Supporting Information

Asymmetric Cationic Polymerization of Benzofuran through a Reversible Chain-Transfer Mechanism: Optically Active Polybenzofuran with Controlled Molecular Weights

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Experimental Section

Materials

Benzofuran (BzF) (TCI, >99.0%) was distilled over calcium hydride under reduced pressure before use. $AlCl_3$ (Aldrich, 99.999%), (*S*)-phenylalanine ((*S*)-**1**) (TCI, >98%), (*S*)-β-phenylalanine ((*S*)-**2**) (Combi-Blocks, 98%), (*R*)-β-phenylalanine ((*R*)-**2**) (Combi-Blocks, 97%), (*R*)-3-aminobutyric acid ((*S*)-**3**) (Combi-Blocks, 98%), (*S*)-3-amino-4-methyl-pentanoic acid ((*S*)-**4**) (Combi-Blocks, 98%), (*S*)-*N*-*t*-Boc-β-phenylalanine ((*S*)-**2a**) (Combi-Blocks, 97%), (*R*)-*N*-Boc-β-phenylalanine ((*R*)-**2a**) (Combi-Blocks, 97%), benzenethiol (TCI, >98.0%), acetic anhydride (TCI, >99.0%), benzoyl chloride (TCI, >98%), and pivalic anhydride (TCI, >98%) were used as received. Phenyl(1-(4-methoxyphenyl)ethyl)thioether (**CTA1**)[1] and (*S*)-β-phenylalanine methyl ester ((*S*)-**2f**)[2] were synthesized according to the literatures. Toluene (Kanto Chemical, >99.5%; H_2O <10 ppm) and dichloromethane (Kanto Chemical, >99.5%; H_2O < 10 ppm) were dried and deoxygenized by passing through columns of a Glass Contour system before use.

Synthesis of (*S*)-*N*-acetyl-β-phenylalanine ((*S*)-**2b**)

(*S*)-*N*-acetyl-β-phenylalanine ((*S*)-**2b**) was synthesized from (*S*)-β-phenylalanine ((*S*)-**2**) and acetic anhydride. Acetic anhydride (2.43 ml, mmol) was added to a solution of (*S*)-**2** (0.50 g, 3.0 mmol) in a mixture of 25% NaOH aqueous solution (0.48 mL) and water (3.0 mL). Then, 25% NaOH solution (1.2 mL) was further added to the reaction mixture. After stirring at 40 °C for 8 h, 35% HCl aqueous solution (1.8 mL) was added to the reaction mixture at 20 °C. Then, the solution was allowed to stand still at 0 °C. The precipitated white solid was filtered and washed acetone and water. After purification by recrystallization with water, (*S*)-**2b** was obtained as a white solid (0.45 g, 2.2 mmol, purity > 99%, yield = 73%, $[\alpha]_D^{25}$ = –93.4). ^{1}H NMR (CD_3OD, r.t.): δ 1.94 (s, 3H), 2.72–2.84 (dd, 2H, J_{vic} = 16.0 Hz, J_{gem} = 6.8 and 8.0 Hz), 5.31–5.35 (t, 1H, J_{gem} = 6.8 and 8.0 Hz), 7.21–7.37 (m, 5H). ^{13}C NMR (CD_3OD, r.t.): δ 22.59 (*C*H_3), 41.61 (*C*H_2), 51.57 (*C*H), 127.60 (Ar-*C*4), 128.46 (Ar-*C*3), 129.58 (Ar-*C*2), 142.89 (Ar-*C*1), 172.37 (N*C*O), 174.05 (*C*OO). IR: 1717, 1616, 1541, 1497, 1294, 1267, 1234, 1198, 1172, 1028, 764 cm^{-1}. HRMS (ESI): Calcd for $C_{11}H_{13}O_3NNa^+$ ([M+Na]$^+$), 230.0788; Found, 230.0789.

Synthesis of (*S*)-*N*-benzoyl-β-phenylalanine ((*S*)-**2c**)

(*S*)-*N*-Benzoyl-β-phenylalanine ((*S*)-**2c**) was synthesized from (*S*)-β-phenylalanine ((*S*)-**2**) and benzoyl chloride. Benzoyl chloride (1.6 mL, mmol) was added to 1.5 M KOH aqueous solution (20 mL) of (*S*)-**2** (1.65 g, 10 mmol) at 0 °C. After 13 h, 35% HCl aqueous solution (0.40 mL) was added to the reaction mixture. The precipitated

white solid was filtered and washed with water. After purification by recrystallization with water, (*S*)-**2c** was obtained as a white solid (1.32 g, 4.9 mmol, purity > 99%, yield = 49%, $[\alpha]_D^{25}$ = +3.0). ^{1}H NMR (CD_3OD, r.t.): δ 2.86–3.01 (dd, 2H, J_{vic} = 16.0 Hz, J_{gem} = 6.0 and 8.6 Hz), 5.56–5.60 (dd, 1H, J_{gem} = 6.0 and 8.6 Hz), 7.23–7.53 (m, 8H), 7.80-7.82 (m, 2H). ^{13}C NMR (CD_3OD, r.t.): δ 41.46 (*C*H_2), 52.11 (*C*H), 127.64 (*C*3 of phenyl), 128.40 (*C*2 of benzoyl), 128.46 (*C*3 of phenyl), 129.51 (*C*2 of phenyl), 129.62 (*C*3 of benzoyl), 132.69 (*C*4 of benzoyl), 135.74 (*C*1 of benzoyl), 143.11 (*C*1 of phenyl), 169.66 (N*C*O), 174.34 (*C*OO). IR: 1698, 1685, 1578, 1521, 1489, 1456, 1418, 1300, 1271, 1028, 700 cm^{-1}.HRMS (ESI): Calcd for $C_{16}H_{15}O_3NNa^+$ ([M+Na]$^+$), 292.0944; Found, 292.0946.

Synthesis of (*S*)-*N*-pivaloyl-β-phenylalanine ((*S*)-2d)

(*S*)-*N*-Pivaloyl-β-phenylalanine ((*S*)-**2d**) was synthesized from (*S*)-β-phenylalanine ((*S*)-**2**) and pivaloyl anhydride. Pivaloyl anhydride (2.43 mL, mmol) was added to a solution of (*S*)-**2** (1.0 g, 6.0 mmol) in a mixture of 25% NaOH aqueous solution (0.96 mL) and water (3.0 mL). Then, 25% NaOH solution (0.50 mL) was further added to the reaction mixture. After stirring at 40 °C for 12 h, 35% HCl aqueous solution (1.5 mL) was added to the reaction mixture at 20 °C. Then, the solvent was removed under reduced pressure, and the product was dissolved in EtOH. The solution was filtered and concentrated. During this procedure, the product underwent esterification with ethanol. The ethyl ester compound was purified by column chromatography on a silica gel column with $CHCl_3$/CH_3OH (9/1) as the eluent. Then, the obtained product was hydrolyzed with 25% NaOH aqueous solutions. After 35% HCl aqueous solution was added to the reaction mixture, the precipitated product was washed with water to obtain (*S*)-**2d** as a white solid (0.36 g, 1.4 mmol, purity > 99%, yield = 24%, $[\alpha]_D^{25}$ = –74.2). ^{1}H NMR (CD_3OD, r.t.): δ 1.18 (s, 9H), 2.76–2.90 (dd, 2H), 5.33–5.39 (dd, 1H), 7.20–7.36 (m, 8H), 7.94-7.95 (d, 1H). ^{13}C NMR (CD_3OD, r.t.): δ 27.78 (*C*H_3), 39.67 (*C*H(CH_3)$_3$), 41.22 (*C*H_2), 51.47 (*C*H), 127.41 (Ar-*C*4), 128.28 (Ar-*C*3), 129.51 (Ar-*C*2), 143.26 (Ar-*C*1), 174.51 (*C*OO), 180.54 (N*C*O). IR: 1705, 1616, 1521, 1456, 1396, 1254, 1219, 1169, 760 cm^{-1}. HRMS (ESI): Calcd for $C_{14}H_{19}O_3NNa^+$ ([M+Na]$^+$), 272.1257; Found, 272.1257.

Synthesis of (*S*)-*N*-isopropyl-β-phenylalanine ((*S*)-2e)

In a 200 mL flask, (*S*)-**2** (1.0 g, 6.0 mmol), acetic acid (10.0 mL, 175 mmol), acetone (0.72 mL, 9.6 mmol), and methanol (74 mL) were placed. After stirring for 1 h at 20 °C, 2-picoline-borane solution (26.0 mL), which was prepared from 2-picoline-borane (1.5 g, 12 mmol) and methanol (30 mL), was added to the reaction mixture. After stirring for 22 h at 20 °C, the reaction mixture was filtered, and EtOAc was added to the filtrate

until unreacted (*S*)-**2** was precipitated. After the solution was filtered, the filtrate was concentrated. The resulting product was washed with acetone to obtain (*S*)-**2e** as a white solid (0.28 g, 0.84 mmol, purity = 98%, yield = 14%, $[\alpha]_D^{25}$ = –58.2). ^{1}H NMR (CD_3OD, r.t.): δ 1.24–1.36 (dd, 6H), 2.65–2.81 (dd, 2H, J_{vic} = 16.4 Hz, J_{gem} = 4.8 and 9.0 Hz), 3.09–3.19 (sep, 1H), 4.59–4.62 (dd, 1H, J_{gem} = 4.8 and 9.0 Hz), 7.41–7.51 (m, 5H). ^{13}C NMR (CD_3OD, r.t.): δ 19.15, 20.53 (CH_3), 40.60 (CH_2), 49.15 ($CH(CH_3)_2$), 59.05 (*C*H), 128.83 (Ar-*C*4), 130.54 (Ar-*C*3), 130.58 (Ar-*C*2), 136.72 (Ar-*C*1), 177.11 (*C*OO). IR: 1570, 1558, 1541, 1521, 1456, 1417, 1387, 1364, 1339, 1331, 1319, 1301, 1273, 1145, 750, 700 cm^{-1}. HRMS (ESI): Calcd for $C_{12}H_{18}O_2N^+$ ($[M+H]^+$), 208.1332; Found, 208.1330.

Synthesis of 2-(phenylthio)-2,3-dihydrobenzofuran (CTA2) and 3-(phenylthio)-2,3-dihydrobenzofuran (CTA3)

Benzofuran (BzF) (5.4 mL, 50 mmol) was added to a solution of benzenethiol (10 mL, 100 mmol) and iodine (1.3 g, 10 mmol) in CH_2Cl_2 (84 mL) at –78 °C. After stirring for 96 h, the reaction was quenched and washed with 1 N NaOH aqueous solution, 1 N HCl aqueous solution, and water. The solvent was removed by evaporation to give the crude product. After purification by column chromatography on silica gel with *n*-hexane/EtOAc (8/2) as the eluent, the thioethers were obtained as white solids (**CTA2**: 0.068 g, purity = 97%, yield = 0.6%, **CTA3**: 0.66 g, purity = 98%, yield = 12%). ^{1}H NMR (**CTA2**) (CD_3Cl, r.t.): δ 3.17–3.22 (dd, 1H, J_{vic} = 5.2 Hz, J_{gem} = 16.6 Hz), 3.65–3.72 (dd, 1H, J_{vic} = 9.2 Hz, J_{gem} = 16.6 Hz), 6.18–6.21 (dd, 1H, J_{vic} = 5.2 and 9.2 Hz), 6.85–6.91 (m, 2H), 7.14-7.20 (m, 2H), 7.28-7.36 (m, 3H), 7.56-7.58 (m, 2H). ^{13}C NMR (**CTA2**) (CD_3Cl, r.t.): δ 36.76 (CH_2), 89.20 (*C*H), 110.34 (*C*6 of the BzF unit), 121.26 (*C*4 of the BzF unit), 124.70 (*C*5 of the BzF unit), 125.91 (*C*3 of the BzF unit), 127.67 (*C*4 of the PhS unit), 128.43 (*C*2 and *C*6 of the PhS unit), 129.07 (*C*1 of the PhS unit), 131.80 (*C*3 and *C*5 of the PhS unit), 134.19 (*C*2 of the BzF unit), 158.10 (*C*1 of the BzF unit). ^{1}H NMR (**CTA3**) (CD_3Cl, r.t.): δ 4.56–4.60 (dd, 1H, J_{vic} = 9.6 Hz, J_{gem} = 4.4 Hz), 4.75–4.80 (dd, 1H, J_{vic} = 8.0 and 9.6 Hz), 4.90–4.93 (dd, 1H, J_{vic} = 8.0 Hz, J_{gem} = 4.4 Hz), 6.77–6.79 (d, 1H), 6.87-6.91 (t, 1H), 7.16-7.20 (t, 1H), 7.25-7.32 (m, 4H), 7.35-7.38 (m, 2H).^{13}C NMR (**CTA3**) (CD_3Cl, r.t.): δ 48.71 (*C*H), 77.46 (CH_2), 110.06 (*C*6 of the BzF unit), 120.92 (*C*4 of the BzF unit), 125.37 (*C*4 of the BzF unit), 126.39 (*C*3 of the BzF unit), 127.64 (*C*4 of the PhS unit), 129.07 (*C*2 and *C*6 of the PhS unit), 129.69 (*C*1 of the PhS unit), 132.25 (*C*3 and *C*5 of the PhS unit), 133.81 (*C*2 of the BzF unit), 159.83 (*C*1 of the BzF unit).

Asymmetric living cationic polymerization of BzF

Cationic polymerization was carried out by the syringe technique under dry nitrogen in

a baked glass tube equipped with a three-way stopcock. A typical example of the polymerization procedure is given below. The catalyst solution was prepared by mixing $AlCl_3$ (0.21 g, 1.54 mmol) and (*S*)-**2a** (0.20 g, 0.77 mmol) in toluene (32 mL) at 20 °C for 24 h. The cationic polymerization was initiated by the addition of 1.0 mL monomer solution, which contained BzF (0.13 mL, 1.2 mmol), **CTA1** (0.05 mL of 517 mM toluene solution, 0.025 mmol), and octane (0.08 mL) as an internal standard in toluene, into the catalyst solution (5.0 mL, $AlCl_3$: 0.24 mmol, (*S*)-**2a**: 0.12 mmol) at –78 °C. In predetermined intervals, the polymerization was terminated with methanol (1.0 mL) containing a small amount of triethylamine. The monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR with *n*-octane as an internal standard (e.g., 100 min, 78% conversion). The quenched reaction mixture was washed with dilute hydrochloric acid and distilled water to remove residual catalyst, evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymers (M_n = 5700, M_w/M_n =1.39, $[\alpha]_D^{25}$ = +67.9).

Measurement

^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS-400 spectrometer operating at 400 MHz. The high-resolution mass spectra were measured on Thermo Fisher scientific Exactive Plus (ESI). Infrared spectra were recorded on Shimadzu IRAffinity-1 spectrometer. MALDI-TOF-MS was performed on a Bruker autoflex max (linear mode) with dithranol as the ionizing matrix and sodium trifluoroacetate as the ion source. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of the product polymer were determined by size-exclusion chromatography (SEC) in THF at 40 °C on two polystyrene gel columns [Shodex KF-805 L (pore size: 20–1000 Å; 8.0 mm i.d. × 30 cm) × 2] connected to a JASCO PU-2080 precision pump and JASCO RI-2031 detector. The columns were calibrated against 10 standard polystyrene samples (Agilent Technologies; M_p = 575–2783000, M_w/M_n = 1.02–1.23). Optical rotation was measured in a 10 cm quartz cell on a JASCO P-2300 polarimeter. The CD spectra were measured in a 1.0 mm quartz cell on a JASCO J-820 spectropolarimeter. The polymer concentration was calculated on the basis of the monomer units and was 0.02 wt%. The glass transition temperature (T_g) of polymers recorded on a Q200 differential scanning calorimeter (TA Instrument Inc.). Samples were first heated 200 °C at 10 °C/min, equilibrated at this temperature for 5 min, and cooled to –20 °C at 5 °C/min. After being held at this temperature for 5 min, the samples were reheated to 250 °C at 10 °C/min. All T_g values were obtained from second scan after removing the thermal history.

References

1. Uchiyama, M.; Satoh, K.; Kamigaito, M. *Macromolecules* **2015**, *48*, 5533–5542.

2. Tishinov, K.; Bayryamov, S.; Nedkov, P.; Stambolieva, N.; Galunsky, B. *J. Mol. Catal. B: Enzym.* **2009**, *59*, 106–110.

Table S1. Asymmetric Cationic Polymerization of BzF Using $AlCl_3$/(*S*)-2a under Various Conditions[a]

entry	$[AlCl_3]_0/[(S)\text{-}\mathbf{2a}]_0$	time (h)	conv[b] (%)	M_n[c]	M_w/M_n[c]	$[\alpha]_D^{25}$[d]
1	1/2	140	>5	–	–	–
2	1/1	140	>5	–	–	–
3	1/0.67	96	31	36100	2.73	+1.8
4	1/0.50	42	>99	98000	2.35	+52.7
5	1/0.25	0.25	>99	107400	5.42	+1.0
6[e]	1/0.50	48	88	99800	3.62	+39.9

[a]Condition: $[BzF]_0/[AlCl_3]_0/[(S)\text{-}\mathbf{2a}]_0$= 200/40/10–80 mM in toluene at –78 °C. [b]Determined by ^{1}H NMR. [c]Determined by SEC. [d]Measured in THF. [e]Without premixing $AlCl_3$ and (*S*)-**2a**.

Table S2. Asymmetric Living Cationic Polymerization of BzF[a]

entry	chiral additive	$[M]_0/[\mathbf{CTA1}]_0$	time (h)	conv[b] (%)	M_n[c]	M_n(Calcd)[d]	M_w/M_n[c]	$[\alpha]_D^{25}$[e]
1	(*S*)-**2**	50	140	97	6900	6000	1.36	–15.1
2[f]	(*S*)-**2**	100	21	99	16700	12000	1.40	+5.4
3[g]	(*S*)-**2**	200	20	90	30500	21500	1.46	+11.0
4	(*R*)-**2**	50	50	97	6500	6000	1.38	+10.0
5	(*R*)-**3**	50	4	>99	6000	6100	1.50	+14.5
6	(*S*)-**2a**	50	1.7	78	5700	4900	1.39	+67.9
7	(*R*)-**2a**	50	2	83	5800	5200	1.43	–77.3
8	(*S*)-**2b**	50	2	>99	7800	6100	1.58	+85.3
9	(*S*)-**2d**	50	3	95	5800	5900	1.48	+123.5

[a]Condition: $[BzF]_0/[\mathbf{CTA1}]_0/[AlCl_3]_0/[\text{chiral additive}]_0$= 200/4.0/40/20 mM in toluene at –78 °C. [b]Determined by ^{1}H NMR. [c]Determined by SEC. [d]M_n(Calcd) = MW(BzF) × ($[M]_0/[\mathbf{CTA1}]_0$) × conv + MW(**CTA1**). [e]Measured in THF. [f] $[\mathbf{CTA1}]_0$ = 2.0 mM. [g]$[\mathbf{CTA1}]_0$ = 1.0 mM.

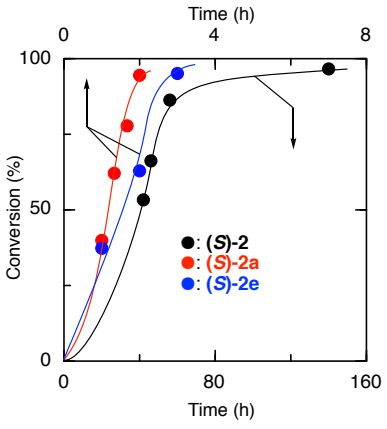

Figure S1. Time-conversion curves in asymmetric living cationic polymerization of BzF in the presence of **CTA1**: $[BzF]_0/[\mathbf{CTA1}]_0/[AlCl_3]_0/[\text{chiral additive}]_0$ = 200/4.0/40/20 mM in toluene at –78 °C.

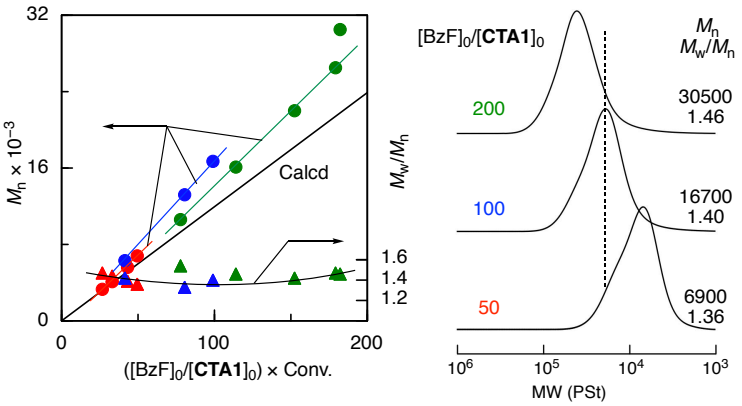

Figure S2. M_n and SEC curves of the polymers obtained in asymmetric living cationic polymerization of BzF by changing the feed ratio of BzF to **CTA1**: [BzF]$_0$/[**CTA1**]$_0$/[$AlCl_3$]$_0$/[(*S*)-**2**]$_0$ = 200/1.0–4.0/40/20 mM in toluene at –78 °C.

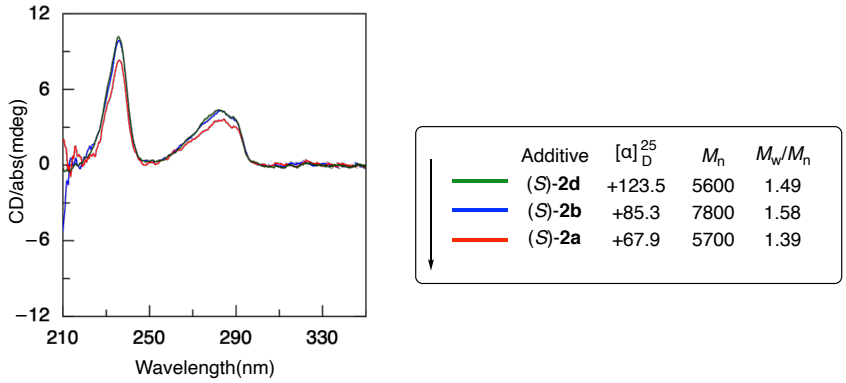

Figure S3. CD spectra of poly(BzF) obtained in asymmetric living cationic polymerization of BzF in the presence of **CTA1**: [BzF]$_0$/[**CTA1**]$_0$/[$AlCl_3$]$_0$/[chiral additive]$_0$ = 200/4.0/40/20 mM in toluene at –78 °C.

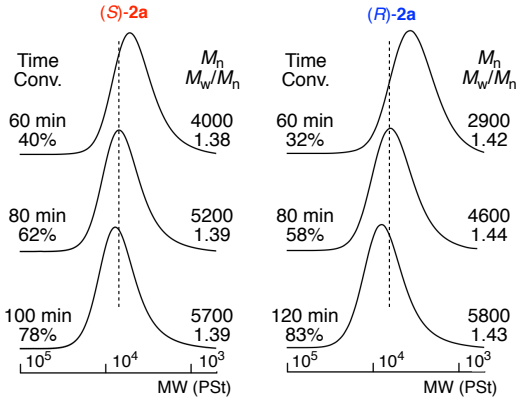

Figure S4. SEC curves of poly(BzF) obtained in living cationic asymmetric polymerization using chiral additives with opposite absolute configurations: [BzF]$_0$/[**CTA1**]$_0$/[$AlCl_3$]$_0$/[(*S*)- or (*R*)-**2a**]$_0$ = 200/4.0/40/20 mM in toluene at –78 °C.

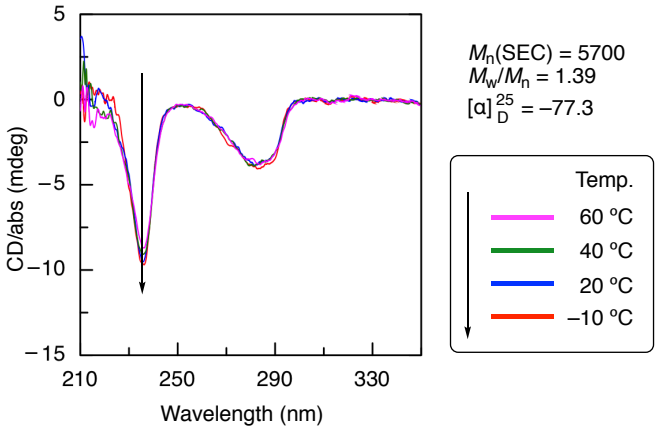

Figure S5. Effect of temperature on CD spectra of poly(BzF) obtained in living cationic asymmetric polymerization using (*R*)-**2a** as a chiral additive.

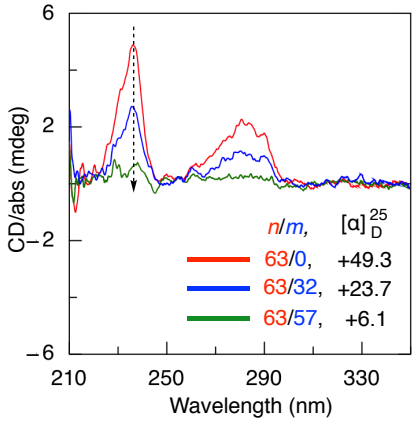

Figure S6. CD spectra of poly(BzF) (macro CTA) obtained with (*S*)-**2a** and asymmetric block poly(BzF) obtained in asymmetric block polymerization with (*R*)-**2a**.

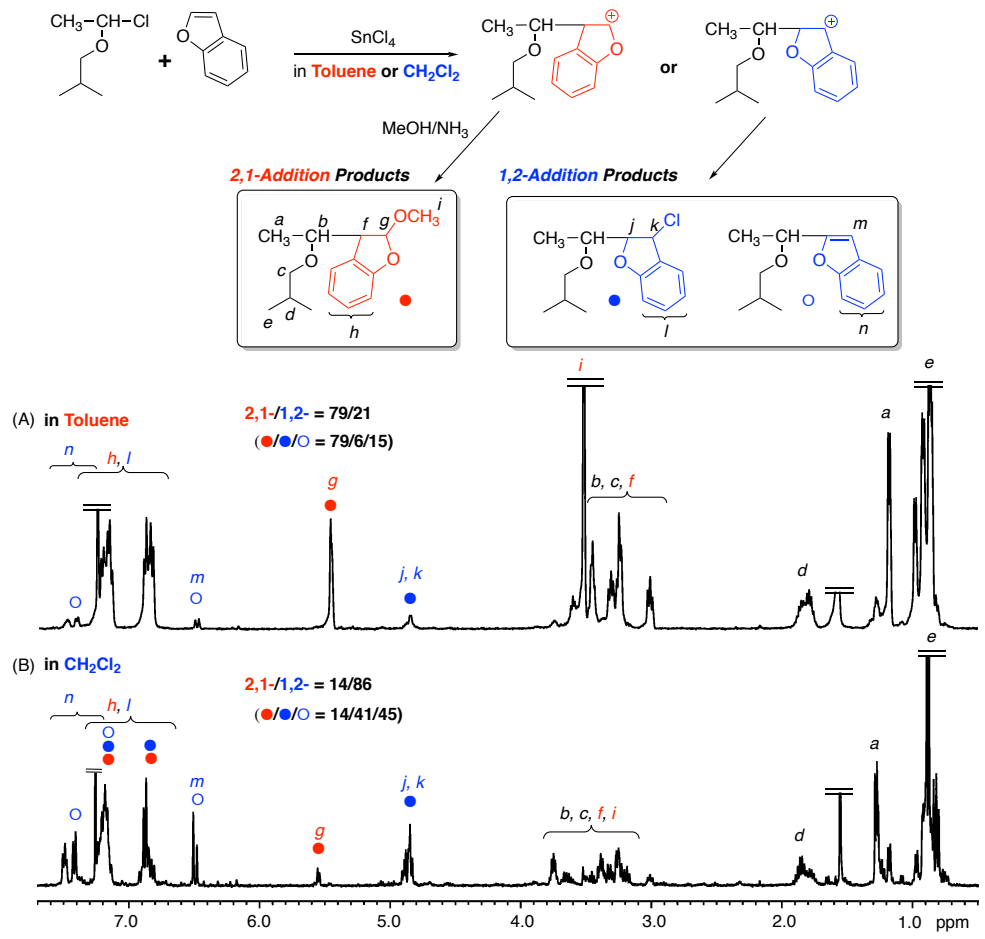

Figure S7. ^{1}H NMR spectra of the products obtained in the cationic addition model reaction between BzF and $CH_3CH(OiBu)Cl$ using $SnCl_4$/EtOAc in toluene (A) and CH_2Cl_2 (B): $[BzF]_0/[CH_3CH(OiBu)Cl]_0/[SnCl_4]_0/[EtOAc]_0$ = 100/200 or 150/10/25 or 100 mM in toluene or CH_2Cl_2 at –78 °C.

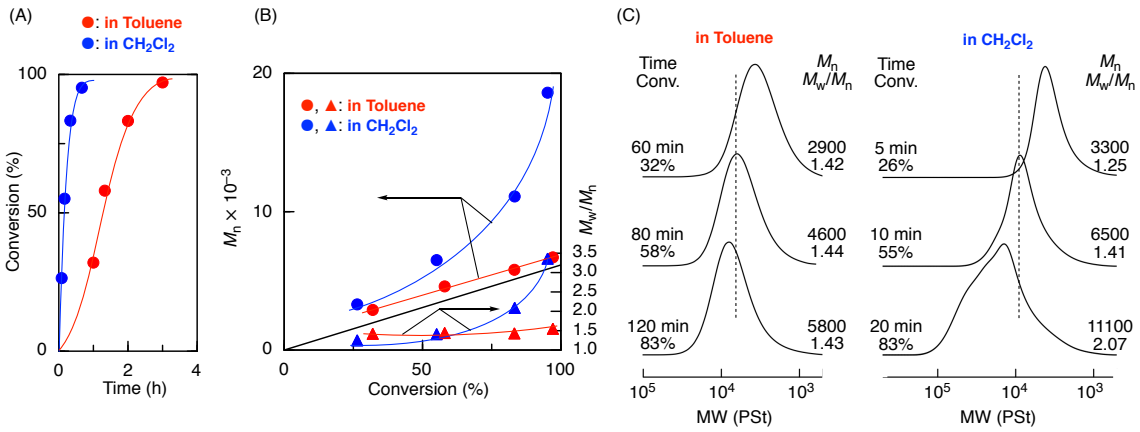

Figure S8. Effect of solvent in asymmetric living cationic polymerization of BzF: $[BzF]_0/[\mathbf{CTA1}]_0/[AlCl_3]_0/[(R)\text{-}\mathbf{2a}]_0$ = 200/4.0/40/20 mM in toluene or CH_2Cl_2 at –78 °C.

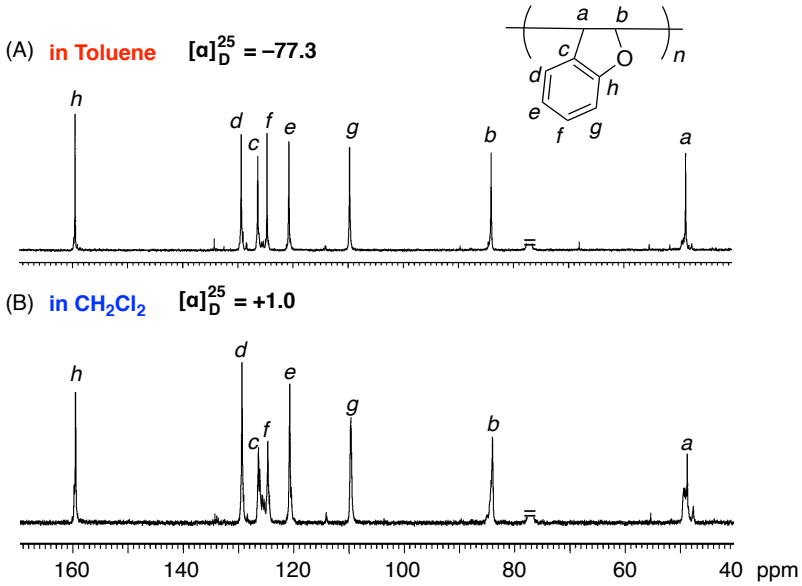

Figure S9. ^{13}C NMR spectra ($CDCl_3$, 55 °C) of poly(BzF) obtained in asymmetric living cationic polymerization under the same condition for Figure S8.

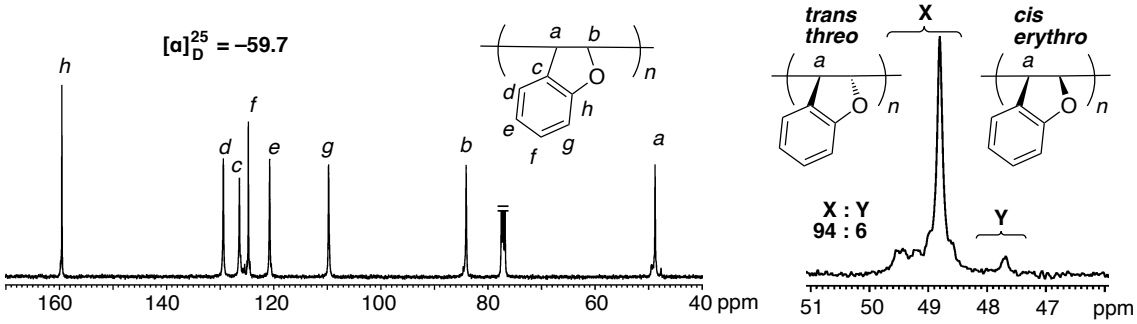

Figure S10. ^{13}C NMR spectrum ($CDCl_3$, 55 °C) of poly(BzF) obtained in asymmetric cationic polymerization using $AlCl_3$/(*R*)-**2a** in the absence of CTA: $[BzF]_0/[AlCl_3]_0/[(R)\text{-}\mathbf{2a}]_0$ = 200/40/20 mM in toluene at –78 °C.

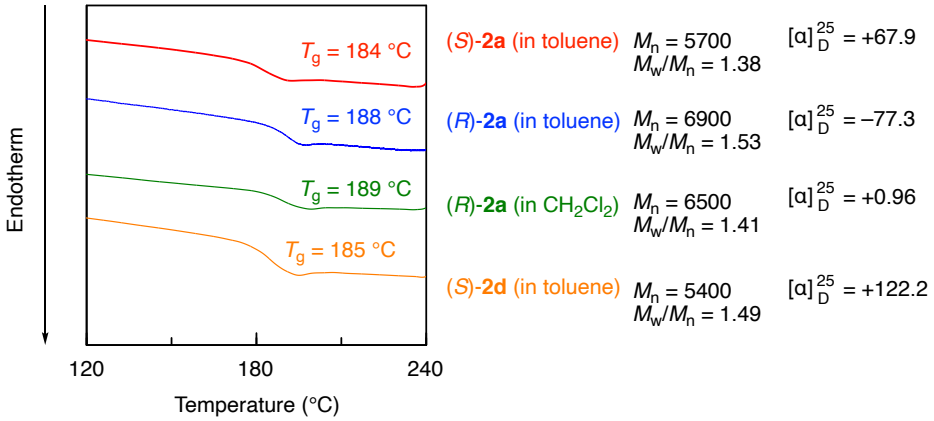

Figure S11. DSC curves of the polymers obtained in asymmetric living cationic polymerization of BzF in the presence of **CTA1**.

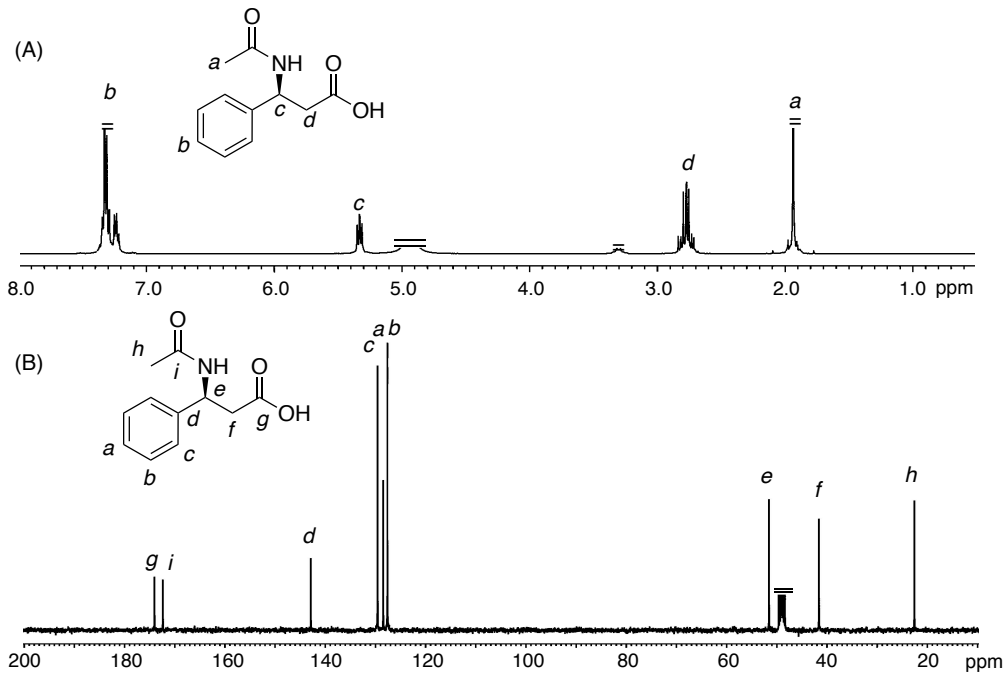

Figure S12. ^{1}H NMR (A) and ^{13}C NMR (B) spectra (CD_3OD, r.t.) of (*S*)-**2b**.

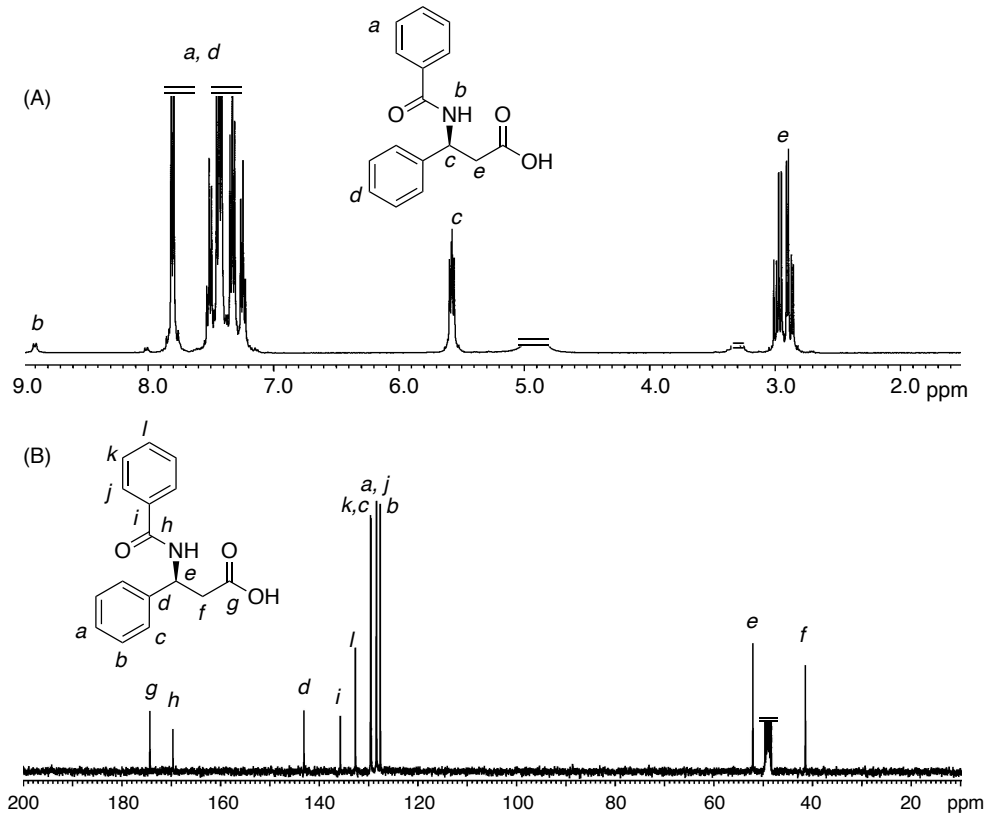

Figure S13. ^{1}H NMR (A) and ^{13}C NMR (B) spectra (CD_3OD, r.t.) of (*S*)-**2c**.

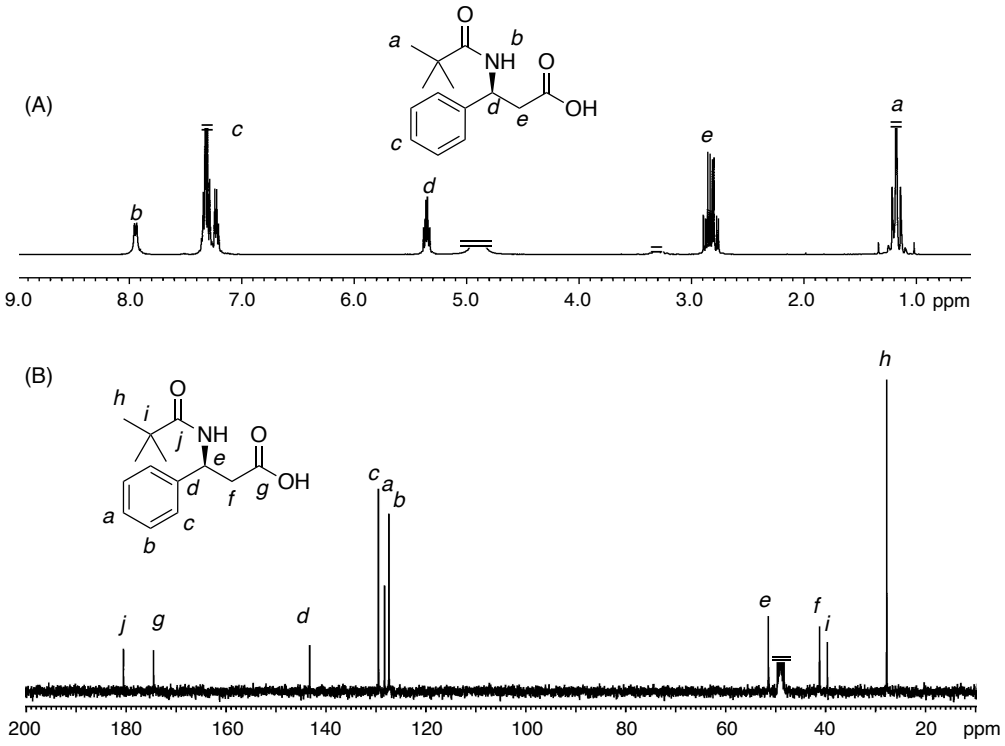

Figure S14. ^{1}H NMR (A) and ^{13}C NMR (B) spectra (CD_3OD, r.t.) of (*S*)-**2d**.

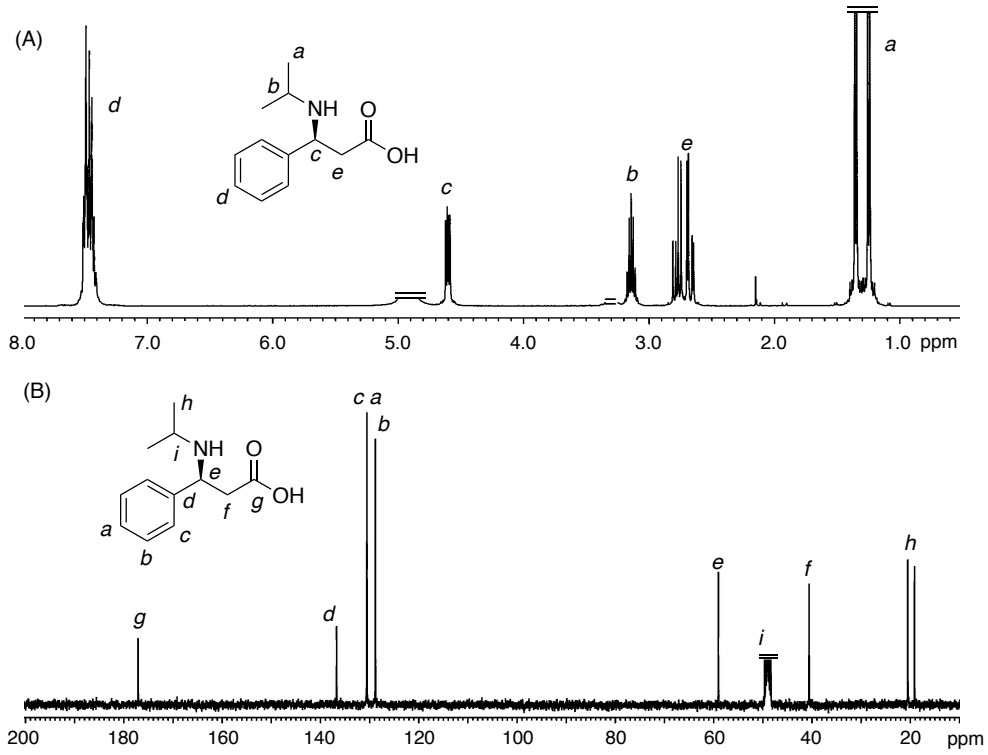

Figure S15. ^{1}H NMR (A) and ^{13}C NMR (B) spectra (CD_3OD, r.t.) of (*S*)-**2e**.

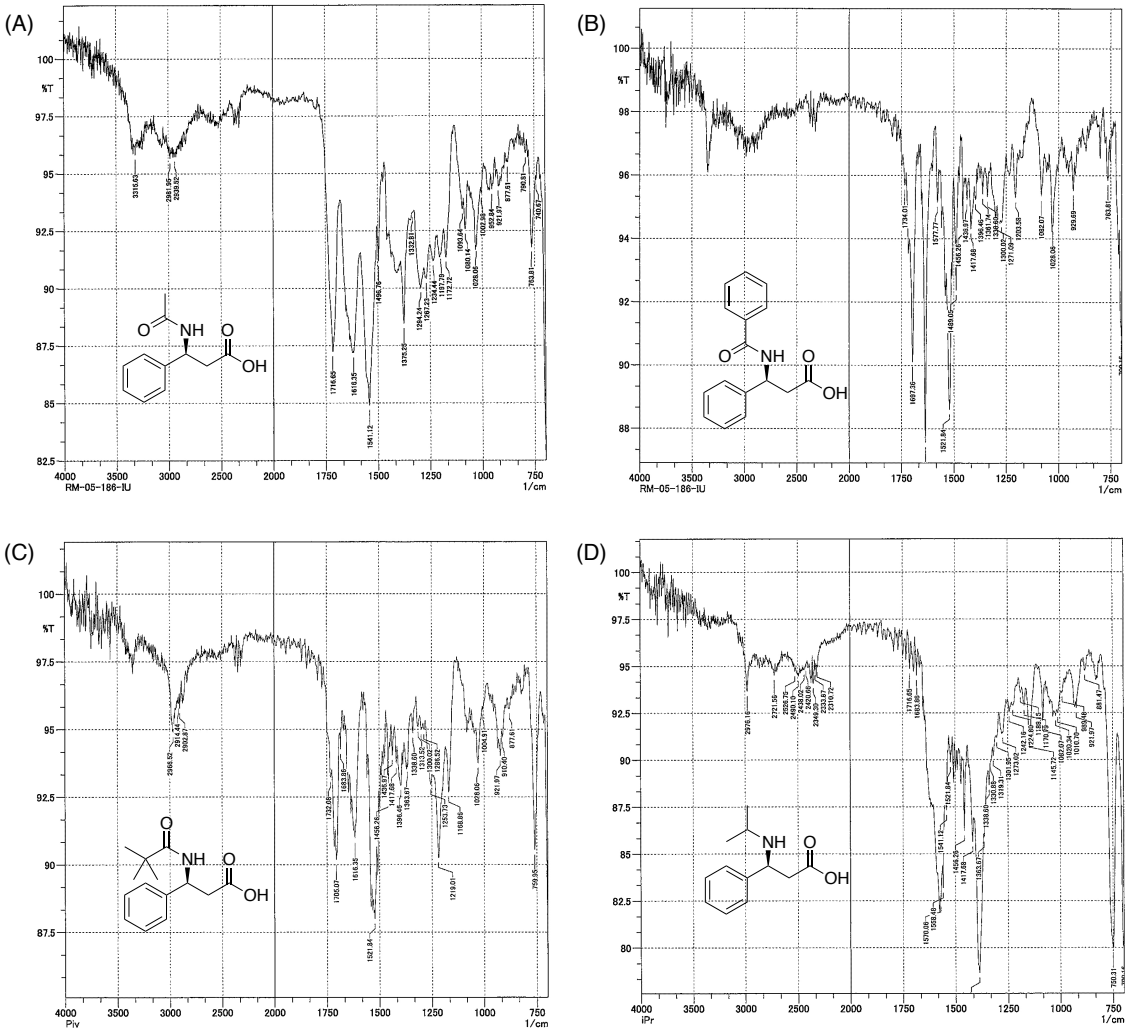

Figure S16. IR spectra of (*S*)-**2b** (A), (*S*)-**2c** (B), (*S*)-**2d** (C), and (*S*)-**2e** (D).

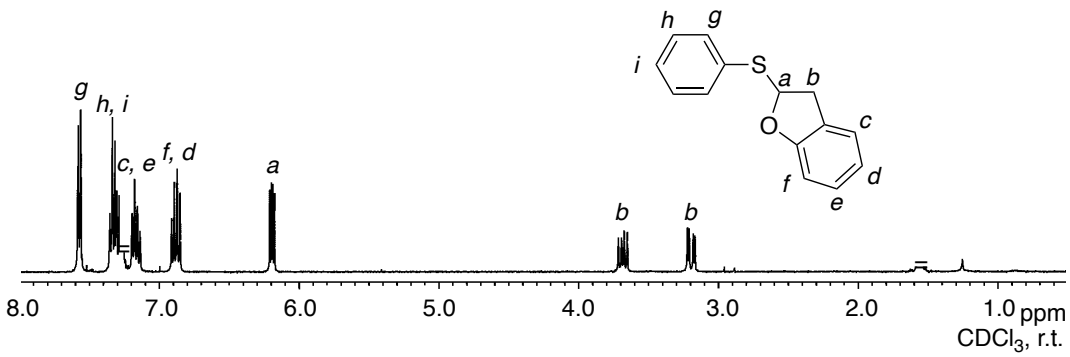

Figure S17. ^{1}H NMR spectrum ($CDCl_3$, r.t.) of **CTA2**.

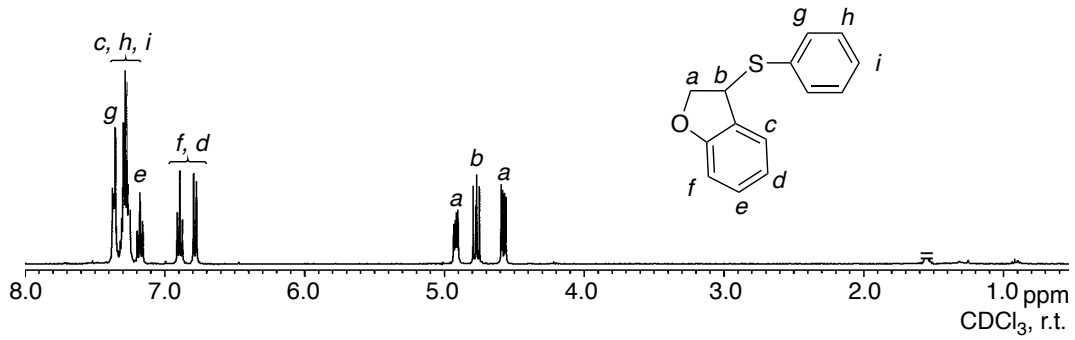

Figure S18. ^{1}H NMR spectrum ($CDCl_3$, r.t.) of **CTA3**.