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Supplementary information

Enantiopure chiral multilayer polymers – design, asymmetric synthesis and property study

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1.General Information

Unless otherwise stated, all reactions were magnetically stirred and conducted in oven-dried glassware in anhydrous solvents under an argon atmosphere. Solvents and liquid reagents, as well as solutions of solid reagents, were transferred via syringe or through stainless-steel/polyethylene cannulae using rubber septa under a gentle argon counterflow. Cooling baths were prepared in Dewar vessels using ice/water (0 °C) or dry ice/acetone (-78 °C). Heated oil baths were used for reactions requiring elevated temperatures. Solvents were removed under reduced pressure at 40-65 °C using a rotary evaporator. All reported yields are isolated yields of chromatographically purified materials whose identity was confirmed by NMR spectroscopy.

Abbreviations. Ethyl acetate (EA, EtOAc), diethyl ether (Et_2O), dichloromethane (DCM), chloroform ($CHCl_3$), tetrahydrofuran (THF), 1,4-dioxane (dioxane), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), acetonitrile (MeCN, ACN), methanol (MeOH), ethanol (EtOH), isopropyl alcohol (IPA, *i*-PrOH), n-butanol (*n*-BuOH), tert-butanol (*t*-BuOH), acetone, toluene (PhMe), hexane (Hex), pyridine (Py), and water (H_2O).

Materials and solvents. All commercially available chemicals were used as received without further purification. Methanol, toluene, ethyl acetate, diethyl ether, dichloromethane, 1,4-dioxane, and acetone were used without further purification. THF and DCM were dispensed from an Innovation Technology solvent purification/delivery system.

NMR Spectroscopy

^1H and ^{13}C NMR spectra were recorded on a JEOL ECS 400 MHz NMR spectrometer. Chemical shifts (δ) are reported in ppm relative to tetramethyl silane (TMS). Residual solvent signals were used for referencing when applicable: $CDCl_3$ (^1H δ 7.26; ^{13}C δ 77.16), DMSO-d_6 (^1H δ 2.50; ^{13}C δ 39.52), and THF-d_8 (^1H δ 3.58 and 1.72; ^{13}C δ 67.21 and 25.31). Data are reported as: chemical shift, multiplicity (s, d, t, m), coupling constant (J, Hz), and integration.

Optical rotation

Optical rotation was measured on a Rudolph Research Analytical AUTOPOL IV automatic polarimeter (model APIV/2W) at room temperature using chloroform ($CHCl_3$) as the solvent at a concentration of c = 0.5 mg mL^{-1}.

Gel Permeation Chromatography (GPC)

GPC measurements were performed on a TOSOH Eco SEC HLC-8320 system equipped with a dual-flow refractive index (RI) detector. THF was used as the eluent at 40 °C with a flow rate of 1.0 mL min^{-1}. To improve solubility, polymer samples were prepared in THF containing 10 vol% $CHCl_3$, filtered through a 0.22 μm PTFE syringe filter, and injected at 10 μL. The installed columns cover a molecular-weight range of 500-10^7 Da, and each run was 20 min. Molecular weights were determined relative to polystyrene (PS) standards (PStQuick C) for calibration.

Circular Dichroism (CD)

Circular dichroism (CD) spectra were recorded on a JASCO J-815 spectropolarimeter equipped with a PMT detector (voltage mode: auto). Measurements were performed in continuous-scan mode over a wavelength range of 400-245 nm with a scanning speed of 100 nm min^{-1}, a spectral bandwidth of 1.0 nm, a data pitch of 0.1 nm, and a digital integration time (D.I.T.) of 1 s. Each reported spectrum represents the average of three accumulations. The CD signal (mdeg) was acquired simultaneously with the PMT high-tension (HT) voltage and absorbance channels. A solvent baseline $CHCl_3$, measured under identical conditions, was subtracted from each sample spectrum. To ensure data fidelity, spectral interpretation was strictly limited to the detector's linear response region; following manufacturer guidance, data points exhibiting an HT voltage 700V were excluded from the analysis (see Supporting Information).

Dynamic Light Scattering (DLS)

Hydrodynamic size distributions were analyzed using a Nanotrac Model NPA250 system (Microtrac Inc.) with CHCl3 as the solvent (c = 0.2 mg mL^{-1}). Sample preparation was critical: prior to analysis, all solutions were centrifuged at 3,600 rpm for 5 min to eliminate dust particles and large artifacts. Measurements were conducted in triplicate to ensure statistical robustness; for each independent aliquot, two consecutive 60-second scans were performed. Data acquisition and processing were executed using the Microtrac FLEX software (version 10.3.14). The final size distributions are reported as the average of the three independent trials, plotted as intensity-weighted percentages versus hydrodynamic diameter.

Scanning Electron Microscopy (SEM)

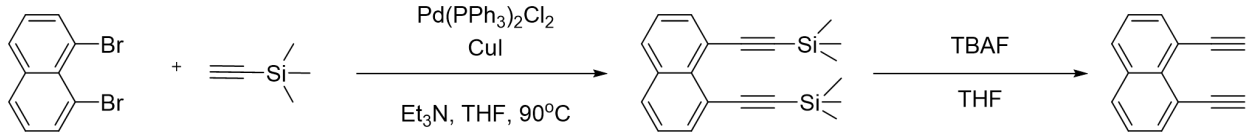
SEM images were acquired on a ZEISS Crossbeam 540 at an accelerating voltage of 5 kV using a secondary electron detector. Polymer powders were dried at 50 °C overnight, gently spread onto adhesive SEM stubs, and sputter-coated with a thin Au layer prior to imaging to mitigate charging effects.

UV-visible spectroscopy (UV)
UV-visible (UV-Vis) absorption spectra were recorded on an Agilent 8453 UV-visible spectrophotometer. Samples were prepared in chloroform ($CHCl_3$) at a concentration of c = 0.05 mg mL^{-1}.

High-Performance Liquid Chromatography (HPLC)
Chiral HPLC analyses were performed on a Thermo Scientific UltiMate 3,000 liquid chromatography system using normal-phase conditions. Samples were prepared at c = 1.0 mg mL^{-1} and injected at 10 µL. Separations were carried out on immobilized polysaccharide-based chiral stationary phases (DAICEL CHIRALPAK IA, IB, IC, or ID, selected according to the specific sample) with n-hexane/2-propanol (*i*PrOH) as the eluent.

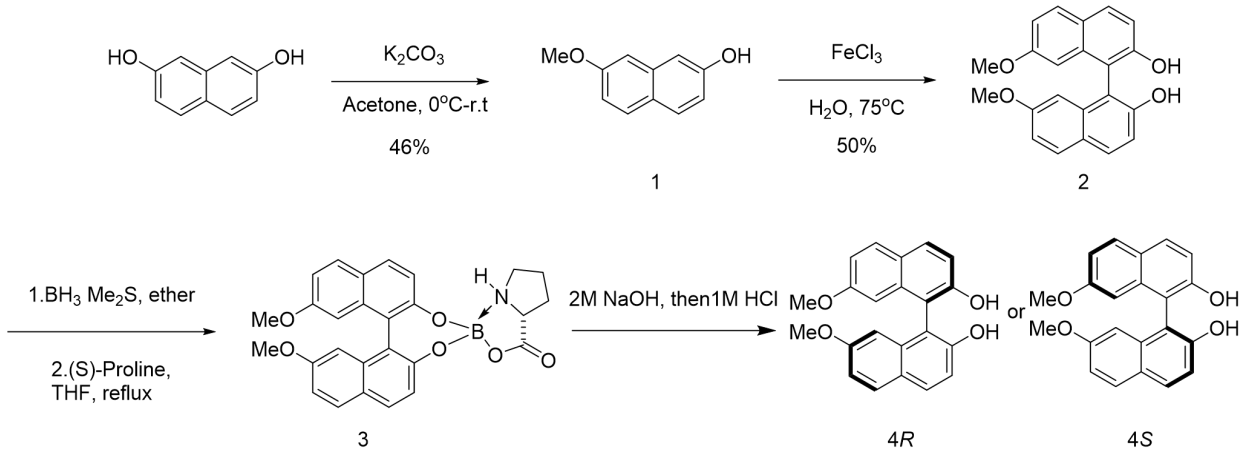
High-resolution mass spectrometry (HRMS)
High-resolution mass spectra were acquired on a Thermo Scientific Orbitrap Fusion Lumos Tribrid mass spectrometer equipped with an electrospray ionization (ESI) source. Data were collected at a resolving power of 120,000 (FWHM, at m/z 200). Samples (c = 1 mg mL^{-1}) were introduced by direct infusion from acetonitrile (CH_3CN).

2.Synthetic Procedures



1,8 bis (trimethylsilyl ethynyl) naphthalene
Add trimethylsilyl acetylene (3.55 ml, 25.0 mmol) to a mixture of 1,8-dibromodonaphthalene (10.0 mmol), CuI (38 mg, 0.20 mmol), $PdCl_2(PPh_3)_2$ (140 mg, 0.20 mmol), and triethylamine (25 mL) in a Schlenk flask. This should be done under Argon at room temperature. Heat the reaction mixture at 110 °C for 1 hour. Once the mixture has cooled to room temperature, filter the suspension through a 2 cm thick layer of Celite. Rinse the Celite thoroughly with ethyl acetate (100 mL). Remove the solvent in vacuo and the residue was purified by silica gel column chromatography with petroleum ether to yield a yellow oil, 1.92 g, 60%.

1,8-diethynylnaphthalene
Add a solution of tetrabutylammonium fluoride in THF (1.0 M, 10 mL) to 1,8 bis (trimethylsilyl ethynyl) naphthalene (4.0 mmol) in 40 mL THF. Stir the mixture for 30 minutes at room temperature. Remove the solvent in vacuo and the residue was purified by silica gel column chromatography with petroleum ether to yield a black solid, 1.73g, 90%. (.[1] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 (td, *J* = 8.2, 7.4, 1.3 Hz, 4H), 7.44 – 7.38 (m, 2H), 3.43 (s, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 136.08, 130.38, 125.59, 85.42.



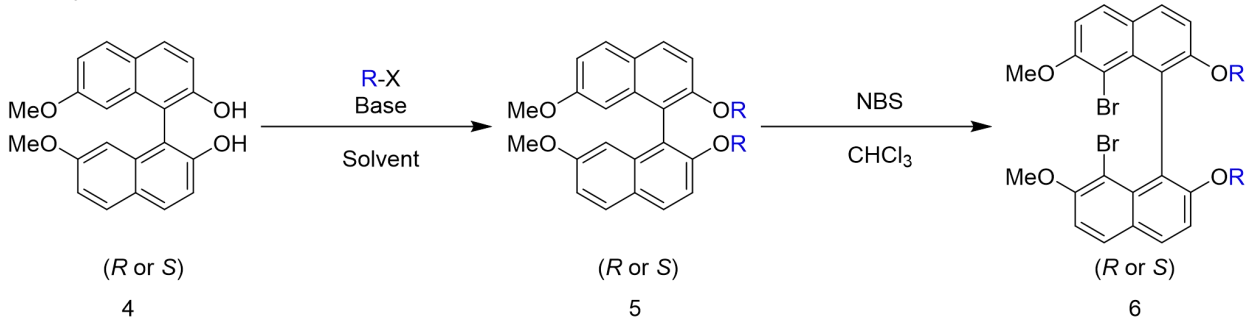
7-methoxynaphthalen-2-ol (1)
Naphthalene-2,7-diol (2.4 g, 15 mmol), K_2CO_3 (2.7 g, 15.0 mmol), and 100 mL of acetone were introduced into a 250 mL round-bottom flask equipped with a stirring bar and a rubber septum. The mixture was cooled to 0°C. The flask was then degassed under vacuum and backfilled with argon three times. Subsequently, CH_3I (0.9 mL, 15.0 mmol) was added dropwise. The reaction slowly warmed to room temperature and stirred overnight. The resulting White solid, (1) was obtained by silica gel column chromatography (eluent: hexane/ethyl acetate = 10:1), yielding 1.21 g (46% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.69 – 7.61 (m, 2H), 7.05 (d, *J* = 2.5 Hz, 1H), 7.02 – 6.96 (m, 2H), 6.93 (dd, *J* = 8.7, 2.5 Hz, 1H), 4.98 (s, 1H), 3.89 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.33, 154.03, 136.05, 129.74, 129.42, 124.49, 116.42, 115.29, 108.95, 104.78, 55.40.

7,7'-dimethoxy-[1,1'-binaphthalene]-2,2'-diol (2)
7-methoxynaphthalen-2-ol (10 g, 57.5 mmol) was added to a solution of $FeCl_3$*$6H_2O$ (31.1 g, 115 mmol) in 150 mL of H_2O. The mixture was stirred at 75 °C for 12 h and then filtered to remove a dark brown precipitate. The solution was diluted by adding 50 mL of water and extracted with diethyl ether. The organic phase was dried over anhydrous $NaSO_4$, remove the solvent in vacuo and the residue was purified by silica gel column chromatography with petroleum ether to yield a white solid (eluent: hexane/ethyl acetate = 20:1) to obtain 7,7'-dimethoxy-[1,1'-binaphthalene]-2,2'-diol **2** (9.88 g, 50%), **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.87 (d, J = 8.8 Hz, 2H), 7.77 (d, J = 8.9 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H), 7.02 (dd, J = 8.9, 2.5 Hz, 2H), 6.47 (d, J = 2.5 Hz, 2H), 5.04 (s, 2H), 3.57 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.00, 159.19, 153.41, 134.77, 131.25, 130.11, 124.87, 116.14, 115.19, 110.09, 103.18, 55.24.

2.1 Synthetic Procedures of Separate Diastereomers

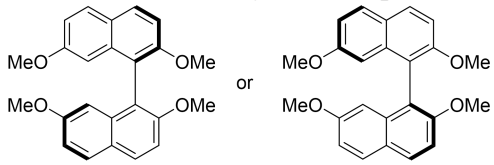
Cool the racemic 7,7'-dimethoxy-[1,1'-binaphthalene]-2,2'-diol (**2**) (10 g, 29mmol) to 0°C, dissolve it in dry ether, and add it to a 250 mL round-bottom flask. Slowly add Borane dimethyl sulfide (BH3*Me2S) (5.8613 g, 77.16 mmol) under an argon atmosphere. Stir the mixture at room temperature for an additional 3 hours. Remove the solvent under vacuum. To the remaining solid, add dry THF (100 mL) followed by (S)-proline (7.32 g, 63.58 mmol). Reflux the mixture for 3 hours, then cool it to room temperature to precipitate a solid from the solution. Filter the solid with THF and dry it under vacuum to yield a mixture of diastereomers (4*R*) and (4*S*). Separate the two diastereomers on a column of silica gel (eluent: hexane/ethyl acetate = 1:4) to obtain 4*R* (1.406 g, 14%) and 4*S* (4.218 g, 42%). [2]

2.2Synthetic Procedures of Substrates



(*R* or *S*) 4 (*R* or *S*) 5 (*R* or *S*) 6

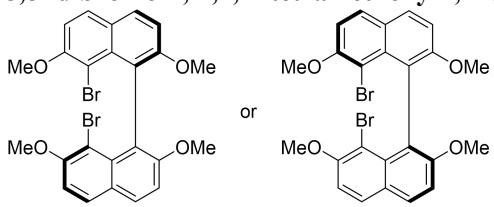
2,2',7,7'-tetramethoxy-1,1'-binaphthalene, 5a (*R* or *S*）



5a***R*** 5a***S***

7,7'-dimethoxy-[1,1'-binaphthalene]-2,2'-diol **4** (*R* or *S*) (2.0 g, 5.8 mmol), K_2CO_3 (3.21 g, 23.2 mmol), and 100 mL of acetone were introduced into a 250 mL round-bottom flask equipped with a stirring bar and a rubber septum. The mixture was cooled to 0°C. The flask was then degassed under vacuum and backfilled with argon three times. Subsequently, CH_3I (4.92 g, 34.6 mmol) was added dropwise. The reaction slowly warmed to room temperature and stirred overnight. The resulting White solid, **5a** (*R* or *S*) was obtained by recrystallization in methanol, yielding 1.2 g (55%, yield). [2] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.84 – 7.77 (m, 2H), 7.68 (d, *J* = 8.9 Hz, 2H), 7.22 (d, *J* = 9.0 Hz, 2H), 6.91 (dd, *J* = 8.9, 2.5 Hz, 2H), 6.36 (d, *J* = 2.5 Hz, 2H), 3.69 (s, 6H), 3.44 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.14, 155.59, 135.25, 129.58, 129.20, 124.93, 118.66, 116.07, 111.58, 103.85, 56.85, 55.07.

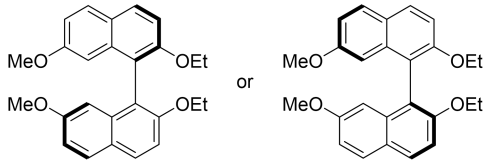
8,8'-dibromo-2,2',7,7'-tetramethoxy-1,1'-binaphthalene, 6a (R or S)



6a***R*** 6a***S***

5a (*R* or *S*) (1 g, 2.67 mmol), N-bromosuccinimide (NBS, 1.901 g, 10.68 mmol), and chloroform ($CHCl_3$, 15 mL) were added to a 50 mL Schlenk flask. The flask was degassed under vacuum and backfilled with argon three times. Subsequently, pyridine (0.9 mL, 11.01 mmol) was added. The mixture was stirred at 75 ℃ overnight. The reaction was then quenched by adding 10 mL of 1M hydrochloric acid (HCl). The reaction mixture was diluted with dichloromethane (CH_2Cl_2, 30 mL) and washed with 20 mL of brine. The organic phase was concentrated, and the residue was purified by recrystallization with methanol, yielding a brown solid (compound **6a** (*R* or *S*), 0.64 g, 45% yield). [2] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 9.0 Hz, 2H), 7.74 (d, *J* = 9.0 Hz, 2H), 7.14 (d, *J* = 8.9 Hz, 2H), 7.04 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 6H), 3.59 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.93, 154.99, 133.71, 130.24, 130.00, 126.63, 121.51, 112.26, 110.91, 106.83, 57.07, 56.94, 29.66. **HRMS** (ESI) m/z: $[M + H]^+$ (M isotope peak) Calcd for $C_{24}H_{21}Br_2O_2$ 530.9801; found 530.9794. **HRMS** (ESI) m/z: $[M + H]^+$ (M+2 isotope peak) Calcd for $C_{24}H_{21}Br_2O_2$ 532.9781; found 532.9775. **HRMS** (ESI) m/z: $[M + H]^+$ (M+4 isotope peak) Calcd for $C_{24}H_{21}Br_2O_2$ 534.9760; found 534.9754.

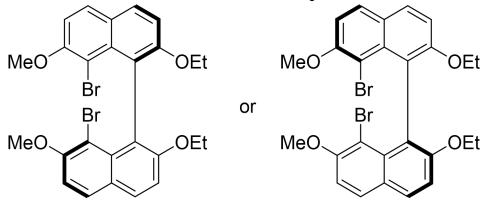
2,2'-diethoxy-7,7'-dimethoxy-1,1'-binaphthalene, 5b (*R* or *S*)



5b*R* 5b*S*

7,7'-dimethoxy-[1,1'-binaphthalene]-2,2'-diol **4** (*R* or *S*) (2.8 g, 8.08 mmol), K_2CO_3 (5.5 g, 32 mmol), and 100 mL of acetone were introduced into a 250 mL round-bottom flask equipped with a stirring bar and a rubber septum. The mixture was cooled to 0°C. The flask was then degassed under vacuum and backfilled with argon three times. Subsequently, CH_3CH_2Br (4.6 g, 48.48 mmol) was added dropwise. The reaction mixture was refluxed overnight. The resulting white solid, **5b** (*R* or *S*) was obtained by recrystallization in methanol, yielding 1.45 g (45 % yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.76 (dd, *J* = 9.0, 1.2 Hz, 2H), 7.66 (dd, *J* = 8.9, 1.3 Hz, 2H), 7.19 – 7.15 (m, 2H), 6.90 (ddd, *J* = 9.0, 2.6, 1.3 Hz, 2H), 6.42 – 6.36 (m, 2H), 3.96 (qdd, *J* = 6.9, 5.3, 1.3 Hz, 4H), 3.43 (d, *J* = 1.3 Hz, 6H), 0.99 (td, *J* = 7.0, 1.3 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform -*d*) δ 157.95, 154.98, 135.44, 129.41, 128.85, 124.94, 119.77, 115.96, 113.20, 104.17, 65.08, 55.04, 15.11, 1.10.

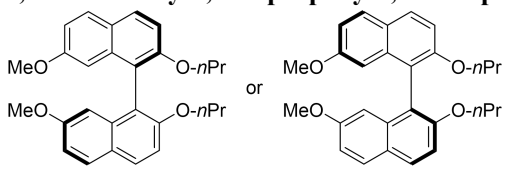
8,8'-dibromo-2,2'-diethoxy-7,7'-dimethoxy-1,1'-binaphthalene, 6b (*R* or *S*)



6b*R* 6b*S*

5b (*R* or *S*) (510 mg, 1.27 mmol), N-bromosuccinimide (NBS, 902.1 mg, 5.1 mmol), and chloroform ($CHCl_3$, 10 mL) were added to a 50 mL Schlenk flask. The flask was degassed under vacuum and backfilled with argon three times. Subsequently, pyridine (301.4 m, 3.81 mmol) was added. The mixture was stirred at 75 ℃ under an argon atmosphere overnight. The reaction was then quenched by adding 10 mL of 1M hydrochloric acid (HCl). The reaction mixture was diluted with dichloromethane (CH_2Cl_2, 30 mL) and washed with 20 mL of brine. The organic phase was concentrated, and the residue was purified by recrystallization with methanol, yielding a brown solid (compound **6b** (R or S), 0.356 g, 50% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 (dd, *J* = 8.9, 7.1 Hz, 4H), 7.18 – 7.08 (m, 4H), 3.98 – 3.83 (m, 10H), 0.82 (td, *J* = 7.0, 0.7 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.12, 154.89, 133.93, 129.74, 129.62, 126.54, 122.39, 113.18, 110.84, 107.56, 70.67, 57.19, 29.79, 22.71, 9.95. **HRMS** (ESI) m/z: [M + H]+ (M isotope peak) Calcd for $C_{26}H_{25}Br_2O_4$ 559.0114; found 559.0109. **HRMS** (ESI) m/z: [M + H]+ (M+2 isotope peak) Calcd for $C_{26}H_{25}Br_2O_4$ 561.0094; found 561.0089. **HRMS** (ESI) m/z: [M + H]+ (M+4 isotope peak) Calcd for $C_{26}H_{25}Br_2O_4$ 563.0073; found 563.0069.

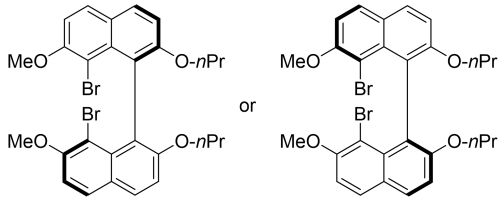
7,7'-dimethoxy-2,2'-dipropoxy-1,1'-binaphthalene, 5c (R or S）



5c*R* 5c*S*

7,7'-dimethoxy-[1,1'-binaphthalene]-2,2'-diol **4** (*R* or *S*) (700mg, 2.02 mmol), K_2CO_3 (1.2 g, 8.08 mmol), and 30 mL of DMF were introduced into a 100 mL round-bottom flask equipped with a stirring bar and a rubber septum. The mixture was cooled to 0°C. The flask was then degassed under vacuum and backfilled with argon three times. Subsequently, 1-iodopropane (1.3 mL, 12.12 mmol) was added dropwise. The reaction mixture was stirred at 70 ℃ overnight. The resulting white solid, 5c, was obtained by chromatography (eluent: hexane: ethyl acetate (10:1)), yielding compound **5c** (*R* or *S*), 0.540 mg, 62% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 (dd, *J* = 9.0, 3.1 Hz, 2H), 7.72 (dd, *J* = 8.8, 3.1 Hz, 2H), 7.25 – 7.20 (m, 2H), 6.96 (dq, *J* = 9.0, 2.4 Hz, 2H), 6.49 (t, *J* = 3.1 Hz, 2H), 3.97 – 3.79 (m, 4H), 3.54 – 3.48 (m, 6H), 1.47 – 1.37 (m, 4H), 0.58 (ddd, *J* = 10.6, 5.3, 2.5 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.91, 155.11, 135.49, 129.38, 128.78, 124.90, 119.69, 113.04, 104.14, 71.04, 55.06, 22.79, 10.24.

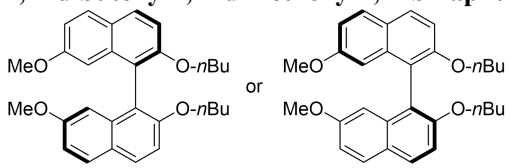
8,8'-dibromo-2,2'- dipropoxy-7,7'-dimethoxy-1,1'-binaphthalene, 6c (*R* or *S*)



6c*R* **6c*S***

5c (*R* or *S*) (860.5 mg, 2 mmol), N-bromosuccinimide (NBS, 1.424 g, 8 mmol), and chloroform ($CHCl_3$, 30 mL) were added to a 50 mL Schlenk flask. The flask was degassed under vacuum and backfilled with argon three times. Subsequently, pyridine (0.7 mL, 8 mmol) was added. The mixture was stirred at 40 ◦C for 2 days. The reaction was then quenched by adding 10 mL of 1M hydrochloric acid (HCl). The reaction mixture was diluted with dichloromethane and washed with brine. The organic phase was concentrated, and the residue was obtained by chromatography (eluent: hexane: ethyl acetate (10:1)), yielding a brown solid (compound **6c** (*R* or *S*), 506 mg, 43% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.71 (m, 4H), 7.12 (dt, *J* = 11.6, 7.3 Hz, 4H), 3.94 – 3.89 (m, 6H), 3.78 (dt, *J* = 11.1, 4.9 Hz, 4H), 0.84 (d, *J* = 6.7 Hz, 4H), 0.34 (td, *J* = 7.2, 1.4 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.13, 154.90, 133.94, 130.45, 129.76, 129.64, 126.55, 122.38, 113.17, 110.84, 107.54, 105.05, 70.67, 57.18, 29.81, 22.72, 10.17, 9.98. **HRMS** (ESI) m/z: [M + H]+ (M isotope peak) Calcd for $C_{28}H_{29}Br_2O_4$ 587.0427; found 587.0425. **HRMS** (ESI) m/z: [M + H]+ (M+2 isotope peak) Calcd for $C_{28}H_{29}Br_2O_4$ 589.0407; found 589.0404. **HRMS** (ESI) m/z: [M + H]+ (M+4 isotope peak) Calcd for $C_{28}H_{29}Br_2O_4$ 591.0386; found 591.0384.

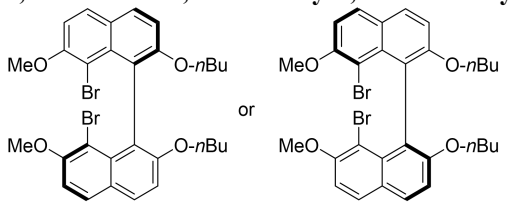
2,2'-dibutoxy-7,7'-dimethoxy-1,1'-binaphthalene, 5d (*R* or *S*)



5d***R*** 5d***S***

7,7'-dimethoxy-[1,1'-binaphthalene] -2,2'-diol **4** (*R* or *S*) (700 mg, 2.02 mmol), K_2CO_3 (1.4 g, 10.1 mmol), and 30 mL of DMF were introduced into a 100 mL round-bottom flask equipped with a stirring bar and a rubber septum. The mixture was cooled to 0 ◦C. The flask was then degassed under vacuum and backfilled with argon three times. Subsequently, bromobutane (1.4 ml, 12.12 mmol) was added dropwise. The reaction mixture was stirred at 95 ℃ overnight. The resulting brown solid, **5d** (*R* or *S*) was obtained by chromatography (eluent: hexane: ethyl acetate (10:1)), yielding 556 mg (60% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ7.82(d, J = 8.9Hz, 2H), 7.73(d, J = 8.9Hz, 2H), 7.24(d, J = 8.9Hz, 2H), 6.98(dd, J = 8.9, 2.5Hz, 2H), 6.50(d, J = 2.5Hz, 2H), 3.94(ddt, J = 27.9, 9.4, 6.5Hz, 4H), 1.41(ddt, J = 13.4, 10.7, 6.6Hz, 4H), 1.11–0.93(m, 4H), 0.66(t, J = 7.4Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.90, 155.15, 135.50, 129.38, 128.77, 124.90, 119.75, 115.88, 113.10, 104.11, 69.21, 55.05, 34.76, 31.70, 31.49, 25.37, 22.76, 18.83, 14.24, 13.68.

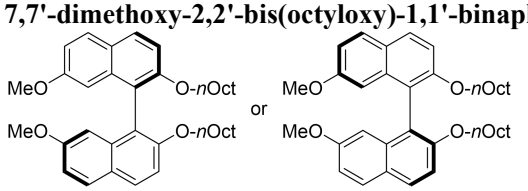
8,8'-dibromo-2,2'-dibutoxy-7,7'-dimethoxy-1,1'-binaphthalene, 6d (*R* or *S*)



6d***R*** 6d***S***

5d (*R* or *S*), (1.2 g, 2.62 mmol), N-bromosuccinimide (NBS, 1.869 g, 10.5 mmol), and chloroform ($CHCl_3$, 30 mL) were added to a 50 mL Schlenk flask. The flask was degassed under vacuum and backfilled with argon three times. Subsequently, pyridine (0.7 mL, 7.86 mmol) was added. The mixture was stirred at 40 ◦C for 2 days. The reaction was then quenched by adding 10 mL of 1M hydrochloric acid (HCl). The reaction mixture was diluted with dichloromethane and washed with brine. The organic phase was concentrated, and the residue was obtained by chromatography (eluent: hexane: ethyl acetate (10:1)) yielding a brown solid (compound **6d** (R or S), 872 mg, 54% yield) **NMR** (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.9 Hz, 2H), 7.73 (dd, *J* = 8.9, 1.1 Hz, 2H), 7.23 (dd, *J* = 9.0, 1.2 Hz, 2H), 6.96 (ddd, *J* = 8.9, 2.6, 1.2 Hz, 2H), 6.47 (d, *J* = 2.4 Hz, 2H), 4.01 – 3.83 (m, 4H), 3.50 (d, *J* = 1.2 Hz, 6H), 1.47 – 1.29 (m, 4H), 1.07 – 0.89 (m, 4H), 0.64 (td, *J* = 7.4, 1.2 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.90, 155.15, 135.50, 129.38, 128.77, 124.90, 119.75, 115.88, 113.10, 104.11, 69.21, 55.05, 34.76, 31.70, 31.49, 25.37, 22.76, 18.83, 14.24, 13.68. **HRMS** (ESI) m/z: [M + H]+ (M isotope peak) Calcd for $C_{30}H_{33}Br_2O_4$ 615.0740; found 615.0745. **HRMS** (ESI) m/z: [M + H]+ (M+2 isotope peak) Calcd for $C_{30}H_{33}Br_2O_4$ 617.0720; found 617.0726. **HRMS** (ESI) m/z: [M + H]+ (M+4 isotope peak) Calcd for $C_{30}H_{33}Br_2O_4$ 619.0699; found 619.0706.

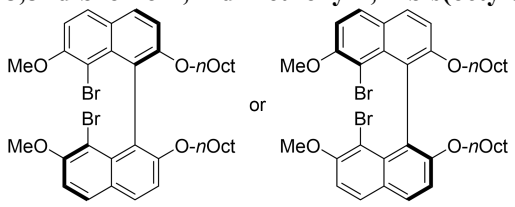
7,7'-dimethoxy-2,2'-bis(octyloxy)-1,1'-binaphthalene, 5e (*R* or *S*)



5e*R* 5e*S*

7,7'-dimethoxy-[1,1'-binaphthalene] -2,2'-diol **4** (*R* or *S*) (2.0 g, 5.8 mmol), K_2CO_3 (4.0 g, 29.0 mmol), and 30 mL of DMF were introduced into a 100 mL round-bottom flask equipped with a stirring bar and a rubber septum. The mixture was cooled to 0 ◦C. The flask was then degassed under vacuum and backfilled with argon three times. Subsequently, Bromo octane (6.0 ml, 34.7 mmol) was added dropwise. The reaction mixture was stirred at 95 ℃ for 16h. The residue was obtained by chromatography (eluent: hexane: ethyl acetate (10:1), yielding **5e** (*R* or *S*), 1.6 g (60% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.9 Hz, 2H), 7.72 (d, *J* = 8.9 Hz, 2H), 7.22 (d, *J* = 8.9 Hz, 2H), 6.95 (dd, *J* = 8.9, 2.5 Hz, 2H), 6.47 (d, *J* = 2.5 Hz, 2H), 3.97 – 3.84 (m, 4H), 3.50 (s, 6H), 1.38 (dq, *J* = 13.0, 6.7 Hz, 4H), 1.21 (dd, *J* = 14.3, 7.2 Hz, 5H), 1.04 (d, *J* = 34.7 Hz, 12H), 0.84 (t, *J* = 7.3 Hz, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 129.36, 128.76, 113.15, 104.13, 69.63, 55.04, 31.79, 29.50, 29.24, 25.75, 22.74, 14.19.

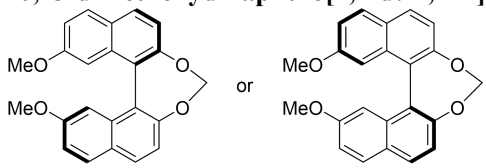
8,8'-dibromo-7,7'-dimethoxy-2,2'-bis(octyloxy)-1,1'-binaphthalene, 6e (*R* or *S*)



6e*R* 6e*S*

5e (*R* or *S*) (2.185 g, 3 mmol), N-bromosuccinimide (NBS, 2.135 g, 12 mmol), and chloroform ($CHCl_3$, 30 mL) were added to a 50 mL Schlenk flask. The flask was degassed under vacuum and backfilled with argon three times. Subsequently, pyridine (0.75 mL, 9 mmol) was added. The mixture was stirred at 40 ◦C or 2 days. The reaction was then quenched by adding 10 mL of 1M hydrochloric acid (HCl). The reaction mixture was diluted with dichloromethane and washed with brine. The organic phase was concentrated, and the residue was obtained by chromatography (eluent: hexane: ethyl acetate (10:1)), compound **6e** (R or S), 1.4 g, 64% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 8.9, 5.5 Hz, 4H), 7.10 (dd, *J* = 11.0, 8.9 Hz, 4H), 3.92 (s, 6H), 3.84 – 3.76 (m, 4H), 1.20 (dddd, *J* = 15.6, 14.0, 7.8, 5.6 Hz, 12H), 1.08 (dt, *J* = 9.3, 7.0 Hz, 4H), 0.97 (ddd, *J* = 9.1, 6.2, 2.6 Hz, 4H), 0.90 – 0.83 (m, 10H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.16, 154.84, 133.93, 129.73, 129.60, 126.54, 122.43, 113.17, 110.73, 107.53, 69.14, 57.10, 31.86, 29.46, 29.25, 29.18, 25.51, 22.77, 14.21. **HRMS** (ESI) m/z: [M + H]+ (M isotope peak) Calcd for $C_{38}H_{49}Br_2O_4$ 727.1992; found 727.1985. **HRMS** (ESI) m/z: [M + H]+ (M+2 isotope peak) Calcd for $C_{38}H_{49}Br_2O_4$ 729.1972; found 729.1969. **HRMS** (ESI) m/z: [M + H]+ (M+4 isotope peak) Calcd for $C_{38}H_{49}Br_2O_4$ 731.1951; found 731.1951.

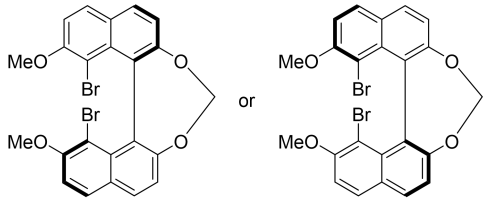
10,13-dimethoxydinaphtho[2,1-d:1',2'-f] [1,3]dioxepine, 5f (*R* or *S*)



5f*R* 5f*S*

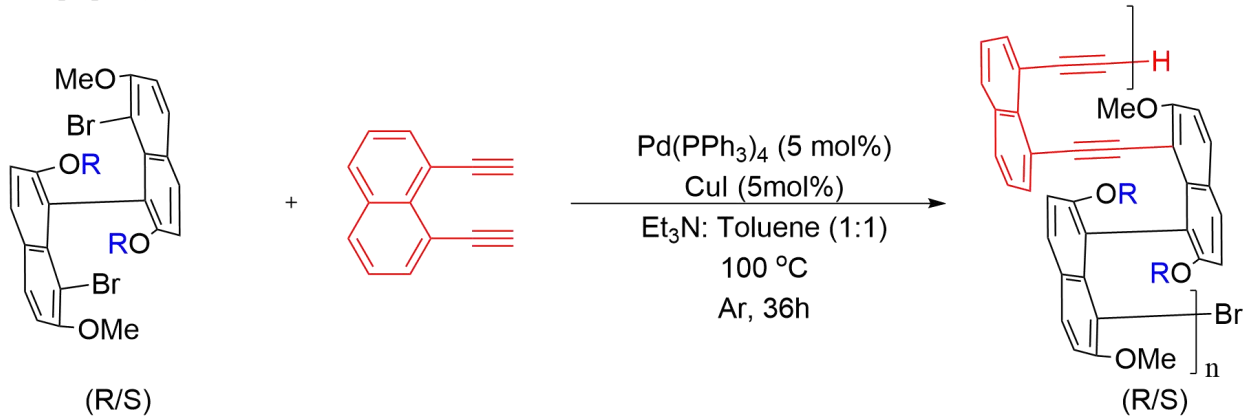
7,7'-dimethoxy-[1,1'-binaphthalene] -2,2'-diol **4** (*R* or *S*) (700 mg, 2.02 mmol) (4), K_2CO_3 (1.68 g, 12.12 mmol), and 10 mL of DMF were introduced into a 50 mL round-bottom flask equipped with a stirring bar and a rubber septum. The mixture was cooled to 0 ◦C. The flask was then degassed under vacuum and backfilled with argon three times. Subsequently, diiodomethane (0.5 ml, 6.06 mmol) was added dropwise. The reaction mixture was stirred at 80 ℃ overnight. The residue was obtained by chromatography (eluent: hexane: ethyl acetate (10:1), yielding a brown solid **5f** (*R* or *S*), 528 mg, 73% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 – 7.86 (m, 2H), 7.81 (d, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.10 (dd, *J* = 9.0, 2.5 Hz, 2H), 6.80 (d, *J* = 2.5 Hz, 2H), 5.68 (s, 2H), 3.45 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.79, 152.03, 132.98, 130.08, 127.38, 125.27, 118.58, 118.00, 105.74, 103.20, 76.85, 55.19.

11,12-dibromo-10,13-dimethoxydinaphtho[2,1-d:1',2'-f] [1,3]dioxepine, 6f (*R* or *S*)

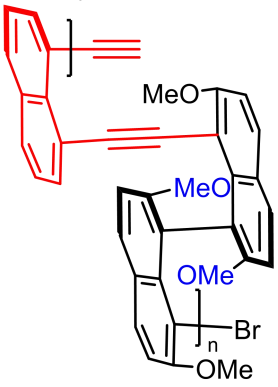


6e*R* **6e*S***

5f (*R* or *S*), (1.05 g, 2.95 mmol), N-bromosuccinimide (NBS, 2.136 mg, 12 mmol), and chloroform ($CHCl_3$, 30 mL) were added to a 50 mL Schlenk flask. The flask was degassed under vacuum and backfilled with argon three times. Subsequently, pyridine (0.75 mL, 9 mmol) was added. The mixture was stirred at 40 ◦C under an argon atmosphere overnight. The reaction was then quenched by adding 10 mL of 1M hydrochloric acid (HCl). The reaction mixture was diluted with dichloromethane and washed with brine. The organic phase was concentrated, and the residue was obtained by chromatography (eluent: hexane: ethyl acetate (10:1)), yielding a brown solid **6f** (R or S),, 1 g, 66% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 – 7.82 (m, 4H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.9 Hz, 2H), 5.64 (s, 2H), 3.86 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.26, 151.37, 134.76, 130.81, 129.92, 129.01, 126.36, 118.80, 112.15, 105.42, 101.38, 56.97. **HRMS** (ESI) m/z: [M + H]+ (M isotope peak) Calcd for $C_{23}H_{17}Br_2O_4$ 514.9488; found 514.9487. **HRMS** (ESI) m/z: [M + H]+ (M+2 isotope peak) Calcd for $C_{23}H_{17}Br_2O_4$ 516.9468; found 516.9466. **HRMS** (ESI) m/z: [M + H]+ (M+4 isotope peak) Calcd for $C_{23}H_{17}Br_2O_4$ 518.9447; found 518.9445.

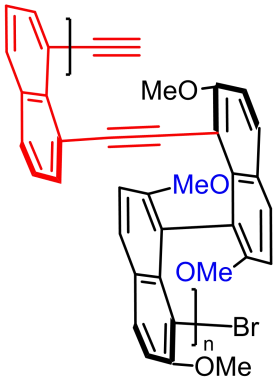


2.3 Synthetic Procedures of Polymers



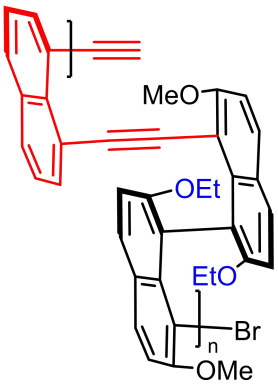
(**1A***R*)

6a (*R* or *S*), (212.892 mg, 0.40 mmol) and 1,8-diethynylnaphthalene (70.488 mg, 0.4 mmol) were placed in a Schlenk flask equipped with a magnetic stir bar. The flask was evacuated and backfilled with argon three times. Degassed toluene (3 mL) and Et_3N (3 mL) were added via syringe under argon to afford a heterogeneous suspension. $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol, 5 mol%) and CuI (3.89 mg, 0.02 mmol, 5 mol%) were added under a gentle argon flow, and the mixture was stirred at 100 °C for 36 h under argon. After cooling to room temperature, the mixture was diluted with $CHCl_3$ (30 mL) and filtered. The filtrate was washed with H_2O and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give a viscous crude polymer. The residue was dissolved in $CHCl_3$ (2 mL) and added dropwise to vigorously stirred MeOH (≈10-fold volume excess relative to the $CHCl_3$ solution). The suspension was stirred for 0.5–1 h and then left to stand at room temperature until precipitation was complete. The solid was collected by suction filtration, washed thoroughly with MeOH, and dried in an oven at 50 °C overnight to afford polymer **1A** (*R* or *S*) as a brown solid (53 mg, 19% yield) M_n= 5606, M_w= 7730, PDI= 1.379. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 6.73 (m, Ar-H), 4.29 – 3.58 (m, OMe-H).



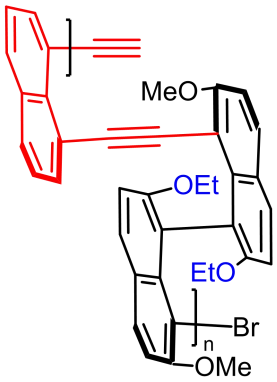
(**1A***S*)

The same synthesis procedure as Polymer **1A***R*, **1A***S* was obtained as brown solid (100 mg, yield: 35%) M_n= 5841, M_w= 7921, PDI= 1.356. ^{1}H NMR (400 MHz, Chloroform-*d*) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 – 6.85 (m, Ar-H), 4.22 – 3.49 (m, OMe-H).



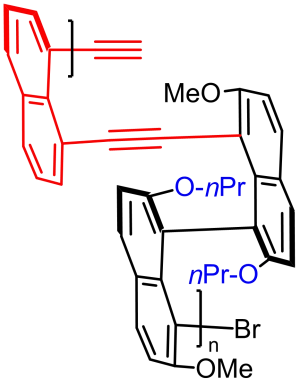
(**2A***R*)

The same synthesis procedure as Polymer **1A***R*, **2A***R* was obtained as brown solid (72.32 mg, yield: 25%) M_n= 5192, M_w= 7378, PDI= 1.421. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.37 (m, Ar-H), 7.17 – 7.07 (m, Ar-H), 4.21 – 3.70 (m, OMe-H & OCH_2-H), 0.81 (t, *J* = 7.0 Hz, CH_3-H).



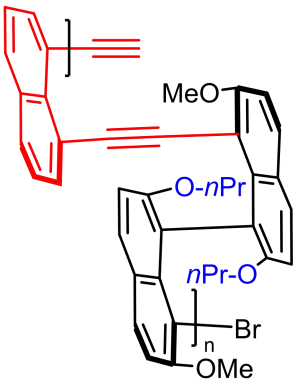
(**2A***S*)

The same synthesis procedure as Polymer **1A***R*, **2A***S* was obtained as brown solid (73.12 mg, yield: 25%) M_n= 6255, M_w= 9053, PDI= 1.447. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.34 (m, Ar-H), 7.12 (dd, *J* = 11.7, 8.9 Hz, Ar-H), 4.13 – 3.72 (m, OMe-H & OCH_2-H), 0.81 (t, *J* = 6.9 Hz, CH_3-H).



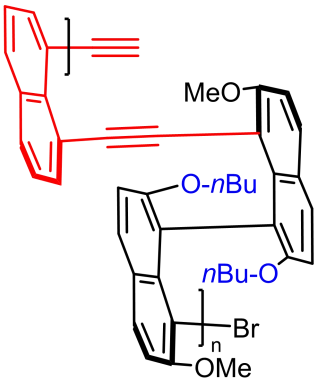
(**3A***R*)

The same synthesis procedure as Polymer **1A***R*, **3A***R* was obtained as brown solid (68 mg, yield: 22%) M_n= 5511, M_w= 7240, PDI= 1.314. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 – 7.39 (m, Ar-H), 7.11 (dd, J = 11.7, 8.9 Hz, Ar-H), 3.91 (s, OMe-H), 3.84 – 3.67 (m, OCH_2-H), 1.40 (t, J = 7.3 Hz, CH_3-H), 1.22 (qt, J = 7.3, 6.2 Hz, CH_2-H).



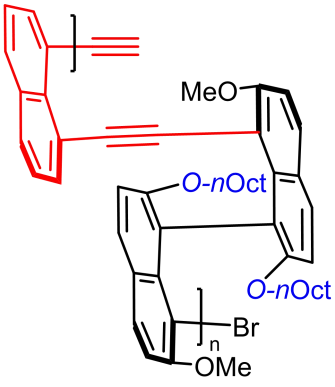
(**3A***S*)

The same synthesis procedure as Polymer **1A***R*, **3A***S* was obtained as brown solid (63 mg, yield: 21%) M_n= 5457, M_w= 7567, PDI= 1.387. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.40 (m, Ar-H), 7.11 (dd, *J* = 11.8, 8.9 Hz, Ar-H), 3.91 (s, OMe-H), 3.84 – 3.66 (m, OCH_2-H), 1.40 (t, *J* = 7.3 Hz, CH_3-H), 1.22 (qt, *J* = 7.3, 6.2 Hz, CH_2-H).



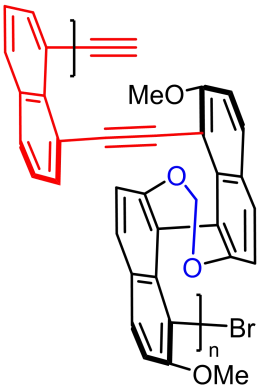
(**4A***S*)

The same synthesis procedure as Polymer **1A***R*, **4A***S* was obtained as brown solid (56.46 mg, yield: 18%) M_n= 5986, M_w= 9462, PDI= 1.581. 1H NMR (400 MHz, Chloroform-d) δ 7.88 – 7.40 (m, Ar-H), 7.11 (t, J = 9.2 Hz, Ar-H), 3.92 (s, OMe-H), 3.80 (tt, J = 6.2, 2.9 Hz, OCH_2-H), 1.26 – 1.03 (m, CH_2-H), 0.74 – 0.65 (m, CH_2-H), 0.65 – 0.43 (m, CH_3-H).



(**5A***S*)

The same synthesis procedure as Polymer **1A***R*, **5A***S* was obtained as brown solid (51.32 mg, yield: 14%) M_n= 4135, M_w= 5939, PDI= 1.436. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.89 – 7.40 (m, Ar-H), 7.10 (dd, J = 10.8, 8.9 Hz, Ar-H), 3.91 (s, OMe-H), 3.84 – 3.68 (m, OCH_2-H), 1.48 – 0.78 (m, C_8H_{17}-H).



(**6A***S*)

The same synthesis procedure as Polymer **1A***R*, **6A***S* was obtained as brown solid (75 mg, yield: 27%) M_n= 4912, M_w= 6667, PDI= 1.357. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.04 (m, Ar-H), 5.64 (s, Bridged-H), 3.86 (s, OMe-H).

3.NMR Spectra

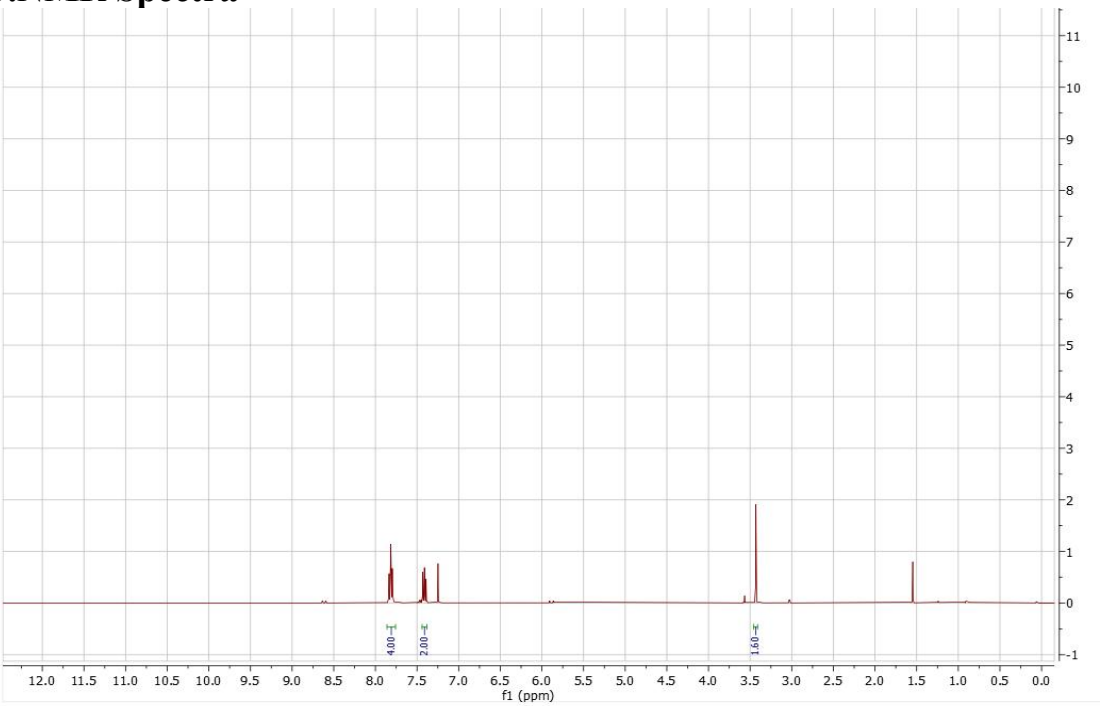


Figure 1. ^{1}H of 1,8 bis (trimethylsilyl ethynyl) naphthalene.

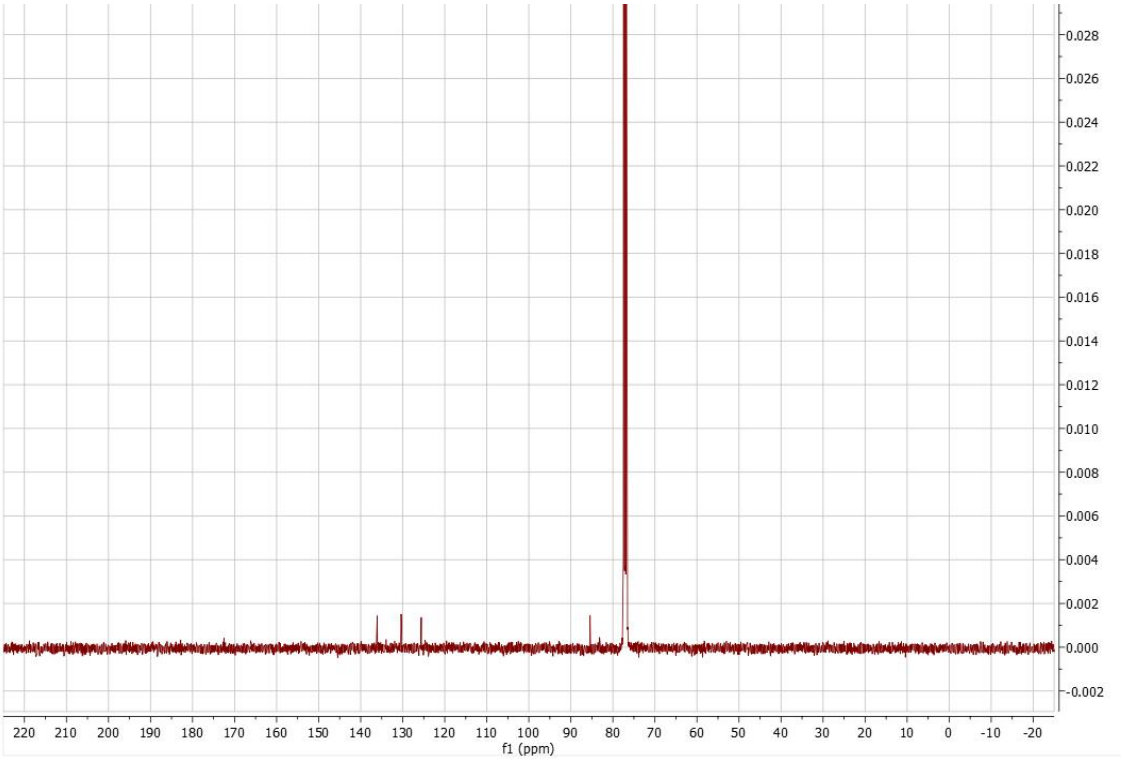


Figure 2. ^{13}C of 1,8 bis (trimethylsilyl ethynyl) naphthalene.

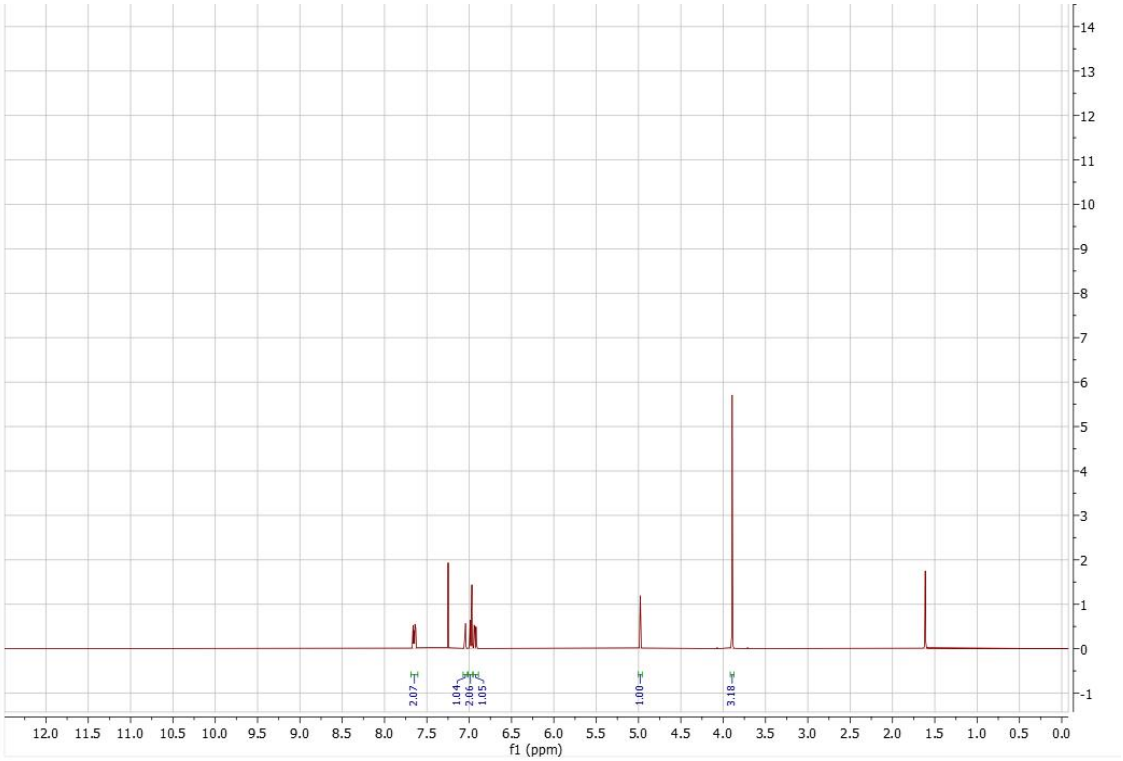


Figure 3. ^{1}H of 7-methoxynaphthalen-2-ol (1).

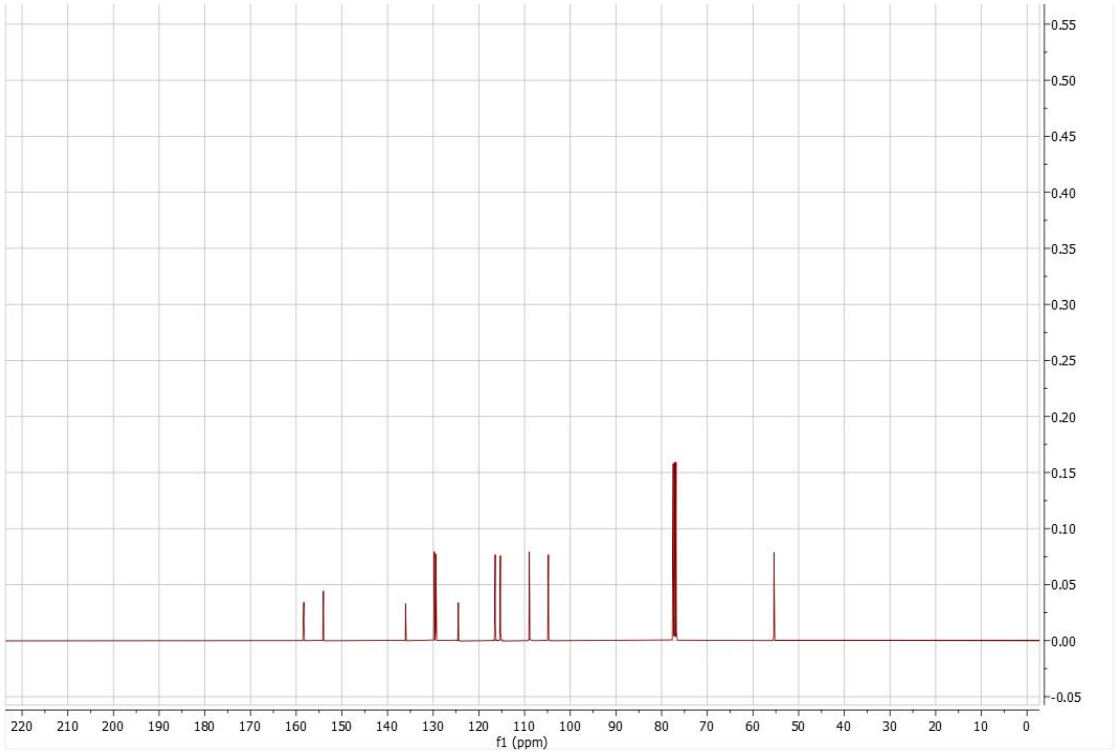


Figure 4. ^{13}C of 7-methoxynaphthalen-2-ol (1).

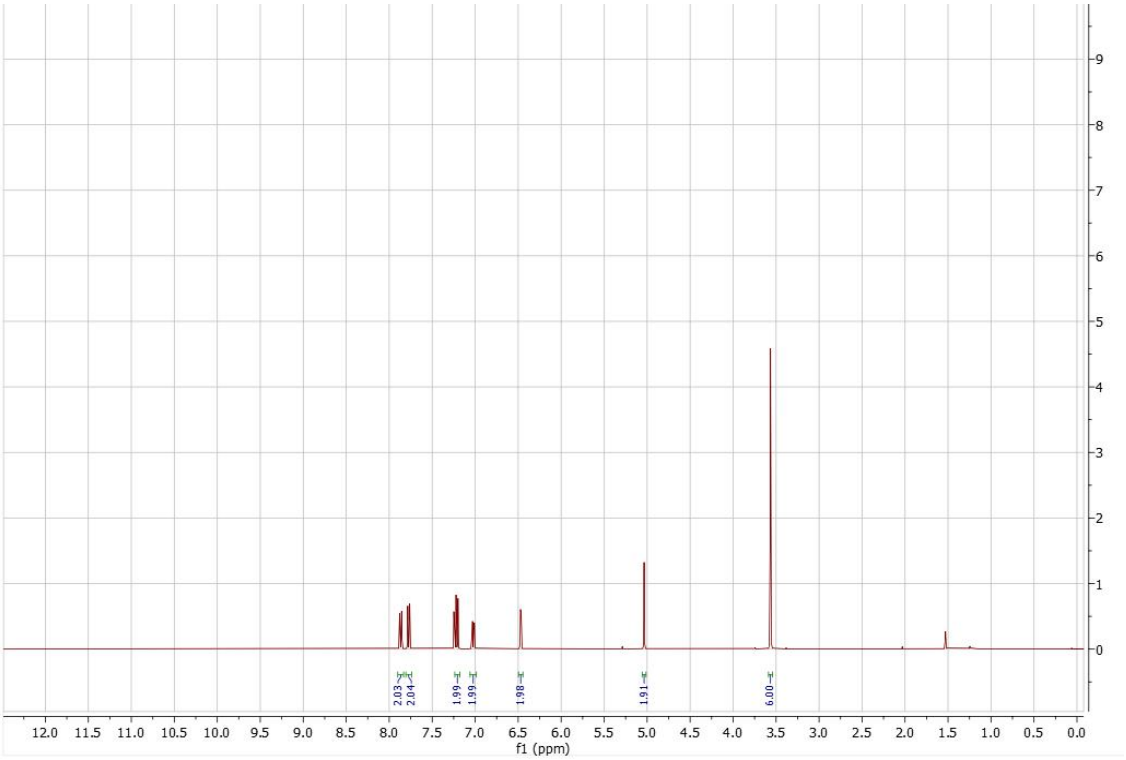


Figure 5. ^{1}H of 7,7'-dimethoxy-[1,1'-binaphthalene]-2,2'-diol (2).

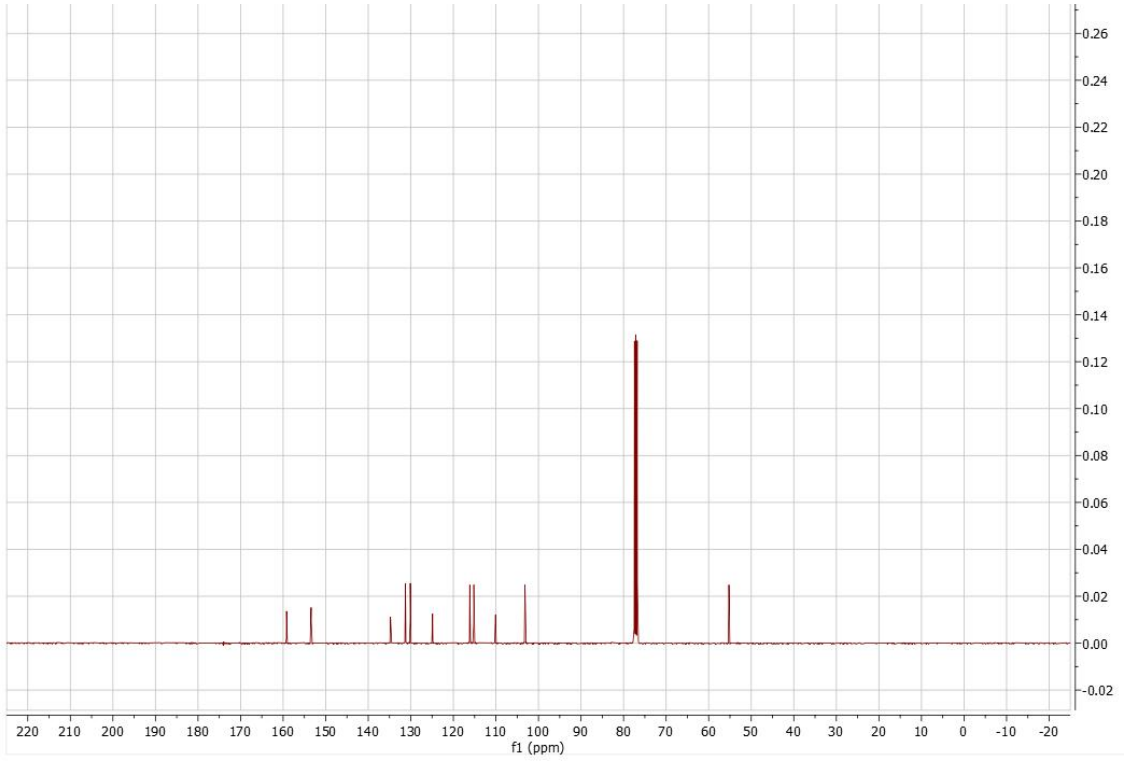


Figure 6. ^{13}C of 7,7'-dimethoxy-[1,1'-binaphthalene]-2,2'-diol (2).

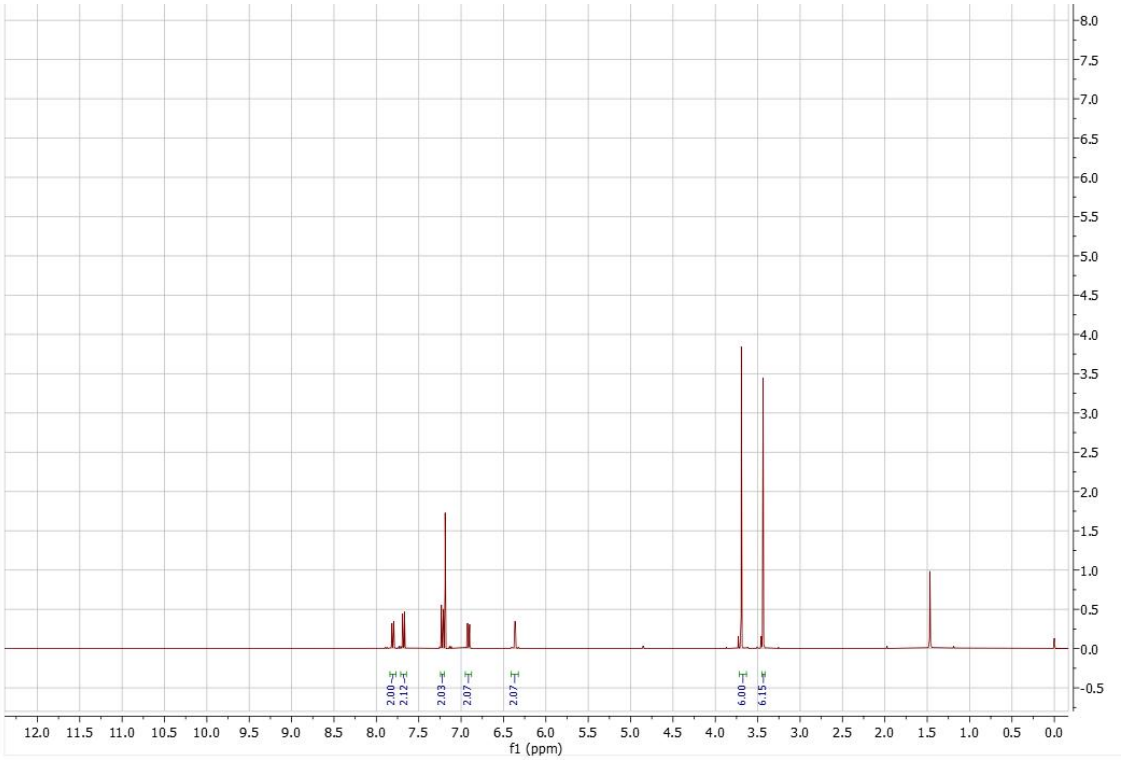


Figure 7. ^{1}H of 2,2',7,7'-tetramethoxy-1,1'-binaphthalene, 5a (R or S).

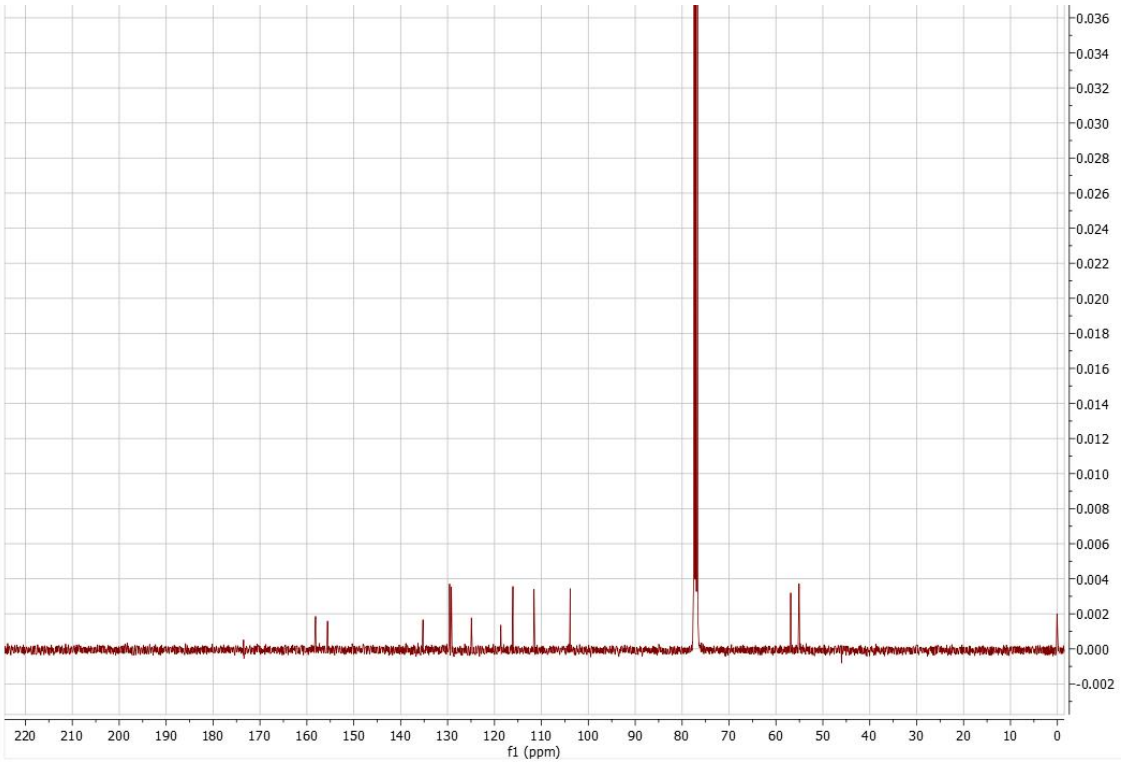


Figure 8. ^{13}C of 2,2',7,7'-tetramethoxy-1,1'-binaphthalene, 5a (R or S).

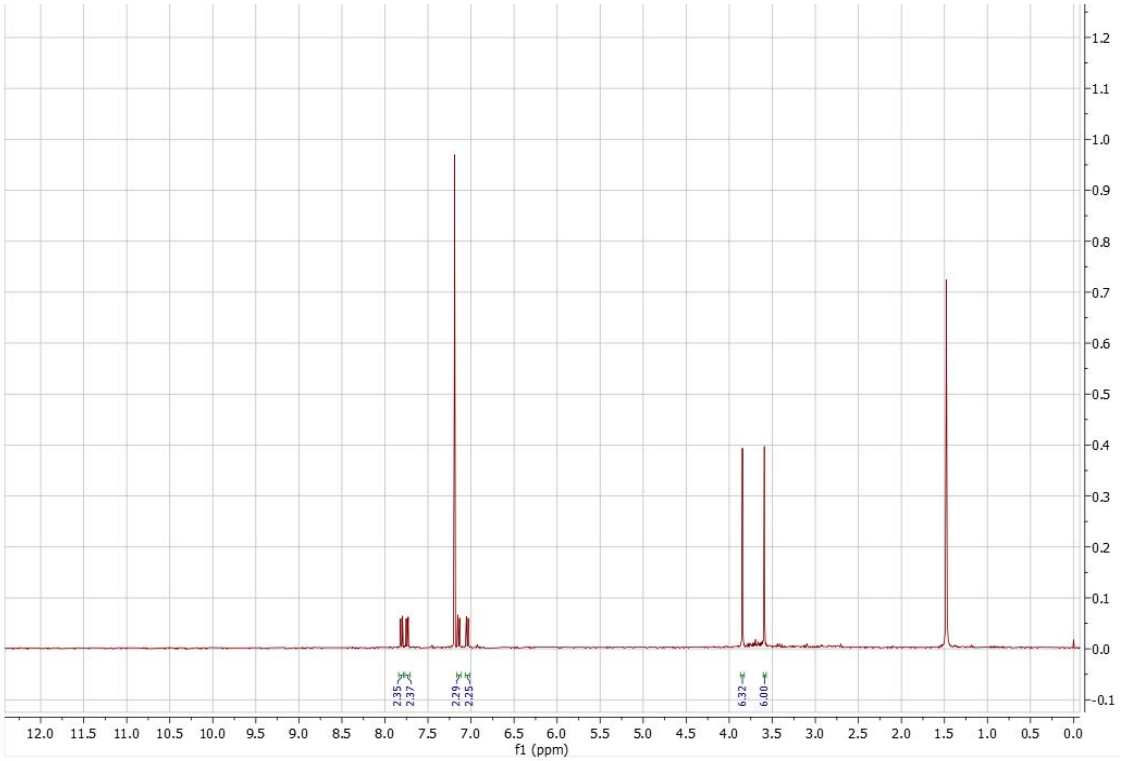


Figure 9. ^{1}H of 8,8'-dibromo-2,2',7,7'-tetramethoxy-1,1'-binaphthalene, 6a.

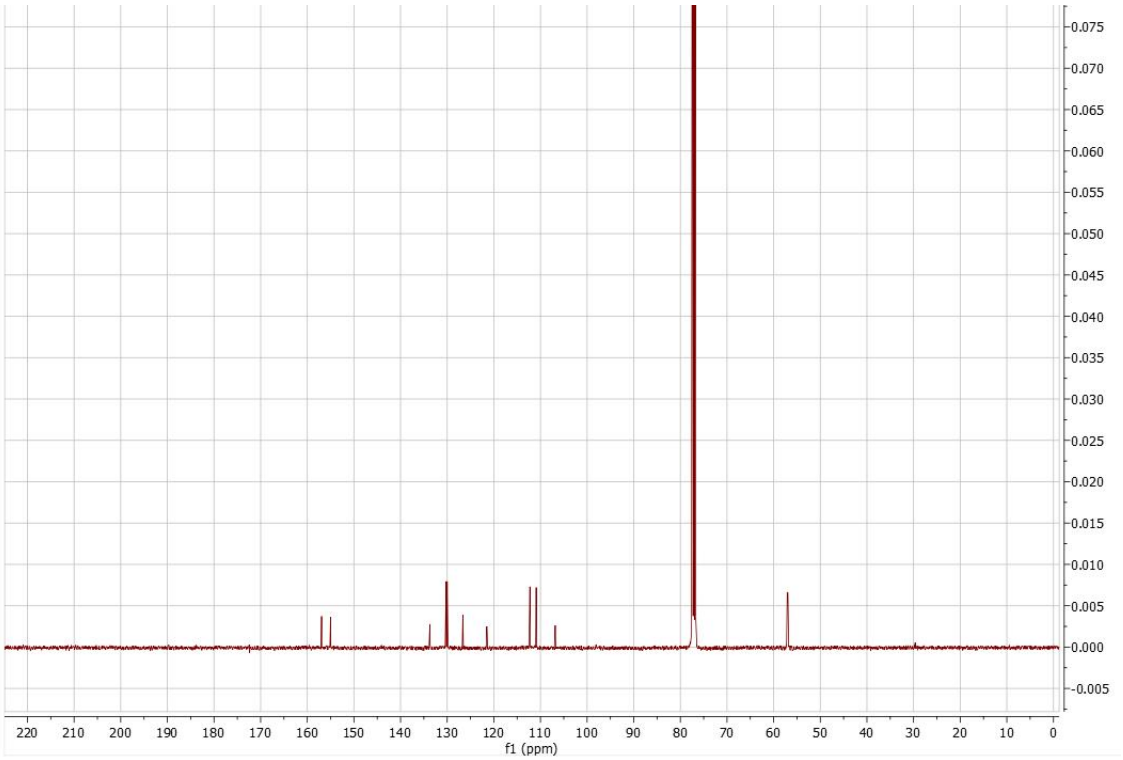


Figure 10. ^{13}C of 8,8'-dibromo-2,2',7,7'-tetramethoxy-1,1'-binaphthalene, 6a.

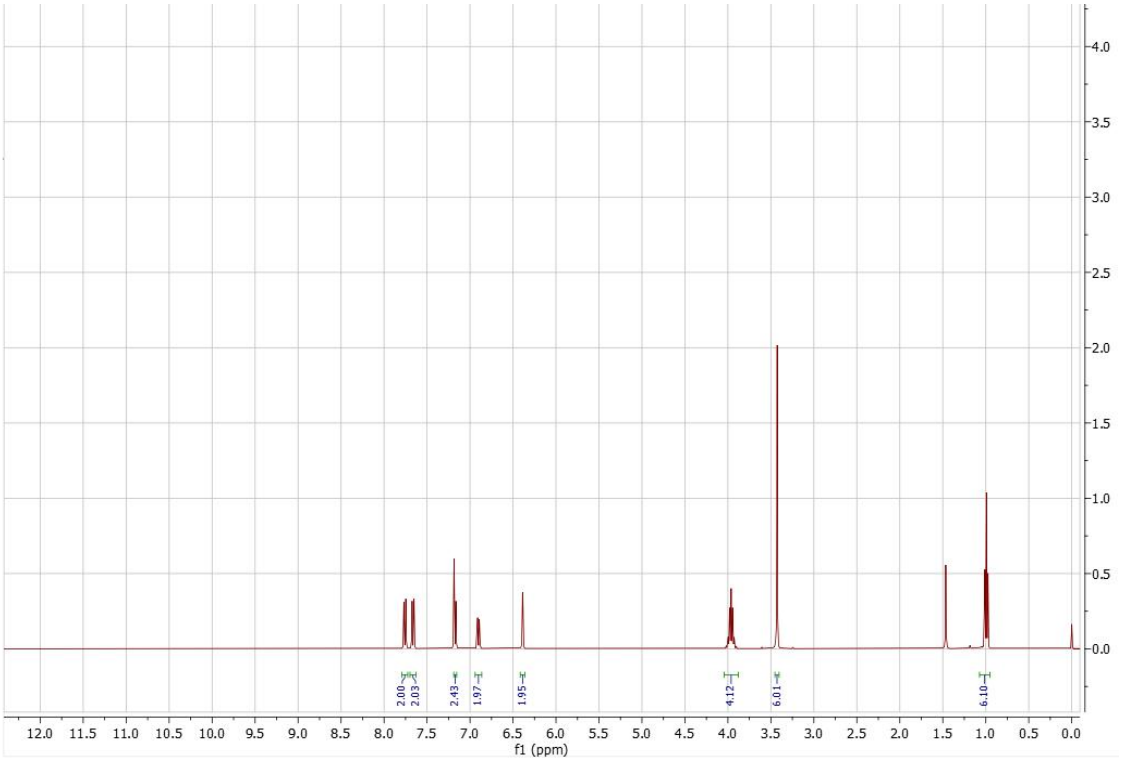


Figure 11. ^{1}H of 2,2'-diethoxy-7,7'-dimethoxy-1,1'-binaphthalene, 5b.

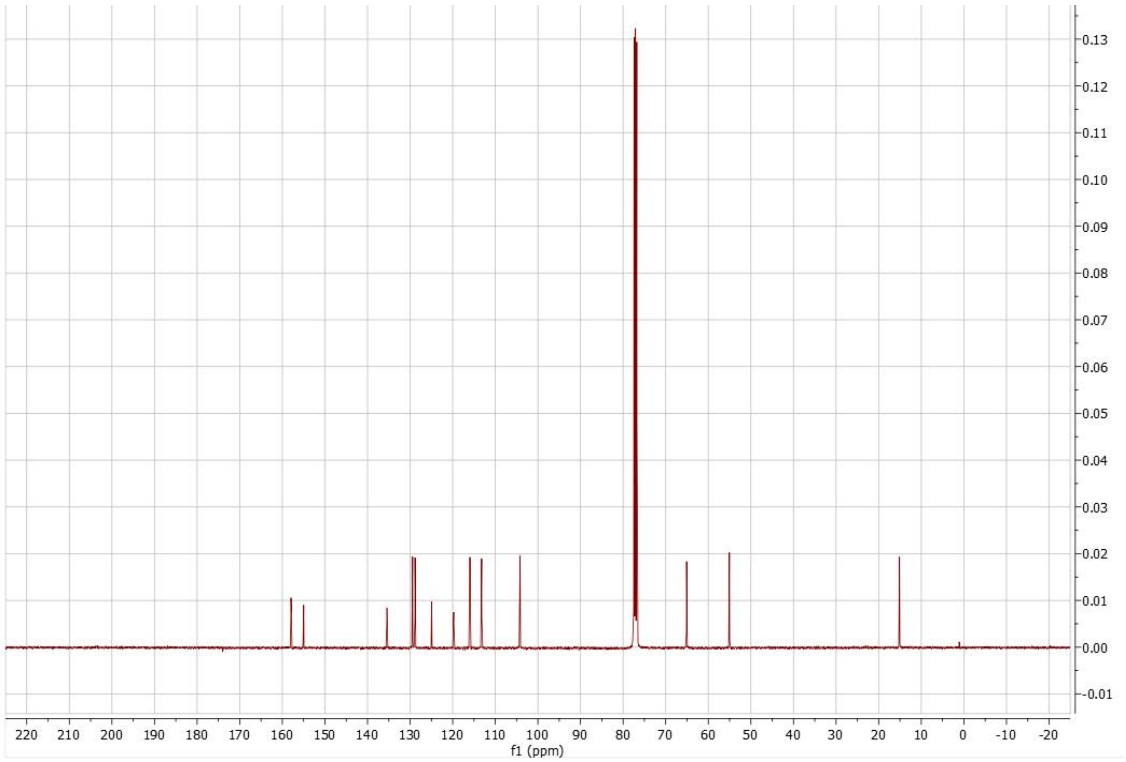


Figure 12. ^{13}C of 2,2'-diethoxy-7,7'-dimethoxy-1,1'-binaphthalene, 5b.

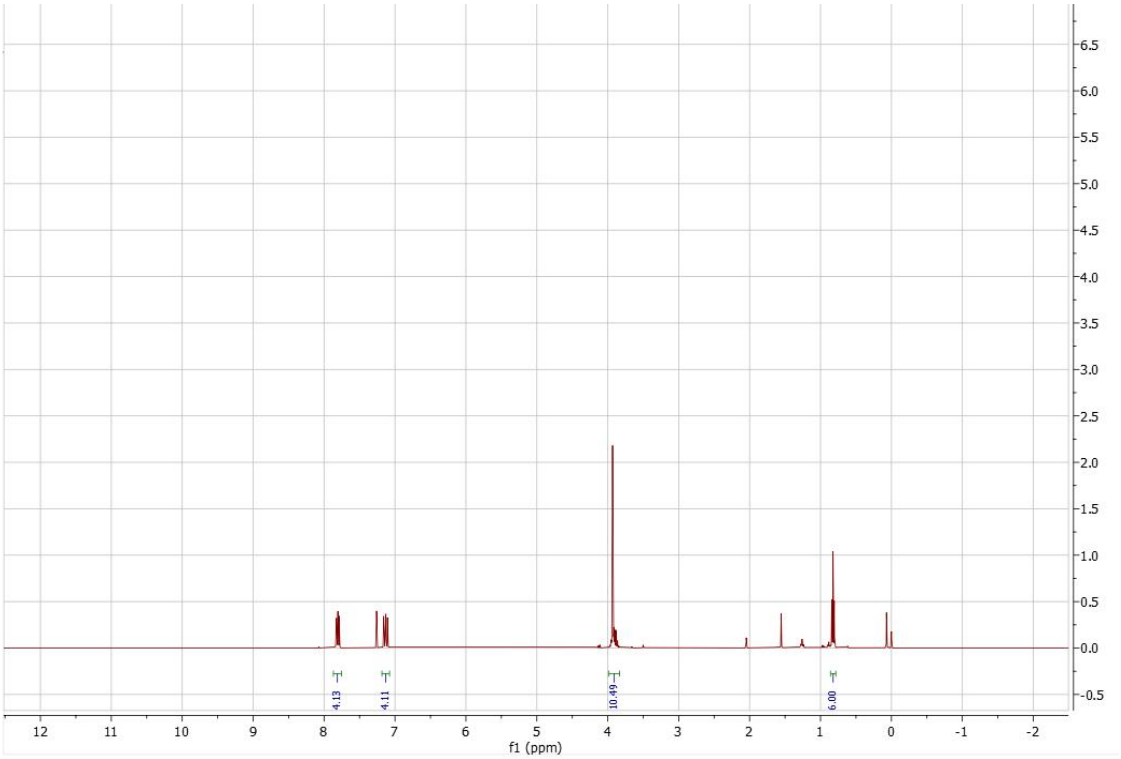


Figure 13. ^{1}H of 8,8'-dibromo-2,2'-diethoxy-7,7'-dimethoxy-1,1'-binaphthalene, 6b.

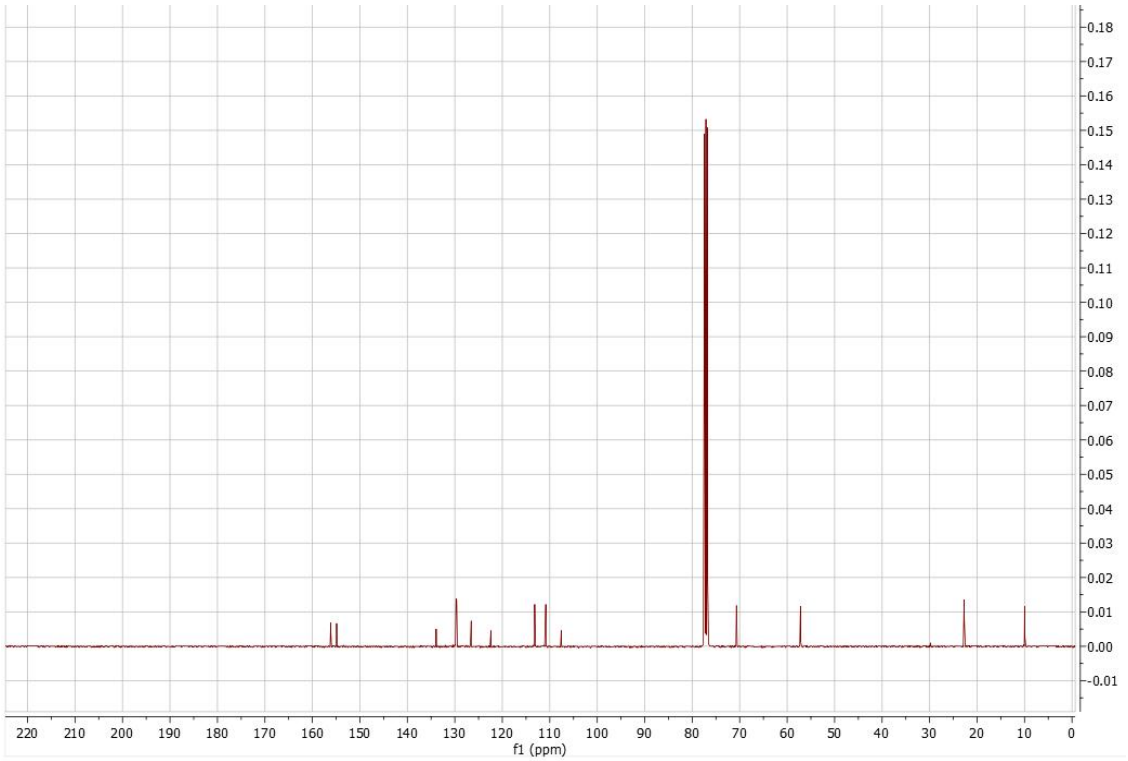


Figure 14. ^{13}C of 8,8'-dibromo-2,2'-diethoxy-7,7'-dimethoxy-1,1'-binaphthalene, 6b.

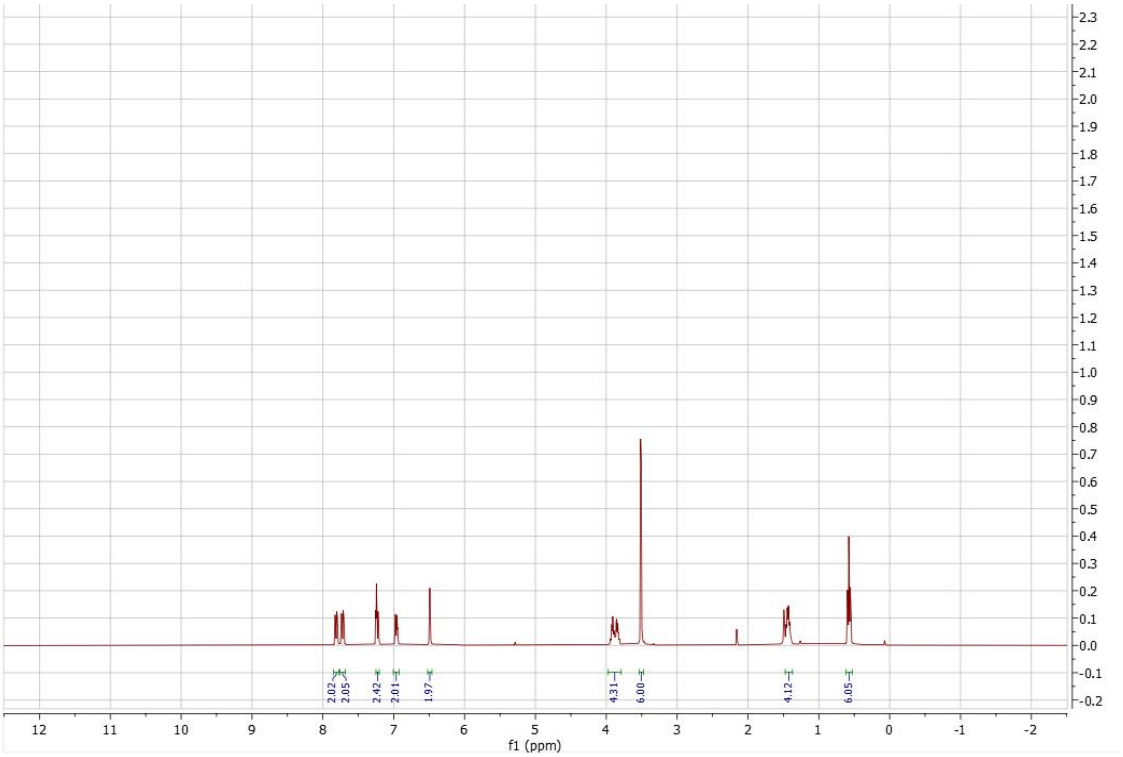


Figure 15. ^{1}H of 7,7'-dimethoxy-2,2'-dipropoxy-1,1'-binaphthalene, 5c.

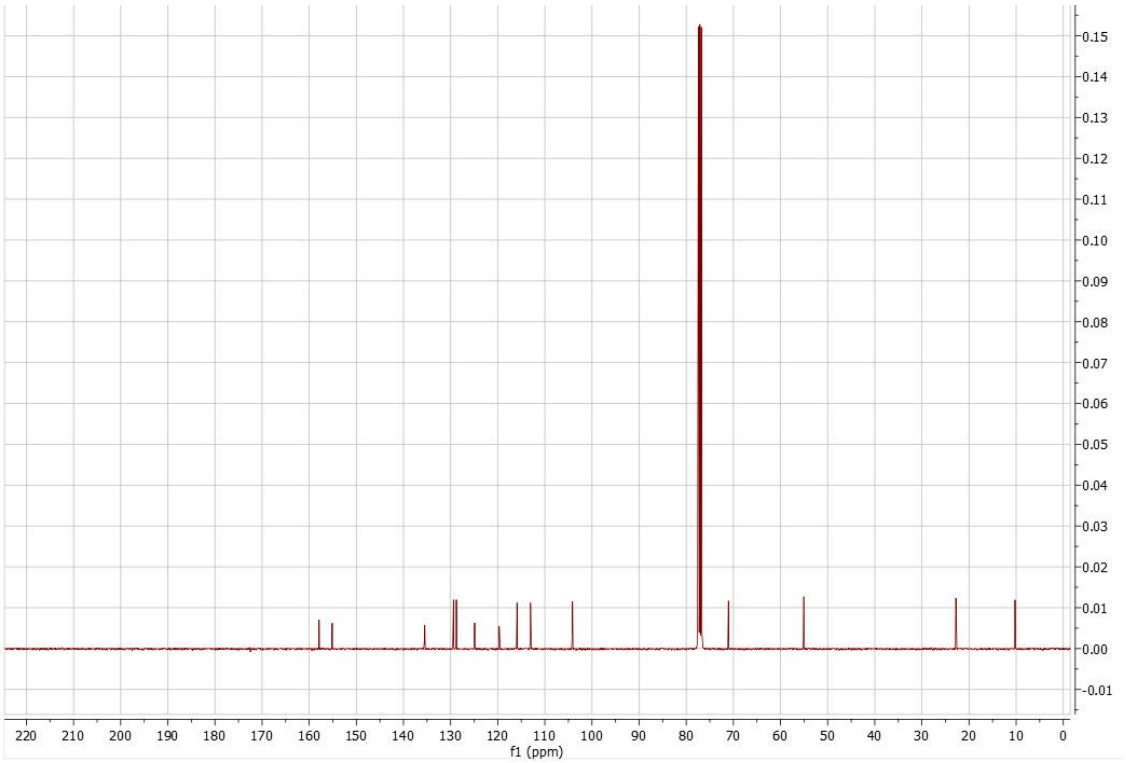


Figure 16. ^{13}C of 7,7'-dimethoxy-2,2'-dipropoxy-1,1'-binaphthalene, 5c.

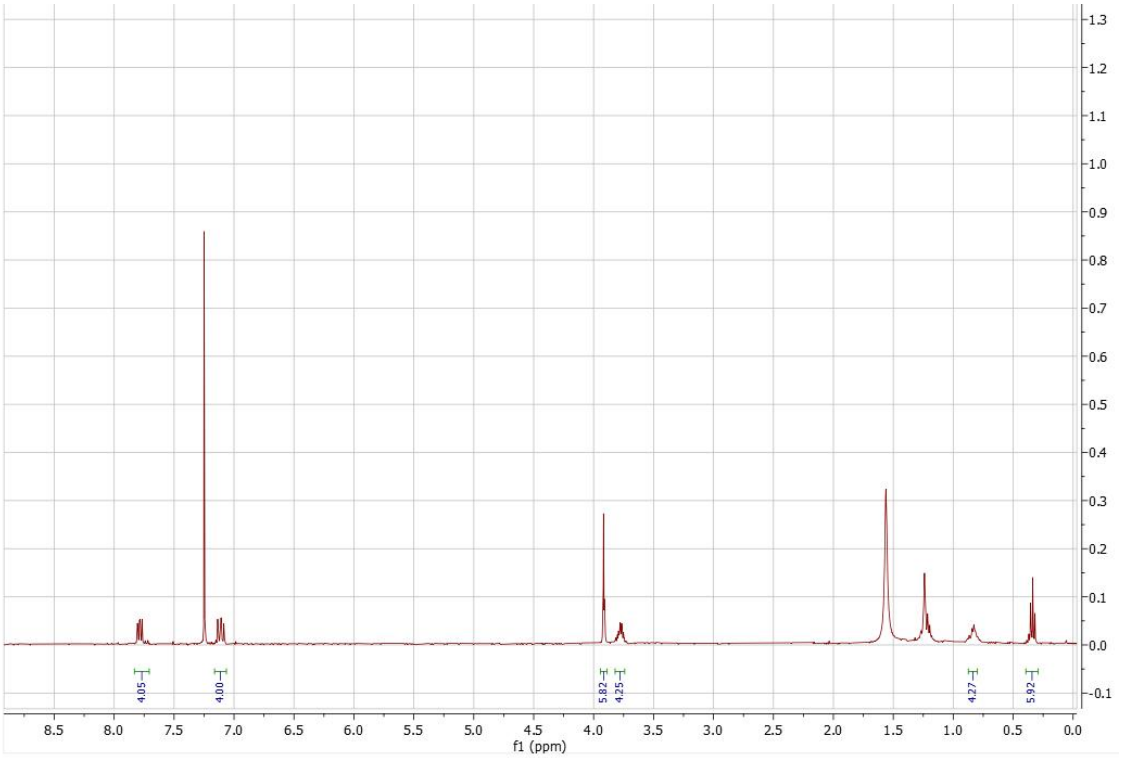


Figure 17. ^{1}H of 8,8'-dibromo-7,7'-dimethoxy-2,2'-dipropoxy-1,1'-binaphthalene, 6c.

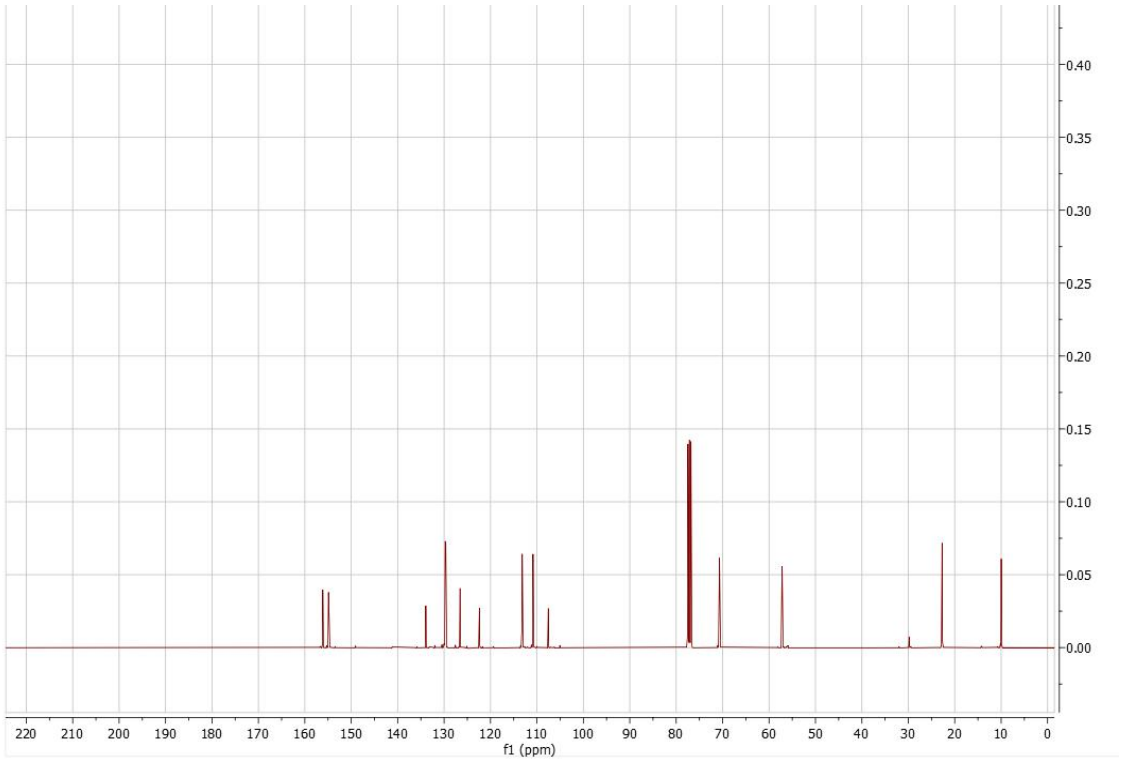


Figure 18. ^{13}C of 8,8'-dibromo-7,7'-dimethoxy-2,2'-dipropoxy-1,1'-binaphthalene, 6c.

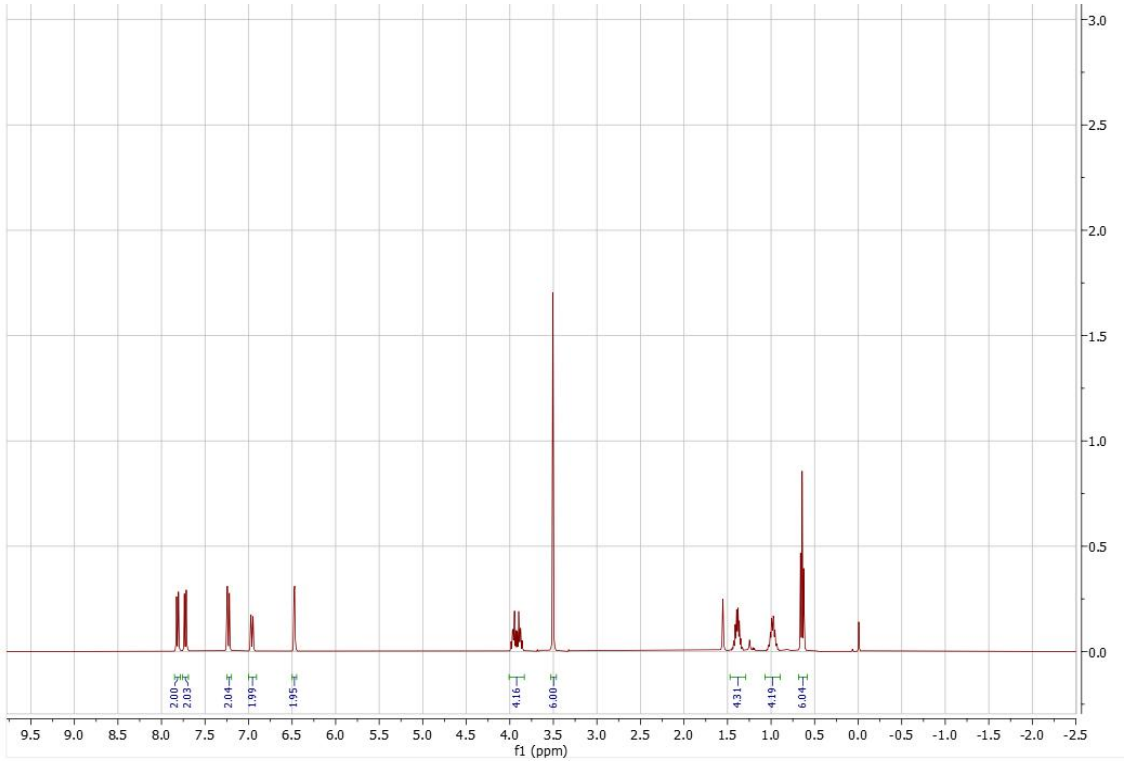


Figure 19. ^{1}H NMR of 2,2'-dibutoxy-7,7'-dimethoxy-1,1'-binaphthalene, 5d.

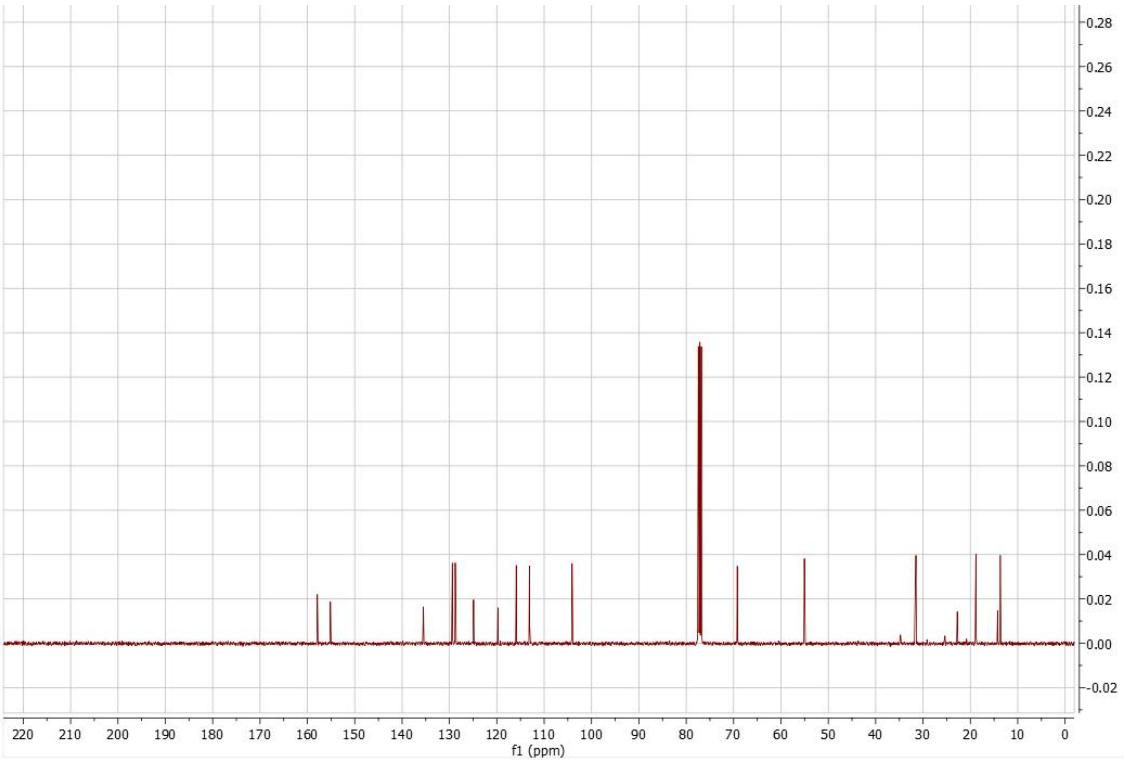


Figure 20. ^{13}C NMR of 2,2'-dibutoxy-7,7'-dimethoxy-1,1'-binaphthalene, 5d.

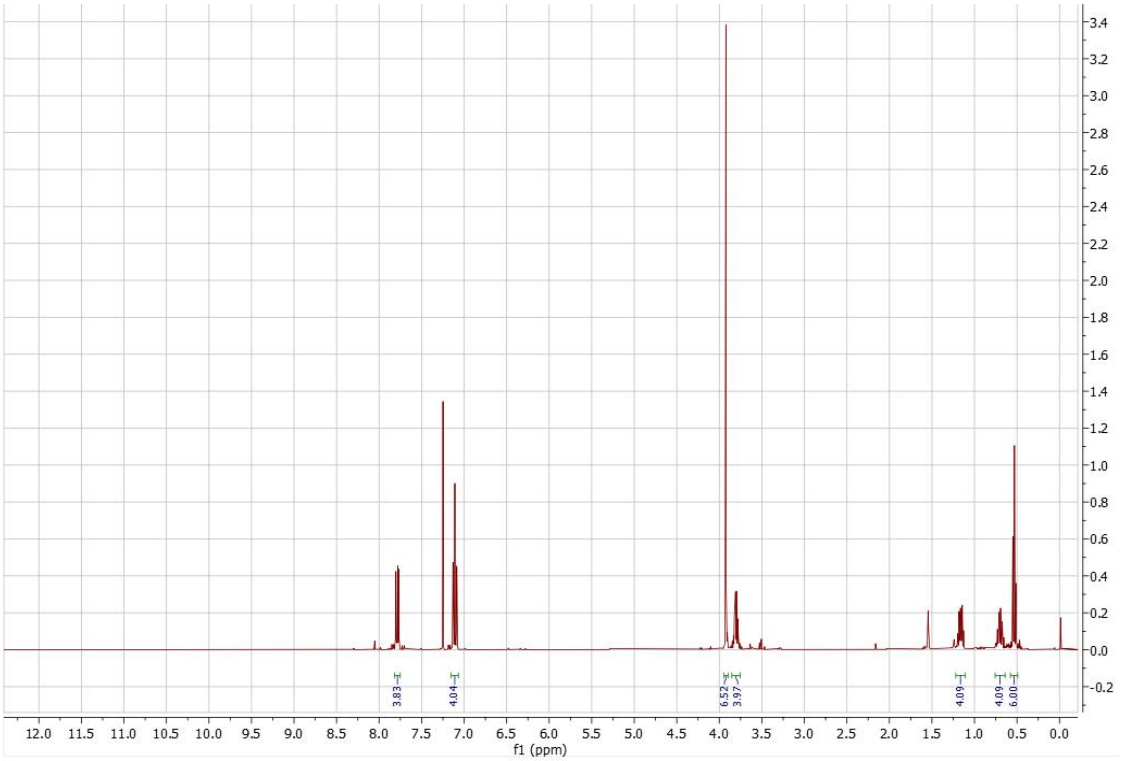


Figure 21. ^{1}H of 8,8'-dibromo-2,2'-dibutoxy-7,7'-dimethoxy-1,1'-binaphthalene, 6d.

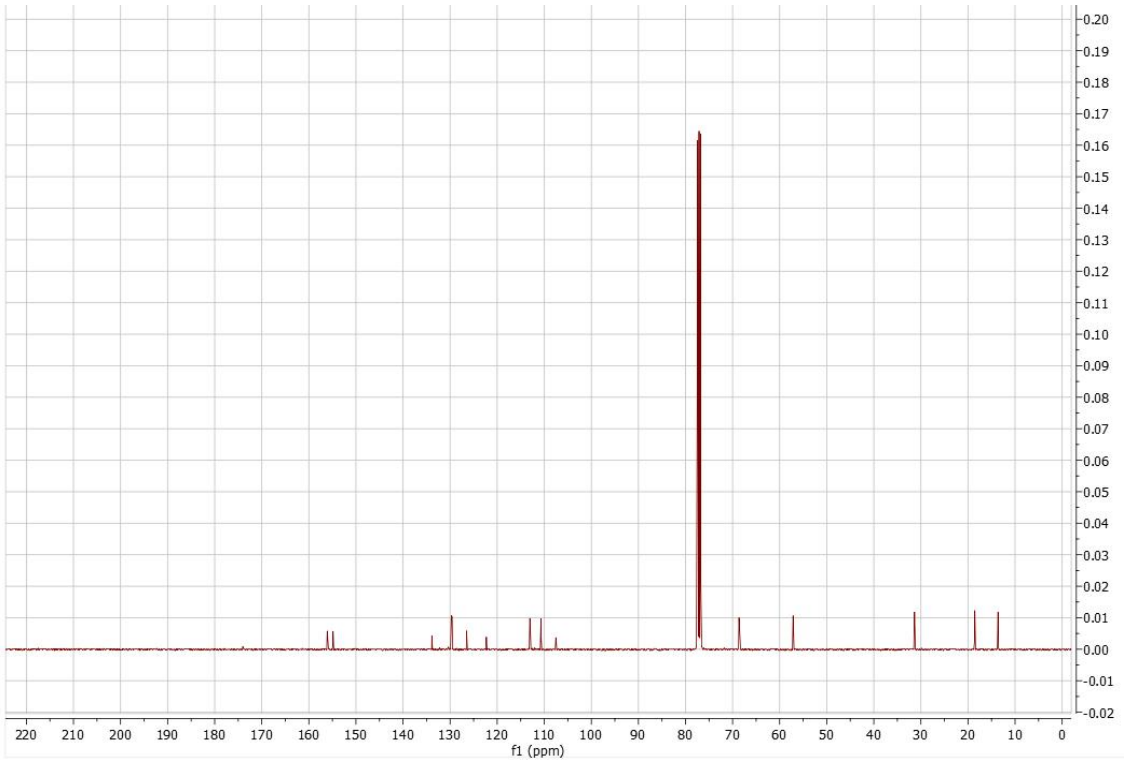


Figure 22. ^{13}C of 8,8'-dibromo-2,2'-dibutoxy-7,7'-dimethoxy-1,1'-binaphthalene, 6d.

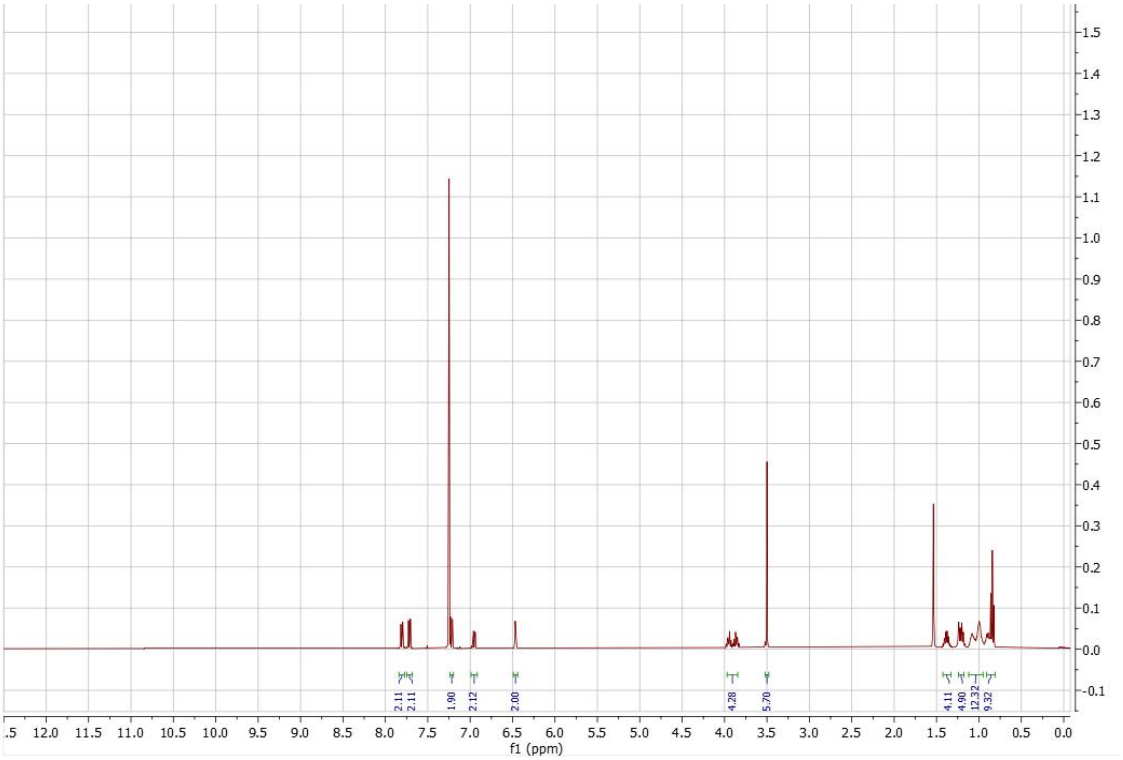


Figure 23. ^{1}H of 7,7'-dimethoxy-2,2'-bis(octyloxy)-1,1'-binaphthalene, 5e.

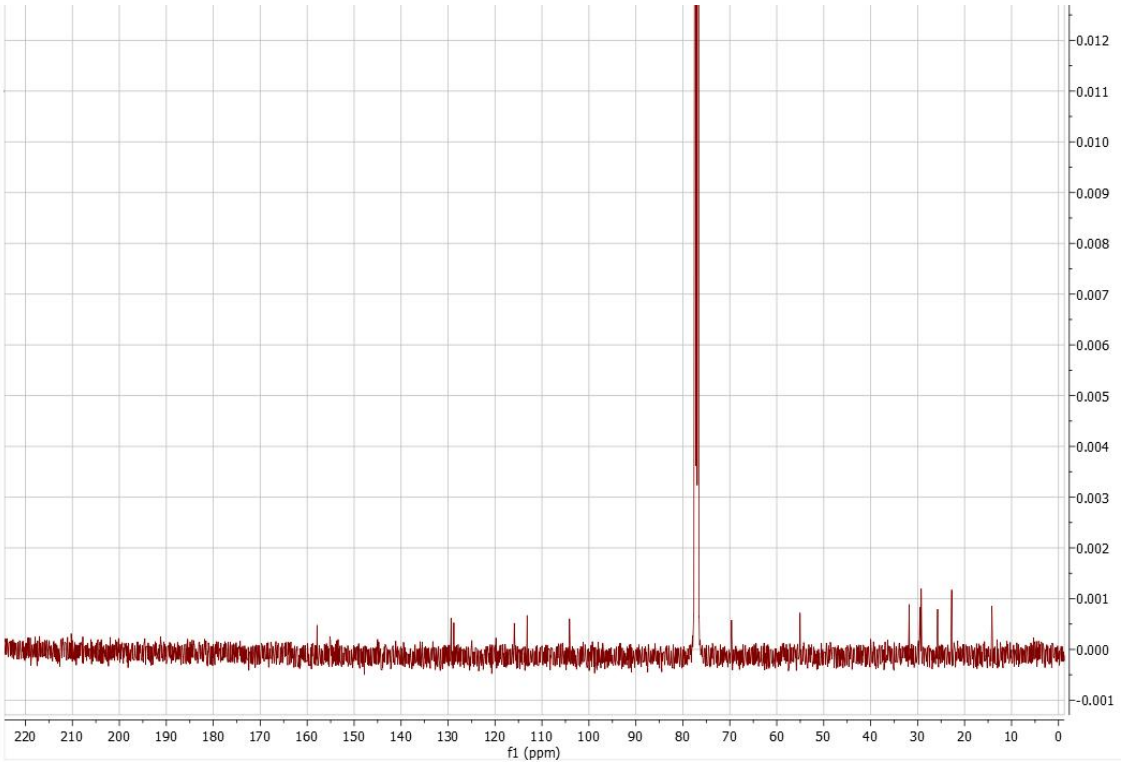


Figure 24. ^{13}C of 7,7'-dimethoxy-2,2'-bis(octyloxy)-1,1'-binaphthalene, 5e.

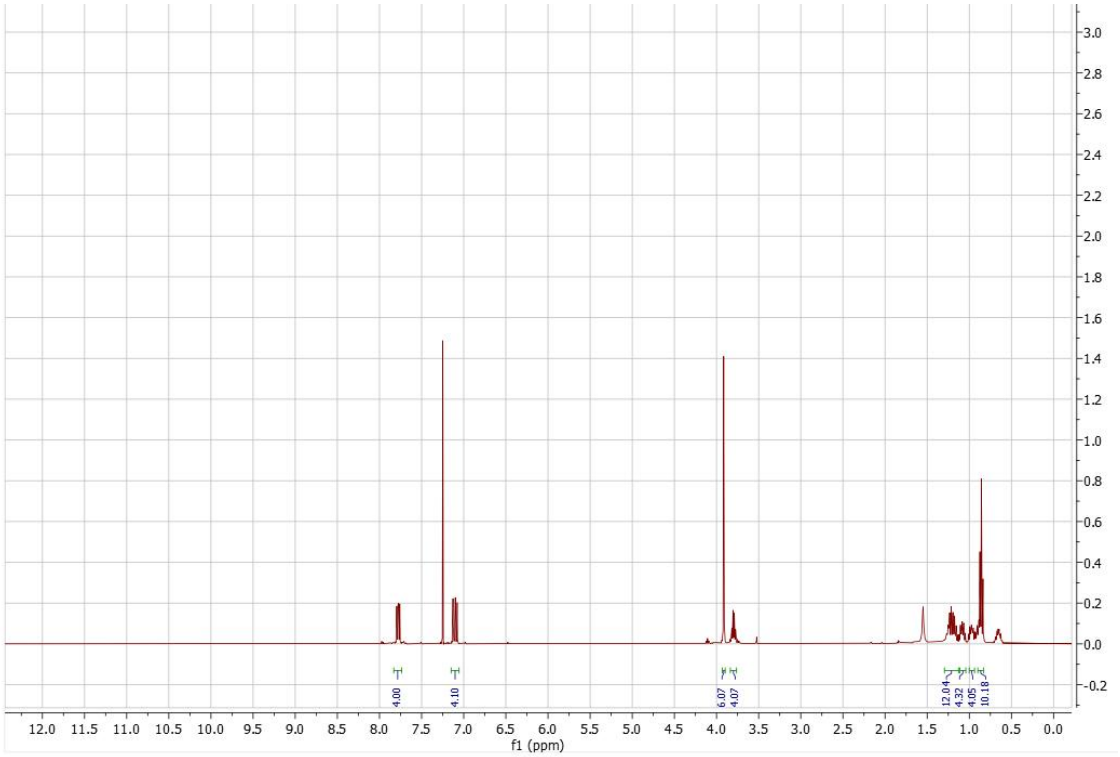


Figure 25. ^{1}H NMR of 8,8'-dibromo-7,7'-dimethoxy-2,2'-bis(octyloxy)-1,1'-binaphthalene, 6e.

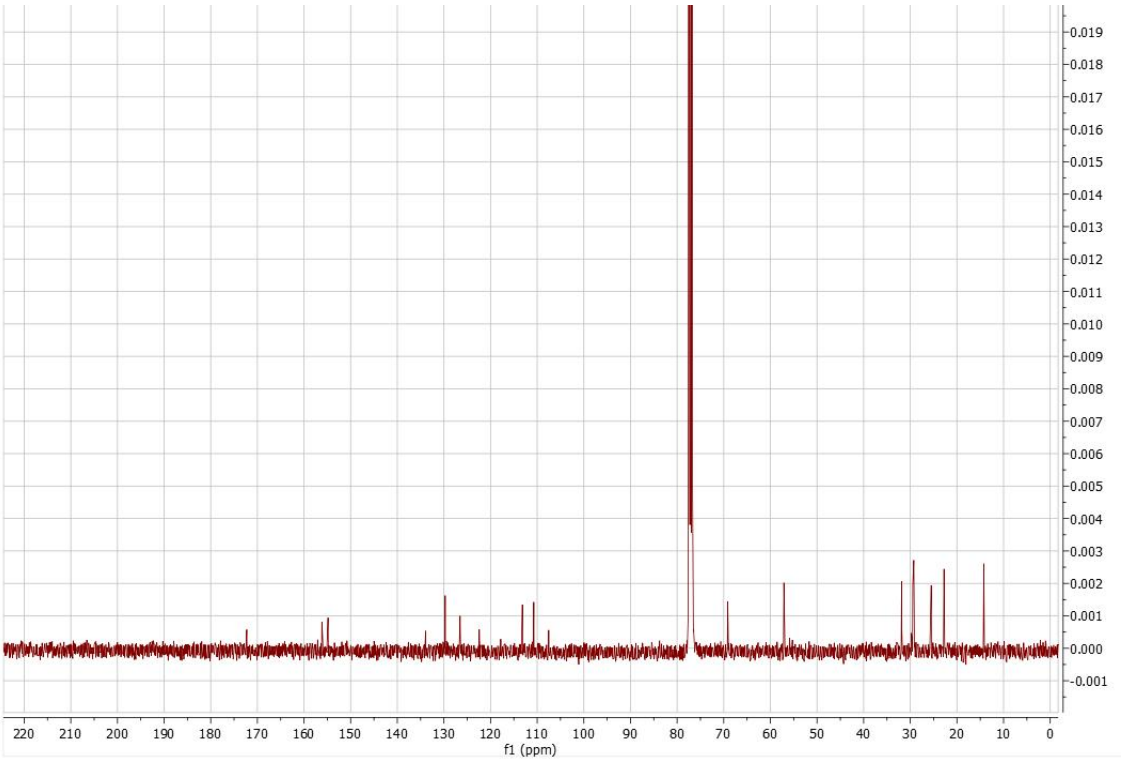


Figure 26. ^{13}C NMR of 8,8'-dibromo-7,7'-dimethoxy-2,2'-bis(octyloxy)-1,1'-binaphthalene, 6e.

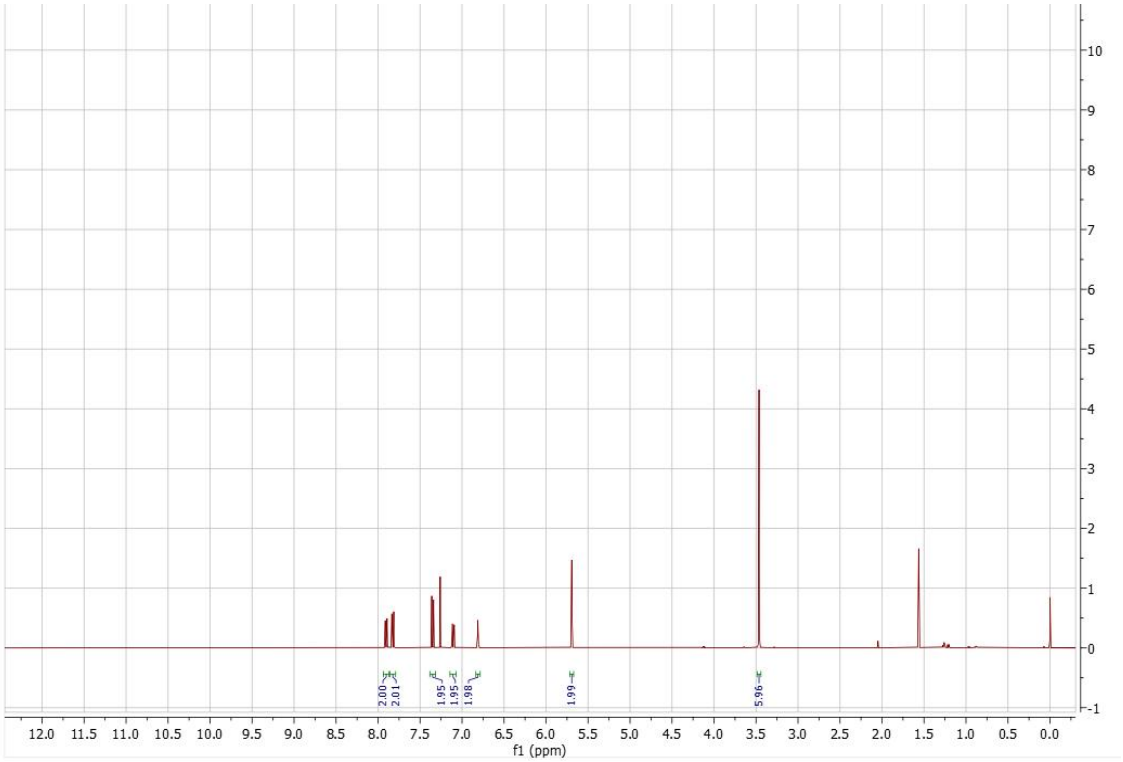


Figure 27. ^{1}H of 10,13-dimethoxydinaphtho[2,1-d:1’,2’-f] [1,3]dioxepine, 5f.

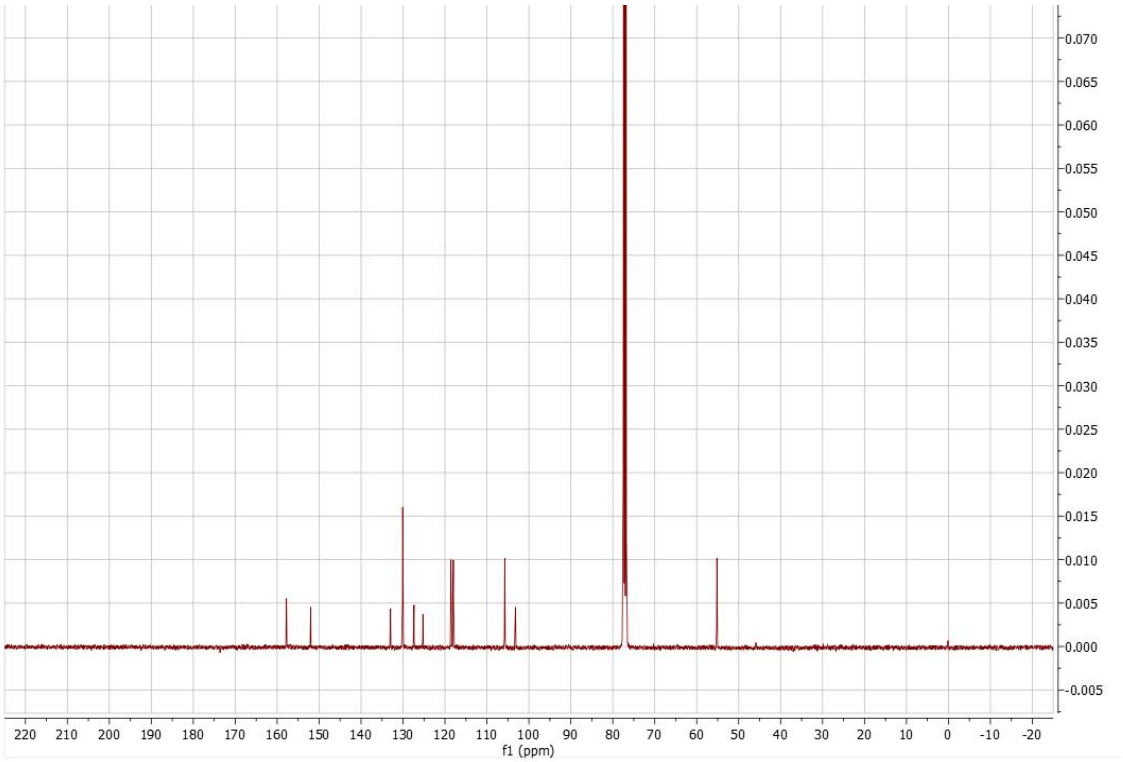


Figure 28. ^{13}C NMR of 10,13-dimethoxydinaphtho[2,1-d:1’,2’-f] [1,3]dioxepine, 5f.

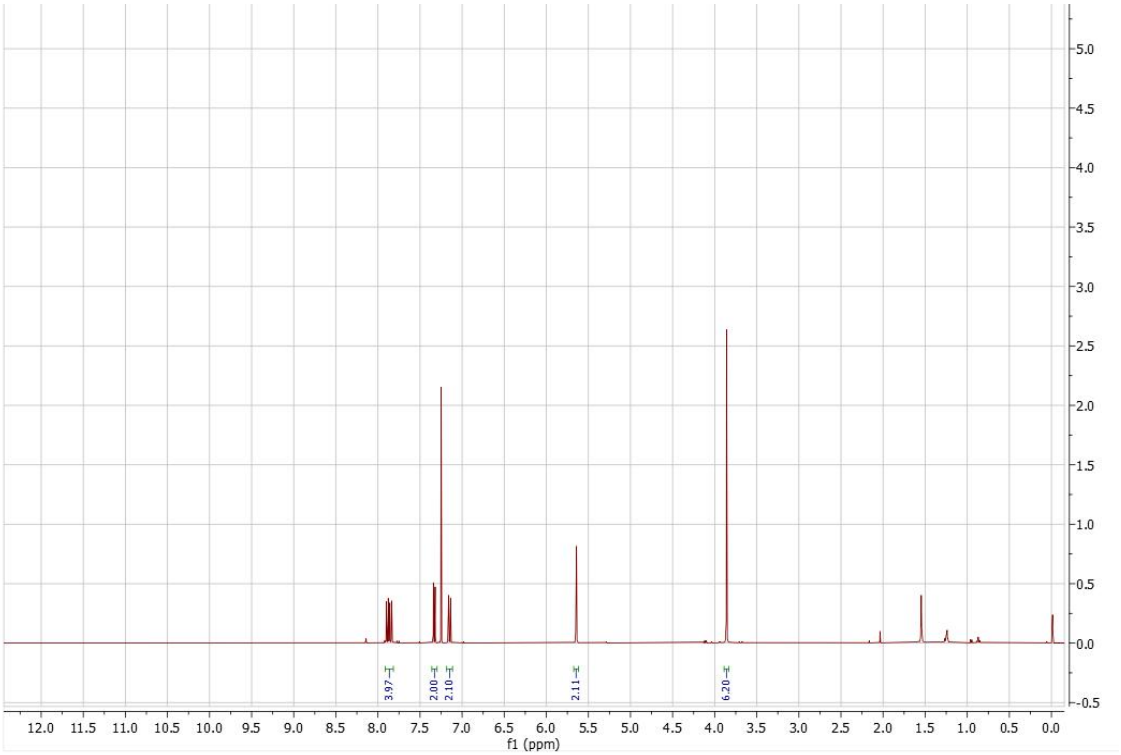


Figure 29. ^{1}H of 11,12-dibromo-10,13-dimethoxydinaphtho[2,1-d:1',2'-f][1,3]dioxepine, 6f.

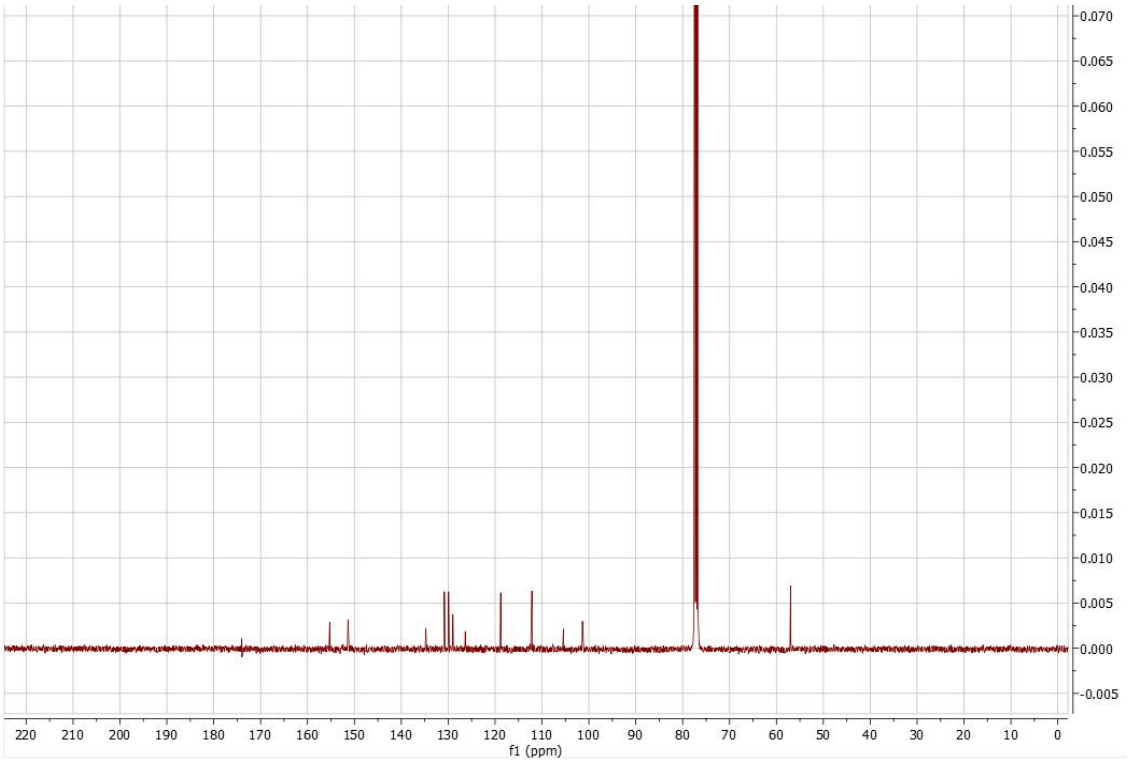


Figure 30. ^{13}C of 11,12-dibromo-10,13-dimethoxydinaphtho[2,1-d:1',2'-f][1,3]dioxepine, 6f.

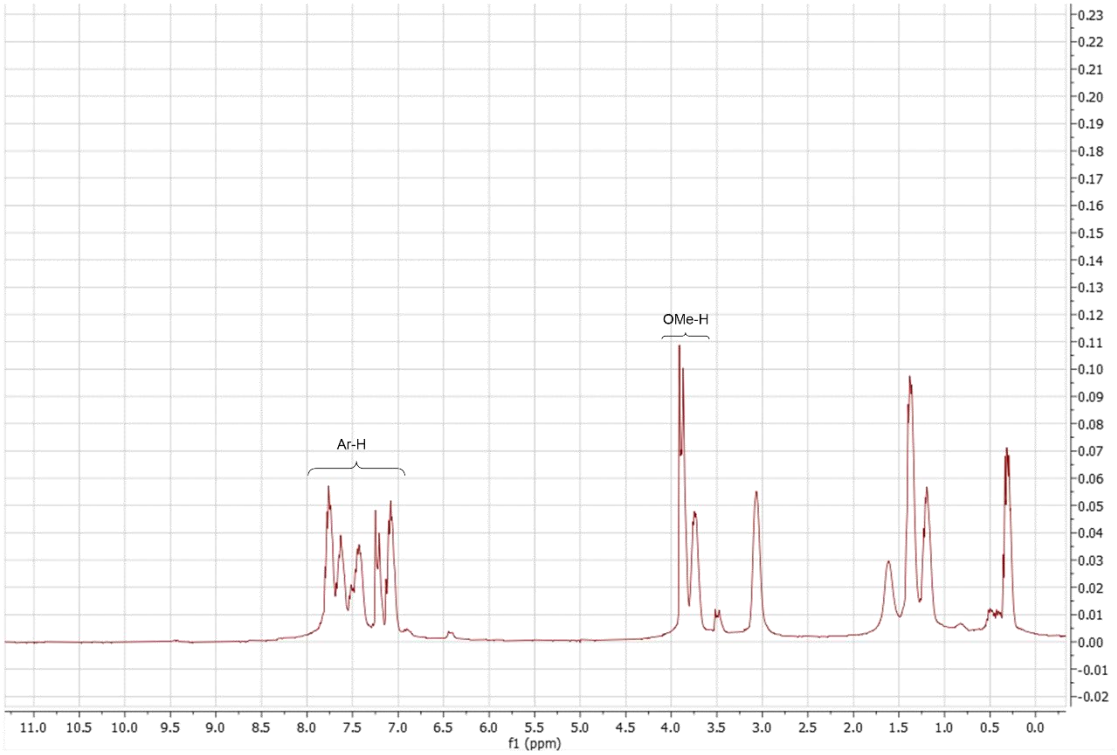


Figure 31. ^{1}H of Polymer **1A**R.

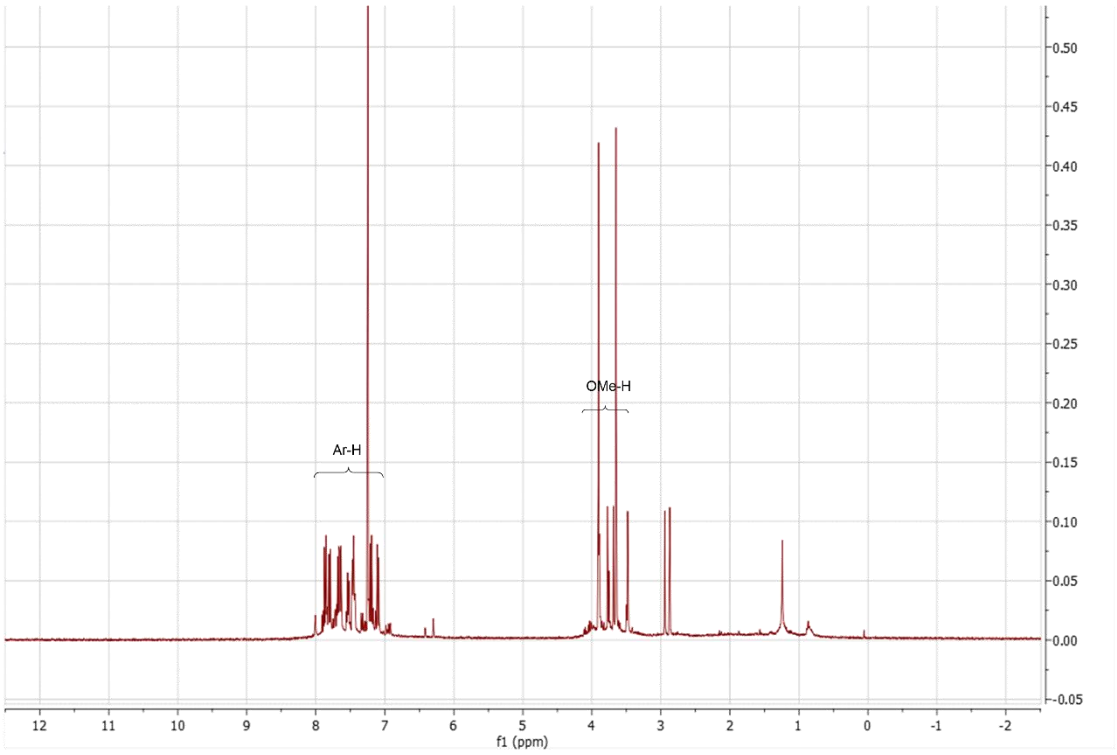


Figure 32. ^{1}H of Polymer **1A**S.

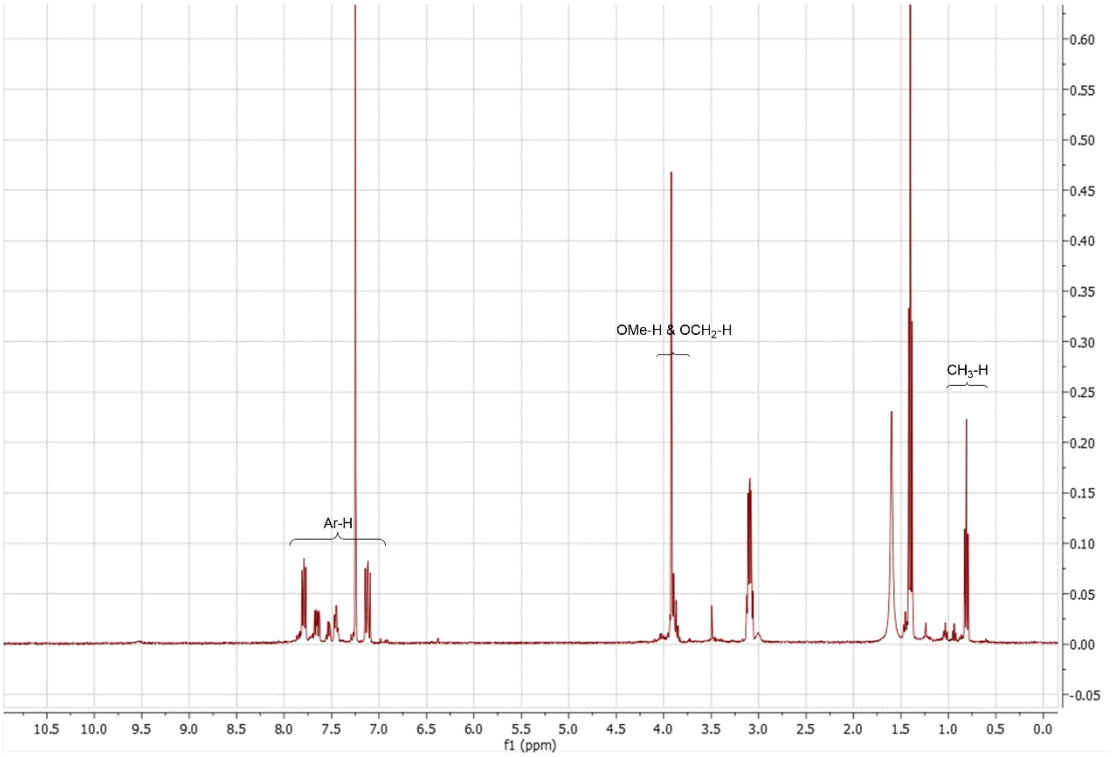


Figure 33. ^{1}H of Polymer **2A**R.

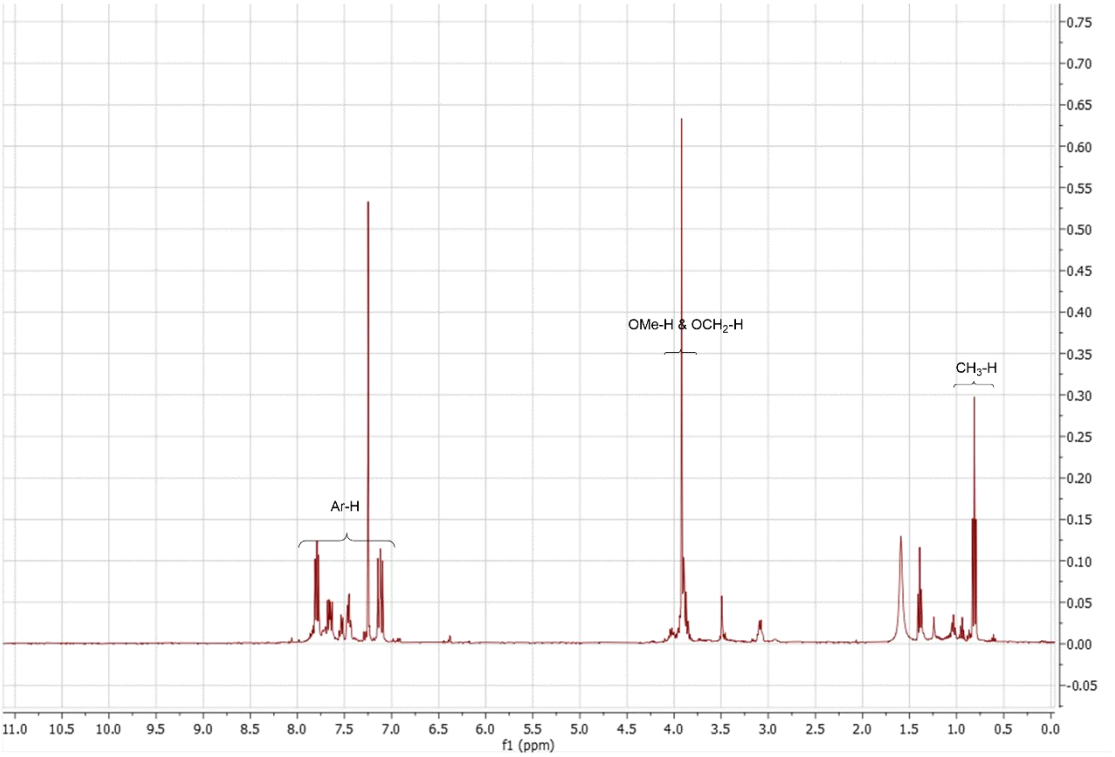


Figure 34. ^{1}H of Polymer **2A**S.

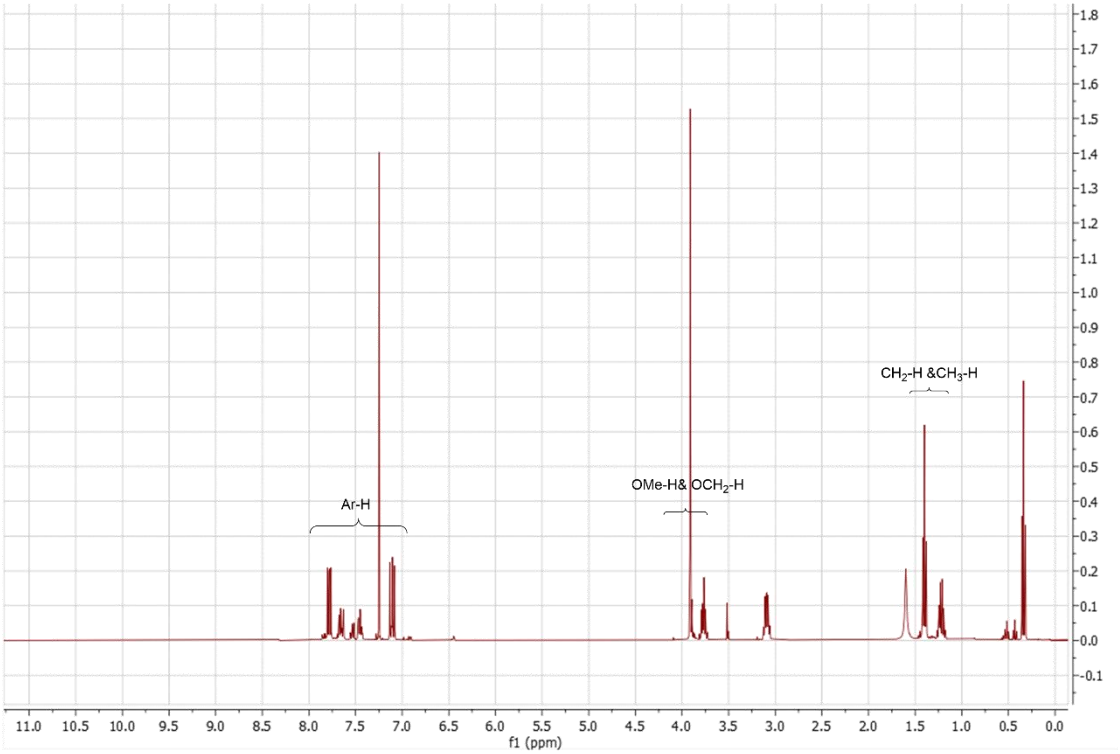


Figure 35. ^{1}H of Polymer **3A**R.

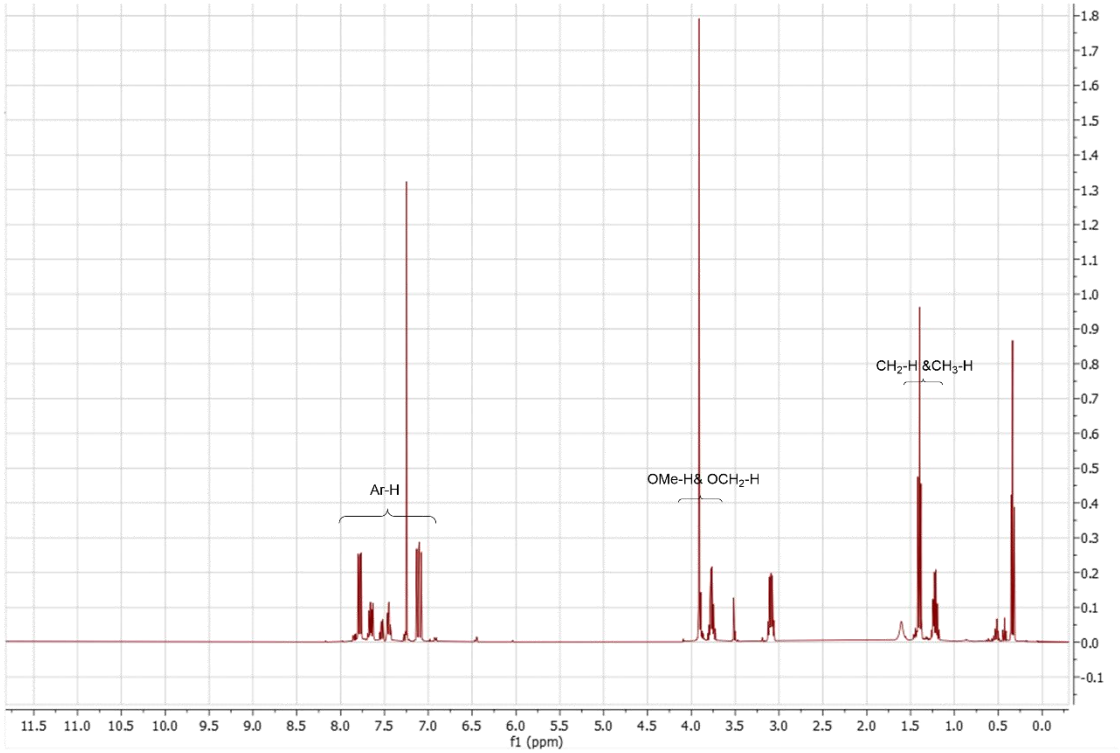


Figure 36. ^{1}H of Polymer **3A**S.

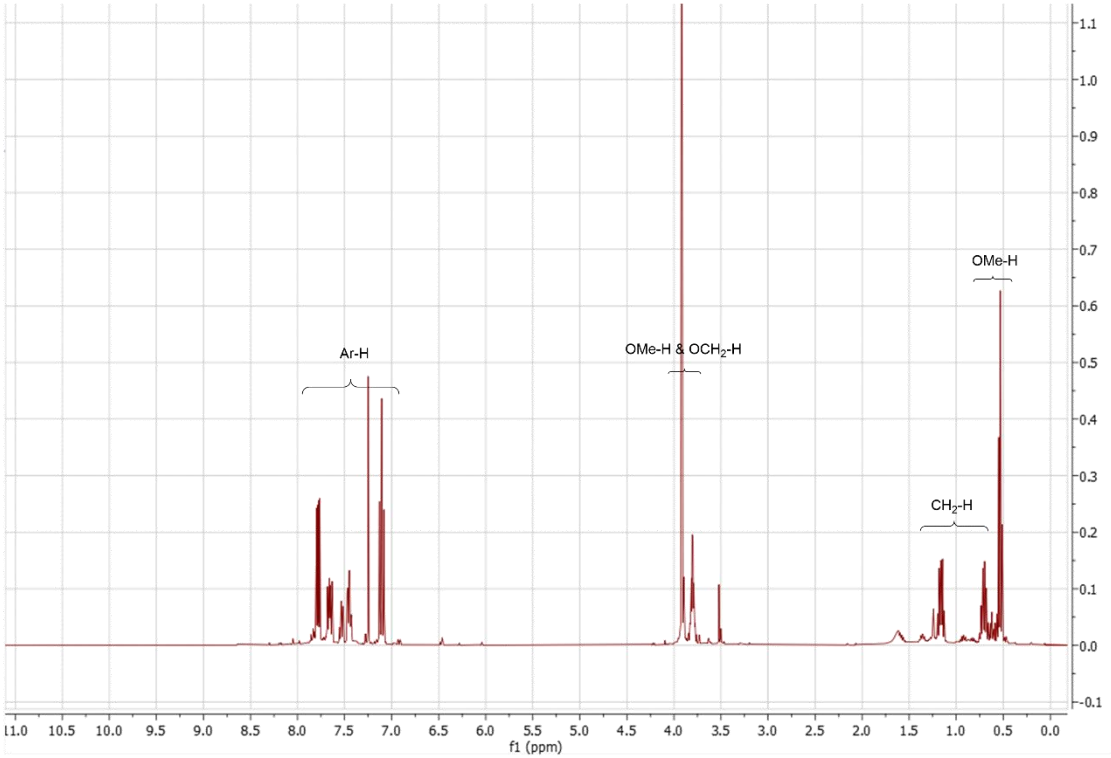


Figure 37. ^{1}H of Polymer **4A**S.

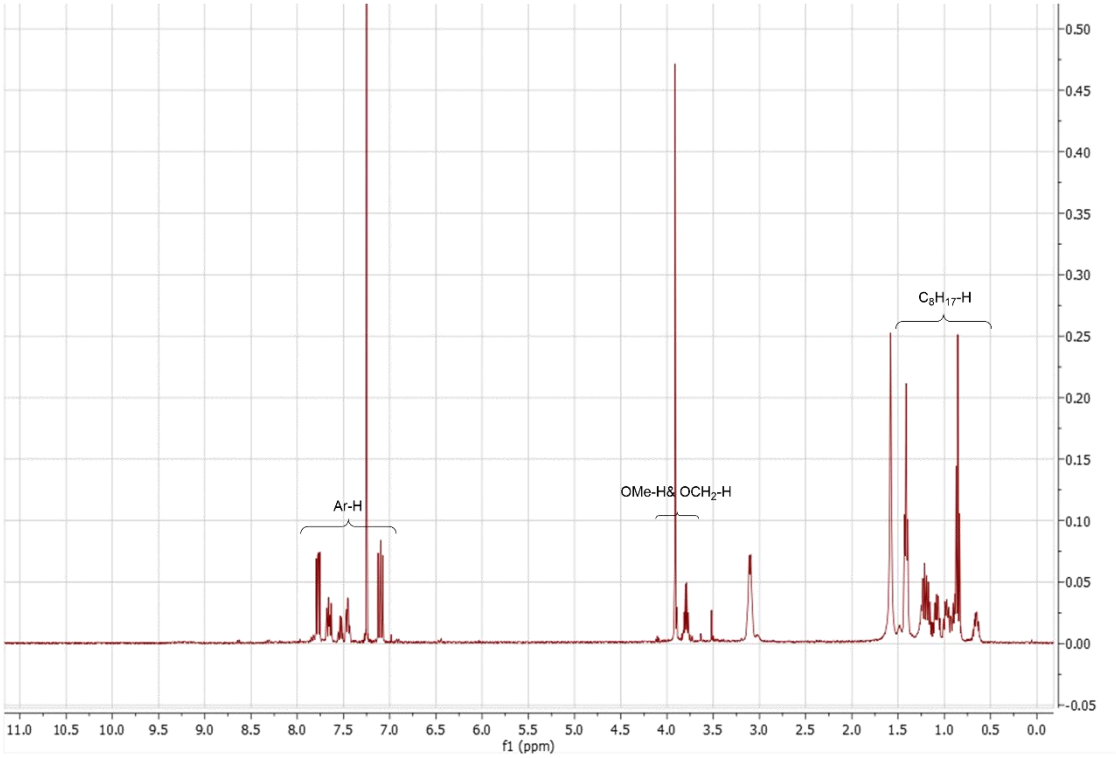


Figure 38. ^{1}H of Polymer **5A**S.

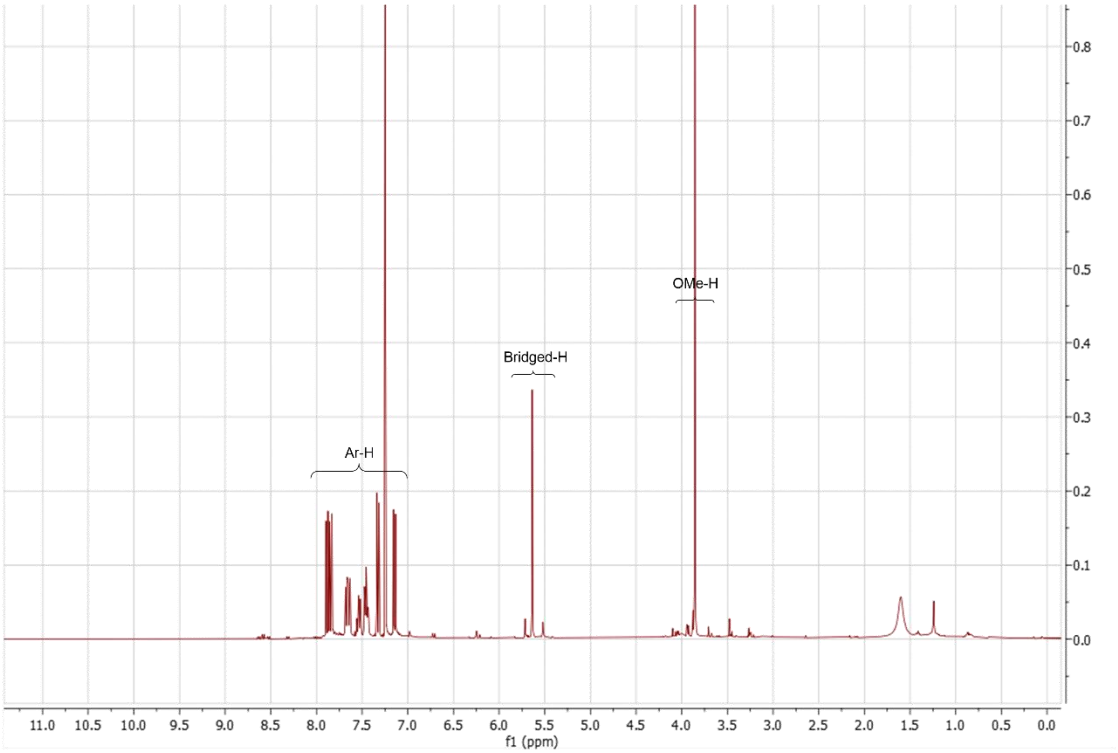
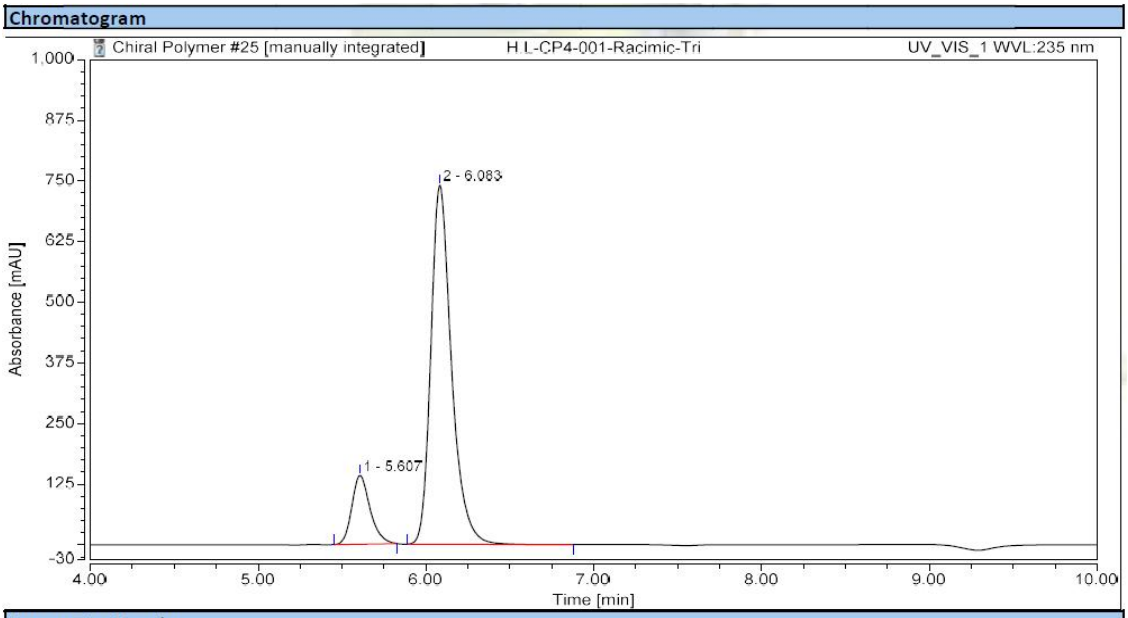


Figure 39. ^{1}H of Polymer **6AS**.

4.HPLC Spectra

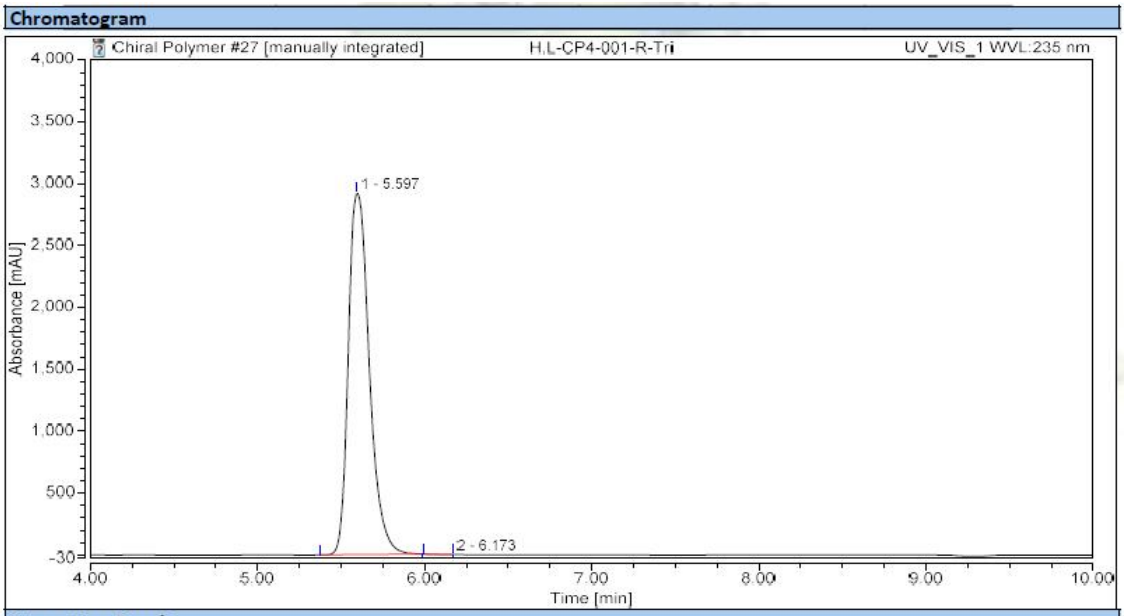
HPLC conditions: Daicel IC column; hexane/2-propanol = 90/10, 1 mL/min



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.607	17.890	141.968	14.47	16.10	n.a.
2		6.083	105.763	739.668	85.53	83.90	n.a.
Total:			**123.653**	**881.636**	**100.00**	**100.00**	

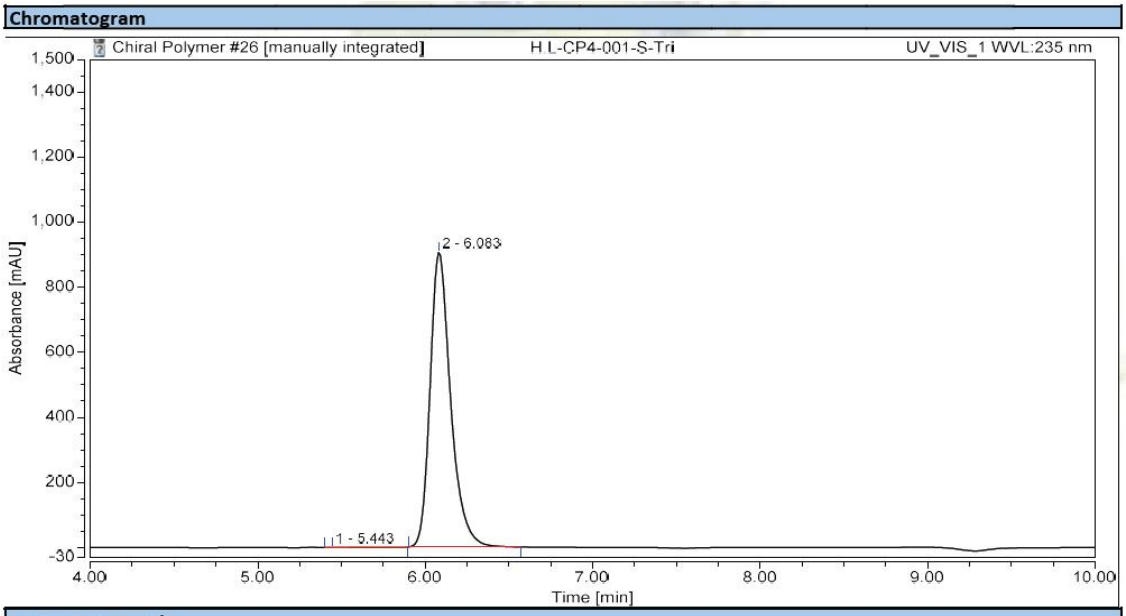
Figure 40. HPLC spectrum of 4a (R or S).



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.597	424.390	2921.539	99.98	100.00	n.a.
2		6.173	0.077	0.000	0.02	0.00	n.a.
Total:			**424.467**	**2921.539**	**100.00**	**100.00**	

Figure 41. HPLC spectrum of 4aR, 99% ee.



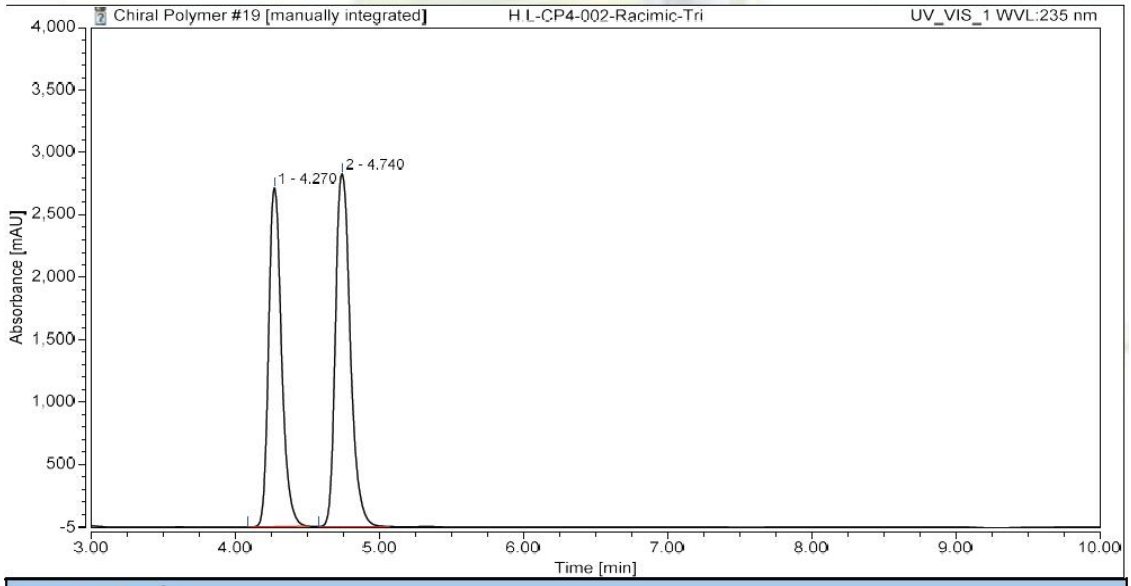
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.443	0.236	0.205	0.18	0.02	n.a.
2		6.083	129.017	906.018	99.82	99.98	n.a.
Total:			**129.253**	**906.224**	**100.00**	**100.00**	

Figure 42. HPLC spectrum of 4aS, 99% ee.

HPLC conditions: Daicel IC column; hexane/2-propanol = 90/10, 1 mL/min

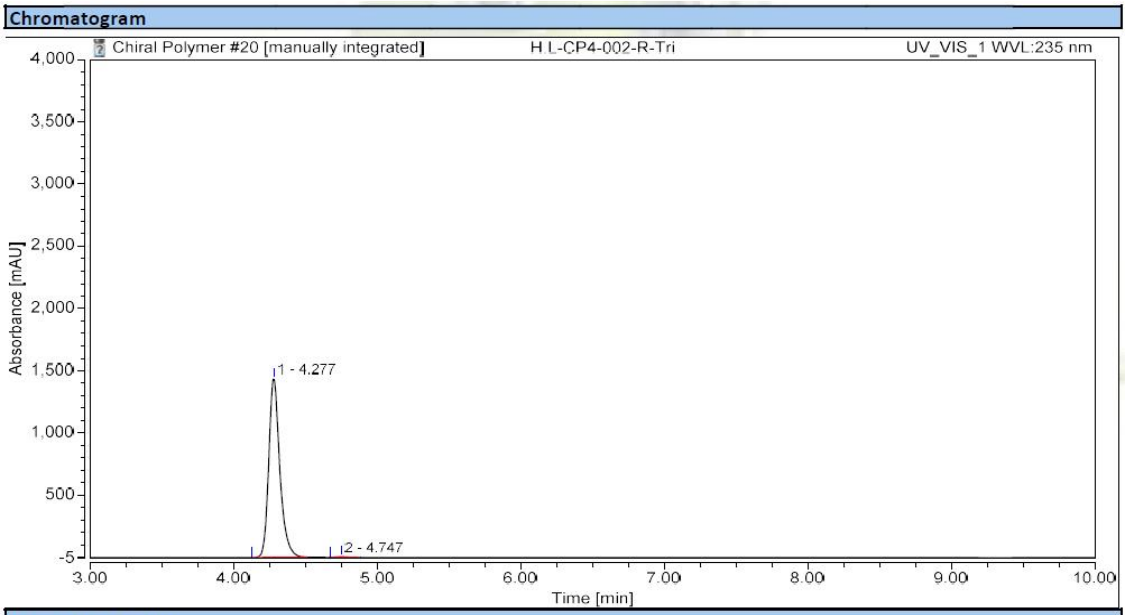
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.270	283.033	2714.846	45.60	48.99	n.a.
2		4.740	337.608	2827.158	54.40	51.01	n.a.
Total:			**620.641**	**5542.004**	**100.00**	**100.00**	

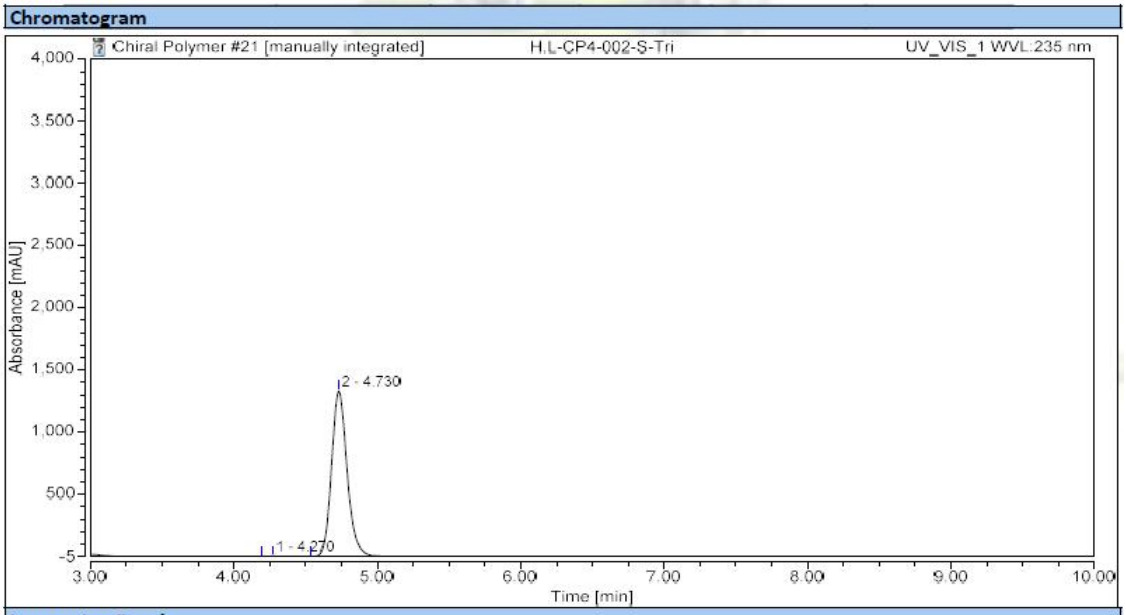
Figure 43. HPLC spectrum of 4b (R or S).



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.277	128.107	1437.123	99.71	99.70	n.a.
2		4.747	0.379	4.367	0.29	0.30	n.a.
Total:			**128.486**	**1441.490**	**100.00**	**100.00**	

Figure 44. HPLC spectrum of 4bR, 99% ee.

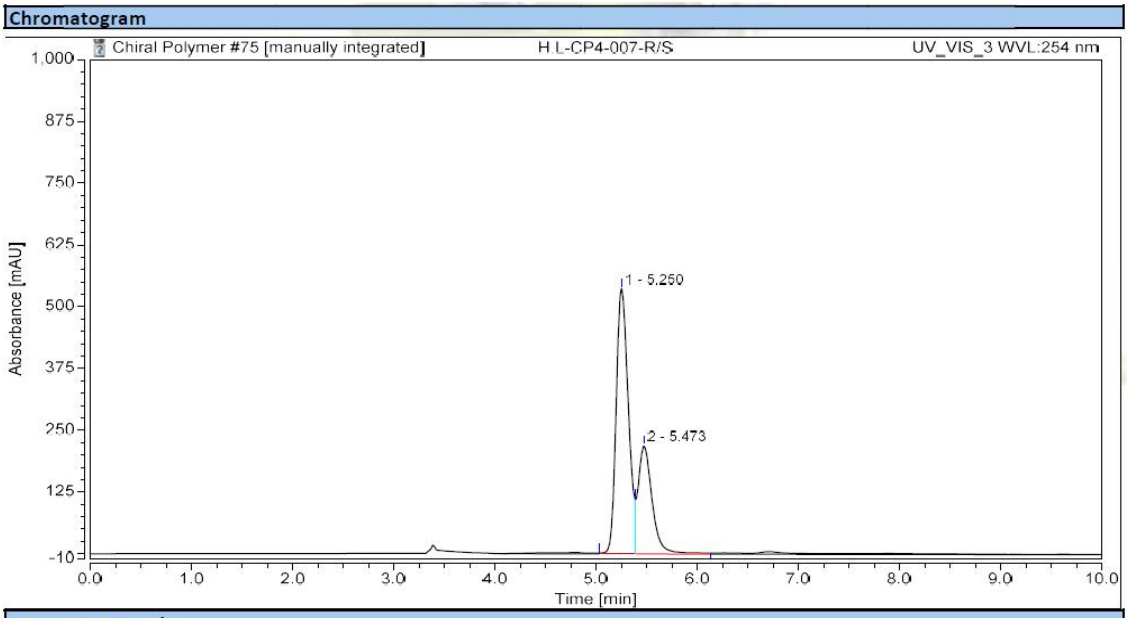


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.270	0.192	2.116	0.12	0.16	n.a.
2		4.730	166.518	1330.560	99.88	99.84	n.a.
Total:			**166.710**	**1332.675**	**100.00**	**100.00**	

Figure 45. HPLC spectrum of 4bS, 99% ee.

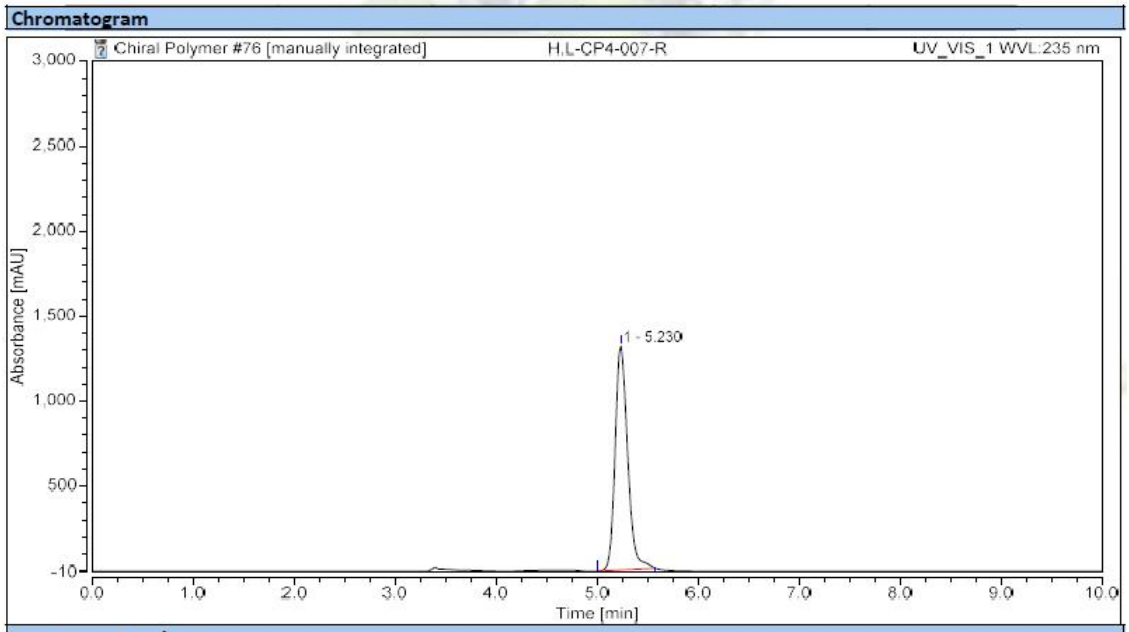
HPLC conditions: Daicel IC column; hexane/2-propanol = 99/1, 1 mL/min



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.250	74.822	536.457	68.19	71.01	n.a.
2		5.473	34.898	218.997	31.81	28.99	n.a.
Total:			**109.720**	**755.454**	**100.00**	**100.00**	

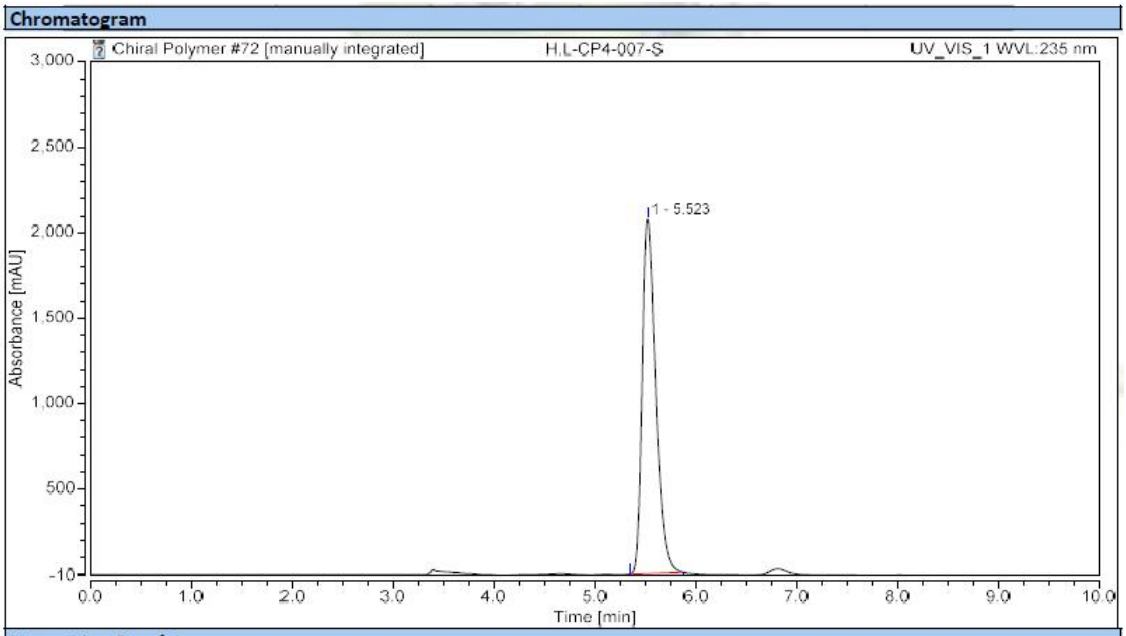
Figure 46. HPLC spectrum of 4c (R or S).



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.230	188.508	1318.039	100.00	100.00	n.a.
Total:			**188.508**	**1318.039**	**100.00**	**100.00**	

Figure 47. HPLC spectrum of 4cR, 99% ee.

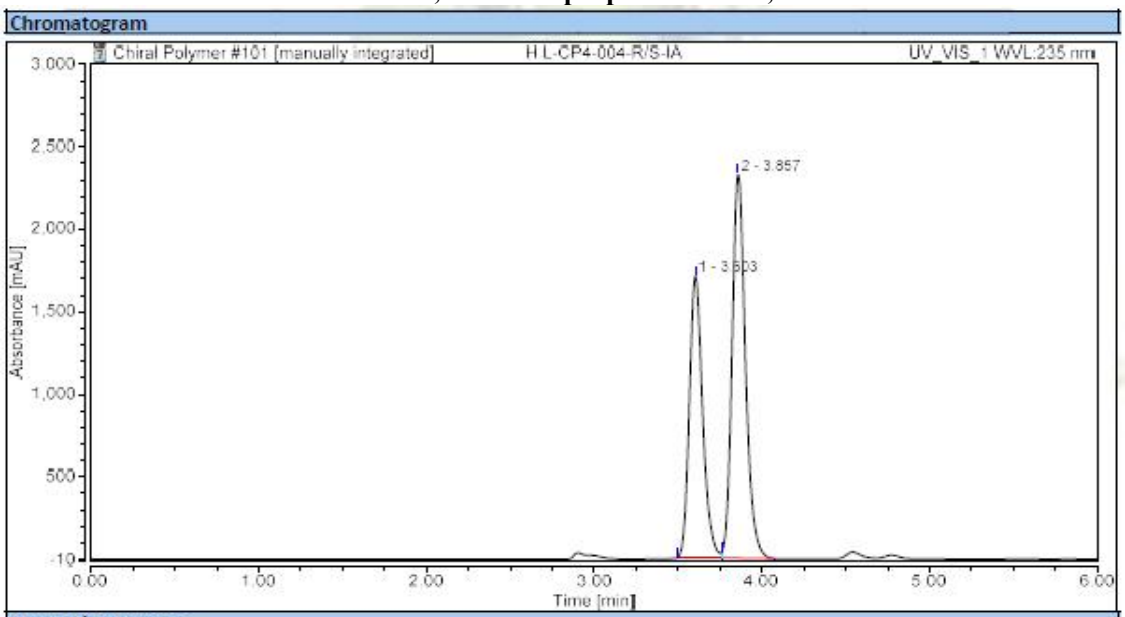


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.523	322.502	2077.078	100.00	100.00	n.a.
Total:			**322.502**	**2077.078**	**100.00**	**100.00**	

Figure 48. HPLC spectrum of 4cS, 99% ee.

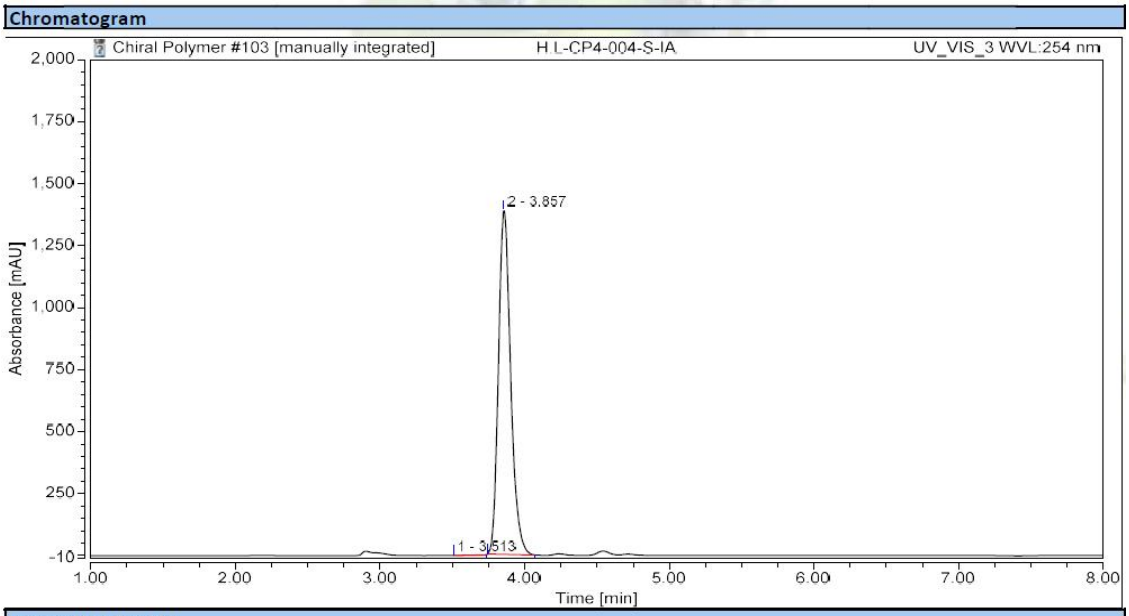
HPLC conditions: Daicel IA column; hexane/2-propanol = 90/10, 1 mL/min



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
n.a.		3.603	155.762	1707.531	42.01	42.35	n.a.
n.a.		3.857	215.015	2324.092	57.99	57.65	n.a.
Total:			**370.777**	**4031.623**	**100.00**	**100.00**	

Figure 49. HPLC spectrum of 4d (R or S).

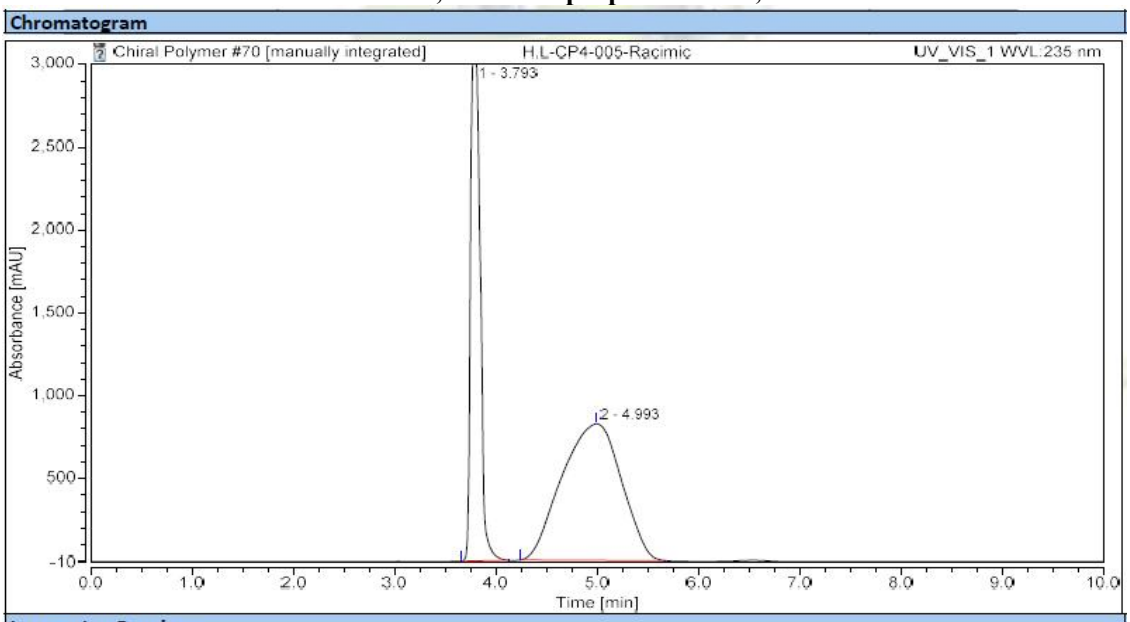


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
n.a.		3.513	0.033	0.000	0.02	0.00	n.a.
n.a.		3.857	135.654	1386.328	99.98	100.00	n.a.
Total:			**135.687**	**1386.328**	**100.00**	**100.00**	

Figure 50. HPLC spectrum of 4d S, 99% ee.

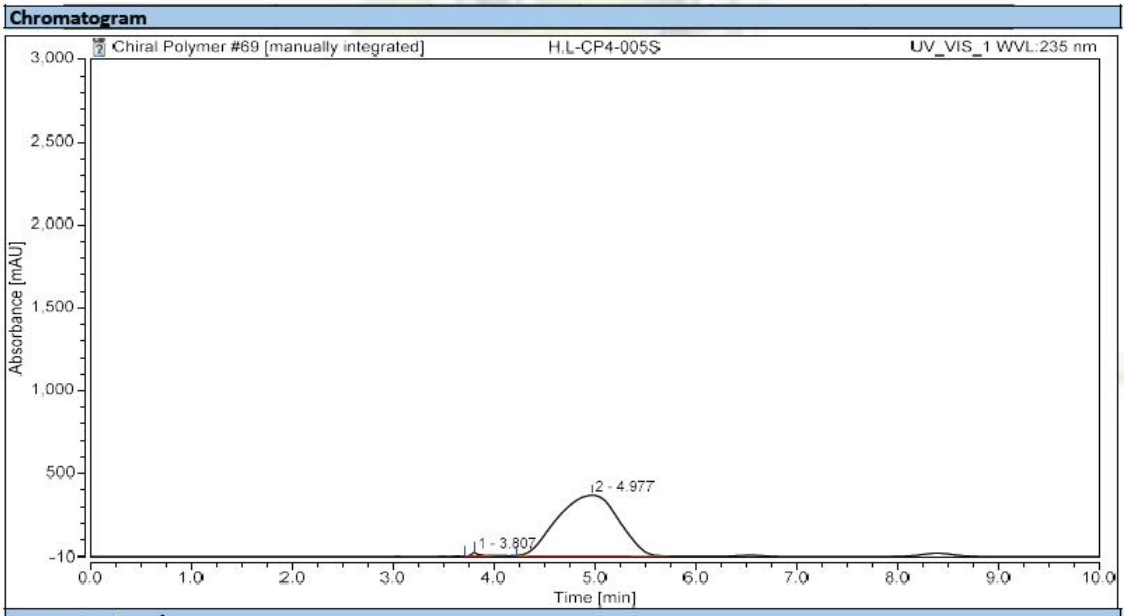
HPLC conditions: Daicel IC column; hexane/2-propanol = 99/1, 1 mL/min



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		3.793	344.399	3105.844	38.06	79.04	n.a.
2		4.993	560.433	823.777	61.94	20.96	n.a.
Total:			**904.832**	**3929.621**	**100.00**	**100.00**	

Figure 51. HPLC spectrum of 4e (R or S).

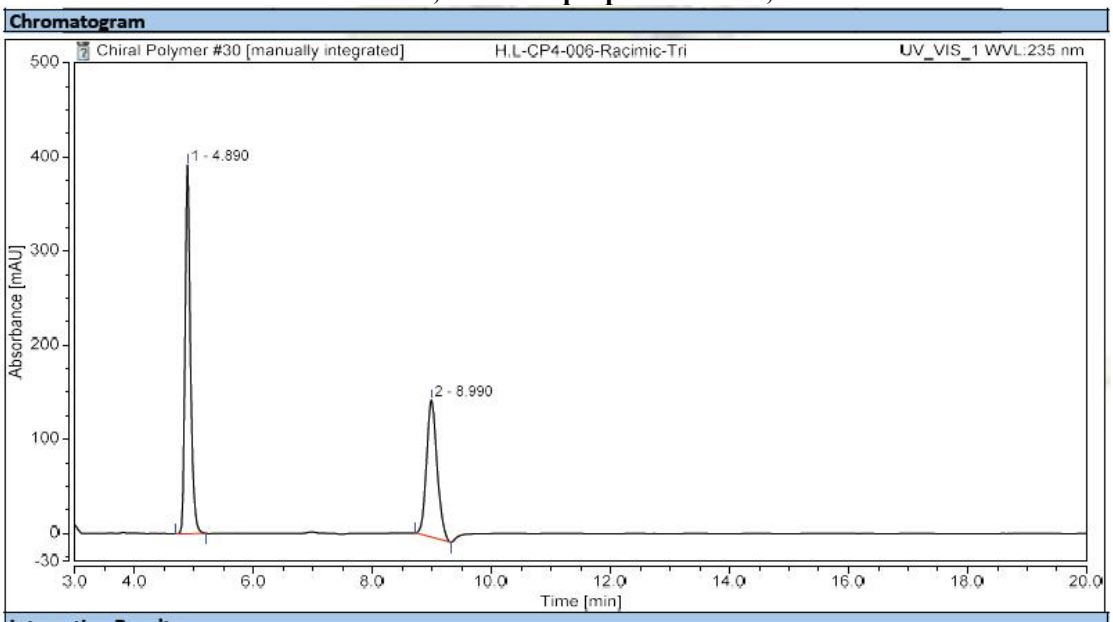


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		3.807	1.538	21.175	0.60	5.48	n.a.
2		4.977	256.377	365.294	99.40	94.52	n.a.
Total:			**257.915**	**386.469**	**100.00**	**100.00**	

Figure 52. HPLC spectrum of 4eS, 98% ee.

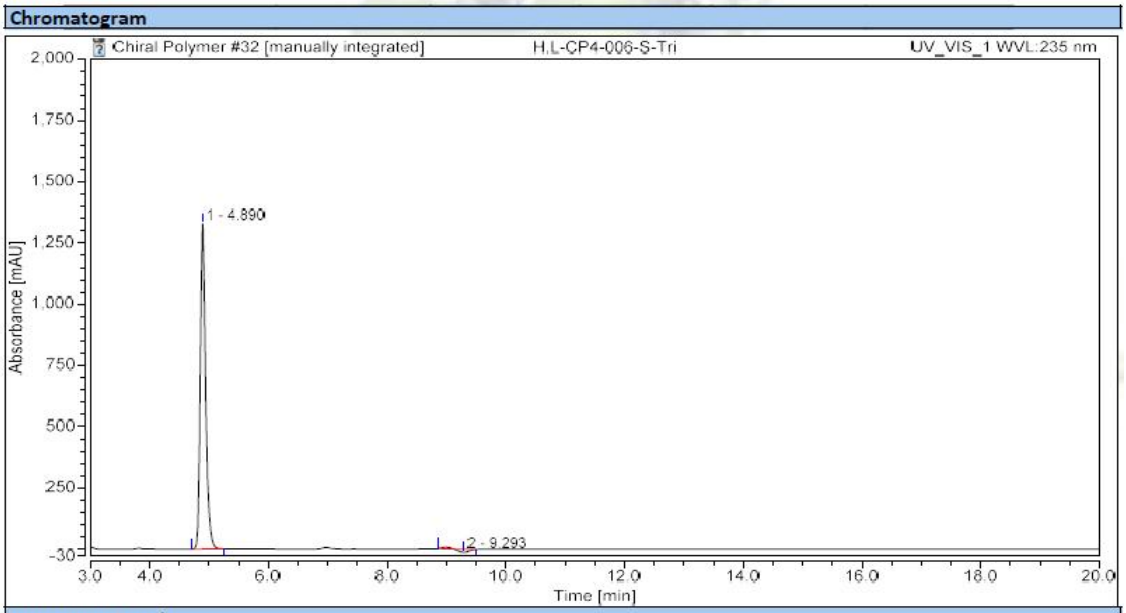
HPLC conditions: Daicel IC column; hexane/2-propanol = 90/10, 1 mL/min



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.890	41.109	391.658	57.85	72.89	n.a.
2		8.990	29.956	145.653	42.15	27.11	n.a.
Total:			**71.065**	**537.312**	**100.00**	**100.00**	

Figure 53. HPLC spectrum of 4f (R or S).

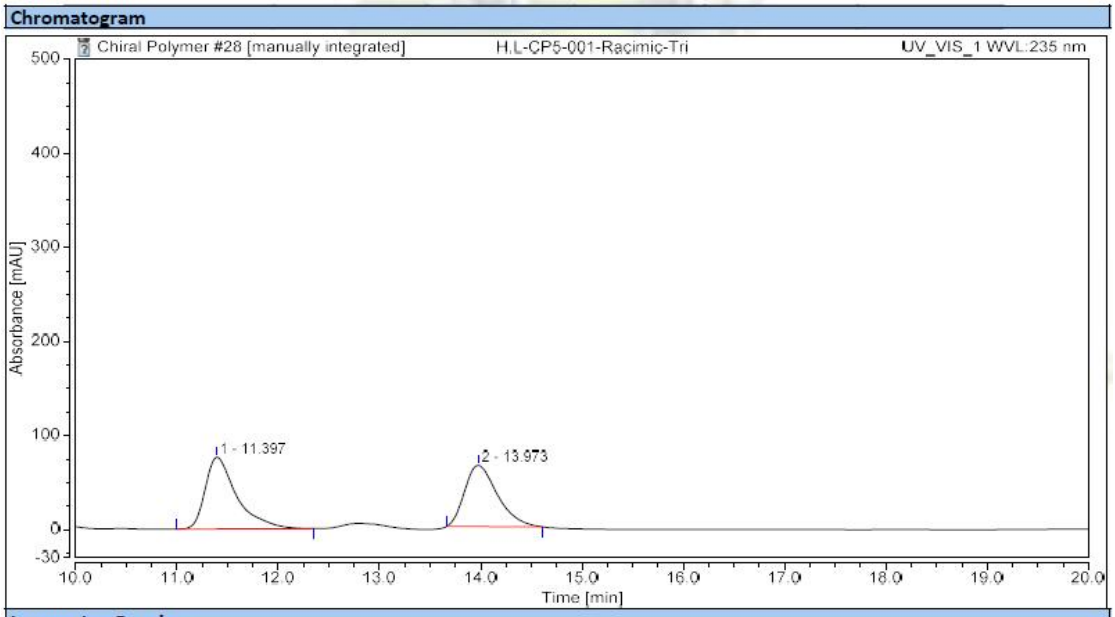


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.890	139.234	1328.638	98.89	99.04	n.a.
2		9.293	1.563	12.917	1.11	0.96	n.a.
Total:			**140.798**	**1341.555**	**100.00**	**100.00**	

Figure 54. HPLC spectrum of 4fS, 97% ee.

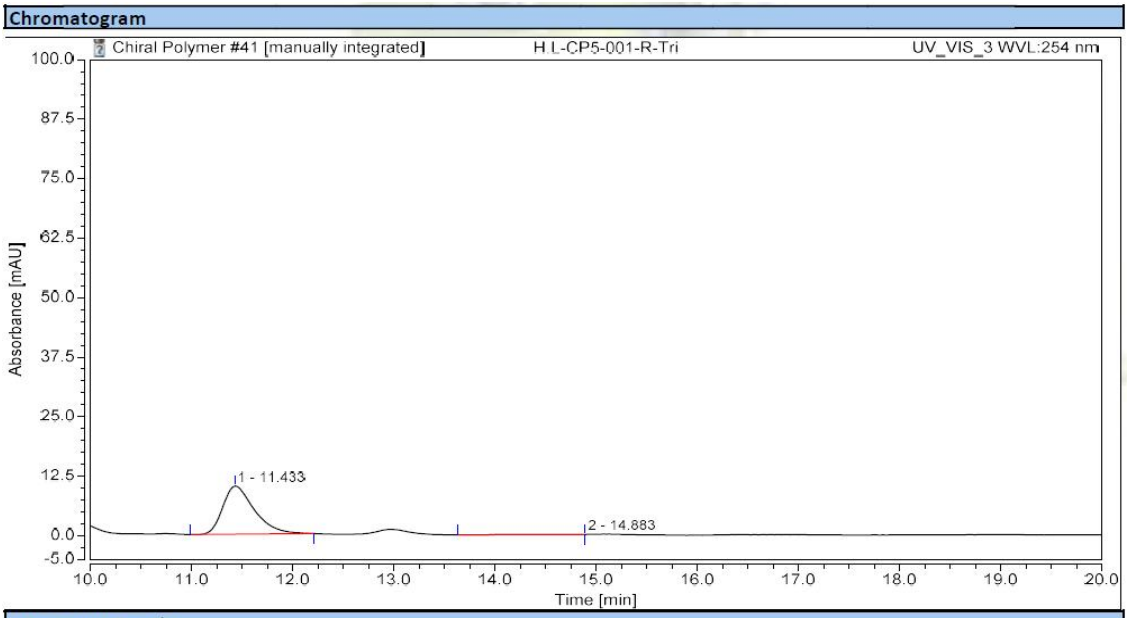
HPLC conditions: Daicel IB column; hexane/2-propanol = 90/10, 1 mL/min



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.397	27.451	76.233	52.99	53.96	n.a.
2		13.973	24.354	65.031	47.01	46.04	n.a.
Total:			**51.805**	**141.264**	**100.00**	**100.00**	

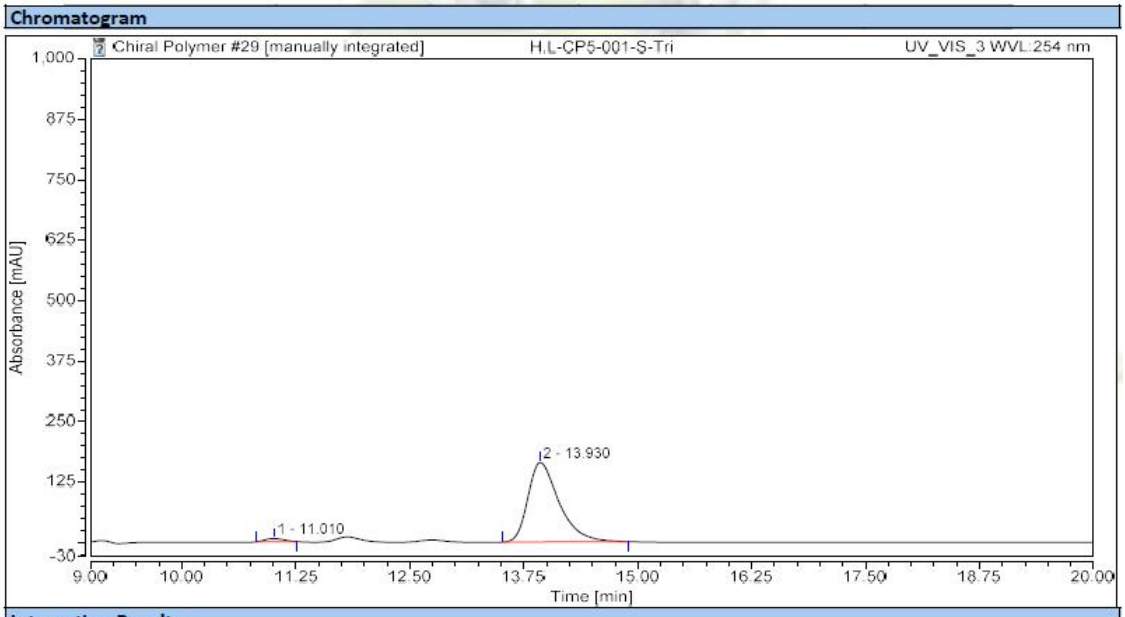
Figure 55. HPLC spectrum of 5a (R or S).



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.433	3.659	10.116	99.97	100.00	n.a.
2		14.883	0.001	0.000	0.03	0.00	n.a.
Total:			**3.660**	**10.116**	**100.00**	**100.00**	

Figure 56. HPLC spectrum of 5aR, 99% ee.

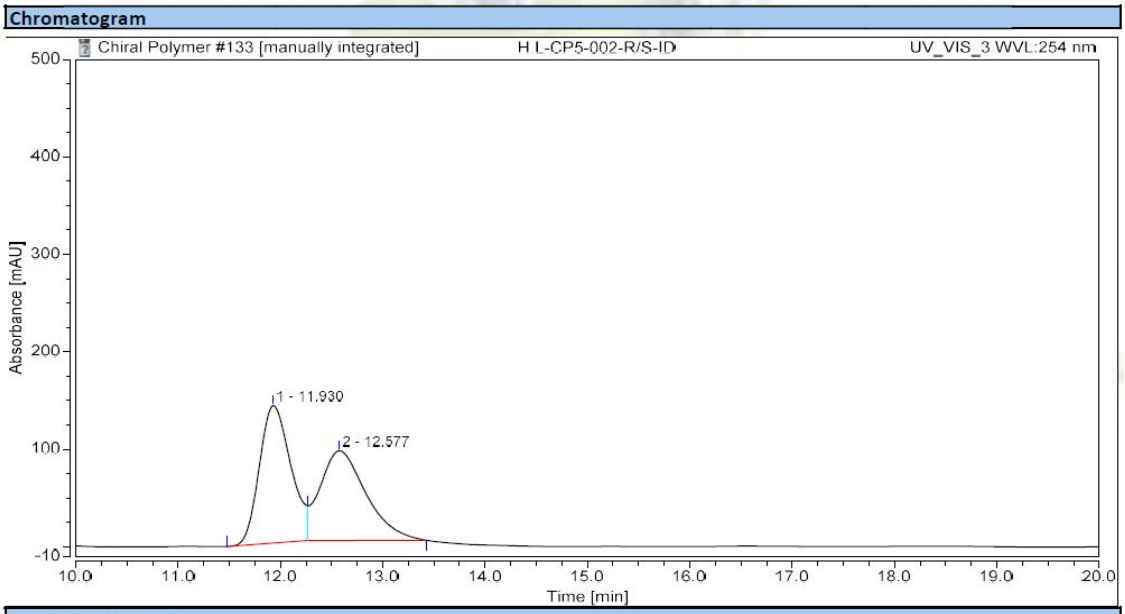


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.010	1.523	6.457	2.28	3.77	n.a.
2		13.930	65.305	164.638	97.72	96.23	n.a.
Total:			**66.828**	**171.095**	**100.00**	**100.00**	

Figure 57. HPLC spectrum of 5aS, 95% ee.

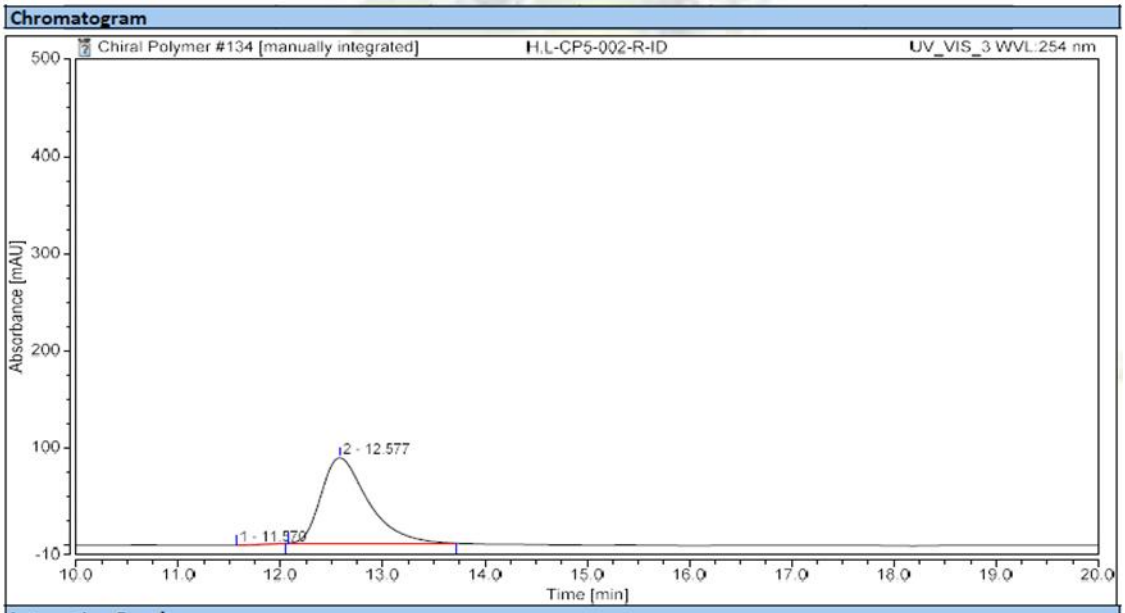
HPLC conditions: Daicel ID column; hexane/2-propanol = 90/10, 1 mL/min



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
n.a.		11.930	50.026	141.112	50.90	60.52	n.a.
n.a.		12.577	48.263	92.066	49.10	39.48	n.a.
Total:			**98.289**	**233.178**	**100.00**	**100.00**	

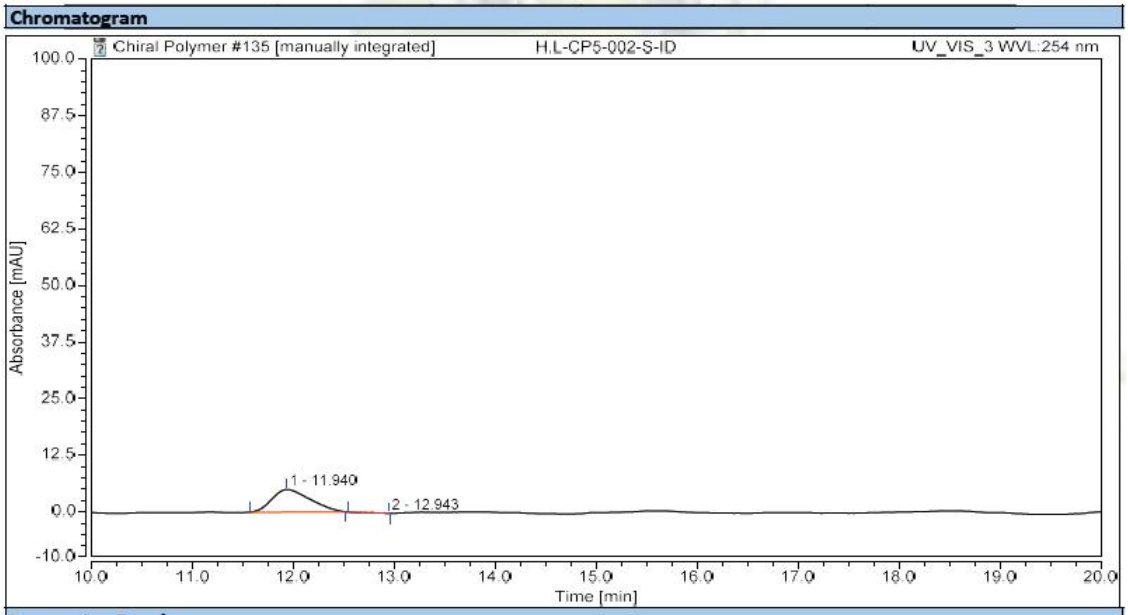
Figure 58. HPLC spectrum of 5b (R or S).



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
n.a.		11.570	0.093	0.000	0.20	0.00	n.a.
n.a.		12.577	46.538	87.857	99.80	100.00	n.a.
Total:			**46.631**	**87.857**	**100.00**	**100.00**	

Figure 59. HPLC spectrum of 5bR, 99% ee.

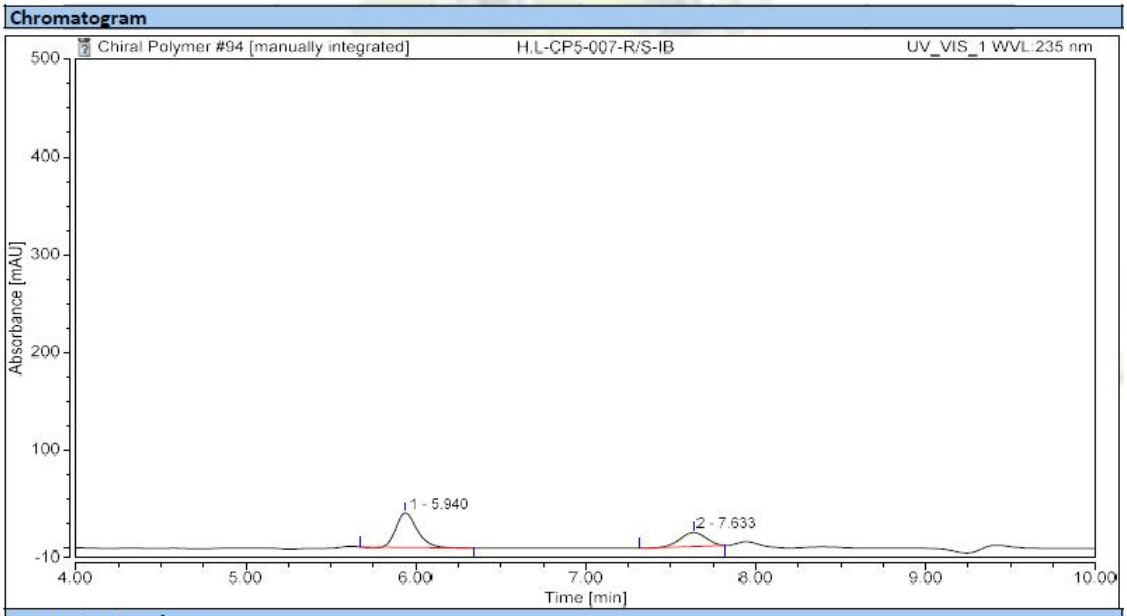


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
n.a.		11.940	2.163	4.988	98.91	99.72	n.a.
n.a.		12.943	0.024	0.014	1.09	0.28	n.a.
Total:			**2.187**	**5.002**	**100.00**	**100.00**	

Figure 60. HPLC spectrum of 5bS, 97% ee.

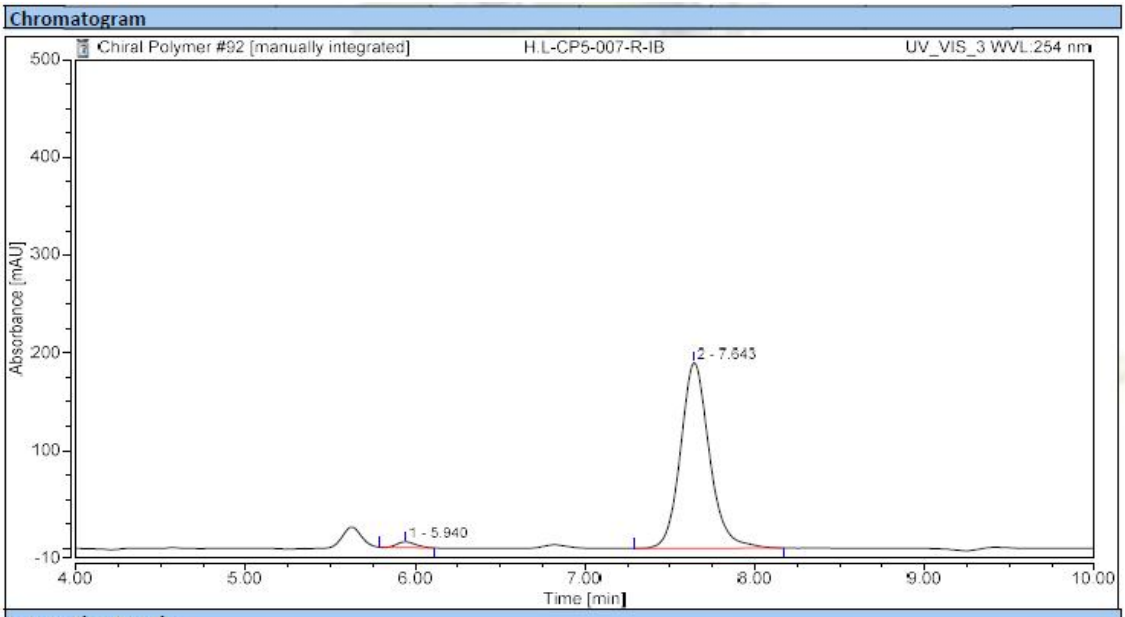
HPLC conditions: Daicel IB column; hexane/2-propanol = 90/10, 1 mL/min



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
n.a.		5.940	5.011	35.358	66.50	71.15	n.a.
n.a.		7.633	2.524	14.338	33.50	28.85	n.a.
Total:			**7.535**	**49.695**	**100.00**	**100.00**	

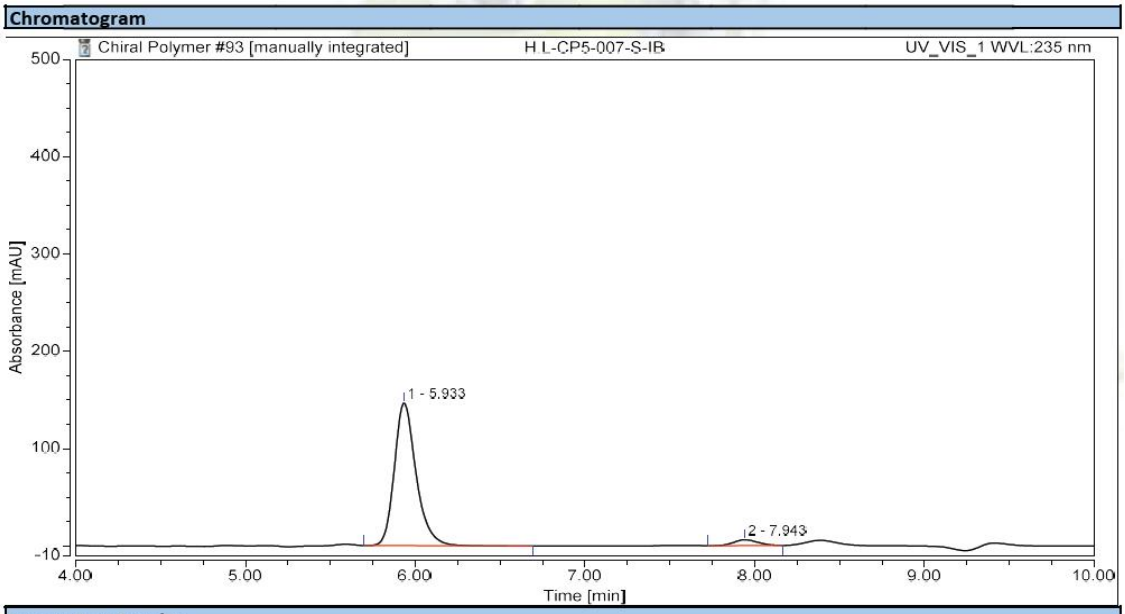
Figure 61. HPLC spectrum of 5c (R or S).



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
n.a.		5.940	0.767	5.956	2.00	3.04	n.a.
n.a.		7.643	37.542	189.850	98.00	96.96	n.a.
Total:			**38.310**	**195.806**	**100.00**	**100.00**	

Figure 62. HPLC spectrum of 5cR, 96% ee.

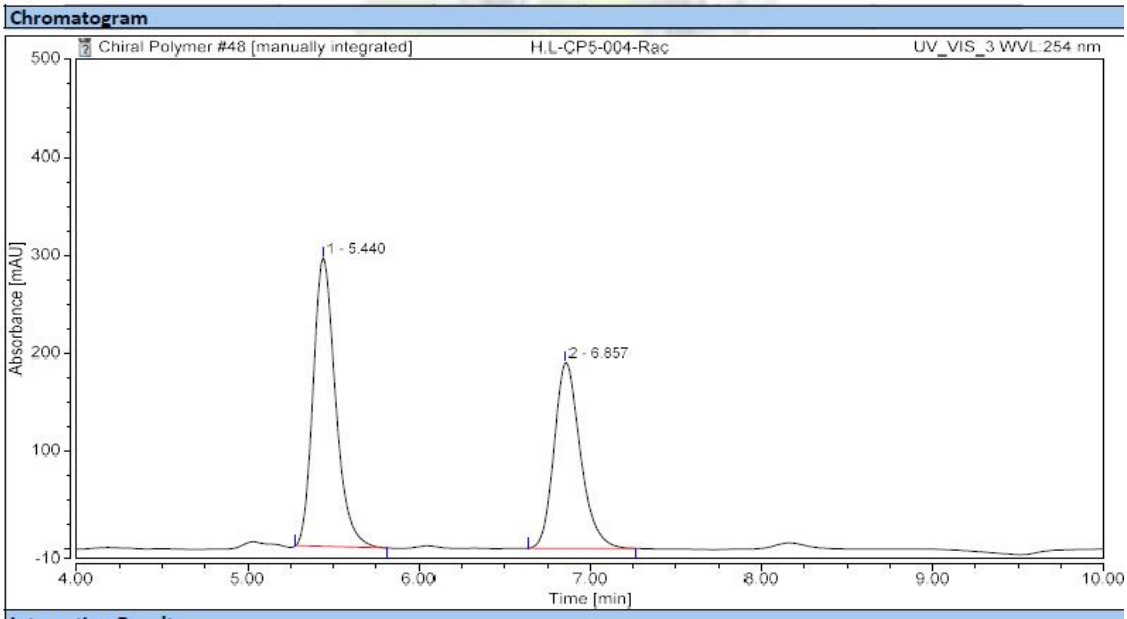


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
n.a.		5.933	21.700	146.712	95.72	96.12	n.a.
n.a.		7.943	0.969	5.921	4.28	3.88	n.a.
Total:			**22.670**	**152.633**	**100.00**	**100.00**	

Figure 63. HPLC spectrum of 5cS, 91% ee.

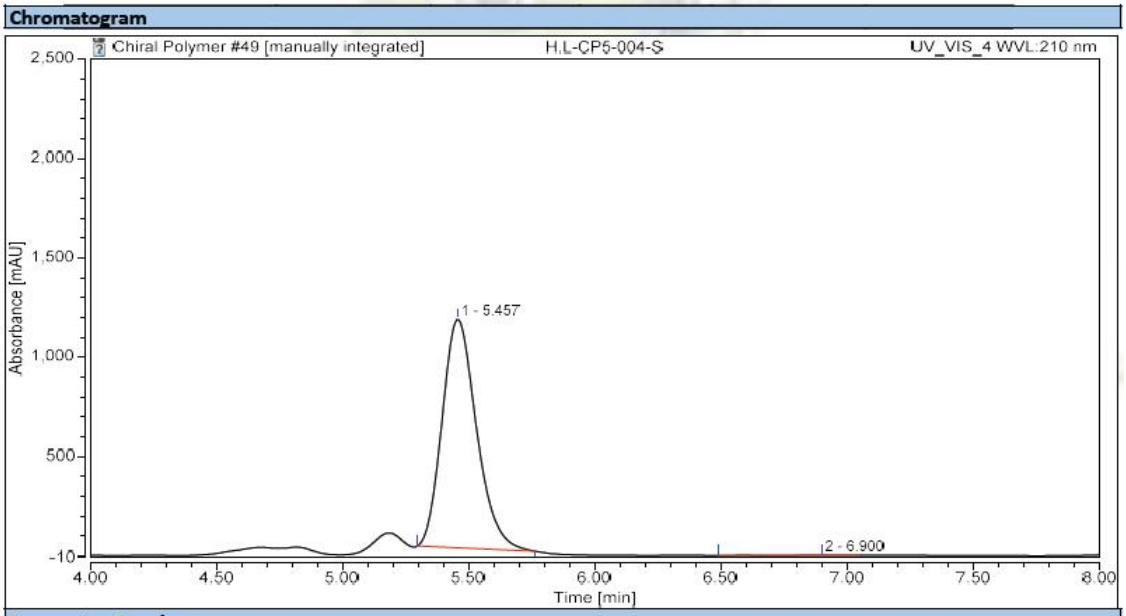
HPLC conditions: Daicel IC column; hexane/2-propanol = 90/10, 1 mL/min



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
n.a.		5.440	44.621	294.575	56.97	60.83	n.a.
n.a.		6.857	33.703	189.670	43.03	39.17	n.a.
Total:			**78.324**	**484.245**	**100.00**	**100.00**	

Figure 64. HPLC spectrum of 5d (R or S).

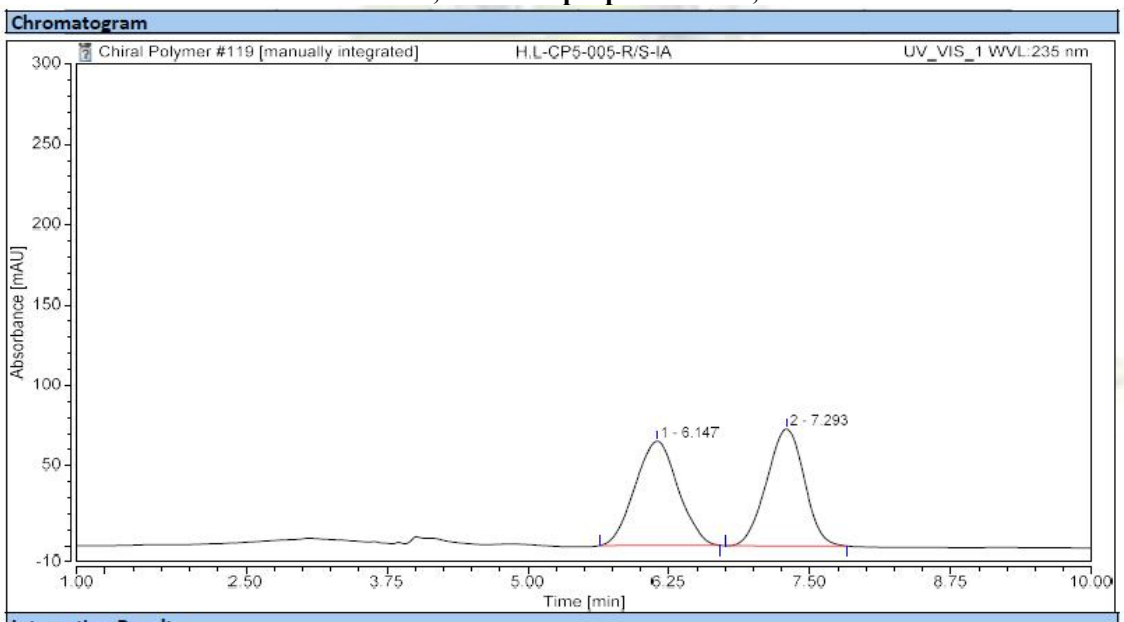


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
n.a.		5.457	181.531	1149.670	99.98	99.97	n.a.
n.a.		6.900	0.031	0.360	0.02	0.03	n.a.
Total:			**181.562**	**1150.029**	**100.00**	**100.00**	

Figure 65. HPLC spectrum of 5dS, 99% ee.

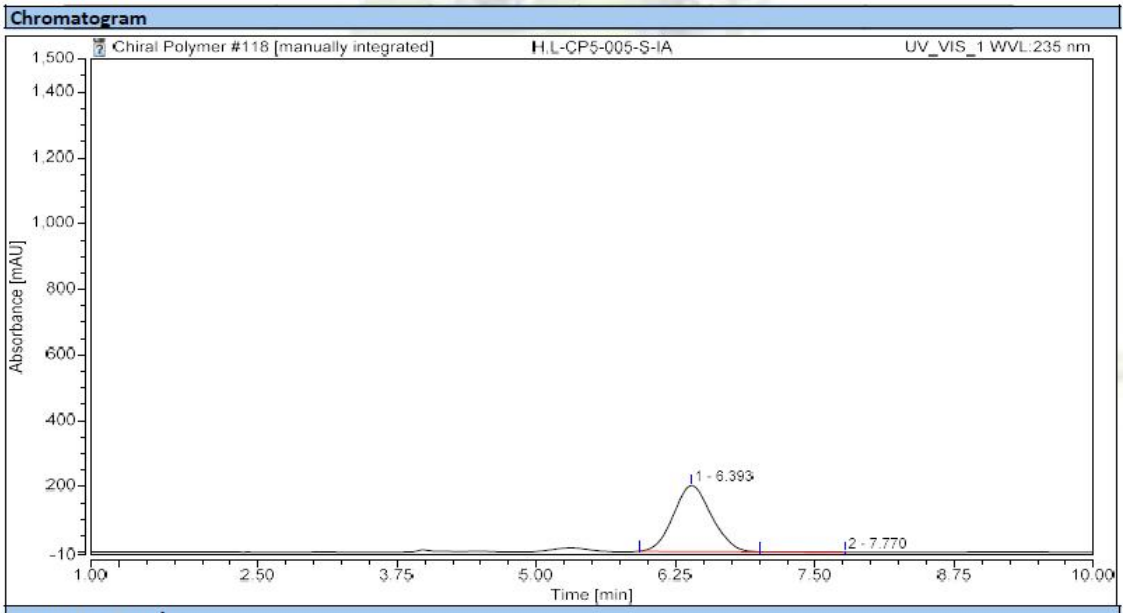
HPLC conditions: Daicel IA column; hexane/2-propanol = 99/1, 1 mL/min



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
n.a.		6.147	28.743	64.915	50.46	47.16	n.a.
n.a.		7.293	28.216	72.731	49.54	52.84	n.a.
Total:			**56.959**	**137.645**	**100.00**	**100.00**	

Figure 66. HPLC spectrum of 5e (R or S).



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
n.a.		6.393	79.541	200.500	99.66	100.00	n.a.
n.a.		7.770	0.270	0.000	0.34	0.00	n.a.
Total:			**79.812**	**200.500**	**100.00**	**100.00**	

Figure 67. HPLC spectrum of 5eS, 99% ee.

For the final 8,8′-dibrominated monomer 6f*S*（6*S in paper*）, the enantiomeric excess could not be determined by chiral HPLC because baseline resolution was not achieved on the available chiral stationary phases under the screened conditions. However, 6eS was prepared from a precursor of 99% ee, and its specific rotation was reproducible and consistent with that expected from the enantioenriched series, supporting retention of configuration during the functionalization step.

6f*S*（6*S in paper*）

Sample	λ (nm)	T (°C)	l (dm)	α (°)	c (g/100 mL)	Solvent	[α]D^T
6S (or 6A)	589	21.8	1.00	0.113	0.05	$CHCl_3$	226

For the single-enantiomer products 4A*S*, 5A*S*, and 6A*S*, CD measurements were conducted.

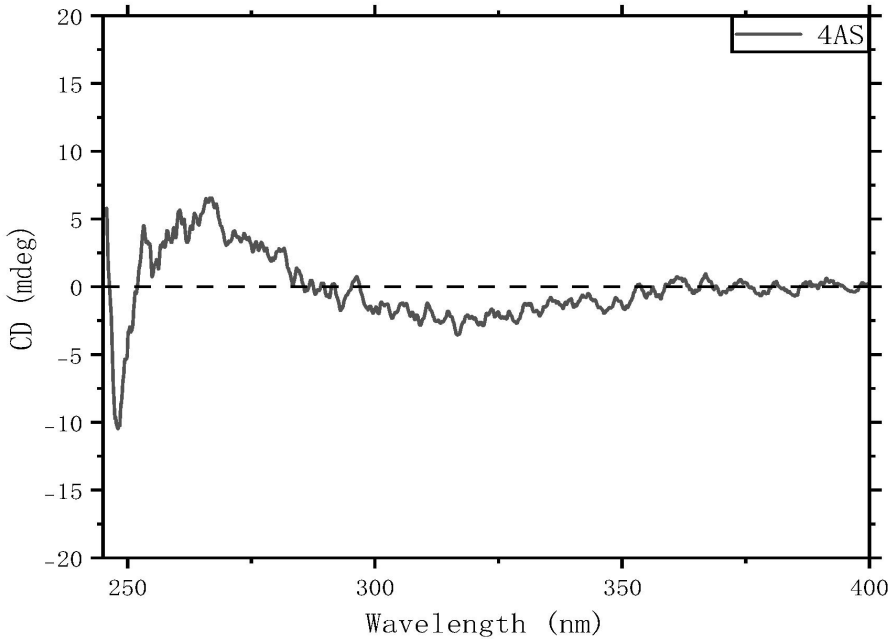


Figure 69. CD spectrum of 4AS.

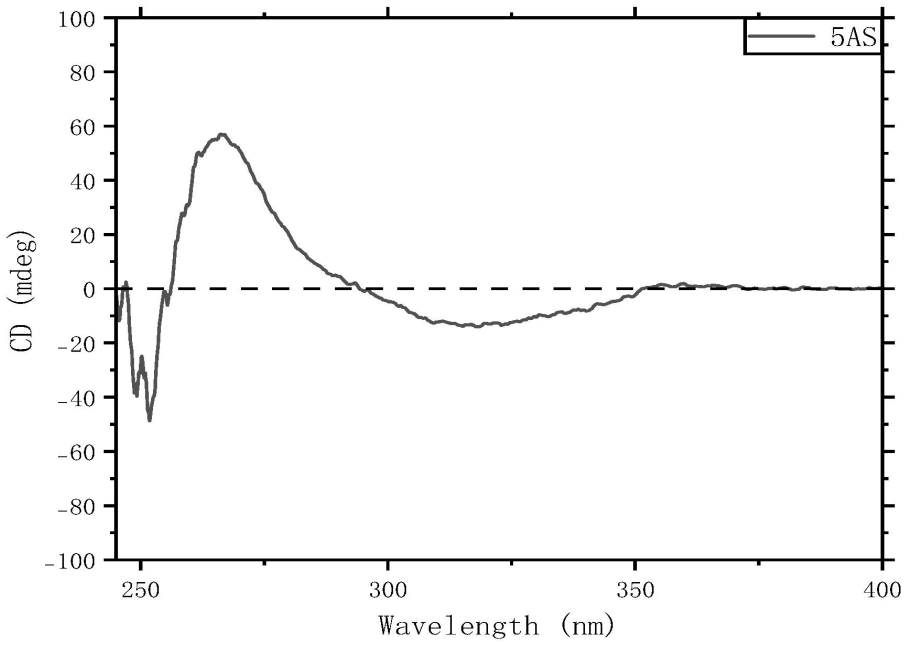


Figure 69. CD spectrum of 5AS.

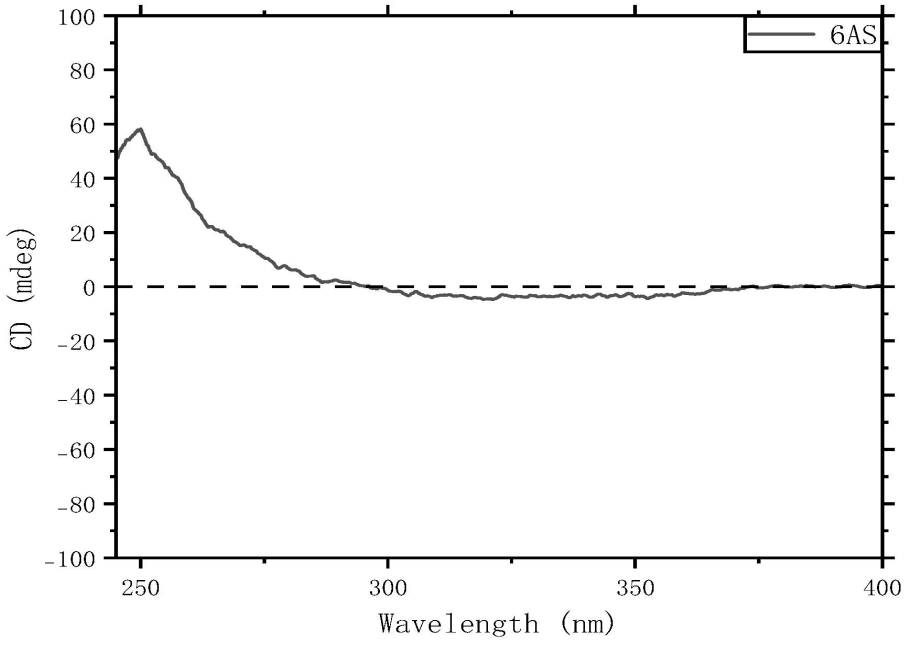
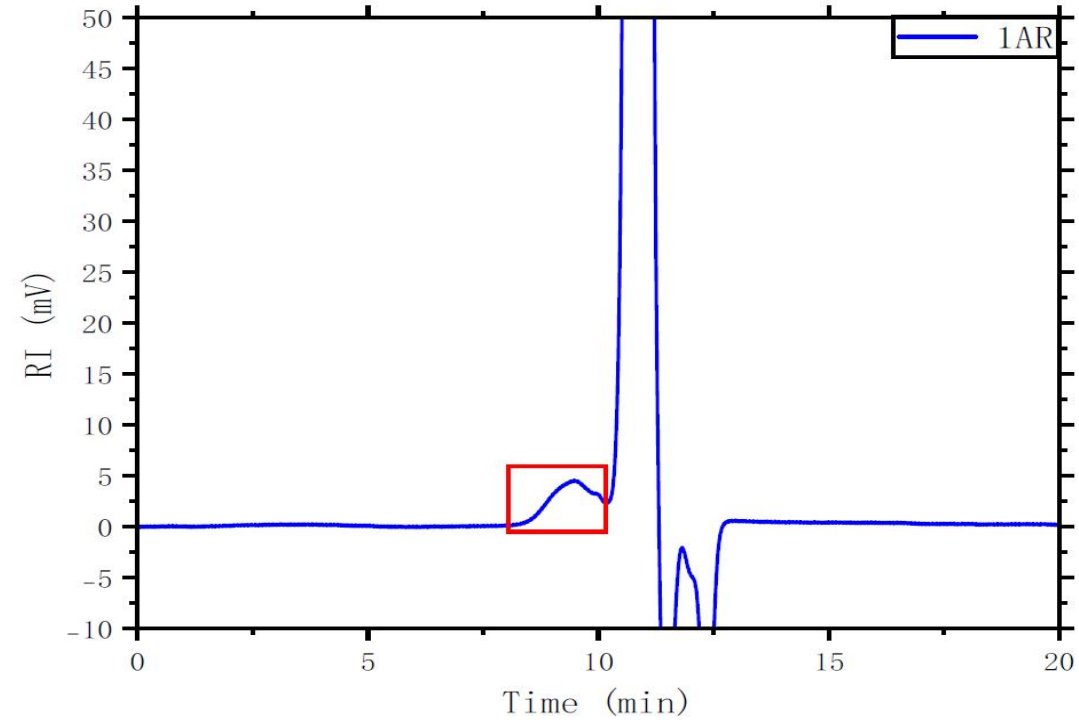
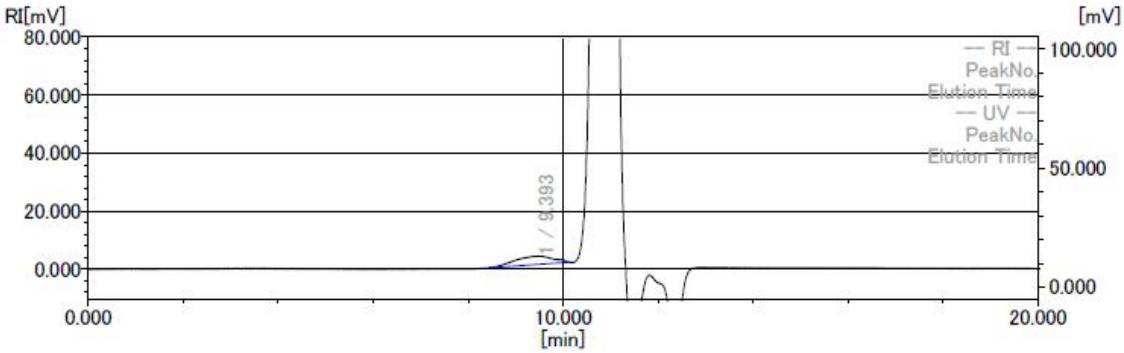


Figure 70. CD spectrum of 6AS.

5.GPC Spectra

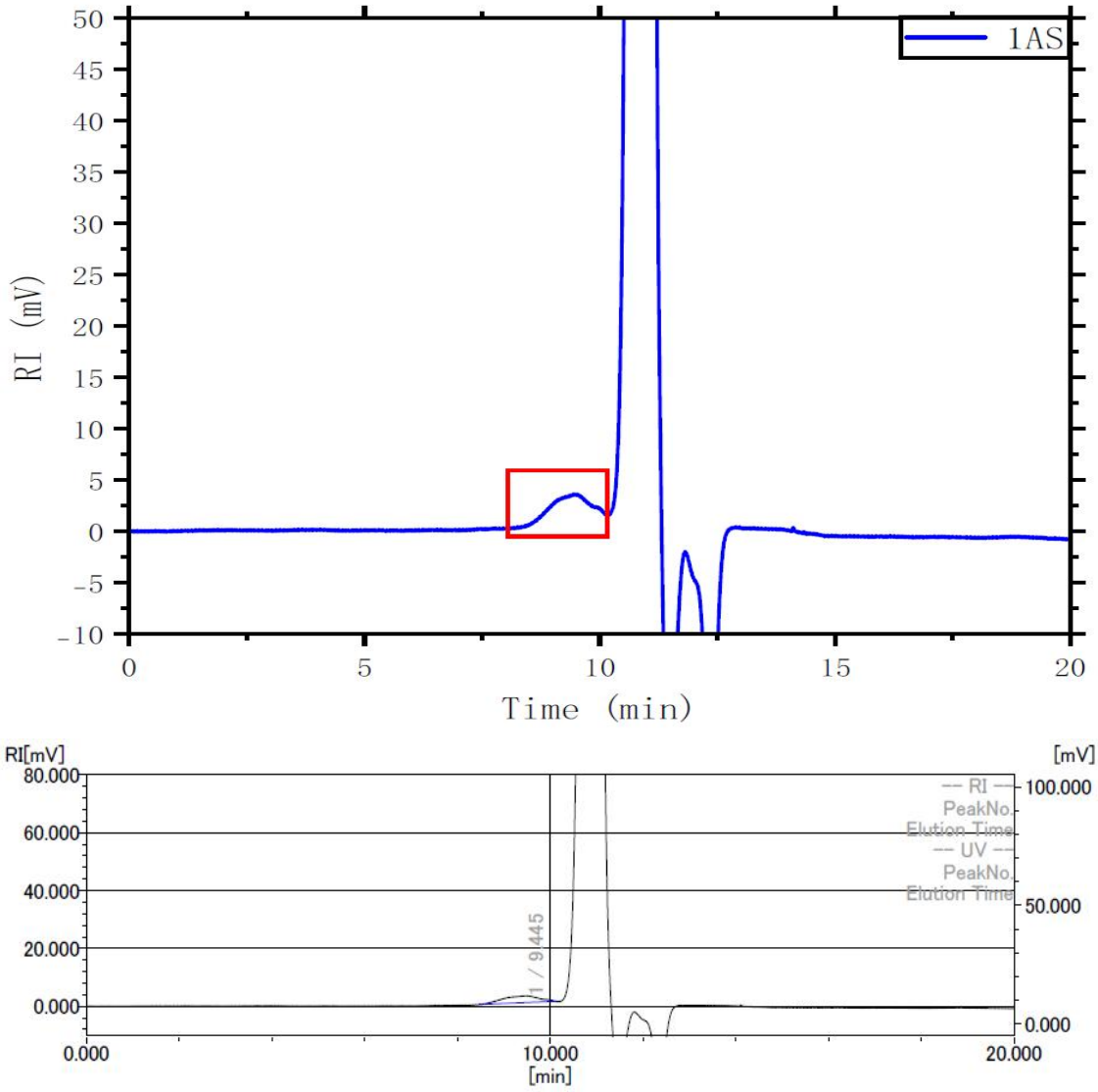




<Result of Molecular Weight Calculation>(RI)
Peak1Base Peak

	[min]	[mV]	[mol]		
Peak Start	8.477	0.518	29185	Mn	5606
Peak Top	9.393	4.489	6225	Mw	7730
Peak End	10.140	2.379	1768	Mz	10415
				Mz+1	13180
				Mv	7730
Height[mV]			2.945	Mp	6226
Area[mV s]			161.344	Mz/Mw	1.347
Area%[%]			100.000	Mw/Mn	1.379
[Eta]			7730.24266	Mz+1/Mw	1.705

Figure 71. GPC spectrum of 1AR.

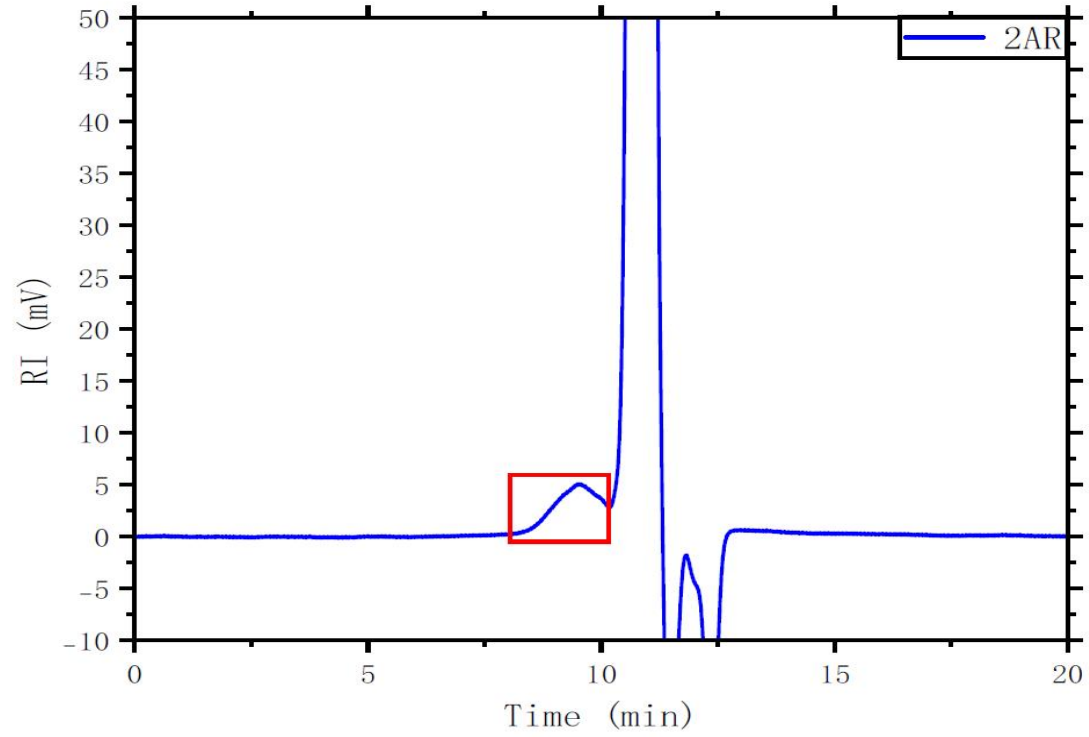


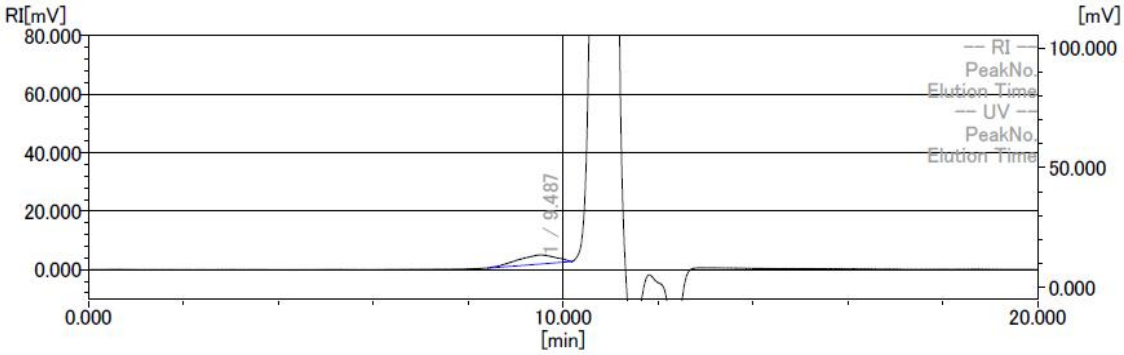
<Result of Molecular Weight Calculation>(RI)

Peak1Base Peak

	[min]	[mV]	[mol]		
Peak Start	8.480	0.613	29021	Mn	5841
Peak Top	9.445	3.643	5706	Mw	7921
Peak End	10.130	1.729	1798	Mz	10494
				Mz+1	13121
				Mv	7921
Height[mV]			2.377	Mp	5707
Area[mV s]			126.838	Mz/Mw	1.325
Area%[%]			100.000	Mw/Mn	1.356
[Eta]			7921.00129	Mz+1/Mw	1.657

Figure 72. GPC spectrum of 1AS.



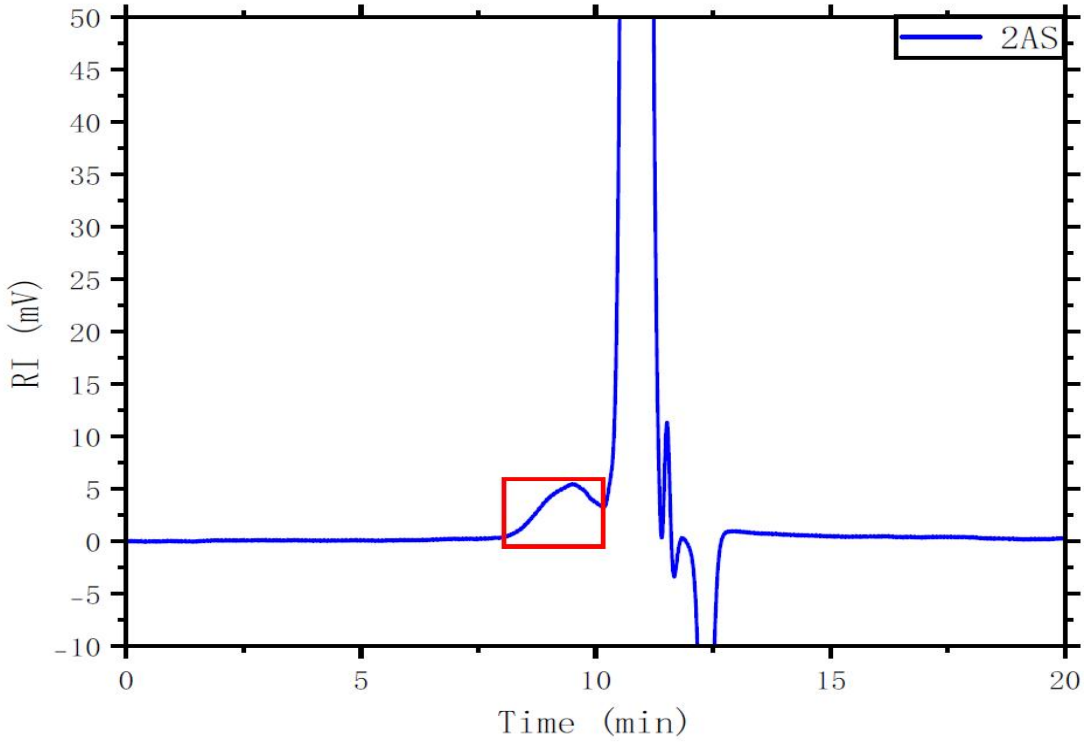


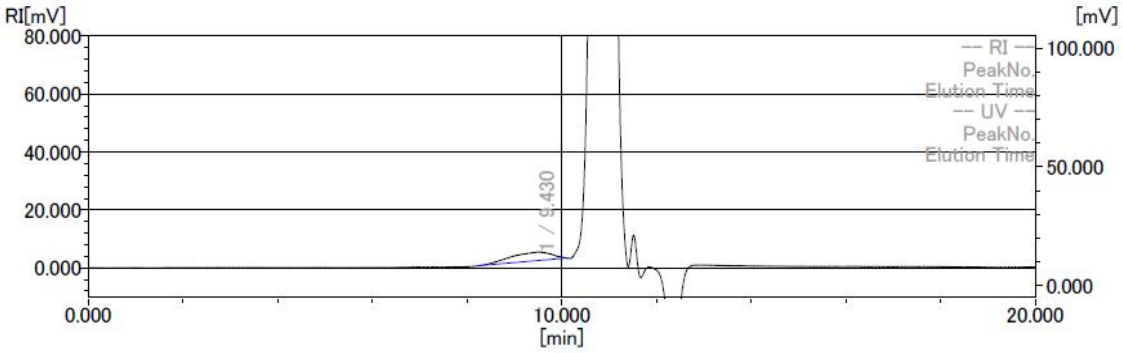
<Result of Molecular Weight Calculation>(RI)

Peak1Base Peak

	[min]	[mV]	[mol]		
Peak Start	8.430	0.516	31573	Mn	5192
Peak Top	9.487	5.068	5319	Mw	7378
Peak End	10.193	2.746	1616	Mz	10464
				Mz+1	13903
				Mv	7378
Height[mV]			3.216	Mp	5320
Area[mV s]			176.910	Mz/Mw	1.418
Area%[%]			100.000	Mw/Mn	1.421
[Eta]			7377.95155	Mz+1/Mw	1.884

Figure 73. GPC spectrum of 2AR.



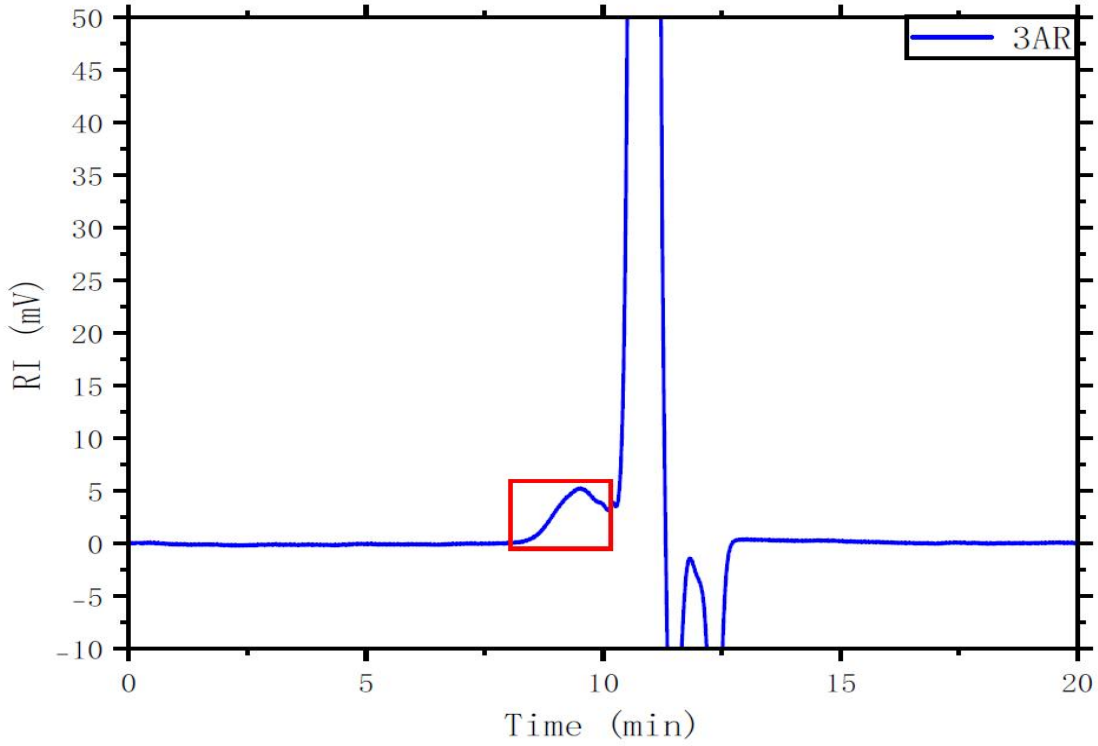


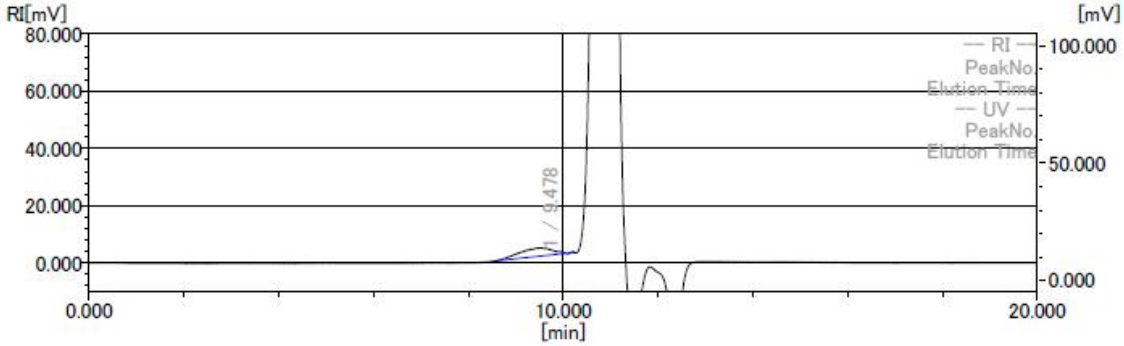
<Result of Molecular Weight Calculation>(RI)

Peak1Base Peak

	[min]	[mV]	[mol]		
Peak Start	8.237	0.761	43735	Mn	6255
Peak Top	9.430	5.404	5852	Mw	9053
Peak End	10.097	3.398	1902	Mz	13022
				Mz+1	17379
				Mv	9053
Height[mV]			2.951	Mp	5380
Area[mV s]			177.510	Mz/Mw	1.439
Area%[%]			100.000	Mw/Mn	1.447
[Eta]			9052.66750	Mz+1/Mw	1.920

Figure 74. GPC spectrum of 2AS.

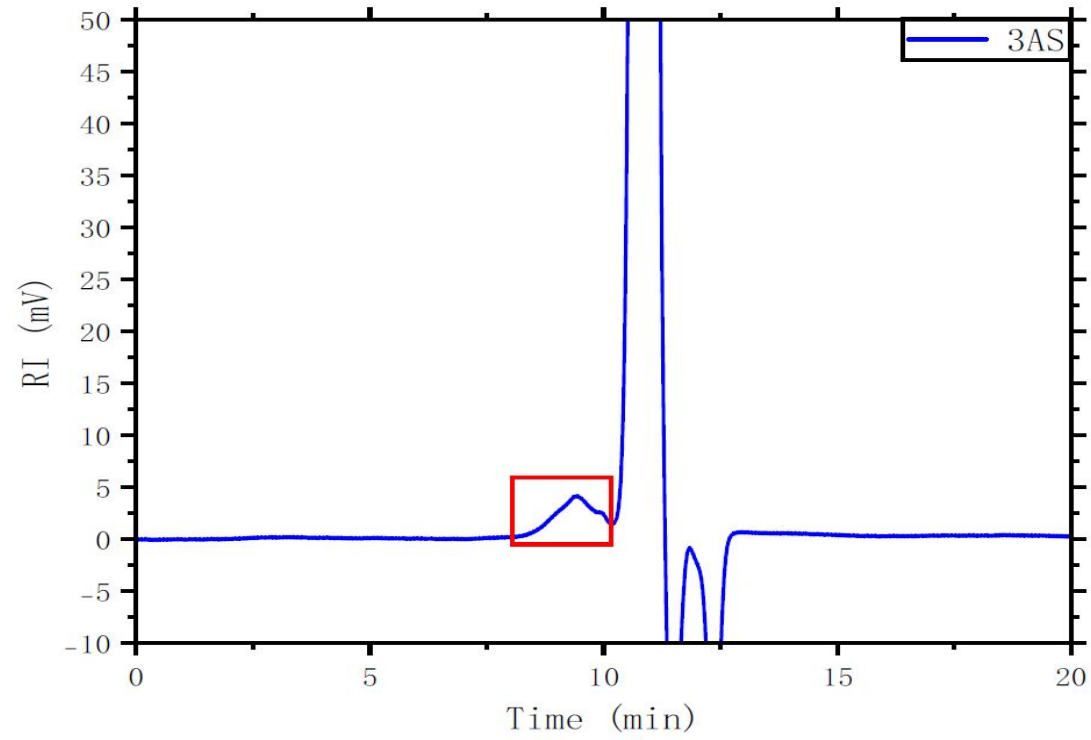


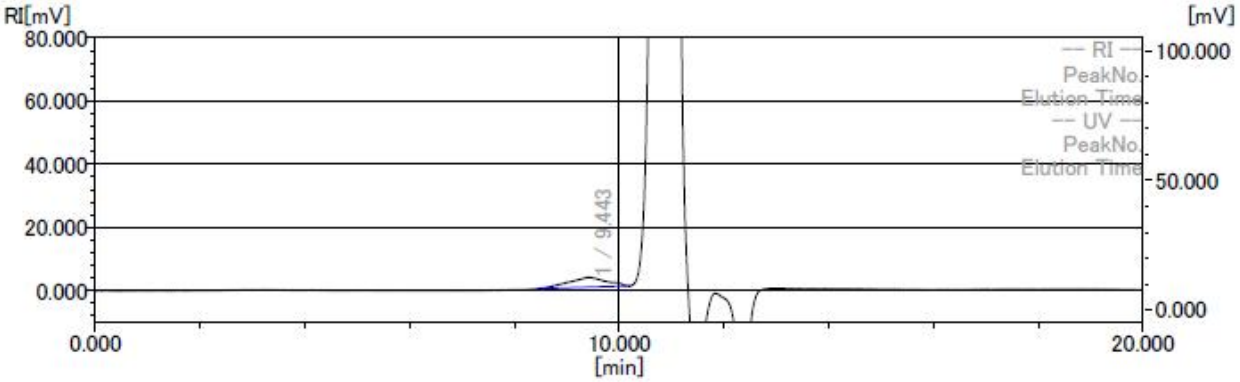


<Result of Molecular Weight Calculation>(RI)
Peak1Base Peak

	[min]	[mV]	[mol]		
Peak Start	8.563	0.658	25219	Mn	5511
Peak Top	9.478	5.253	5394	Mw	7240
Peak End	10.233	3.674	1511	Mz	9332
				Mz+1	11500
				Mv	7240
Height[mV]			2.943	Mp	5395
Area[mV s]			144.168	Mz/Mw	1.289
Area%[%]			100.000	Mw/Mn	1.314
[Eta]			7240.15405	Mz+1/Mw	1.588

Figure 75. GPC spectrum of 3AR.

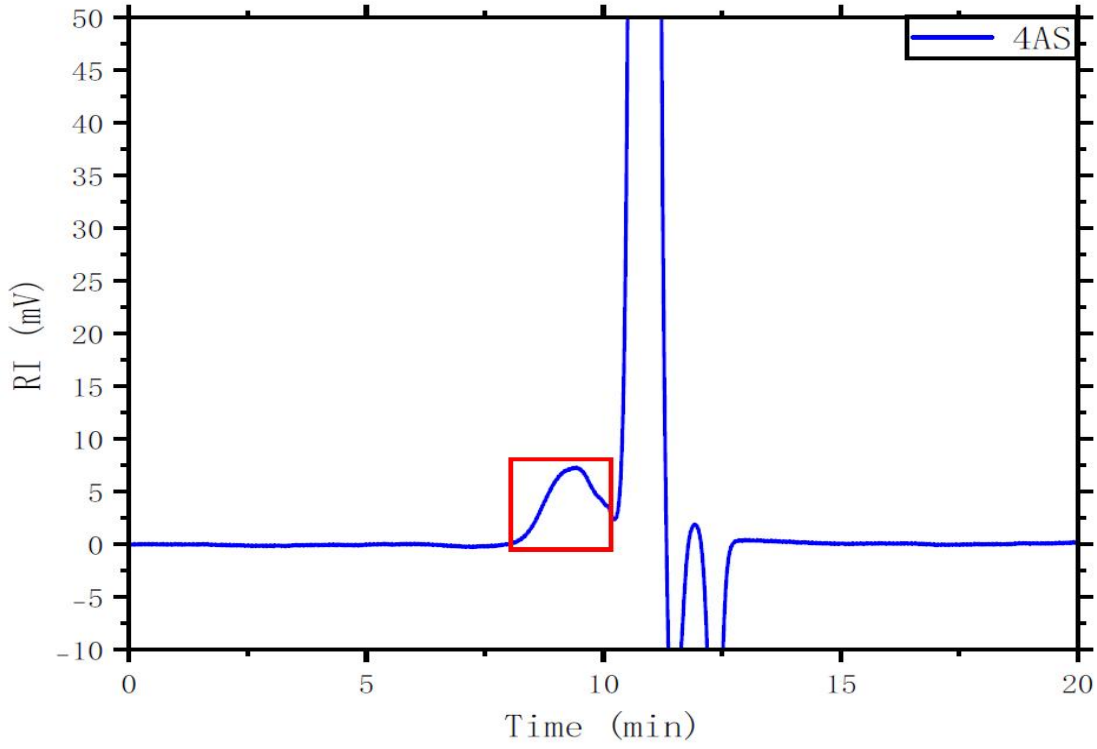


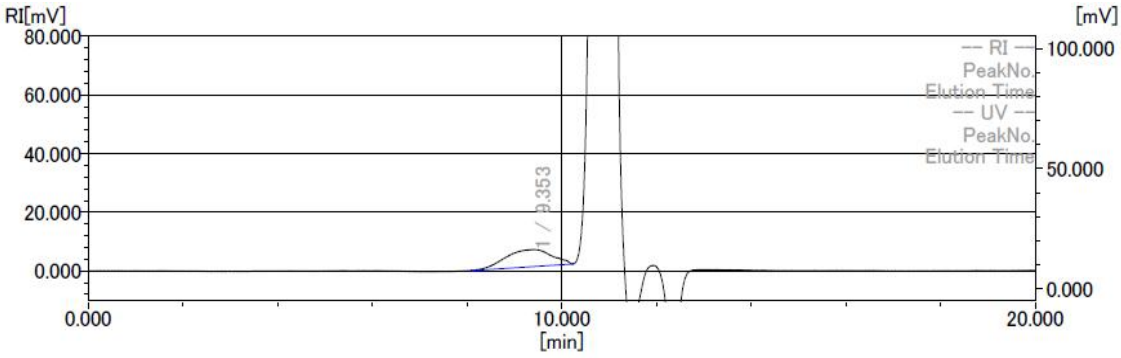


<Result of Molecular Weight Calculation>(RI)
Peak1Base Peak

	[min]	[mV]	[mol]		
Peak Start	8.468	0.584	29598	Mn	5457
Peak Top	9.443	4.216	5722	Mw	7567
Peak End	10.192	1.483	1621	Mz	10362
				Mz+1	13380
				Mv	7567
Height[mV]			3.123	Mp	5723
Area[mV s]			155.640	Mz/Mw	1.369
Area%[%]			100.000	Mw/Mn	1.387
[Eta]			7566.52977	Mz+1/Mw	1.768

Figure 76. GPC spectrum of 3AS.



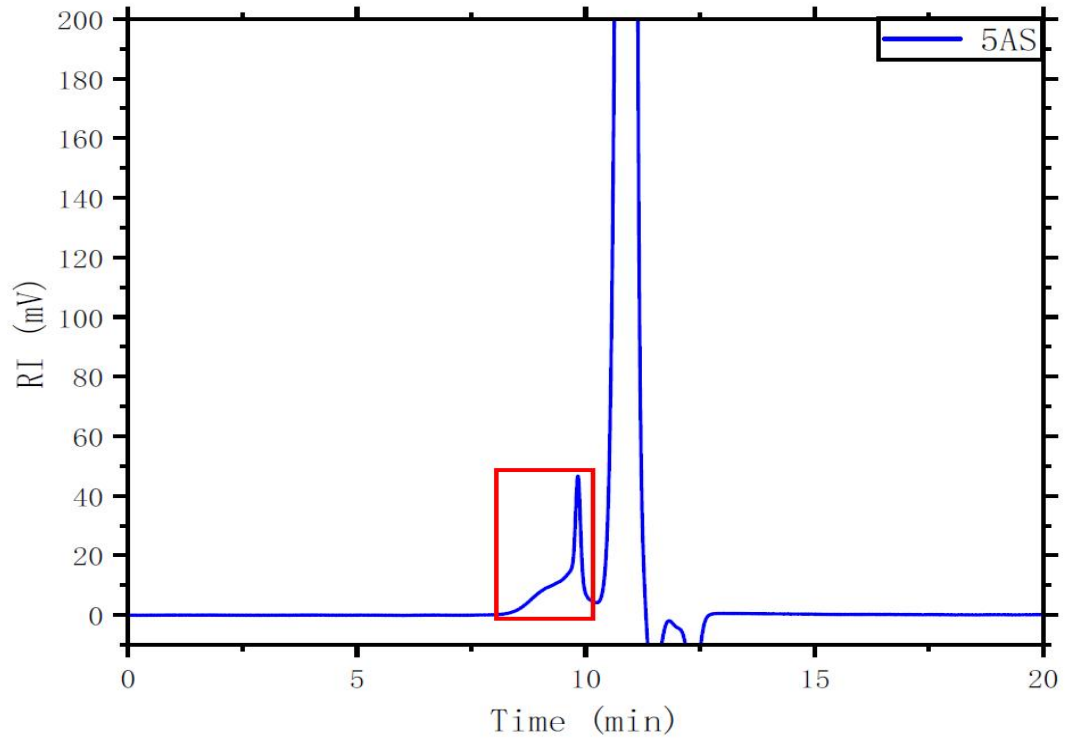


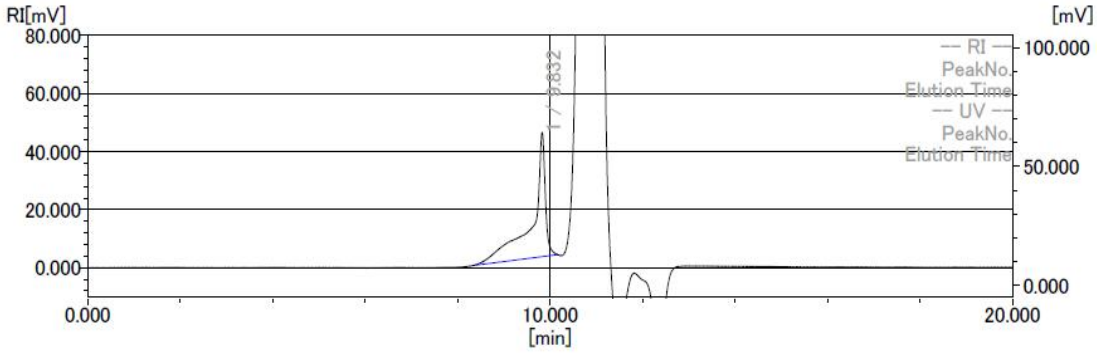
<Result of Molecular Weight Calculation>(RI)

Peak1Base Peak

	[min]	[mV]	[mol]		
Peak Start	8.103	0.105	54755	Mn	5986
Peak Top	9.353	7.292	6660	Mw	9462
Peak End	10.243	2.349	1486	Mz	14442
				Mz+1	20028
				Mv	9462
Height[mV]			5.876	Mp	6660
Area[mV s]			396.434	Mz/Mw	1.526
Area%[%]			100.000	Mw/Mn	1.581
[Eta]			9462.09978	Mz+1/Mw	2.117

Figure 77. GPC spectrum of 4AS.



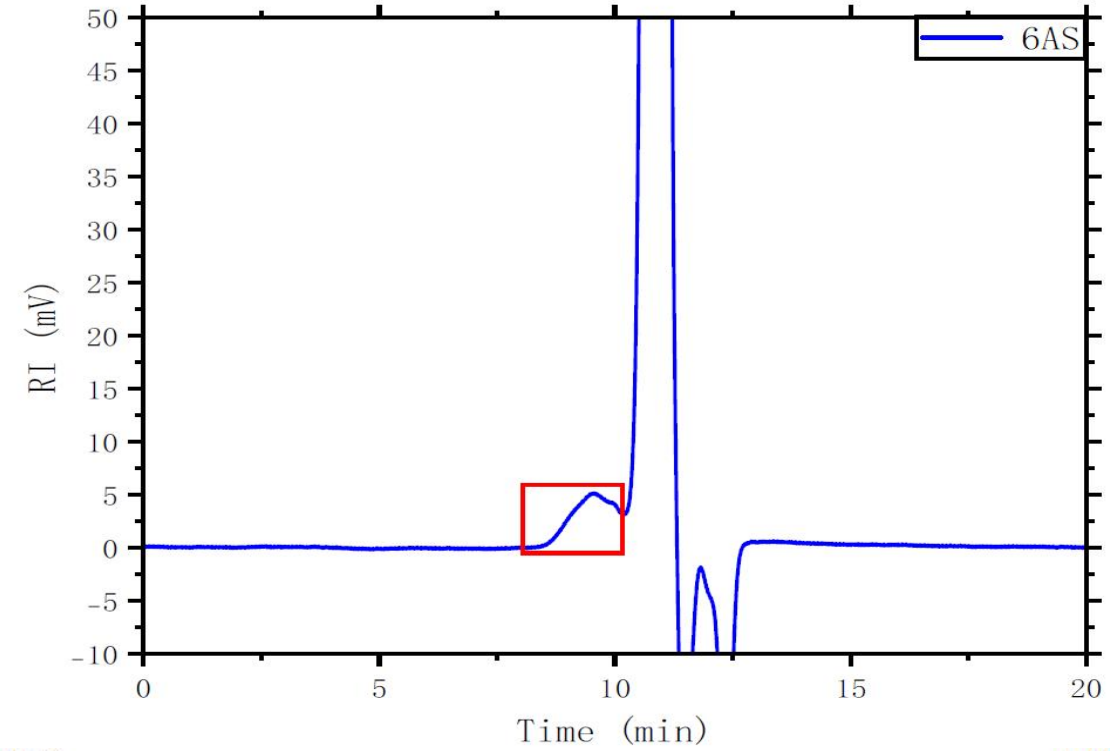


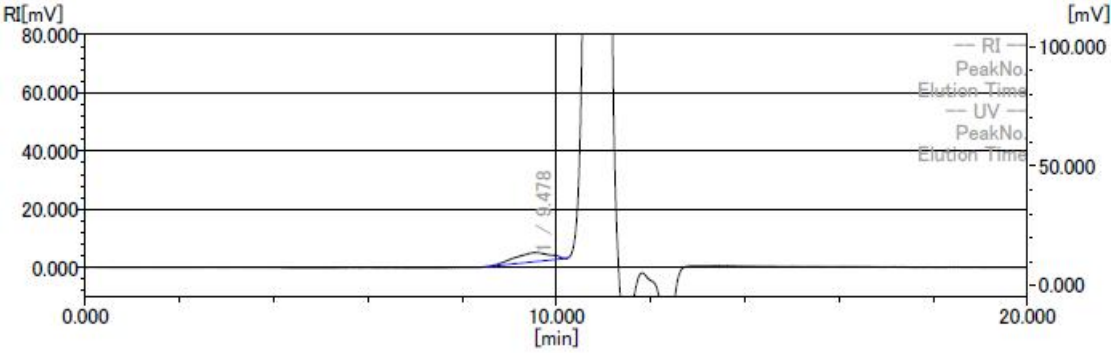
<Result of Molecular Weight Calculation>(RI)

Peak1Base Peak

	[min]	[mV]	[mol]		
Peak Start	8.365	0.797	35229	Mn	4135
Peak Top	9.832	46.632	2974	Mw	5939
Peak End	10.172	4.489	1676	Mz	9551
				Mz+1	14105
				Mv	5939
Height[mV]			42.838	Mp	2974
Area[mV s]			841.837	Mz/Mw	1.608
Area%[%]			100.000	Mw/Mn	1.436
[Eta]			5939.24298	Mz+1/Mw	2.375

Figure 78. GPC spectrum of 5AS.





<Result of Molecular Weight Calculation>(RI)
Peak1Base Peak

	[min]	[mV]	[mol]		
Peak Start	8.492	0.217	28456	Mn	4912
Peak Top	9.478	5.108	5394	Mw	6667
Peak End	10.210	3.117	1571	Mz	8961
				Mz+1	11424
				Mv	6667
Height[mV]			3.226	Mp	5395
Area[mV s]			167.197	Mz/Mw	1.344
Area%[%]			100.000	Mw/Mn	1.357
[Eta]			6667.20981	Mz+1/Mw	1.714

Figure 79. GPC spectrum of 6AS.

6.SEM Imagines

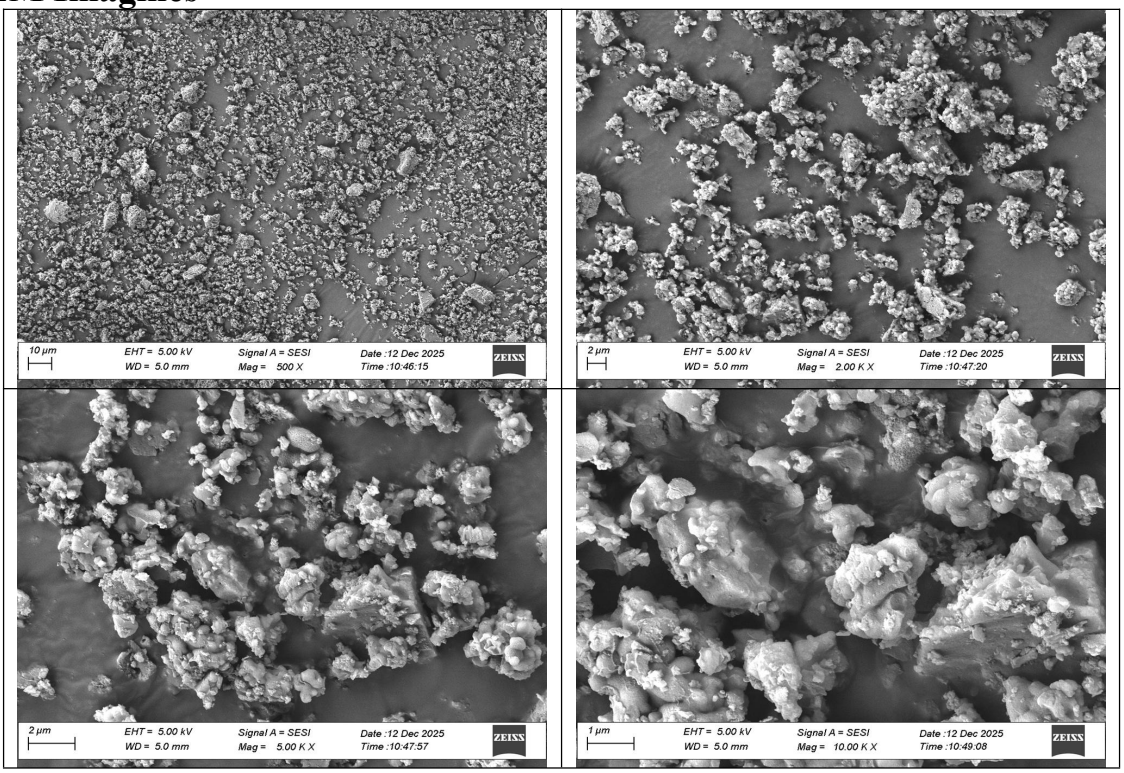


Figure 80. SEM imagines of 1AR.

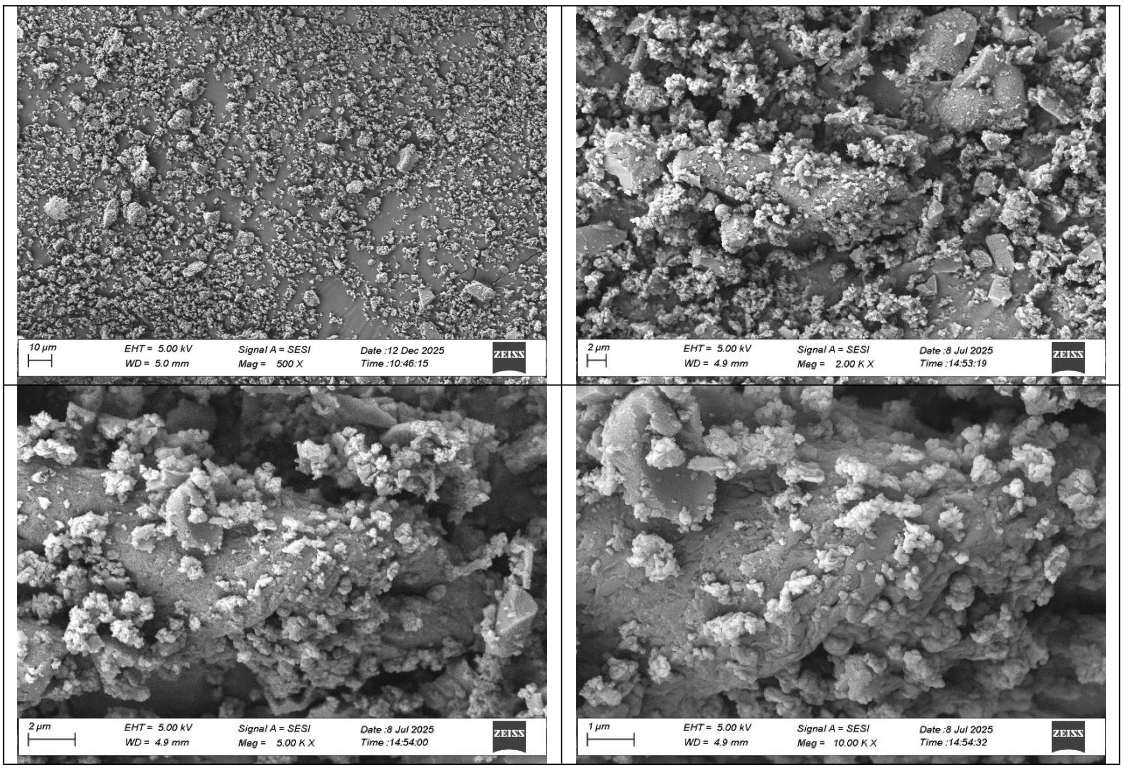


Figure 81. SEM imagines of 1AS.

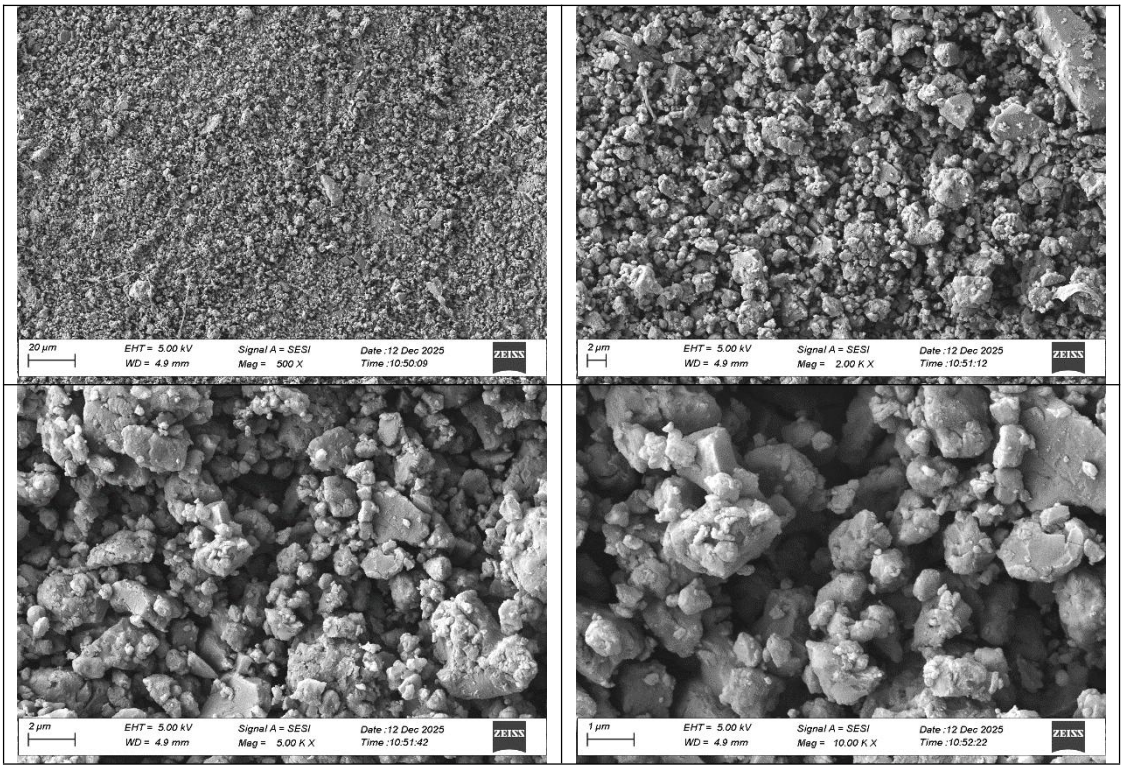


Figure 80. SEM imagines of 2AR.

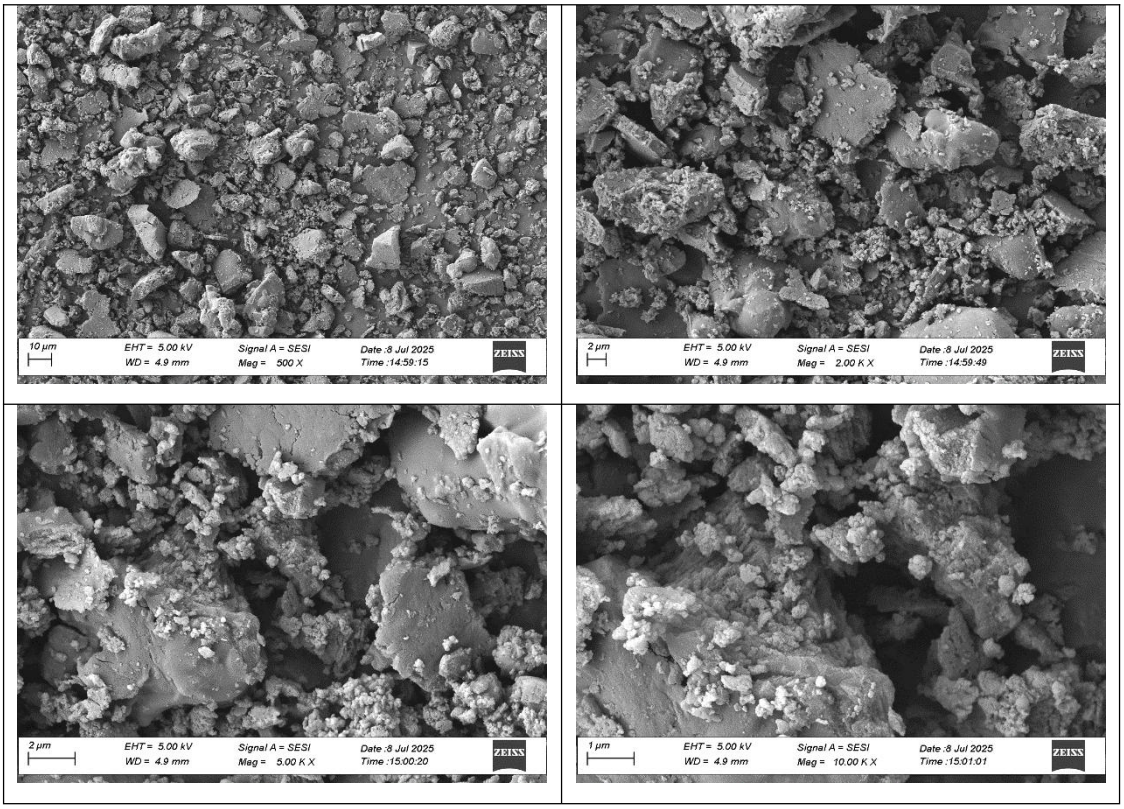


Figure 81. SEM imagines of 2AS.

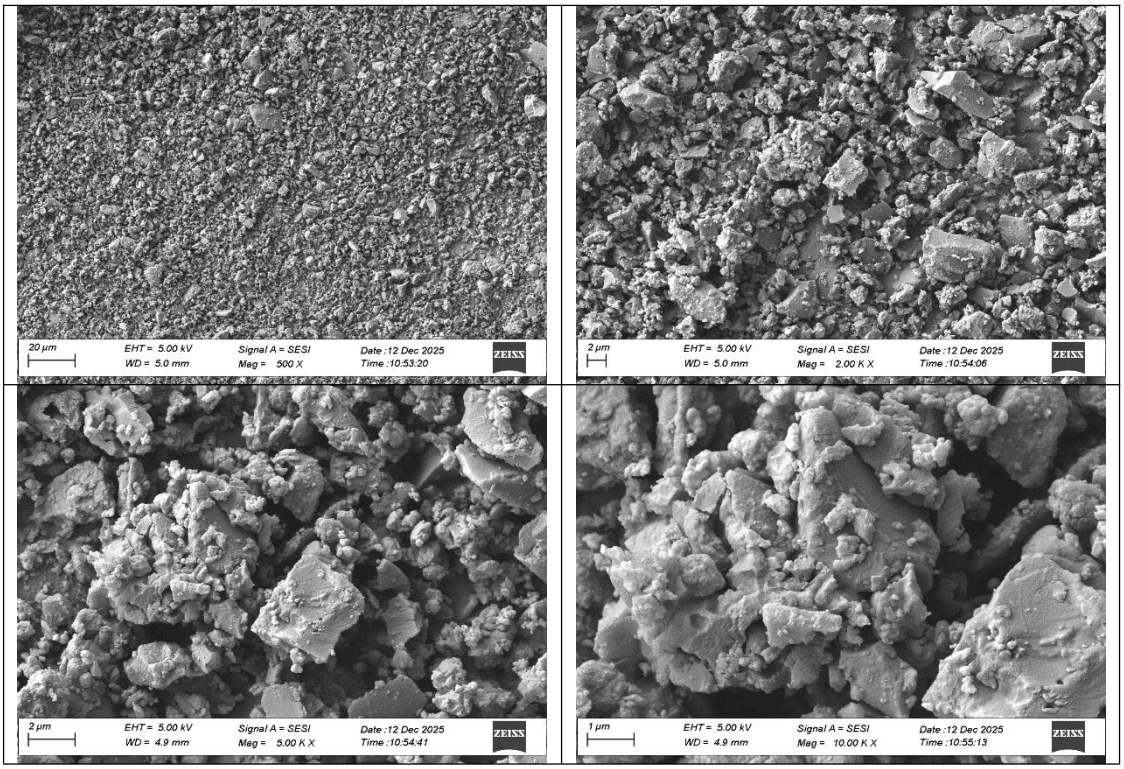


Figure 80. SEM imagines of 3AR.

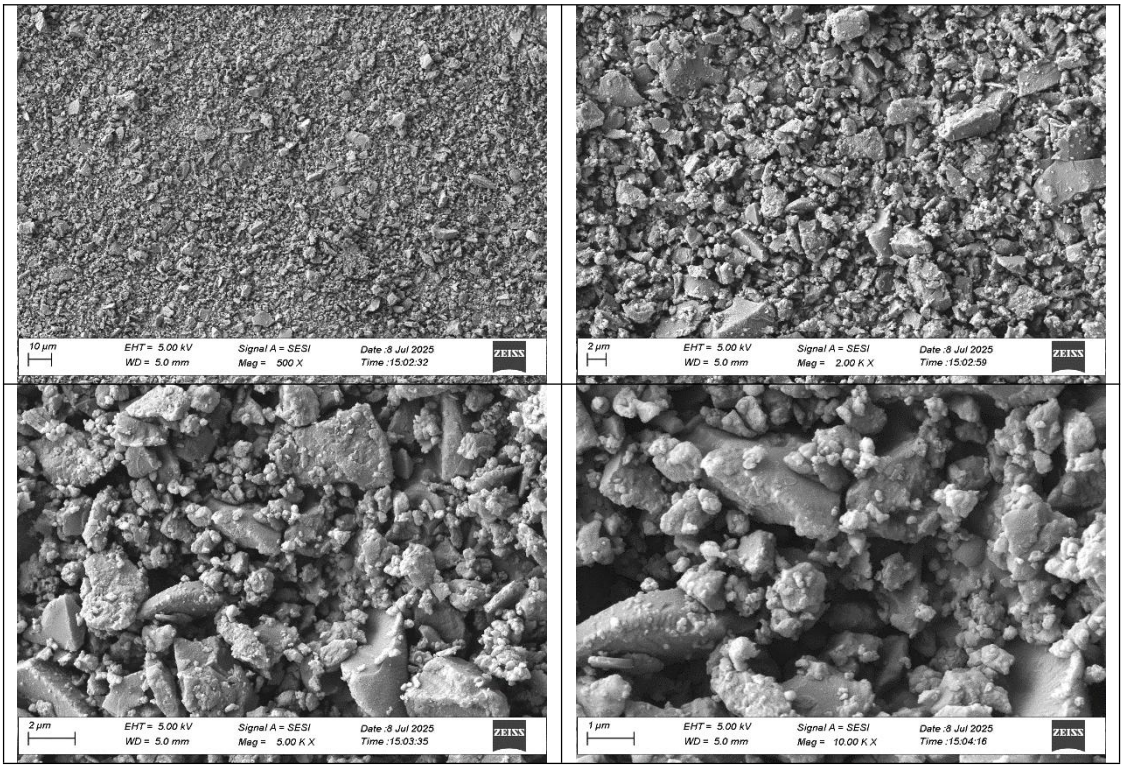


Figure 81. SEM imagines of 3AS.

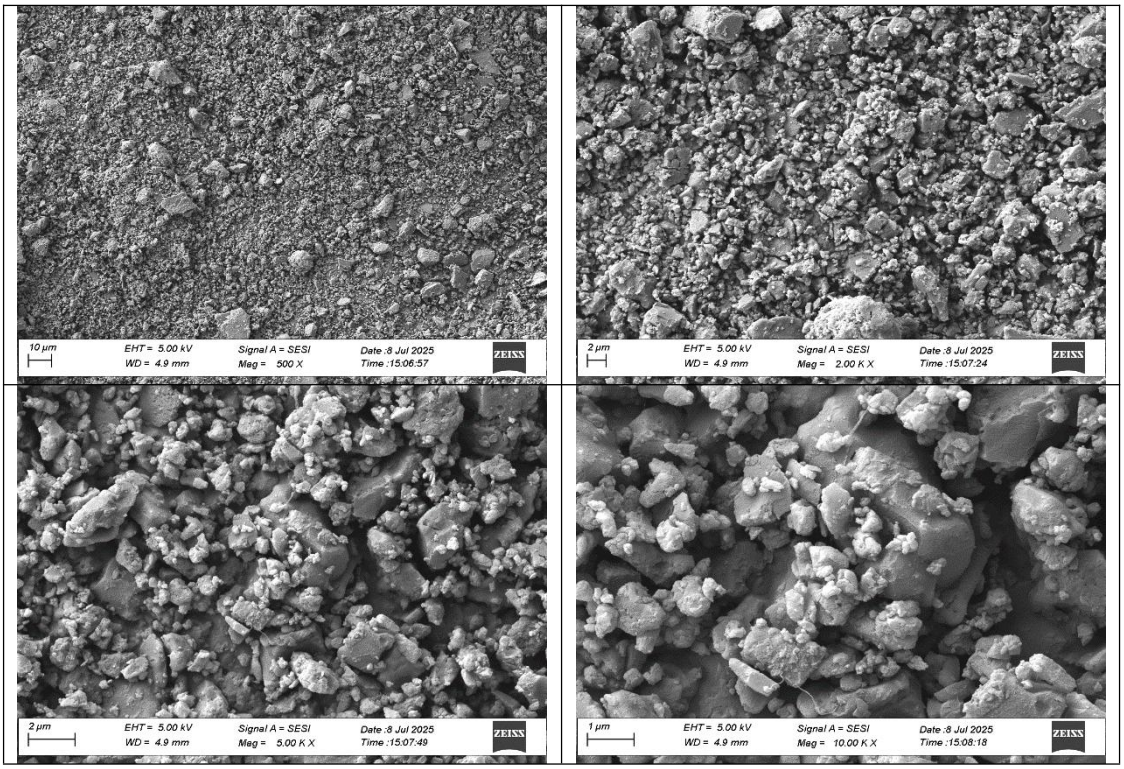


Figure 80. SEM imagines of 4AS.

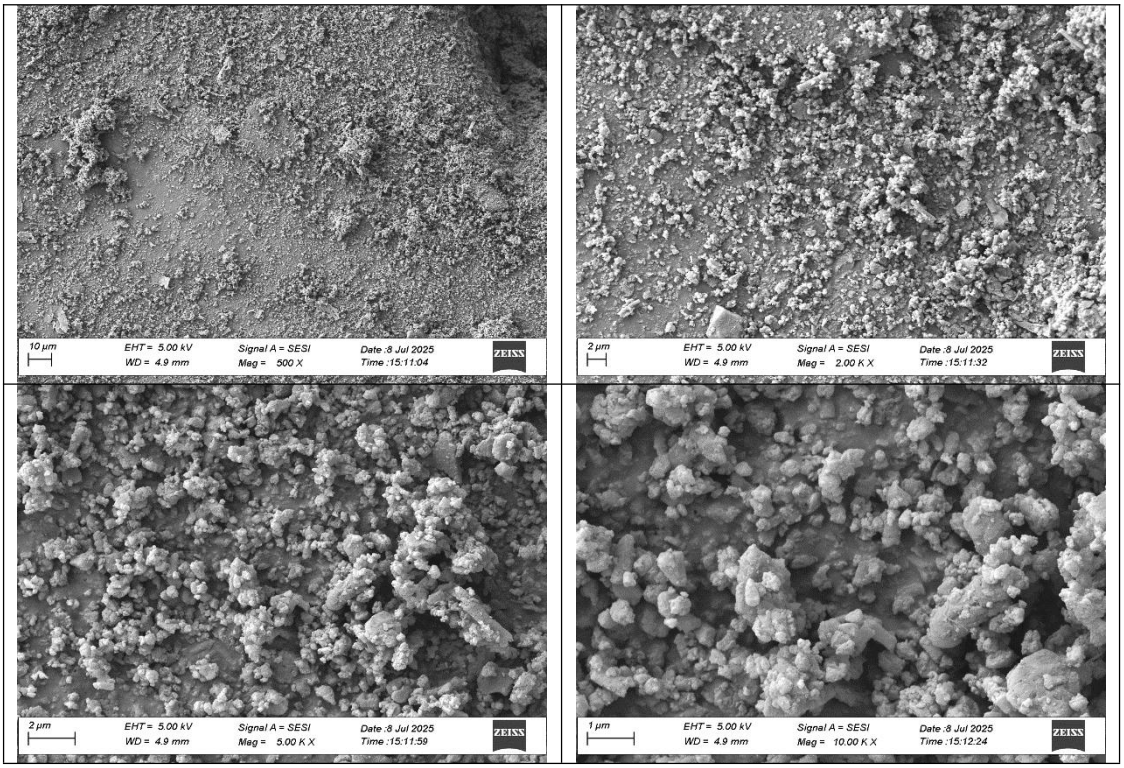


Figure 81. SEM imagines of 5AS.

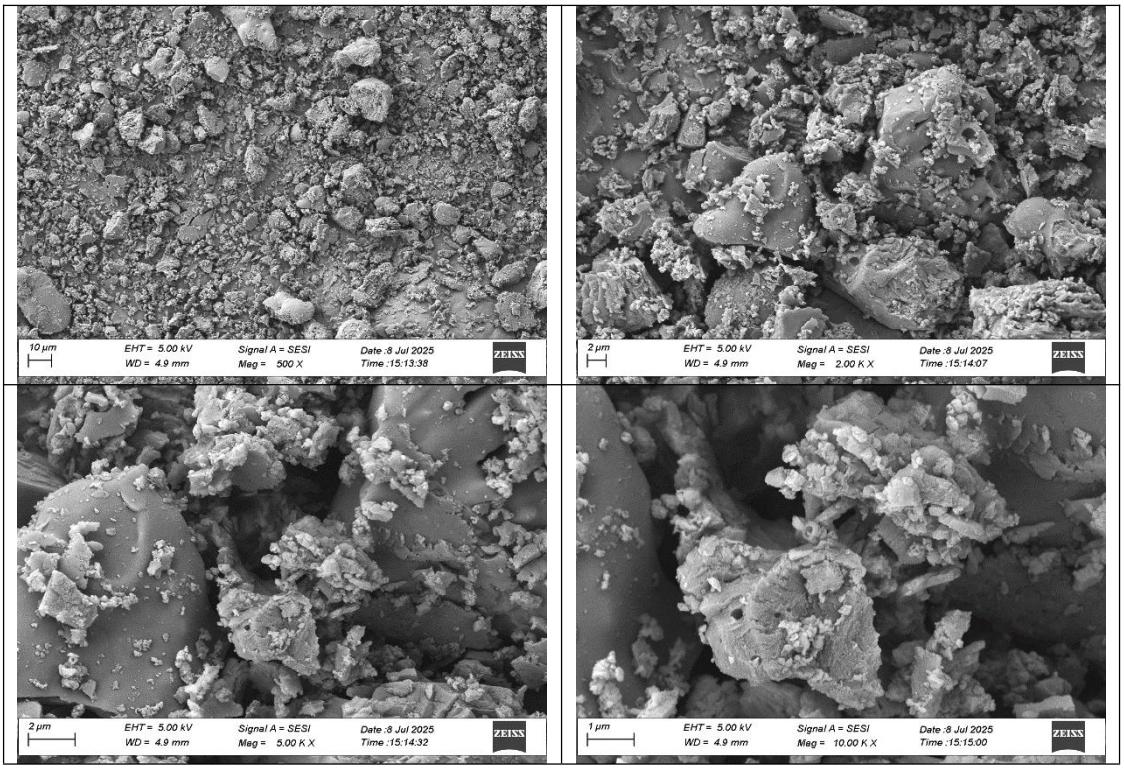


Figure 80. SEM imagines of 6AS.

7.AIE Spectra

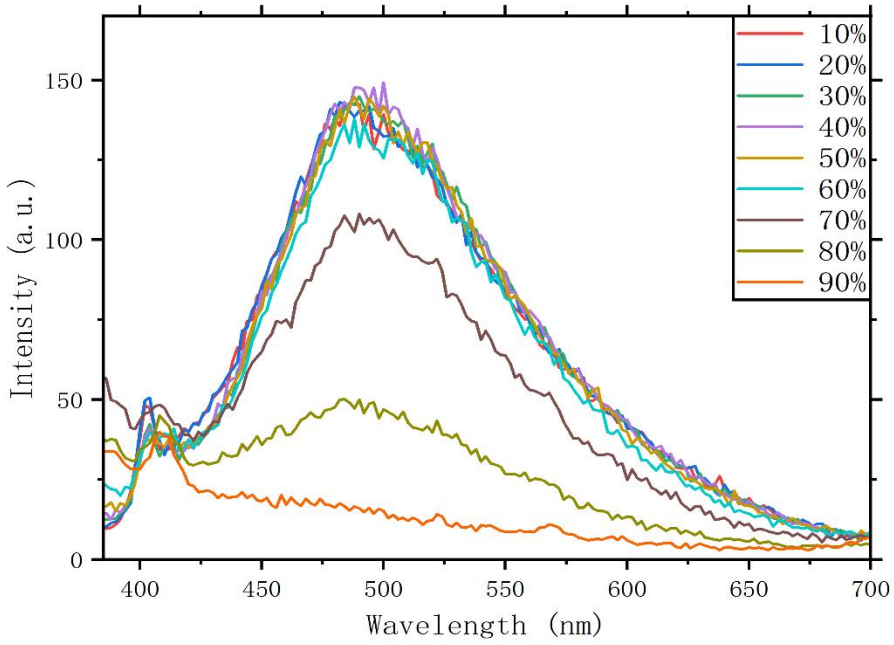


Figure 89. PL Spectra of 1AR.

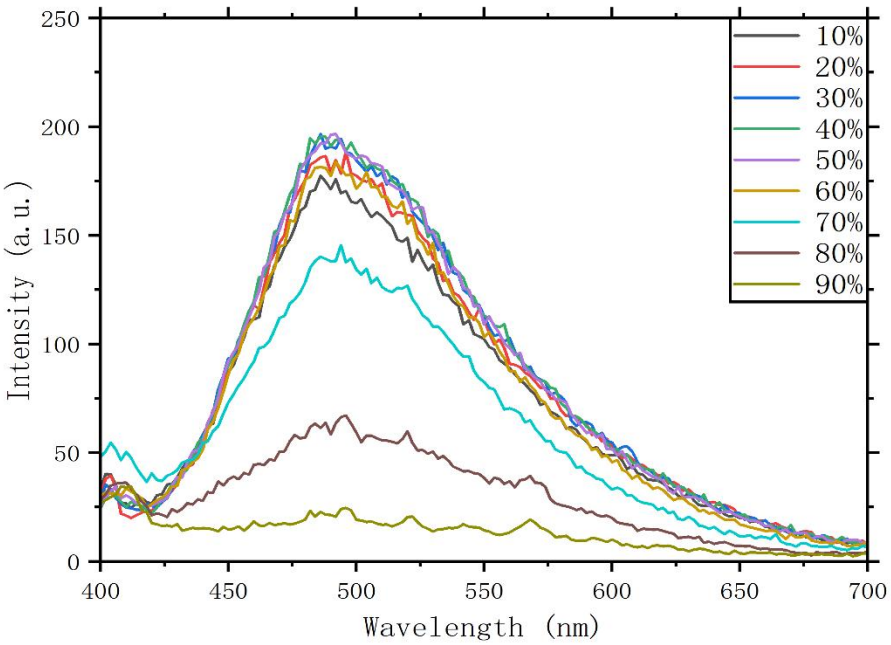


Figure 90. PL Spectra of 2AR.

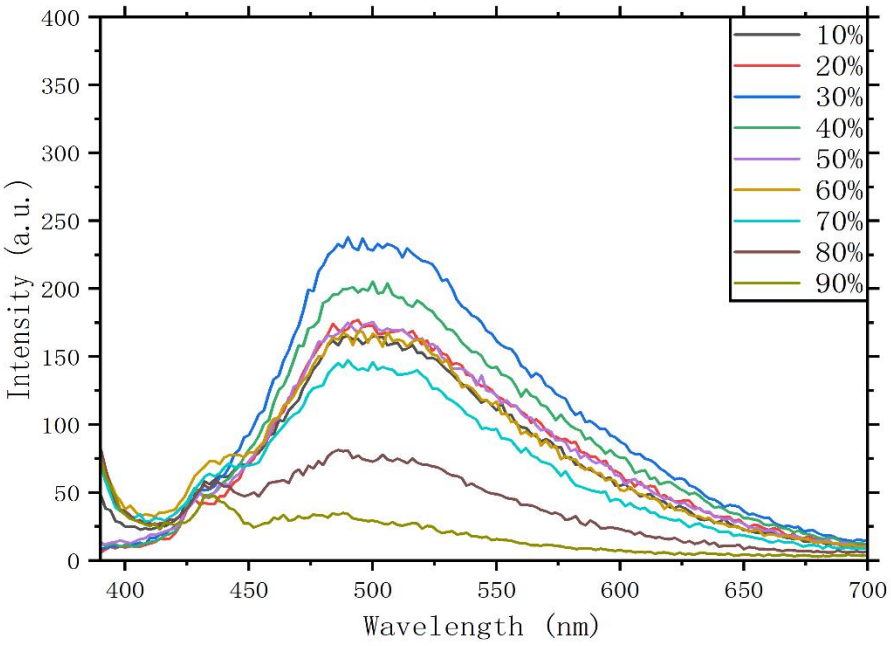


Figure 91. PL Spectra of 3AR.

8.CD (Additional Spectra)

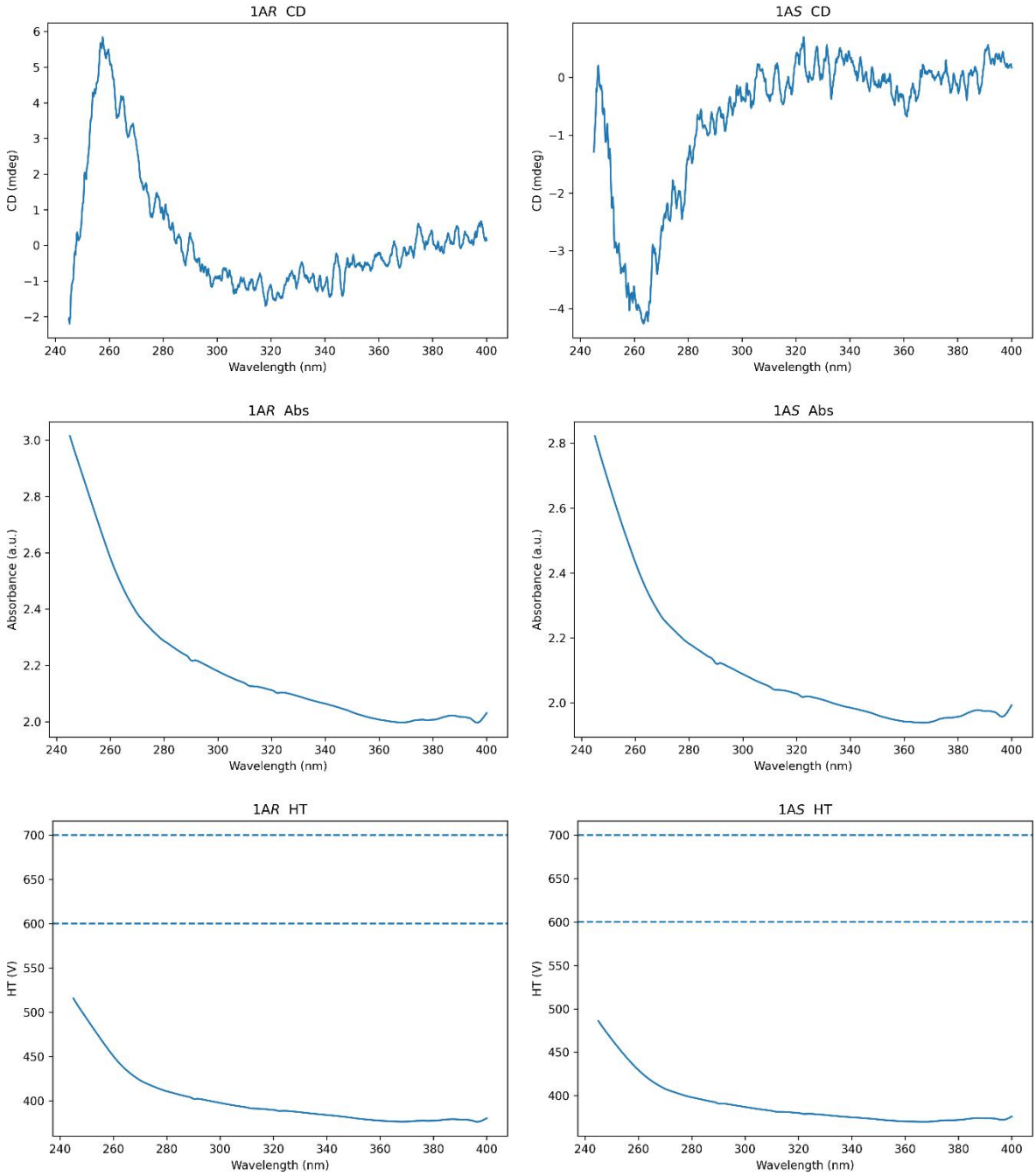


Figure 92. CD Spectra of Polymer 1A (R/S).

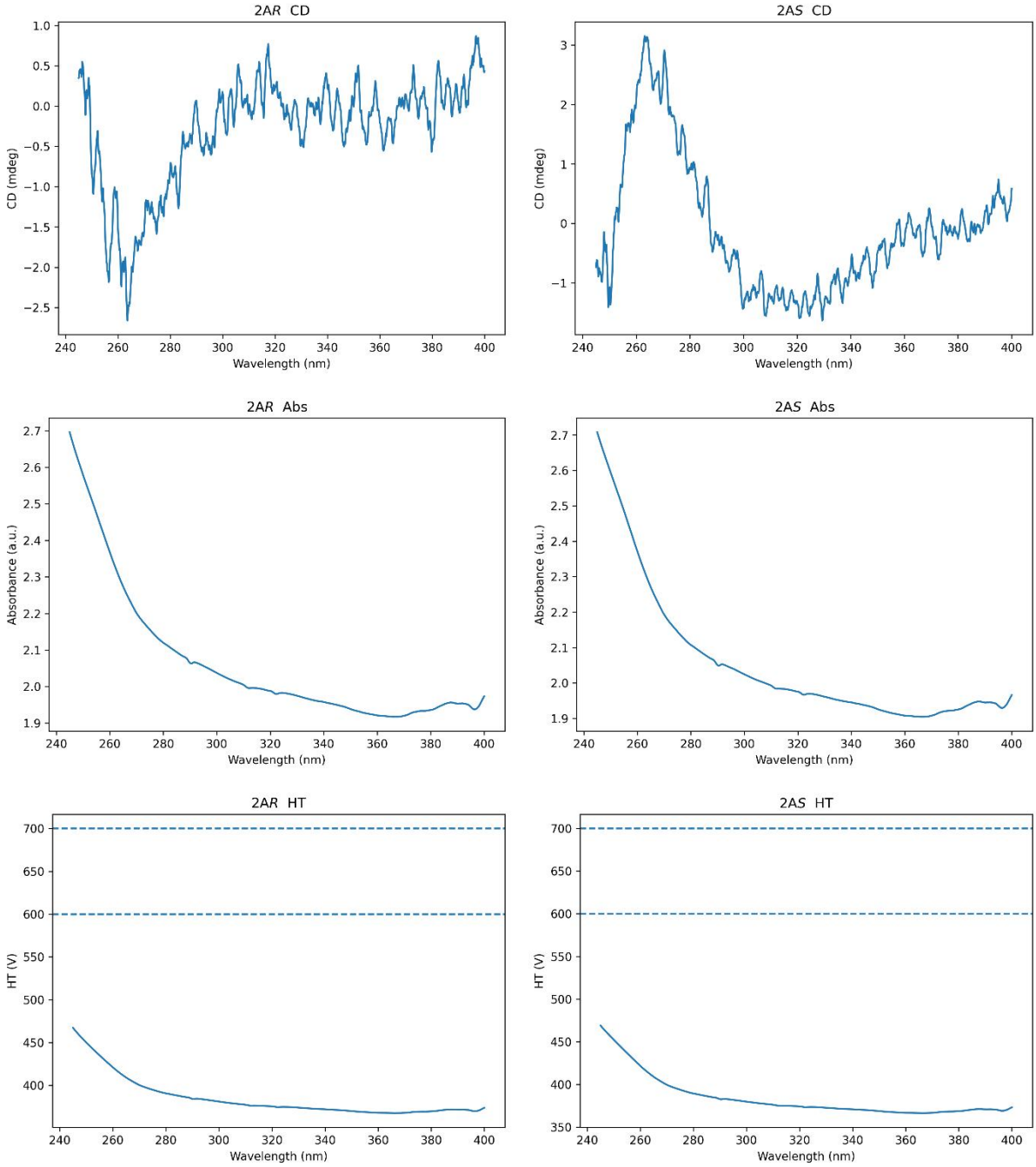


Figure 93. CD Spectra of Polymer 2A (R/S).

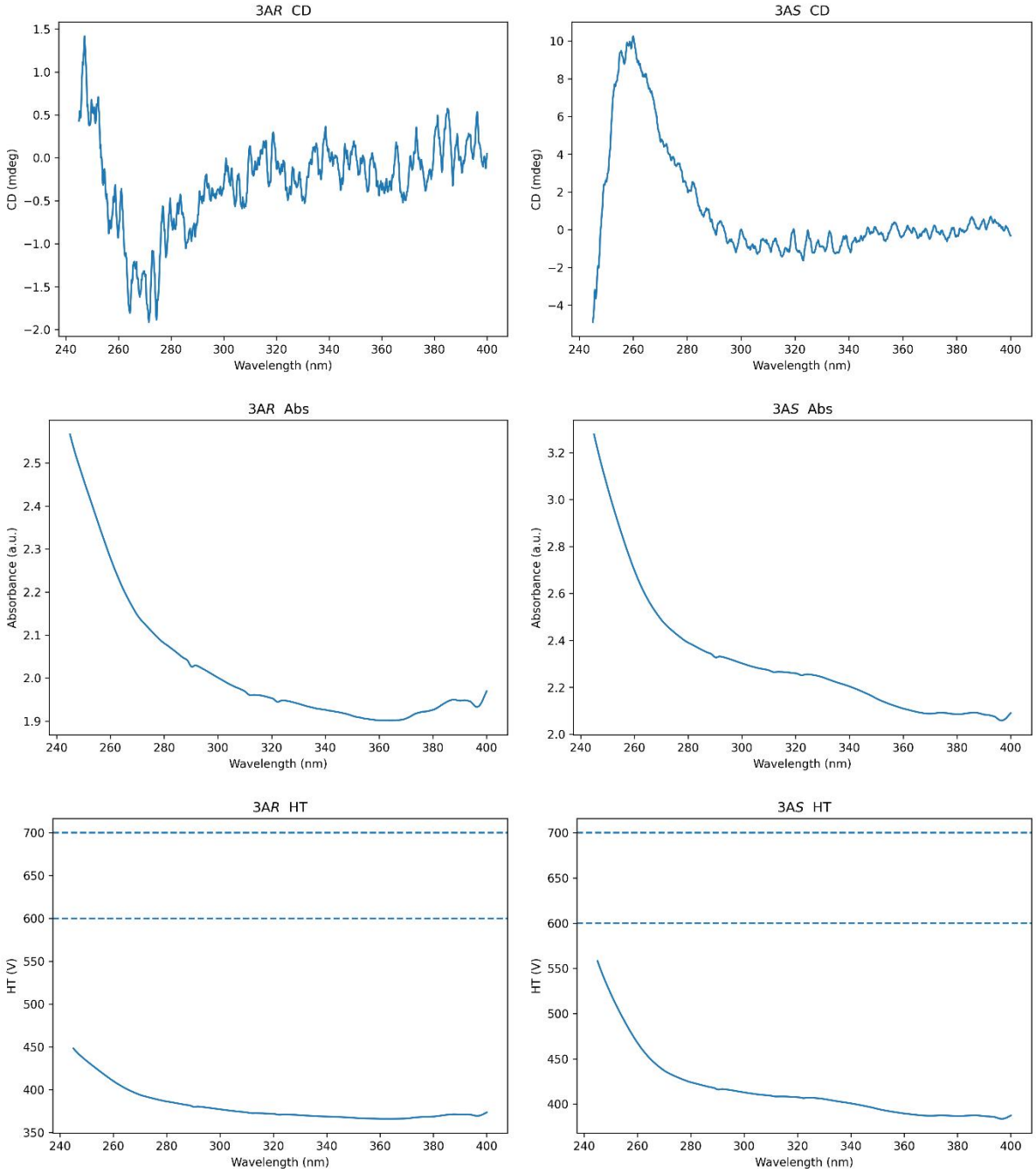


Figure 94. CD Spectra of Polymer 3A (R/S).

9.Tyndall Tests

Tyndall-effect tests were performed in HPLC grade $CHCl_3$ using the same sample concentration as that used for the CD measurements. All samples were filtered through a 0.22 µm syringe filter prior to testing, and pure HPLC grade $CHCl_3$ was used as the blank control.

Figure 95.Tyndall Test of blank sample (pure HPLC grade Chloroform).

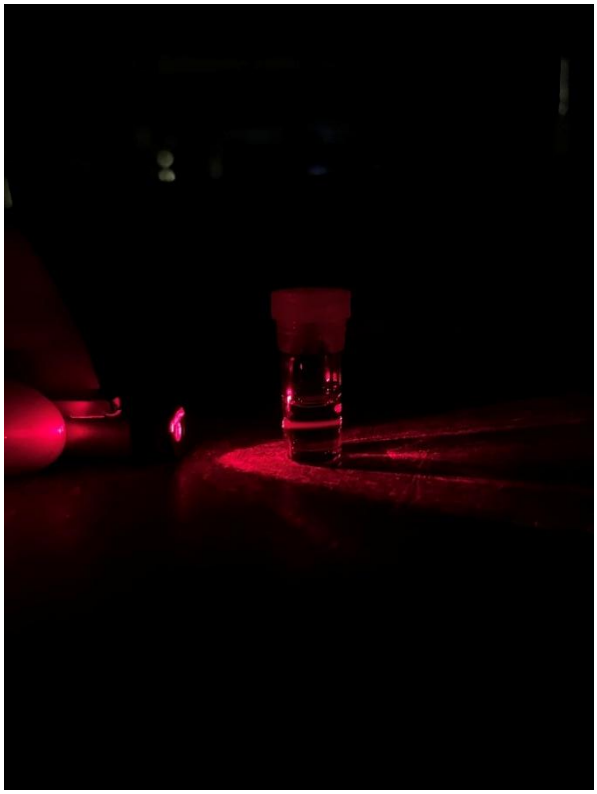


Figure 96. Tyndall Test of Polymer 1AR.

Figure 97. Tyndall Test of Polymer 1AS.

Figure 98 Tyndall Test of Polymer 2AR.

Figure 99. Tyndall Test of Polymer 2AS.

Figure 100. Tyndall Test of Polymer 3AR.


Figure 101. Tyndall Test of Polymer 3AS.

References

1.Liu, X., Yi, Q., Han, Y., Liang, Z., Shen, C., Zhou, Z., Sun, J., Li, Y., Du, W., & Cao, R. Angew. Chem. Int. Ed. 2014, 54(6), 1846–1850.
2.Tang Y, Yuan Q, Zhang S. Enantioselective synthesis of [1, 1′-binaphthalene]-8, 8′-diyl bis (diphenylphosphane) and its derivatives. RSC advances. 2024. 14(4):2792–2795.