Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Synthesis of Optically Active Polymer Containing a Planar Phthalimide Backbone by Asymmetric Polymerization

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1. Experimental Section

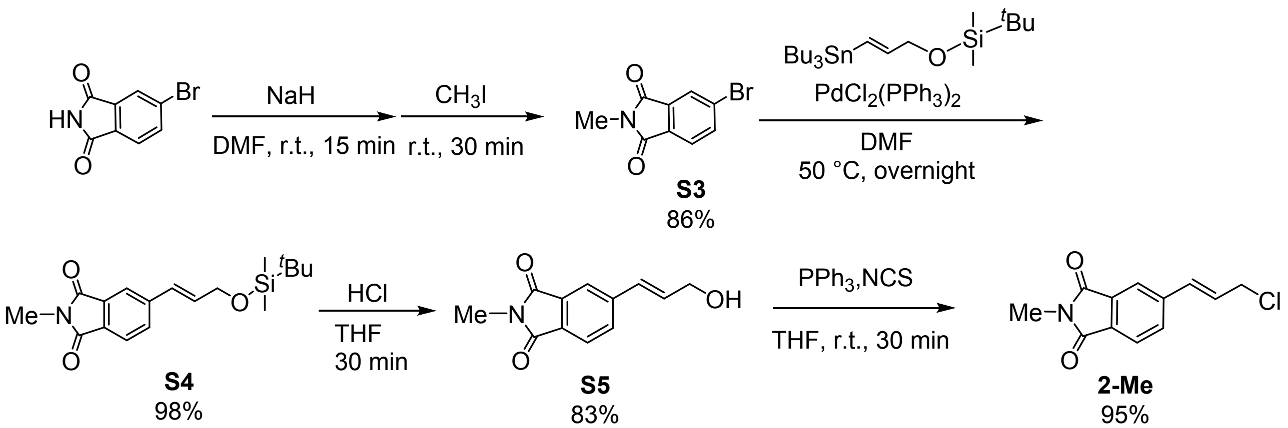
1.1. General.

All reactions were carried out under an Ar atmosphere, whereas the workup was performed in air. ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-ECS400, and JEOL JNM-ECA500 spectrometers using $SiMe_4$ as an internal standard. HR-MS measurement was carried out on Thermo Fisher Scientific LTQ-Orbitrap XL. The enantiomeric excess was determined by HPLC analysis using Shimadzu LC-10 and SPD-10AV equipped with DAICEL Chiralcel OD-H. The number of molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymer were determined by size exclusion chromatography (SEC) in chloroform at 40 °C with polystyrene gel column [Tosoh; TSKgel GMH_{HR}-M × 2 (exclusion molecular weight = 4 × 10^6); flow rate 0.7 mL min^{-1}] connected by Shimadzu LC-10AS, SPD-10A UV-vis detector. CD spectra were obtained with JASCO J-720WO with cryostat at –35-45 °C. UV−vis spectra were obtained with a Shimadzu UV 3100PC.

1.2. Material.

All solvents used for reactions were passed through purification columns just before use. And tetrahydrofuran was dried by sodium-benzophenone. Planar-chiral Cp'Ru complexes (*R*)-**I** and (*S*)-**I** were prepared as reported previously.[1] Allyltributyltin,[2] $NaBAr^F{}_4$,[3] and $NaB(C_6F_5)_4$,[4] were prepared as reported previously. 4-Bromophtallic anhydride, were purchased from TCI. Sodium carbonate, methyl iodide and sodium hydride were purchased from Nacalai tesque. *N*-Chlorosuccinimide was purchased from Aldrich.

1.3. Synthesis of Model Compounds



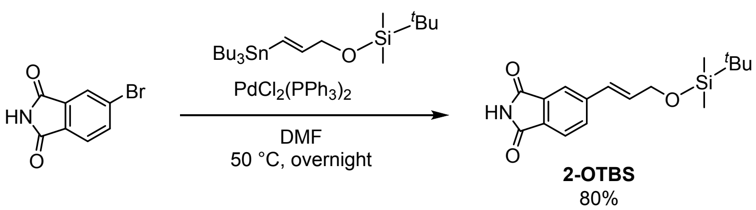
Synthesis of *(E)*-5-(3-chloroprop-1-en-1-yl)-2-methylisoindoline-1,3-dione (2-Me)

Synthesis of S3; To a dimethylformamide (89 mL) solution of 60% sodium hydride (1.02 g, 26 mmol) was added 4-bromophthalimide (4.52 g, 20 mmol) and stirred at room temperature. After 15 min., iodomethane (2.79 mL, 44.8 mmol) was added at room temperature. After stirred for 30 minutes, quenched with brine. The reaction mixture was extracted with ethyl acetate, and the organic layer was washed with brine and dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel; CH_2Cl_2/*n*-hexane = 10/7, 1/1, 10/14) to obtain the white solid, (4.13 g, 86% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, 1H, *J* = 1.5 Hz, Ar), 7.85 (dd, 1H, *J* = 8.0, 1.5 Hz, Ar), 7.71 (d, 1H, *J* = 8.0 Hz, Ar), 3.18 (s, 3H, C*H*$_3$), ^{13}C NMR ($(CD_3)_2CO$, 500 MHz): δ 168.0, 167.4, 137.3, 134.2, 131.1, 129.2, 126.9, 124.9, 24.5

Synthesis of S4; To a solution of **S3** (2.7 g, 12 mmol) and $PdCl_2(PPh_3)_2$ (147.4 mg, 3 mol%) in DMF (15 mL) was added (*E*)-1-(tributylstannyl)-3-(tert-butyldimethylsiloxy)-1-propene (4.89 g, 10.6 mmol). The yellow reaction mixture was heated to 50 °C in a preheated oil bath. After stirring overnight, the reaction mixture was cooled to r.t. and added ethyl acetate and brine sequentially. The organic layer was washed with brine, dried over sodium sulfate and concentrated under reduced pressure. The residue was washed with *n*-hexane. The residue was purified by column chromatography (silica gel; *n*-hexane/ethyl acetate = 50/1 to 5/1) to obtain the yellow solid (2.29 g, 98%yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (d, 1H, *J* = 1.4 Hz, Ar), 7.77 (d, 1H, *J* = 7.6 Hz, Ar), 7.64 (dd, 1H, *J* = 7.6, 1.4 Hz, Ar), 6.73 (dt, 1H, *J* = 16.0, 1.9 Hz, –C*H*═CHCH$_2$), 6.50 (dt, 1H, *J* = 16.0, 4.4 Hz, –CH═C*H*CH$_2$), 4.40 (dd, 2H, *J* = 4.4, 1.9 Hz, –CH═CHC*H*$_2$), 3.18 (s, 3H), 0.96−0.95 (s, 9H, ^{t}Bu), 0.13–0.11 (s, 6H, −Si(C*H*$_3$)$_2$).

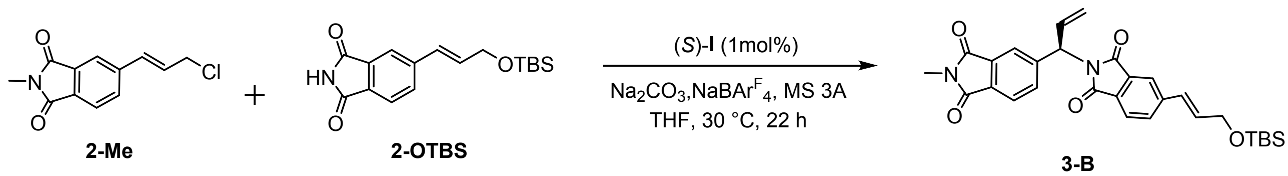
Synthesis of S5; To a tetrahydrofuran solution (28 mL) of **S4** (2.29 g, 6.9 mmol) was added 1M HCl (14 mL) at 0 °C and the mixture was stirred for 30 min at r.t. Then Ethyl acetate and sodium bicarbonate was added to the reaction mixture at 0 °C. The organic layer was extracted with dichloromethane and washed with brine. The organic layer was washed with sodium bicarbonate and brine. After dried over sodium sulfate, the solvent was removed under reduced pressure. The residue was washed with *n*-hexane to give white solid (1.24 g, 83 % yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, 1H, *J* = 1.2 Hz, Ar), 7.78 (d, 1H, *J* = 7.7 Hz, Ar), 7.65 (dd, 1H, *J* = 1.2, 7.7 Hz, Ar), 6.75 (dt, 1H, *J* = 16, 2.0 Hz, –C*H*═CHCH$_2$), 6.56 (dt, 1H, *J* = 16, 5.4 Hz, –CH═C*H*CH$_2$), 4.41 (td, 2H, *J* = 5.4, 2.0 Hz, –CH═CHC*H*$_2$), 3.18 (s, 1H, C*H*$_3$), 1.58 (t, *J* = 5.5 Hz, 1H, O*H*), ^{13}C NMR ($CDCl_3$, 500 MHz): δ 168.6, 168.4, 143.1, 133.2, 133.1, 132.0, 130.9, 128.8, 123.7, 120.7, 63.3, 24.1.

Synthesis of 2-Me; To a tetrahydrofuran solution (50 mL) of **S5** (1.2 g, 5.5 mmol), triphenylphosphine (2.09 g, 8.0 mmol) and lithium chloride (233 mol, 5.5 mmol) was added tetrahydrofuran solution (35 mL) of *N*-chlorosuccinimide (1.04 g, 7.8 mmol). After stirred at r.t. for 40 min., the reaction mixture was added ethyl acetate and washed with brine. The organic layer was dried over sodium sulfate. After removal of the solvent, the residue was purified by column chromatography (silica gel; dichloromethane/ethyl acetate = 17/1 to 15/1) to obtain the yellow solid (1.23 g, 95% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, 1H, *J* = 1.2 Hz, Ar), 7.80 (d, 1H, *J* = 7.9 Hz, Ar), 7.67 (dd, 1H, *J* = 7.9, 1.2 Hz, Ar), 6.76 (d, 1H, *J* = 15 Hz, −C*H*═CHCH$_2$), 6.53 (dt, 1H, *J* = 15, 7.0 Hz, −CH═C*H*CH$_2$), 4.27 (d, 2H, *J* = 7.0 Hz, −CH═CHC*H*$_2$), 3.19 (s, 3H, C*H*$_3$), ^{13}C NMR ($CDCl_3$, 500 MHz): δ 168.5, 168.4, 142.4, 133.4, 132.5, 131.7, 129.5, 124.0, 121.1, 44.8, 24.4.



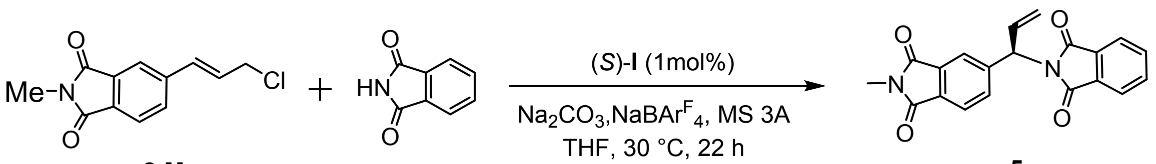
2-OTBS
80%

Synthesis of 2-OTBS; To a solution of 4-bromophthalimide (2.7 g, 12 mmol) and $PdCl_2(PPh_3)_2$ (252.7 mg, 3 mol%) in DMF (20 mL) was added (*E*)-1-(tributylstannyl)-3-(*tert*-butyldimethylsiloxy)-1-propene (8.3 g, 18 mmol). The reaction mixture was heated to 50 °C. After stirring overnight, the reaction mixture was cooled to r.t. and added dichloromethane sequentially. The organic layer was washed with brine, dried over sodium sulfate and concentrated under reduced pressure. The residue was washed with *n*-hexane. After removal of the solvent, the residue was purified by column chromatography (silica gel; CH_2Cl_2/ethyl acetate = 10/1 to 6/1) to obtain the yellow solid (3.04 g, 80%yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (s, 1H, Ar), 7.79 (dd, 1H, *J* = 7.4, 1.0 Hz, Ar), 7.69 (d, 1H, *J* = 7.4 Hz, Ar), 7.55 (bs, 1H, N*H*), 6.75 (dd, 1H, *J* = 16.0, 1.0 Hz, –C*H*=CHCH$_2$), 6.52 (ddt, 1H, *J* = 16.0, 4.2, 2.1 Hz, −CH=C*H*CH$_2$), 4.41 (dd, 2H, *J* = 4.2, 2.1 Hz, −CH=C*H*CH$_2$), 0.95 (s, 9H, ^{t}Bu), 0.13 (s, 6H, −Si(C*H*$_3$)$_2$), ^{13}C NMR ($CDCl_3$, 500 MHz): δ 207.4, 144.1, 133.5, 133.4, 132.3, 130.9, 127.3, 124.1, 121.0, 63.3, 26.0, 18.6, –5.1.



2-Me **2-OTBS** **3-B**

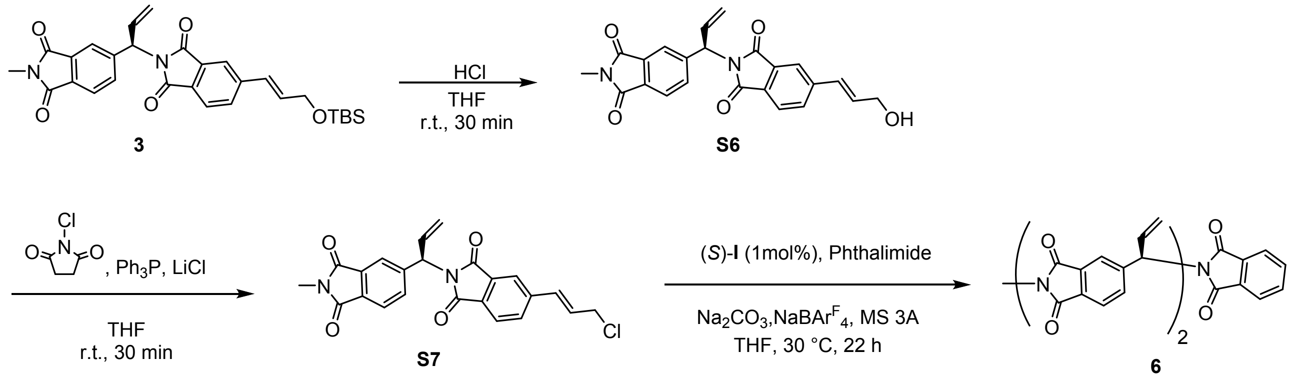
Synthesis of 3-B; Sodium carbonate (63.6 mg, 0.3 mmol) and MS 3A 863.6 mg) was dried by heat gun. Then NaBAr^F$_4$ (92.22 mg, 20 mol%), **2-Me** (117.84 mg, 0.5 mmol), **2-OTBS** (158.73 mg, 0.5 mmol), (*S*)-**I** (3.6 mg, 1 mol%) were filled in the flask under Ar flow, followed by addition of THF (0.4 mL) and the reaction mixture was stirred at 30 °C. After 24 h, dichloromethane was added to the reaction mixture. The insoluble part was filtered through Celite. The solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography (silica gel; CH_2C1_2/ethyl acetate = 50/1 to 30/1) to obtain the yellow oil (188.1 mg, 73%yield). HPLC analysis: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95/5 (v/v), 1.0 mL, 220 nm; major enantiomer: *t* = 33.7 min, minor enantiomer: *t* = 44.5 min, 99% ee. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, 1H, *J* = 0.6 Hz, Ar), 7.85(s, 1H, Ar), 7.80 (d, 1H, *J* = 7.9 Hz, Ar), 7.78 (d, 1H, *J* = 7.9 Hz, Ar), 7.74 (td, 1H, *J* = 7.9, 0.6 Hz, Ar), 7.67 (d, 1H, *J* = 7.9 Hz, Ar),6.73 (dt, 1H, *J* = 16.0, 2.0 Hz, −C*H*=CHCH$_2$), 6.63-6.55 (m, 1H, −CHC*H*=CH$_2$), 6.51 (dt,1H *J* = 16, 4.4 Hz, −CH=C*H*CH$_2$), 6.02 (d, 1H, *J* = 8.0 Hz, −C*H*CH=CH$_2$), 5.44 (dd, 1H, *J* = 17.0, 10.0 Hz,−CHCH=C*H*$_2$), 4.41 (dd, 2H, *J* = 4.4, 2.0 Hz, −CH=CHC*H*$_2$), 3.16 (s, 3H, C*H*$_3$), 0.95 (s, 9H, ^{t}Bu), 0.12 (s, 6H, −Si(C*H*$_3$)$_2$), ^{13}C NMR ($CDCl_3$, 500 MHz): δ 168.3, 168.2, 167.5, 167.4, 145.4, 144.1, 134.3, 133.1, 132.8, 132.5, 132.3, 132.1, 131.6, 129.8, 127.2, 124.0, 123.5, 122.4, 120.9, 120.8, 63.3, 56.3, 26.0, 24.1, 18.4, –5.2.



2-Me **5**

Synthesis of 5

Sodium carbonate (25.44 mg, 0.24 mmol) and MS3A (25.44 mg) was dried by heat gun under Ar atmosphere. Then NaBAr^F$_4$ (36.89 mg, 20 mol%), **2** (47.13 mg, 0.2 mmol), phthalimide (29.43 mg, 0.2 mmol), (*S*)-**1** (1.8 mg, 1 mol%) were filled in the flask the under Ar flow, followed by addition of THF (0.4 mL) and the reaction mixture was stirred at 30 °C. After 24 h, dichloromethane was added to the reaction mixture. The insoluble part was filtered through Celite. The solvent was removed under reduced pressure, and the reaction mixture was purified by a flash column (silica gel; CH_2C1_2/ethyl acetate = 100/0, 50/1 to 40/1) to obtain the colorless oil (61.1 mg, 84%yield). HPLC analysis: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95/5 (v/v), 1.0 mL, 220 nm; major enantiomer: *t* = 48.9 min, minor enantiomer: *t* = 59.7 min, 94% ee. ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.88 (t, 1H, *J* = 0.74 Hz, Ar), 7.86 (dd, 2H, *J* = 3.0 Hz, Ar), 7.81 (d, 1H, *J* = 7.8 Hz, Ar), 7.76 (m, 2H, Ar), 7.74 (d, 1H, *J* = 3.0 Hz, Ar), 6.64 (q, 1H, *J* = 18.0, 7.8 Hz, −CH═C*H*CH_2), 6.04 (d, 1H, *J* = 7.8 Hz, −C*H*═CHCH_2), 5.45 (dd, 2H, *J* = 18.0, 7.8 Hz, −CH═CHCH_2), 3.19 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 500 MHz): δ 168.3, 168.2, 167.6, 145.4, 134.6, 134.5, 133.2, 132.9, 131.9, 131.7, 123.8, 121.0, 56.3, 24.1. HRMS (ESI): Calcd for $C_{21}H_{18}N_2O_4$ ([M + Na]$^+$): m/z 369.0851, Found: m/z 369.0848.

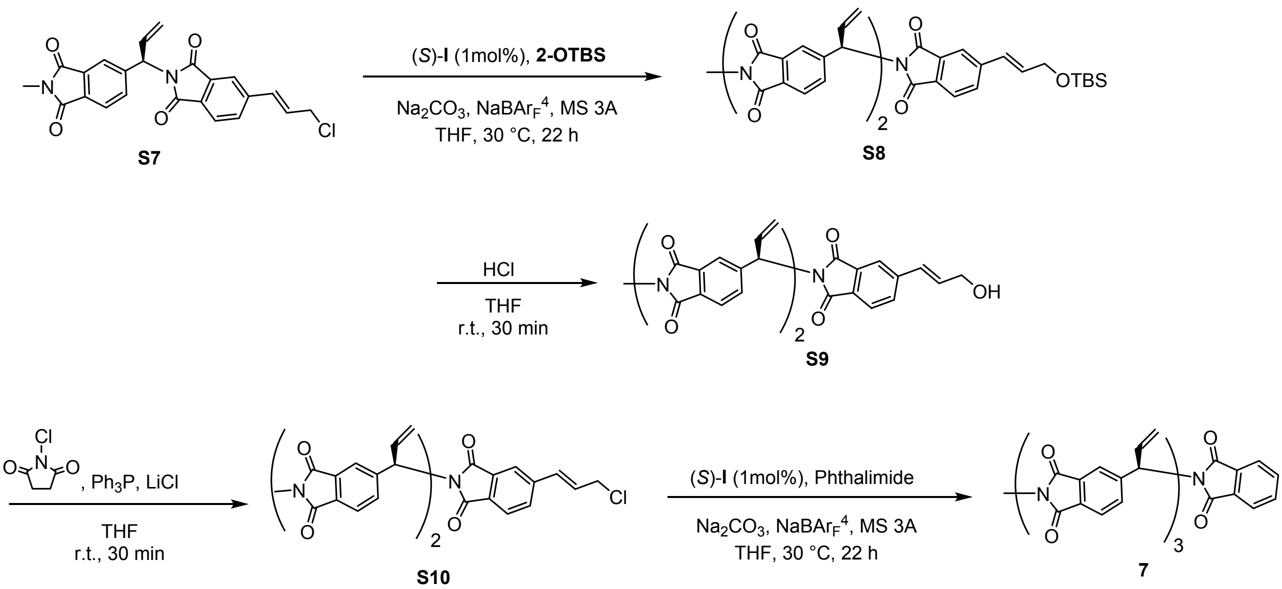


Synthesis of 6

Synthesis of S6; To a tetrahydrofuran solution (2.0 mL) of **3** (243.1 mg, 0.47 mmol) was added 1M HCl (1.0 mL) at 0 °C, and stirred for 30 min at r.t. The reaction mixture was added ethyl acetate and $NaHCO_3$ aq at 0 °C. The organic layer was separated, and washed with $NaHCO_3$ aq. and brine. After dried over sodium sulfate, the solvent was removed under reduced pressure. The residue was washed with *n*-hexane to give white solid (186.7 mg, 99% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (t, 1H, *J* = 0.7 Hz, Ar), 7.86 (s, 1H, Ar), 7.80 (d, 1H, *J* = 4.5 Hz, Ar), 7.79 (d, 1H, *J* = 4.5 Hz, Ar), 7.75 (dd, 1H, *J* = 1.4, 0.7 Hz, Ar), 7.73 (dd, 1H, *J* = 1.4, 0.7 Hz, Ar), 7.69 (dd, 1H, *J* = 1.4, 0.7 Hz, Ar), 6.76 (dt, 1H, *J* = 16.0, 2.0 Hz, −C*H*═CHCH_2), 6.63–6.54 (m, 2H, *J* = 16, 2.0 Hz, −CH═C*H*CH_2 and −CHC*H*═CH_2), 6.02 (d, 1H, *J* = 8.0 Hz, −C*H*CH═CH_2), 5.43 (dd, 1H, *J* = 17, 10 Hz,−CHCH═CH_2), 4.41 (dd, 2H, *J* = 4.4 Hz, −CH═CHCH_2), 3.16 (s, 3H, CH_3), 1.26 (bs, 1H, O*H*). ^{13}C NMR ($CDCl_3$, 500 MHz): δ 168.1, 167.9, 167.2, 167.1, 145.2, 143.5, 133.4, 132.9, 132.6, 132.3, 132.2, 131.4, 129.9, 128.2, 123.9, 123.4, 123.3, 122.2, 120.8, 120.7, 62.9, 56.1, 23.9.

Synthesis of S7; To a tetrahydrofuran solution (3.5 mL) of triphenylphosphine (175.7 mg, 0.67 mmol), lithium chloride (19.5 mg, 0.46 mmol) and **c3** (186.7 mg, 0.46 mmol) was added tetrahydrofuran solution (6 mL) of *N*-chlorosuccinimide (86.8 mg, 0.65 mmol). After stirred at r.t., ethyl acetate was added, and the mixture was washed with water and brine and dried over sodium sulfate. After removal of the solvent, the residue was purified by column chromatography (silica gel; *n*-hexane/ethyl acetate = 5/1 to 2/1) to obtain the colorless oil (140 mg, 72%yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (s, 2H, Ar), 7.81–7.84 (m, 2H, Ar), 7.75 (d, 1H, *J* = 7.7 Hz, Ar), 7.71 (d, 1H, *J* = 7.7 Hz, Ar), 6.78 (d, 1H, *J* = 17.0 Hz, −C*H*═CHCH_2), 6.62–6.52 (m, 2H, −CH═C*H*CH_2 and −CHC*H*═CH_2), 6.04 (d, 1H *J* = 7.8 Hz, −C*H*CH═CH_2), 5.46 (t, 2H, *J* = 11.0, 18.0 Hz, −CHCH═CH_2), 4.28 (d, 2H, *J* = 7.0 Hz, −CH═CHCH_2), 3.15 (s, 3H, CH_3), ^{13}C NMR ($CDCl_3$, 400 MHz): δ 168.1, 168.0, 167.1, 167.0, 145.2, 145.6, 133.0, 132.7, 132.6, 132.5, 131.8, 131.6, 130.7, 129.6, 124.0, 123.4, 122.3, 121.3, 120.8, 56.3, 44.4, 24.0. HRMS (ESI): Calcd for $C_{12}H_{10}ClNO_2$ ([M + Na + CH_3OH]$^+$): m/z 290.0554, Found: m/z 290.0566.

Synthesis of 6; Sodium carbonate (12.1 mg, 0.11 mmol) and MS 3A (12.1 mg) was dried by heat gun under vacuum. After filling the Schlenk flask with argon, then $NaBAr^F{}_4$ (17.5 mg, 20 mol%) and **S7** (40 mg, 0.095 mmol), phthalimide (14.0 mg, 0.095 mmol), (*S*)-**I** (0.68 mg, 1 mol%) were filled in the flask the under Ar flow, followed by addition of THF (0.4 mL) and the reaction mixture was stirred at 30 °C. After 22 h, dichloromethane was added to the reaction mixture. The insoluble part was filtered through Celite. The solvent was removed under reduced pressure and purified by column chromatography (silica gel; *n*-hexane/ethyl acetate = 3/1 to 1/1) to obtain the white solid (22.9 mg, 45%yield). ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.83 (s, 1H, Ar), 7.78–7.77 (m, 2H, Ar), 7.73 (s, 1H, Ar), 7.71 (d, 1H, *J* = 7.7 Hz, Ar), 7.67 (d, 1H, *J* = 2.9 Hz, Ar), 7.66 (d, 1H, *J* = 2.9 Hz, Ar), 7.64 (d, 1H, *J* = 7.7 Hz, Ar), 6.55–6.45 (m, 2H, −CHC*H*═CH$_2$), 5.95 (dd, 2H, *J* = 8.0 Hz, −C*H*CH═CH$_2$), 5.41–5.32 (m, 4H, −CHCH═C*H*$_2$), 3.07 (s, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$, 400 MHz) : δ 168.2, 167.5, 167.2, 167.1, 146.0, 145.3, 134.5, 133.8, 133.1, 132.9, 132.7, 132.3, 131.8, 131.7, 131.1, 124.0, 123.8, 123.5, 122.9, 122.4, 121.0, 121.0, 56.3, 24.1. HRMS (ESI): Calcd for $C_{31}H_{21}N_3O_6$ ([M + Na + CH_3OH]$^+$): m/z 586.1590, Found: m/z 586.1581.



Synthesis of 7

Synthesis of S8; Sodium carbonate (26.5 mg, 0.25 mmol) and MS 3A (26.5 mg) was dried by heat gun under vaccum. After filling the Schlenk flask with argon, $NaBAr^F{}_4$ (38.7 mg, 20 mol%) **S7** and **2-OTBS** (87.4 mg, 0.21 mmol), **a2** (66.7 mg, 0.21 mmol), (*S*)-**I** (1.5 mg, 1 mol%) were filled in the flask the under Ar flow, followed by addition of THF (0.85 mL) and the reaction mixture was stirred at 30 °C. After 22 h, dichloromethane was added to the reaction mixture. The insoluble part was filtered through Celite. The solvent was removed under reduced pressure and purified by column chromatography (silica gel; *n*-hexane/ethyl acetate = 5/1 to 2/1) to obtain the colorless oil (89.1 mg, 60%yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (s, 1H, Ar), 7.75 (d, 2H, *J* = 7.7 Hz, Ar), 7.71 (s, 2H, Ar), 7.68 (d, 2H, *J* = 7.7 Hz, Ar), 7.62 (s, 1H, Ar), 7.58 (d, 1H, *J* = 7.7 Hz, Ar), 7.71 (s, 2H, Ar), 7.68 (t, 2H, *J* = 7.7 Hz, Ar), 7.62 (d, 1H, *J* = 7.7 Hz, Ar), 7.58 (d, 1H, *J* = 7.7 Hz, Ar), 6.65 (d, 1H, *J* = 16.0 Hz, −C*H*═CHCH$_2$), 6.53–6.46 (m, 2H, −CHC*H*═CH$_2$), 6.43 (dt, 1H, *J* = 16, 4.4 Hz, −CH═C*H*CH$_2$), 5.93 (t, 2H, *J* = 8.3 Hz, −C*H*CH═CH$_2$), 5.39–5.31 (m, 4H, −CHCH═C*H*$_2$), 4.32–4.31 (dd, 2H, *J* = 4.4 Hz, −CH═CHC*H*$_2$), 3.05 (s, 3H, C*H*$_3$), 0.86 (s, 9H, ^{t}Bu), 0.033 (s, 6H, −Si(C*H*$_3$)$_2$), ^{13}C NMR ($CDCl_3$, 400 MHz): δ 168.1, 168.0, 167.4, 167.2, 167.1, 167.0, 146.0, 145.2, 144.0, 134.4, 133.7, 133.0, 132.8, 132.7, 132.4, 132.2, 131.6, 131.0, 129.7, 127.1, 123.9, 123.4, 122.9, 122.4, 120.9, 120.8, 63.2, 56.2, 26.0, 24.0, 18.5, –5.2

Synthesis of S9; To a tetrahydrofuran solution (0.5 mL) of **S8** (89.1 mg, 0.13 mmol) was added 1M HCl (0.25 mL) at 0 °C, and the mixture was stirred for 30 min at r.t. The reaction mixture was added ethyl acetate and $NaHCO_3$ aq. at 0 °C. The organic layer was separated, and washed with sodium bicarbonate and brine. After dried over sodium sulfate, the solvent was removed under reduced pressure. The residue was washed with *n*-hexane to give white solid (79.0 mg, 92% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (s, 1H, Ar), 7.84 (d, 2H, *J* = 8.0 Hz, Ar), 7.82 (d, 1H, *J* = 8.0 Hz, Ar), 7.80 (d, 1H, *J* = 5.5 Hz, Ar), 7.78 (d, 1H, *J* = 5.5 Hz, Ar), 7.77 (d, 1H, *J* = 5.5 Hz, Ar), 7.71 (d, 1H, *J* = 8.0 Hz, Ar), 7.67 (d, 1H, *J* = 8.0 Hz, Ar),6.73 (d, 1H, *J* = 16.0 Hz,), 7.90 (s, 1H, Ar), 7.85–7.76 (m, 6H, Ar), 7.72 (d, 1H, *J* = 8.0 Hz, Ar), 7.67 (d, 1H, *J* = 8.0 Hz, Ar), 6.75 (d, 1H, *J* = 16 Hz, −C*H*═CHCH$_2$), 6.60–6.00 (m, 1H, −CH═C*H*CH$_2$ and −CHC*H*═CH$_2$), 6.02 (t, 2H, *J* = 7.0 Hz, −C*H*CH=CH$_2$), 5.49–5.40 (m, 4H, −CHCH═C*H*$_2$), 4.40 (d, 2H, *J* = 4.0 Hz, −CH═CHC*H*$_2$), 3.14 (s, 3H, C*H*$_3$), 1.26 (t, 1H, *J* = 7.1 Hz, O*H*), ^{13}C NMR ($CDCl_3$, 400 MHz): δ 168.2, 168.1, 167.4, 167.2, 167.1, 146.0, 145.3, 143.7, 133.9, 133.7, 133.1, 132.8, 132.7, 132.5, 132.3, 132.3, 131.6, 131.1, 130.0, 128.2, 124.1, 123.9, 123.5, 122.9, 122.4, 121.0, 62.9, 56.3, 25.7

Synthesis of S10; To a tetrahydrofuran solution (1.0 mL) of **S9** (70.3 mg, 0.12 mmol), triphenylphosphine (45.6 mg, 0.17 mmol) and lithium chloride (5.1 mg, 0.12 mmol) was added tetrahydrofuran solution (1.5 mL) of *N*-chlorosuccinimide (22.7 mg, 0.17 mmol). After stirred at r.t. for 90 min, the reaction mixture was added dichloromethane, and washed with brine. The organic layer was dried over sodium sulfate. After removal of the solvent, the residue was purified by column chromatography (silica gel; *n*-hexane/ethyl acetate = 5/1 to 2/1) to obtain the colorless oil (60.3 mg, 83%yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (s, 1H, Ar), 7.86 (s, 1H, Ar), 7.85 (s, 1H, Ar), 7.81 (s, 2H, Ar), 7.78 (d, 2H, *J* = 7.1 Hz, Ar), 7.72 (d, 2H, *J* = 7.1 Hz, Ar), 7.70 (d, 1H, *J* = 7.1 Hz, Ar), 6.77 (d, 2H, *J* = 16.0 Hz, −C*H*═CHCH$_2$), 6.63–6.49 (m, 3H, −CH=C*H*CH$_2$ and −CHC*H*═CH$_2$), 6.03 (t, 2H, *J* = 8.5 Hz, −C*H*CH═CH$_2$), 5.50–5.40 (m, 4H, −CHCH═C*H*$_2$), 4.27 (d, 2H, *J* = 7.0 Hz, −CH═CHC*H*$_2$), 3.15 (s, 3H, C*H*$_3$) ^{13}C NMR ($CDCl_3$, 400 MHz): δ 168.2, 168.1, 167.2, 167.1, 167.0, 145.9, 145.2, 142.7, 133.7, 133.1, 132.8, 132.7, 132.6, 132.5, 132.3, 131.9, 131.6, 131.1, 130.7, 130.0, 124.1, 123.9, 123.4, 122.9, 122.4, 121.3, 121.0, 120.9, 56.3, 44.4, 24.0

Synthesis of 7; A solution of **d4** (94.3 mg, 0.4 mmol), sodium carbonate (12.7 mg, 0.10 mmol), NaBAr$^F{}_4$ (18.4 mg, 20 mol%), Phthalimide (14.7 mg, 0.10 mmol) and (*S*)-**I** (1.0 mg, 1mol%) in THF (0.4 mL) was stirred at 30 °C. After 26 h, the reaction mixture was added dichloromethane. The insoluble part was filtered through Celite. The solvent was removed under reduced pressure, and the residue was purified by a flash column (silica gel; CH_2C1_2/ethyl acetate = 50/1 to 30/1) to obtain the colorless oil (28.9 mg, 40%yield). ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.89-7.88 (d, 2H, *J* = 6.4 Hz, Ar), 7.88–7.86 (m, 4H, Ar), 7.81–7.79 (d, 3H, *J* = 5.4 Hz, Ar), 7.77–7.76 (m, 2H, Ar), 7.72–7.70 (d, 2H, *J* = 7.8 Hz, Ar), 6.60–6.52 (m, 3H, *J* = 10, 7.0 Hz, −CHC*H*═CH$_2$), 6.05–6.03 (m, 3H, *J* = 8.1, 4.3 Hz, −C*H*CH═CH$_2$), 5.49–5.40 (m, 6H, *J* = 10, 8.1, 4.3 Hz, −CHCH═C*H*$_2$), 3.15 (s,3H, C*H*$_3$), ^{13}C NMR ($CDCl_3$, 400 MHz): δ 168.2, 168.1, 167.5, 167.2, 167.1, 167.1, 146.1, 145.9, 145.3, 134.5, 134.4, 133.8, 133.7, 133.1, 132.8, 132.7, 132.6, 132.3, 131.7, 131.6, 131.1, 124.0, 123.8, 123.7, 123.5, 122.9, 122.4, 121.0, 56.3, 24.1, HRMS (ESI): Calcd for $C_{42}H_{28}N_4O_8$ ([M + Na + $CH_3OH]^+$): m/z 771.2067, Found: m/z 771.2062.

Standard method for the polymerization of 2.

Under Ar vacuum, base (0.3 mmol) and MS3A were dried by heat gun. After filling the Schlenk flask with argon, $NaBAr^F{}_4$ (dried by dryer, 11.53 mg, 5 mol%), **2** (50.4 mg, 0.25 mmol) and **(*S*)-I** (1.8 mg, 1 mol%) were filled in the flask the under Ar flow, followed by addition of THF (0.5 mL), and the reaction mixture was stirred at 30 °C. After 22 h, dichloromethane was added to the reaction mixture. The insoluble part was filtered through Celite. The solvent was removed under reduced pressure to obtain brown oil. Crude compound was purified by silica gel column chromatography eluted by dichloromethane/ethyl acetate = 10/1 as cyclic oligomer and dichloromethane/methanol = 5/1 as polymer.

Standard method of thiol-ene reaction of poly-2

To a THF solution (3.0 mL) of **poly-2** (10 mg, 0.054 mmol) and DMPA (13.8 mg, 0.054 mmol) was added thiol **4** (0.32 mmol) and the reaction mixture was irradiated with LED light (365 nm) for 3 hours. The crude product was purified by using an SEC column (Shodex; KF 2003 × 2; flow rate 3.0 mL min^{-1}) to give the target product.

Synthesis of poly-4a.

According to the standard method, thiol-ene reaction was conducted using **poly-2** (M_w = 4200, M_w/M_n = 2.1) and 1-dodecanethiol (**4a**) to yield **poly-4a** (M_w = 7700, M_w/M_n = 2.9)**.** ^{1}H NMR ($CDCl_3$, 500 MHz) 8.01 (brs, 1H, Ar), 7.90–7.80 (m, 1H, Ar), 7.79–7.72 (m, 1H, Ar), 5.62 (br, 1H, −C*H*CH_2CH_2S−), 2.85 (br, 1H, −CHC*H*$_2$$CH_2$S−), 2.75−2.41 (m, 7H, −CHC*H*$_2$$CH_2$S−, −CHC*i*$_2$C*H*$_2$S−, and −$CHCH_2CH_2$SC*H*$_2$–), 1.79–1.14 (m, 20H, –$SCH_2$(C*H*$_2$)$_{10}$$CH_3$), 0.87 (t, 3H, –$SCH_2(CH_2)_{10}$C*H*$_3$).

Synthesis of poly-4b.

According to the standard method, thiol-ene reaction was conducted using **poly-2** (M_w = 4200, M_w/M_n = 2.1) and thiol **4b** to yield **poly-4b** (M_w = 7900, M_w/M_n = 1.3)**.** ^{1}H NMR ($CDCl_3$, 500 MHz) 8.01 (brs, 1H, Ar), 7.88 (br, 1H, Ar), 7.81 (br, 1H, Ar), 5.65 (br, 1H, −C*H*CH_2CH_2S−), 2.96 (br, 1H), 2.75 (br, 2H), 2.59 (br, 3H), 2.37 (br, 2H).

Synthesis of poly-4c.

According to the standard method, thiol-ene reaction was conducted using **poly-2** (M_w = 4200, M_w/M_n = 2.1) and thiol **4c** to yield **poly-4c** (M_w = 7800, M_w/M_n = 1.4)**.** ^{1}H NMR ($CDCl_3$, 500 MHz) 7.97 (br, 1H, Ar), 7.83 (br, 1H, Ar), 7.76 (br, 1H, Ar), 5.62 (br, 1H, −C*H*CH_2CH_2S−), 3.70–3.55(m, 8H, –O(C*H*$_2$)$_2$O–), 3.54–3.51 (m, 2H, –SCH_2C*H*$_2$O–), 3.36 (s, 3H, –OCH_3), 2.86 (br, 1H, −CHC*H*$_2$$CH_2$S−), 2.67 (br, 1H, −CHC*H*$_2$$CH_2$S−), 2.60–2.48 (m, 2H, −$CHCH_2$C*H*$_2$S−).

Synthesis of poly-4d.

According to the standard method, thiol-ene reaction was conducted using **poly-2** (M_w = 4200, M_w/M_n = 2.1) and thiol **4d** to yield **poly-4d** (M_w = 7300, M_w/M_n = 1.9)**.** ^{1}H NMR ($CDCl_3$, 500 MHz) 7.96 (br, 1H, Ar), 7.85 (br, 1H, Ar), 7.76 (br, 1H, Ar), 5.60 (br, 1H, −C*H*CH_2CH_2S−), 3.80–3.47(m, 18H, –O(CH_2)$_2$O–), 3.37 (s, 3H, –OCH_3), 2.87 (br, 1H, −CHC$H_2$$CH_2$S−), 2.67 (br, 1H, −CHC$H_2$$CH_2$S−), 2.55 (br, 2H, −CH$CH_2CH_2$S−).

Synthesis of poly-4f.

According to the standard method, thiol-ene reaction was conducted using **poly-2** (M_w = 4200, M_w/M_n = 2.1) and thiol **4e** to yield **poly-4e** (The molecular weight was not determined)**.** ^{1}H NMR (($(CD_3)_2CO$, 500 MHz) 7.89 (br, 2H, Ar), 7.77 (br, 1H, Ar), 5.61 (br, 1H, −C*H*CH_2CH_2S−), 3.10 (br, 1H, −CHC$H_2$$CH_2$S−), 2.99–2.42 (br, 7H, −CHC$H_2$$CH_2$S−, −CH$CH_2CH_2$S−, −SC$H_2CH_2$−).

Synthesis of poly-4g

According to the standard method, thiol-ene reaction was conducted using **poly-2** (M_w = 4200, M_w/M_n = 2.1) and thiol **4g** to yield **poly-4g** (Because the SEC chart is tailing, the molecular weight can't be accurately estimated)**.** ^{1}H NMR ($CDCl_3$, 500 MHz) 7.88 (br, 1H, Ar), 7.76 (br, 1H, Ar), 7.69 (br, 1H, Ar), 5.54 (br, 1H, −C*H*CH_2CH_2S−), 4.86 (br, 1H, NH), 3.17 (br, 2H, –CH_2NH–) 2.81 (br, 1H, −CHC$H_2$$CH_2$S−), 2.67−2.36 (br, 5H, −CHC$H_2$$CH_2$S−, −CH$CH_2CH_2$S−, and −CH$CH_2CH_2SCH_2$–), 1.32 (s, 9H, ^{t}Bu).

Synthesis of poly-4h

According to the standard method, thiol-ene reaction was conducted using **poly-2** (M_w = 4200, M_w/M_n = 2.1) and thiol **4h** to yield **poly-4h** (M_w = 4300, M_w/M_n = 2.7)**.** ^{1}H NMR ($CDCl_3$, 500 MHz) 7.92 (br, 1H, Ar), 7.86 (br, 1H, Ar), 7.74 (br, 1H, Ar), 5.59 (br, 1H, −C*H*CH_2CH_2S−), 3.65 (br, 2H, –CH_2NH–) 3.11 (br, 4H), 2.61 (br, 2H), 1.84–0.81 (br, 14H, ^{i}Pr).

Synthesis of poly-4i

According to the standard method, thiol-ene reaction was conducted using **poly-2-((*S*)-I)** (M_w = 4200, M_w/M_n = 2.1) and thiol **4i** to yield **poly-4i-((*S*)-I)** (M_w = 10,000, M_w/M_n = 1.3)**.** ^{1}H NMR ($CDCl_3$, 500 MHz) 7.96 (br, 1H, Ar), 7.82 (br, 1H, Ar), 7.76 (br, 1H, Ar), 5.64 (br, 1H, −C*H*CH_2CH_2S−), 5.19 (t, 1H, *J* = 9.7 Hz, CH(OAc)C*H*(OAc)CH(OAc)), 5.04 (t, 1H, *J* = 9.7 Hz, S(O)CHC*H*(OAc)CH), 4.98 (t, 1H, *J* = 9.7 Hz, CH_2(O)CHC*H*(OAc)CH), 4.49 (d, 1H, *J* = 9.7 Hz, S(O)C*H*CH(OAc)CH), 4.16 (dd, 1H, *J* = 12.3, 4.4 Hz, AcOCH_2CH), 4.02 (d, 1H, *J* = 10.6 Hz, AcOCH_2CH), 3.70 (br, 1H, AcOCH_2C*H*(O)CH), 2.91 (br, 1H, −CHC$H_2$$CH_2$S−), 2.73 (br, 1H, −CHC$H_2$$CH_2$S−), 2.62 (br, 2H, −CH$CH_2CH_2$S−), 2.04 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.93 (s, 3H, OAc).

2. NMR Analysis

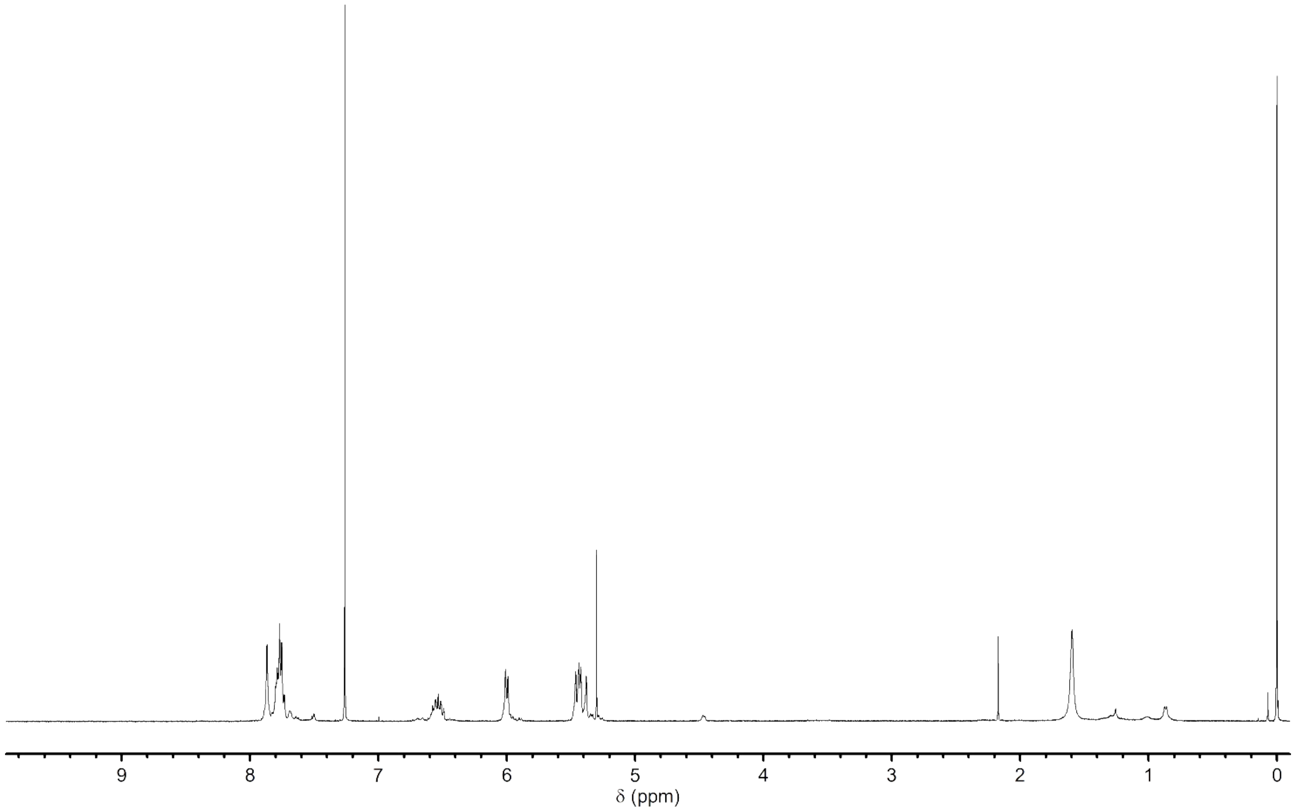


Fig. S1 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **poly-2** (entry 6 in Table 1).

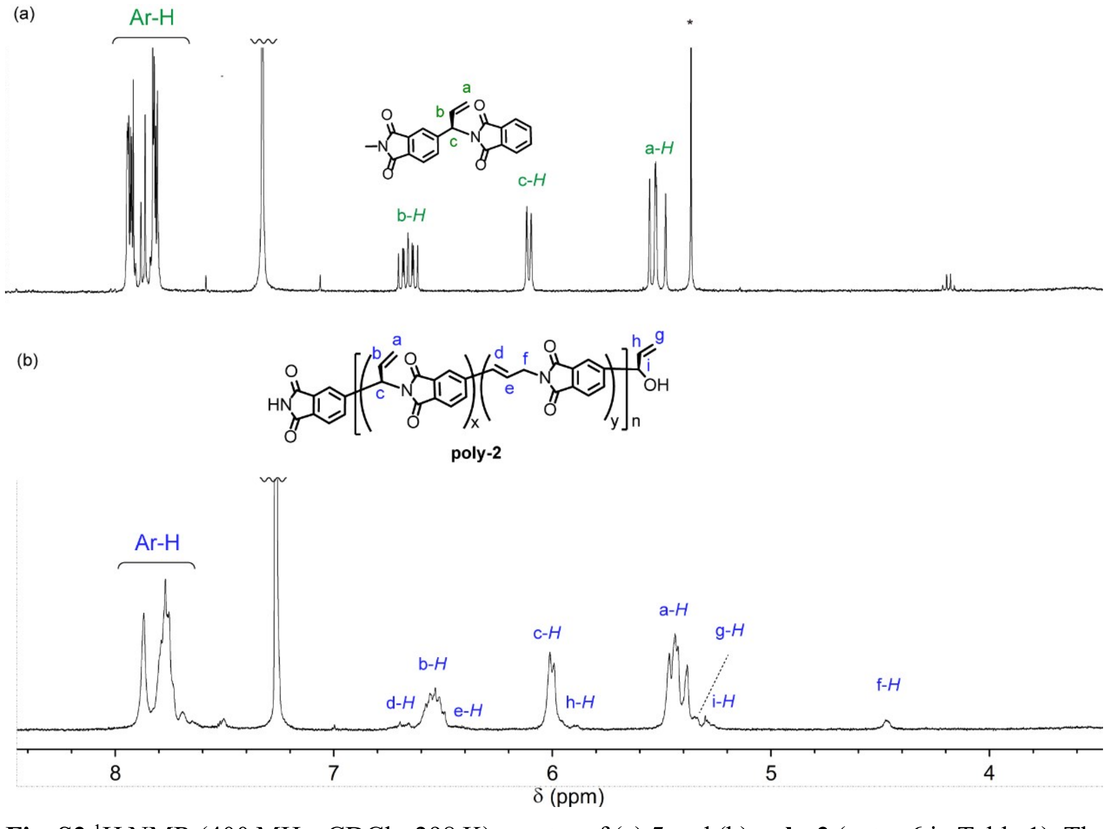


Fig. S2 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectra of (a) **5** and (b) **poly-2** (entry 6 in Table 1). The asterisk denotes the CH_2Cl_2.

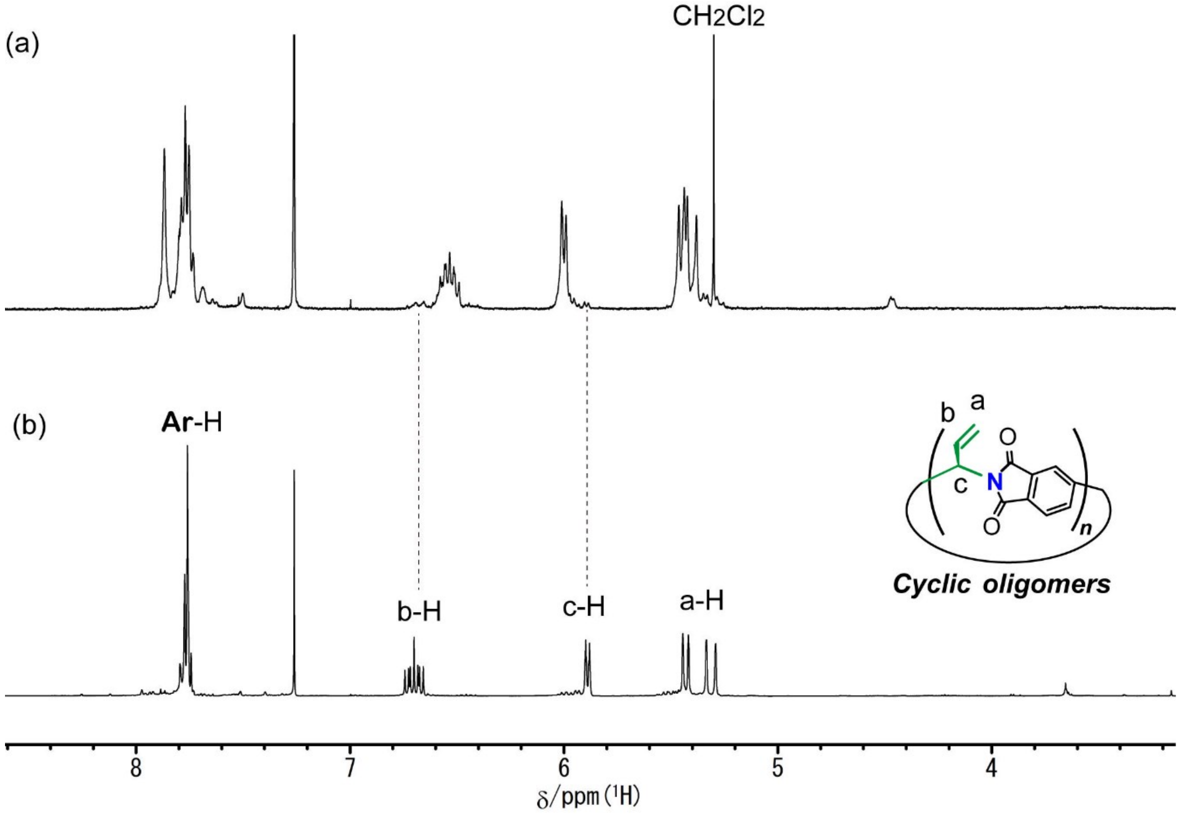


Fig. S3 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectra of (a) **poly-2** (entry 6 in Table 1) and cyclic compound (n = 4).

Cyclic oligomer (n = 4) was purified by silica gel column chromatography eluted by CH2 Cl 2 /AcOEt = 10/1) and preparative SEC. Further purification with preparative TLC (Eluent; Hexne/AcOEt = 3/2) gave cyclic oligomer (n = 4).

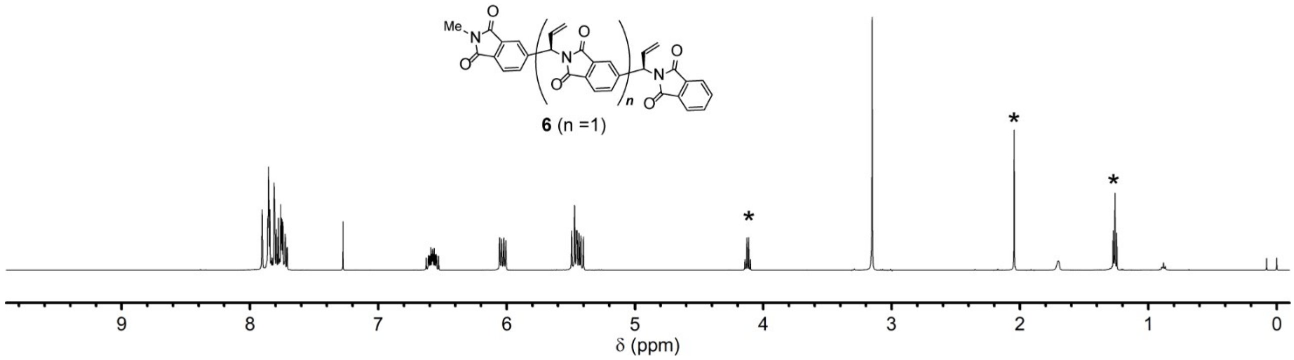


Fig. S4 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **b** (n = 1). The asterisk denotes ethyl acetate.

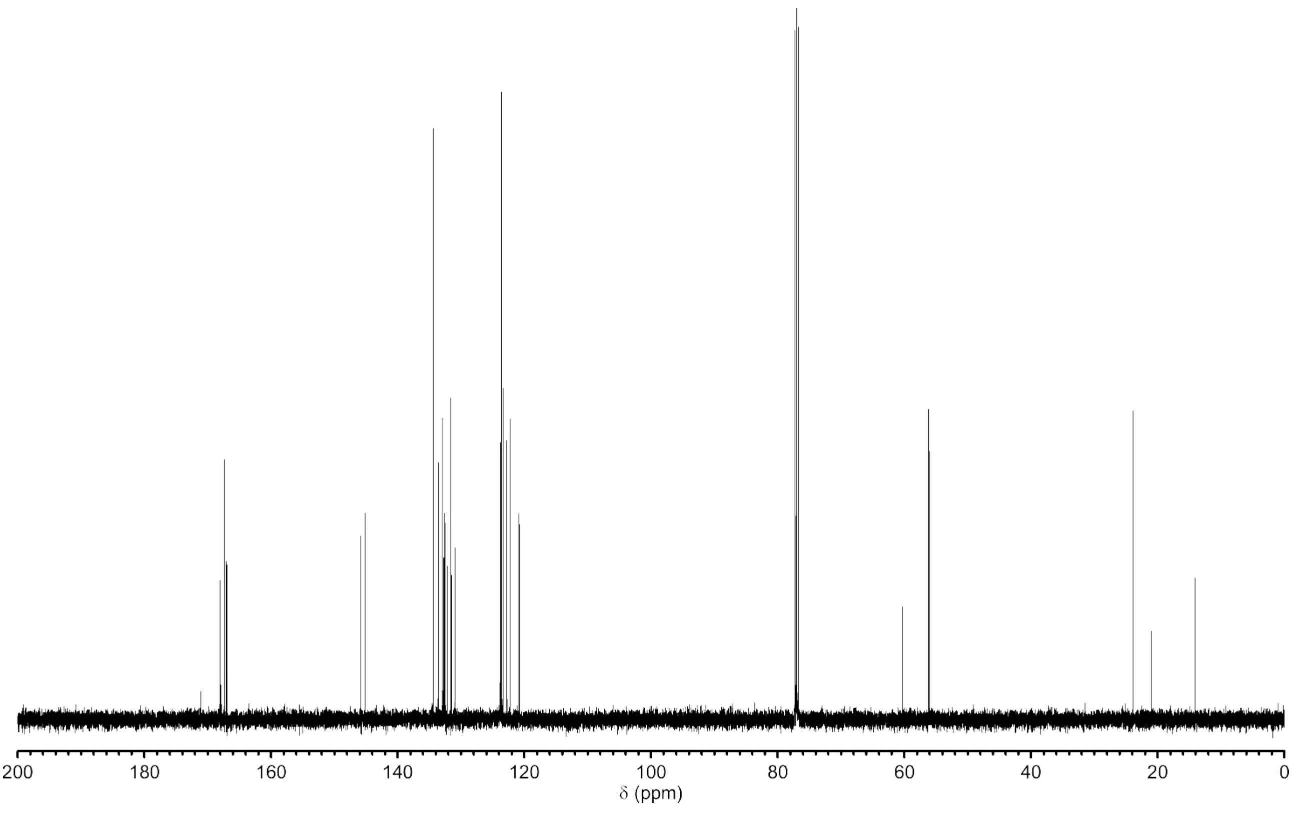
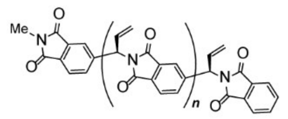


Fig. S5 ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) spectrum of **6** (n = 1).



7 (n = 2)

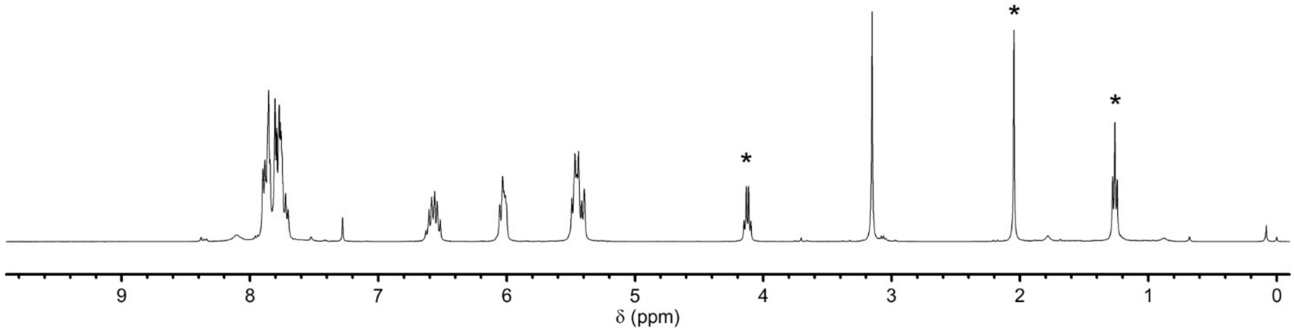


Fig. S6 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **7** (n = 2). The asterisk denotes ethyl acetate.

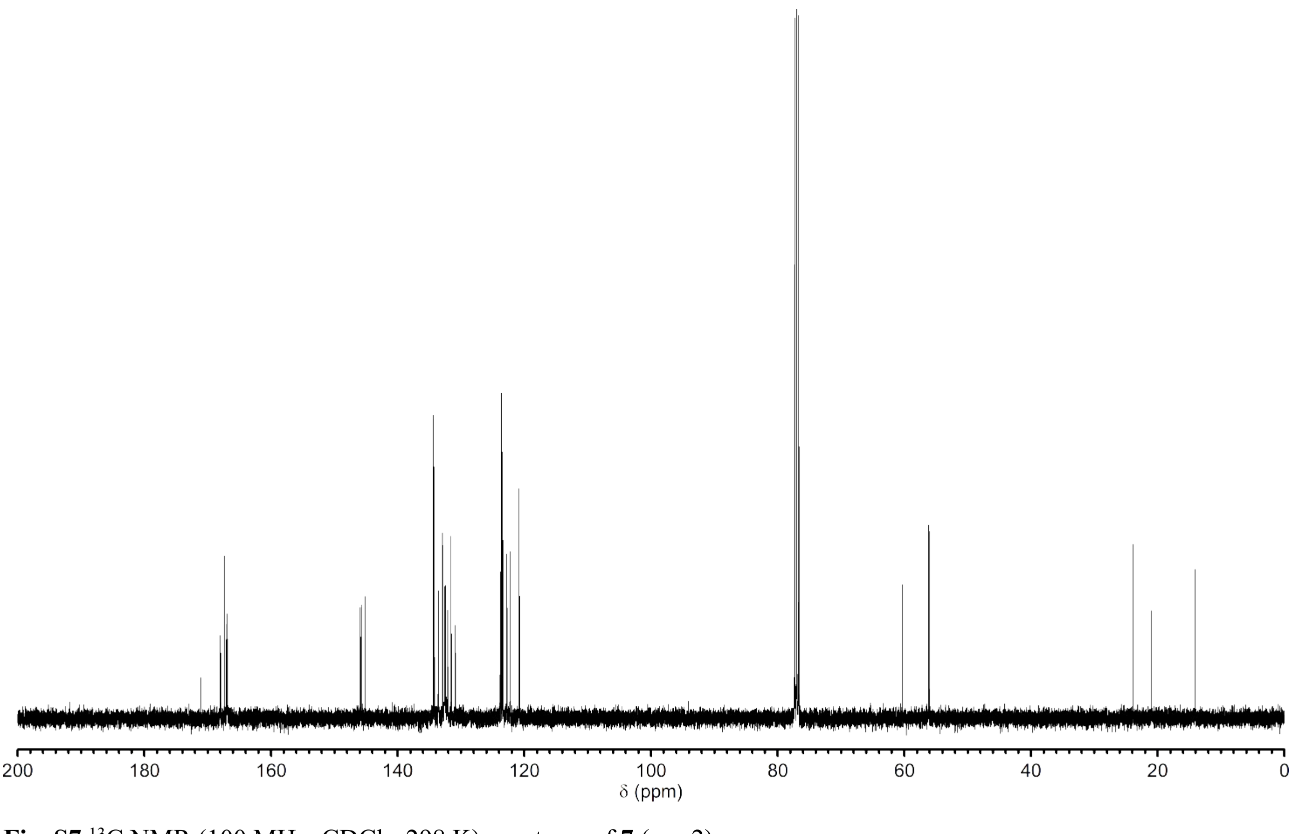


Fig. S7 ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) spectrum of **7** (n = 2).

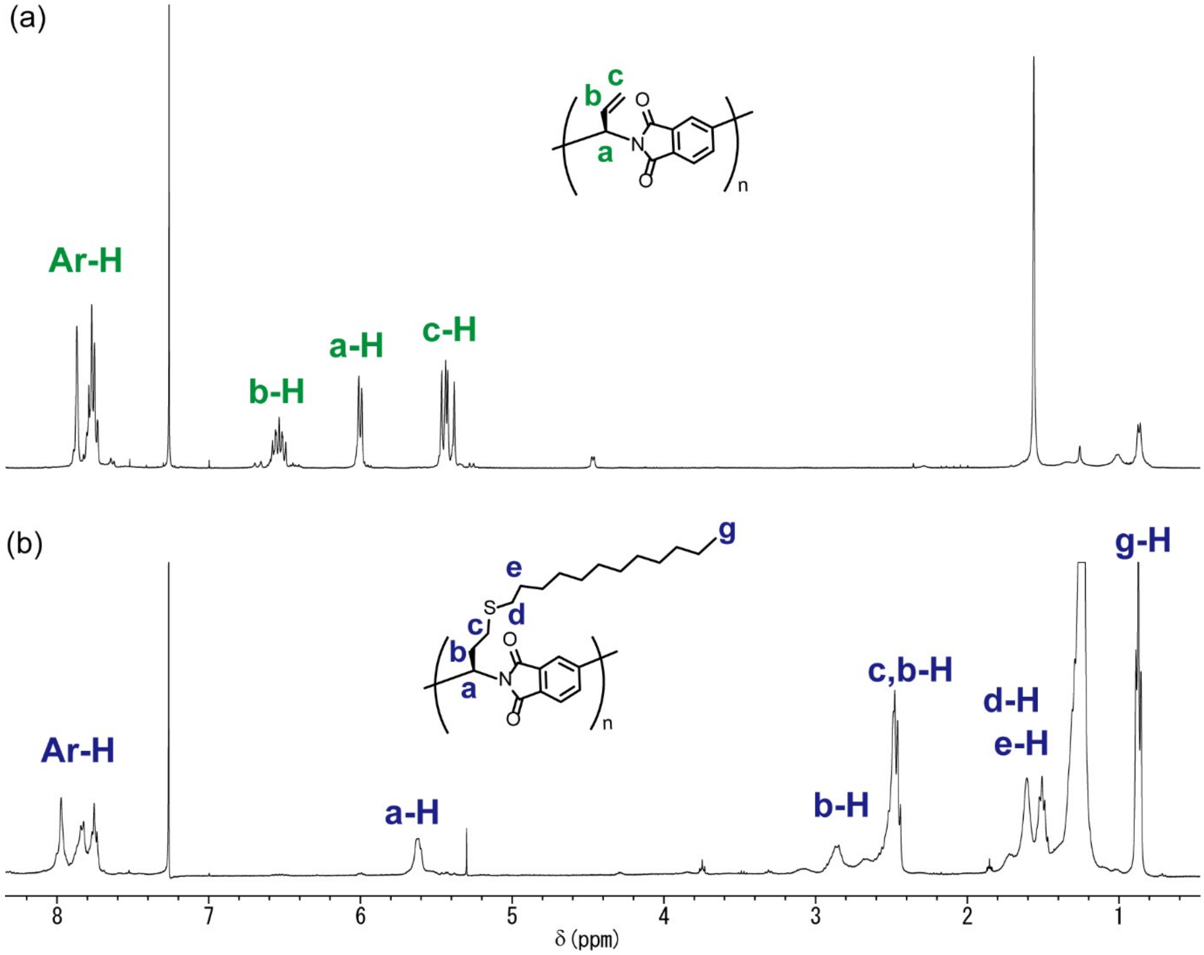


Fig. S8 [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectra of (a) **poly-2** and (b) **poly-4a**.

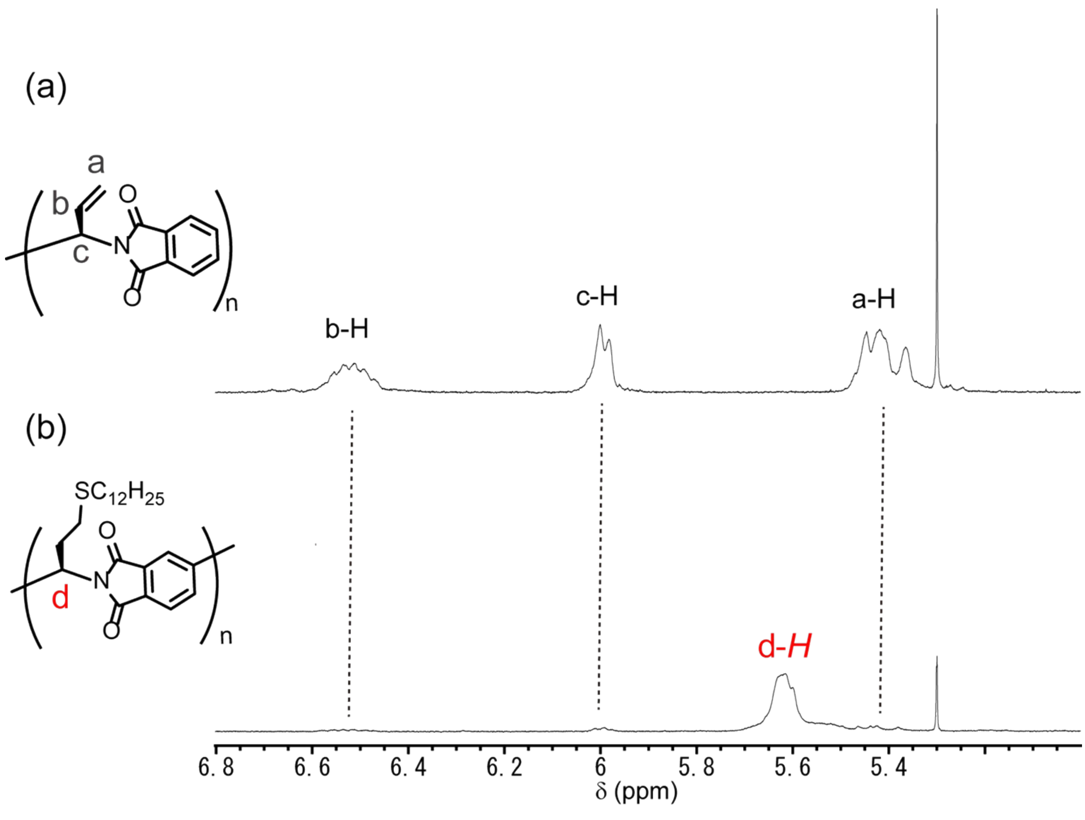


Fig. S9 [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectra of (a) **poly-2** and (b) **poly-4a**.

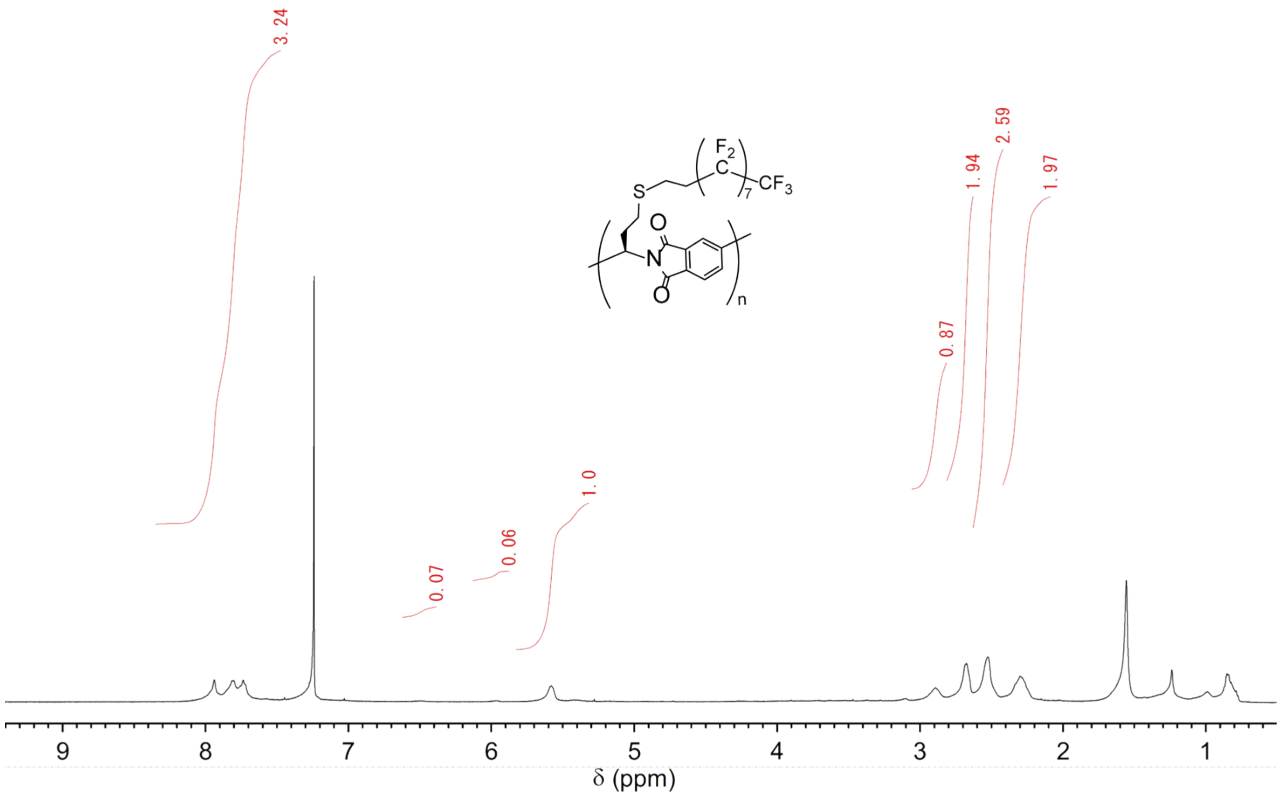


Fig. S10 [1]H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **poly-4b**.

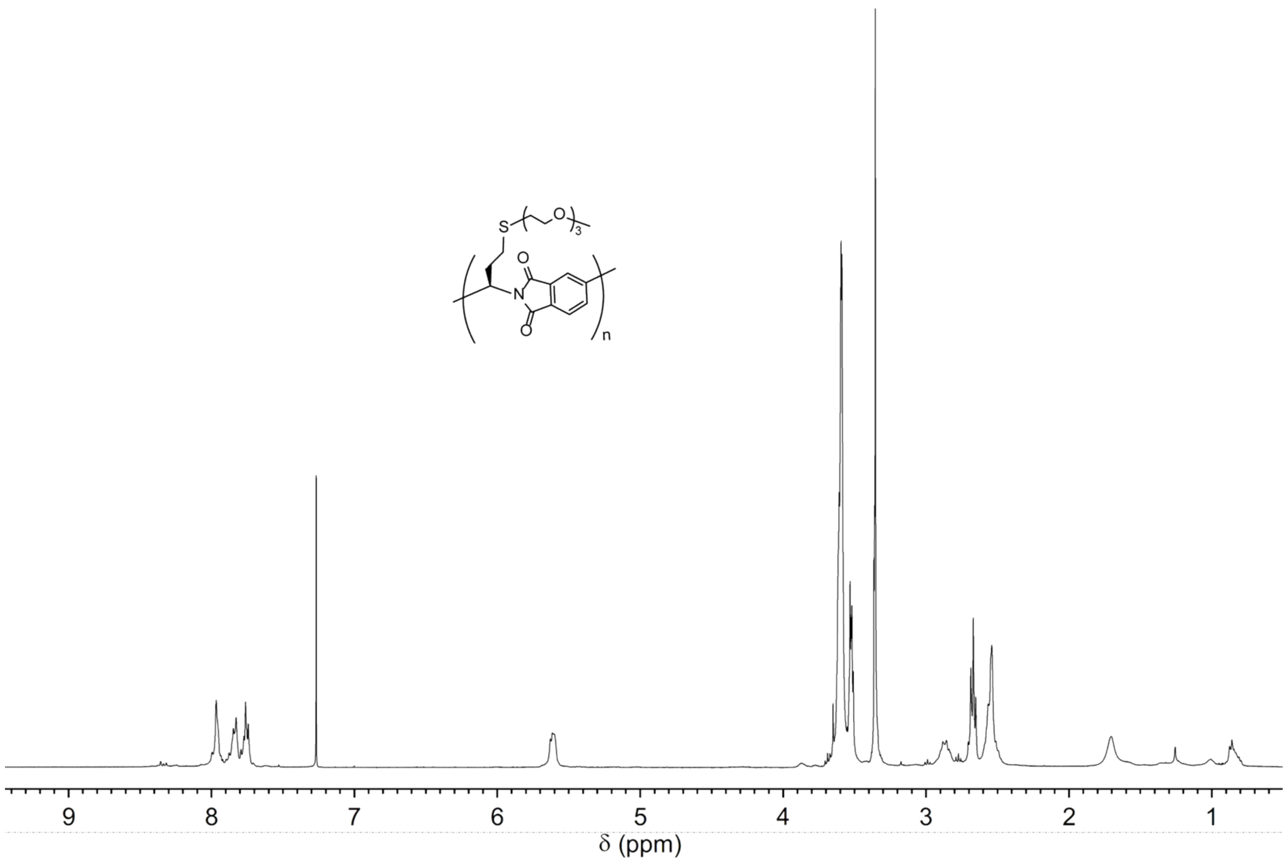


Fig. S11 [1]H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **poly-4c**.

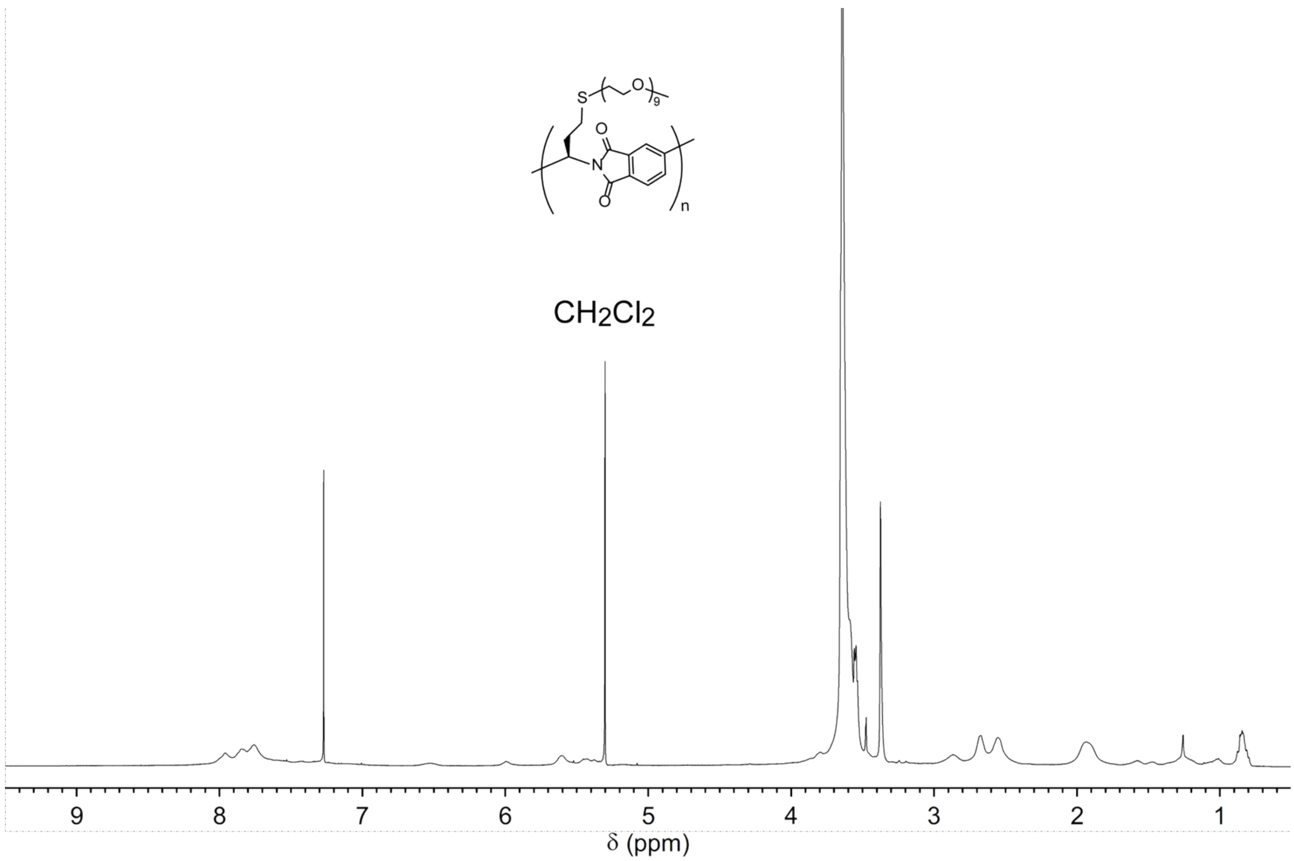


Fig. S12 [1]H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **poly-4d**.

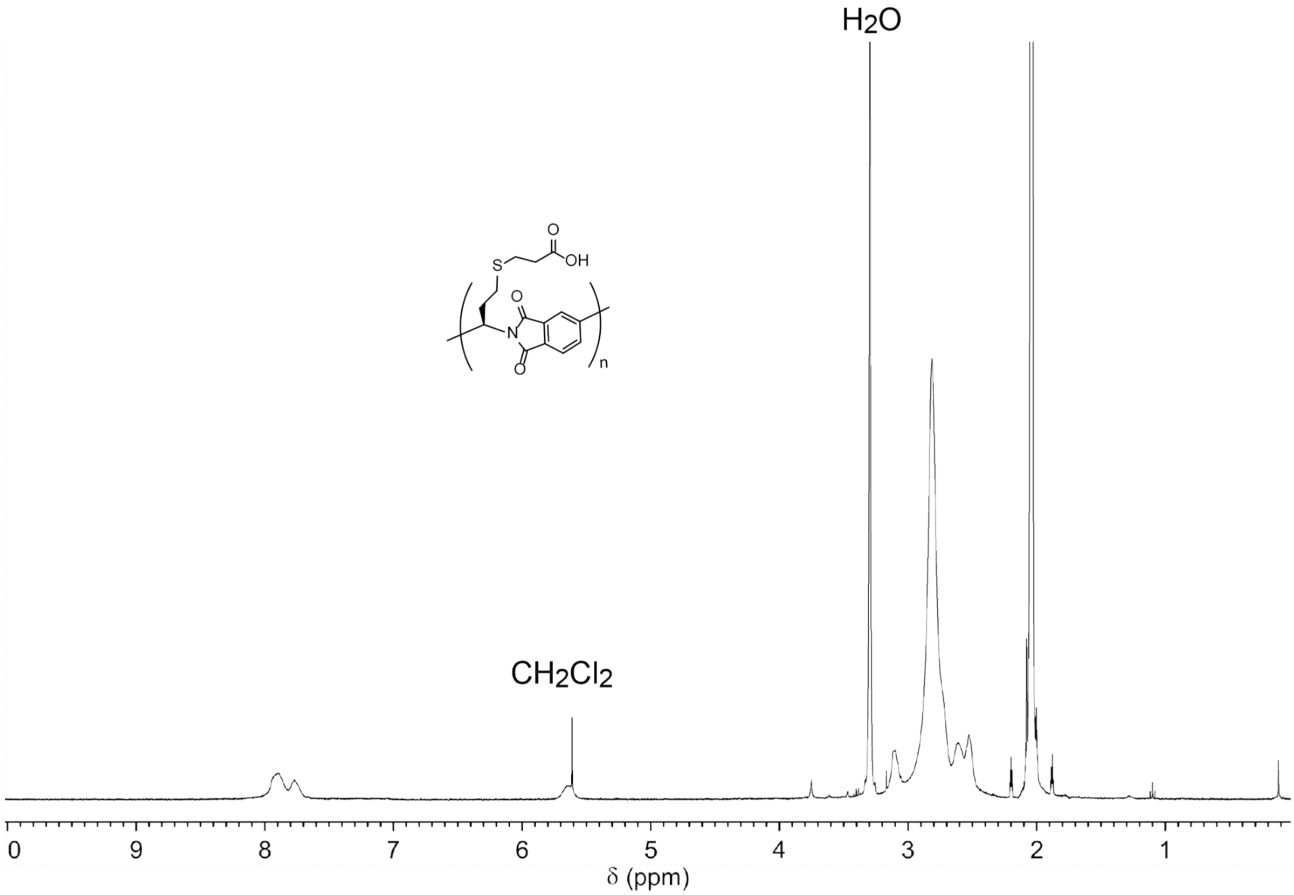


Fig. S13 [1]H NMR (500 MHz, $(CD_3)_2CO$, 298 K) spectrum of **poly-4f**.

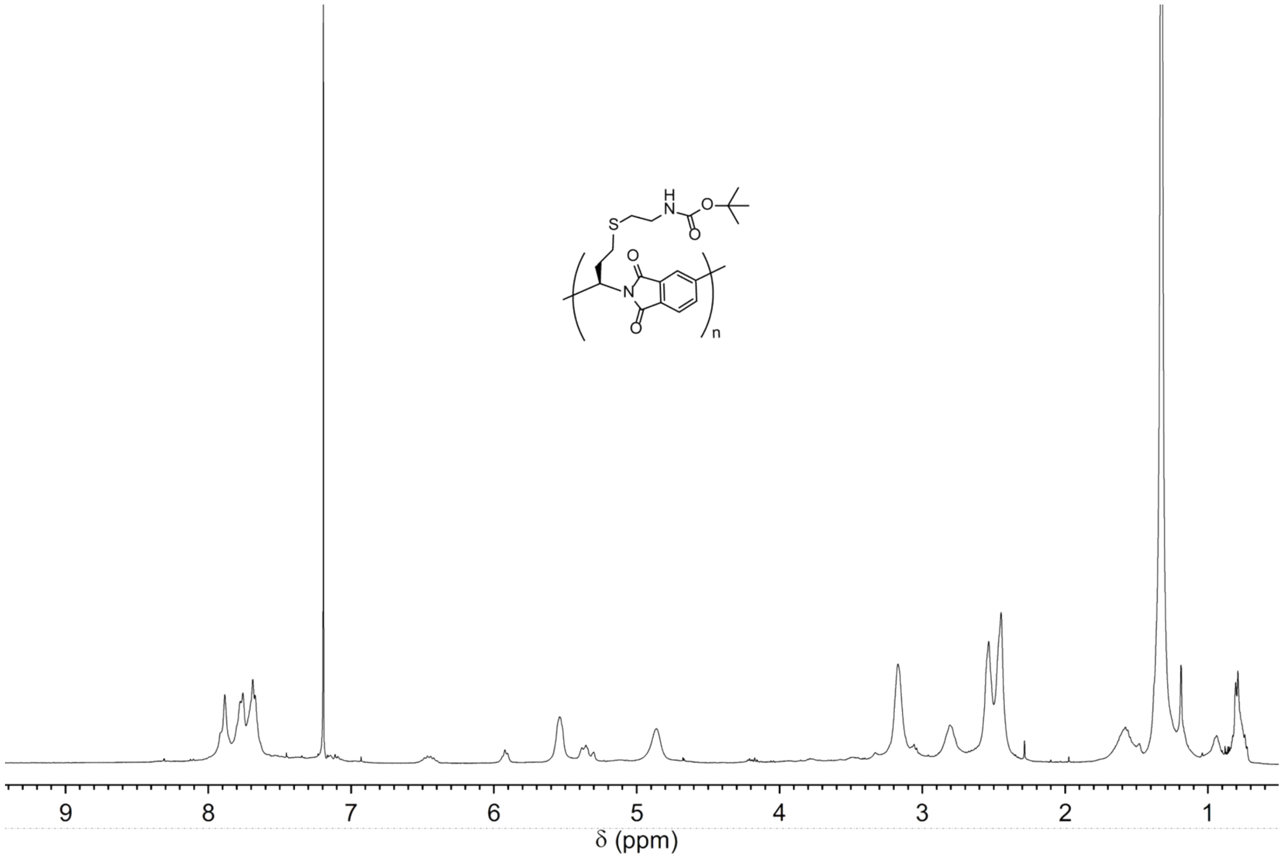


Fig. S14 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **poly-4g**.

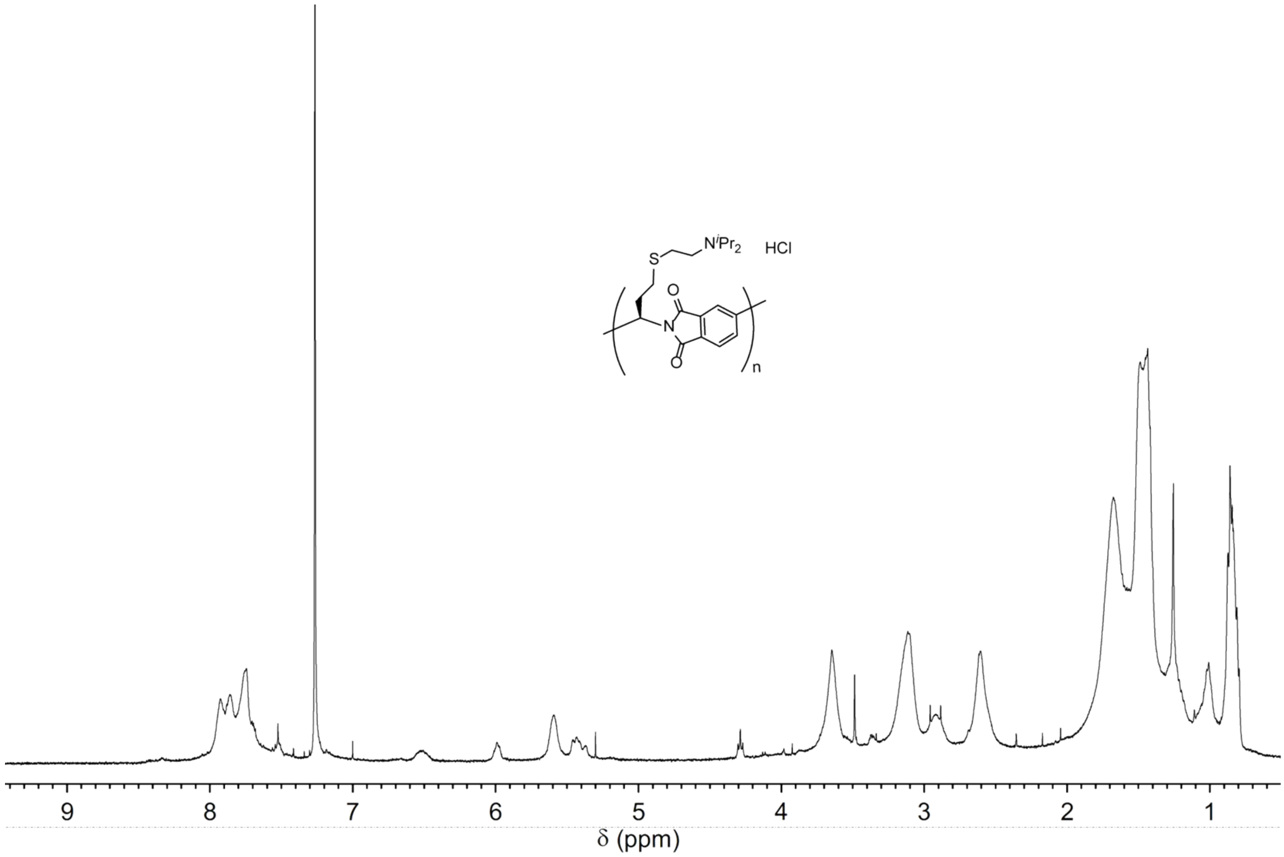


Fig. S15 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **poly-4h**.

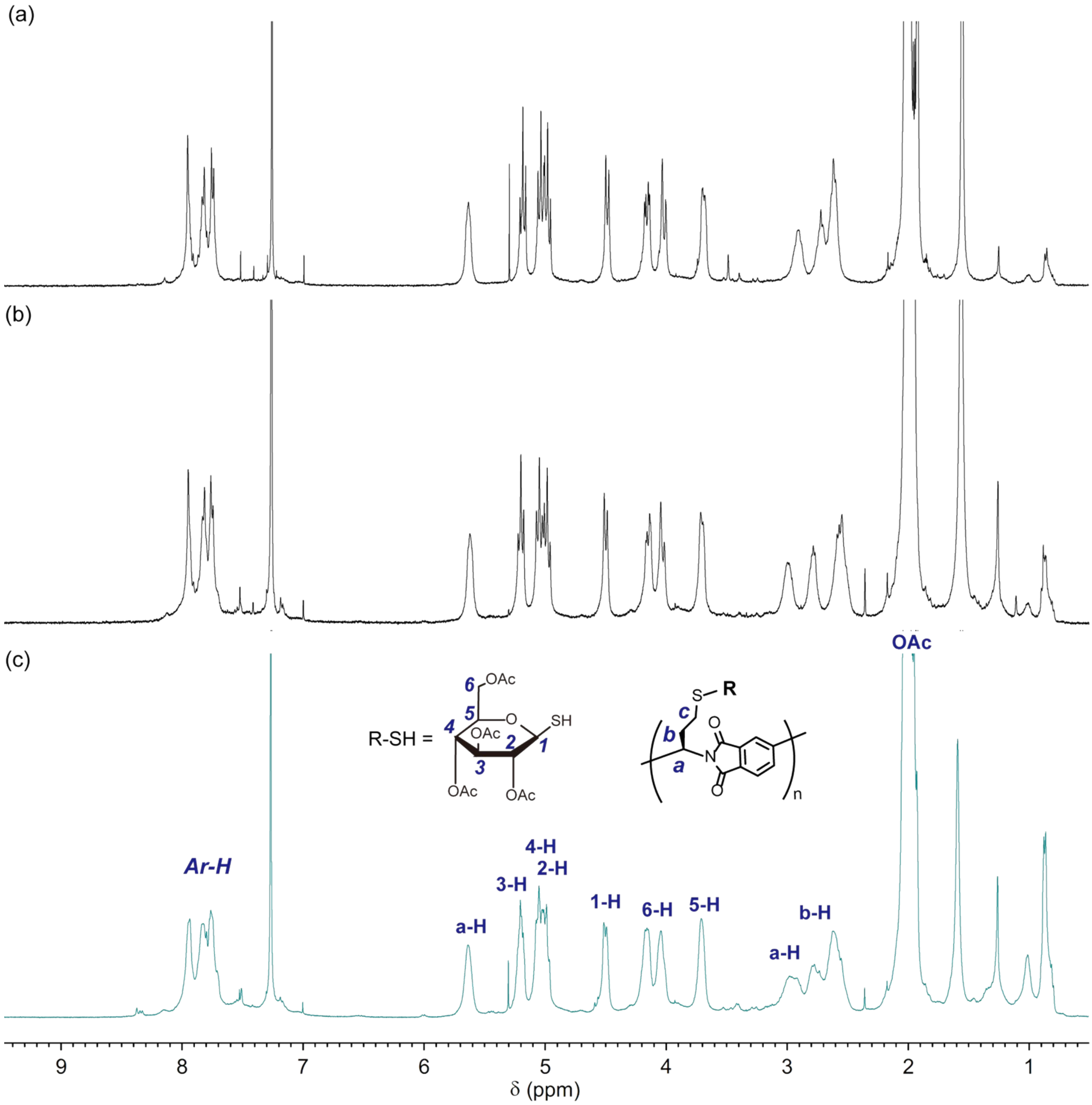


Fig. S16 [1]H NMR (500 MHz, $CDCl_3$, 298 K) spectra of (a) **poly-4i-((*S*)-I)**, (b) **poly-4i-((*R*)-I)**, and (c) **poly-4i-((*rac*)-I)**

3. SEC Analysis

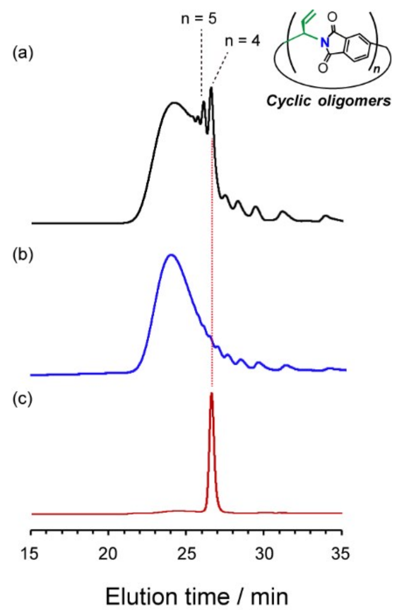


Fig. S17 SEC chromatograms of **poly-2** in chloroform: (a) crude product of entry6 in Table 1, (b) after pirification of **poly-2**, and (c) cyclic oligomer (n = 4).

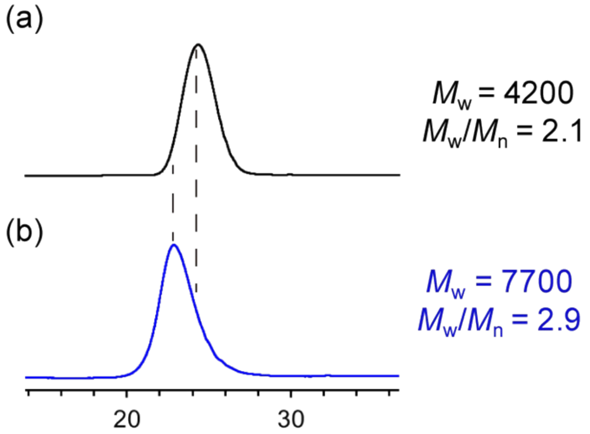
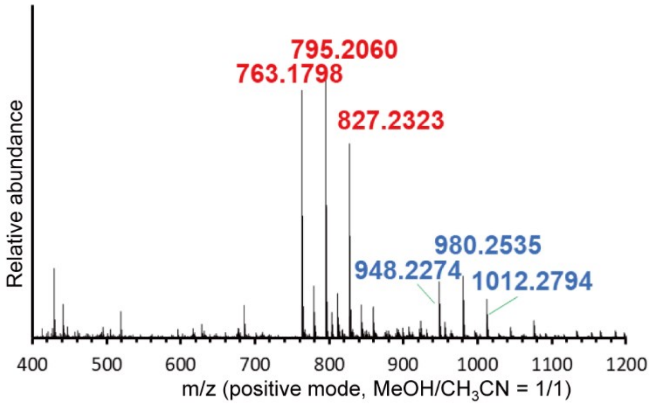
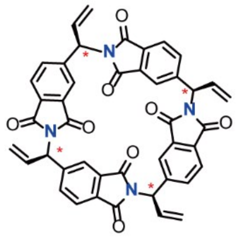


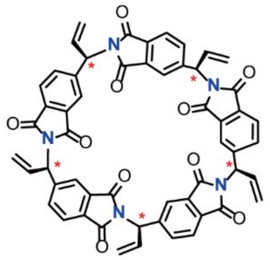
Fig. S18 SEC chromatograms of (a) **poly-2** and (b) **poly-4a** in chloroform.

5. ESI-MS Analysis





$[M+Na]^+$	Found 763.1798, Calcd. 763.1805
$[M+Na+MeOH]^+$	Found 769.2060, Calcd. 795.2097
$[M+Na+2MeOH]^+$	Found 827.2323, Calcd. 827.2329

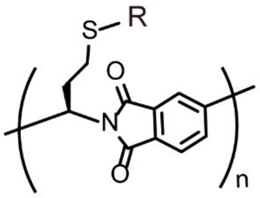


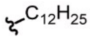
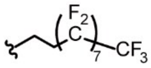
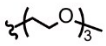
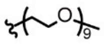
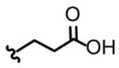
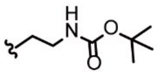
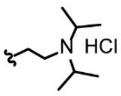
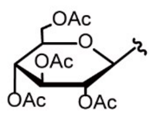
$[M+Na]^+$	Found 948.2274, Calcd. 948.2282
$[M+Na+MeOH]^+$	Found 980.2535, Calcd. 980.2544
$[M+Na+2MeOH]^+$	Found 1012.2794, Calcd. 1012.2806

Fig. S19 ESI-MS spectrum of the oligomers removed during purification.

5. Solubility of Polymers (poly-4)

Table S1



entry	ξ—SR		cyclohexane	$CHCl_3$	THF	CH_3CN	CH_3OH	H_2O
1		**poly-2**	×	○	○	×	×	×
2		**poly-4a**	○	○	○	×	×	×
3		**poly-4b**	×	○	×	×	×	×
4		**poly-4c**	×	○	○	○	△	×
5		**poly-4d**	×	○	○	○	○	○
6		**poly-4f**	×	△	○	△	×	×
7		**poly-4g**	×	○	○	○	×	×
8		**poly-4h**	×	○	△	△	○	○
9		**poly-4i**	×	○	○	△	×	×

Soluble: ○ Partially soluble: △ Insoluble: × ([polymer: 1.0 mg]/[solvent: 1.0 mL])

6. UV and CD spectra

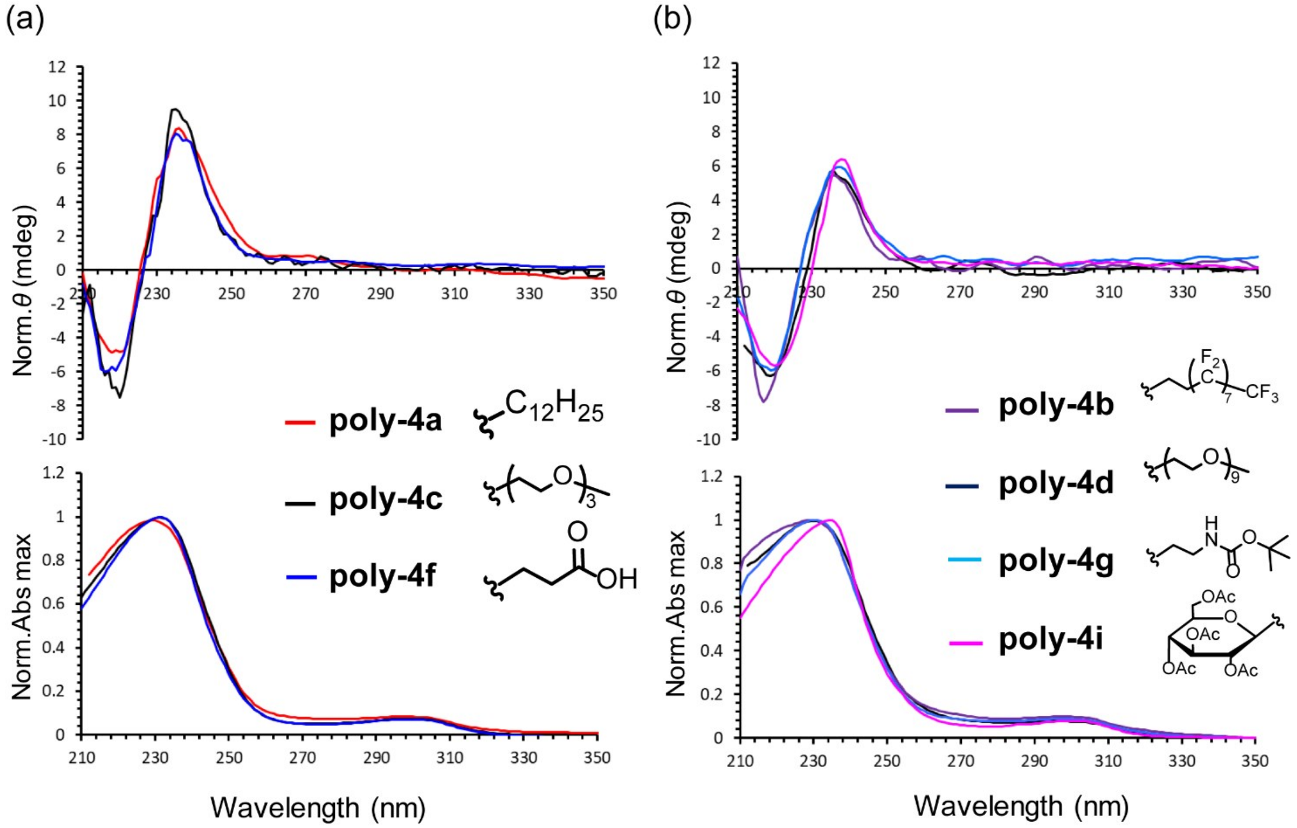


Fig. S20 CD and UV spectra in THF (298 K): (a) **poly-4a**, **poly-4c**, and **poly-4f**, (b) **poly-4b**, **poly-4d**, **poly-4g**, and **poly-4i**. The vertical axes are nomarized on the basis of the absorption maxima.

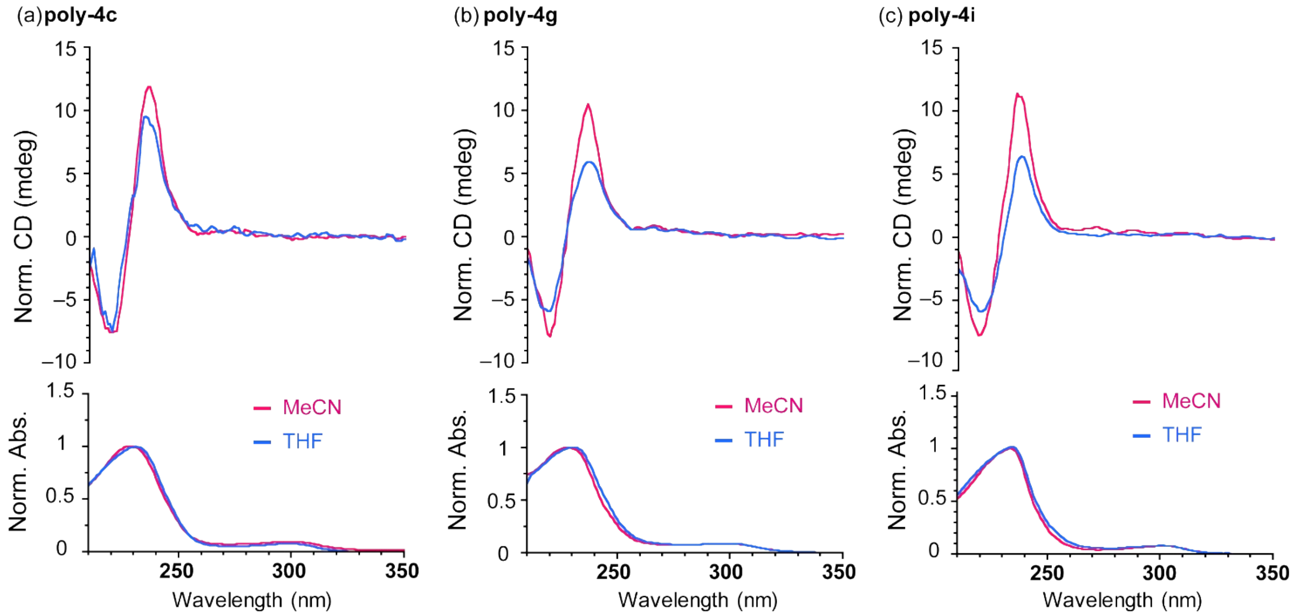


Fig. S21 Normalized CD and UV spectra of (a) **poly-4c**, (b) **poly-4g**, (c) **poly-4i** in THF (red line) and acetonitrile (blue line) at 25 °C.

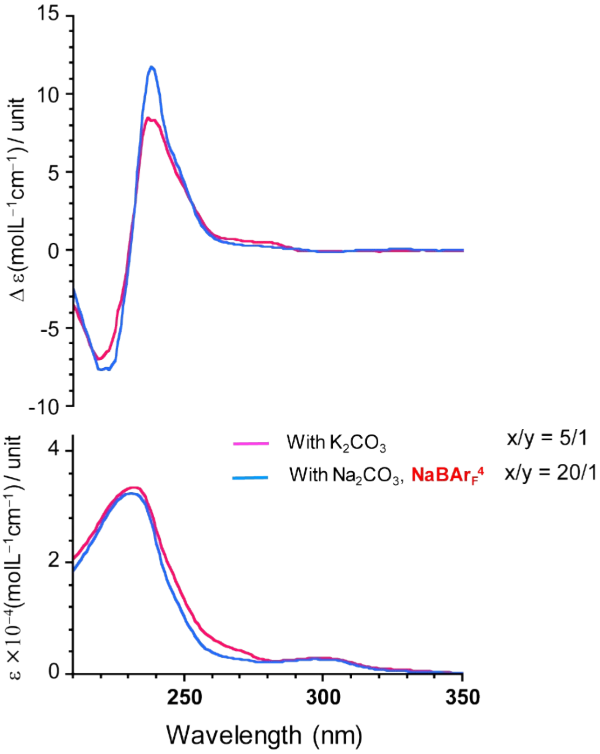


Fig. S22 CD and UV spectra in THF (298 K). Red line; **poly-2** (M_w = 9000, M_w/M_n = 2.6, x/y 5/1: entry 1 in Table 1, in the absence of $NaBAr^F{}_4$). Blue line; **poly-2** (M_w = 4200, M_w/M_n = 2.1, x/y 20/1: entry 7 in Table 1, in the presence of $NaBAr^F{}_4$).

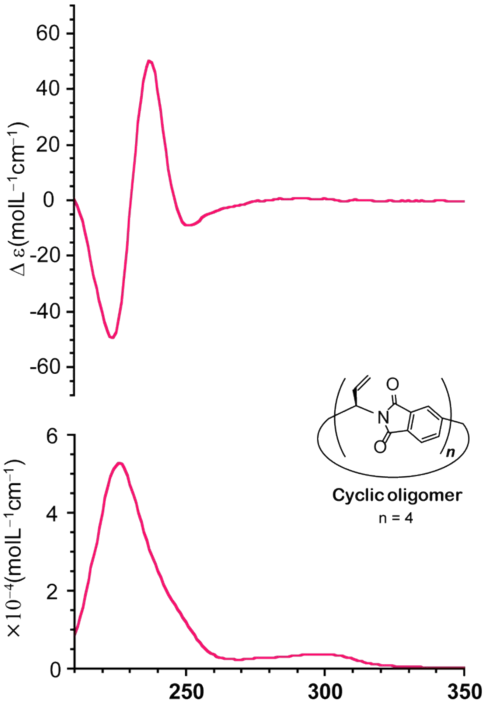


Fig. S23 CD and UV spectra of cyclic tetramer in THF (298 K).

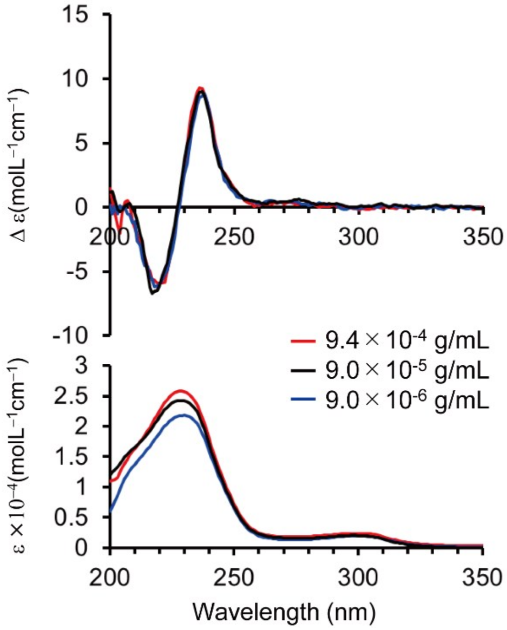
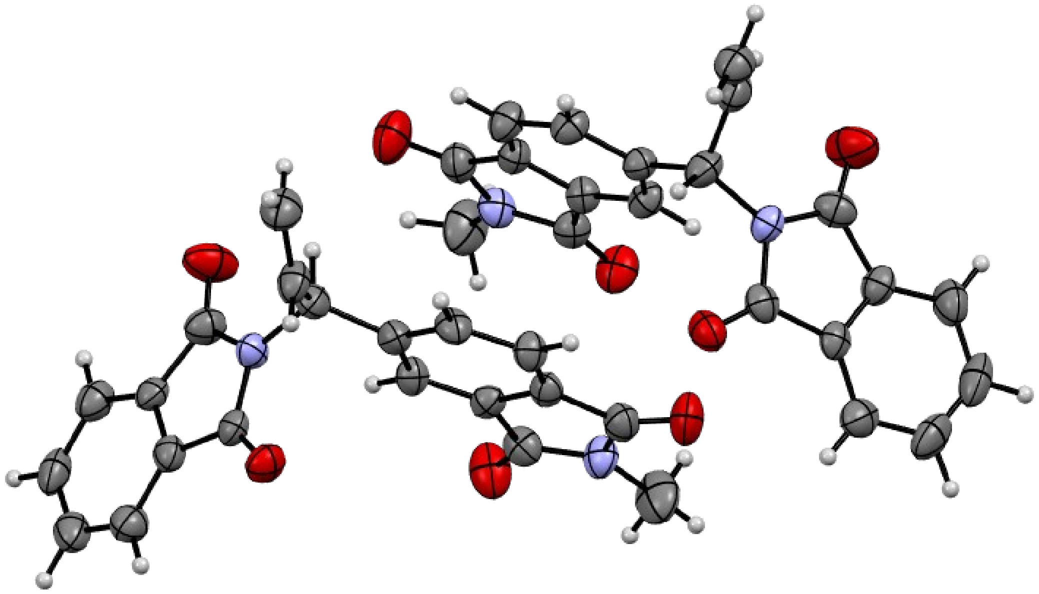


Fig. S24 CD and UV spectra of **poly-4c** (9.4×10^{-4} – 9.0×10^{-6} g/mL) in THF (298 K)

7. X-ray crystallography



	5
fomula	$C_{20}H_{14}N_2O_4$
fw	346.34
cryst syst	Monoclinic
space group	$P2_1$
a, Å	7.6121(6)
b, Å	27.2894(18)
c, Å	8.5005(5)
β, deg	107.255(8)
V, Å^3	1686.3(2)
Z	4
d_{calc}, g cm^{-1}	1.363
μ, mm^{-1}	0.966
GOF	1.032
$R1^a$ [I > 2σ(I)]	0.0567
wR2^b (all data)	0.1080

8. Stable Conformation Search of the Polymer

To investigate the stable secondary structure of **poly-2**, the conformational search with energy minimization based on the crystal structure **5** (φ = 91.1°, ψ = –167.7°) was performed using MacroModel 11.9 with an OPLS3e[5] as the force field, and several pairs of dihedral angles yielded. The resluts was shown in Fig. S20 and Table S2.

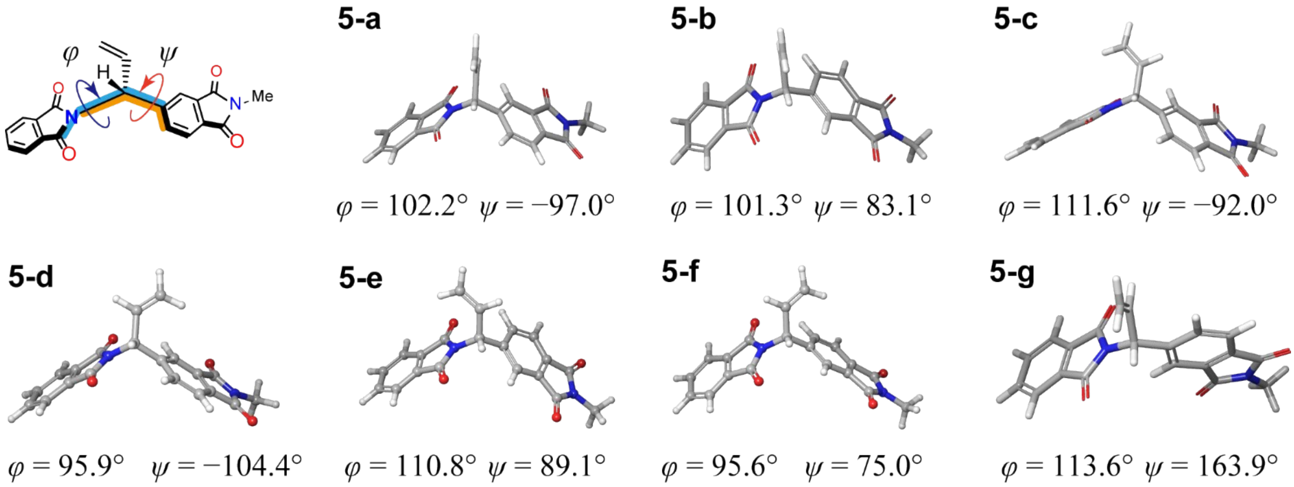


Fig. S25 Stable conformers of **5** obtained by conformational search with energy minimization using MacroModel 11.9 with an OPLS3e as the force field.

Table S2 Potential energy of possible conformers of **5**

Conformer	φ (°)	ψ (°)	Potential Energy (Δ, kcal/mol)
5-a	102.2	–97.0	39.299 (± 0)
5-b	101.3	83.1	39.600 (+0.301)
5-c	111.6	–92.0	44.755 (+5.456)
5-d	95.9	–104.4	45.008 (+5.709)
5-e	110.8	89.1	45.380 (+6.081)
5-f	95.6	75.0	45.594 (+6.295)
5-g	113.6	163.9	49.959 (+10.660)

Based on the stable conformers of **5-a** and **5-b**, the main chain was extended to **7-a** and **7-b**, molecular mechanics minimizations was conducted using MacroModel, followed by molecular dynamics (MD) simulations at 300 K for 300 ps with no solvent. In the case of **7-a** and **7-b**, the rigid phthalimide backbones form the turn conformation, which was stable in MD simulation. Potential energy of **7-a** is more stable than **7-b**

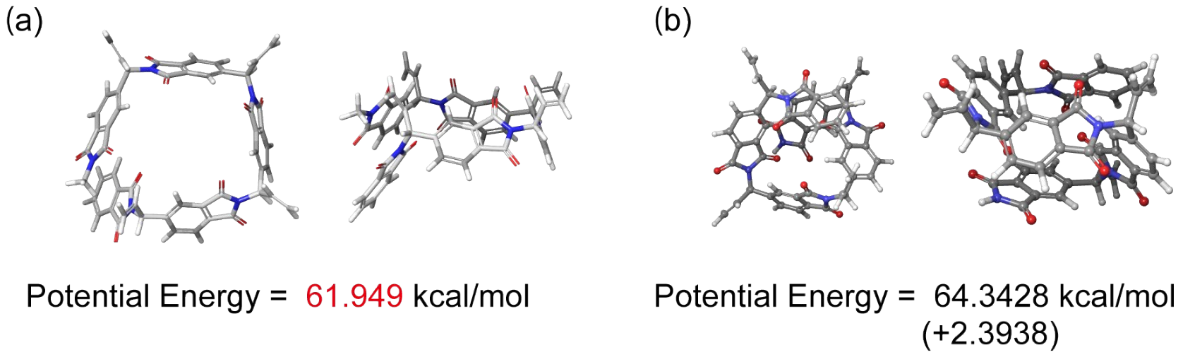


Fig. 26 Optimized structures of (a) **7-a** and (b) **7-b**.

Based on the most stable conformer of **7-a**, the main chain was extended as same methods. The optimized structures of **poly-2 (n = 6)** and **poly-2 (n = 12)** were shown in Fig. 22(a) and (b). In addition, overlay structures of **poly-2 (n = 6)** and **poly-2 (n = 12)** in molecular dynamic simulation (300 K for 300 ps) ever 20 ps were shown in Fig 22 (c) and (d). The same simulation was conducted based on the second low energy conformer of **7-b**. The resulting **poly-2 (n = 6)** collapses the tern conformation after molecular dynamics simulation 300 K for 300 ps .

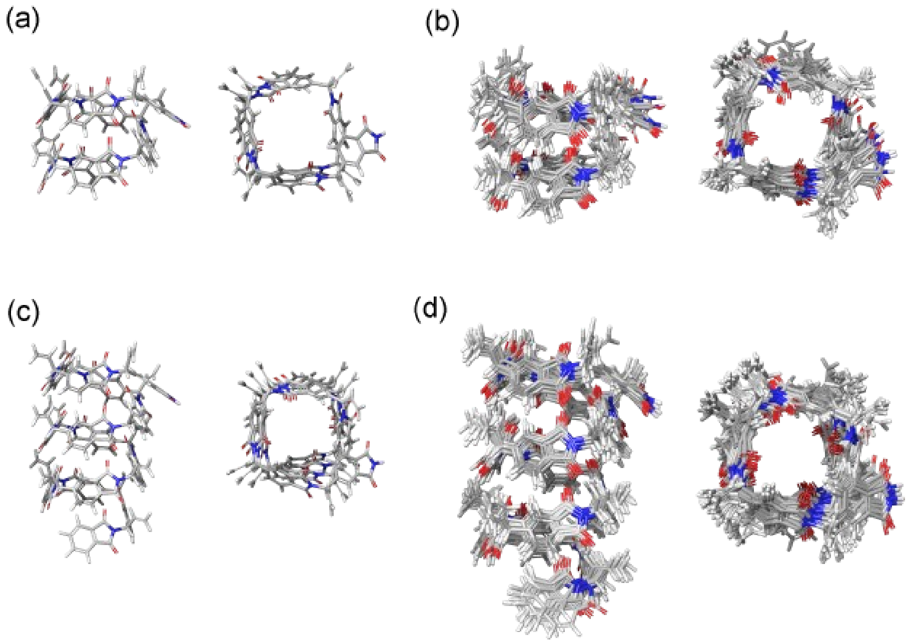


Fig. 27 Optimized structures of **poly-2** (n = 6) and **poly-2** (n = 12).

MD simulation of **poly-2’** (n = 6), the terminal N-Me of phthalimide substituted N–H, was conducted. The N–H proton of terminal phthalimide interacts with the carbonyl group of the neighbouring phthalimide skeleton (i ± 4) through a hydrogen bond.

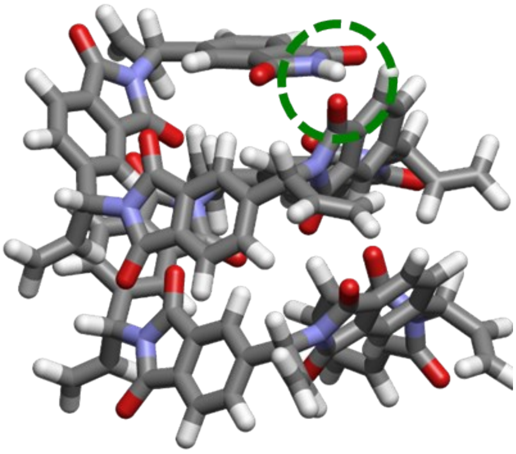


Fig. 28 One of the images in the MD simulation of **poly-2’** (n = 6).

9. References

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