Electronic Supplementary Information

Synthesis of Optically Active Polymers Containing a Main-Chain Hydroxamic Acid Backbone via Asymmetric Polymerization

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1. Experimental Section

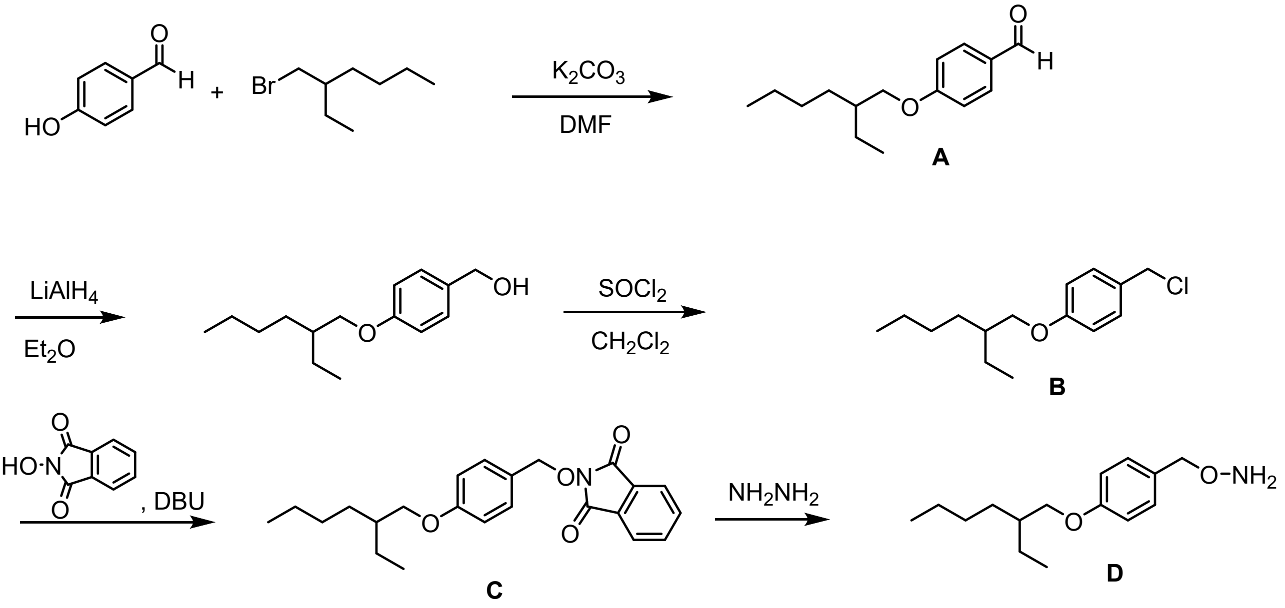
1.1 General. All reactions were carried out under an Ar atmosphere, whereas the workup was performed in air. NMR spectra were recorded in $CDCl_3$ or THF-d_8 on JEOL JNM-ECS400, JEOL JNM-ECA500. In ^{1}H and ^{13}C NMR, $SiMe_4$ was used as an internal standard. HR-MS measurement was carried out on Thermo Fisher Scientific LTQ-Orbitrap XL. The molecular weights (M_n) and its distributions (M_w/M_n) of the polymers were determined by size-exclusion chromatography (SEC) in chloroform at 40 °C with polystyrene gel column [Tosoh; TSKgel GMHHR-M × 3 (exclusion molecular weight = 4×10^6); flow rate 0.7 mL min^{-1}] connected to ShimadzuLC10-AD and Shimadzu SPD-10A UV-vis detectors, calibrated with polystyrene standards. CD spectra were obtained by JASCO J-720WO. UV-vis spectra were obtained by SHIMADZU UV 3100PC.

1.2 Materials

All solvents used for reactions were passed through purification columns just before use. Planar-chiral Cp′Ru complexes (*S*)-**I** was prepared as reported previously.[1, 2]

1.3 Synthesis

Synthesis of Monomer 1



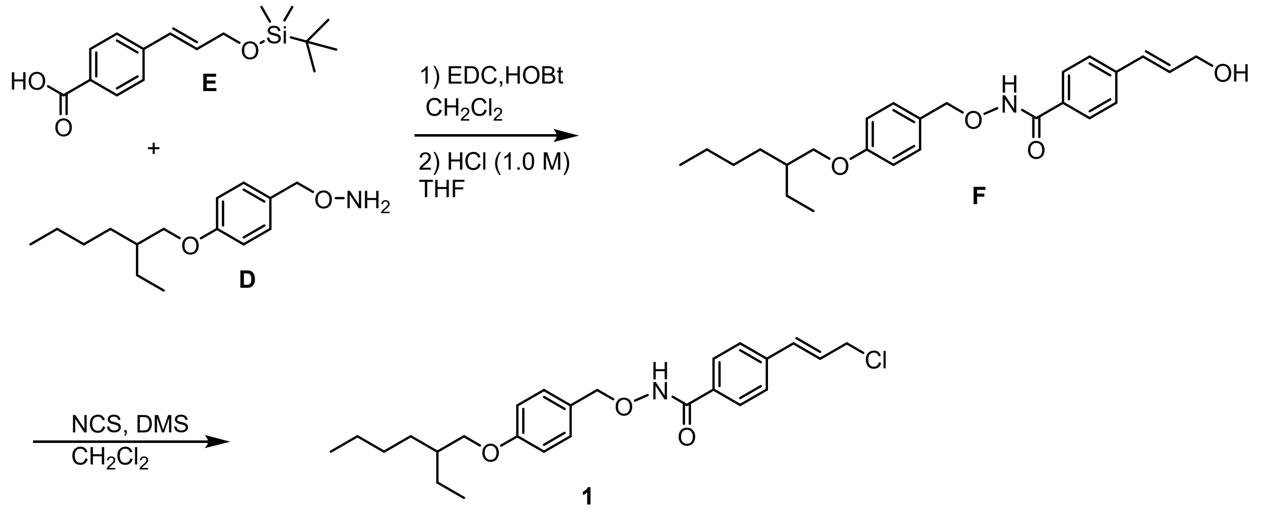
Synthesis of 1-(chloromethyl)-4-[(2-ethylhexyl)oxy]benzene (B). To a DMF solution (80.0 mL) of 4-hydroxybenzaldehyde (4.88 g, 40.0 mmol) and K_2CO_3 (6.08 g, 44.0 mmol), a DMF solution (20.0 mL) of 3-(bromomethyl)heptane (7.68 g, 40.0 mmol) was added dropwise. The reaction mixture was stirred at 80 °C for 12 hours. After cooling to room temperature, ethyl acetate was added to the reaction mixture, and the organic layer was separated. The organic layer was washed three times with brine, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 9:1), affording a yellow oil (A: 7.19 g, 94%).

To a diethyl ether solution (100 mL) of compound A, $LiAlH_4$ (1.53 g, 40.3 mmol) was added slowly at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2 hours. The reaction was quenched by the addition of a saturated potassium tartrate solution (100 mL) at 0 °C, then warmed to room temperature and stirred for an additional 2 hours. The reaction mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, yielding a colorless oil.

The oil was dissolved in CH_2Cl_2 (100 mL) and cooled to 0 °C. Thionyl chloride ($SOCl_2$, 2.2 mL, 30.7 mmol) was added dropwise to the solution. The reaction mixture was warmed to room temperature and stirred for 1 hour. The reaction was quenched by the addition of aqueous $NaHCO_3$ solution (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with aqueous $NaHCO_3$ solution and brine, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, yielding a colorless oil (**B**: 5.93 g, 52%).

^1H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 8.5 Hz, 2H, Ar), 6.88 (d, *J* = 8.5 Hz, 2H, Ar), 4.57 (s, 2H, CH_2–Cl), 3.84 (d, *J* = 5.7 Hz, 2H, OCH_2), 1.73 (sep, *J* = 5.8 Hz, 1H, CH), 1.51–1.30 (m, 8H, CH_2), 0.95–0.90 (m, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6, 130.1, 129.5, 114.8, 70.6, 46.5, 39.4, 30.6, 29.2, 23.9, 23.1, 14.2, 11.2.

Synthesis of D. To a solution of **B** (8.00 g, 31.5 mmol) and *N*-hydroxyphthalimide (5.05 g, 31.5 mmol) in DMF (30 mL) was added a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 4.86 g, 32.0 mmol) in DMF (10 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 15 hours. After completion, brine and ethyl acetate were added to the reaction mixture. The organic layer was separated and washed four times with brine. The combined organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure to afford a yellow solid. The resulting solid was dissolved in CH_2Cl_2 (150 mL), and hydrazine monohydrate (3.0 mL) was added at 0 °C. After 1 minute, a white precipitate formed, and the reaction mixture was warmed to room temperature and stirred for 2 hours. The reaction mixture was concentrated under reduced pressure, and diethyl ether was added to the residue. The mixture was filtered through Celite, and the filtrate was concentrated under reduced pressure to yield a pale yellow oil (6.6 g, 83%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.27 (d, 2H, *J* = 8.5 Hz, Ar), 6.88 (d, 2H, *J* = 8.5 Hz, Ar), 5.32 (s, 2H, NH_2), 4.60 (2H, s, NH_2OCH_2–), 3.83 (2H, d, *J* = 6.0 Hz, OCH_2–), 1.72 (1H, sep, *J* = 6.0 Hz, C*H*), 1.53–1.28 (m, 8H, CH_2), 0.92 (t, 3H, *J* = 7.6 Hz, CH_3), 0.90 (t, 3H, *J* = 6.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 159.2, 129.9, 129.0, 114.4, 77.6, 70.4, 39.3, 30.4, 29.0, 23.7, 22.9, 14.0, 11.0. HRMS (ESI): Calcd for $C_{15}H_{25}NNaO_2$ ($[M+Na]^+$): m/z 274.1783, Found: m/z 274.1777.



Synthesis of F. To a dichloromethane solution (10.0 mL) containing (*E*)-2-[3-(tert-butyldimethylsilyloxy)prop-1-en-yl]benzoic acid (2.92 g, 10.0 mmol),[3] 1-hydroxybenzotriazole (HOBt, 1.49 g, 10.0 mmol), and triethylamine (2.0 g, 20.0 mmol), a dichloromethane solution (10.0 mL) of *N*-[3-(dimethylamino)propyl]-*N*'-ethylcarbodiimide hydrochloride (EDC·HCl, 2.29 g, 12.0 mmol) was added slowly at room temperature, followed by a dichloromethane solution (10.0 mL) of *O*-{4-[(2-ethylhexyl)oxy]benzyl}hydroxylamine (2.85 g, 11.3 mmol). The reaction mixture was stirred at room temperature for 16 hours. After completion, dichloromethane and water were added to the mixture, and the organic layer was separated. The organic layer was washed sequentially with water and a saturated $NaHCO_3$ solution, then dried over Na_2SO_4. The solvent was removed under reduced pressure, affording a yellow oil.

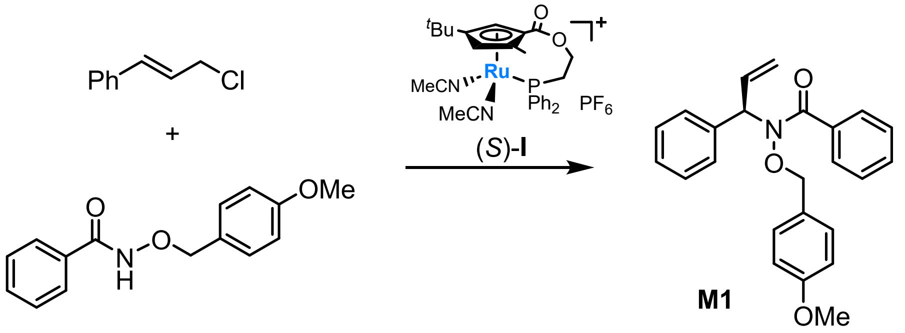
The resulting yellow oil was dissolved in tetrahydrofuran (50.0 mL), and 1 M HCl (60.0 mL) was added. The mixture was stirred for 30 minutes, and ethyl acetate was then added. The organic layer was separated and washed with brine, then dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was washed with n-hexane to yield a white solid (3.64 g, 89%).

^{1}H NMR (acetone-d_6, 400 MHz): δ 10.7 (s, 1H, NH), 7.76 (d, 2H, J = 8.5 Hz, Ar), 7.49 (d, 2H, J = 8.3 Hz, Ar), 7.38 (d, 2H, J = 8.3 Hz, Ar), 6.93 (d, 2H, J = 8.5 Hz, Ar), 6.67 (d, 2H J = 16.0 Hz, C*H*=CHCH$_2$), 6.52 (dt, 1H, J = 16.0, 4.8 Hz, CH=C*H*CH$_2$), 4.91 (2H, s, ArCH$_2$O–), 3.90 (d, 2H, J = 4.8 Hz, CH=CHC*H*$_2$), 3.90 (d, 2H, J = 5.8 Hz, –CHC*H*$_2$Ar), 1.72 (sep, 1H, J = 5.8 Hz, –C*H*CH$_2$Ar), 1.57–1.28 (m, 8H, CH$_2$), 0.93 (t, 3H, J = 7.3 Hz, CH$_3$), 0.89 (t, 3H, J = 7.1 Hz, CH$_3$). ^{13}C NMR (acetone-d_6, 101 MHz): δ 164.6, 159.7, 140.6, 132.6, 130.8, 128.2, 127.9, 127.4, 126.1, 114.2, 77.1, 70.1, 62.1, 39.4, 30.4, 23.7, 22.8, 13.4, 10.5. One peak was missing due to overlapping. HRMS (ESI): $C_{25}H_{33}NNaO_4$ ([M+Na]$^+$): m/z 434.2307, Found: m/z 434.2309.

Synthesis of 1. To a dichloromethane solution (10.0 mL) of *N*-chlorosuccinimide (2.14 g, 16 mmol), dimethyl sulfide (1.02 g, 16 mmol) was added dropwise at −25 °C. The resulting white suspension was stirred for 5 minutes. Subsequently, a dichloromethane solution (60.0 mL) of **F** (3.64 g, 8.85 mmol) was added, and the mixture was warmed to 0 °C and stirred for 4 hours.

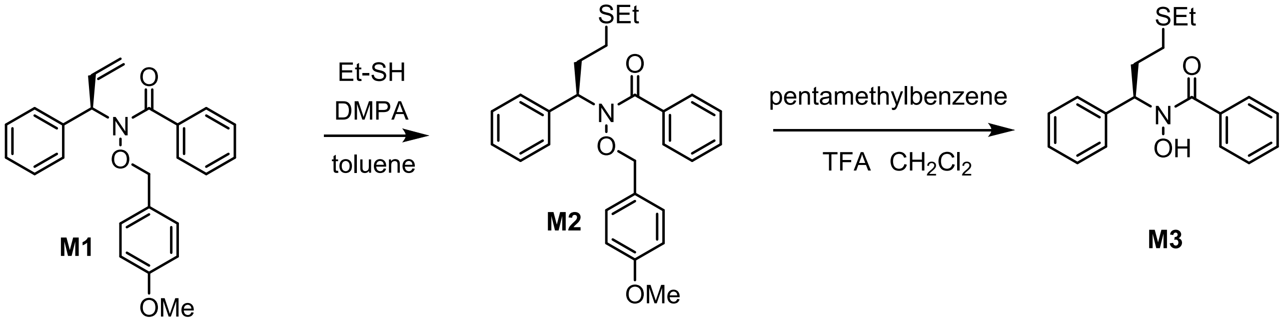
Water was then added to the reaction mixture. The organic layer was separated, washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was washed with n-hexane to afford a white solid (3.57 g, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.90 (s, 1H, NH), 7.63 (d, 2H, J = 8.0 Hz, Ar), 7.37 (d, 2H, J = 8.0 Hz, Ar), 7.32 (d, 2H, J = 8.3 Hz, Ar), 6.87 (d, 2H, J = 8.3 Hz, Ar), 6.63 (d, 1H, J = 15.8 Hz, C*H*=$CHCH_2$), 6.35 (dt, 1H, J = 15.8, 7.2 Hz, CH=C*H*CH_2), 4.92 (s, 2H, $ArCH_2O$–), 4.22 (d, 2H, J = 7.2 Hz, CH=CHCH_2), 3.82 (d, 2H, J = 5.7 Hz, –CHCH_2Ar), 1.70 (sep, 1H, J = 6.0 Hz, –C*H*CH_2Ar), 1.52–1.29 (m, 8H, CH_2), 0.91 (t, 3H, J = 7.5 Hz, CH_3), 0.89 (t, 3H, J = 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 101 MHz): 165.9, 159.9, 139.4, 132.8, 131.4, 131.0, 127.5, 127.2, 126.9, 126.8, 114.5, 78.0, 70.5, 44.9, 39.3, 30.4, 29.0, 23.8, 23.0, 14.0, 11.0. HRMS (ESI): $C_{25}H_{32}ClNNaO_3$ ($[M+Na]^+$): m/z 452.1968, Found: m/z 452.1971.

Synthesis of M1



To a mixture of Na_2CO_3 (127.2 mg, 1.20 mmol), (*S*)-**I** (7.8 mg, 10 μmol), *N*-((4-methoxybenzyl)oxy)benzamide (257 mg, 1.00 mmol), and molecular sieves 3A, a solution of cinnamyl chloride (152 mg, 1.00 mmol) in THF (2.0 mL) was added. The reaction mixture was stirred at 30 °C for 15 hours. After dilution with diethyl ether, the reaction mixture was filtered through Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/diethyl ether = 10:1), affording a colorless oil (300 mg, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 (d, 2H, J = 6.6 Hz, Ar), 7.52 (d, 2H, J = 8.0 Hz, Ar), 7.46 (d, 1H, J = 7.1 Hz, Ar), 7.43–7.32 (m, 5H, Ar), 6.72 (s, 4H, Ar), 6.31 (ddd, 1H, J = 17.1, 10.4, 6.8 Hz, –CHC*H*=CH_2), 6.16 (d, 1H, J = 6.8 Hz, –C*H*CH=CH_2), 5.40 (d, 1H, J = 17.1 Hz, –CHCH=CH_2), 5.38 (d, 1H, J = 10.4 Hz, –CHCH=CH_2), 4.40 (d, 1H, J = 7.8 Hz, –OCH_2Ar), 4.02 (d, 1H, J = 7.8 Hz, –OCH_2Ar), 3.74 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 170.5, 160.0, 138.2, 135.1, 134.4, 131.3, 130.6, 129.0, 128.7, 128.4, 128.3, 128.2, 126.3, 118.6, 113.7, 78.3, 64.1, 55.3. HRMS (ESI): $C_{25}H_{32}ClNNaO_3$ ($[M+Na]^+$): m/z 452.1968, Found: m/z 452.1971.

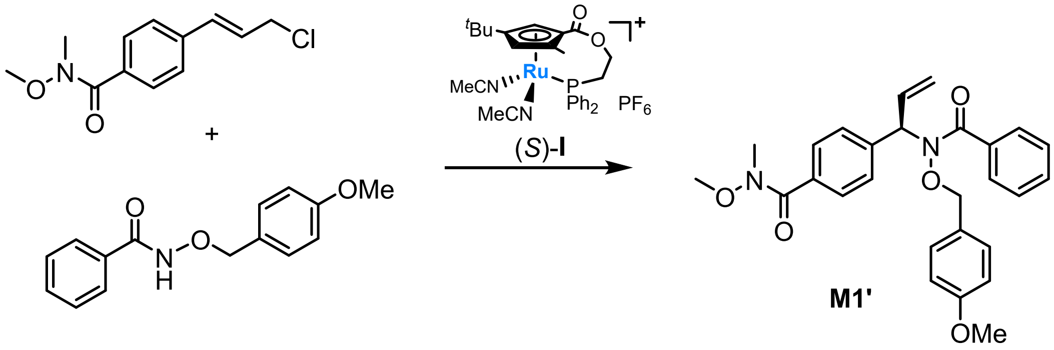
Synthesis of M3



To a solution of **M1** (105.8 mg, 0.23 mmol) and 2,2-dimethoxy-2-phenylacetophenone (DMPA, 19 mg, 0.074 mmol) in toluene (0.2 mL), 1-ethanethiol (0.1 mL, 1.3 mmol) was added. The reaction mixture was irradiated with a 500 W high-pressure mercury lamp for 3 hours. After completion, the residue was purified by silica gel column chromatography (*n*-hexane/diethyl ether = 8:2, followed by 1:1) to afford a colorless oil (96.9 mg, 83%).

To a solution of 4-(3-(ethylthio)-1-(*N*-((4-methoxybenzyl)oxy)benzamido)propyl)-*N*-methoxy-*N*-methylbenzamide (80.5 mg, 0.15 mmol) and pentamethylbenzene (111 mg, 0.75 mmol) in dichloromethane (1.0 mL), trifluoroacetic acid (TFA, 0.5 mL) was added at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 hours. After cooling the mixture to 0 °C, the reaction was quenched with saturated $NaHCO_3$ aqueous solution. Dichloromethane was added, and the organic layer was separated. The organic layer was washed with $NaHCO_3$ aqueous solution, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (n-hexane/diethyl ether = 8:2, followed by 1:1), yielding a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.42 (brs, 1H, OH), 7.49 (t, 3H, J = 7.2 Hz, Ar), 7.43 (t, 2H, J = 7.2 Hz, Ar), 7.36–7.29 (m, 5H, Ar), 5.22 (brs, 1H, CH), 2.64–2.55 (m, 2H, –$CHCH_2CH_2S$–) 2.55–2.49 (m, 1H, –$CHCH_2CH_2S$–), 2.50 (q, 2H, J = 7.5 Hz, –SCH_2CH_3), 2.01–2.07 (m, 1H, –$CHCH_2CH_2S$–), 1.22 (t, 3H, –SCH_2CH_3). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 168.3, 139.0, 132.6, 131.1, 128.8, 128.6, 128.1, 127.1, 126.7, 62.9, 32.6, 28.4, 26.0, 14.8. HRMS (ESI): $C_{18}H_{21}NNaO_2S$ ($[M+Na]^+$): m/z 338.1191, Found: m/z 338.1183.

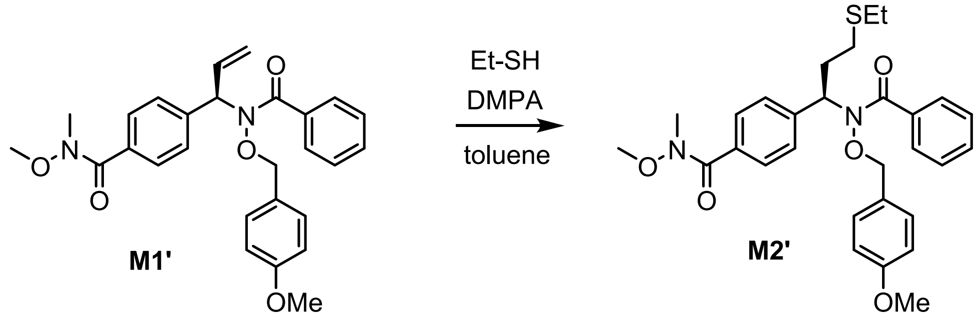
Synthesis of M1'



To a mixture of Na_2CO_3 (63.6 mg, 0.6 mmol), (*S*)-**I** (3.9 mg, 5 μmol), *N*-((4-methoxybenzyl)oxy)benzamide (141 mg, 0.5 mmol), and molecular sieves 3A, a solution of (*E*)-4-(3-chloroprop-1-en-1-yl)-*N*-methoxy-*N*-methylbenzamide[3] (119.5 mg, 0.5 mmol) in THF (2.0 mL) was added. The reaction mixture was stirred at 30 °C for 15 hours. After dilution with diethyl ether, the reaction mixture was filtered through Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (n-hexane/diethyl ether = 10:1, followed by 1:1) to afford a brown oil (212.7 mg, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, 2H, J = 8.5 Hz, Ar), 7.70 (d, 2H, J = 7.8 Hz, Ar), 7.55 (d, 2H, J = 8.5 Hz, Ar), 7.49 (t, 1H, J = 7.8 Hz, Ar), 7.42 (t, 2H, J = 7.8 Hz, Ar), 6.78–6.72 (m, 4H, Ar), 6.32 (ddd, 1H, J = 17.1, 10.3, 7.1 Hz, –$CHCH{=}CH_2$), 6.17 (d, 1H, J = 6.6 Hz, –$CHCH{=}CH_2$), 5.42 (d, 1H, J = 10.3 Hz, –$CHCH{=}CH_2$), 5.41 (d, 1H, J = 17.1 Hz, –$CHCH{=}CH_2$), 4.56 (d, 1H, J = 8.5 Hz, –OCH_2Ar), 4.12 (d, 1H, J = 8.5 Hz, –

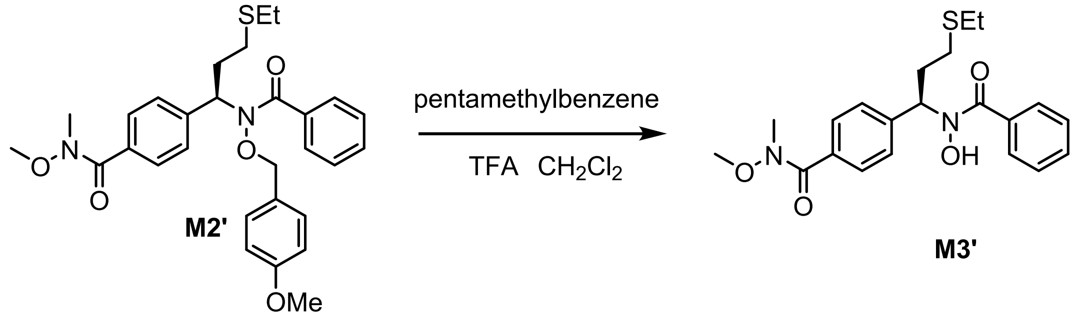
OCH_2Ar), 3.76 (s, 3H, CH_3), 3.53 (s, 3H, CH_3), 3.36 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 170.6, 169.5, 160.0, 141.0, 134.8, 133.9, 133.8, 131.2, 130.7, 128.6, 128.4, 128.2, 126.1, 119.4, 113.8, 78.4, 63.9, 61.2, 55.3, 33.8. One peak was missing due to overlapping. HRMS (ESI): $C_{29}H_{28}N_2NaO_5$ ($[M+Na]^+$): m/z 483.1896, Found: m/z 483.1885.

Synthesis of M2'



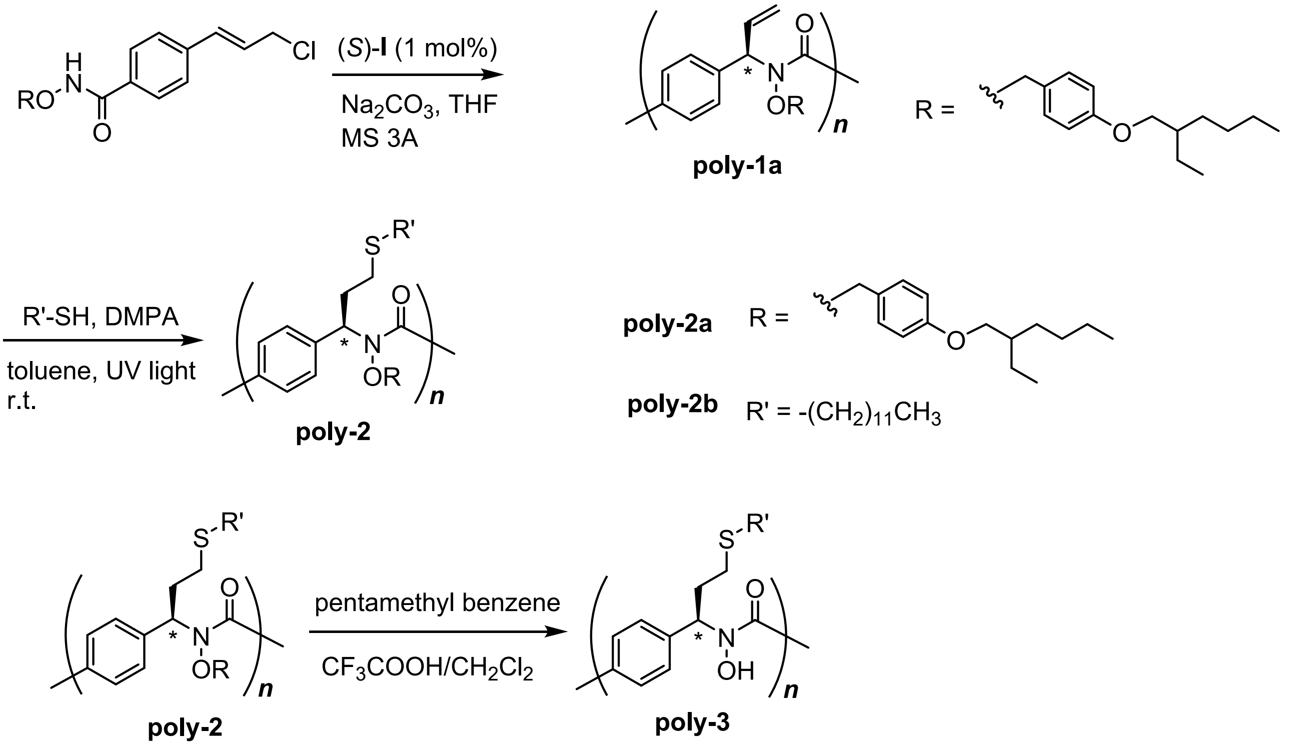
To a solution of *N*-methoxy-4-(1-{*N*-[(4-methoxybenzyl)oxy]benzamido}allyl)-*N*-methylbenzamide (105.8 mg, 0.23 mmol) and 2,2-dimethoxy-2-phenylacetophenone (DMPA, 19 mg, 0.074 mmol) in toluene (0.2 mL), 1-ethanethiol (0.1 mL, 1.3 mmol) was added. The reaction mixture was irradiated with a 500 W high-pressure mercury lamp for 3 hours. After completion, the residue was purified by silica gel column chromatography (*n*-hexane/diethyl ether = 8:2, followed by 1:1) to afford a colorless oil (96.9 mg, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, 2H, J = 8.0 Hz, Ar), 7.65 (d, 2H, J = 7.6 Hz, Ar), 7.57 (d, 2H, J = 8.0 Hz, Ar), 7.50 (t, 1H, J = 7.6 Hz, Ar), 7.42 (t, 2H, J = 7.6 Hz, Ar), 6.79–6.74 (m, 4H, Ar), 5.76 (brs, 1H, CH), 4.32 (d, 1H, J = 6.4 Hz, –OCH_2Ar), 4.07 (d, 1H, J = 6.4 Hz, –OCH_2Ar), 3.77 (s, 3H, CH_3), 3.54 (s, 3H, CH_3), 3.37 (s, 3H, CH_3), 2.60–2.55 (m, 3H, –CH$CH_2$$CH_2$S– and –CH$CH_2$$CH_2$S–), 2.52 (q, 2H, J = 8.0 Hz, –S$CH_2$$CH_3$), 2.38–2.32 (m, 1H, –CH$CH_2$$CH_2$S–), 1.21 (t, 3H, –S$CH_2$$CH_3$). ^{13}C NMR ($CDCl_3$, 101 MHz): 170.8, 169.5, 160.1, 141.3, 134.8, 134.0, 131.2, 130.8, 128.8, 128.3, 128.2, 126.3, 113.8, 78.3, 61.2, 60.2, 55.3, 33.8, 31.0, 28.3, 26.0, 14.8. One peak was missing due to overlapping. HRMS (ESI): $C_{29}H_{34}N_2NaO_5S$ ($[M+Na]^+$): m/z 545.2086, Found: m/z 545.2090.

Synthesis of M3'



To a solution of 4-(3-(ethylthio)-1-(*N*-((4-methoxybenzyl)oxy)benzamido)propyl)-*N*-methoxy-*N*-methylbenzamide (80.5 mg, 0.15 mmol) and pentamethylbenzene (111 mg, 0.75 mmol) in dichloromethane (1.0 mL), trifluoroacetic acid (TFA, 0.5 mL) was added at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 3 hours. After cooling the mixture to 0

°C, the reaction was quenched with saturated $NaHCO_3$ aqueous solution. Dichloromethane was added, and the organic layer was separated. The organic layer was washed with $NaHCO_3$ aqueous solution, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (n-hexane/diethyl ether = 8:2, followed by 1:1), affording a colorless oil (61.0 mg, 90%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.61 (brs, 1H, OH), 7.65 (d, $J = 8.0$ Hz, Ar), 7.49–7.36 (m, 7H, Ar), 5.28 (brs, 1H, CH), 3.57 (s, 3H, CH_3), 3.36 (s, 3H, CH_3), 2.63–2.55 (m, 3H, $–CHCH_2CH_2S–$ and $–CHCH_2CH_2S–$), 2.50 (q, 2H, $J = 8.0$ Hz, $–SCH_2CH_3$), 2.16–2.02 (m, 1H, $–CHCH_2CH_2S–$), 1.22 (t, 3H, $–SCH_2CH_3$). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.5, 168.6, 141.7, 133.7, 132.3, 131.2, 128.7, 128.0, 126.8, 62.6, 61.2, 33.8, 32.5, 28.3, 26.0, 14.8. One peak was missing due to overlapping. HRMS (ESI): $C_{21}H_{25}N_2NaO_4S$ ($[M+Na]^+$): m/z 425.1511, Found: m/z 425.1505.



Synthesis of poly-1

The polymerization of **1** was conducted according to the previous method. To a solution of sodium carbonate (226 mg, 2.2 mmol), MS 3A 120 mg, and (*S*)-I catalyst (6 mg, 8 μ mol) in THF (0.7 mL) was added **1** (430 mg, 1.0 mmol), and the reaction mixture was stirred at 25 °C. After 36 h, dichloromethane (10.0 mL) was added to the reaction mixture. The insoluble part was filtered through Celite. The combined organic layer was washed with water. After drying over Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography with CH_2Cl_2 and dried under vacuum to give a pale-yellow solid (287 mg).

Synthesis of poly-2a

To a toluene solution (0.6 mL) of **poly-1** (112 mg, 0.28 mmol of C═C groups) and 2,2-dmethoxy-2-phenylacetophenone (35.8 mg, 0.14 mmol) was added 1-dodecanthiol (339 mg, 1.7 mmol), and the reaction mixture was irradiated with a 500 W high-pressure mercury lamp for 12 h. 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 (80%, 132.1 mg).

Synthesis of poly-2b

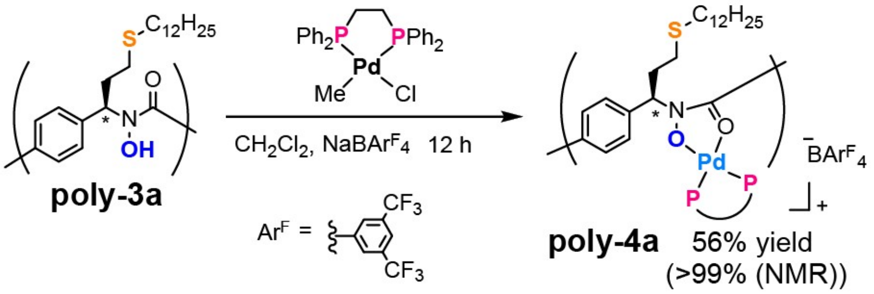
Poly-2b was obtained as a pale yellow solid (66 mg, 50%) from poly-1 (91.6 mg, 0.23 mmol of C═C groups) according to the above method.

Synthesis of poly-3a

To a solution of **poly-2a** and pentamethylbenzene (119 mg, 0.8 mmol) in CH_2Cl_2 (1.0 mL) was added trifluoroacetic acid (1.0 mL) at 0 °C, and the reaction mixture was stirred at 25 °C for 4 h. After the reaction, MeOH was added, and the reaction mixture was concentrated under reduced pressure. This procedure was repeated twice. The crude product was purified by SEC (Shodex; KF-2003 × 2; flow rate, 3.0 mL min^{-1}) to give the target product (37.7 mg, 77%).

Synthesis of poly-3b

Poly-3b was obtained as a pale yellow solid (21 mg, 74%) from **poly-2b** (45 mg, 0.08 mmol of C═C groups) according to the above method.



Synthesis of poly-4a

To a solution of **poly-3a** (9.7 mg, 0.025 mmol) in CH_2Cl_2 (0.5 mL) was added 1,2-bis(diphenylphosphino)ethanePdMeCl (13.0 mg, 0.030 mmol) at room temperature, followed by the addition of $NaBAr^F_4$ (27.0 mg, 0.030 mmol). The reaction mixture was filtered through a pad of Celite and concentrated under reduced pressure. The crude product was then washed with hexane and diethyl ether to remove excess metal complex and borate salts, affording the product as an ocher solid (24.5 mg, 56%).

2. NMR analysis

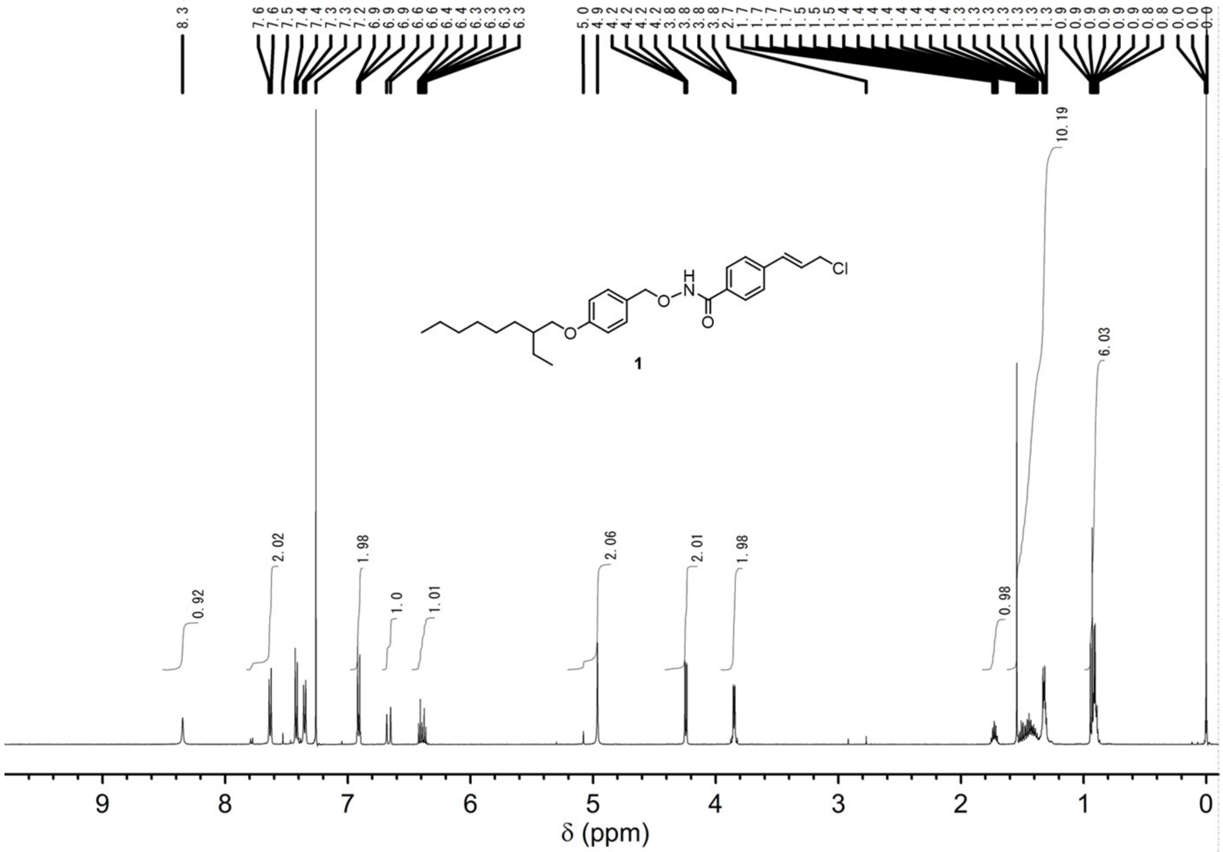


Fig. S1 ^{1}H NMR (500 MHz) spectrum of **1** in CDCl$_3$.

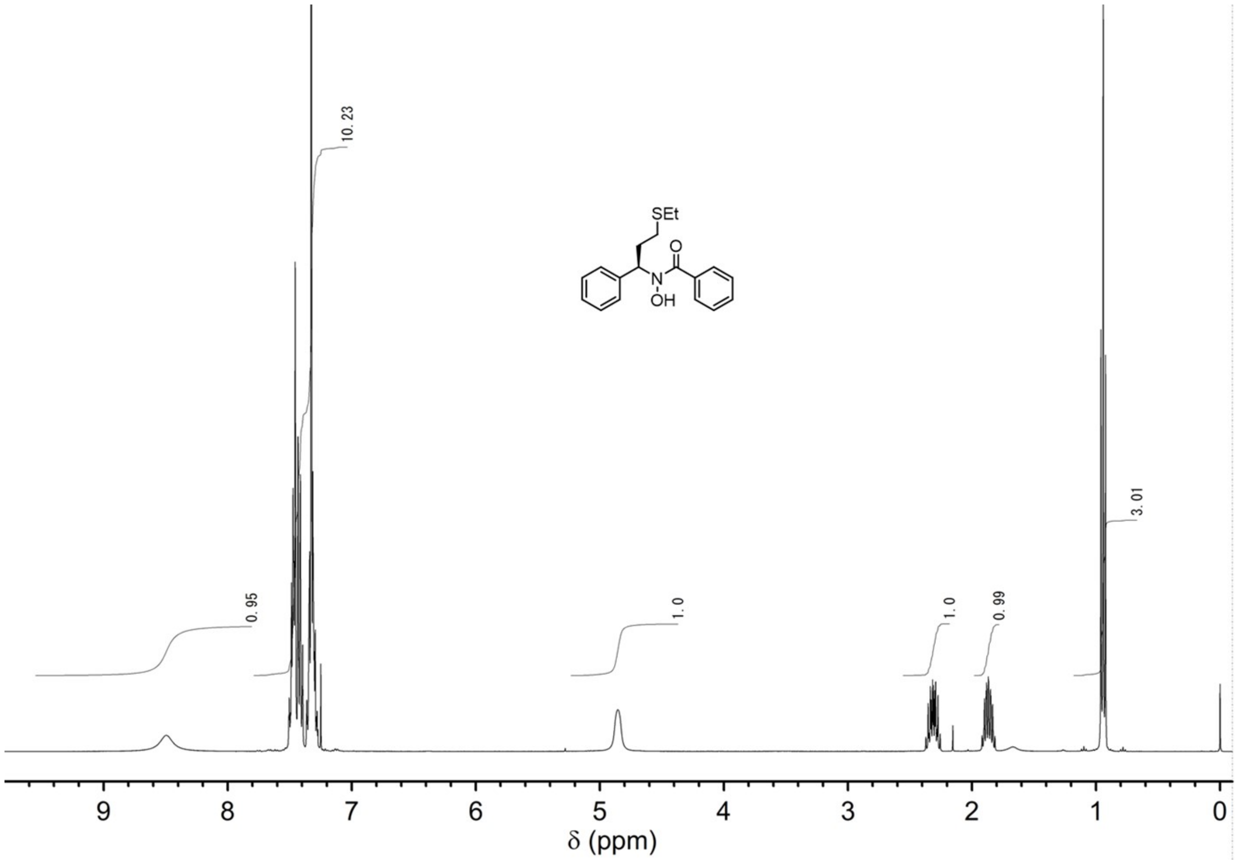


Fig. S2 ^{1}H NMR (500 MHz) spectrum of **M3** in CDCl$_3$.

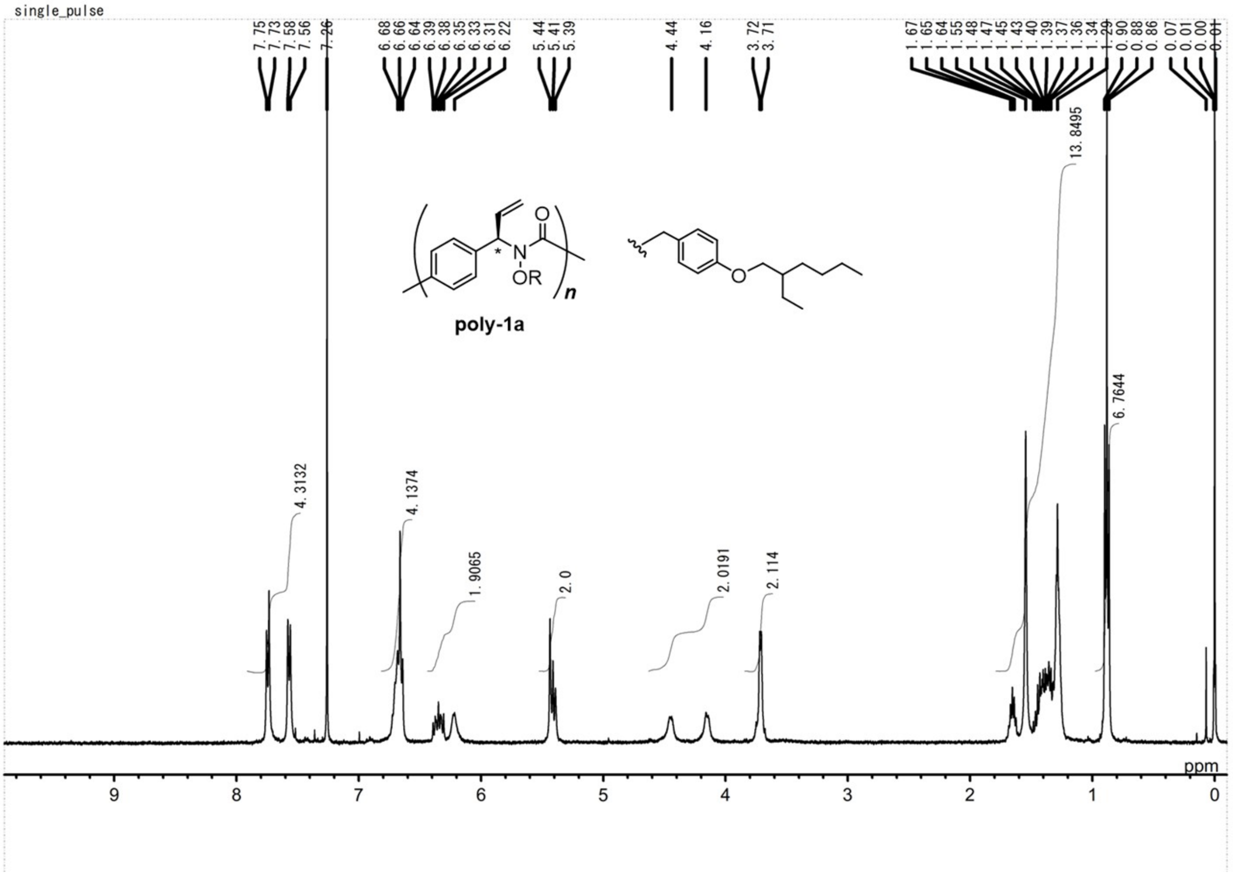


Fig. S3 ^{1}H NMR (500 MHz) spectrum of **poly-1** in $CDCl_3$.

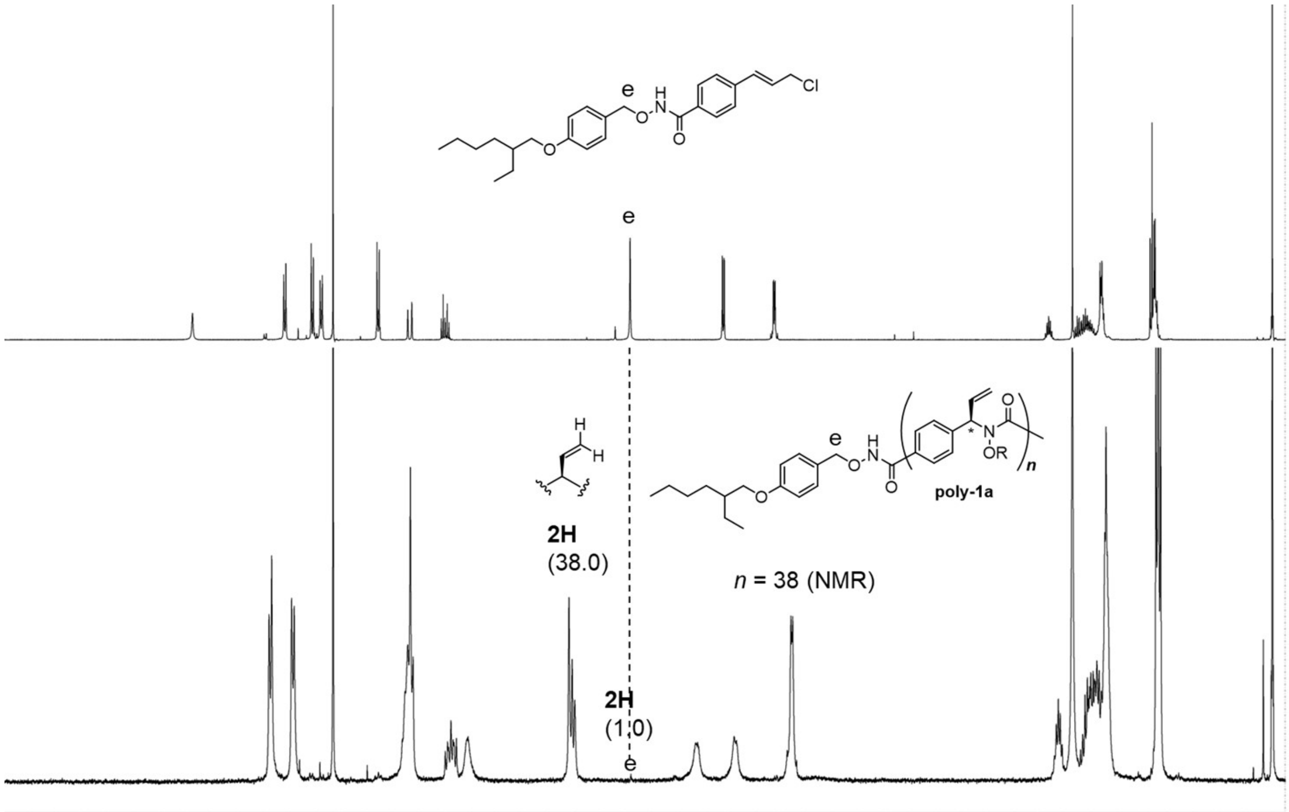


Fig S3-2 ^{1}H NMR (500 MHz) spectrum of **poly-1** in $CDCl_3$.

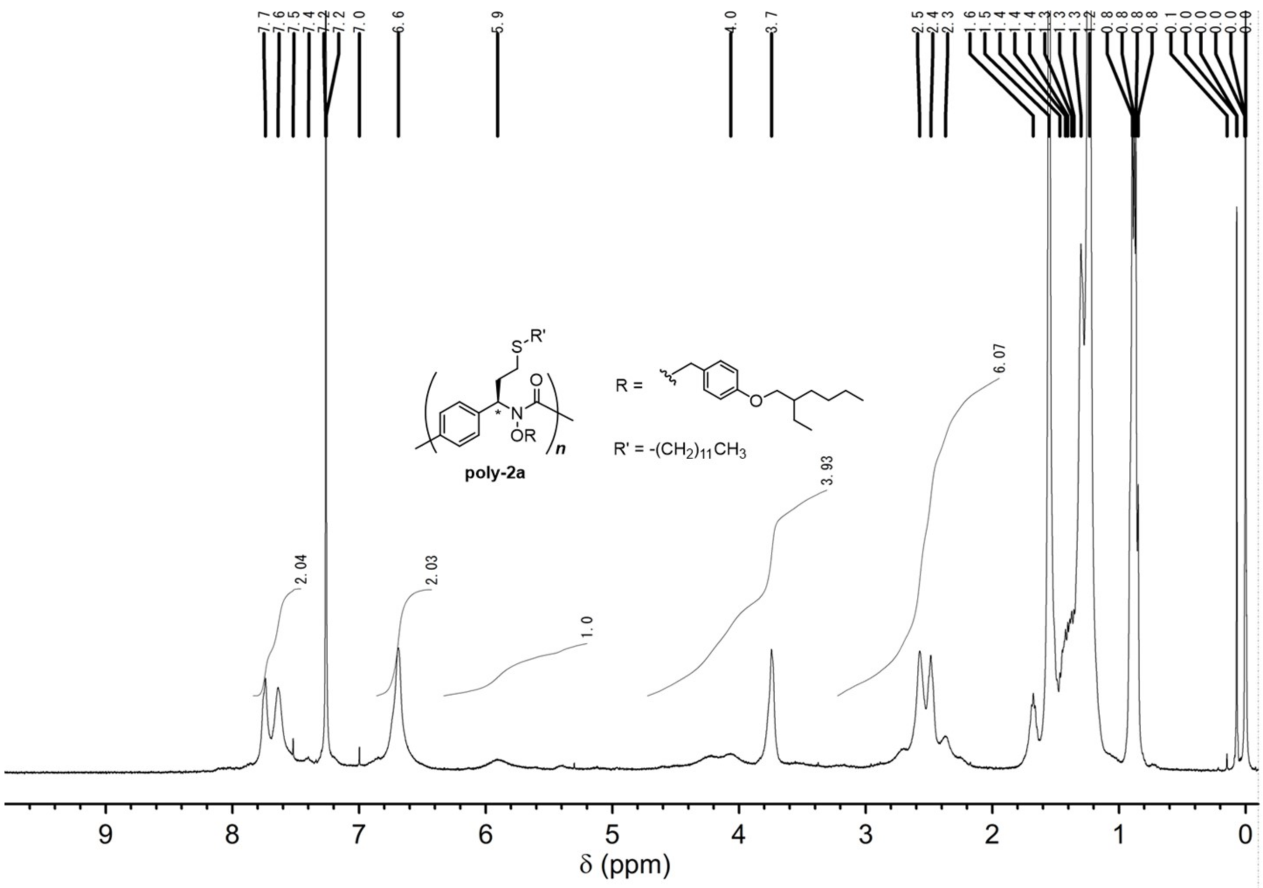


Fig. S4 ^{1}H NMR (500 MHz) spectrum of **poly-2a** in $CDCl_3$.

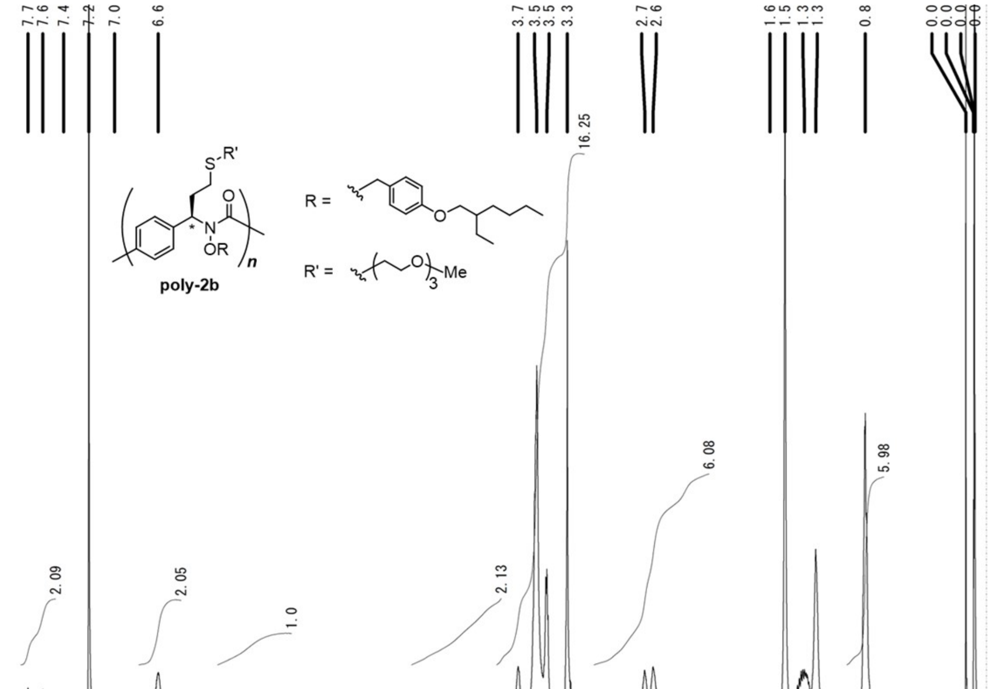


Fig. S5 ^{1}H NMR (500 MHz) spectrum of **poly-2b** in $CDCl_3$.

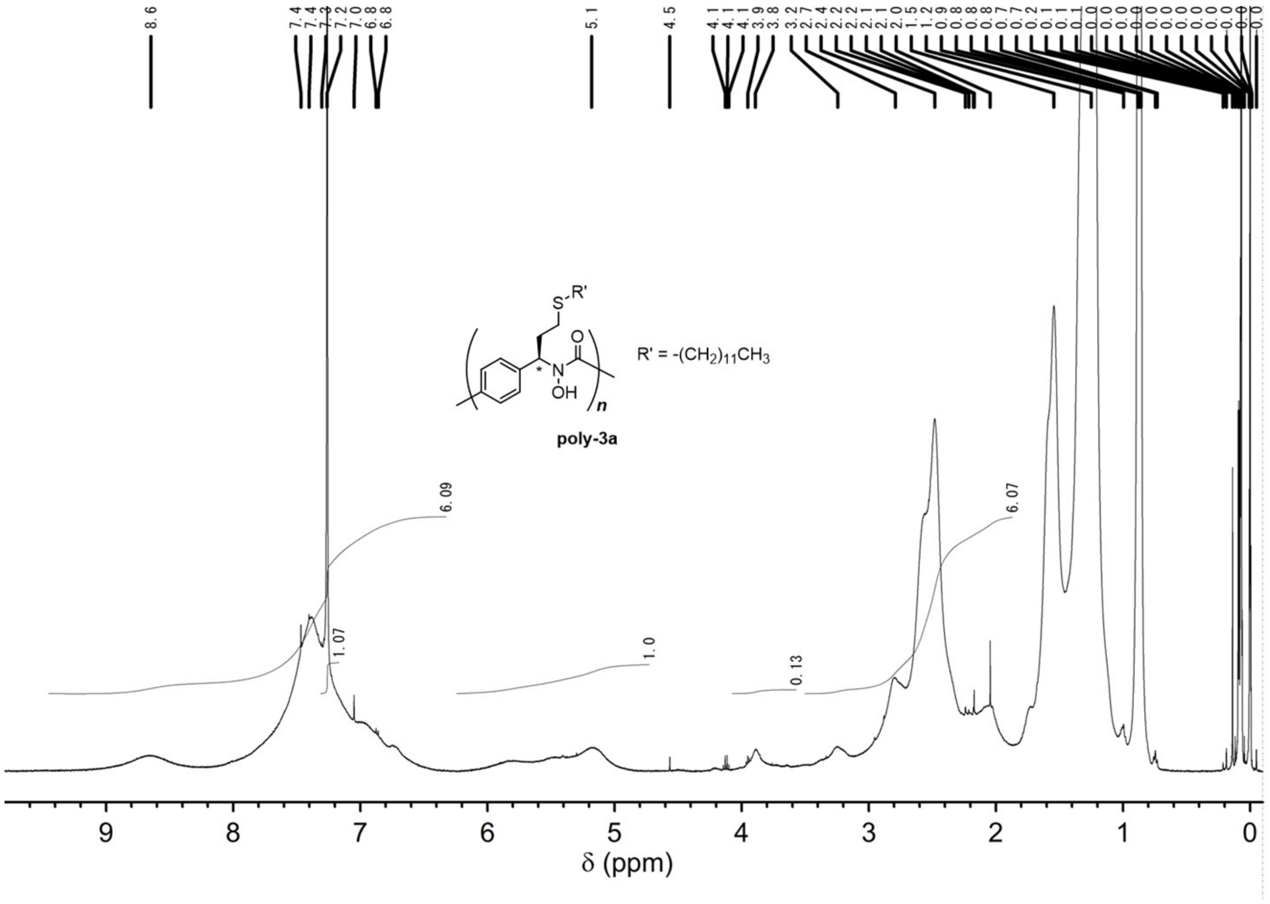


Fig. S6 ^{1}H NMR (500 MHz) spectrum of **poly-3a** in CDCl$_3$.

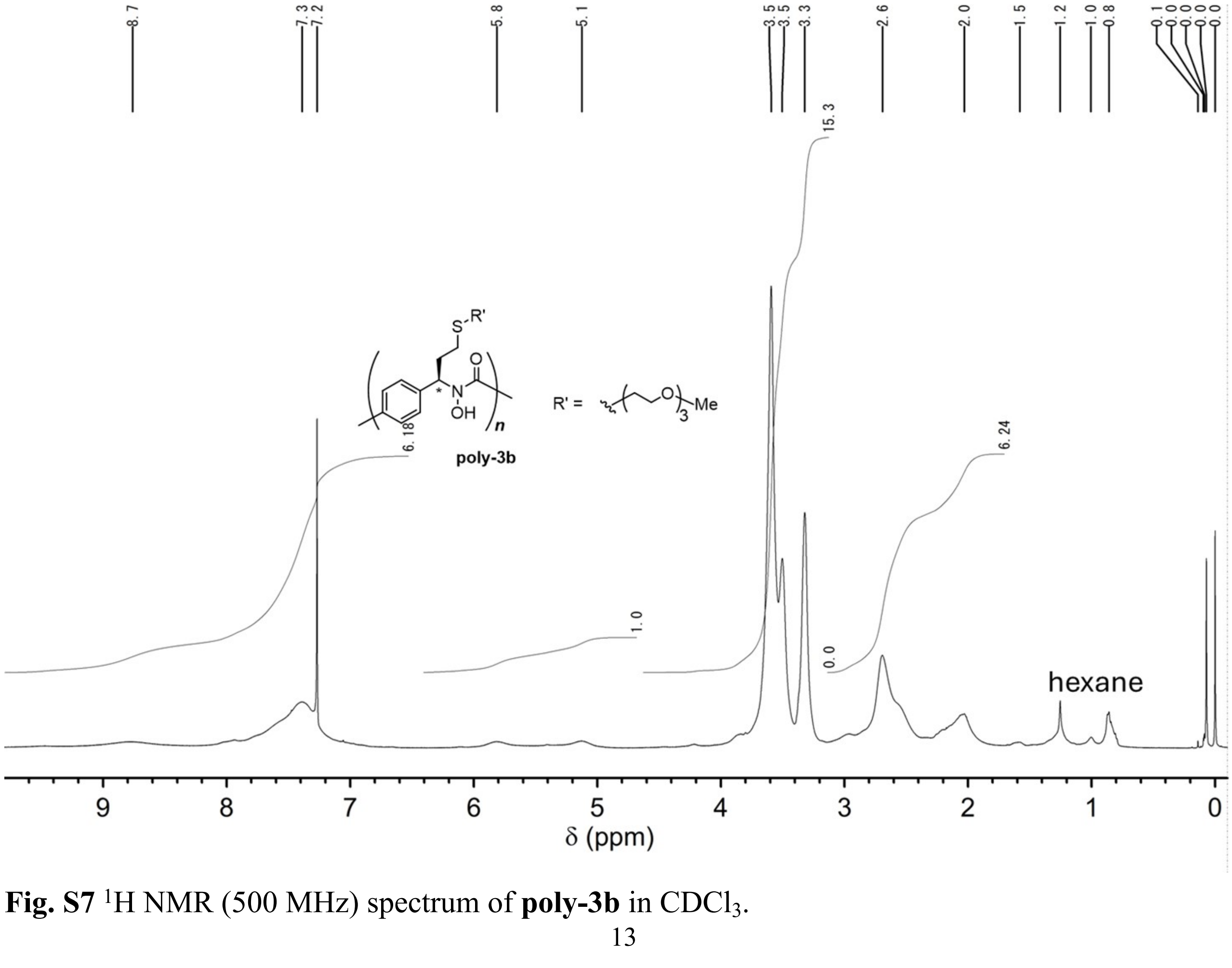


Fig. S7 ^{1}H NMR (500 MHz) spectrum of **poly-3b** in CDCl$_3$.

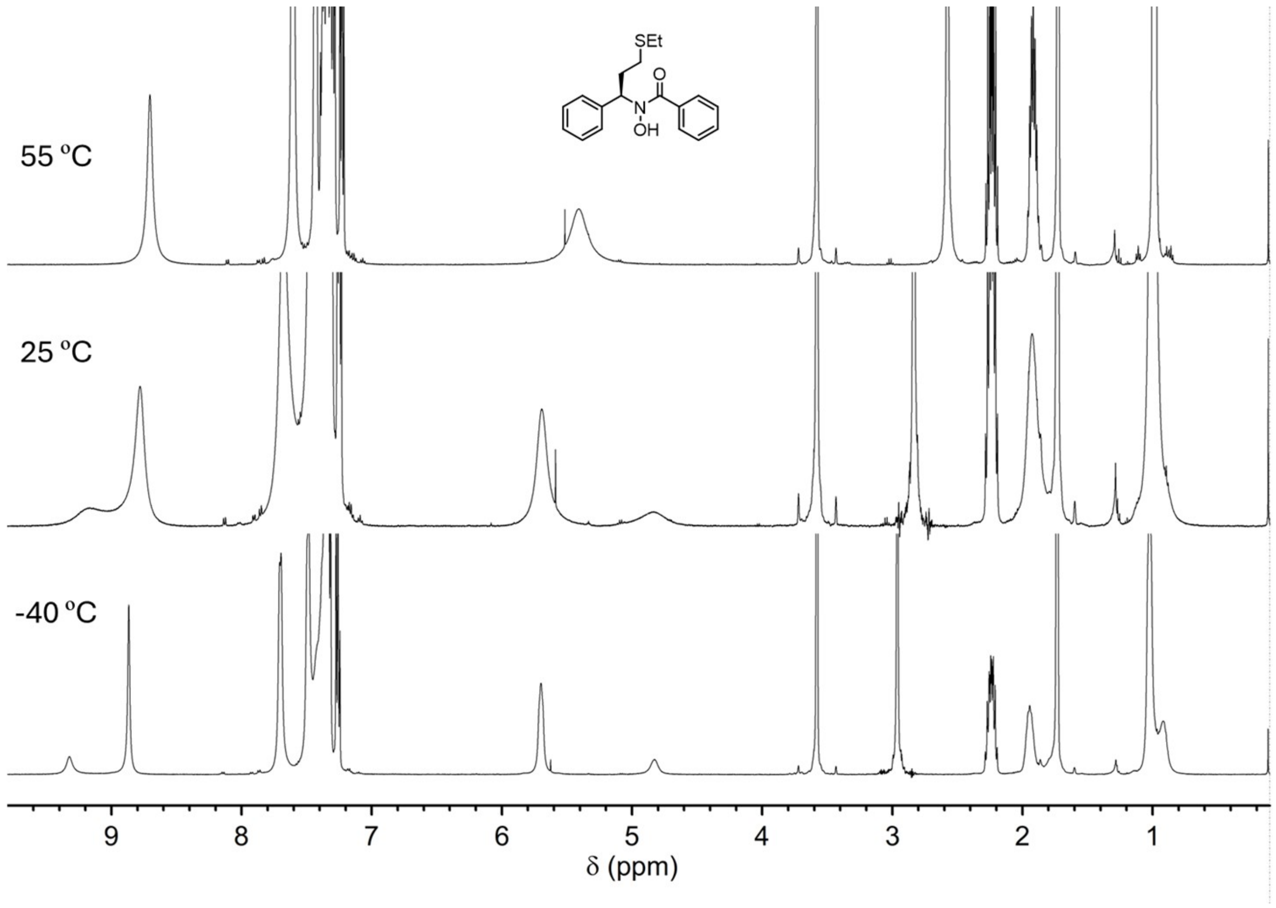


Fig. S8 Temperature dependence of model compound **M3** in THF-d_8.

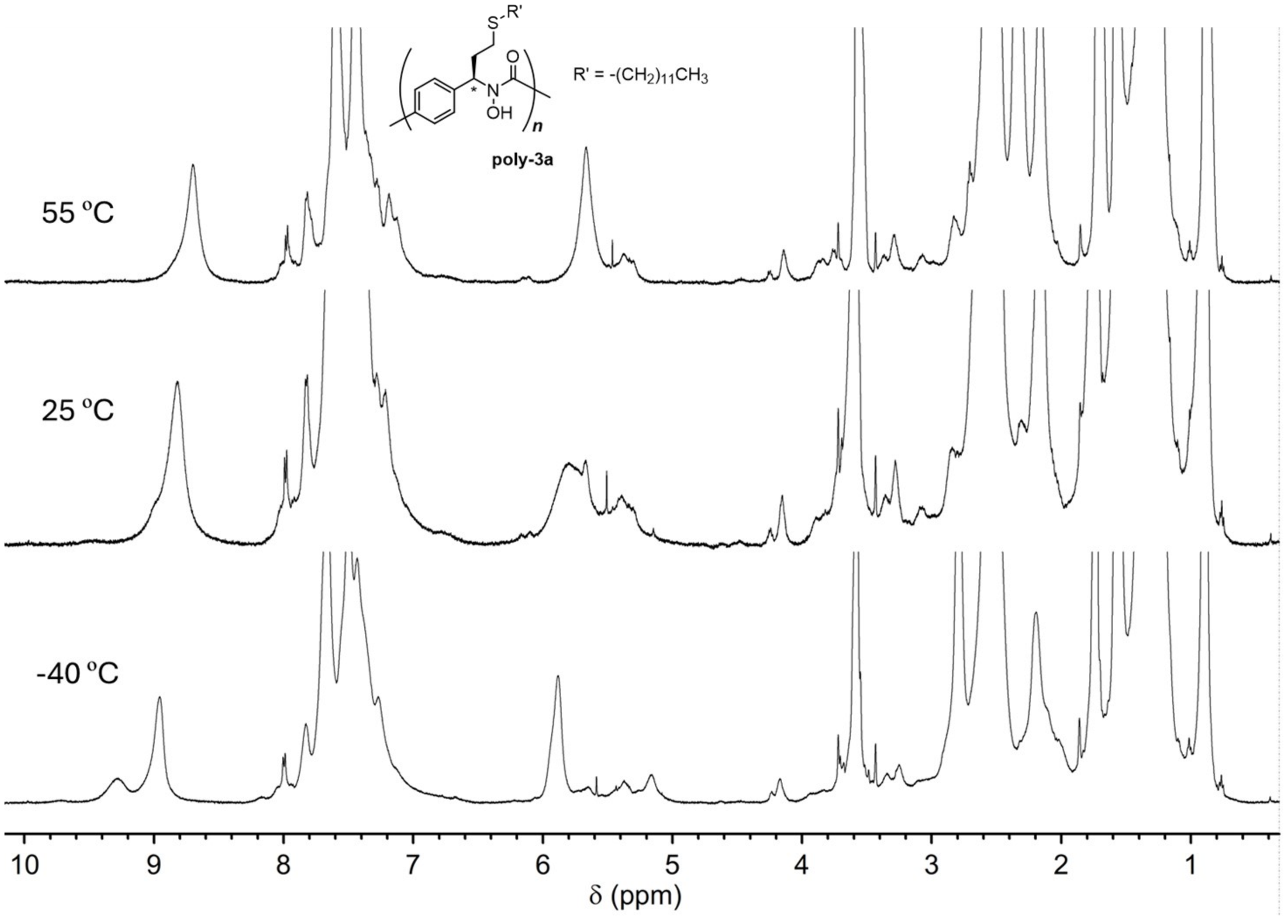


Fig. S9 Temperature dependence of model compound **poly-3a** in THF-d_8.

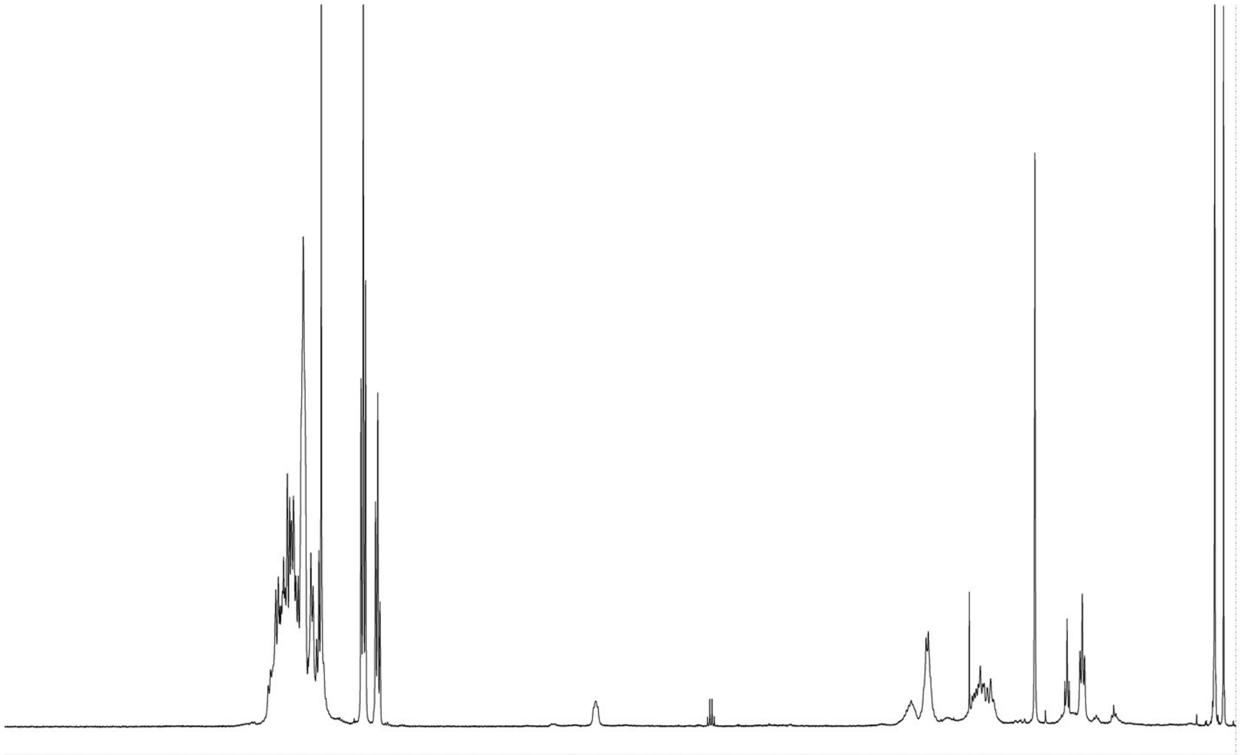


Fig. S10 ^{1}H NMR (500 MHz) spectrum of **M4** in $CDCl_3$.

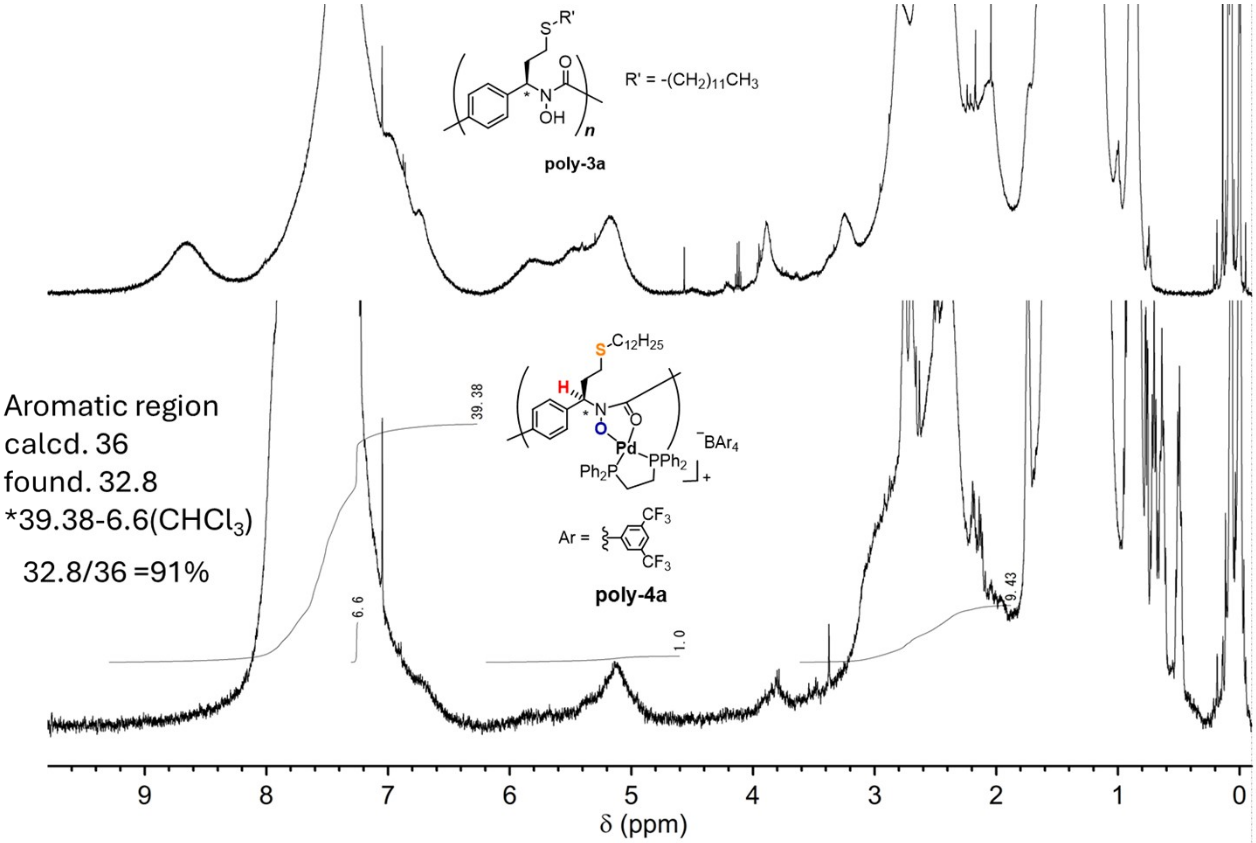


Fig. S11 ^{1}H NMR (500 MHz) spectrum of **poly-3a** and **poly-4a** in $CDCl_3$.

3. IR Spectra

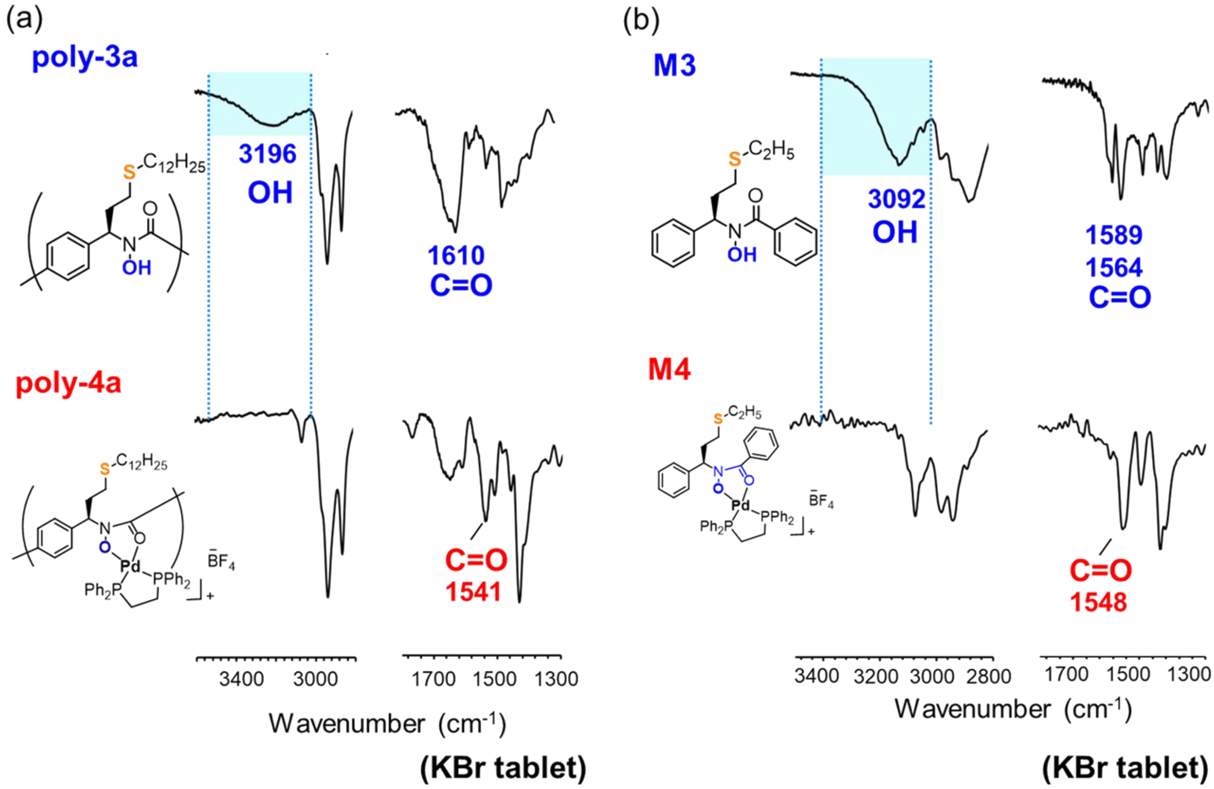


Fig. S12 IR Spectra of (a) **poly3a** and **poly-4a**, (b) **M3** and **M4** (KBr tablet).

4. References

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(3) Kanbayashi, N.; Okamura, T.; Onitsuka, K. New Method for Asymmetric Polymerization: Asymmetric Allylic Substitution Catalyzed by a Planar-Chiral Ruthenium Complex. *Macromolecules* **2014**, *47* (13), 4178-4185.