Supplementary Information

Design of main-chain polymer of chiral imidazolidinone for asymmetric organocatalysis application

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General

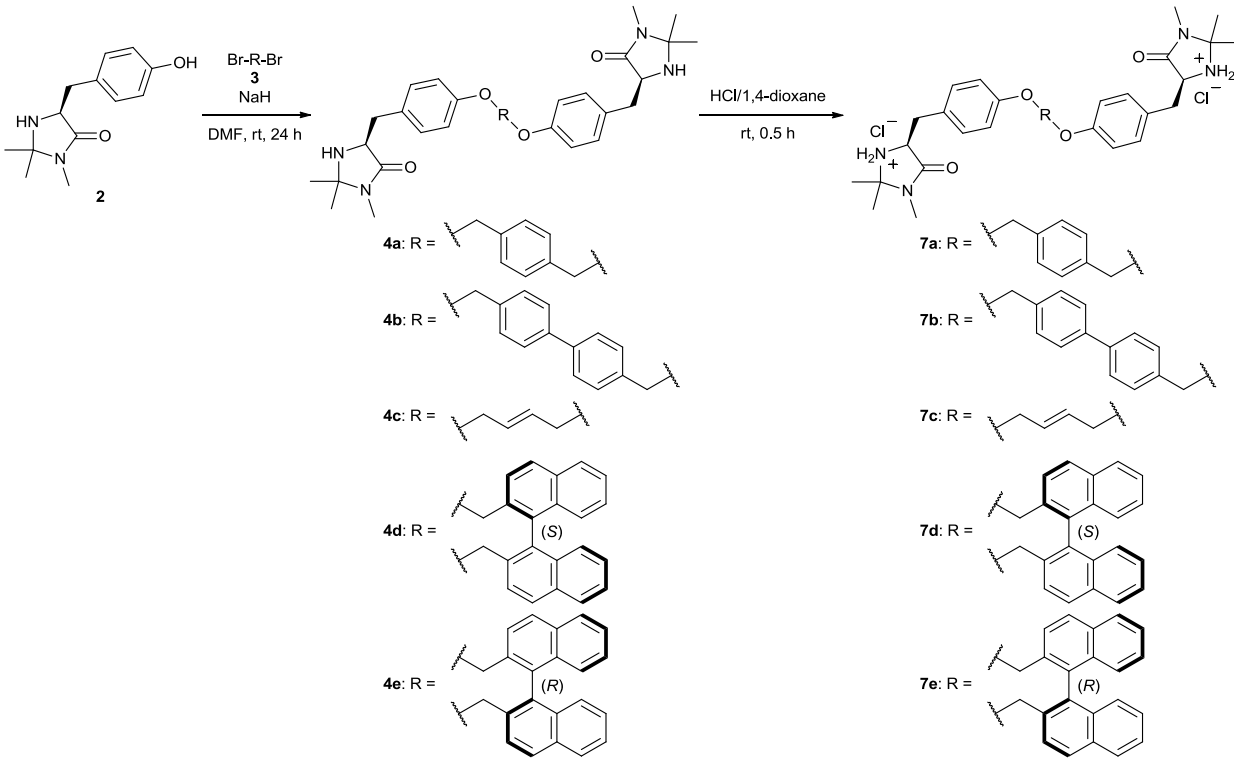
Materials. All solvent and reagents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Ltd., or Tokyo Chemical Industry Co., Ltd. at the highest available purity and used as is unless noted otherwise. Cyclopentadiene was obtained by the pyrolysis of dicyclopentadiene at 200 ^{o}C.

Measurements. Reactions were monitored by thin-layer chromatography (TLC) using Merck precoated silica gel plates (Merck 5554, 60F254). Column chromatography was performed with a silica gel column (Wakogel C-200, 100−200 mesh). Melting points were recorded using a Yanaco micro melting apparatus and are uncorrected. ^{1}H (300 MHz) and ^{13}C (75 MHz) spectra were measured on a Varian Mercury 300 spectrometer and ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra were measured on a JEOL JNM-ECS 400SS. The J values are reported in Hertz. IR spectra were recorded with a JEOL JIR-7000 FT-IR spectrometer and were reported in reciprocal centimeters (cm^{-1}). Elemental analyses were performed at the Microanalytical Center of Kyoto University. Size exclusion chromatography (SEC) was obtained with Tosoh instrument with HLC 8020 UV (254 nm) or refractive index detection. DMF was used as a carrier solvent at a flow rate of 1.0 mL/min at 40 ^{o}C. Two polystyrene gel columns of bead size 10 μm were used. A calibration curve was made to determine number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) values with polystyrene standards. GC analyses were performed with a Shimadzu

Capillary Gas Chromatograph GC-2014 equipped with a capillary column (Astec CHIRALDEX B-PH, 30 m x 0.25 mm). Optical rotations were recorded with a JASCO DIP-149 digital polarimeter using 10 cm thermostated microcell.

Synthesis of (*S*)-5-(4-hydroxybenzyl)-2,2,3-trimethylimidazolidin-4-one (2). The synthesis of **2** was carried out according to the similar procedure reported in reference 1. **2** was obtaiend as a yellowish liquid. yield 99%; The ^{1}H NMR data was in good agreement with the values of reference **2**.

Synthesis of Chiral Imidazolidinone Dimers (7a-7e)



Synthesis of **7a:** A 50 mL round-bottomed flask equipped with a magnetic stirring bar was charged with **2** (0.703 g, 3.00 mmol) and 10 mL of dry DMF. NaH (0.0864 g, 3.60 mmol), α,α'-dibromo-*p*-xylene (0.317g, 1.20 mmol), and 5 mL of dry DMF was then added to the mixture at 0 ^{o}C and the mixture was stirred at room temperature for 12 h. Excess NaH was quenched with methanol and the solvent of mixture was removed with a vacuum pump. After adding CH_2Cl_2 and H_2O to the residue, the organic layer was separated and dried with anhydrous $MgSO_4$. $MgSO_4$ was removed by filtration and the solvent was removed with a vacuum pump. The reside was purified by silica gel column chromatography (with CH_2Cl_2 as an eluent). **4a** (0.494 g, 0.865 mmol) was obtaiend as a yellowwish liquid.

4a was added to 4.0 M HCl in 1,4-dioxane at rrom temperature and stiired for 0.5 h. Removal of solvent under high vacum gave **7a** as a yellowwish solid. yield 72%; $[\alpha]_D$ = −57.3 (*c* = 1.01 g/dL in CH_3OH); ^1H NMR (300 MHz, $CDCl_3$, δ = 0 ($(CH_3)_4Si$)): δ = 1.40 (s, 6H, CH_3), 1.67 (s, 6H, CH_3), 2.78 (s, 6H, NCH_3), 3.32 (m, 4H, CH_2), 3.76 (s, 2H, CH), 4.93 (s, 4H, OCH_2), 6.85 (d, *J* = 9.0 Hz, 4H, Ar), 7.29 (s, 4H, Ar), 7.35 (d, *J* = 6.0 Hz, 4H, Ar), 10.20 (br, 2H, NH), 11.46 ppm (br, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$, δ = 77.1 ($CDCl_3$)): δ = 24.48, 24.75, 25.29, 33.80, 58.45, 67.24, 69.70, 77.95, 115.39, 126.68, 127.83, 131.30, 136.75, 158.22, 166.20 ppm; FT-IR (KBr): ν = 1713 (C=O) cm^{-1}.

Synthesis of **7b**: The synthetic procedure is similar to that of **7a**. Final purification of **4b** was carried out by silica gel column chromatography (with 1:4 ethanol/ethyl acetate as an eluent). **7b** was obtaiend as a yellowwish solid. yield 88%; $[\alpha]_D$ = −64.0 (*c* = 1.00 g/dL in CH_3OH); ^1H NMR (300 MHz, $CDCl_3$, δ = 0 ($(CH_3)_4Si$)): δ = 1.53 (s, 6H, CH_3), 1.70 (s, 6H, CH_3), 2.78 (s, 6H, NCH_3), 3.39 (m, 4H, CH_2), 4.36 (s, 2H, CH), 4.93 (s, 4H, OCH_2), 6.93 (d, *J* = 9.0 Hz, 4H, Ar), 7.35 (m, 4H, Ar), 7.48 (d, *J* = 9.0 Hz, 4H, Ar), 10.16 (br, 2H, NH), 10.41 ppm (br, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$, δ = 77.1 ($CDCl_3$)): δ = 24.37, 24.80, 25.27, 33.75, 58.30, 67.24, 69.70, 77.86, 115.27, 126.75, 127.32, 128.13, 131.26, 136.07, 140.44, 158.37, 166.20 ppm; FT-IR (KBr): ν = 1711 (C=O) cm^{-1}.

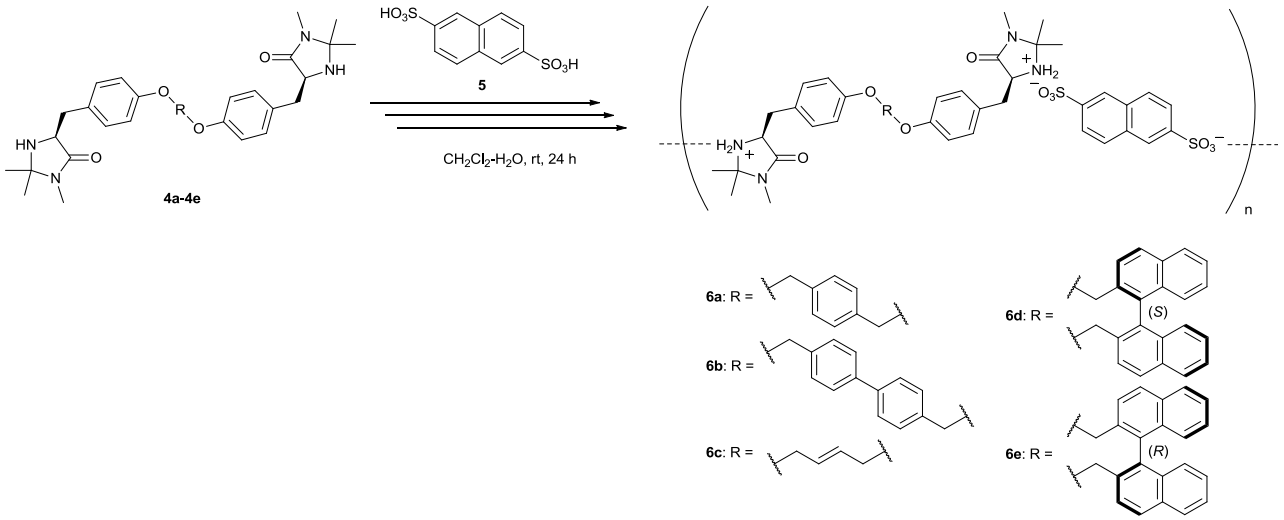
Synthesis of **7c**: The synthetic procedure is similar to that of **7a**. Final purification of **4c** was carried out by silica gel column chromatography (with 1:4 ethanol/ethyl acetate as an eluent). **7c** was obtaiend as a brownwish solid. yield 51%; $[\alpha]_D$ = −43.5 (*c* = 1.00 g/dL in CH_3OH); ^1H NMR (300 MHz, $CDCl_3$, δ = 0 ($(CH_3)_4Si$)): δ = 1.52 (s, 6H, CH_3), 1.71 (s, 6H, CH_3), 2.79 (s, 6H, NCH_3), 3.37 (m, 4H, CH_2), 4.35 (s, 2H, CH), 4.42 (s, 4H, OCH_2), 5.89 (s, 2H, -CH=), 6.81 (d, *J* = 9.0 Hz, 4H, Ar), 7.35 (d, *J* = 9.0 Hz, 4H, Ar), 10.23 (br, 2H, NH), 11.45 ppm (br, 2H, NH); ^{13}C NMR (75 MHz, $CDCl_3$, δ = 77.1 ($CDCl_3$)): δ = 24.19, 24.64, 25.21, 33.56, 58.31, 67.09, 67.57, 77.78, 114.99, 126.70, 128.25, 131.11, 157.88, 166.11 ppm; FT-IR (KBr): ν = 1713 (C=O) cm^{-1}.

Synthesis of **7d**: The synthetic procedure is similar to that of **7a**. Final purification of **4d** was carried out by silica gel column chromatography (with 1:11

ethanol/ethyl acetate as an eluent). **7d** was obtaiend as a yellowwish solid. yield 60%; $[\alpha]_D$ = −34.9 (*c* = 1.00 g/dL in CH_3OH); ^1H NMR (400 MHz, $CDCl_3$, δ = 0 ($(CH_3)_4Si$)): δ = 1.60 (s, 6H, CH_3), 1.68 (s, 6H, CH_3), 2.75 (s, 6H, NCH_3), 3.19 (m, 4H, CH_2), 4.26 (s, 2H, CH), 4.66 (m, 4H, OCH_2), 6.64 (dd, *J* = 6.4, 2.0 Hz, 4H, Ar), 7.08 (d, *J* = 8.0 Hz, 4H, Ar), 7.17 (dd, *J* = 8.0 Hz, 4H, Ar), 7.26 (t, *J* = 8.0 Hz, 4H, Ar), 7.46 (t, *J* = 4.0 Hz, 4H, Ar), 7.78 (d, *J* = 6.1, 2.5 Hz, 4H, Ar), 7.92 (d, *J* = 8.0 Hz, 4H, Ar), 7.97 (dd, *J* = 6.4, 2.0 Hz, 4H, Ar), 9.97 (br, 2H, NH), 11.14 ppm (br, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$, δ = 77.1 ($CDCl_3$)): δ = 24.16, 24.99, 25.28, 25.74, 34.05, 58.28, 67.21, 68.12, 68.19, 78.01, 115.53, 125.66, 125.87, 126.39, 126.94, 127.02, 128.40, 128.84, 130.93, 132.67, 133.24, 133.25, 133.65, 158.02, 166.23 ppm; FT-IR (KBr): ν = 1711 (C=O) cm^{-1}.

Synthesis of **7e**: The synthetic procedure is similar to that of **7a**. Final purification of **4e** was carried out by silica gel column chromatography (with 1:11 ethanol/ethyl acetate as an eluent). **7e** was obtaiend as a yellowwish solid. yield 24%; $[\alpha]_D$ = −44.5 (*c* = 1.02 g/dL in CH_3OH); ^1H NMR (400 MHz, $CDCl_3$, δ = 0 ($(CH_3)_4Si$)): δ = 1.53 (s, 6H, CH_3), 1.68 (s, 6H, CH_3), 2.78 (s, 6H, NCH_3), 3.23 (s, 4H, CH_2), 4.23 (s, 2H, CH), 4.55 (m, 4H, OCH_2), 6.60 (d, *J* = 4.0 Hz, 4H, Ar), 7.07 (d, *J* = 8.0 Hz, 4H, Ar), 7.14 (d, *J* = 8.0 Hz, 4H, Ar), 7.25 (m, 4H, Ar), 7.47 (t, *J* = 8.0 Hz, 4H, Ar), 7.81 (dd, *J* = 5.0, 3.5 Hz, 4H, Ar), 7.93 (d, *J* = 8.0 Hz, 4H, Ar), 8.01 (d, *J* = 4.0 Hz, 4H, Ar), 10.24 ppm (br, 4H, NH); ^{13}C NMR (100 MHz, $CDCl_3$, δ = 77.1 ($CDCl_3$)): δ = 23.61, 24.85, 25.32, 33.88, 57.98, 67.24, 68.65, 77.68, 115.83, 125.84, 125.96, 126.38, 126.92, 127.57, 128.37, 128.84, 130.49, 132.75, 133.25, 133.31, 133.81, 158.06, 166.45 ppm; FT-IR (KBr): ν = 1710 (C=O) cm^{-1}.

Synthesis of Main-chain Polymers of Chiral Imidazolidinone (6a-6e)



Synthesis of **6a**: A 50 mL round-bottomed flask equipped with a magnetic stirring bar was charged with 2,6-naphthalene disulfonic acid (**5**) (0.288 g, 1.00 mmol) and 6 mL of H_2O. **4a** (0.571 g, 1.00 mmol) in 12 mL of CH_2Cl_2 was then added to the mixture at room temperature and the mixture was vigorously stirred for 24 h. After the solvent was removed by a vacumm pump, the residue was washed with CH_2Cl_2 and H_2O. The solid was dried under vacuum to give **6a** (0.825 g) as an off-white powder. yield 96%; ^{1}H NMR (300 MHz, DMSO-d_6, δ = 2.50 (DMSO)):δ = 1.46 (s, 6H, CH_3), 1.60 (s, 6H, CH_3), 2.77 (s, 6H, NCH_3), 2.90 (m, 2H, CH_2), 3.22 (m, 2H, CH_2), 4.56 (s, 2H, CH), 5.09 (s, 4H, OCH_2), 6.98 (d, *J* = 9.0 Hz, 4H, Ar), 7.28 (d, *J* = 9.0 Hz, 4H, Ar), 7.45 (s, 4H, Ar), 7.71 (d, *J* = 6.0 Hz, 4H, Ar), 7.93 (d, *J* = 9.0 Hz, 4H, Ar), 8.13 ppm (s, 4H, Ar); ^{13}C NMR (75 MHz, DMSO-d_6, δ = 39.51 (DMSO)): δ = 21.77, 23.84, 24.92, 32.78, 57.53, 68.90, 76.76, 114.81, 123.90, 124.29, 127.80, 128.02, 128.22, 130.31, 131.99, 136.75, 145.78, 157.40, 166.64 ppm; FT-IR (KBr): ν = 1716 (C=O), 1237 (SO_3), 1020 (SO_3) cm^{-1}; $M_{n(SEC)}$ = 58.9 kg/mol, $M_{w(SEC)}$ = 193 kg/mol, M_w/M_n = 3.28.

Synthesis of **6b**: The synthetic procedure is similar to that of **6a**. **6b** was obtaiend as an off-white powder. yield 99%; ^{1}H NMR (300 MHz, DMSO-d_6, δ = 2.50 (DMSO)): δ = 1.35 (s, 6H, CH_3), 1.47 (s, 6H, CH_3), 2.72 (s, 6H, NCH_3), 2.88 (m, 2H, CH_2), 3.11 (m, 2H, CH_2), 4.19 (br, 2H, CH), 5.14 (s, 4H, OCH_2), 6.98 (d, *J* = 6.0 Hz, 4H, Ar), 7.28 (d, *J* = 5.4 Hz, 4H, Ar), 7.53 (d, *J* = 5.4 Hz, 4H, Ar), 7.69 (d, *J* = 6.0 Hz, 4H, Ar), 7.74 (d, *J* = 9.0 Hz, 2H, Ar), 7.93 (dd, *J* = 4.8, 1.7 Hz, 2H, Ar), 8.16 ppm (s, 2H, Ar),; ^{13}C NMR (75 MHz, DMSO-d_6, δ = 39.51 (DMSO)): δ = 23.72, 24.03, 25.54, 30.82, 58.24, 68.79, 76.24, 85.54, 114.77, 123.91, 124.34, 126.76, 128.20,

130.24, 132.00, 136.54, 139.28, 145.87, 157.18 ppm; FT-IR (KBr): ν = 1717 (C=O), 1234 (SO_3), 1030 (SO_3) cm^{-1}; $M_{n(SEC)}$ = 18.6 kg/mol, $M_{w(SEC)}$ = 42.5 kg/mol, M_w/M_n = 2.28.

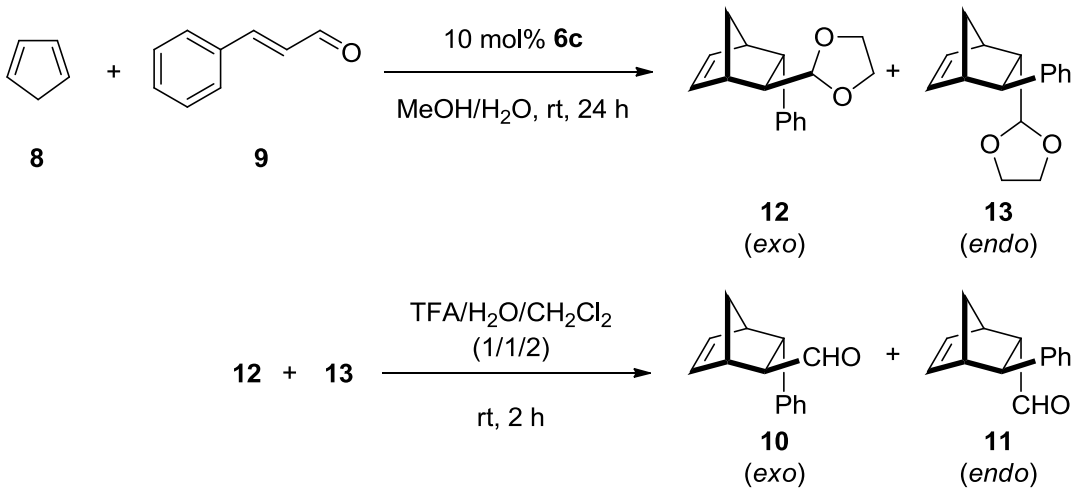
Synthesis of **6c**: The synthetic procedure is similar to that of **6a**. **6c** was obtaiend as a brownwish powder. yield 88%; ^{1}H NMR (300 MHz, DMSO-d_6, δ = 2.50 (DMSO)): δ = 1.47 (s, 6H, CH_3), 1.60 (s, 6H, CH_3), 2.78 (s, 6H, NCH_3), 2.89 (m, 2H, CH_2), 3.22 (m, 2H, CH_2), 4.57 (m, 6H, CH, OCH_2), 6.05 (s, 2H, -CH=), 6.93 (d, *J* = 6.0 Hz, 4H, Ar), 7.28 (d, *J* = 9.0 Hz, 4H, Ar), 7.70 (d, *J* = 6.0 Hz, 2H, Ar), 7.92 (dd, *J* = 6.0, 2.4 Hz, 2H, Ar), 8.12 ppm (s, 2H, Ar); ^{13}C NMR (75 MHz, DMSO-d_6, δ = 39.51 (DMSO)): δ = 21.78, 23.74, 24.96, 32.57, 48.73, 57.59, 67.23, 76.73, 114.71, 123.96, 124.33, 128.29, 128.40, 130.40, 132.04, 145.75, 157.32, 166.53 ppm; FT-IR (KBr): ν = 1718 (C=O), 1236 (SO_3), 1021 (SO_3) cm^{-1}; $M_{n(SEC)}$ = 26.2 kg/mol, $M_{w(SEC)}$ = 89.1 kg/mol, M_w/M_n = 3.40.

Synthesis of **6d**: The synthetic procedure is similar to that of **6a**. **6d** was obtaiend as an off-white powder. yield >99%; ^{1}H NMR (300 MHz, DMSO-d_6, δ = 2.50 (DMSO)): δ = 1.26 (m, 12H, CH_3), 2.66 (s, 6H, NCH_3), 2.69 (s, 2H, CH_2), 3.00 (m, 2H, CH_2), 3.77 (br, 2H, CH), 4.66 (dd, *J* = 21, 12 Hz, 4H, OCH_2), 6.61 (d, *J* = 9.0 Hz, 4H, Ar), 7.04 (m, 4H, Ar), 7.25 (d, *J* = 9.0 Hz, 2H, Ar), 7.35 (t, *J* = 6.0 Hz, 2H, Ar), 7.53 (t, *J* = 7.5 Hz, 2H, Ar), 7.71 (d, *J* = 9.0 Hz, 2H, Ar), 7.81 (d, *J* = 9.0 Hz, 2H, Ar), 7.91 (d, *J* = 6.0 Hz, 2H, Ar), 8.05 (d, *J* = 9.0 Hz, 2H, Ar), 8.11 ppm (m, 4H, Ar); ^{13}C NMR (75 MHz, DMSO-d_6, δ = 39.51 (DMSO)): δ = 23.78, 24.80, 25.97, 35.54, 58.70, 68.04, 75.71, 114.31, 116.01, 123.92, 124.35, 125.64, 126.41, 126.82, 128.21, 128.28, 128.61, 130.24, 130.41, 132.01, 132.07, 132.83, 133.55, 133.59, 145.88, 155.01, 156.90 ppm; FT-IR (KBr): ν = 1683 (C=O), 1234 (SO_3), 1018 (SO_3) cm^{-1}; $M_{n(SEC)}$ = 92.5 kg/mol, $M_{w(SEC)}$ = 240 kg/mol, M_w/M_n = 2.59.

Synthesis of **6e**: The synthetic procedure is similar to that of **6a**. **6e** was obtaiend as an off-white powder. yield 79%; ^{1}H NMR (300 MHz, DMSO-d_6, δ = 2.50 (DMSO)): δ = 1.41 (s, 6H, CH_3), 1.56 (s, 6H, CH_3), 2.74 (m, 8H, NCH_3, CH_2), 3.16 (br, 2H, CH_2), 3.48 (br, 2H, CH), 4.70 (dd, *J* = 60, 12 Hz, 4H, OCH_2), 6.64 (d, *J* = 9.0 Hz, 2H, Ar), 6.88 (dd, *J* = 14, 8.3 Hz, 2H, Ar), 7.12 (d, *J* = 6.0 Hz, 4H, Ar), 7.38 (m, 2H, Ar), 7.58 (m, 2H, Ar), 7.69 (d, *J* = 9.0 Hz, 2H, Ar), 7.88 (m, 2H, Ar), 8.10 (m, 4H, Ar), 8.24 ppm (m, 2H, Ar); ^{13}C NMR (75 MHz, DMSO-d_6, δ = 39.51 (DMSO)): δ = 22.81,

24.86, 33.99, 58.24, 68.79, 76.24, 114.77, 123.91, 124.34, 126.76, 128.20, 128.29, 128.54, 130.24, 130.37, 132.00, 136.54, 139.28, 145.87, 157.18 ppm; FT-IR (KBr): ν = 1703 (C=O), 1173 (SO_3), 1023 (SO_3) cm^{-1}; $M_{n(SEC)}$ = 24.7 kg/mol, $M_{w(SEC)}$ = 56.6 kg/mol, M_w/M_n = 2.29.

Asymmetric Diels-Alder reaction of 1,3-cyclopentadiene and *trans*-cinnamaldehyde with use of 8c (entry 3 in Table 3).



A 5 mL round-bottom flask equipped with a magnetic stirring bar was charged with *trans*-cinnamaldehyde (**9**) (0.264 g, 2.00 mmol), a main-chain polymer of chiral imidazolidinone (**6c**) 0.162 g (0.20 mmol of catalyst), and 1.0 mL of CH_3OH/H_2O (95/5, *v*/*v*) mixed solvent. After three cycles of freeze-thaw under liquid nitrogen, the mixture was stirred at room temperature for 10 min. 1,3-Cyclopentadiene (**8**) (0.397 g, 6.00 mmol) was added to the mixture and stirred at room temperature for 24 h. After removing solvents by a vacuum pump, the residue was washed with CH_2Cl_2. The organic layer was collected and dried with anhydrous $MgSO_4$. After removing $MgSO_4$ by filtration, solvent of the filtrate was removed with a vacuum pump and the residual liquid was purified by silica gel column chromatography (with 1:19 ethyl acetate/hexanes as an eluent). The products with diethyl acetal **12** and **13** were obtained as colorless liquids.

Hydrolysis of **12** and **13** was performed by adding 1 mL of trifluoroacetic acid, 1 mL of H_2O, and 2 mL of CH_2Cl_2. After stirring the mixture at room temperature for 2 h, the mixture was neutrized by saturated $NaHCO_3$ aqueous solution. The mixture was extracted with 5 mL of Et_2O three times and the organic layer was dried with anhydrous $MgSO_4$. After removing $MgSO_4$ by filtration, solvent of the filtrate was removed with a vacuum pump and the residual liquid was purified by silica gel column chromatography (with 1:19 ethyl acetate/hexanes as an eluent). The products **10** and **11** were obtained as colorless liquids. ^{1}H NMR (300 MHz, $CDCl_3$, δ = 0 ($(CH_3)_4Si$): δ = 1.52-1.64(m, CH_2, 1H), 1.82(d, J = 8.7 Hz, CH_2, 1H), 2.60(m, 0.55H, *exo*-CH),

2.99(m, 0.45H, *endo*-CH), 3.08-3.14(m, 1H, CH), 3.23(m, 1H, CH), 3.34(m, 0.45H, *endo*-CH), 3.73(m, 0.55H, *exo*-CH), 6.08(m, 0.55H, *exo*-CH=), 6.18(m, 0.45H, *endo*-CH=), 6.35(m, 0.55H, *exo*-CH=), 6.42(m, 0.45H, *endo*-CH=), 7.13-7.32(m, 5H Ar), 9.61(m, 0.45H, *endo*-CHO), 9.93(m, 0.55H, *exo*-CHO). Conversion and *Exo*/*endo* ratio were determined by ^{1}H NMR with the comparison of proton signals of the aldehyde. The enantiomeric excess (93% ee (*exo*) and 97% ee (*endo*)) was determined by GC analysis (Astec CHIRALDEX B-PH; injection temperature 180 ^{o}C, detection temperature 180 ^{o}C, column temperature was increased from 120 ^{o}C to 150 ^{o}C with 5 ^{o}C/min and then to 180 ^{o}C with 1 ^{o}C/min; retention time: 26.2 min (*exo*(2*R*)), 26.8 min (*exo*(2*S*)), 27.3 min (*endo*(2*R*)), and 27.7 min (*endo*(2*S*)).

Reuse test of Main-chain Polymer of Chiral Imidazolidinone (6c): Recovered **6c** was dried with a vacuum pump at room temperature. A 5 mL round-bottom flask equipped with a magnetic stirring bar was charged with **9** (0.264 g, 2.00 mmol), recovered **6c**, and 1.0 mL of CH_3OH/H_2O (95/5, *v*/*v*) mixed solvent. After three cycles of freeze-thaw under liquid nitrogen, the mixture was stirred at room temperature for 10 min. **8** (0.397 g, 6.00 mmol) was added to the mixture and stirred at room temperature. The reaction was monitored by TLC or ^{1}H NMR. The procedures of the following work up and the hydrolysis were as same as those of the first reaction.

Table S1 Characterization of the main-chain polymers of chiral imidazolidinone

Entry	Polymer	Yield (%)	M_n[a] (kg/mol)	M_w[a] (kg/mol)	M_w/M_n[a]	DP[b]
1	**6a**	96	58.9	193	3.28	62
2	**6b**	99	18.6	42.5	2.28	20
3	**6c**	88	26.2	89.1	3.40	30
4	**6d**	>99	92.5	240	2.59	87
5	**6e**	79	24.7	56.6	2.29	23
6[c]	**6c**	-	27.1	90.0	3.28	32

[a] Measured by GPC. [b] DP (Degree of Polymerization) = $M_{n(polymer)}/M_{n(\mathbf{4}+\mathbf{5})}$. [c] Reused **6c**.

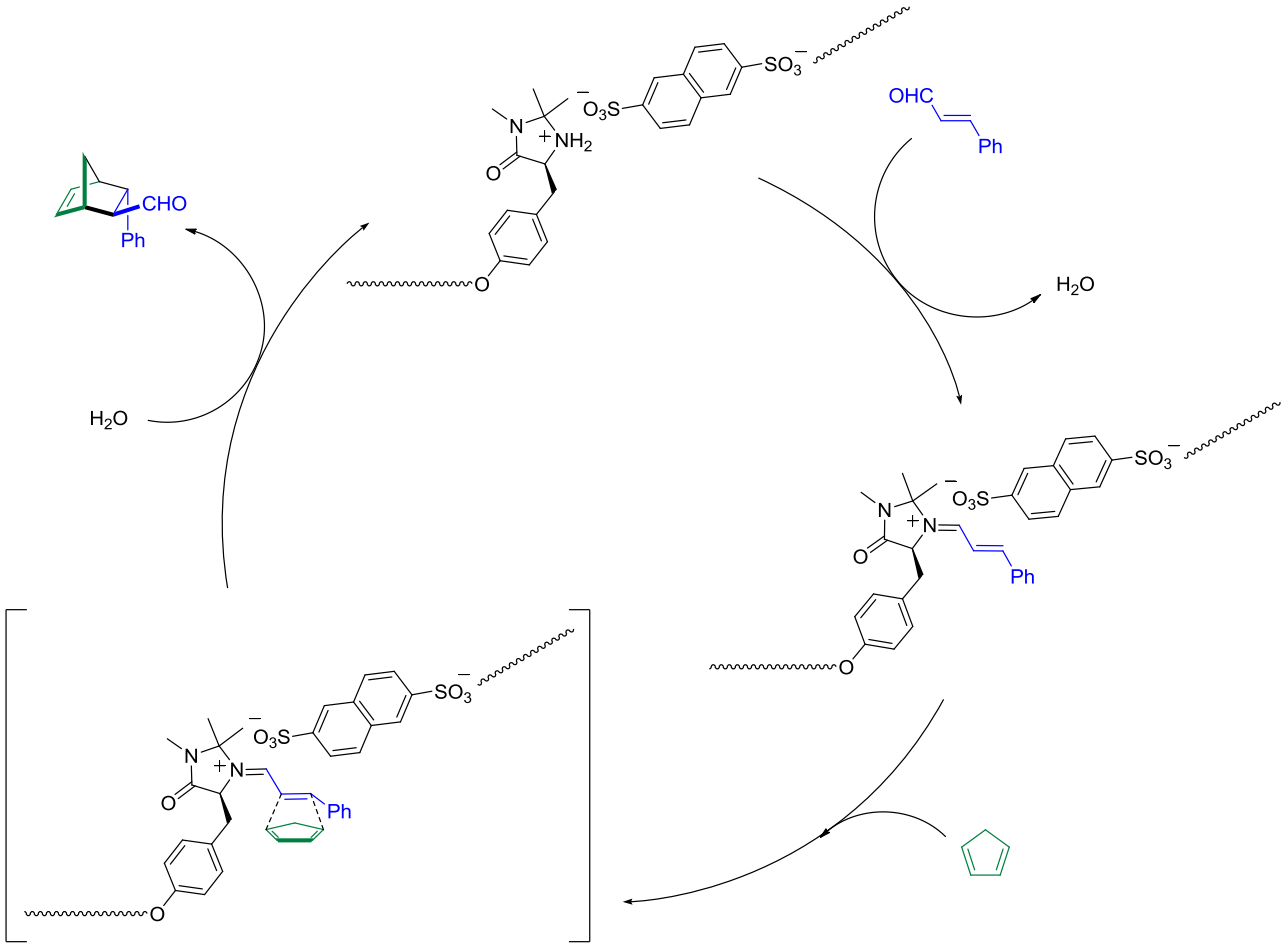


Figure S1. Estimated reaction mechanism with polymeric chiral imidazolidinone catalyst.

References

1. K. A. Ahrendt, C. J. Borths and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2000, **122**, 4243-4244.
2. Y. Zhang, L. Zhao, S. S. Lee and J. Y. Ying, *Adv. Synth. Catal.*, 2006, **348**, 2027–2032.

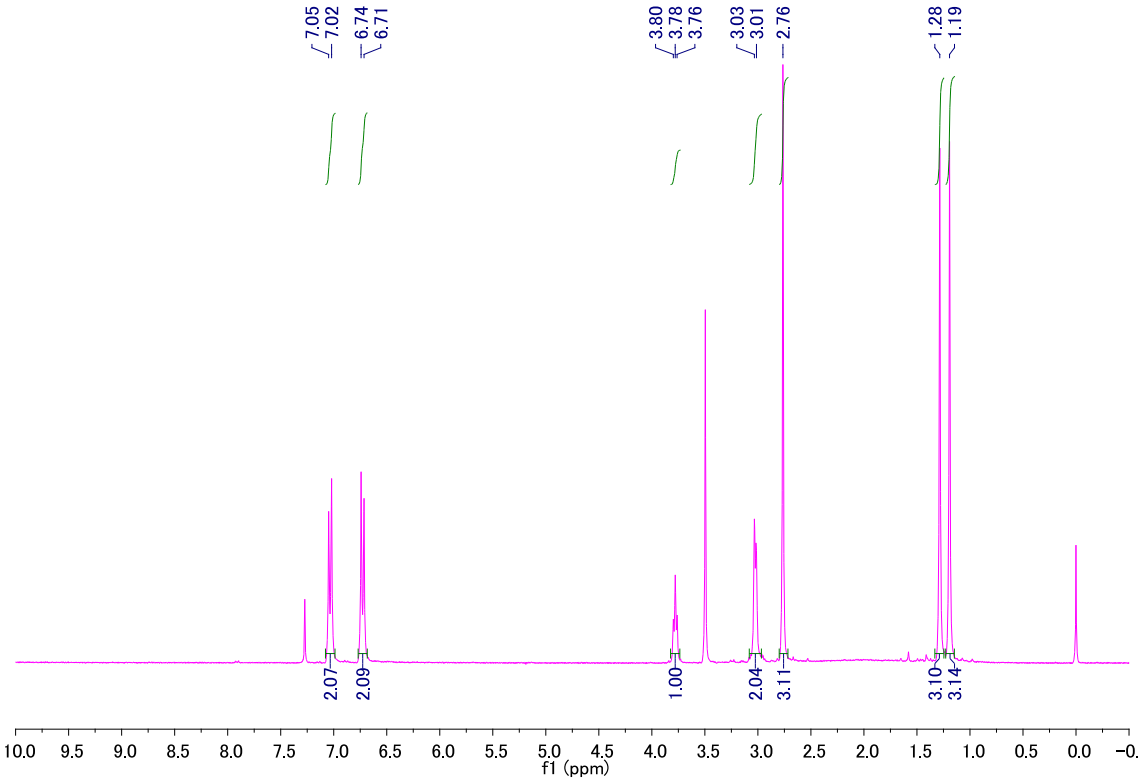


Figure S2. ^{1}H-NMR spectrum of **2**.

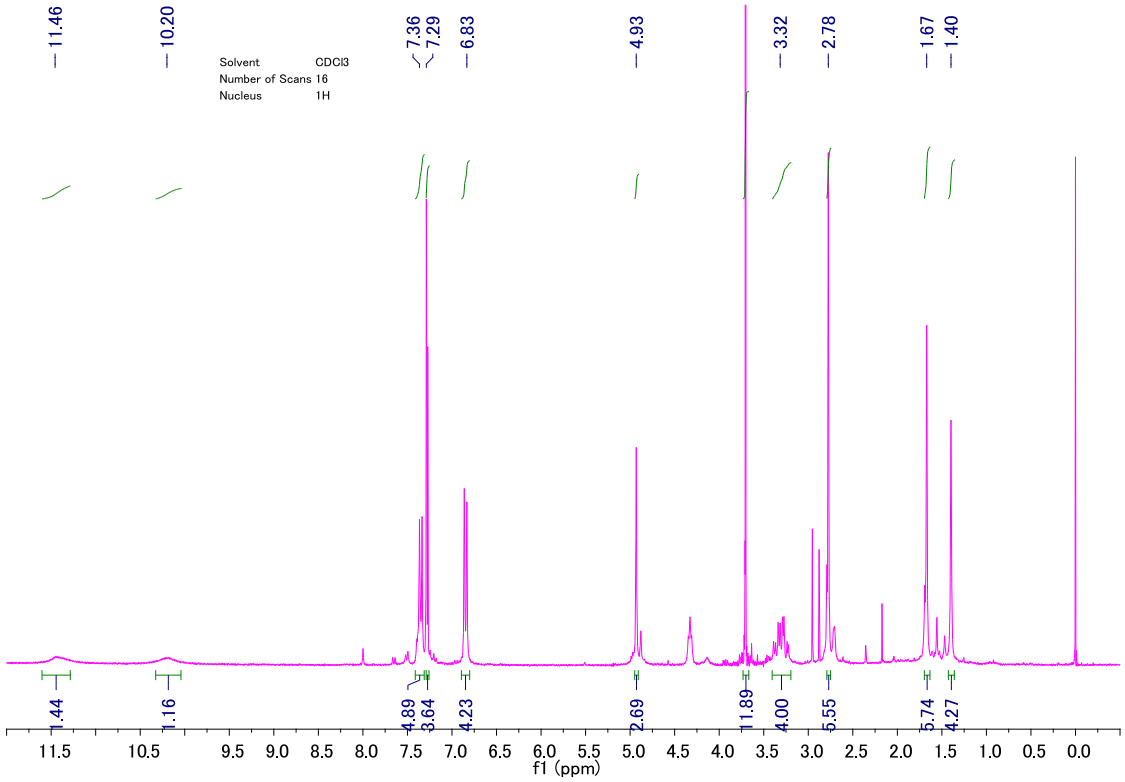


Figure S3. ^{1}H-NMR spectrum of **7a**.

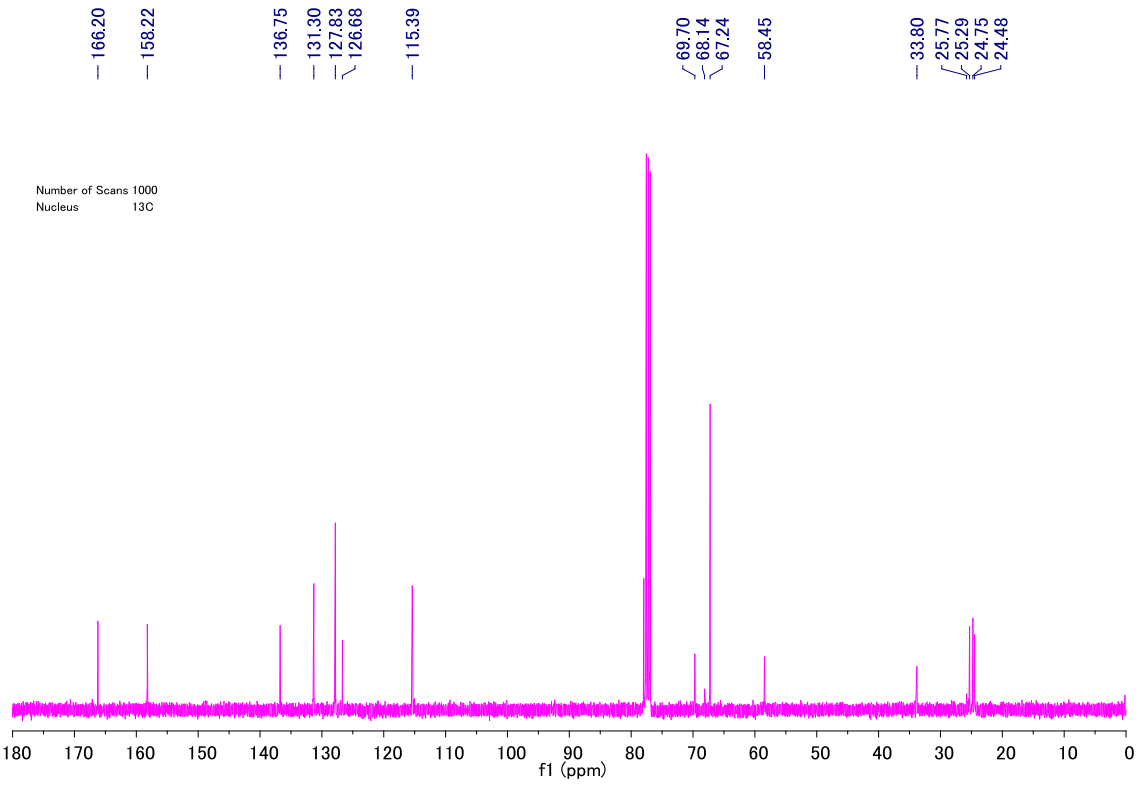


Figure S4. ^{13}C-NMR spectrum of **7a**.

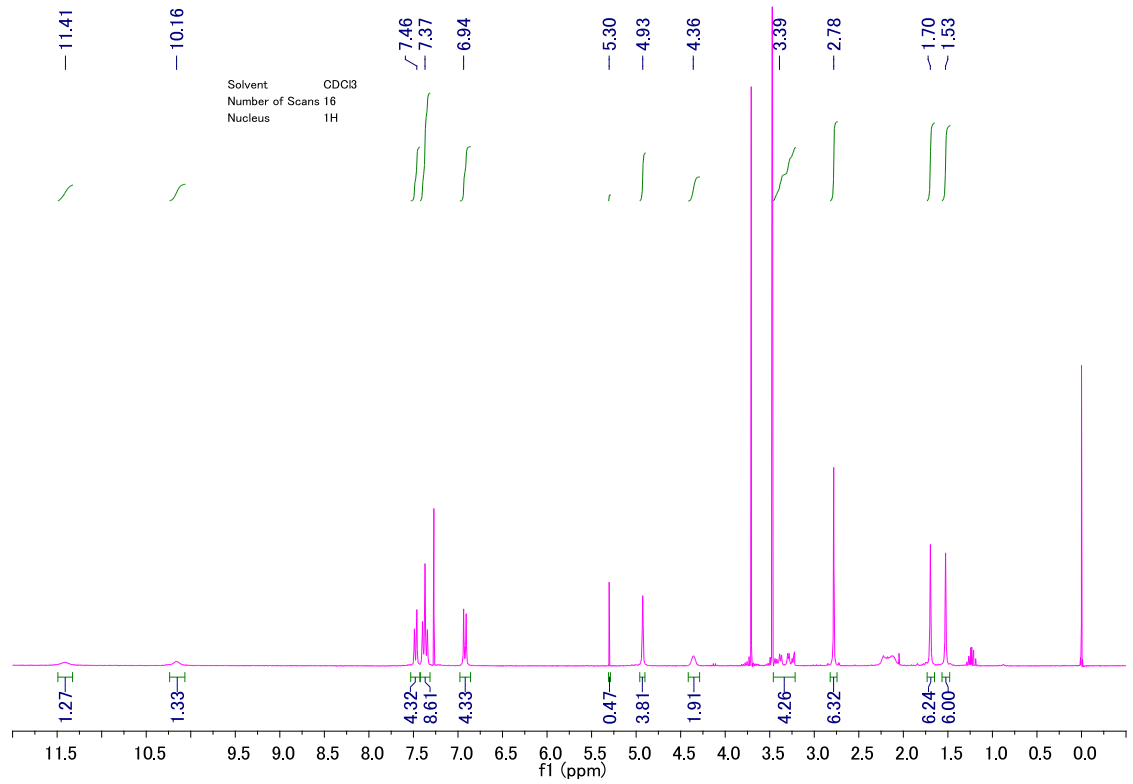


Figure S5. ^{1}H-NMR spectrum of **7b**.

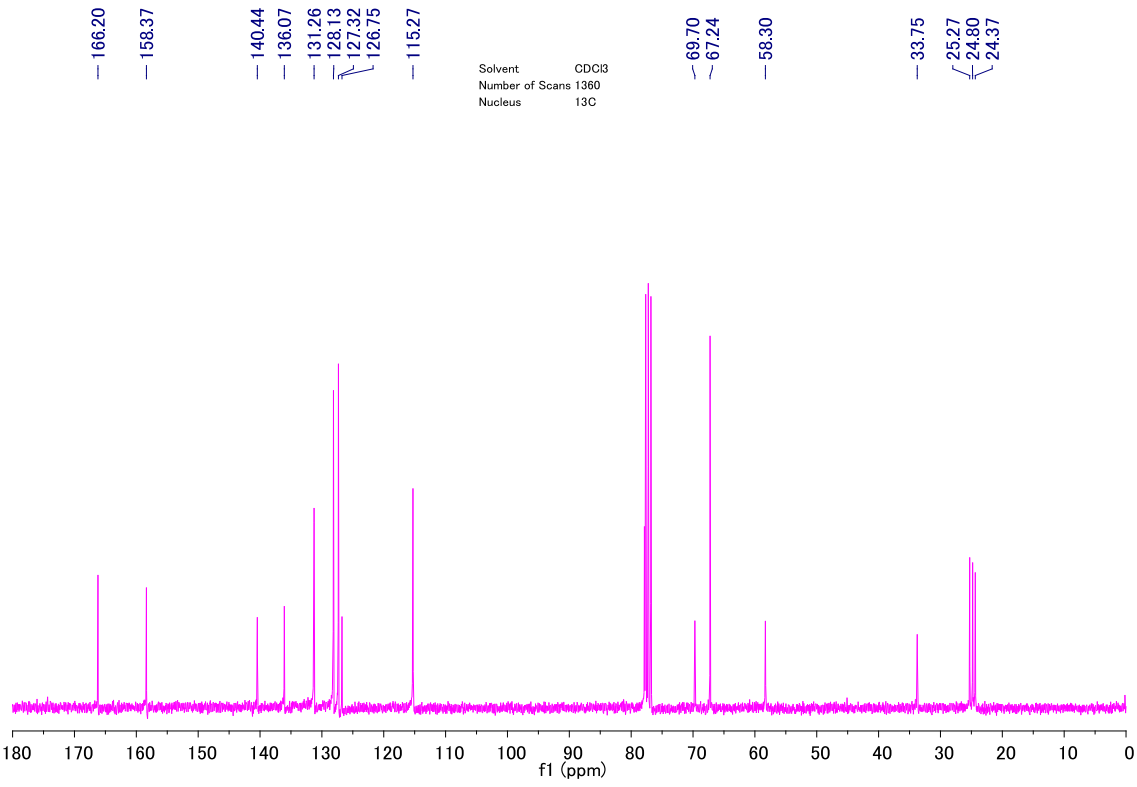


Figure S6. ^{13}C-NMR spectrum of **7b**.

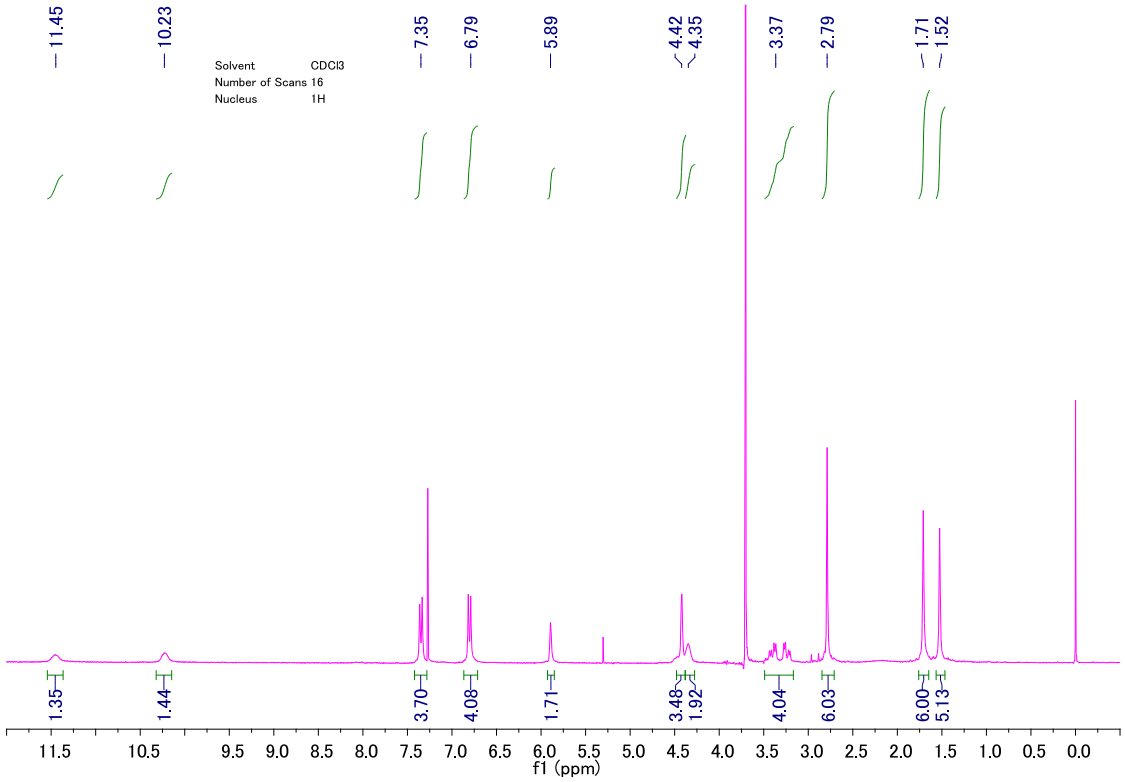


Figure S7. ^{1}H-NMR spectrum of **7c**.

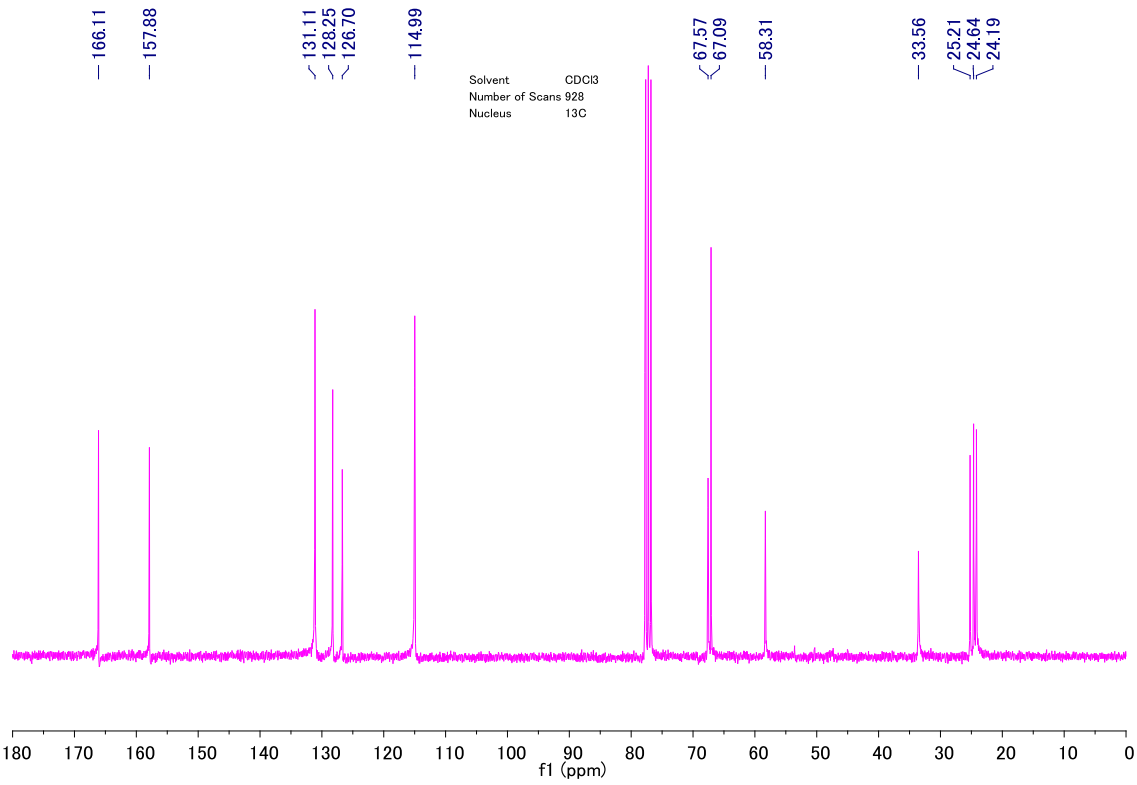


Figure S8. ^{13}C-NMR spectrum of **7c**.

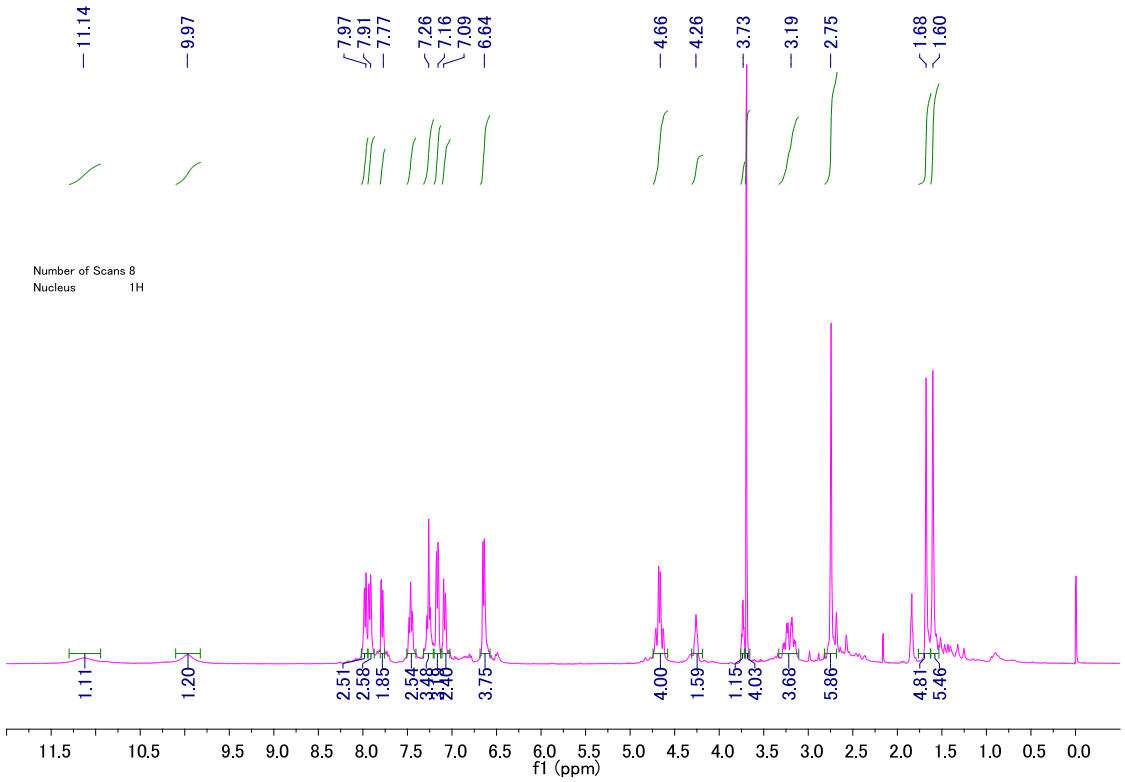


Figure S9. ^{1}H-NMR spectrum of **7d**.

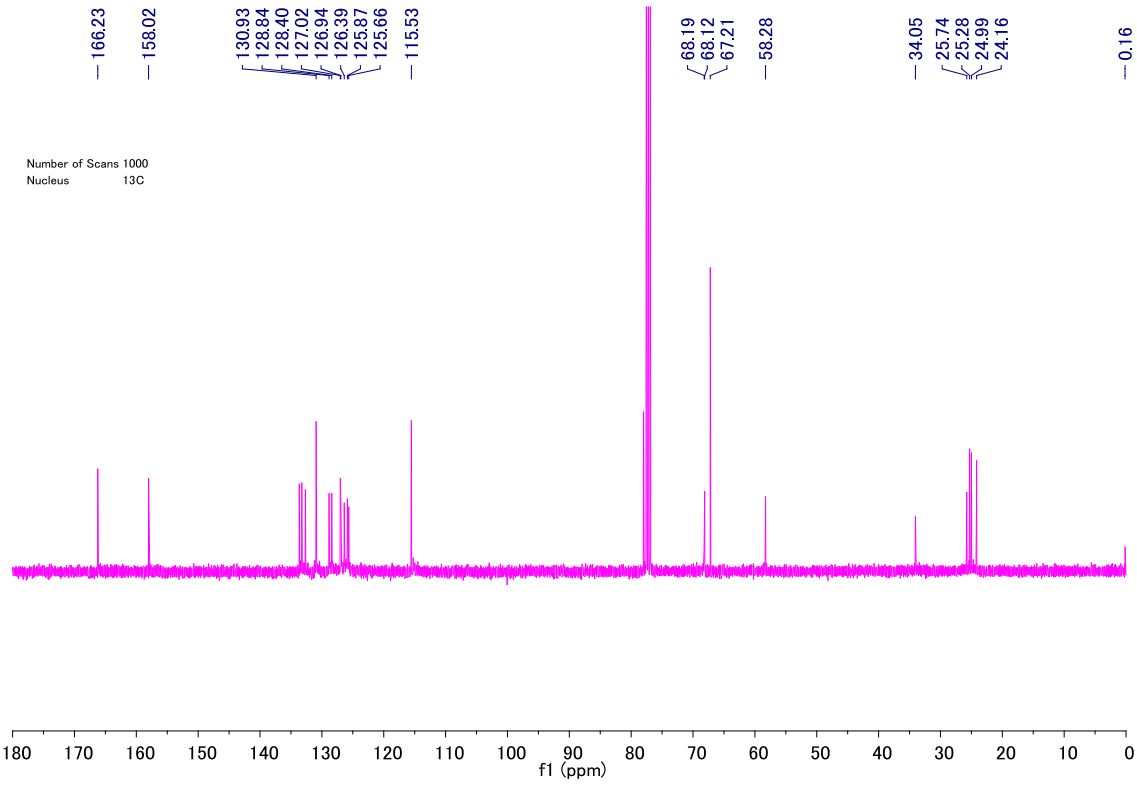


Figure S10. ^{13}C-NMR spectrum of **7d**.

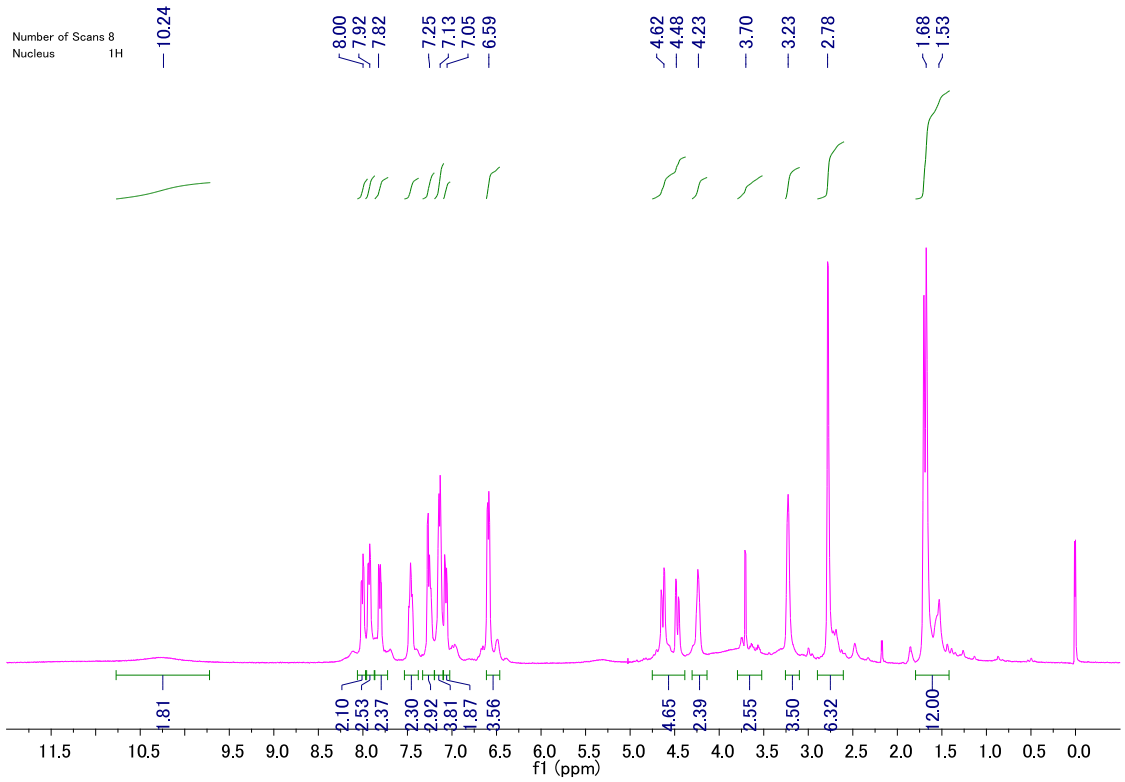


Figure S11. ^{1}H-NMR spectrum of **7e**.

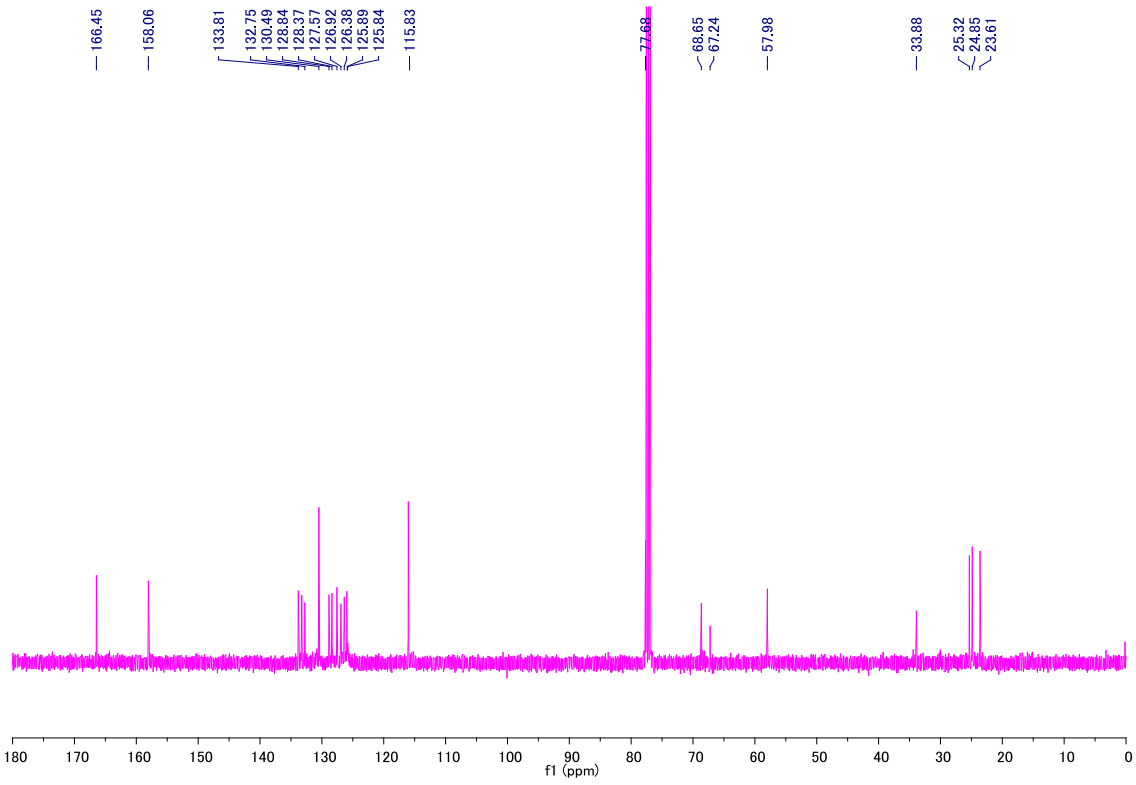


Figure S12. ^{13}C-NMR spectrum of **7e**.

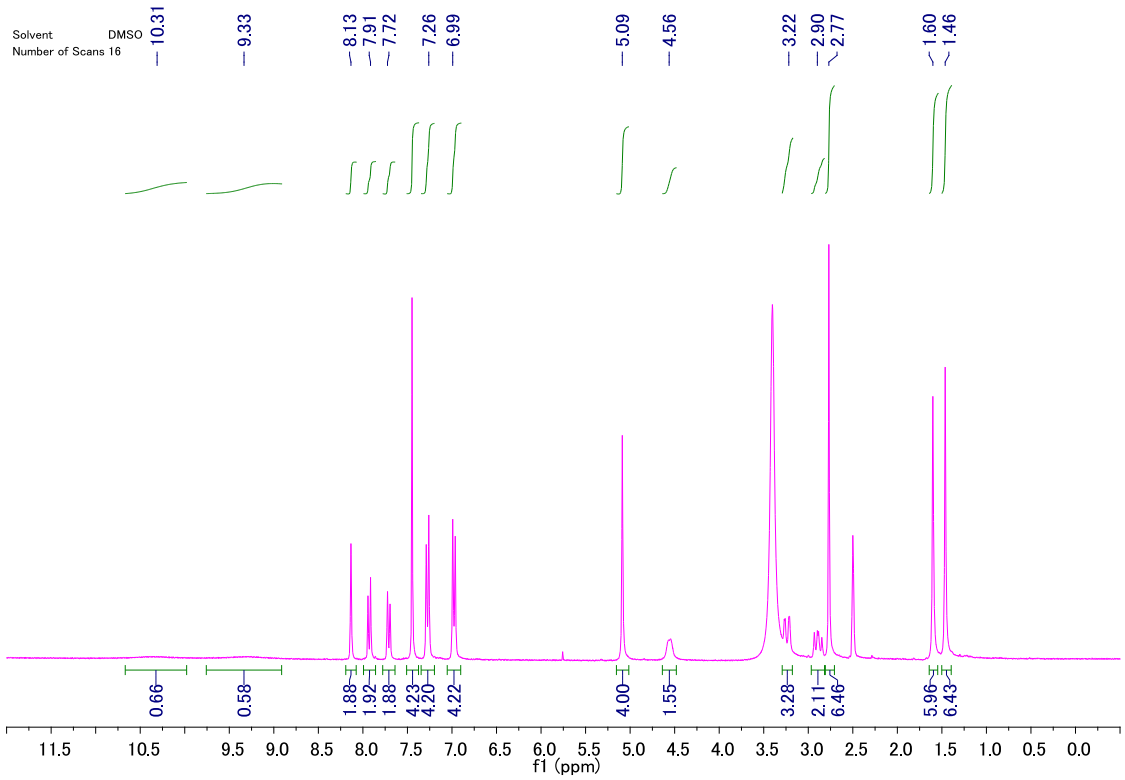


Figure S13. ^{1}H-NMR spectrum of **6a**.

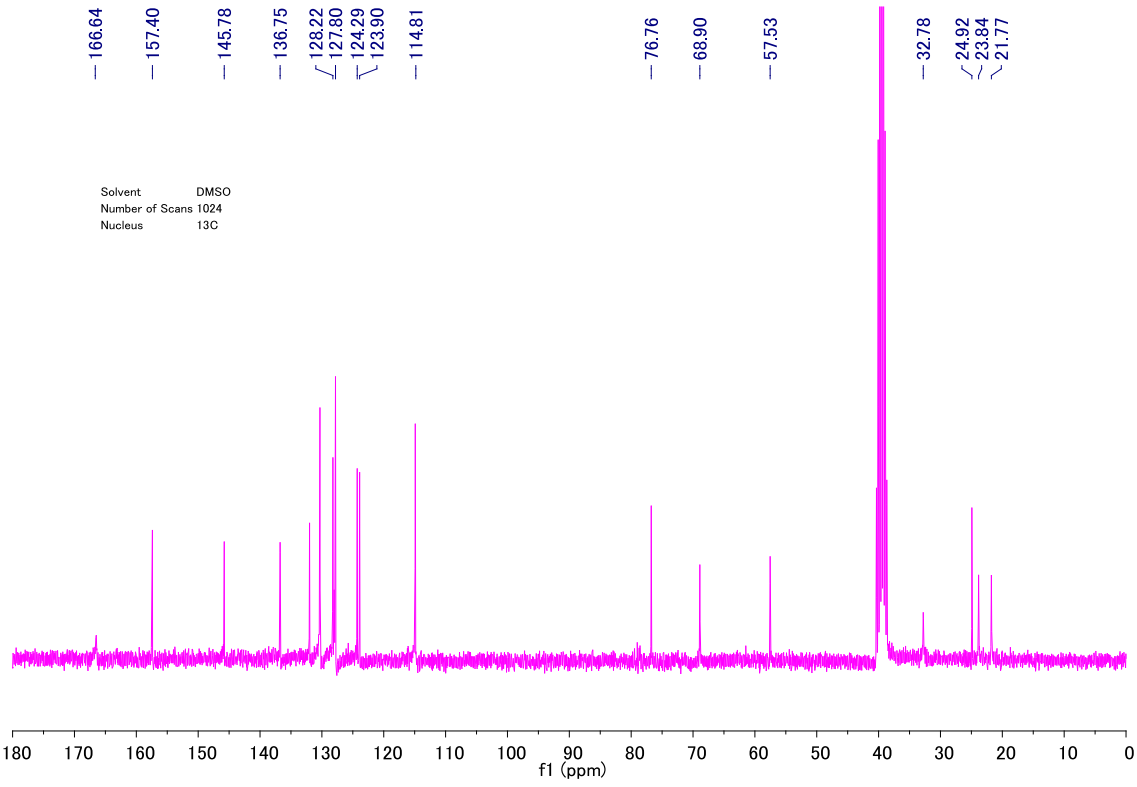


Figure S14. ^{13}C-NMR spectrum of **6a**.

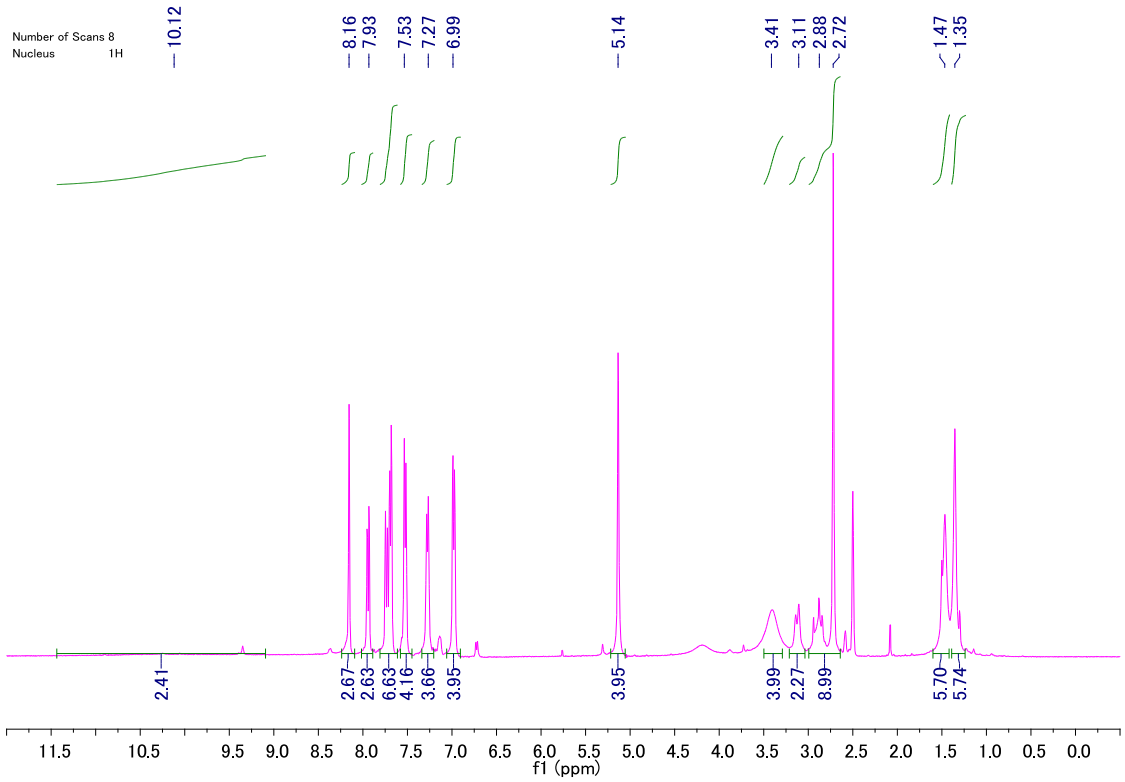


Figure S15. ^{1}H-NMR spectrum of **6b**.

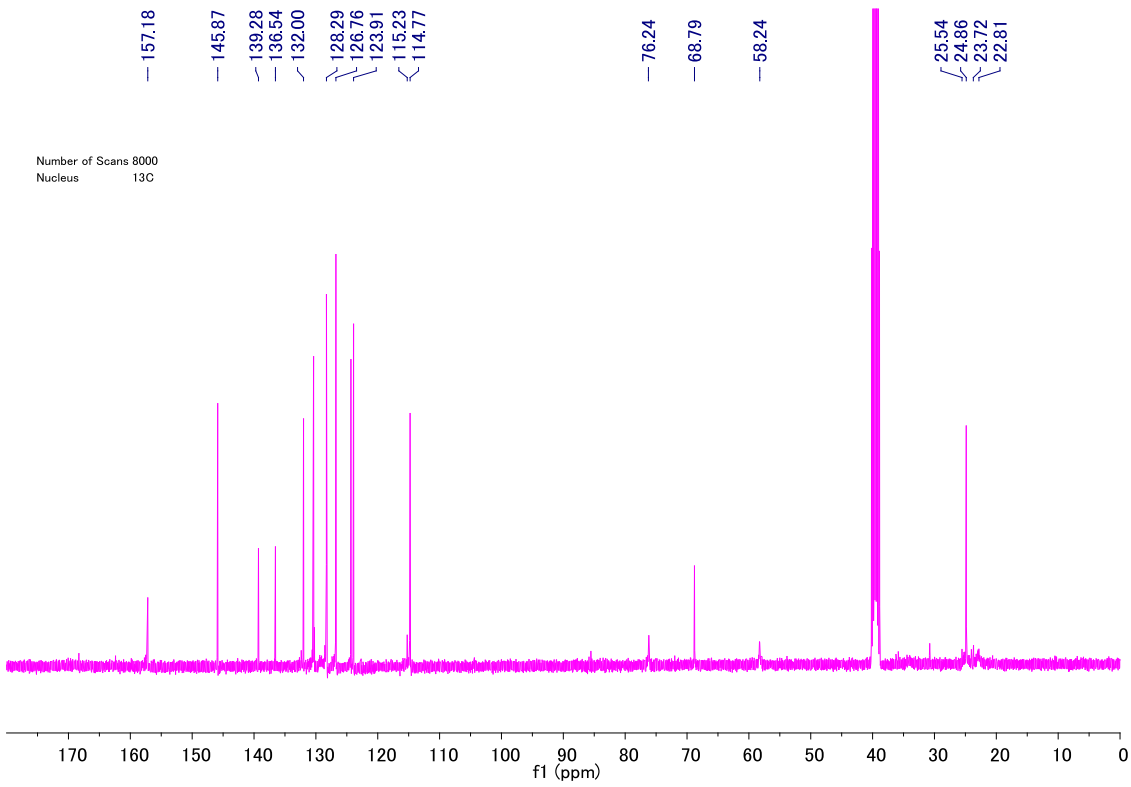


Figure S16. ^{13}C-NMR spectrum of **6b**.

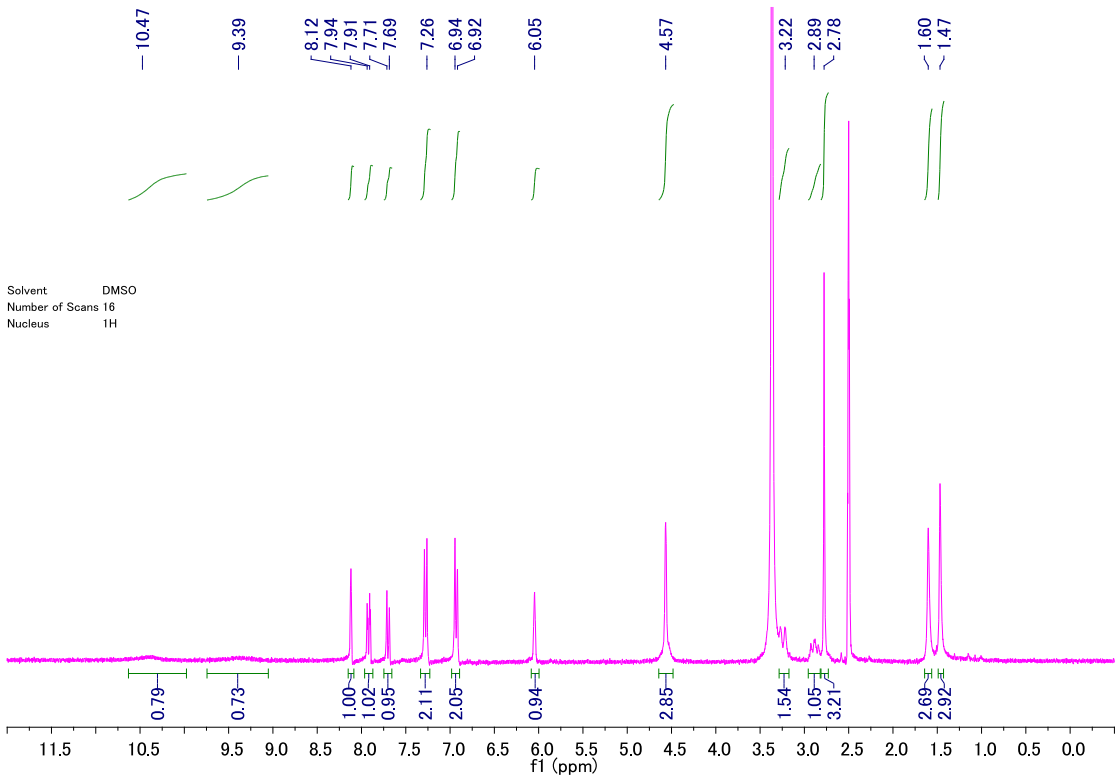


Figure S17. ^{1}H-NMR spectrum of **6c**.

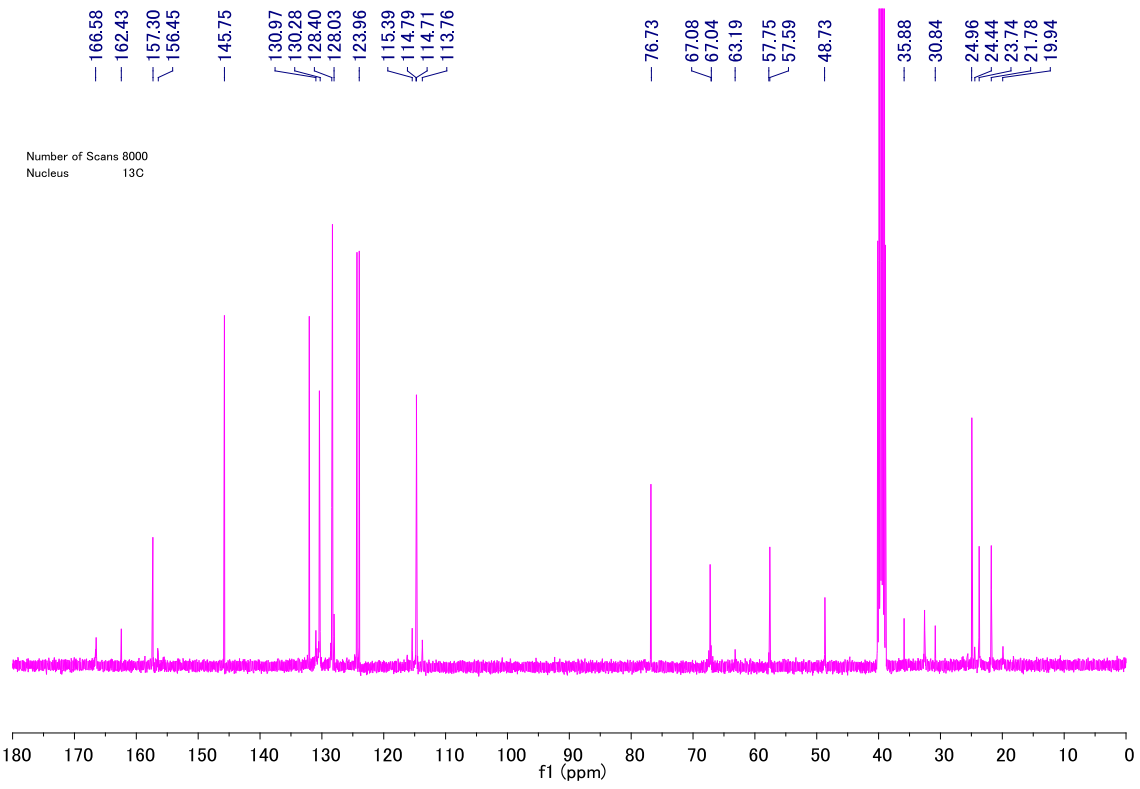


Figure S18. ^{13}C-NMR spectrum of **6c**.

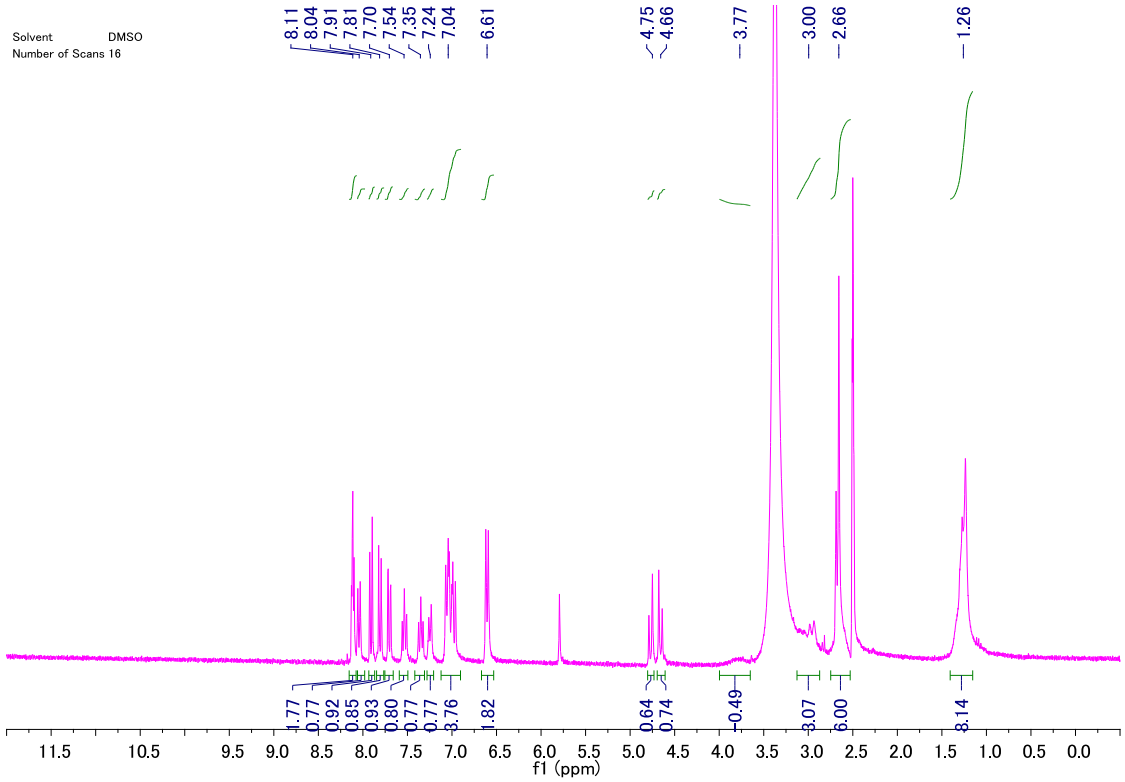


Figure S19. ^{1}H-NMR spectrum of **6d**.

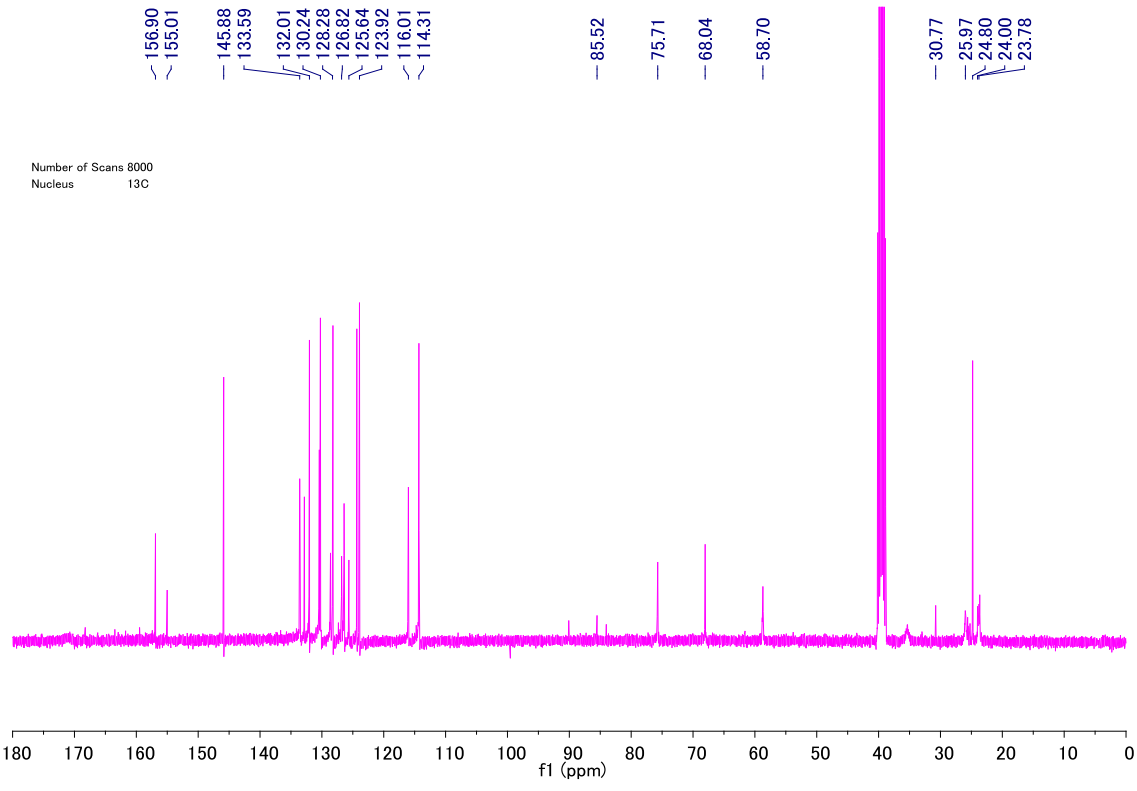


Figure S20. ^{13}C-NMR spectrum of **6d**.

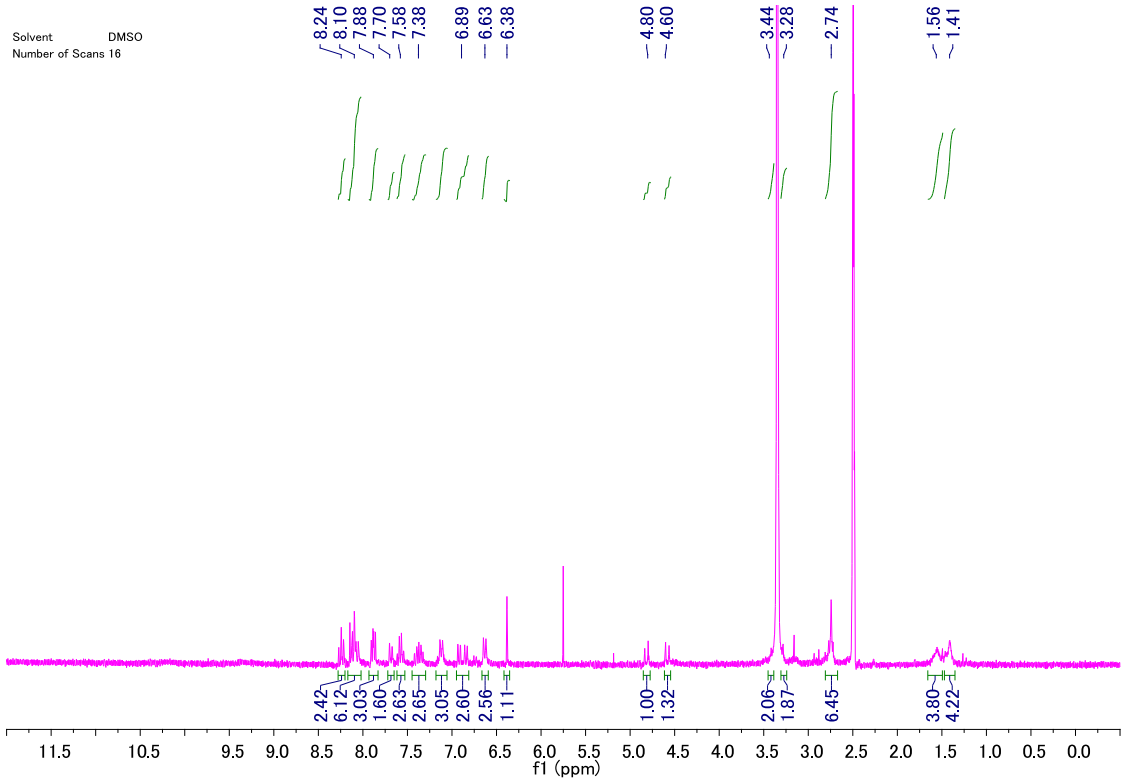


Figure S21. ^{1}H-NMR spectrum of **6e**.

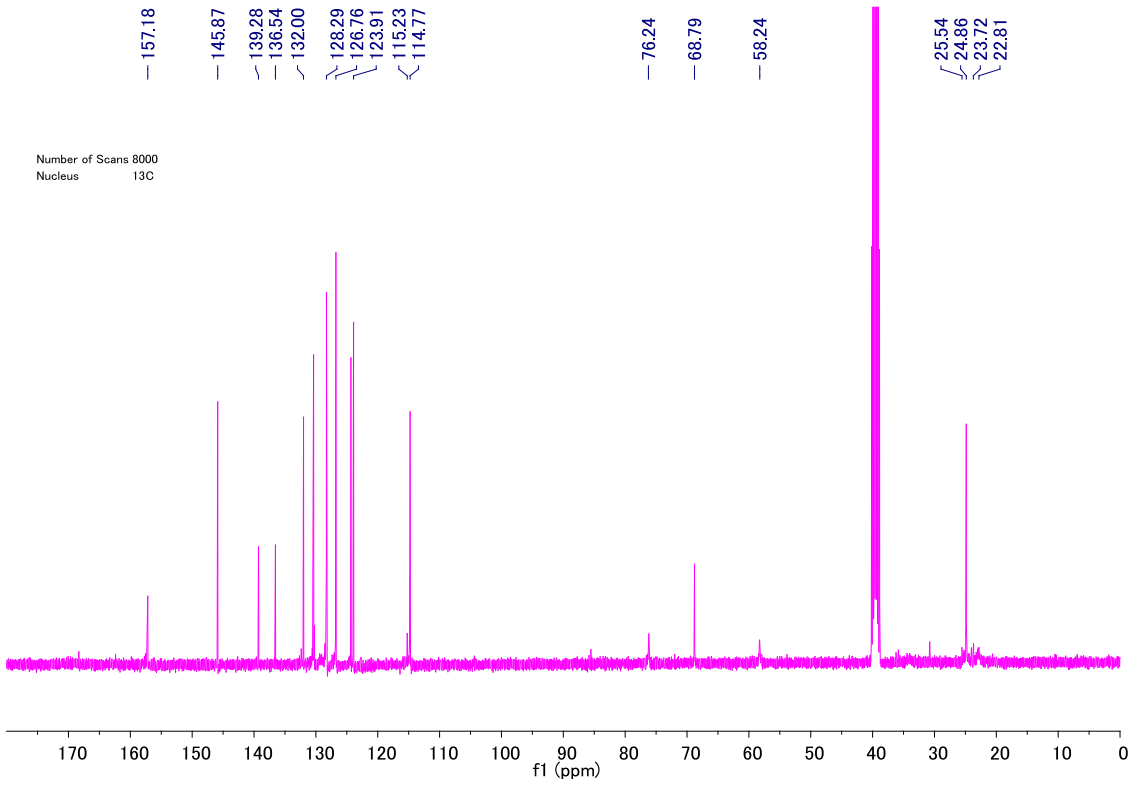


Figure S22. ^{13}C-NMR spectrum of **6e**.

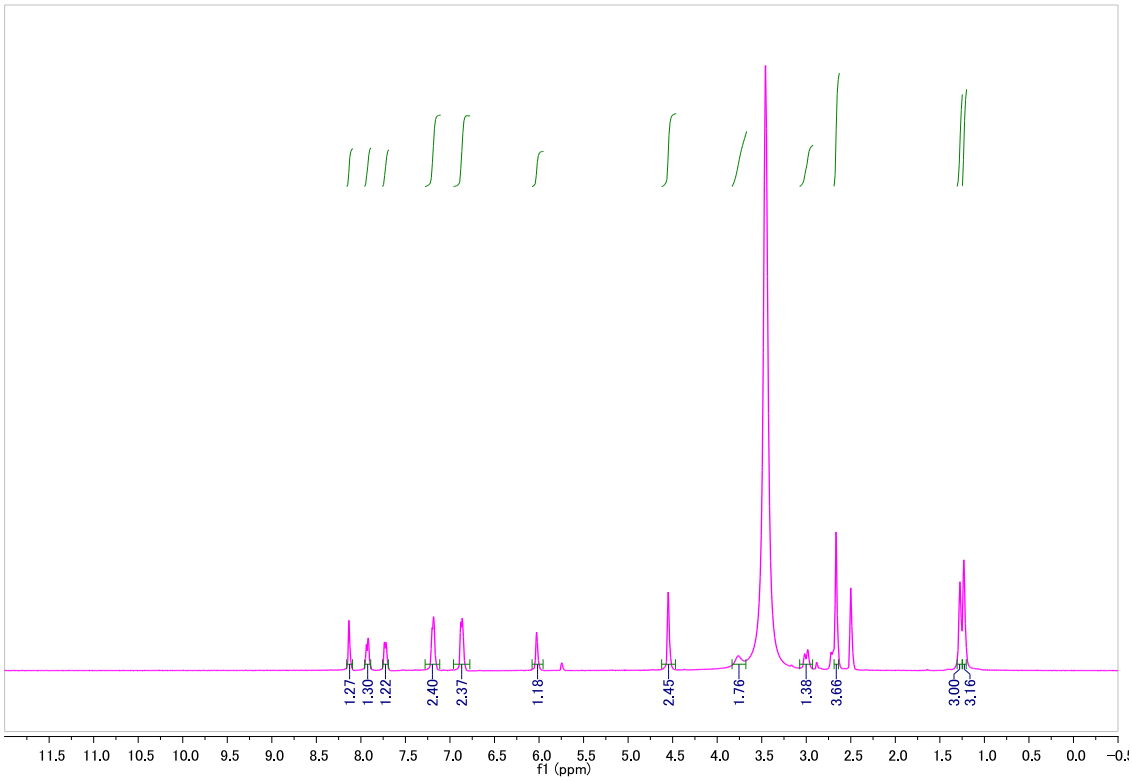


Figure S23. ^{1}H-NMR spectrum of reused **6c**.

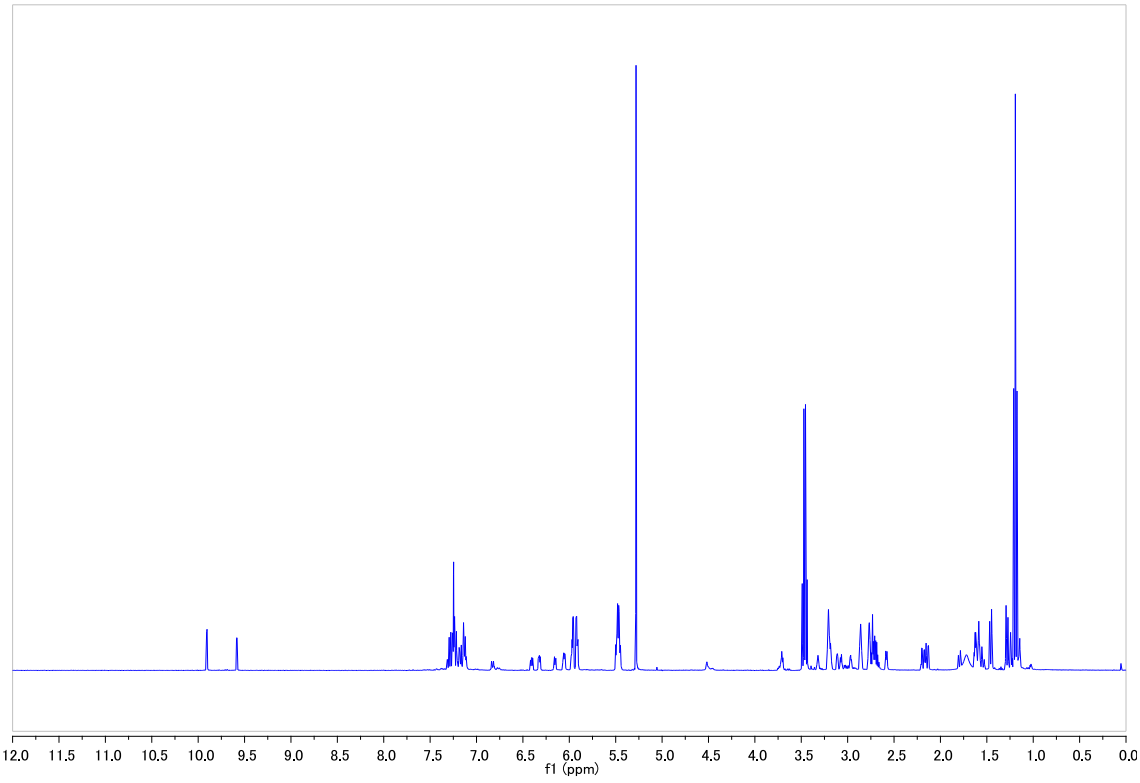


Figure S23. ^{1}H-NMR spectrum of **10** and **11**.