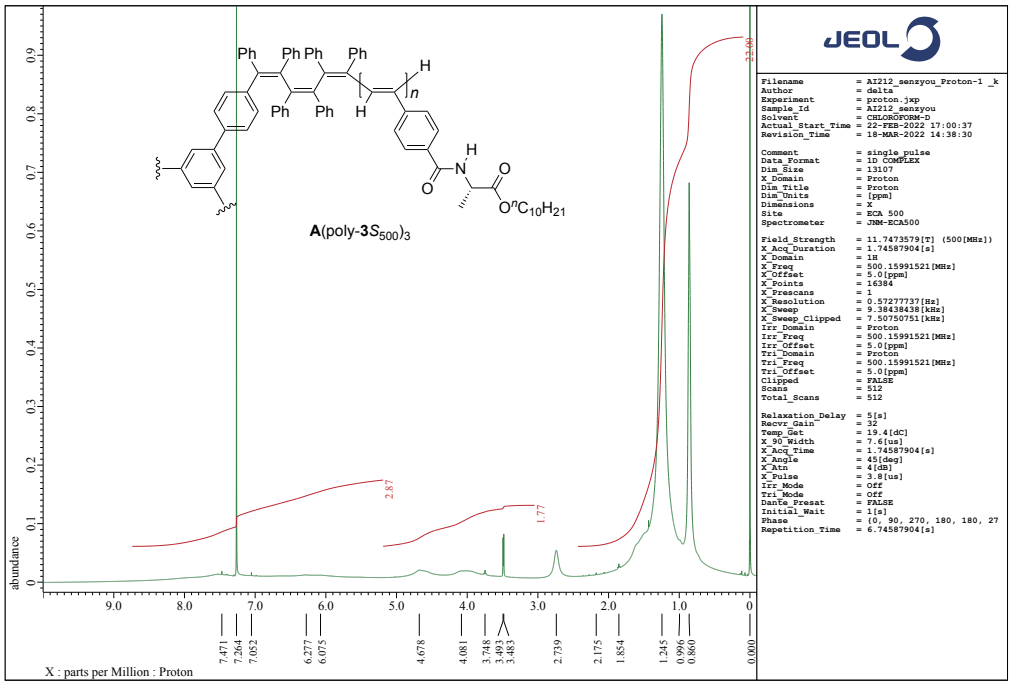


Figure S22. ^{1}H NMR (500 MHz, $CDCl_3$, 19 °C) spectrum of **A**(poly-**3**S_{500})$_3$.

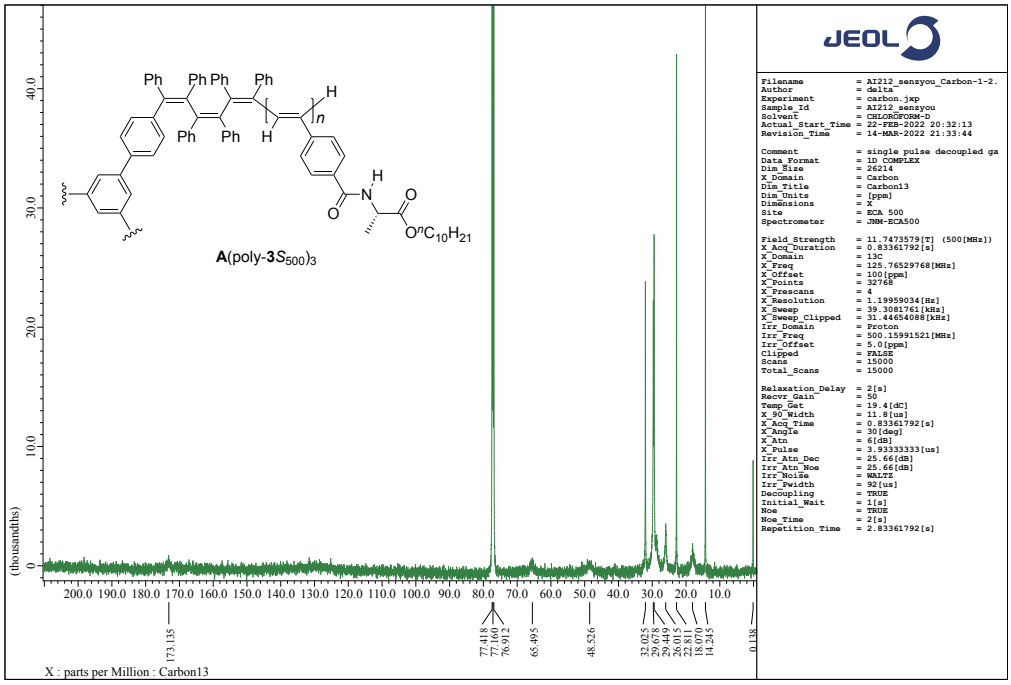


Figure S23. ^{13}C NMR (125 MHz, $CDCl_3$, 19 °C) spectrum of **A**(poly-**3**S_{500})$_3$.

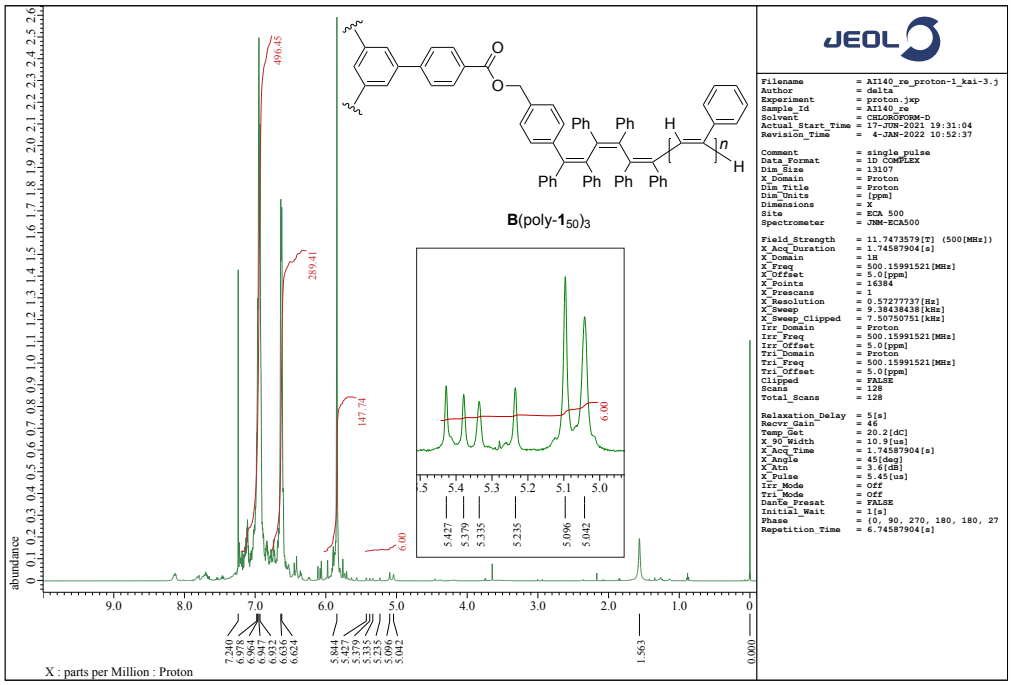


Figure S24. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) spectrum of **B**(poly-**1**$_{50}$)$_3$.

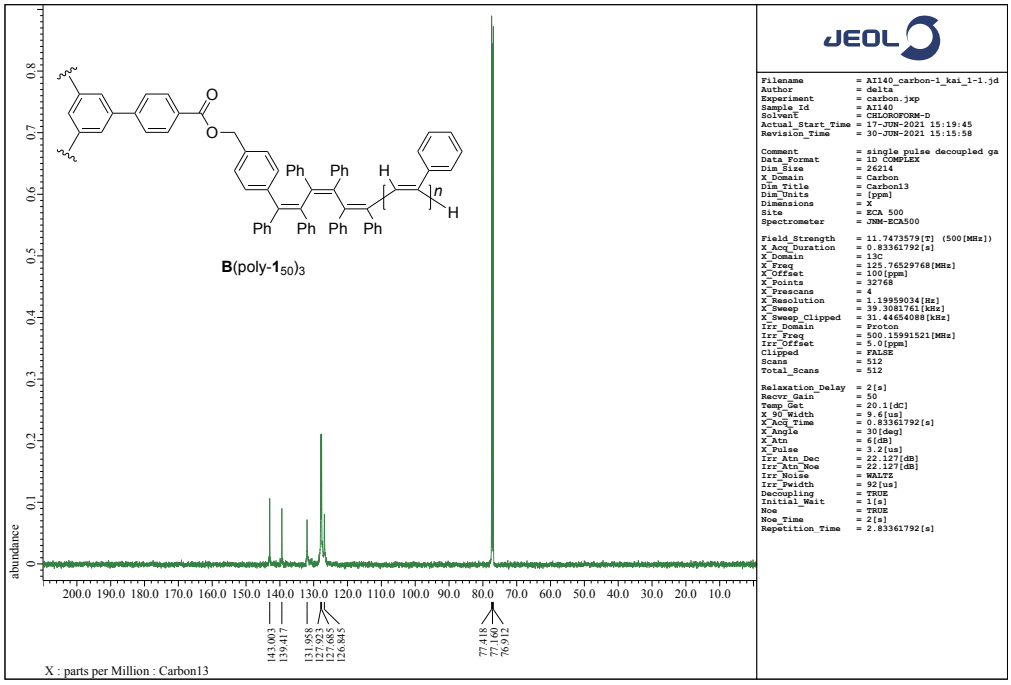


Figure S25. ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) spectrum of **B**(poly-**1**$_{50}$)$_3$.

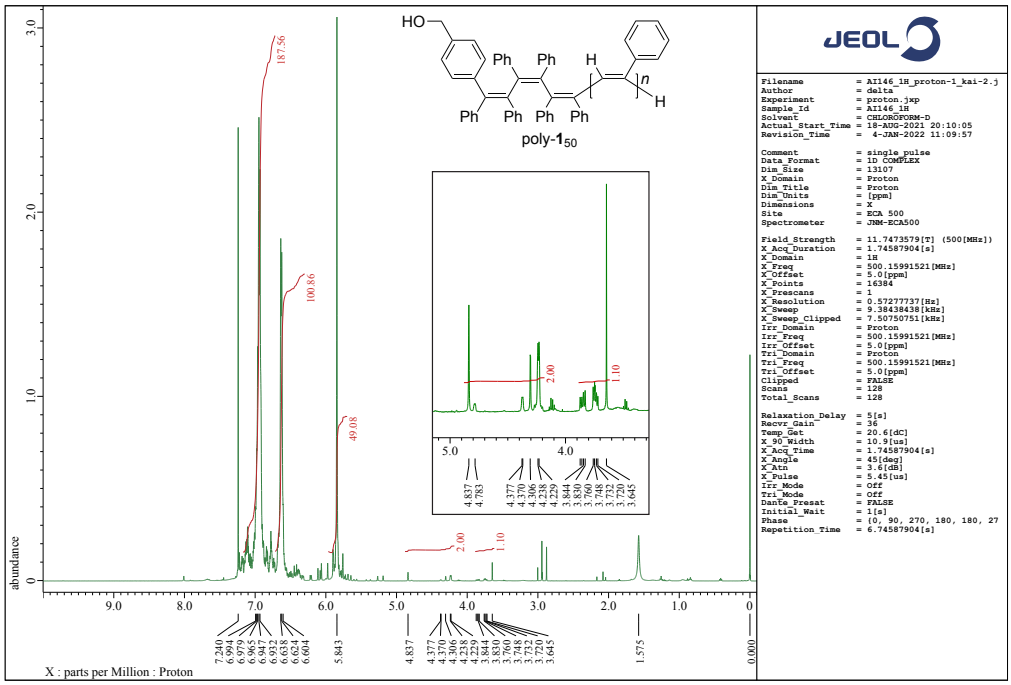


Figure S26. ^{1}H NMR (500 MHz, $CDCl_3$, 21 °C) spectrum of poly-**1**$_{50}$.

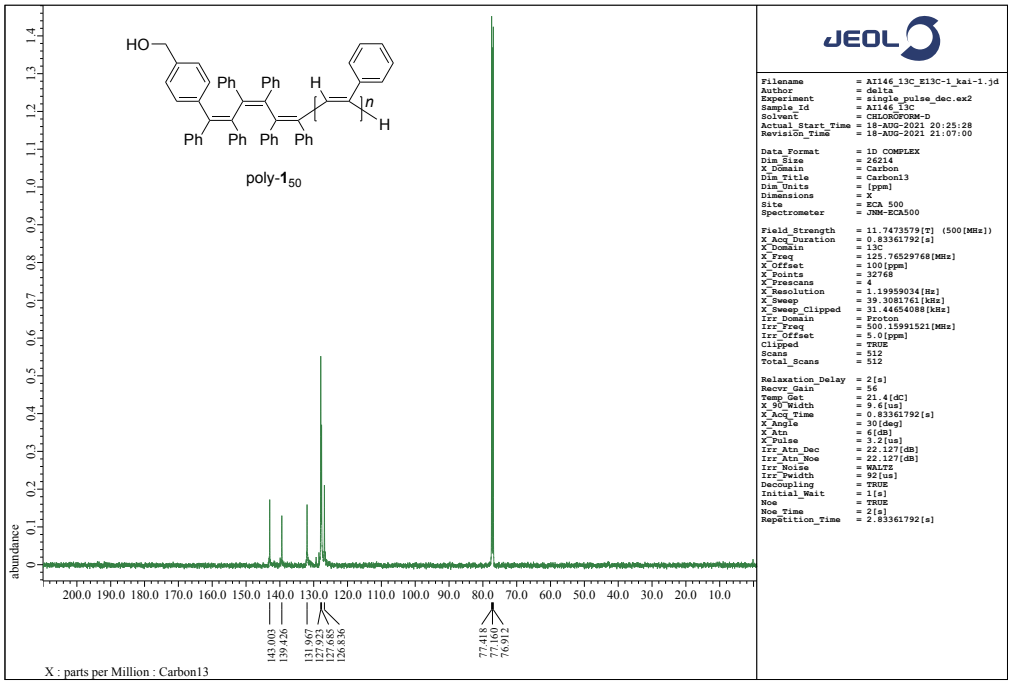


Figure S27. ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C) spectrum of poly-**1**$_{50}$.

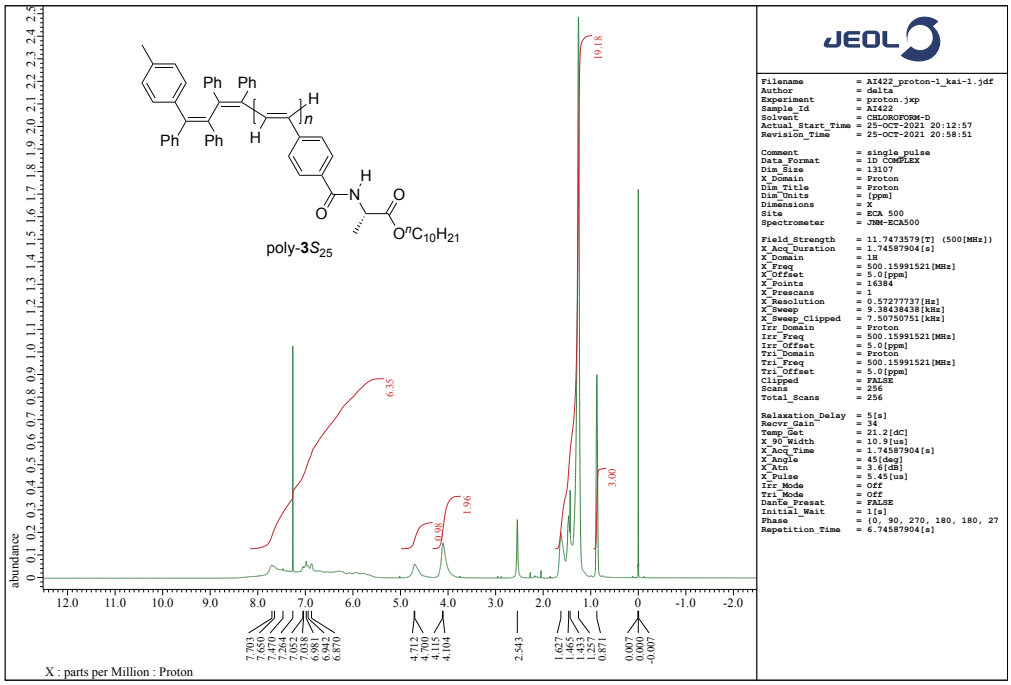


Figure S28. ^{1}H NMR (500 MHz, $CDCl_3$, 21 °C) spectrum of poly-**3**S_{25}.

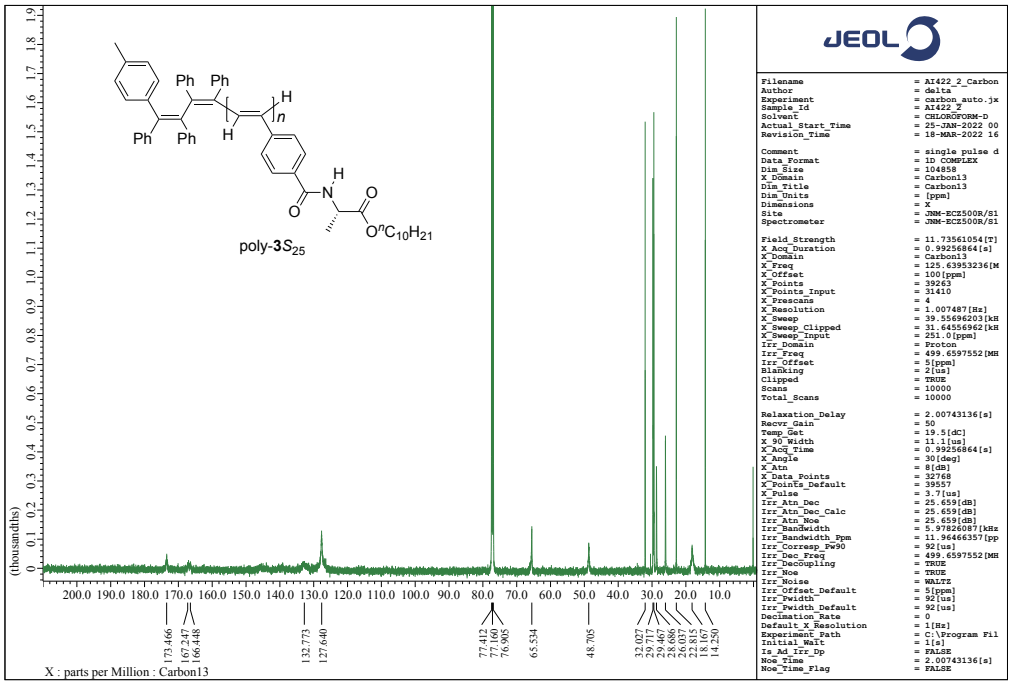


Figure S29. ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) spectrum of poly-**3**S_{25}.

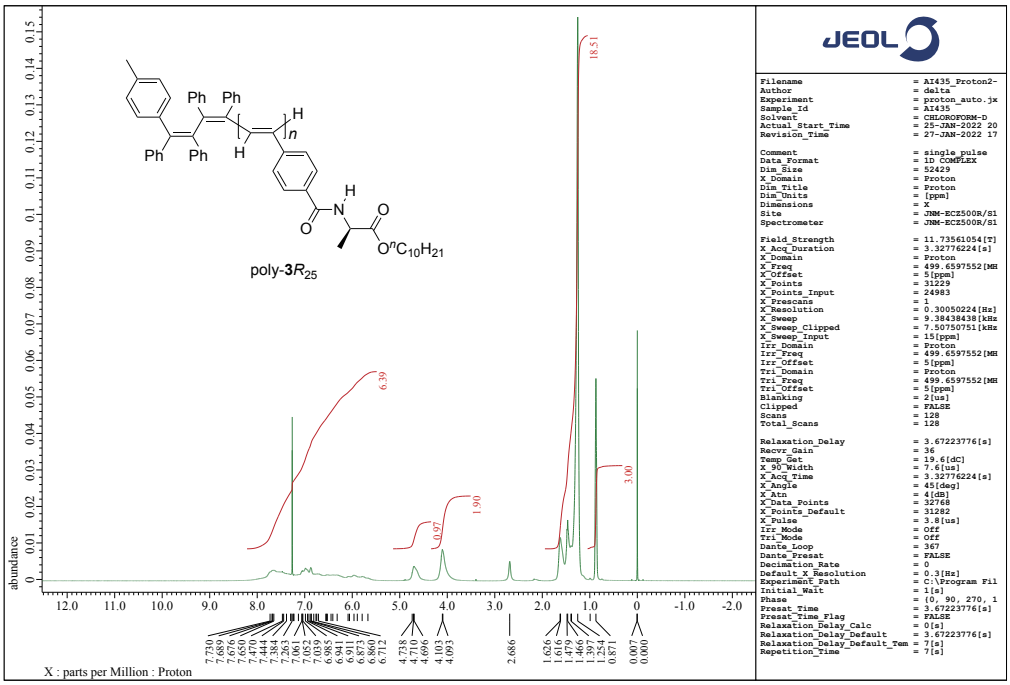


Figure S30. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) spectrum of poly-**3**R_{25}.

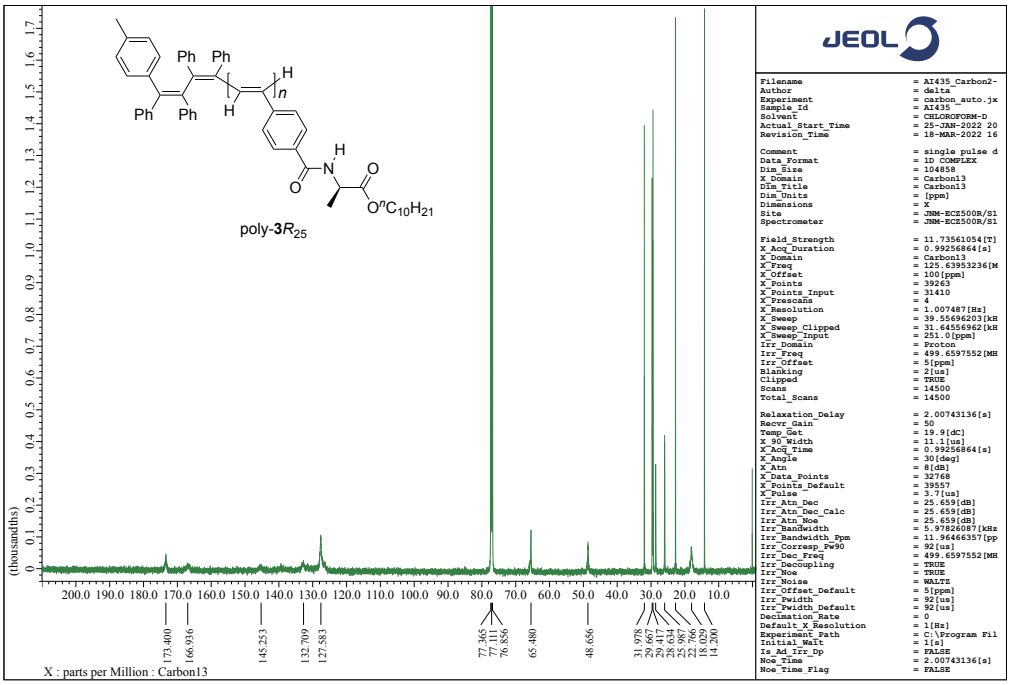


Figure S31. ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) spectrum of poly-**3**R_{25}.