Supporting Information for:

Diastereoselective Imine-Bond Forming Reaction through Complementary Double Helix Formation

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1. Materials and Instruments

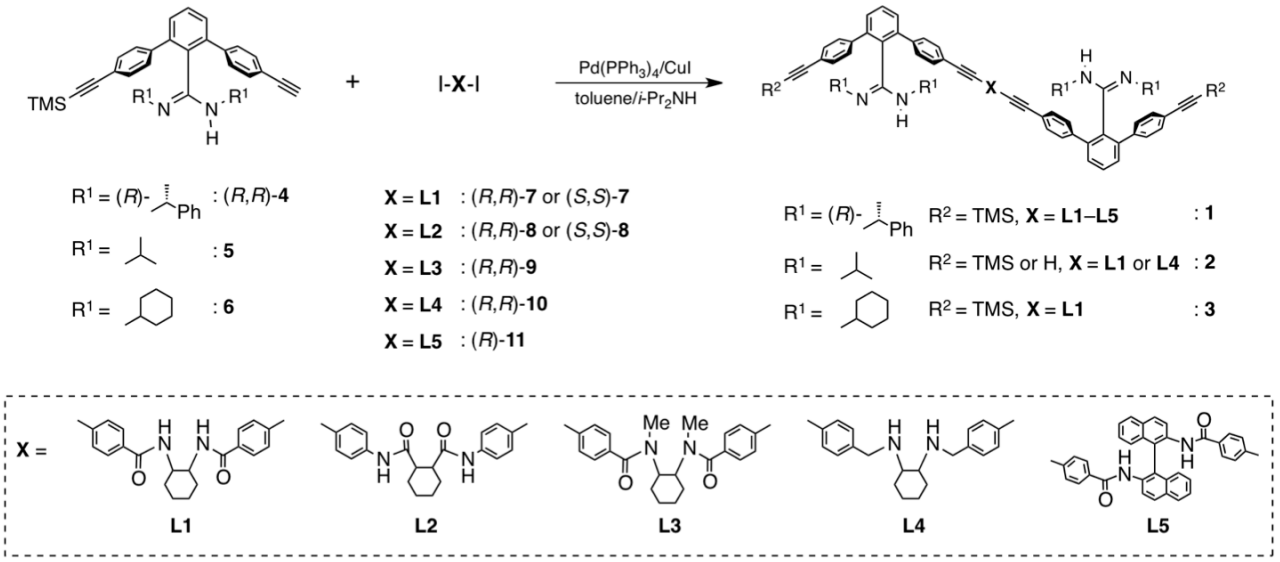
Materials. All starting materials and dehydrated solvents were purchased from Aldrich, Wako Pure Chemical Industries (Osaka, Japan), Kokusan Chemical (Tokyo, Japan), and Tokyo Kasei Kogyo (TCI) (Tokyo, Japan) unless otherwise noted. Silica gel (SiO_2) and aminopropyl-modified silica gel (NH-SiO_2) for the flash chromatography were purchased from Merck and Fuji Silysia Chemical Ltd. (Kasugai, Japan), respectively. Bio-Beads SX-1 for the SEC was purchased from Bio-Rad Laboratories. The monoethynyl amidine monomers (*R*,*R*)-**4**, **5**, and **6**, amidine dimer (*R*,*R*,*R*,*R*)-**1h**, and carboxylic acid monomer **A** were synthesized according to the reported methods.[1-4]

Instruments. The melting points were measured using a Yanaco MP-500D melting point apparatus (Kyoto, Japan) and were uncorrected. The NMR spectra were obtained using a Varian UNITY INOVA 500AS spectrometer operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C. Chemical shifts are reported in parts per million (δ) downfield from tetramethysilane (TMS) as the internal standard in $CDCl_3$ or DMSO-d_6. The recycling preparative HPLC was performed with an LC-928R liquid chromatograph (Japan Analytical Industry, Tokyo, Japan) equipped with two SEC columns (JALGEL-1H (1 x 60 cm) and JALGEL-2H (1 x 60 cm)) in series and a UV-visible detector (254 nm, JAI UV-310), and chloroform was used as the eluent. The electron spray ionization (ESI) mass spectra were recorded using a JEOL JMS-T100CS spectrometer (Akishima, Japan). The elemental analyses were performed by the laboratory of elemental analyses in the Department of Agriculture, Nagoya University. The IR spectra were recorded using a JASCO Fourier Transform IR-680 spectrophotometer (Hachioji, Japan). The absorption and CD spectra were measured in a 0.1-mm

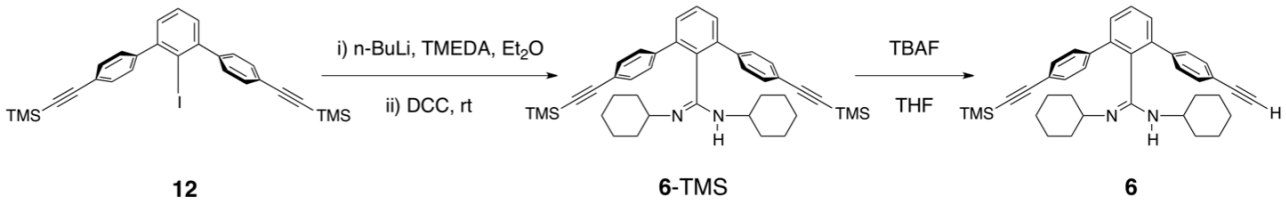
quartz cell on a JASCO V-570 spectrophotometer and a JASCO J-820 spectropolarimeter, respectively. The optical rotations were taken using a JASCO P-1030 polarimeter in a 2-cm quartz cell equipped with a temperature controller (EYELA NCB-2100).

2. Synthetic Procedures

Scheme S1. Synthesis of Amidine Templates **1**-**3**.



Scheme S2. Synthesis of **6**-TMS and **6**.



6-TMS. *n*-BuLi (1.6 M in *n*-hexane, 1.26 mL, 2.12 mmol) and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) (0.30 mL, 234 mg, 2.02 mmol) were added dropwise to a solution of iodide **12** (1.00 g, 1.83 mmol), which had been prepared according to the previously reported method,[1] in Et_2O (8.0 mL) at 0 ºC. After 15 min, a solution of *N*,*N*'-dicyclohexylcarbodiimide (416 mg, 2.02 mmol) in THF (2.0 mL) was added dropwise to the reaction mixture at 0 ºC. After the mixture was stirred at room temperature for 18 h, water (10 mL) was added to the reaction mixture at 0 ºC, and the mixture was extracted with Et_2O (3 × 10 mL). The organic layer was washed with brine (10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated to dryness and the residue was then purified by column chromatography

(NH-SiO_2, *n*-hexane/Et_2O = 20/1 to 10/1 (v/v)) to afford **6**-TMS (691 mg, 60% yield) as a white solid. Mp: 218–220 ºC. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as **6**-TMS·CH_3CO_2H): δ 10.16 (br s, 2H, NH), 7.72 (t, J = 7.7 Hz, 1H, ArH), 7.57–7.55 (m, 6H, ArH), 7.50–7.48 (m, 4H, ArH), 2.67–2.62 (m, 2H, CHN), 2.08 (s, CH_3CO_2), 1.56–1.53 (m, 4H, CH_2), 1.41–1.39 (m, 2H, CH_2), 1.26–1.19 (m, 4H, CH_2), 1.03–0.97 (m, 2H, CH_2), 0.85–0.75 (m, 8H, CH_2), 0.27 (s, 18H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, as **6**-TMS·CH_3CO_2H): δ 177.50, 161.32, 140.90, 138.55, 132.76, 131.97, 130.90, 128.66, 124.00, 122.23, 104.11, 96.59, 54.78, 32.30, 25.39, 24.54, 21.15, 0.13. IR (KBr, cm^{-1}): 2157 ($\nu_{C\equiv C}$), 1634 ($\nu_{C=N}$). Anal. Calcd for $C_{41}H_{52}N_2Si_2$: C, 78.28; H, 8.33; N, 4.45. Found: C, 78.24; H, 8.31; N, 4.43.

6. A solution of tetra-*n*-butylammonium fluoride (TBAF) in THF (8 mM, 3.0 mL, 0.024 mmol) was added to a solution of **6**-TMS (500 mg, 0.795 mmol) in THF (15.0 mL) at 0 ºC, and the mixture was stirred at 0 °C for 5 min. After 1 M HCl (0.5 mL) was added at 0 ºC, the reaction mixture was evaporated to dryness. The residue was dissolved in Et_2O (30 mL), and the resultant solution was washed with 0.5 M NaOH (10 mL), water (10 mL), and brine (10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated to dryness and the residue was then purified by column chromatography (NH-SiO_2, *n*-hexane/Et_2O = 10/1 (v/v)) to afford **6** (85 mg, 30% yield) as a white solid. Mp: 173–174 ºC. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as **6**·CH_3CO_2H): δ 12.62 (br s, 2H, NH), 7.72 (t, J = 5.0 Hz, 1H, ArH), 7.61–7.50 (m, 10H, ArH), 3.17 (s, 1H, C≡C–H), 2.70–2.57 (m, 2H, CHN), 2.00 (s, CH_3CO_2), 1.60–1.50 (m, 4H, CH_2), 1.44–1.36 (m, 2H, CH_2), 1.31–1.17 (m, 4H, CH_2), 1.09–0.97 (m, 2H, CH_2), 0.90–0.73 (m, 8H, CH_2), 0.27 (s, 9H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as **6**·CH_3CO_2H): δ 179.06, 161.17, 140.86, 140.70, 139.20, 138.68, 132.90, 132.70, 131.79, 130.90, 130.81, 128.85, 128.70, 123.90, 122.80, 122.75, 104.19, 95.50, 82.88, 79.10, 54.61, 32.55, 32.52, 25.40, 24.56, –0.05. IR (KBr, cm^{-1}): 2157 ($\nu_{C\equiv C}$), 1634 ($\nu_{C=N}$). Anal. Calcd for $C_{38}H_{44}N_2Si$: C, 81.96; H, 7.96; N, 5.03. Found: C, 81.75; H, 8.08; N, 4.96.

(*R*,*R*)-**7** and (*S*,*S*)-**7**. 4-*N*,*N*-dimethylaminopyridine (58.1 mg, 0.476 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (1.49 g, 7.77 mmol) were added to a suspension of *p*-iodobenzoic acid (1.79 g, 7.22 mmol) and (1*R*,2*R*)-(-)-1,2-cyclohexanediamine (362 mg, 3.17 mmol) in dichloromethane (15 mL) at 0 °C, and the mixture was stirred at room temperature for 2.5 h. The obtained precipitate was collected and washed with water and $CHCl_3$ to afford (*R*,*R*)-**7** (1.38 g, 76% yield) as a white solid. In the same way, (*S*,*S*)-**7** was also prepared in 65% yield.

(*R*,*R*)-**7**. M.p. = 333–336 °C. $[\alpha]_D^{20}$ –229 (*c* = 0.1 in DMSO). ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C) δ 8.30 (d, *J* = 8.0 Hz, 2H, NH), 7.77 (d, *J* = 8.5 Hz, 4H, ArH), 7.47 (d, *J* = 8.5 Hz, 4H, ArH), 3.93–3.87 (m, 2H, NCH), 1.90–1.83 (m, 2H, CH), 1.77–1.68 (m, 2H, CH), 1.55–1.43 (m, 2H, CH), 1.32–1.22 (m, 2H, CH). ^{13}C NMR (125 MHz, DMSO-d_6, 25 °C) δ 165.62, 136.96, 134.32, 129.12, 98.40, 52.92, 31.50, 24.67. IR (KBr, cm^{-1}): 3291 ($\nu_{N\text{-}H}$), 1627 ($\nu_{C\text{-}O}$), 1532 ($\nu_{C\text{-}N}$). Anal. Calcd for $C_{20}H_{20}I_2N_2O_2$: C, 41.83; H, 3.51; N, 4.88. Found: C, 41.85; H, 3.53; N, 4.83.

(*S*,*S*)-**7**. M.p. = 339–341 °C. $[\alpha]_D^{20}$ 225 (*c* = 0.1 in DMSO). ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C) δ 8.30 (d, *J* = 8.0 Hz, 2H, NH), 7.77 (d, *J* = 8.5 Hz, 4H, ArH), 7.47 (d, *J* = 8.5 Hz, 4H, ArH), 3.93–3.87 (m, 2H, NCH), 1.90–1.83 (m, 2H, CH), 1.77–1.68 (m, 2H, CH), 1.55–1.43 (m, 2H, CH), 1.32–1.22 (m, 2H, CH). ^{13}C NMR (125 MHz, DMSO-d_6, 25 °C) δ 165.65, 136.98, 134.33, 129.13, 98.42, 52.93, 31.51, 24.68. IR (KBr, cm^{-1}): 3291 ($\nu_{N\text{-}H}$), 1627 ($\nu_{C\text{-}O}$), 1532 ($\nu_{C\text{-}N}$). Anal. Calcd for $C_{20}H_{20}I_2N_2O_2$: C, 41.83; H, 3.51; N, 4.88. Found: C, 41.96; H, 3.55; N, 4.95.

(*R*,*R*)-**8** and (*S*,*S*)-**8**. Thionyl chloride (0.21 mL, 2.9 mmol) and a catalytic amount of DMF were added to (1*R*,2*R*)-(-)-1,2-cyclohexanedicarboxylic acid (100 mg, 0.581 mmol), and the mixture was stirred at room temperature for 3 h. After removing the solvent and the excess amount of thionyl chloride, the residue was dissolved in anhydrous $CHCl_3$ (1.0 mL), and it was then added to an anhydrous $CHCl_3$ solution (1.0 mL) of 4-iodoaniline (262 mg, 1.20 mmol) and triethylamine (0.41 mL, 2.90 mmol) at 0 °C. The mixture was stirred at room temperature for 3 h. The obtained precipitate was collected and washed with water and $CHCl_3$ to afford (*R*,*R*)-**8** (30 mg, 9% yield) as a white solid. In the same way, (*S*,*S*)-**8** was also prepared in 25% yield.

(*R*,*R*)-**8**. M.p. = 302–305 °C. $[\alpha]_D^{20}$ 34 (*c* = 0.1 in DMSO). ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C) δ 10.07 (s, 2H, NH), 7.57 (d, *J* = 9.0 Hz, 4H, ArH), 7.39 (d, *J* = 9.0 Hz, 4H, ArH), 2.73–2.65 (m, 2H, COCH), 2.01–1.94 (m, 2H, CH), 1.82–1.75 (m, 2H, CH), 1.38–1.25 (m, 4H, CH). ^{13}C NMR (125 MHz, DMSO-d_6, 25 °C) δ 173.72, 139.22, 137.21, 121.05, 86.06, 46.20, 29.61, 25.15. IR (KBr, cm^{-1}): 3277 ($\nu_{N\text{-}H}$), 1660 ($\nu_{C\text{-}O}$). Anal. Calcd for $C_{20}H_{20}I_2N_2O_2$: C, 41.83; H, 3.51; N, 4.88. Found: C, 41.81; H, 3.77; N, 5.06.

(*S*,*S*)-**8**. M.p. = 306–308 °C. $[\alpha]_D^{20}$ –28 (*c* = 0.1 in DMSO). ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C) δ 10.07 (s, 2H, NH), 7.57 (d, *J* = 9.0 Hz, 4H, ArH), 7.39 (d, *J* = 9.0 Hz, 4H, ArH), 2.73–2.65 (m, 2H, COCH), 2.01–1.94 (m, 2H, CH), 1.82–1.75 (m, 2H, CH), 1.38–1.25 (m, 4H, CH). ^{13}C NMR (125 MHz, DMSO-d_6, 25 °C) δ 173.77, 139.24, 137.24, 121.09, 86.10, 46.23, 29.64,

25.18. IR (KBr, cm^{-1}): 3277 (ν_{N-H}), 1661 (ν_{C-O}). Anal. Calcd for $C_{20}H_{20}I_2N_2O_2$: C, 41.83; H, 3.51; N, 4.88. Found: C, 41.85; H, 3.38; N, 4.92.

(*R*,*R*)-**9**. Methyl iodide (29.2 mg, 469 μmol) was added to a suspension of (*R*,*R*)-**7** (52.2 mg, 90.9 μmol) and sodium hydride (60% oil dispersion, 21.2 mg, 530 μmol) in DMF (3.0 mL). After the mixture was stirred at room temperature for 16 h under nitrogen, the solvent was evaporated to dryness. The residue was dissolved in $CHCl_3$, and the resultant solution was washed with brine and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated to dryness and the residue was then purified by column chromatography (SiO_2, *n*-hexane/EtOAc) to afford (*R*,*R*)-**9** (39.8 mg, 73% yield) as a white solid. M.p. = 235–237 °C. $[\alpha]_D^{20}$ 168 (*c* = 0.1 in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.73 (d, *J* = 8.5 Hz, 4H, ArH), 7.08 (d, *J* = 8.5 Hz, 4H, ArH), 4.86–4.81 (m, 2H, NCH), 2.92 (s, 6H, CH_3) 1.94–1.83 (m, 4H, CH), 1.83–1.68 (m, 2H, CH), 1.48–1.40 (m, 2H, CH). ^{13}C NMR (125 MHz, $CDCl_3$, 40 °C) δ 170.99, 137.78, 136.43, 128.75, 95.76, 52.66, 32.60, 29.46, 25.24. IR (KBr, cm^{-1}): 1619 (ν_{C-O}). Anal. Calcd for $C_{22}H_{24}I_2N_2O_2$: C, 43.87; H, 4.02; N, 4.65. Found: C, 43.87; H, 3.96; N, 4.71.

(*R*,*R*)-**10**. A mixture of (1*R*,2*R*)-(-)-1,2-cyclohexanediamine (115 mg, 1.01 mmol) and *p*-iodobenzaldehyde (467 mg, 2.01 mmol) in EtOH (10 mL) was refluxed for 24 h, and to this was added $NaBH_4$ (178 mg, 4.71 mmol) at 0 °C. After the mixture was stirred at room temperature for 5 h, the solvent was evaporated to dryness. The residue was then purified by column chromatography (SiO_2, *n*-hexane/EtOAc) to afford (*R*,*R*)-**10** (194 mg, 35% yield) as a yellow oil. $[\alpha]_D^{20}$ 23 (*c* = 1.0 in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.62 (d, *J* = 8.5 Hz, 4H, ArH), 7.04 (d, *J* = 8.5 Hz, 4H, ArH), 3.82 (d *J* = 13.5 Hz 2H, PhCHN), 3.58 (d *J* = 13.5 Hz 2H, PhCHN), 2.22–2.18 (m, 2H, CH), 2.15–2.09 (m, 2H, CH), 1.74–1.69 (m, 2H, CH), 1.24–1.18 (m, 2H, CH) 1.05–0.95 (m, 2H, CH). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ 140.85, 137.54, 130.20, 92.15, 60.98, 50.43, 31.65, 25.11. IR (NaCl, cm^{-1}): 3294 (ν_{N-H}). HRMS(ESI): m/z calcd for $[M(C_{20}H_{24}I_2N_2)+H]^+$, 547.0107; found 547.0103.

(*R*)-**11**. Thioyl chloride (0.37 mL, 5.10 mmol) and a catalytic amount of DMF were added to an anhydrous $CHCl_3$ solution (3.0 mL) of *p*-iodobenzoic acid (506 mg, 2.04 mmol), and the mixture was stirred at room temperature for 5 h. After removing the solvent and the excess amount of thionyl chloride, the residue was dissolved in anhydrous $CHCl_3$ (2.5 mL). To this was added an anhydrous $CHCl_3$ solution (2.0 mL) of (*R*)-(+)-1,1'-binaphthyl-2,2'-diamine (289 mg, 1.02 mmol) and *N*,*N*-diisopropylethylamine (1.80 mL, 24.3 mmol) at 0 °C. After the mixture was stirred at

room temperature for 12 h, the solvents were evaporated to dryness. The residue was then dissolved in $CHCl_3$, and the resultant solution was washed with 1M HCl and brine and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated to dryness and the residue was purified by column chromatography (SiO_2, *n*-hexane/EtOAc) and preparative recycling HPLC to afford (*R*)-**11** (249 mg, 33% yield) as a pale yellow solid. M.p. = 121–123 °C. $[\alpha]_D^{20}$ 74 (*c* = 0.1 in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 8.61 (d, *J* = 9.5 Hz, 2H, ArH), 8.12 (d, *J* = 9.0 Hz, 2H, ArH), 8.00 (d, *J* = 8.0 Hz, 2H, ArH), 7.70 (s, 2H, NH), 7.55 (d, *J* = 8.5 Hz, 4H, ArH), 7.58–7.42 (m, 2H, ArH), 7.38–7.33 (m, 2H, ArH), 7.24 (d, *J* = 8.5 Hz, 2H, ArH), 6.90 (d, *J* = 8.5 Hz, 4H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ 165.30, 138.05, 135.10, 133.75, 132.28, 131.64, 130.49, 128.80, 128.45, 128.00, 126.16, 125.17, 121.85, 121.51, 99.29. IR (KBr, cm^{-1}): 3278 ($\nu_{N\text{-}H}$), 1656 ($\nu_{C\text{-}O}$). Anal. Calcd for $C_{34}H_{22}I_2N_2O_2$: C, 54.86; H, 2.98; N, 3.76. Found: C, 54.87; H, 2.94; N, 3.83.

General Procedures for the Preparation of Templates 1, 2, and 3. A typical experimental procedure is described below. CuI (0.54 mg, 2.8 μmol) was added to a solution of monoethynyl amidine (*R*,*R*)-**4** (27.1 mg, 45.1 μmol), (*R*,*R*)-**7** (12.9 mg, 22.5 μmol), and $Pd(PPh_3)_4$ (4.5 mg, 3.9 μmol) in toluene-diisopropylamine (8/2 (v/v), 1.5 mL). After the mixture was stirred at 65 °C for 11 h under nitrogen, the solvents were evaporated to dryness. The residue was then purified by column chromatography (NH-SiO_2, *n*-hexane/EtOAc) and Bio-Beads (SX-1, $CHCl_3$) to afford (*R*,*R*,*R*,*R*,*R*,*R*)-**1a** (21.5 mg, 63% yield) as a pale yellow solid. In the same way, (*R*,*R*,*R*,*R*,*R*,*R*)-**1b**, (*R*,*R*,*S*,*S*,*R*,*R*)-**1c**, (*R*,*R*,*S*,*S*,*R*,*R*)-**1d**, (*R*,*R*,*R*,*R*,*R*,*R*)-**1e**, (*R*,*R*,*R*,*R*,*R*,*R*)-**1f**, (*R*,*R*,*R*,*R*,*R*)-**1g**, (*R*,*R*,*R*,*R*)-**1h**, (*R*,*R*)-**2a**, (*R*,*R*)-**2b**, and (*R*,*R*)-**3a** were prepared.

(*R*,*R*,*R*,*R*,*R*,*R*)-**1a**. M.p. = 181–183 °C. $[\alpha]_D^{20}$ –334 (*c* = 0.1 in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as (*R*,*R*,*R*,*R*,*R*,*R*)-**1a**·$(CH_3CO_2H)_2$) δ 13.28 (br, 4H, NH), 7.77–7.72 (m, 6H, ArH), 7.56–7.50 (m, 8H, ArH), 7.32–7.20 (m, 20H, ArH), 7.05 (d, *J* = 7.0 Hz, 4H, ArH), 7.04 (d, *J* = 7.0 Hz, 4H, ArH), 6.87 (d, *J* = 7.5 Hz, 2H, NH), 6.71 (d, *J* = 8.5 Hz, 4H, ArH), 6.66 (d, *J* = 8.5 Hz, 4H, ArH), 4.02 (m, 2H, C*H*NH), 3.91 (m, 4H, PhCHN), 2.28–2.20 (m, 2H, CH), 2.09 (s, CH_3CO_2), 1.91–1.82 (m, 2H, CH), 1.52–1.38 (m, 4H, CH), 0.71 (d, *J* = 6.5 Hz, 12H, CH_3CHN), 0.25 (s, 18H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as (*R*,*R*,*R*,*R*,*R*,*R*)-**1a**·$(CH_3CO_2H)_2$) δ 178.12, 167.67, 162.66, 142.84, 142.79, 141.71, 141.61, 138.29, 138.13, 133.69, 132.37, 132.11, 132.00, 131.90, 130.73, 130.66, 129.18, 129.15, 128.74, 128.55, 128.09, 128.08, 127.15, 126.69, 126.67, 126.42, 123.41, 123.08, 122.60, 104.29, 96.18, 91.07, 90.29, 55.56, 54.82, 32.48, 24.92, 23.52, 22.34, 0.04. IR (KBr, cm^{-1}): 3431 ($\nu_{N\text{-}H}$), 2156 ($\nu_{C\text{-}C}$), 1638 ($\nu_{C=N}$). HRMS(ESI): m/z calcd for

$[M(C_{104}H_{98}N_6O_2Si_2)+2H]^{2+}$, 760.3723; found 760.3723. Anal. Calcd for $C_{104}H_{98}N_6O_2Si_2$: C, 82.17; H, 6.50; N, 5.53. Found: C, 82.37; H, 6.57; N, 5.58.

(*R*,*R*,*R*,*R*,*R*,*R*)-**1b**. 65% yield. M.p. = 177–179 °C. $[\alpha]_D^{20}$ –190 (*c* = 0.1 in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as (*R*,*R*,*R*,*R*,*R*,*R*)-**1b**·$(CH_3CO_2H)_2$) δ 13.23 (br, 4H, NH), 7.77–7.72 (m, 4H, ArH), 7.53–7.40 (m, 12H, ArH), 7.30–7.20 (m, 18H, ArH), 7.06–7.02 (m, 8H, ArH), 6.69 (d, *J* = 8.5 Hz, 4H, ArH), 6.66 (d, *J* = 8.5 Hz, 4H, ArH), 3.94–3.88 (m, 4H, PhCHN), 2.70–2.62 (m, 2H, C*H*NH), 2.10 (s, CH_3CO_2), 2.10–2.02 (m, 2H, CH), 1.92–1.85 (m, 2H, CH), 1.73–1.63 (m, 2H, CH), 1.43–1.35 (m, 2H, CH), 0.70 (d, *J* = 6.5 Hz, 12H, CH_3CHN), 0.25 (s, 18H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as (*R*,*R*,*R*,*R*,*R*,*R*)-**1b**·$(CH_3CO_2H)_2$) δ 176.99, 174.06, 162.82, 142.58, 141.77, 141.68, 138.11, 137.90, 137.66, 132.49, 132.39, 132.07, 131.97, 130.70, 130.65, 129.22, 129.19, 128.65, 128.54, 128.22, 128.19, 128.15, 126.69, 123.76, 123.49, 122.46, 120.01, 118.94, 104.28, 96.22, 91.02, 88.46, 55.66, 48.58, 29.31, 25.00, 22.18, 21.17, 0.04. IR (KBr, cm^{-1}): 3423 (ν_{N-H}), 2156 (ν_{C-C}), 1638 ($\nu_{C=N}$). HRMS(ESI): m/z calcd for $[M(C_{104}H_{98}N_6O_2Si_2)+H]^+$, 1519.7368; found 1519.7308.

(*R*,*R*,*S*,*S*,*R*,*R*)-**1c**. 31% yield. M.p. = 178–180 °C. $[\alpha]_D^{20}$ 357 (*c* = 0.1 in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as (*R*,*R*,*S*,*S*,*R*,*R*)-**1c**·$(CH_3CO_2H)_2$) δ 13.40 (br, 4H, NH), 7.75 (t, *J* = 8.0 Hz, 2H, ArH), 7.57–7.49 (m, 8H, ArH), 7.31–7.20 (m, 18H, ArH), 7.05 (t, *J* = 7.0 Hz, 8H, ArH), 6.81 (d, *J* = 7.5 Hz, 2H, NH), 6.72 (d, *J* = 8.5 Hz, 4H, ArH), 6.67 (d, *J* = 8.5 Hz, 4H, ArH), 4.06–3.98 (m, 2H, C*H*NH), 3.95–3.88 (m, 4H, PhCHN), 2.30–2.20 (m, 2H, CH), 2.10 (s, CH_3CO_2), 1.92–1.82 (m, 2H, CH), 1.52–1.38 (m, 4H, CH), 0.71 (d, *J* = 6.5 Hz, 12H, CH_3CHN), 0.25 (s, 18H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as (*R*,*R*,*S*,*S*,*R*,*R*)-**1c**·$(CH_3CO_2H)_2$) δ 177.91, 167.64, 162.67, 142.96, 142.90 141.77, 141.66, 138.15, 138.18, 133.73, 132.38, 132.13, 131.96, 131.92, 130.73, 130.67, 129.18, 129.15, 128.79, 128.59, 128.09, 128.07, 127.15, 126.73, 126.70, 126.47, 123.47, 123.13, 122.71, 104.34, 96.19, 91.12, 90.31, 55.59, 54.89, 32.55, 24.95, 23.41, 22.40, 0.06. IR (KBr, cm^{-1}): 3424 (ν_{N-H}), 2156 (ν_{C-C}), 1638 ($\nu_{C=N}$). HRMS(ESI): m/z calcd for $[M(C_{104}H_{98}N_6O_2Si_2)+H]^+$, 1519.7368; found 1519.7312.

(*R*,*R*,*S*,*S*,*R*,*R*)-**1d**. 16% yield. M.p. = 179–182 °C. $[\alpha]_D^{20}$ –155 (*c* = 0.1 in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as (*R*,*R*,*S*,*S*,*R*,*R*)-**1d**·$(CH_3CO_2H)_2$) δ 13.20 (br, 4H, NH), 7.81 (s, 2H, NH), 7.74 (t, *J* = 7.5 Hz, 2H, ArH), 7.55–7.40 (m, 12H, ArH), 7.30–7.19 (m, 18H, ArH), 7.08–7.00 (m, 8H, ArH), 6.69 (d, *J* = 8.5 Hz, 4H, ArH), 6.66 (d, *J* = 8.5 Hz, 4H, ArH), 3.95–3.88 (m, 4H, PhCHN), 2.70–2.62 (m, 2H, C*H*NH), 2.10 (s, CH_3CO_2), 2.10–2.02 (m, 2H, CH), 1.92–1.85 (m, 2H, CH),

1.73–1.63 (m, 2H, CH), 1.43–1.35 (m, 2H, CH), 0.70 (d, J = 6.5 Hz, 12H, CH_3CHN), 0.25 (s, 18H, SiCH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as (*R*,*R*,*S*,*S*,*R*,*R*)-**1d**·$(CH_3CO_2H)_2$) δ 176.60, 173.65, 162.70, 142.88, 141.79, 141.71, 138.22, 137.94, 137.79, 132.53, 132.38, 132.37, 131.95, 130.69, 130.63, 129.18, 129.14, 128.69, 128.58, 128.10, 128.09, 128.06, 126.71, 123.69, 123.44, 122.66, 119.84, 118.87, 104.35, 96.16, 90.95, 88.51, 55.58, 48.54, 29.43, 25.05, 22.40, 22.29, 0.06. IR (KBr, cm^{-1}): 3423 (ν_{N-H}), 2157 (ν_{C-C}), 1637 ($\nu_{C=N}$). HRMS(ESI): m/z calcd for $[M(C_{104}H_{98}N_6O_2Si_2)+H]^+$, 1519.7368; found 1519.7309.

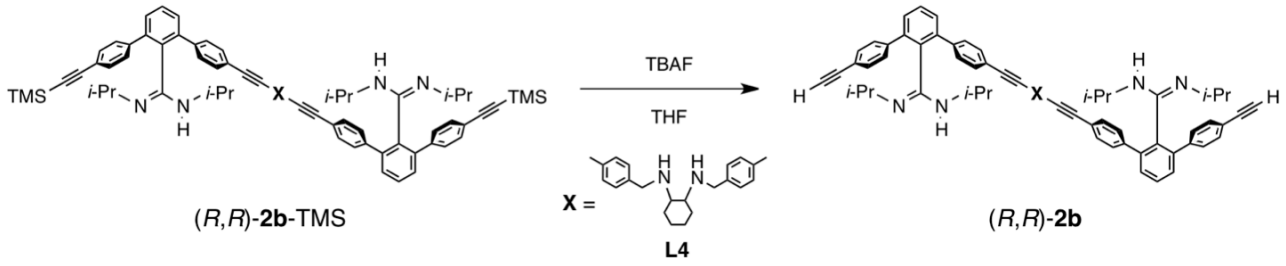
(*R*,*R*,*R*,*R*,*R*,*R*)-**1e**. 78% yield. M.p. = 156–158 °C. $[\alpha]_D^{20}$ –127 (c = 0.1 in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as (*R*,*R*,*R*,*R*,*R*,*R*)-**1e**·$(CH_3CO_2H)_2$) δ 12.83 (br, 4H, NH), 7.77 (t, J = 7.5 Hz, 2H, ArH), 7.70–7.65 (m, 2H, ArH), 7.58–7.43 (m, 8H, ArH), 7.38 (d, J = 8.5 Hz, 4H, ArH), 7.33–7.20 (m, 18H, ArH), 7.06–7.00 (m, 8H, ArH), 6.71 (d, J = 8.5 Hz, 4H, ArH), 6.66 (d, J = 8.5 Hz, 4H, ArH), 4.95–4.86 (m, 2H, C*H*NH), 3.95–3.90 (m, 4H, PhCHN), 2.97 (s, 6H, NCH_3), 2.09 (s, CH_3CO_2), 1.97–1.88 (m, 4H, CH), 1.83–1.73 (m, 2H, CH), 1.52–1.45 (m, 2H, CH), 0.714 (d, J = 6.5 Hz, 6H, CH_3CHN), 0.707 (d, J = 6.5 Hz, 6H, CH_3CHN), 0.25 (s, 18H, SiCH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as (*R*,*R*,*R*,*R*,*R*,*R*)-**1e**·$(CH_3CO_2H)_2$) δ 177.17, 171.43, 162.82, 142.58, 142.54, 141.73, 141.68, 138.12, 138.08, 136.50, 132.41, 132.33, 132.25, 132.14, 131.82, 130.74, 129.25, 129.21, 128.74, 128.65, 128.55, 128.22, 127.25, 126.72, 126.69, 124.55, 123.53, 123.30, 122.47, 110.03, 104.27, 96.25, 90.23, 55.70, 52.69, 32.69, 29.41, 25.21, 22.18, 21.18, 0.05. IR (KBr, cm^{-1}): 3434 (ν_{N-H}), 2156 (ν_{C-C}), 1637 ($\nu_{C=N}$). HRMS(ESI): m/z calcd for $[M(C_{106}H_{102}N_6O_2Si_2)+H]^+$, 1547.7681; found 1547.7642.

(*R*,*R*,*R*,*R*,*R*,*R*)-**1f**. 41% yield. M.p. = 122–124 °C. $[\alpha]_D^{20}$ –114 (c = 0.1 in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as (*R*,*R*,*R*,*R*,*R*,*R*)-**1f**·$(CH_3CO_2H)_2$) δ 12.71 (br, 4H, NH), 7.76 (t, J = 7.5 Hz, 2H, ArH), 7.70–7.64 (m, 2H, ArH), 7.54–7.50 (m, 8H, ArH), 7.38 (d, J = 8.0 Hz, 4H, ArH), 7.32–7.20 (m, 18H, ArH), 7.05–6.98 (m, 8H, ArH), 6.71 (d, J = 8.5 Hz, 4H, ArH), 6.66 (d, J = 8.5 Hz, 4H, ArH), 4.09 (d, J = 13.5 Hz, 2H, CH), 3.96–3.90 (m, 4H, PhCHN), 3.88 (d, J = 13.5 Hz, 2H, CH), 2.65–2.58 (m, 2H, CH), 2.25–2.18 (m, 2H, CH), 2.09 (s, CH_3CO_2), 1.83–1.772 (m, 2H, CH), 1.35–1.20 (m, 4H, CH), 0.71 (d, J = 6.5 Hz, 6H, CH_3CHN), 0.70 (d, J = 6.5 Hz, 6H, CH_3CHN), 0.25 (s, 18H, SiCH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as (*R*,*R*,*R*,*R*,*R*,*R*)-**1f**·$(CH_3CO_2H)_2$) δ 177.37, 162.86, 142.53, 142.48, 141.72, 141.70, 138.05, 137.94, 13.69, 132.41, 132.34, 132.26, 132.08, 130.71, 129.24, 129.23, 128.97, 128.75, 128.71, 128.65, 128.54, 128.21, 126.71, 126.69, 123.55, 123.52, 122.96, 122.42, 104.25, 96.27, 90.70, 89.37, 58.50, 55.71, 48.58, 29.30, 24.55,

22.16, 21.20, 0.05. IR (KBr, cm^{-1}): 3432 ($\nu_{N\text{-}H}$), 2156 ($\nu_{C\text{-}C}$), 1637 ($\nu_{C=N}$). HRMS(ESI): m/z calcd for $[M(C_{104}H_{102}N_6Si_2)+H]^+$, 1491.7783; found 1491.7738.

(*R*,*R*,*R*,*R*,*R*)-**1g**. 76% yield. M.p. = 174–176 °C. $[\alpha]_D^{20}$ –315 (*c* = 0.1 in $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, 25 °C, as (*R*,*R*,*R*,*R*,*R*)-**1g**·$(CH_3CO_2H)_2$) δ 12.99 (br, 4H, NH), 8.73 (d, *J* = 9.0 Hz, 2H, ArH), 8.18 (d, *J* = 9.0 Hz, 2H, ArH), 8.05 (d, *J* = 9.0 Hz, 2H, ArH), 7.81–7.77 (m, 4H, ArH), 7.57–7.52 (m, 6H, ArH), 7.43–7.37 (m, 6H, ArH), 7.34–7.23 (m, 22H, ArH), 7.19 (d, *J* = 8.5 Hz, 2H, ArH), 7.08–7.03 (m, 8H, ArH), 6.72 (d, *J* = 8.5 Hz, 4H, ArH), 6.68 (d, *J* = 8.5 Hz, 4H, ArH), 3.97–3.91 (m, 4H, PhCHN) 2.12 (s, CH_3CO_2), 0.73 (d, *J* = 6.5 Hz, 6H, C*H*$_3$CHN), 0.72 (d, *J* = 6.5 Hz, 6H, C*H*$_3$CHN), 0.28 (s, 18H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as (*R*,*R*,*R*,*R*,*R*)-**1g**·$(CH_3CO_2H)_2$) δ 177.04, 165.21, 162.75, 142.65, 142.58, 141.75, 141.60, 138.31, 138.05, 135.26, 133.79, 132.40, 132.20, 132.11, 132.09, 131.92, 131.55, 130.78, 130.65, 130.47, 129.22, 129.20, 128.77, 128.75, 128.55, 128.17, 127.98, 126.91, 126.75, 126.71, 126.68, 126.04, 125.11, 123.53, 123.04, 122.53, 121.64, 121.03, 104.26, 96.26, 91.40, 90.08, 55.67, 55.65, 22.23, 22.20, 21.77, 0.05. IR (KBr, cm^{-1}): 3422 ($\nu_{N\text{-}H}$), 2156 ($\nu_{C\text{-}C}$), 1637 ($\nu_{C=N}$). HRMS(ESI): m/z calcd for $[M(C_{118}H_{100}N_6O_2Si_2)+H]^+$, 1689.7525; found 1689.7529.

(*R*,*R*)-**2a**. 34% yield. M.p. = 128–123 °C. $[\alpha]_D^{20}$ –246 (*c* = 0.1 in $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, 25 °C, as (*R*,*R*)-**2a**·$(CH_3CO_2H)_2$) δ 11.99 (br, 4H, NH), 7.74 (d, *J* = 8.5 Hz, 4H, ArH), 7.72–7.70 (m, 2H, ArH), 7.66 (d, *J* = 8.5 Hz, 4H, ArH), 7.62–7.53 (m, 16H, ArH), 7.50 (d, *J* = 8.5 Hz, 4H, ArH), 6.92 (d, *J* = 7.5 Hz, 2H, NH), 4.10–4.00 (m, 2H, C*H*NH), 3.15–3.17 (m, 4H, CH_3C*H*N), 2.28–2.20 (m, 2H, CH), 2.04 (s, CH_3CO_2), 1.91–1.82 (m, 2H, CH), 1.52–1.38 (m, 4H, CH), 0.75 (d, *J* = 6.5 Hz, 24H, C*H*$_3$CHN), 0.27 (s, 18H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as (*R*,*R*)-**2a**·$(CH_3CO_2H)_2$) δ 176.56, 167.71, 161.54, 140.81, 140.72, 138.54, 138.35, 133.76, 132.83, 132.59, 131.96 131.03, 130.92, 130.89, 128.96, 128.75, 127.20, 126.39, 123.98, 123.63, 122.38, 104.10, 96.66, 90.92, 90.62, 68.30, 54.80, 30.49, 23.88, 22.52, 21.98, 0.04. IR (KBr, cm^{-1}): 3337 ($\nu_{N\text{-}H}$), 2157 ($\nu_{C\text{-}C}$), 1637 ($\nu_{C=N}$). HRMS(ESI): m/z calcd for $[M(C_{84}H_{90}N_6O_2Si_2)+2H]^{2+}$, 636.3410; found 636.3378.



(*R*,*R*)-**2b**. During the purification of (*R*,*R*)-**2b**-TMS by column chromatography (NH-SiO_2), the TMS groups were partially deprotected, and therefore, the product was treated with tetra-*n*-butylammonium fluoride (TBAF) to afford desilylated (*R*,*R*)-**2b** (15% yield). M.p. = 99.7–102.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as (*R*,*R*)-**2b**·$(CH_3CO_2H)_2$) δ 11.85 (br, 4H, NH), 7.75 (t, J = 8.0 Hz, 2H, ArH), 7.69 (d, J = 8.5 Hz, 4H, ArH), 7.67–7.53 (m, 20H, ArH), 7.40 (d, J = 8.0 Hz, 4H, ArH), 4.11 (d, J = 13 Hz, 2H, PhCHN), 3.86 (d, J = 13 Hz, 2H, PhCHN), 3.20 (s, 2H, C≡CH), 3.16–3.12 (m, 4H, CH_3CHN), 2.60–2.52 (m, 2H, CH), 2.23–2.18 (m, 2H, CH), 2.11 (s, CH_3CO_2), 1.86–1.80 (m, 2H, CH), 1.35–1.23 (m, 4H, CH), 0.79 (d, J = 6.5 Hz, 24H, CH_3CHN). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as (*R*,*R*)-**4**·$(CH_3CO_2H)_2$) δ 176.85, 161.56, 140.81, 140.68, 138.79, 138.18, 133.04, 132.52, 132.35, 132.23, 132.05, 130.99, 130.89, 129.79, 128.91, 128.88, 124.00, 122.95, 122.78, 122.30, 91.04, 89.18, 82.78, 79.29, 58.59, 48.66, 29.84, 29.45, 24.59, 22.46, 21.9. IR (KBr, cm^{-1}): 3425 ($\nu_{N\text{-}H}$), 3296 ($\nu_{C\text{-}CH}$), 1631 ($\nu_{C=N}$). HRMS(ESI): m/z calcd for $[M(C_{78}H_{78}N_6)+2H]^{2+}$, 550.3222; found 550.3212.

(*R*,*R*)-**3a**. 26% yield. M.p. = 167–169 °C. $[\alpha]_D^{20}$ –201 (c = 0.1 in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as (*R*,*R*)-**3a**·$(CH_3CO_2H)_2$) δ 12.33 (br, 4H, NH), 7.77–7.71 (m, 6H, ArH), 7.64 (d, J = 8.5 Hz, 4H, ArH), 7.61–7.55 (m, 16H, ArH), 7.52 (d, J = 8.5 Hz, 4H, ArH), 6.87 (d, J = 7.5 Hz, 2H, NH), 4.10–4.00 (m, 2H, CHN), 2.70–2.60 (m, 4H, CH_2CHN), 2.28–2.20 (m, 2H, CH), 2.01 (s, CH_3CO_2), 1.91–1.84 (m, 2H, CH), 1.58–1.51 (m, 8H, CH), 1.49–1.35 (m, 8H, CH), 1.30–1.19 (m, 8H, CH), 1.09–0.96 (m, 4H, CH), 0.91–0.75 (m, 16H, CH), 0.27 (s, 18H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as (*R*,*R*)-**3a**·$(CH_3CO_2H)_2$) δ 177.65, 167.66, 161.24, 140.87, 140.77, 138.87, 138.67, 133.77, 132.71, 132.147, 131.97 131.86, 130.88, 130.85, 128.92, 128.70, 127.18, 126.43, 123.90, 123.53, 122.59, 104.18, 96.50, 90.99, 90.50, 54.86, 54.65, 32.50, 32.48, 25.40, 24.93, 24.57, 23.54, 0.05. IR (KBr, cm^{-1}): 3423 ($\nu_{N\text{-}H}$), 2157 ($\nu_{C\text{-}C}$), 1637 ($\nu_{C=N}$). HRMS(ESI): m/z calcd for $[M(C_{96}H_{106}N_6O_2Si_2)+H]^+$, 1431.7994; found 1431.8063.

3. General Procedures for Template-Directed Imine-Bond Forming Reactions

A typical experimental procedure for the imine-bond forming reaction between **A** and (*S*,*S*)-**B** in the presence of the amidine dimer (*R*,*R*,*R*,*R*,*R*,*R*)-**1a** as a template is described below. Stock solutions of (*R*,*R*,*R*,*R*,*R*,*R*)-**1a** (2.0 mM), **A** (2.0 mM), and (*S*,*S*)-**B** (2.0 mM) were prepared in dry $CDCl_3$ (1.0 mL). 200 μL (0.40 μmol) and 400 μL (0.80 μmol) of the stock solutions of (*R*,*R*,*R*,*R*,*R*,*R*)-**1a** and **A**, respectively, were transferred to an NMR tube (5-mm (i.d.)) by a syringe under nitrogen. To this was added a 200 μL aliquot of the stock solution of (*S*,*S*)-**B** (0.40 μmol), and the solution was mixed with a vibrator at room temperature. The reaction's progress was monitored by ^{1}H NMR spectroscopy at 25 °C (Figures 1a and S1a) to determine the conversion of (*S*,*S*)-**B** and the diastereomeric excess (*de*) of the product. In the same way, the time-dependent UV-vis and CD spectral changes were followed.

References and Notes

(1) Tanaka, Y.; Katagiri, H.; Furusho, Y.; Yashima, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 3867–3870.

(2) Hasegawa, T.; Furusho, Y.; Katagiri, H.; Yashima, E. *Angew. Chem., Int. Ed.* **2007**, *46*, 5885–5888.

(3) Furusho, Y.; Tanaka, Y.; Maeda, T.; Ikeda, M.; Yashima, E. *Chem. Commun.* **2007**, *43*, 3174–3176.

(4) Yamada, H.; Furusho, Y.; Ito, H.; Yashima, E. *Chem. Commun.* **2010**, *46*, 3487–3489.

4. Imine-Bond Forming Reaction in the Presence of Chiral Amidine Templates

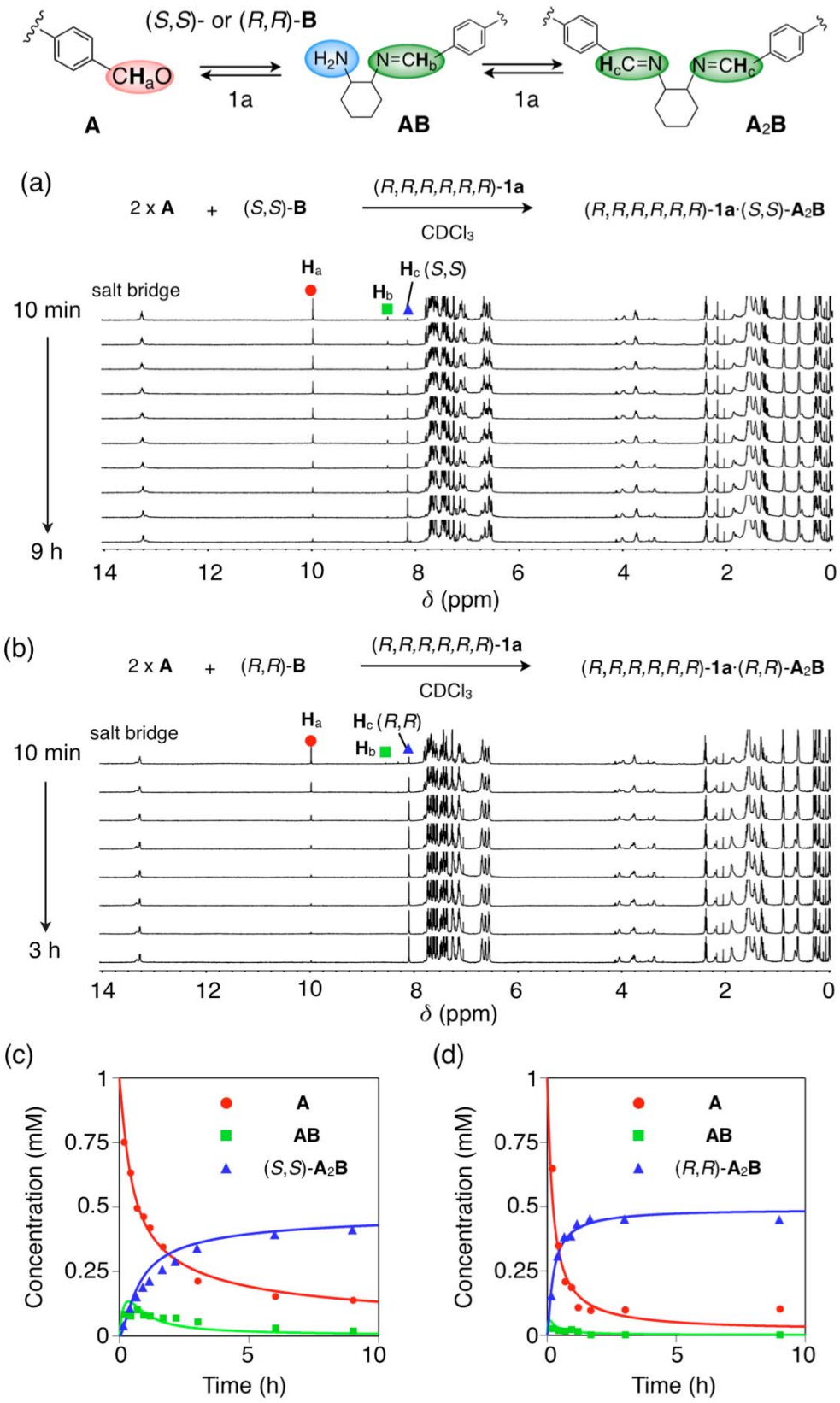


Figure S1. Time-dependent ^{1}H NMR spectral changes (a and b) and time-concentration plots (c and d) of the mixture of **A** (1.0 mM) and (1*S*,2*S*)-**B** (0.50 mM) (a and c) and (1*R*,2*R*)-**B** (0.50 mM) (b and d) in the presence of (*R*,*R*,*R*,*R*,*R*,*R*)-**1a** (0.50 mM) in $CDCl_3$ at 25 °C. The curves in the plots were obtained using the determined rate constants (*k*).

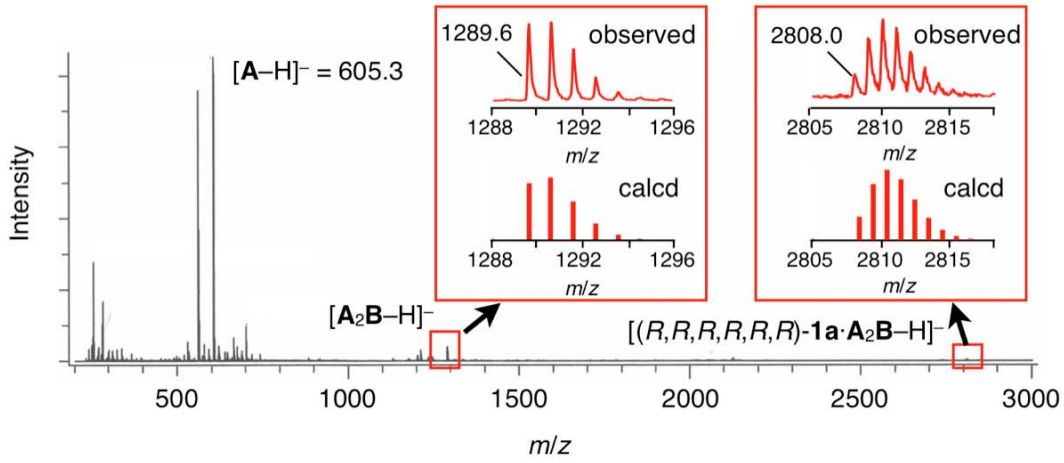


Figure S2. Negative mode ESI-MS ($CHCl_3$/MeOH = 1/1 as a solvent) spectrum of (*R*,*R*,*R*,*R*,*R*,*R*)-**1a**·$\mathbf{A_2B}$.

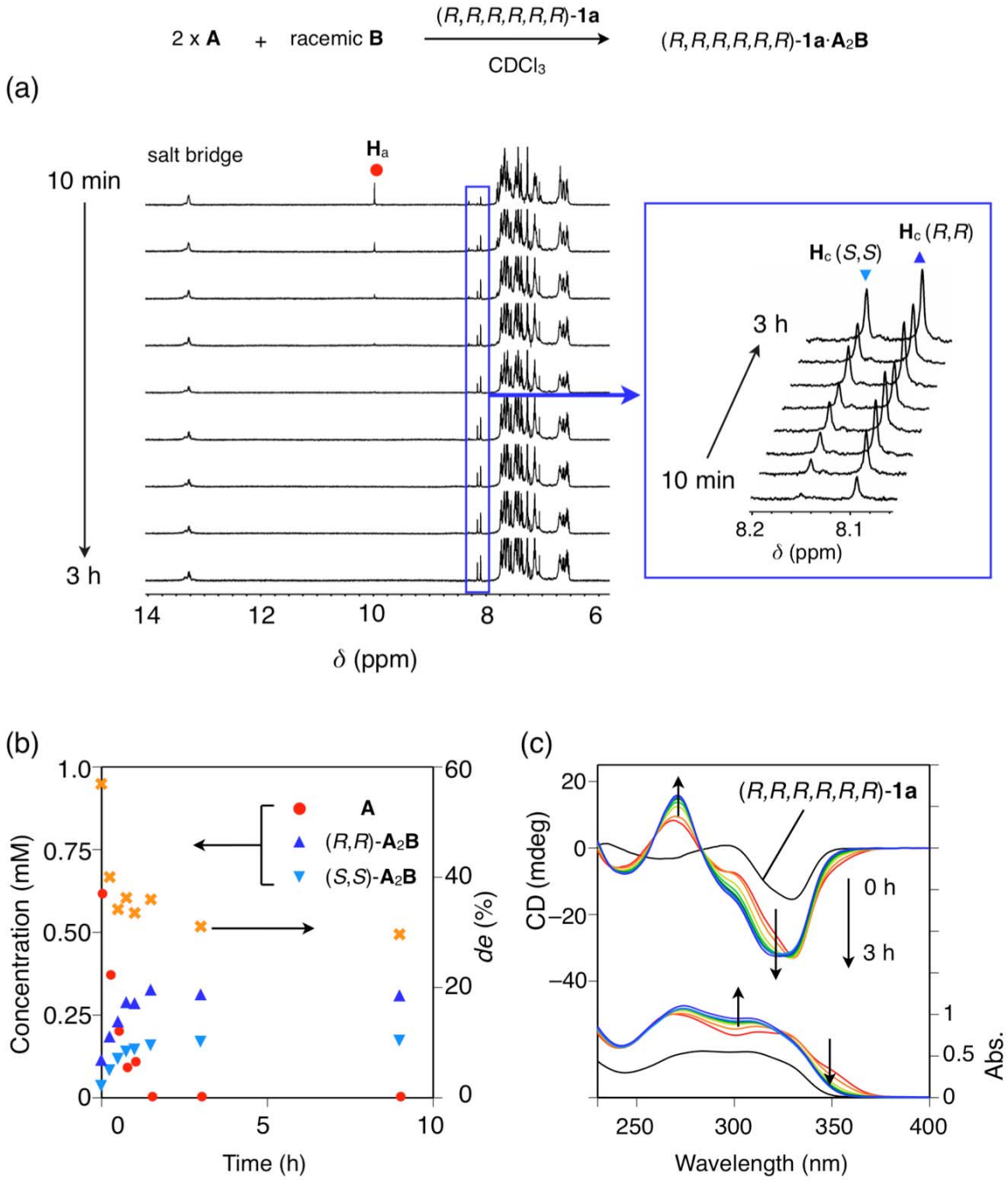


Figure S3. Time-dependent ^{1}H NMR spectral changes (a), time-concentration plots (b), and time-dependent CD and absorption spectral changes (c) of the mixture of **A** (1.0 mM) and racemic **B** (1.0 mM) in the presence of (*R*,*R*,*R*,*R*,*R*,*R*)-**1a** (0.50 mM) in $CDCl_3$ at 25 °C.

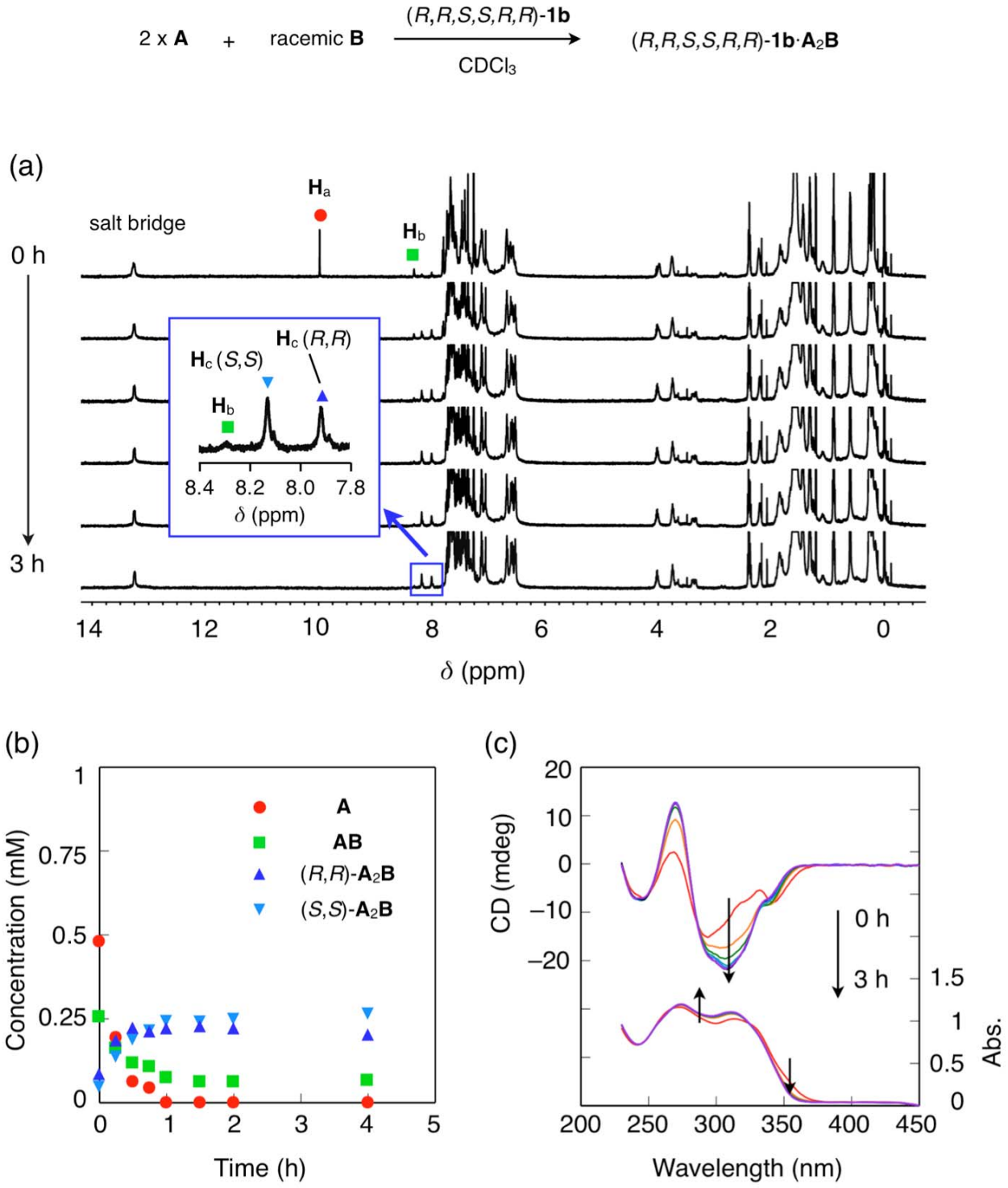


Figure S4. Time-dependent ^{1}H NMR spectral changes (a), time-concentration plots (b), and time-dependent CD and absorption spectral changes (c) of the mixture of **A** (1.0 mM) and racemic **B** (1.0 mM) in the presence of (*R*,*R*,*S*,*S*,*R*,*R*)-**1b** (0.50 mM) in $CDCl_3$ at 25 °C.

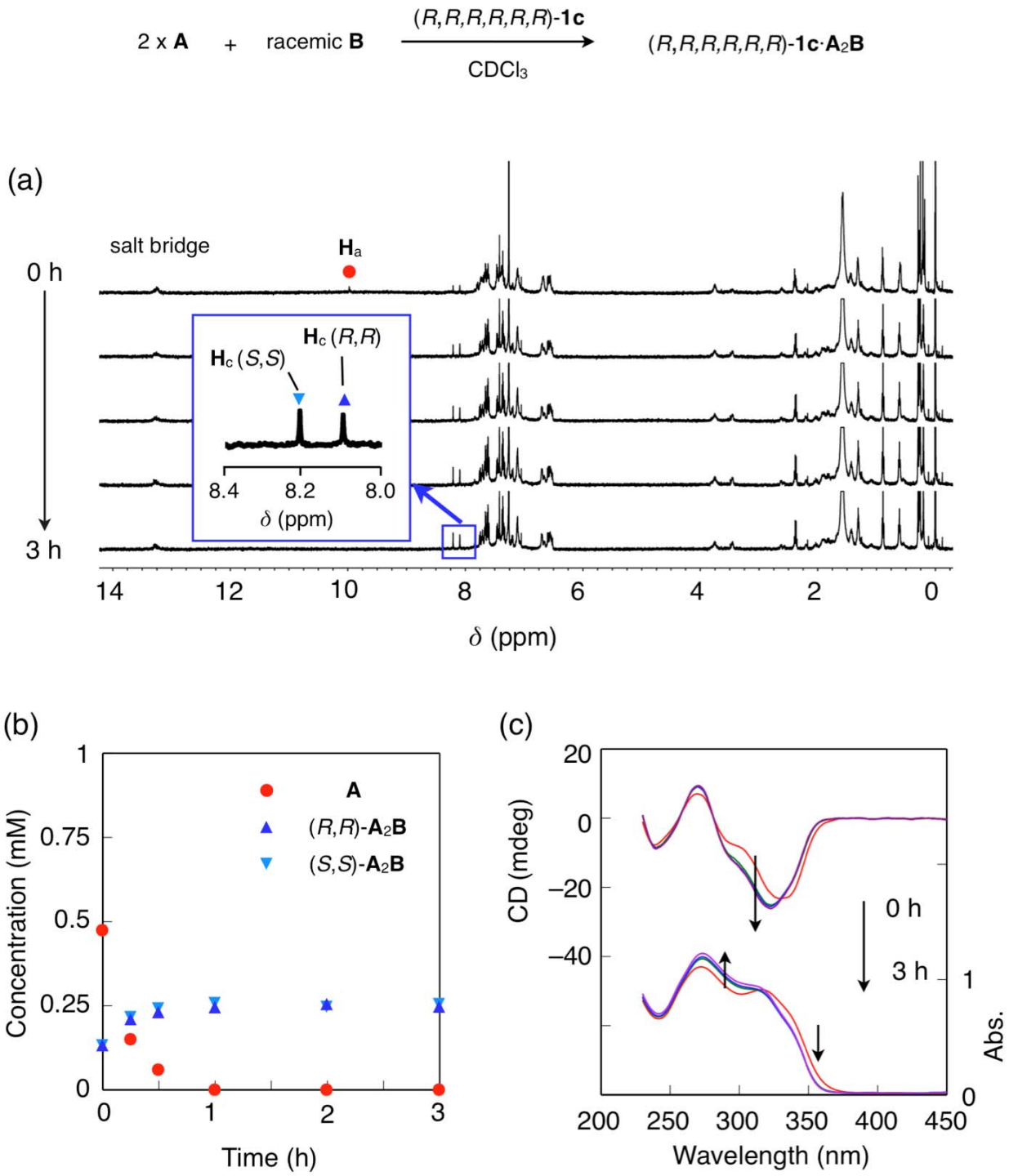


Figure S5. Time-dependent ^{1}H NMR spectral changes (a), time-concentration plots (b), and time-dependent CD and absorption spectral changes (c) of the mixture of **A** (1.0 mM) and racemic **B** (1.0 mM) in the presence of (*R*,*R*,*R*,*R*,*R*,*R*)-**1c** (0.50 mM) in $CDCl_3$ at 25 °C.

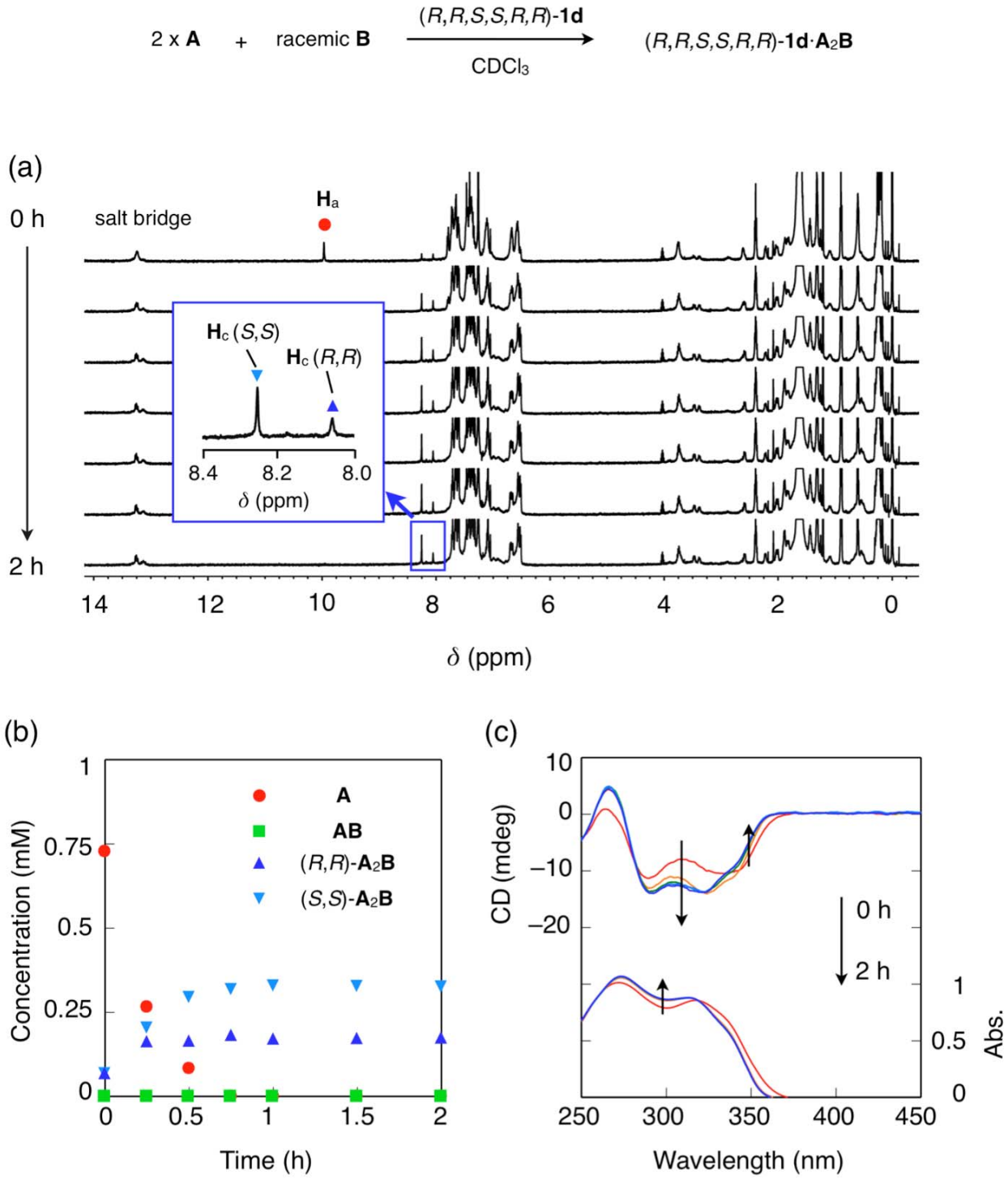


Figure S6. Time-dependent ^{1}H NMR spectral changes (a), time-concentration plots (b), and time-dependent CD and absorption spectral changes (c) of the mixture of **A** (1.0 mM) and racemic **B** (1.0 mM) in the presence of (*R*,*R*,*S*,*S*,*R*,*R*)-**1d** (0.50 mM) in $CDCl_3$ at 25 °C.

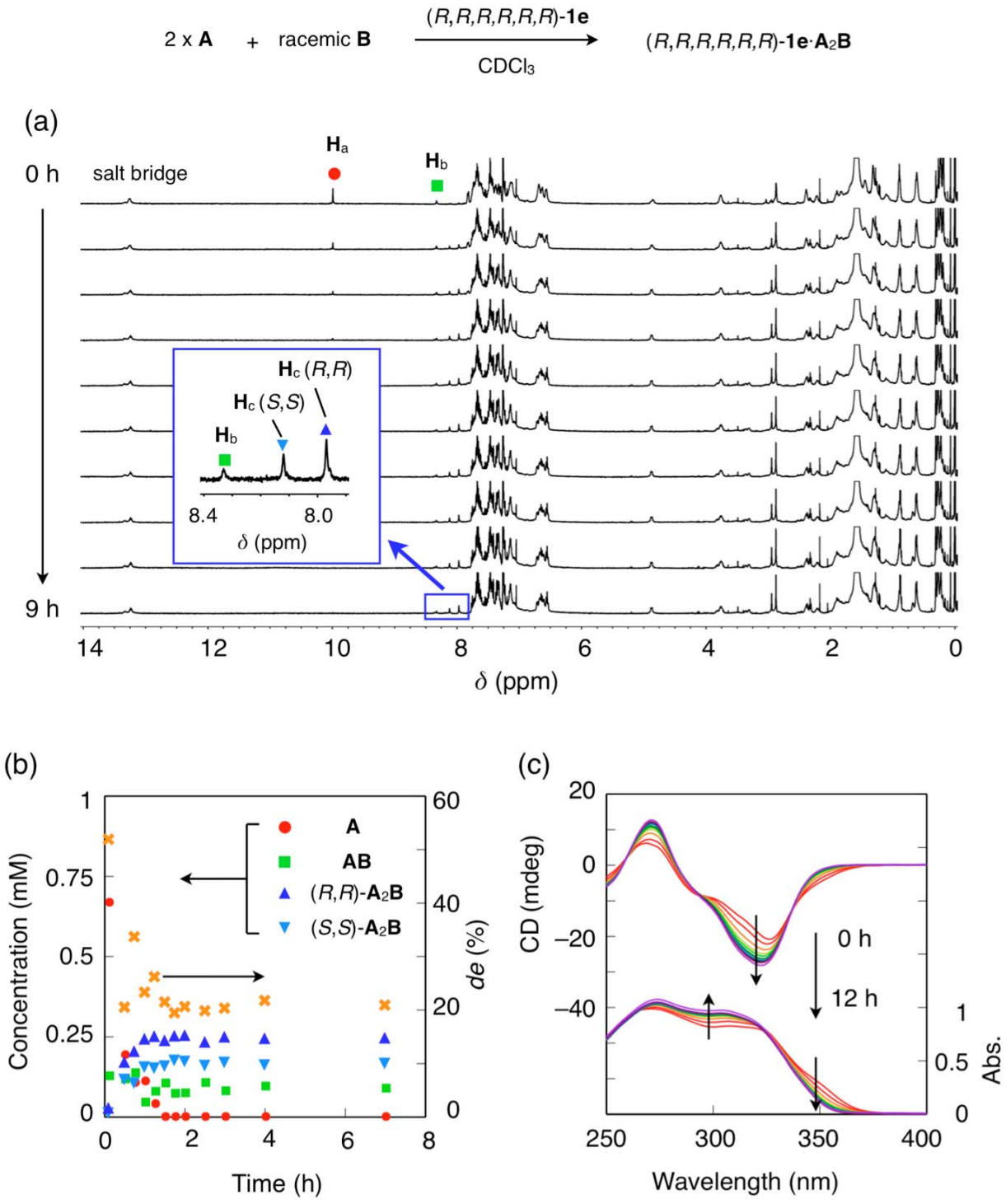


Figure S7. Time-dependent ^{1}H NMR spectral changes (a), time-concentration plots (b), and time-dependent CD and absorption spectral changes (c) of the mixture of **A** (1.0 mM) and racemic **B** (1.0 mM) in the presence of (*R*,*R*,*R*,*R*,*R*,*R*)-**1e** (0.50 mM) in $CDCl_3$ at 25 °C.

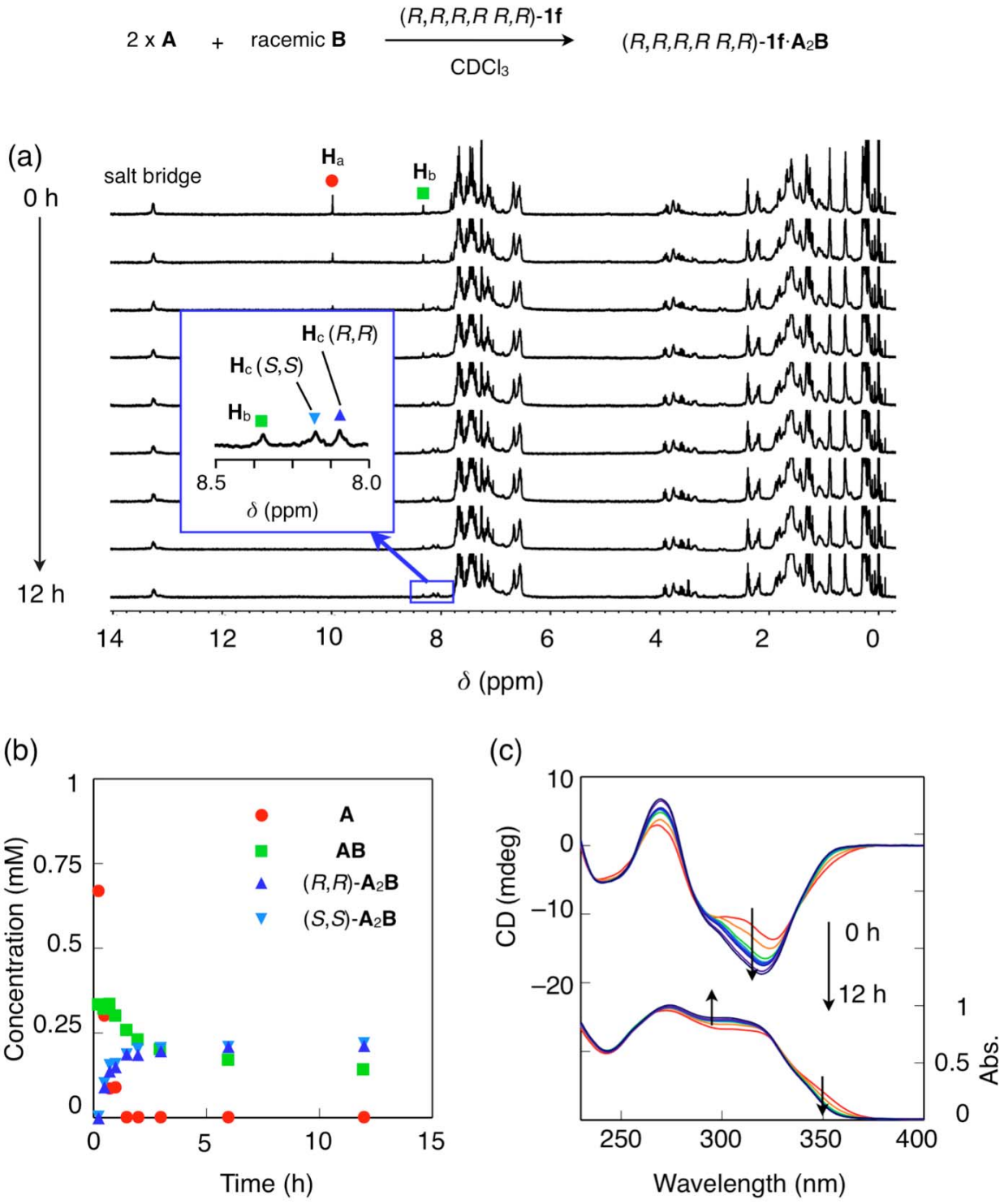


Figure S8. Time-dependent ^{1}H NMR spectral changes (a), time-concentration plots (b), and time-dependent CD and absorption spectral changes (c) of the mixture of **A** (1.0 mM) and racemic **B** (1.0 mM) in the presence of (*R*,*R*,*R*,*R*,*R*,*R*)-**1f** (0.50 mM) in $CDCl_3$ at 25 °C.

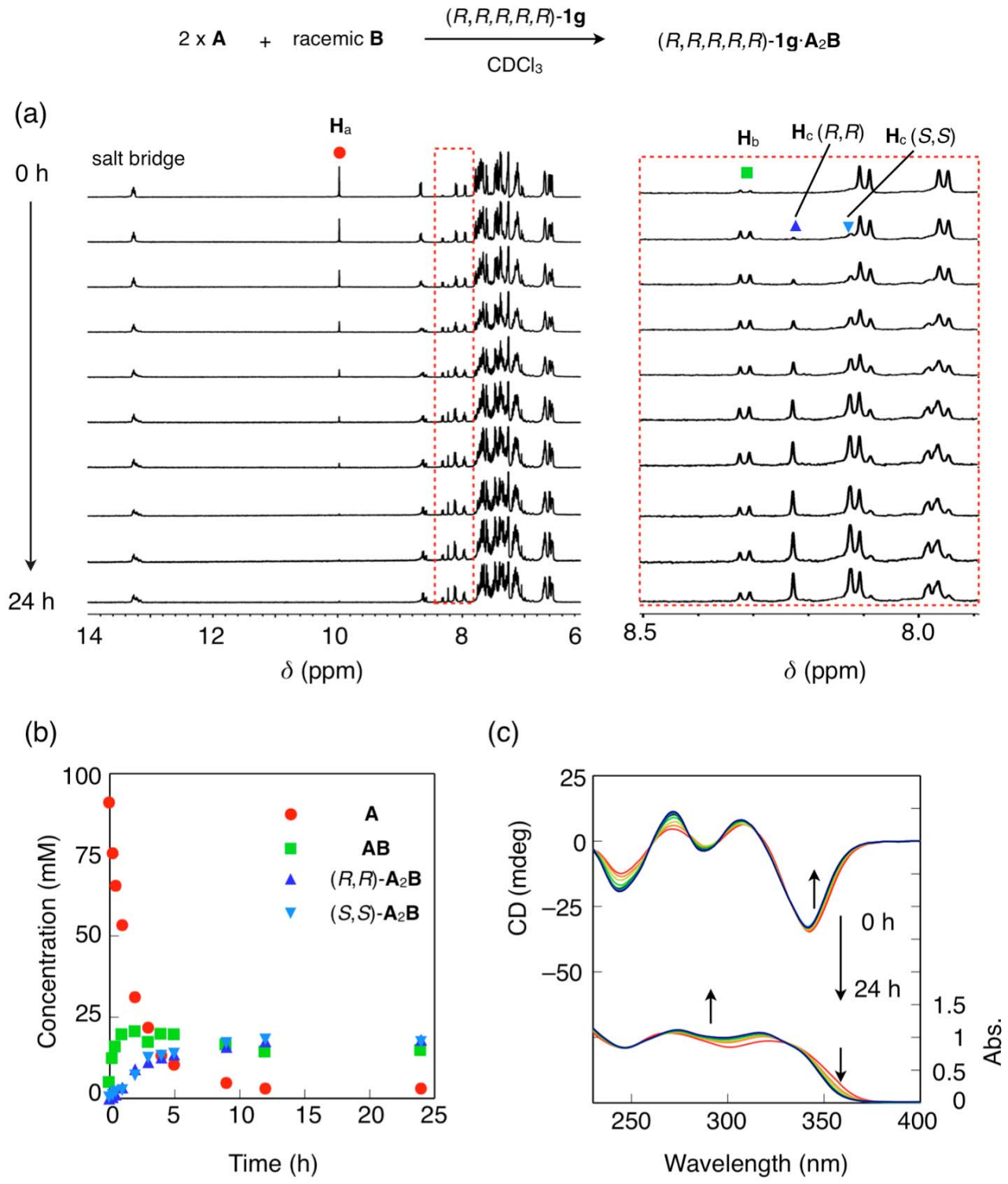


Figure S9. Time-dependent ^{1}H NMR spectral changes (a), time-concentration plots (b), and time-dependent CD and absorption spectral changes (c) of the mixture of **A** (1.0 mM) and racemic **B** (1.0 mM) in the presence of (*R*,*R*,*R*,*R*,*R*)-**1g** (0.50 mM) in $CDCl_3$ at 25 °C.

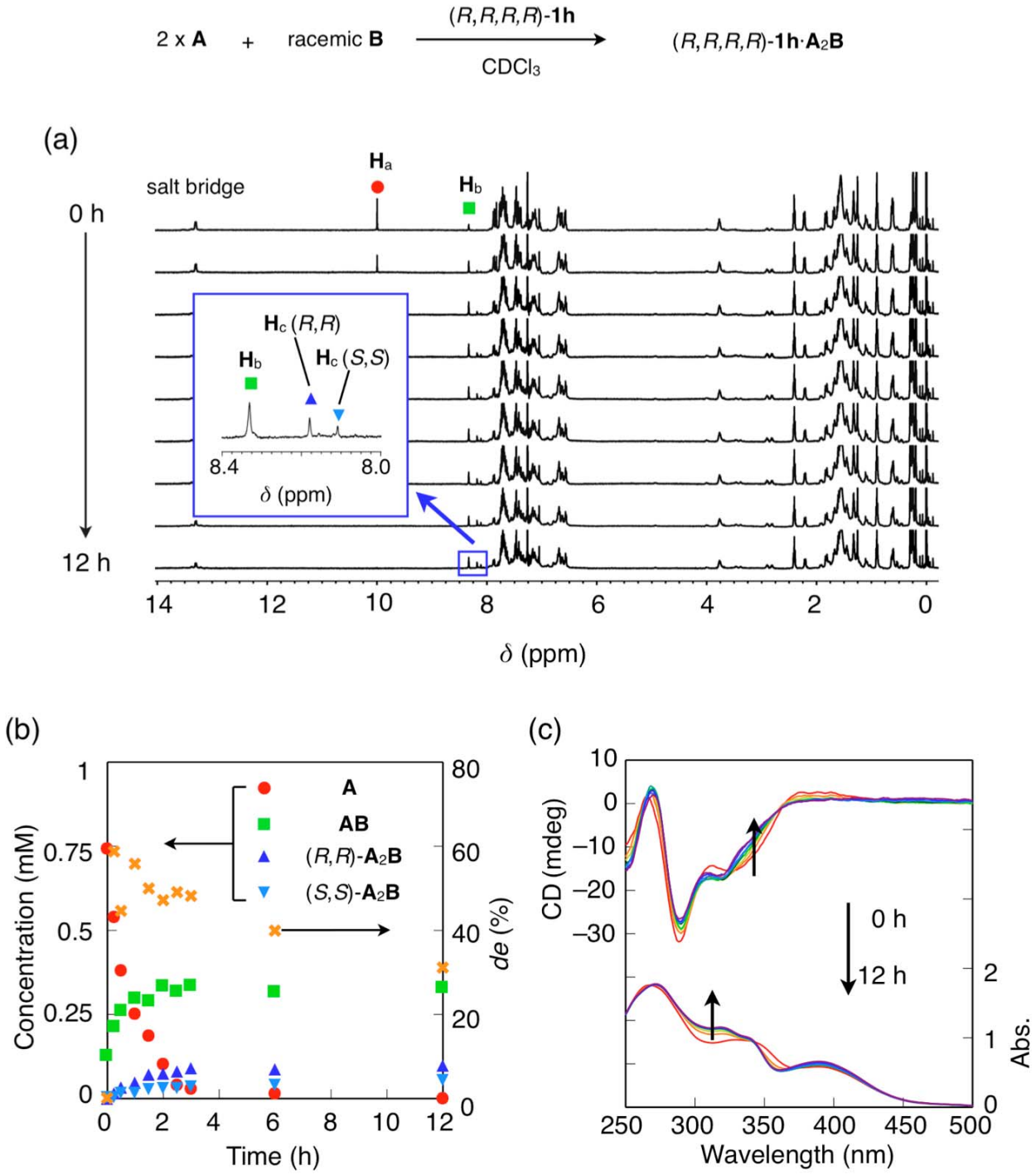


Figure S10. Time-dependent ^{1}H NMR spectral changes (a), time-concentration plots (b), and time-dependent CD and absorption spectral changes (c) of the mixture of **A** (1.0 mM) and racemic **B** (1.0 mM) in the presence of (*R*,*R*,*R*,*R*)-**1h** (0.50 mM) in $CDCl_3$ at 25 °C.

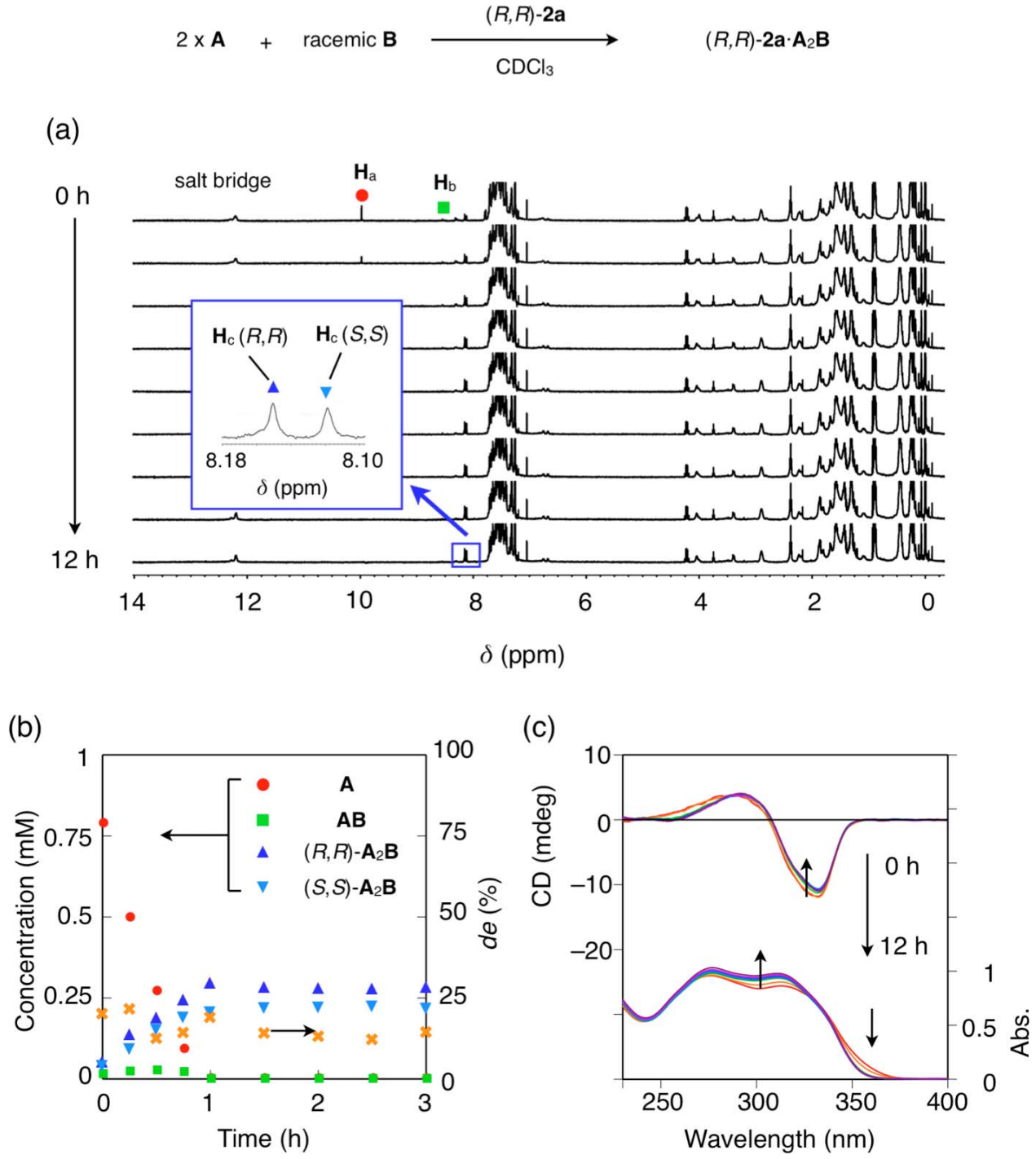


Figure S11. Time-dependent ^{1}H NMR spectral changes (a), time-concentration plots (b), and time-dependent CD and absorption spectral changes (c) of the mixture of **A** (1.0 mM) and racemic **B** (1.0 mM) in the presence of (*R*,*R*)-**2a** (0.50 mM) in $CDCl_3$ at 25 °C.

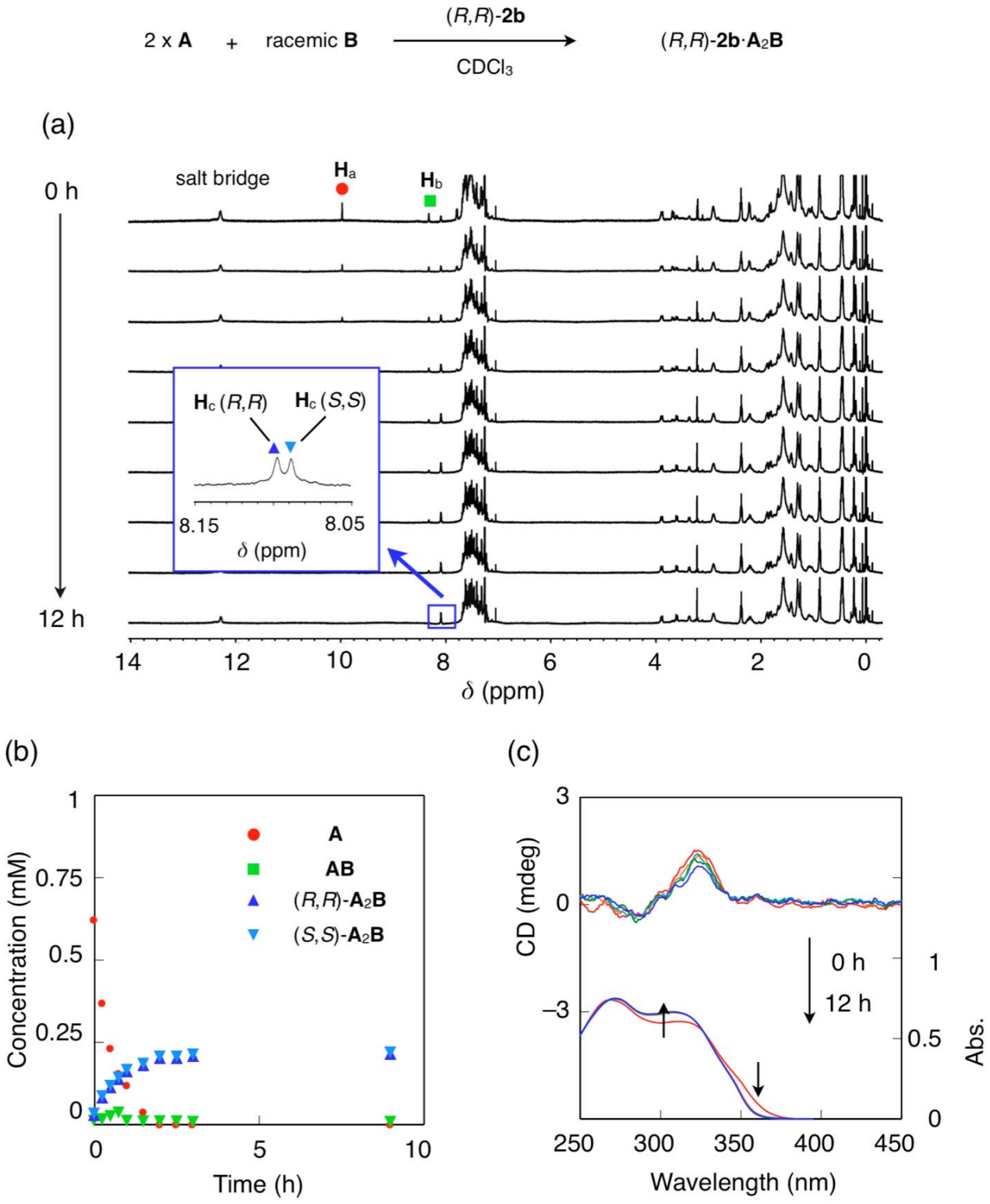


Figure S12. Time-dependent ^{1}H NMR spectral changes (a), time-concentration plots (b), and time-dependent CD and absorption spectral changes (c) of the mixture of **A** (1.0 mM) and racemic **B** (1.0 mM) in the presence of (*R*,*R*)-**2b** (0.50 mM) in $CDCl_3$ at 25 °C.

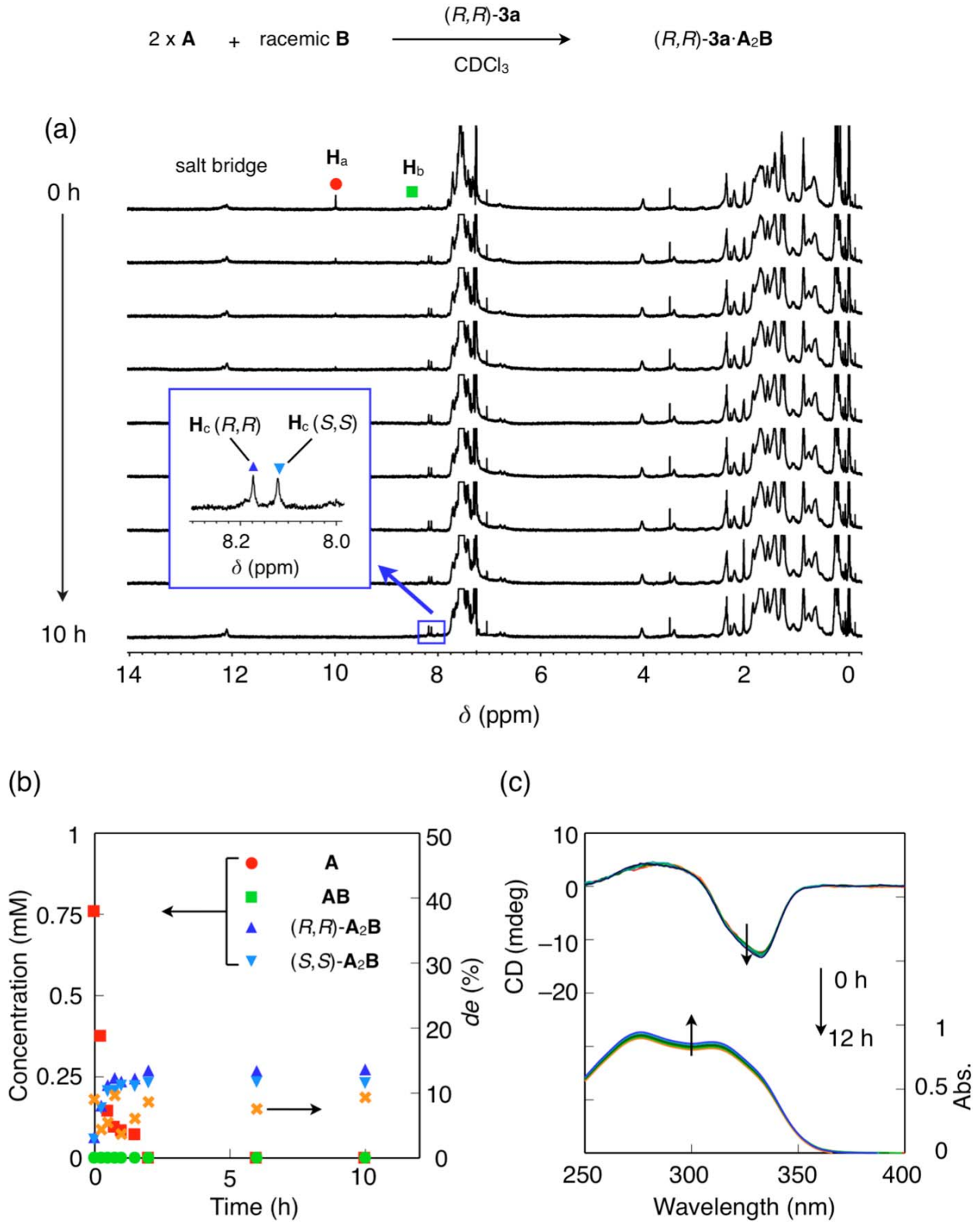


Figure S13. Time-dependent ^{1}H NMR spectral changes (a), time-concentration plots (b), and time-dependent CD and absorption spectral changes (c) of the mixture of **A** (1.0 mM) and racemic **B** (1.0 mM) in the presence of (*R*,*R*)-**3a** (0.50 mM) in $CDCl_3$ at 25 °C.

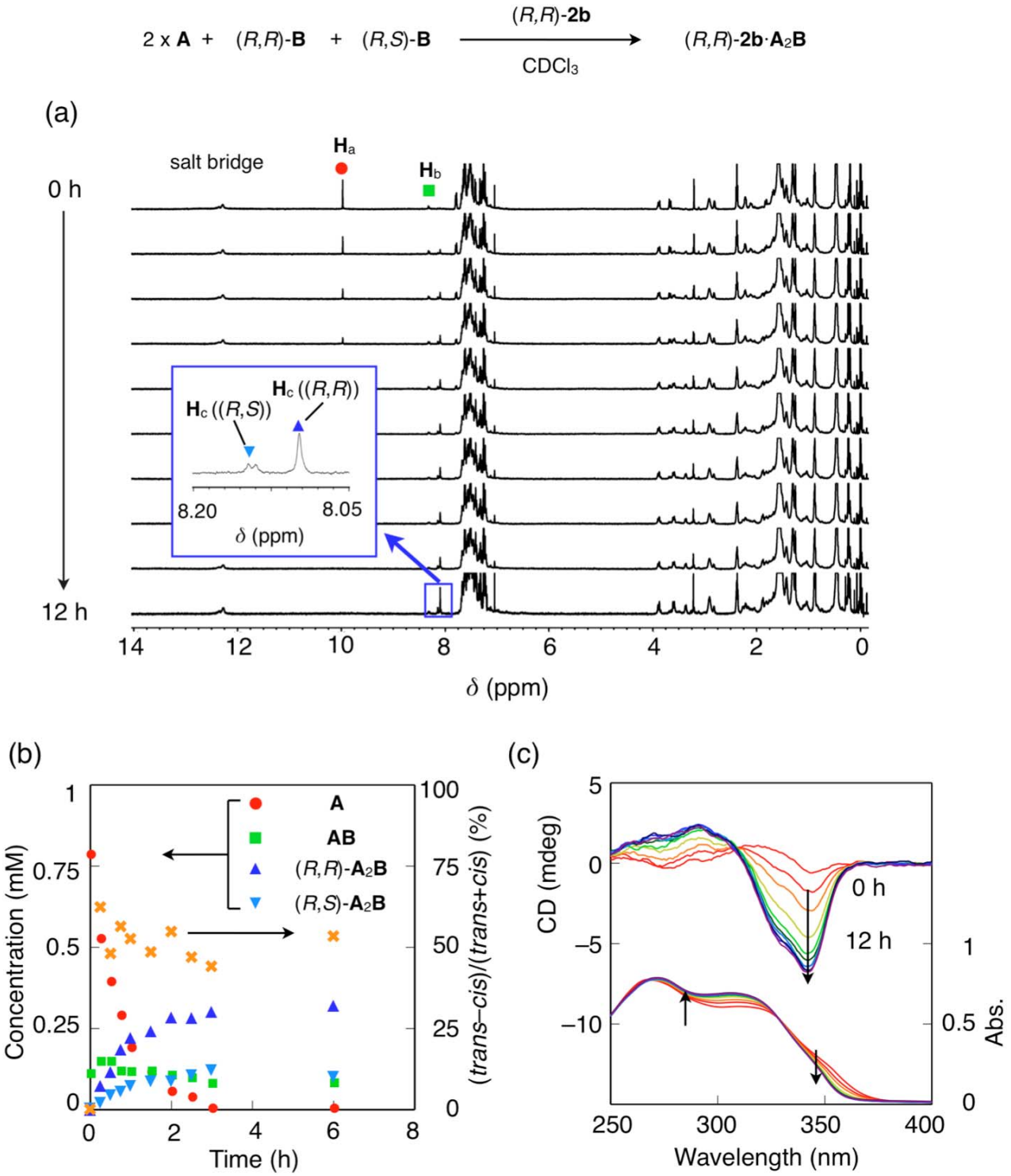


Figure S14. Time-dependent ^{1}H NMR spectral changes (a), time-concentration plots (b), and time-dependent CD and absorption spectral changes (c) of the mixture of **A** (1.0 mM), (*R*,*R*)-**B** (0.50 mM), and (*R*,*S*)-**B** (0.50 mM) in the presence of (*R*,*R*)-**2b** (0.50 mM) in $CDCl_3$ at 25 °C.

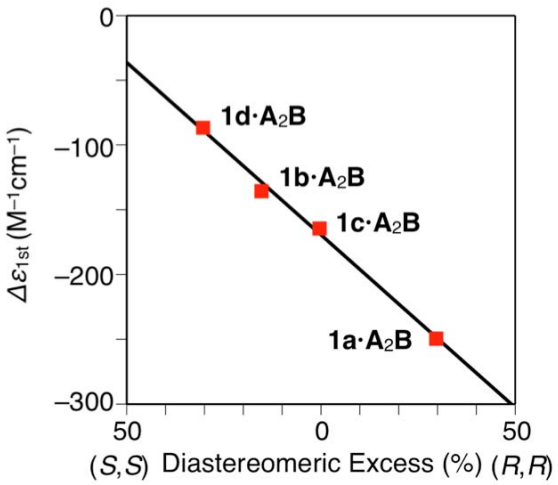


Figure S15. The relationship between CD intensities ($\Delta\varepsilon_{1st}$) of the duplexes **1a**·$\mathbf{A_2B}$, **1b**·$\mathbf{A_2B}$, **1c**·$\mathbf{A_2B}$, and **1d**·$\mathbf{A_2B}$ and their diastereomeric excess (*de*) values at equilibrium in $CDCl_3$ at 25 °C.

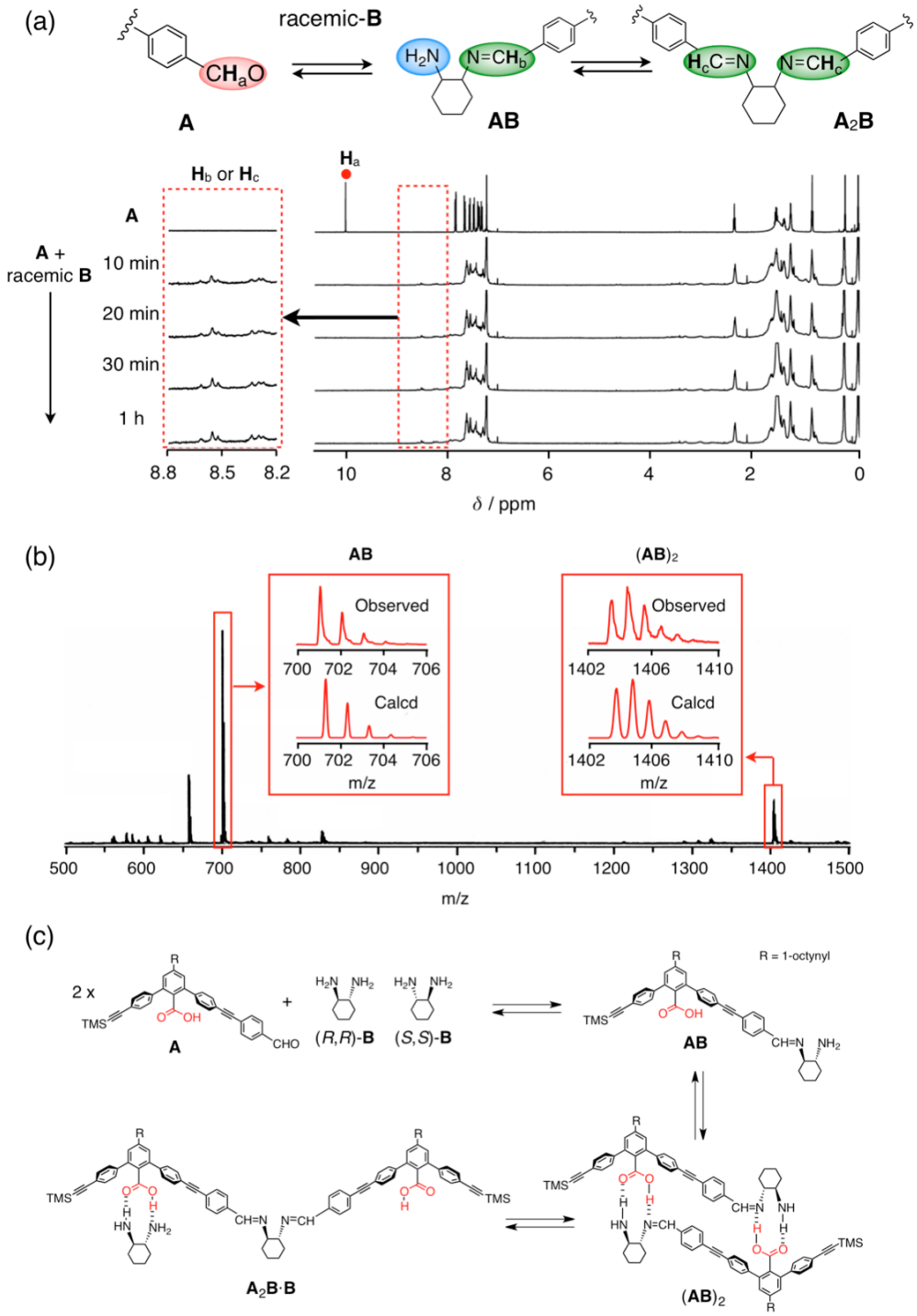


Figure S16. (a) Time-dependent ^{1}H NMR spectral changes of the mixture of **A** (1.0 mM) and racemic-**B** (1.0 mM) in $CDCl_3$ at 25 °C. (b) Negative mode ESI-MS ($CHCl_3$/MeOH = 1/1 as a solvent) spectrum of the equimolar mixture of **A** and racemic-**B**. (c) Possible structures of imine derivatives formed from **A** and **B**.

It is well known that imine-bond forming reaction between aldehydes and amines is catalyzed by acids, and therefore, in the absence of the amidine template, the carboxylic acid monomer **A** bearing a terminal aldehyde group self-catalyzed the imine-bond forming reaction with the racemic amine **B**, and the aldehyde (**A**) was consumed within 10 min. However, the products were complexed mixtures of the monomer (**AB**) and dimer (**A$_2$B**), and the monomer **AB** was predominantly formed, as revealed by the time-dependent ^{1}H NMR spectral changes of the reaction mixture and the ESI-MS measurement results of the products. Consequently, the amidine templates are essential to preferentially produce the carboxylic acid dimer (**A$_2$B**) with an optical activity.

5. Theoretical Formulae

The kinetics of the imine-bond forming reaction was analyzed as the two-step reversible reactions, as shown in eq (1).

$$\mathbf{A} + \mathbf{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{AB} + H_2O \qquad \mathbf{A} + \mathbf{AB} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathbf{A_2B} + H_2O \tag{1}$$

time / s	concentration / M				
	A	**B**	**AB**	**A_2B**	H_2O
t_0	a_0	b_0	0	0	0
t	x	y	$2b_0 - a_0 + x - 2y$	$a_0 - b_0 - x + y$	$a_0 - x$

When the concentrations of **A** and **B** are a_0 and b_0 at initial stage (= t_0), respectively, the imine-bond forming reaction obeys the following equations.

$$\begin{aligned} dx/dt &= d[\mathbf{A}]/dt \\ &= -k_1[\mathbf{A}][\mathbf{B}] + k_{-1}[\mathbf{AB}][H_2O] - k_2[\mathbf{A}][\mathbf{AB}] + k_{-2}[\mathbf{A_2B}][H_2O] \\ &= -k_1xy + k_{-1}(2b_0 - a_0 + x - 2y)(a_0 - x) - k_2x(2b_0 - a_0 + x - 2y) \\ &\quad + k_{-2}(a_0 - b_0 - x + y)(a_0 - x) \end{aligned} \tag{2}$$

$$\begin{aligned} dy/dt &= d[\mathbf{B}]/dt \\ &= -k_1[\mathbf{A}][\mathbf{B}] + k_{-1}[\mathbf{AB}][H_2O] \\ &= -k_1xy + k_{-1}(2b_0 - a_0 + x - 2y)(a_0 - x) \end{aligned} \tag{3}$$

Since the eqs (2) and (3) were difficult to solve analytically, the kinetic data were fitted by numerical integration using the fourth-order Runge-Kutta method. Using this procedure, a time course of concentrations for the reaction of **A** and **B** was generated. The concentration of each species was then plotted as a function of time and it was then compared to the observed concentrations. Using a least-squares curve fitting method, best-fit rate constants were obtained. C-language source code for this method is shown below.

```
#include <stdio.h>
#include <stdlib.h>
#include <math.h>

typedef struct PARAMSET {
	double k1;
	double k_1;
	double k2;
	double k_2;
	double A0;
	double B0;
} PARAMSET;

typedef struct DATASET{
	double t;
	double A;
	double A2B;
	double AB;
} DATASET;


double f(PARAMSET, double x, double y);
double g(PARAMSET, double x, double y);

int main(void)
{

	double t, h;
	double s1, s2, s3, s4, t1, t2, t3, t4;
	double k1m, k1M, k_1m, k_1M, k2m, k2M,k_2m, k_2M;
	double dev, dev_m;
	PARAMSET ps, ps_best;
	DATASET ds[25];

	int d, i, j, k, l, m, d_j, d_k, d_l, d_m, n_ds, i_ds, step, trial;

	double x[100001];
	double y[100001];
	double A;
	double AB;
	double A2B;


	FILE *fp;


	x[0] = ps.A0 = 0.0010;
	y[0] = ps.B0 = 0.0005;


	printf("2A+B-><-AB2+2H2O¥nTrial No:");
	scanf("%d", &trial);

	printf("¥nnumber of data:");
	scanf("%d", &n_ds);

	for(i_ds=0; i_ds <= n_ds -1; i_ds++){
		printf("¥ninput data (t[sec] A [M] AB [M] A2B [M]):");
		scanf("%lf%lf%lf%lf", &(ds[i_ds].t), &(ds[i_ds].A), &(ds[i_ds].AB), &(ds[i_ds].A2B));
	}
```

```
printf("¥nterminal time(sec):");
scanf("%lf", &t);

printf("¥nk1min, MAX [M^-1 s^-1] and div:");
scanf("%lf%lf%d", &k1m, &k1M, &d_j);

printf("¥nk_1min, MAX[M^-1 s^-1] and div:");
scanf("%lf%lf%d", &k_1m, &k_1M, &d_k);

printf("¥nk2min, MAX [M^-1 s^-1] and div:");
scanf("%lf%lf%d", &k2m, &k2M, &d_l);

printf("¥nk_2min, MAX[M^-1 s^-1] and div:");
scanf("%lf%lf%d", &k_2m, &k_2M, &d_m);

printf("¥ndivision number for RK(max1000):");
scanf("%d", &d);


h = t / d;
printf("h=%f¥n", h);


if((fp = fopen("runge-kutta.csv", "a")) == NULL){
        printf("file open error¥n");
        exit(1);
}

fprintf(fp, "¥ntrial# %d,RK div:%d,,,¥n", trial, d);
fprintf(fp, "k1,k_1,k2,k_2,dev¥n");
fprintf(fp, "k1:%f-%f,k_1:%f-%f,k2:%f-%f, k_2:%f-%f¥n", k1m, k1M, k_1m, k_1M, k2m, k2M, k_2m, k_2M);
fprintf(fp, "div:%d,div:%d,div:%d,div:%d,¥n", d_j, d_k, d_l, d_m);



for(j=0; j <= d_j; j++){
        for(k=0; k <= d_k; k++){
                        for(l=0; l <= d_l; l++){
                                        for(m=0; m <= d_m; m++){


                        ps.k1 = k1m + j * ( k1M - k1m) / (double)d_j;
                        ps.k_1 = k_1m + k * (k_1M - k_1m) / (double)d_k;
                        ps.k2 = k2m + l * ( k2M - k2m) / (double)d_l;
                        ps.k_2 = k_2m + k * (k_2M - k_2m) / (double)d_m;

        for(i = 1; i <= d; i++) {
                        s1 = f(ps, x[i-1], y[i-1]) * h;
                        t1 = g(ps, x[i-1], y[i-1]) * h;

                        s2 = f(ps, x[i-1] + s1 / 2.0, y[i-1] + t1 / 2.0) * h;
                        t2 = g(ps, x[i-1] + s1 / 2.0, y[i-1] + t1 / 2.0) * h;

                        s3 = f(ps, x[i-1] + s2 / 2.0, y[i-1] + t2 / 2.0) * h;
                        t3 = g(ps, x[i-1] + s2 / 2.0, y[i-1] + t2 / 2.0) * h;

                        s4 = f(ps, x[i-1] + s3, y[i-1] + t3) * h;
                        t4 = g(ps, x[i-1] + s3, y[i-1] + t3) * h;

                        x[i] = x[i-1] + (s1 + 2.0 * s2 + 2.0 * s3 + s4) / 6.0;
                        y[i] = y[i-1] + (t1 + 2.0 * t2 + 2.0 * t3 + t4) / 6.0;
                        }
```

```
		dev = 0.0;
		for(i_ds = 0; i_ds <= n_ds - 1; i_ds++){
				step = (int)(ds[i_ds].t / h);
				A = x[step];
				AB = 2.0 * ps.B0 - ps.A0 + x[step] - 2.0 * y[step];
				A2B = ps.A0 - ps.B0 - x[step] + y[step];
				dev += pow(ds[i_ds].A - A, 2.0) + pow(ds[i_ds].AB - AB, 2.0) + pow(ds[i_ds].A2B - A2B,
2.0);
				}

				printf("%d %d %d %d¥n", j, k, l, m);

				if((j==0 && k==0 && l==0 && m==0) || dev < dev_m){
						ps_best = ps;
						dev_m = dev;
						fprintf(fp, "%e,%e,%e,%e¥n", ps_best.k1, ps_best.k_1,ps_best.k2, ps_best.k_2,
dev_m);

}
}
}
}
}



printf("k1=%f, k_1=%f,k2=%f, k_2=%f, dev=%.10f¥n", ps_best.k1, ps_best.k_1, ps_best.k2, ps_best.k_2, dev_m);

fclose(fp);

return 0;

}



double f(PARAMSET ps, double x, double y){
double ey, ey1, ey2, ey3;

	ey1 = - 1.0 * ps.k1 * x * y +ps.k_1 * (2.0 * ps.B0 - ps.A0 + x - 2.0 * y) * (ps.A0 - x);
	ey2 = - 1.0 * ps.k2 * (2.0 * ps.B0 - ps.A0 + x - 2.0 * y ) * x;
	ey3 = ps.k_2 * (ps.A0 - ps.B0 - x + y ) * (ps.A0 - x );

	ey = ey1 + ey2 + ey3;

	return ey;

}

double g(PARAMSET ps, double x, double y)
{
		double yf;

		yf = - 1.0 * ps.k1 * x * y + ps.k_1 * (2.0 * ps.B0 - ps.A0 + x - 2.0 * y) * (ps.A0 - x );


		return yf;

}
```

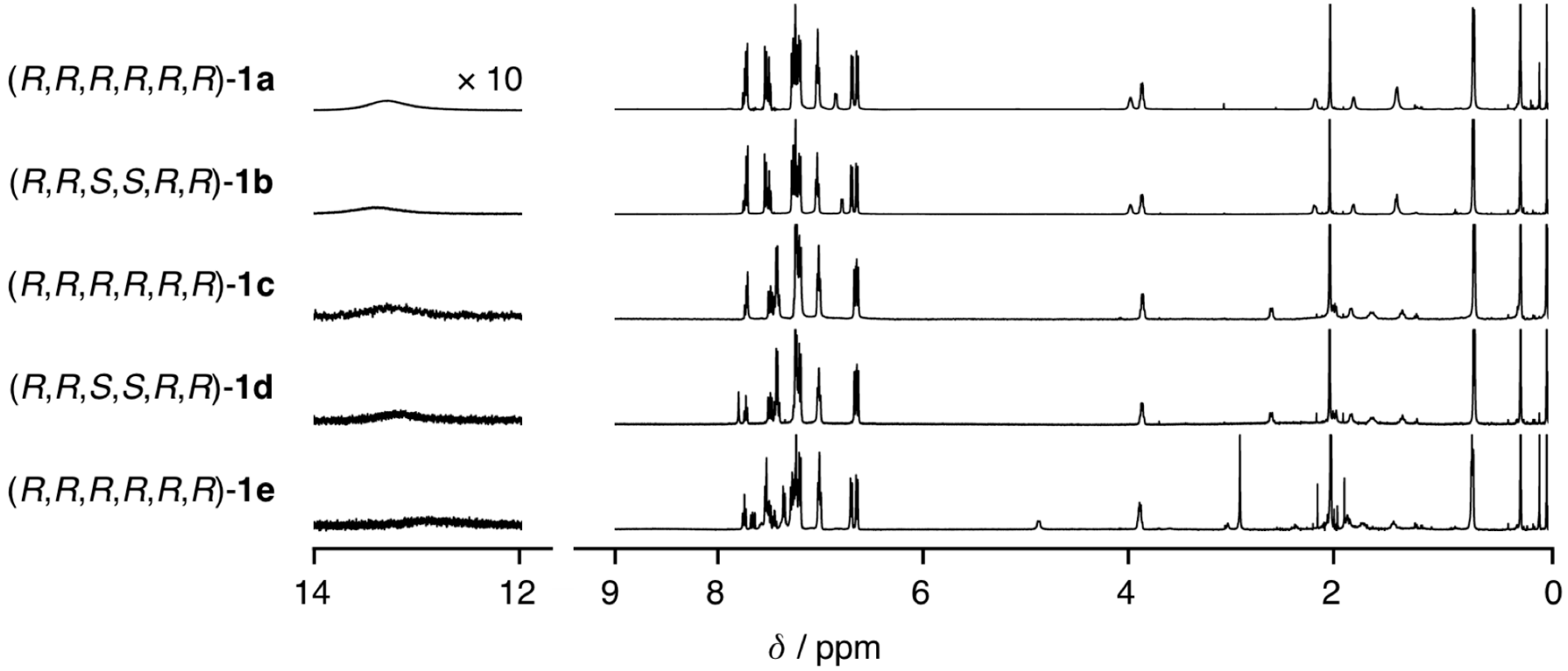


Figure S17. ^{1}H NMR spectra (500 MHz) of (*R*,*R*,*R*,*R*,*R*,*R*)-**1a**, (*R*,*R*,*S*,*S*,*R*,*R*)-**1b**, (*R*,*R*,*R*,*R*,*R*,*R*)-**1c**, (*R*,*R*,*S*,*S*,*R*,*R*)-**1d**, and (*R*,*R*,*R*,*R*,*R*,*R*)-**1e** in the presence of acetic acid in $CDCl_3$ at 25 °C.

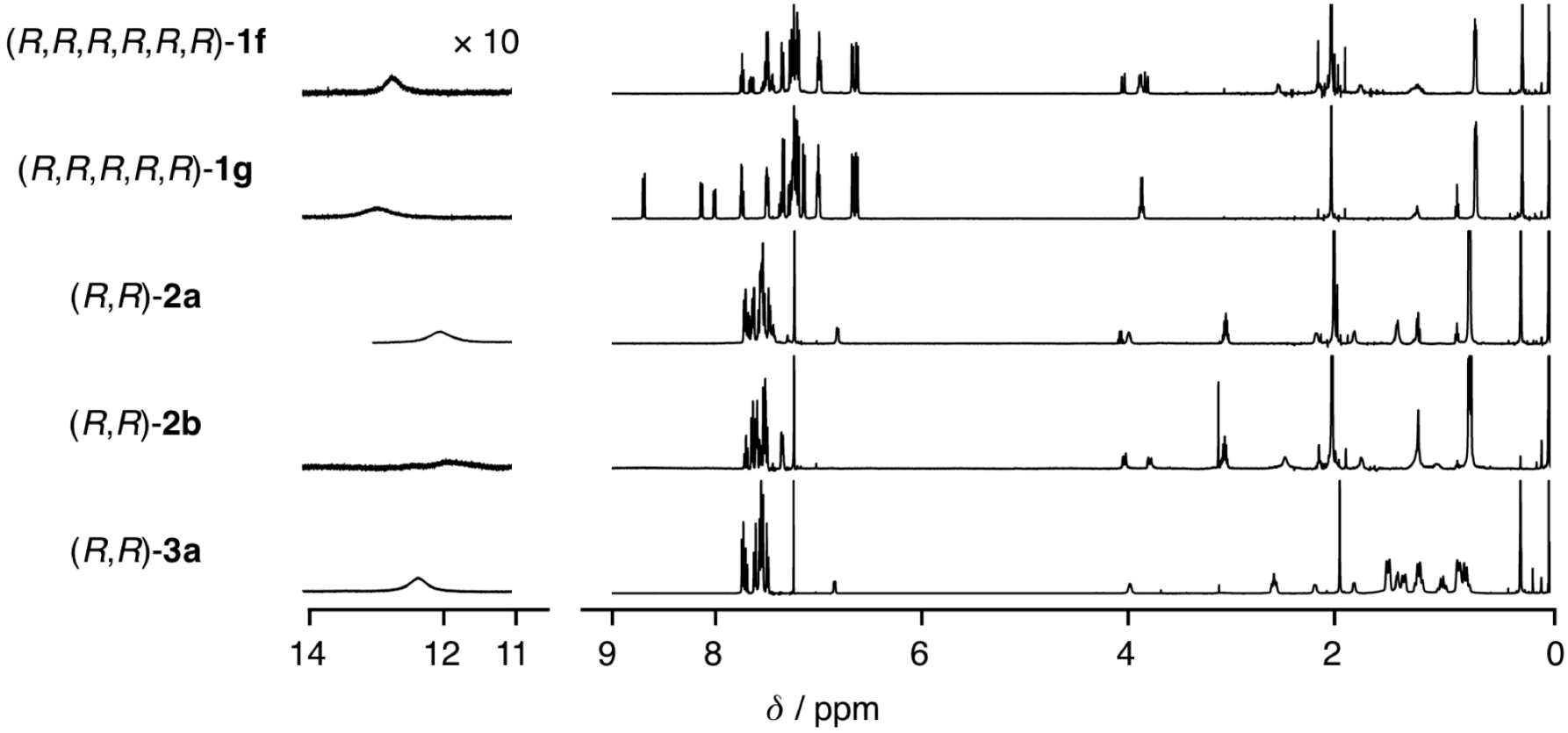


Figure S18. ^{1}H NMR spectra (500 MHz) of (*R*,*R*,*R*,*R*,*R*,*R*)-**1f**, (*R*,*R*,*R*,*R*,*R*)-**1g**, (*R*,*R*)-**2a**, (*R*,*R*)-**2b**, and (*R*,*R*)-**3a** in the presence of acetic acid in $CDCl_3$ at 25 °C.