Electronic supplementary information for:

A hetero-stranded double helix composed of *m*-diethynylbenzene-based complementary molecular strands stabilized by amidinium–carboxylate salt bridges

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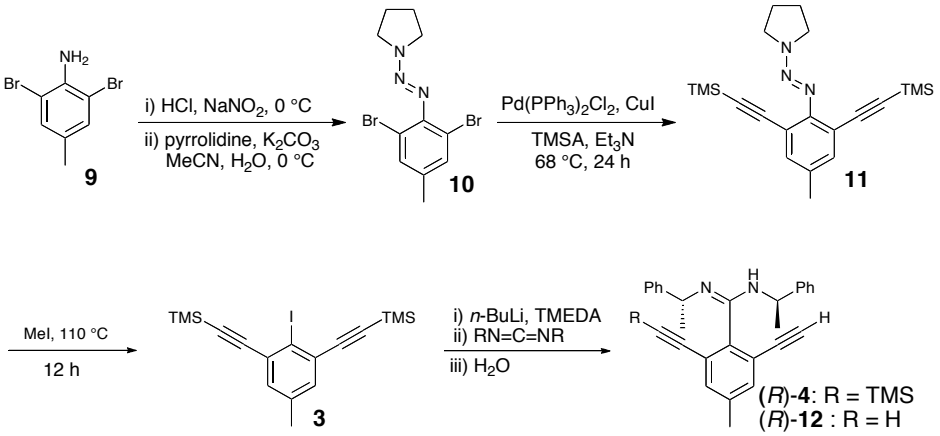
1. Instruments.

The melting points were measured using a Yanaco MP-500D melting point apparatus (Kyoto, Japan) and were uncorrected. The NMR spectra were taken using a Varian UNITY INOVA 500AS spectrometer operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C using TMS as the internal standard. The electron spray ionization mass spectra (ESI-MS) were recorded on 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 FT/IR-680 spectrometer (JASCO, Tokyo, Japan). The absorption and CD spectra were obtained in a 1.0-mm quartz cell at 25 °C using a JASCO V570 spectrophotometer and a JASCO J820 spectropolarimeter, respectively. The temperature was controlled by a JASCO PTC-423L apparatus (–10 to 60 °C). The optical rotations were measured in a 2-cm quartz cell on a JASCO P-1030 polarimeter equipped with an EYELA NCB-2100 temperature controller. Fluorescence spectra were measured in a 10-mm quartz cell by use of a JASCO FP 6500 spectrofluorometer. Molecular modeling and molecular mechanics calculations were performed by using Spartan 08 packages (Wavefunction, Inc., Irvine, CA, 2008). The geometries were further refined by the density functional theory (DFT) calculations using the Gaussian 03 program (Gaussian, Inc., Pittsburgh, PA).

2. Materials.

Anhydrous solvents were purchased from Wako (Osaka, Japan) and stored under dry nitrogen. All starting materials were purchased from commercial suppliers and were used without further purification unless otherwise noted. *N,N'*-Bis[(*R*)-1-phenylethyl]carbodiimide was prepared according to the literature method.[1]

3. Synthetic Procedures



Scheme S1. **Synthesis of amidine (*R*)-4.**

Triazene 10: A solution of 2,6-dibromo-4-methylaniline (**9**，4.90 g, 18.5 mmol) in 7.5 mL of conc. HCl was cooled in an ice bath while a solution of $NaNO_2$ (1.40 g, 20.3 mmol) in 40 mL of cold water was added dropwise. After the resulting solution of the diazonium salt was stirred at 0 °C for 30 min, this solution was added at once to a solution of pyrrolidine (3.00 g, 41.7 mmol) and K_2CO_3 (13.0 g, 94.2 mmol) in 1:2 CH_3CN/water (30 mL). The reaction mixture was then stirred at 0 °C for 30 min and was extracted with $CHCl_3$ (3 × 50 mL). The organic layer was washed twice with brine, dried over Na_2SO_4, filtered, and concentrated by evaporation. The crude product was purified by flash chromatography (SiO_2, *n*-hexane) to give the pure product **10** (5.55 g, 87% yield) as a yellow solid: ^{1}H NMR (500 MHz, $CDCl_3$, 10 mM, 25 °C): δ 7.35 (s, 2H, aromatic), 3.95 (br s, 2H, CH_2N), 3.72 (br s 2H, CH_2N), 2.28 (s,

3H, CH_3), 2.07 (brs, 4H, CH_2).

Triazene 11: A mixture of compound **10** (5.00 g, 14.5 mmol), CuI (78.7 mg, 0.410 mmol), and $PdCl_2(PPh_3)_2$ (280 mg, 0.410 mmol) in a 50 mL two-necked flask was degassed and back-filled with Ar. After this procedure was repeated three times, triethylamine (65.0 mL) and trimethylsilylacetylene (5.10 mL, 36.9 mmol) were introduced into the flask via a syringe. The reaction mixture was stirred at 68 °C for 24 h. After the solvents were evaporated to dryness, the residue was triturated with *n*-hexane (100 mL), and the mixture was filtered. The filtrate was then evaporated to dryness. The residue was further purified by column chromatography (SiO_2, *n*-hexane/EtOAc = 20/1) to afford the triazene **11** (4.69 g, 85% yield) as a white solid: M.p. = 138.0–139.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 10 mM, 25 °C): δ 7.23 (s, 2H, aromatic), 3.91 (broad, 2H, CH_2N), 3.74 (broad, 2H, CH_2N), 2.23 (s, 3H, CH_3), 2.05 (broad, 4H, $C\underline{H_2}CH_2N$), 0.20 (s, 18H, TMS); ^{13}C NMR (125 MHz, $CDCl_3$, 10 mM, 25 °C): δ 152.74, 134.61, 133.63, 116.05, 103.52, 96.97, 50.92, 46.35, 24.09, 20.55, 0.17; Anal. Calcd for $C_{21}H_{31}N_3Si_2$: C, 66.09; H, 8.19; N, 11.01. Found: C, 66.00; H, 8.09; N, 10.93.

Iodide 3: Triazene **11** (1.10 g, 2.89 mmol) was dissolved in iodomethane (7.00 mL) and the solution was heated in a sealed heavy-walled tube at 110 °C for 12 h. The reaction mixture was cooled, and the solvent was evaporated to dryness. The residue was then dissolved in $CHCl_3$ and the solution was filtered through a short plug of silica gel. After evaporation, the crude product was purified by column chromatography (SiO_2, *n*-hexane) to afford the iodide **3** (1.06 g, 90% yield) as a white solid: M.p. = 120.5–121.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 10 mM, 25 °C): δ 7.21 (s, 2H, aromatic), 2.22 (s, 3H, CH_3), 0.28 (s, 18H, TMS); ^{13}C NMR (125 MHz, $CDCl_3$, 10 mM, 25 °C): δ 137.66, 133.32, 130.68, 106.97, 103.92, 98.63, 20.61, 0.07; Anal. Calcd for $C_{17}H_{23}ISi_2$: C, 49.75; H, 5.65. Found: C, 49.87; H, 5.59.

Amidine (*R*)-4: *n*-BuLi (1.6 M in *n*-hexane, 1.56 mL, 2.50 mmol) and then

N,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) (0.38 mL, 294 mg, 2.53 mmol) were added dropwise to a solution of iodide **3** (920 mg, 2.24 mmol) in Et_2O (12 mL) at 0 °C. After 15 min, a solution of *N,N'*-bis[(*R*)-1-phenylethyl]carbodiimide[1] (617 mg, 2.46 mmol) in THF (2.0 mL) was added dropwise to the reaction mixture at 0 °C under stirring. The reaction was further continued at ambient temperature. After 18 h, water (12 mL) was added at 0 °C, and the mixture was then extracted with Et_2O (3 × 15 mL). The extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was purified by column chromatography (NH-SiO_2, *n*-hexane/AcOEt = 15/1) to afford the amidine (*R*)-**4** (519 mg, 50% yield) as a yellow solid: M.p. = 55.0–56.0 °C; $[\alpha]_D^{22}$ +23.6 (*c* 0.1 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, (*R*)-**4** (4.0 mM), CH_3CO_2H (67 mM), 25 °C): δ 9.71 (s, 2H, NH), 7.30 (s, 1H, aromatic), 7.27 (s, 1H, aromatic), 7.22–7.20 (m, 6H, aromatic), 7.03–7.02 (m, 4H, aromatic), 4.04–3.97 (m, 2H, NCH), 2.92 (s, 1H, C≡CH), 2.39 (s, 3H, CH_3), 2.10 (s, 50H, $C\underline{H_3}CO_2H$), 1.56–1.53 (m, 6H, $CHC\underline{H_3}$), 0.08 (s, 9H, TMS); ^{13}C NMR (125 MHz, $CDCl_3$, (*R*)-**4** (4.0 mM), CH_3CO_2H (67 mM), 25 °C): δ 176.78, 163.13, 142.87, 142.72, 141.69, 133.41, 133.01, 131.88, 128.63, 128.54, 127.54, 127.42, 126.45, 126.24, 122.51, 122.35, 121.51, 95.12, 86.43, 83.32, 78.31, 62.76, 55.83, 33.00, 27.87, 23.41, 23.25, 21.15; FT-IR (KBr, cm^{-1}): ν = 2158 (C≡C), 1642 (C=N) cm^{-1}; Anal. Calcd for $C_{31}H_{34}N_2Si$: C, 80.47; H, 7.41; N, 6.05. Found: C, 80.48; H, 7.32; N, 6.12.

Amidine (*R*)-12: In the preparation of (*R*)-**4**, (*R*)-**12** was isolated in 15% yield as a dark yellow solid: M.p. = 65.0–66.0 °C; $[\alpha]_D^{22}$ +22.6 (*c* 0.1 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, (*R*)-**12** (4.0 mM), CH_3CO_2H (28 mM), 25 °C): δ 13.35 (s, 2H, NH), 7.30 (s, 2H, aromatic), 7.22–7.18 (m, 6H, aromatic), 7.04–7.02 (m, 4H, aromatic), 3.99 (dd, J_1 = 6.9 Hz, J_2 = 0.7 Hz, 2H, NCH), 2.90 (s, 2H, C≡CH), 2.39 (s, 3H, CH_3), 2.07 (s, 22H, $C\underline{H_3}CO_2H$), 1.55 (d, J = 6.9 Hz, 6H, $CHC\underline{H_3}$); ^{13}C NMR (125 MHz, $CDCl_3$, (*R*)-**12** (4.0 mM), CH_3CO_2H (28 mM), 25 °C):

δ 176.61, 162.74, 142.89, 141.47, 133.88, 128.57, 127.42, 126.40, 121.60, 83.34, 78.17, 55.80, 23.39, 22.25, 21.16,; FT-IR (KBr, cm^{-1}): ν = 2172 (C≡C), 1637 (C=N) cm^{-1}; Anal. Calcd for $C_{28}H_{26}N_2$: C, 86.12; H, 6.71; N, 7.17. Found: C, 86.13; H, 6.75; N, 7.16.

Diamidine (*R*)-1: A mixture of the amidine (*R*)-**4** (71.0 mg, 0.153 mmol), 1,4-diiodobenzene (25.3 mg, 0.0770 mmol), CuI (2.10 mg, 0.0110 mmol), and $PdCl_2(PPh_3)_2$ (12.0 mg, 0.0170 mmol) in a 50 mL two-necked flask was degassed and back-filled with Ar. After this procedure was repeated three times, triethylamine (15.0 mL) was introduced into the flask via a syringe, and the reaction mixture was stirred at ambient temperature for 6 h. After the solvents were evaporated to dryness, the residue was dissolved in AcOEt (25 mL) and the solution was washed with water (2 × 8 mL) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was then purified by column chromatography (NH-SiO_2, *n*-hexane/AcOEt = 2/1) to afford the diamidine (*R*)-**1** (46 mg, 70% yield) as a reddish solid: M.p. = 101.1–102.2 °C; $[\alpha]_D^{22}$ –25.4 (*c* 0.1 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, (*R*)-**1** (5 mM), CH_3CO_2H (70 mM), 25 °C): δ 13.23 (br s, 4H, NH), 7.37 (s, 2H, aromatic), 7.34 (s, 2H, aromatic), 7.32 (s, 4H, aromatic), 7.24–7.22 (m, 8H, aromatic) 7.11–7.04 (m, 12H, aromatic), 4.13–4.04 (m, 4H, NCH), 2.95 (s, 2H, C≡CH), 2.44 (s, 6H, CH_3), 2.12 (s, 42H, $C\underline{H_3}CO_2H$), 1.58 (d, *J* = 6.9 Hz, 6H, $CHC\underline{H_3}$) 1.52 (d, *J* = 6.9 Hz, 6H, $CHC\underline{H_3}$); ^{13}C NMR (125 MHz, $CDCl_3$, (*R*)-**1** (5 mM), CH_3CO_2H (70 mM), 25 °C): δ 176.78, 163.13, 142.87, 142.72, 141.69, 133.41, 133.01, 131.88, 128.63, 128.54, 127.54, 127.42, 126.45, 126.24, 122.51, 122.35, 121.51, 95.12, 86.43, 83.32, 78.31, 62.76, 55.83, 27.87, 23.41, 23.25, 21.15; FT-IR (KBr, cm^{-1}): ν = 2212 (C≡C), 2103 (C≡C), 1716 (C=O) 1654 (C=N) cm^{-1}; Anal. Calcd for $C_{62}H_{54}N_4$: C, 87.08; H, 6.37; N, 6.55. Found: C, 87.06; H, 6.57; N, 6.39.

Carboxylic Acid 5: *n*-BuLi (1.6 M in *n*-hexane, 1.12 mL, 1.79 mmol) and then TMEDA

(0.27 mL, 209 mg, 1.79 mmol) were added dropwise to a solution of the iodide **3** (670 mg, 1.63 mmol) in THF (15.0 mL) at 0 °C. After 15 min, CO_2 was bubbled into the solution at 0 °C for 1.5 h. The mixture was further stirred at ambient temperature under CO_2 atmosphere for 12 h. To this was added a 10 mL of aqueous 1 M HCl at 0 °C, and the mixture was extracted with EtOAc (2 × 20 mL). The extracts were sequentially washed with water (10 mL) and brine (10 mL). The organic layer was then dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by column chromatography (SiO_2, *n*-hexane/AcOEt = 6/1) to afford the carboxylic acid **5** (472 mg, 88% yield) as a white solid: M.p. = 137.8–138.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 5 mM, 25 °C): δ 7.31 (s, 2H, aromatic), 2.31 (s, 3H, CH_3), 0.23 (s, 18H, TMS); ^{13}C NMR (125 MHz, $CDCl_3$, 5 mM, 25 °C): δ 140.49, 134.82, 133.67, 122.89, 101.70, 99.76, 20.99, 0.15; FT-IR (KBr, cm^{-1}): ν = 2160 (C≡C), 1707 (C=O) cm^{-1}; Anal. Calcd for $C_{18}H_{24}O_2Si_2$: C, 65.80; H, 7.36. Found: C, 66.08; H, 7.63.

Carboxylic Acid 6: A solution of *n*-tetrabutylammonium fluoride (TBAF) in THF (0.0460 M, 7.00 mL, 0.322 mmol) was added portionwise (1.0 mL at a time) to a solution of the carboxylic acid **5** (200 mg, 0.698 mmol) in THF (15.0 mL) at 0 °C. The reaction progress was monitored by TLC (eluent: *n*-hexane/EtOAc = 2/1; Rf values: **5** = 0.8; **6** = 0.4; the product with no TMS group = 0.1). The reaction was quenched with 1 M HCl (2 mL) at 0 °C, and the mixture was extracted with EtOAc (2 × 15 mL). The extracts were sequentially washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was then purified by column chromatography (SiO_2, *n*-hexane/EtOAc = 2/1) to afford the carboxylic acid **6** (80.0 mg, 51% yield) as a white solid: M.p. = 131.0–131.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 10 mM, 25 °C): δ 7.35 (s, 2H, aromatic), 3.24 (s, 1H, CH), 2.33 (s, 3H, CH_3), 0.24 (s, 9H, TMS); ^{13}C NMR (125 MHz, $CDCl_3$, 10 mM, 25 °C): δ 164.89, 151.13, 145.27, 140.12, 136.05, 122.65, 121.48, 120.74, 103.51, 99.44, 90.91, 22.93, 0.14;

FT-IR (KBr, cm^{-1}): ν = 2160 (C≡C), 1706 (C=O) cm^{-1}; Anal. Calcd for $C_{15}H_{16}Si$: C, 70.27; H, 6.29. Found: C, 69.98; H, 6.30.

7: To a solution of the carboxylic acid **6** (100 mg, 0.391 mmol) and triethylamine (0.5 mL) in THF (5.0 mL) was added chloro(methoxy)methane (MOMCl, 74.5 mg, 0.391 mmol). The reaction mixture was stirred at 0 °C for 10 min, and extracted with EtOAc (2 × 15 mL). The extracts were sequentially washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was then purified by column chromatography (NH-SiO_2, *n*-hexane/EtOAc = 8/1) to afford the compound **7** (111 mg, 95% yield) as a yellow liquid: ^{1}H NMR (500 MHz, $CDCl_3$, 10 mM, 25 °C): δ 7.33 (s, 1H, aromatic), 7.32 (s, 1H, aromatic) 5.48 (s, 2H, OCH_2), 3.58 (s, 3H, OCH_3), 3.19 (s, 1H, C≡CH), 2.32 (s, 3H, CH_3), 0.22 (s, 9H, TMS); ^{13}C NMR (125 MHz, $CDCl_3$, 10 mM, 25 °C): δ 166.84, 139.87, 136.41, 133.90, 133.73, 121.44, 120.28, 101.49, 99.07, 91.78, 81.14, 80.56, 58.20, 21.01, 0.15; Anal. Calcd for $C_{17}H_{20}O_3Si$: C, 67.96; H, 6.71. Found: C, 67.93; H, 6.66.

8: A mixture of the compound **7** (80.0 mg, 0.267 mmol), 1,4-diiodobenzene (44.0 mg, 0.134 mmol), CuI (2.10 mg, 0.0110 mmol), and $PdCl_2(PPh_3)_2$ (12.0 mg, 0.0170 mmol) in a 50 mL two-necked flask was degassed and back-filled with Ar. After this procedure was repeated three times, triethylamine (15 mL) was introduced into the flask via a syringe. The reaction mixture was stirred at 50 °C for 6 h. After evaporation, the residue was dissolved in AcOEt (30 mL) and the solution was washed sequentially with water (2 × 15 mL) and brine (8 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was then purified by column chromatography (NH-SiO_2, *n*-hexane/AcOEt = 2/1) to afford the compound **8** (63 mg, 63% yield) as a yellow solid: M.p. > 280 °C (dec.); ^{1}H NMR (500 MHz, $CDCl_3$, 10 mM, 25 °C): δ 7.46 (s, 4H, aromatic), 7.35 (s, 2H, aromatic), 7.32 (s, 2H, aromatic), 5.51 (s, 4H, OCH_2), 3.53 (s, 6H, OCH_3), 2.35 (s, 6H, CH_3), 0.23 (s, 18H,

TMS); ^{13}C NMR (125 MHz, $CDCl_3$, 10 mM, 25 °C): δ 166.93, 139.89, 135.84, 133.53, 133.01, 131.76, 123.12, 121.46, 121.21, 99.04, 92.80, 91.59, 88.46, 58.10, 21.07, –0.08; FT-IR (KBr, cm^{-1}): ν = 2158 (C≡C), 1732 (C=O) cm^{-1}; Anal. Calcd for $C_{40}H_{42}O_6Si_2$: C, 71.18; H, 6.27. Found: C, 71.15; H, 6.10.

Dicarboxylic Acid 2: A mixture of aqueous 1 M HCl (0.5 mL) and the compound **8** (35.0 mg, 0.052 mmol) in THF (5.0 mL) was stirred at 45 °C for 4 h. The mixture was then extracted with EtOAc (2 × 15 mL), the extracts were washed with brine (10 mL), and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated to dryness, and the residue was purified by column chromatography (SiO_2, *n*-hexane/EtOAc = 2/1) to afford the dicarboxylic acid **2** (24 mg, 80% yield) as a white solid: M.p. > 280 °C (dec.); ^{1}H NMR (500 MHz, $CDCl_3$, 10 mM, 25 °C): δ 7.37 (s, 2H, aromatic), 7.36 (s, 2H, aromatic), 7.15 (s, 4H, aromatic), 2.36 (s, 6H, CH_3), 0.27 (s, 18H, TMS); ^{13}C NMR (125 MHz, $CDCl_3$, 10 mM, 25 °C): δ 174.27, 140.42, 135.19, 133.34, 132.73, 131.48, 122.56, 121.71, 121.52, 101.46, 99.80, 93.53, 87.84, 67.24, 21.12, 0.15; FT-IR (KBr, cm^{-1}): ν = 2160 (C≡C), 1705 (C=O) cm^{-1}; Anal. Calcd for $C_{36}H_{34}O_4Si_2$: C, 73.68; H, 5.84. Found: C, 73.55; H, 6.01.

Complex (*R*)-1·2: The diamidine (*R*)-**1** (6.97 mg, 0.00815 mmol) and dicarboxylic acid **2** (4.78 mg, 0.00815 mmol) were dissolved in $CHCl_3$ (5.00 mL). After the solution was filtered through a membrane filter (0.45 μm), the filtrate was then evaporated to dryness to afford the complex (*R*)-**1**·**2** (11.5 mg, 98% yield) as a yellow solid: M.p. = 156.6–157.5 °C; $[\alpha]_D^{22}$ +80.2 (*c* 0.1 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 0.4 mM, 25 °C): δ 13.83 (s, 2H, NH) 13.77 (s, 2H, NH) 7.33 (s, 2H, aromatic), 7.31 (s, 2H, aromatic), 7.28 (s, 2H, aromatic), 7.25 (s, 2H, aromatic), 7.20–7.16 (m, 8H, aromatic), 7.07–7.04 (m, 8H, aromatic), 7.01–6.99 (s, 8H, aromatic), 6.87 (s, 4H, aromatic), 4.17–4.12 (m, 2H, CHN), 4.07–4.03 (m, 2H, CHN), 2.88 (s, 2H, C≡CH), 2.43 (s, 6H, CH_3), 2.30 (s, 6H, CH_3), 1.65 (d, *J* = 6.9 Hz, 6H, NCHC$\underline{H_3}$), 1.37 (d,

J = 6.9 Hz, 6H, NCHC<u>H</u>$_3$), 0.24 (s, 18H, TMS); ^{13}C NMR (125 MHz, $CDCl_3$, 0.7 mM, 25 °C): δ 177.19, 163.45, 142.78, 141.34, 133.70, 133.15, 133.04, 132.98, 132.22, 132.08, 131.25, 130.26, 130.04, 128.60, 128.53, 127.46, 127.24, 126.50, 122.83, 122.53, 122.30, 121.42, 120.01, 94.85, 86.50, 82.79, 78.57, 62.48, 56.01, 27.61, 23.96, 23.76, 21.24, 20.88, 0.28; FT-IR (KBr, cm^{-1}): ν = 2214 (C≡C), 2157 (C≡C), 1715 (C=O), 1651 (C=N) cm^{-1}; Anal. Calcd for $C_{98}H_{88}N_4O_4Si_2$: C, 81.63; H, 6.15; N, 3.89. Found: C, 81.66; H, 6.41; N, 3.73.

4. Structural Analysis of Double Helical (*R*)-1·2

4-1. ESI-MS Spectrum of (*R*)-1·2

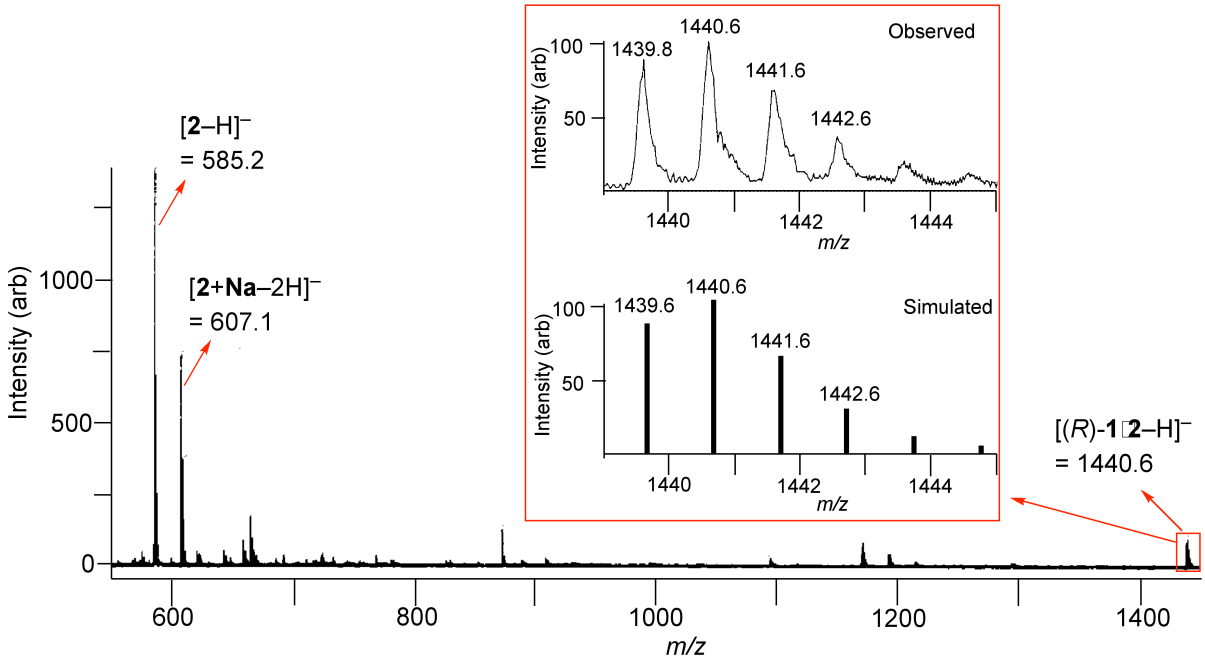


Fig. S1. Negative mode ESI-MS ($CHCl_3$/MeOH = 8/2 (v/v)) spectrum of (*R*)-**1·2**.

4-2. gCOSY Spectrum of (*R*)-1·2

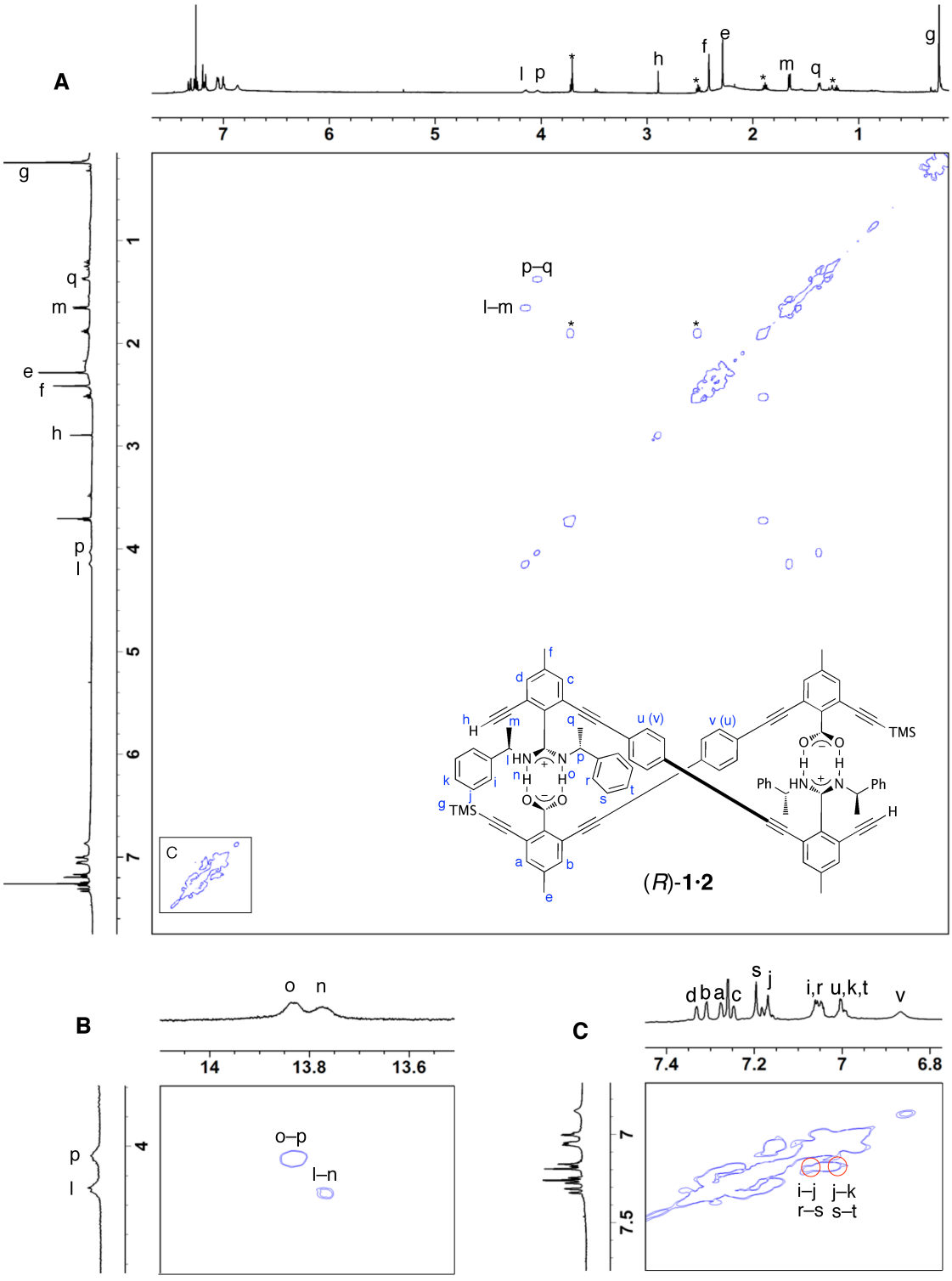


Fig. S2. Partial gCOSY (500 MHz, $CDCl_3$, 25 °C) spectra of (*R*)-**1·2** (2.0 mM). The asterisks denote impurities contained in the solvent.

4-3. ROESY Spectrum of (*R*)-1·2

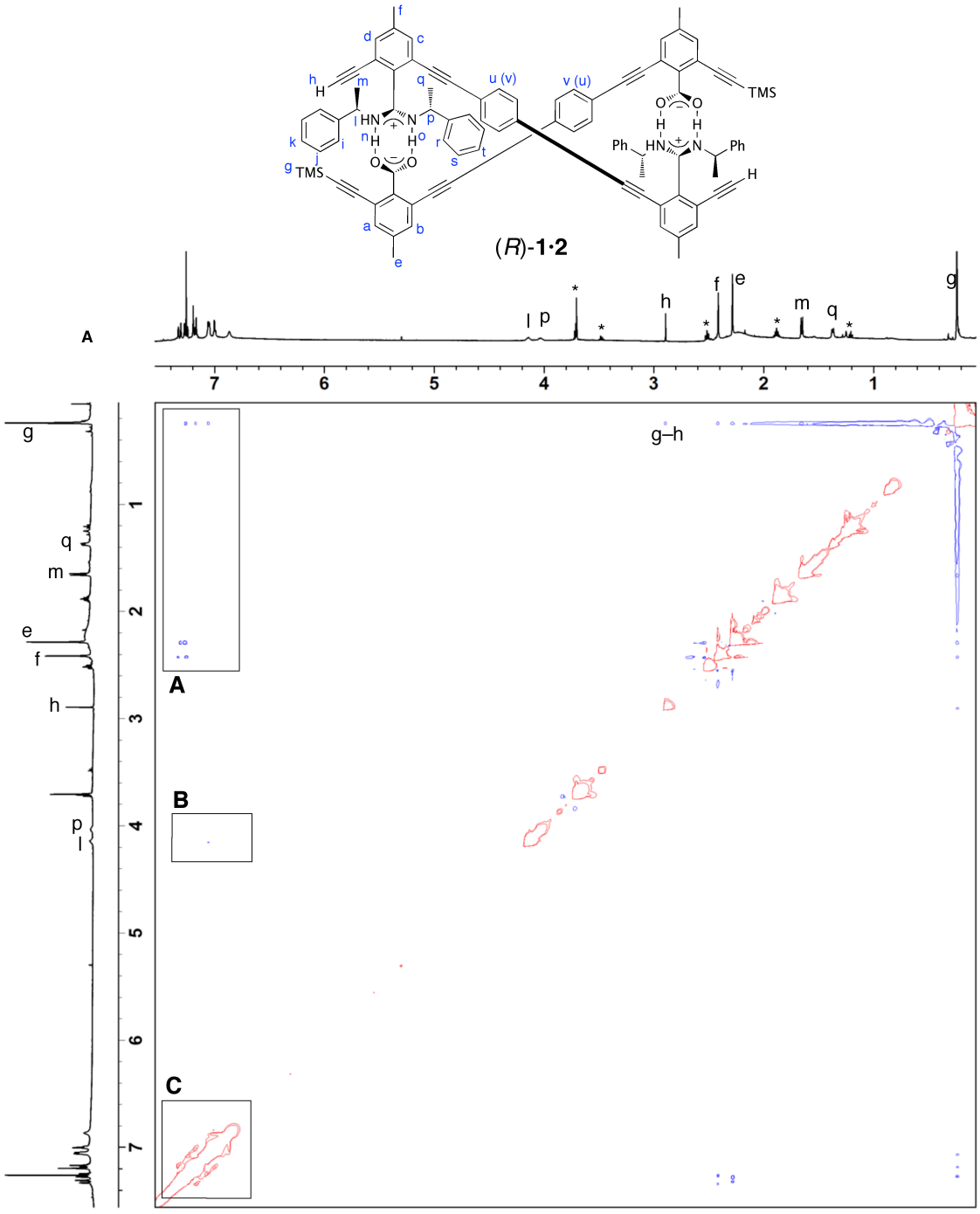


Fig. S3. Partial ROESY (500 MHz, $CDCl_3$, 25 °C, mixing time = 500 ms) spectrum of (*R*)-**1·2** (2.0 mM). The asterisks denote impurities contained in the solvent.

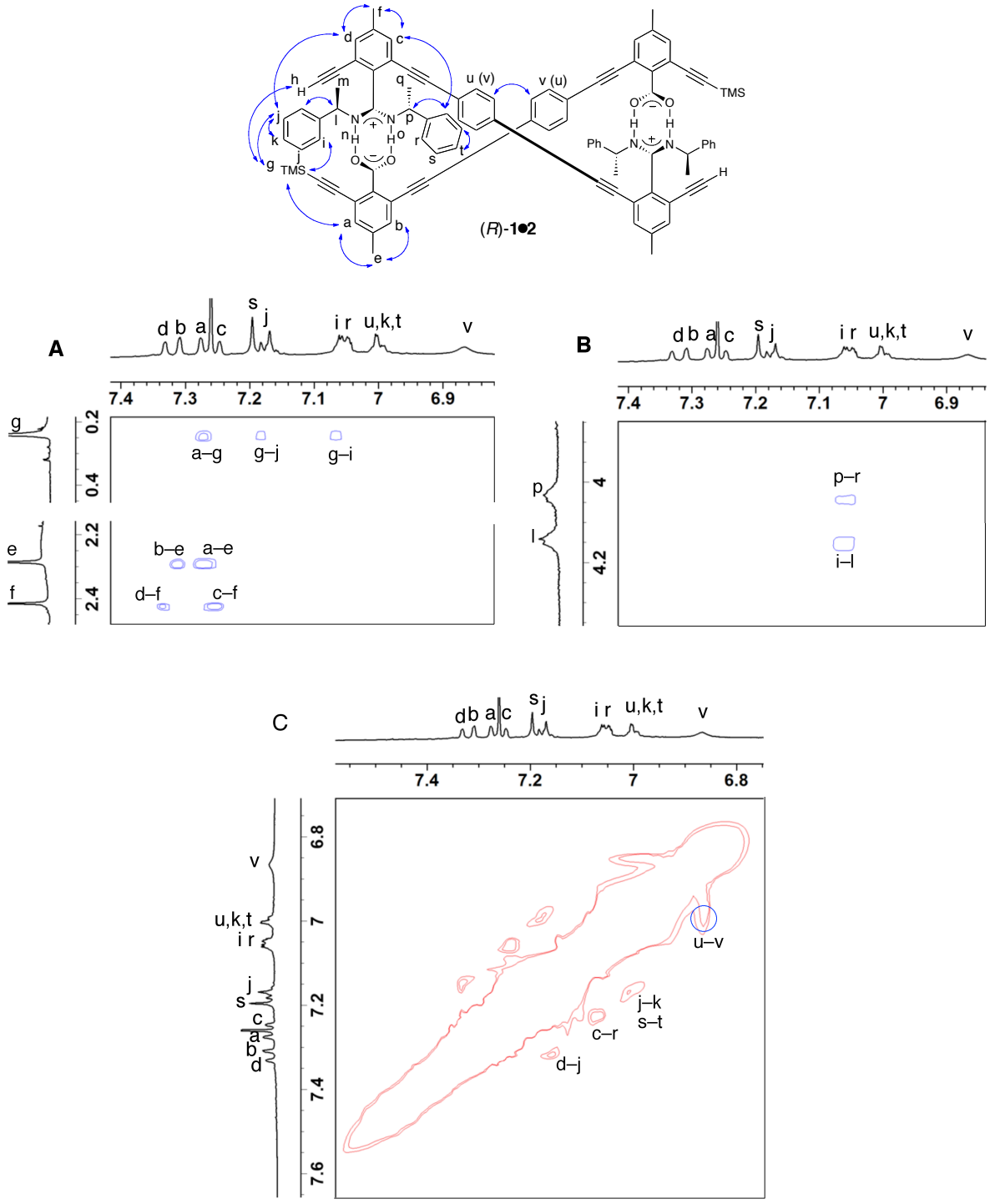


Fig. S4. Partial ROESY (500 MHz, $CDCl_3$, 25 °C, mixing time = 500 ms) spectra of (*R*)-**1**·**2** (2.0 mM).

4-4. Variable-Temperature CD Spectra of (*R*)-1·2

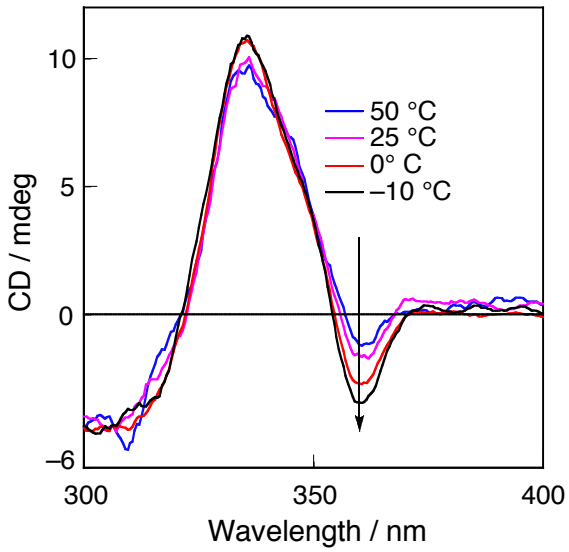


Fig. S5. CD spectra of (*R*)-**1·2** in $CHCl_3$ measured at various temperatures (c = 0.2 mM, 0.1 cm cell).

4-5. Association Constant of Monomeric Amidine (*R*)-12 with Carboxylic Acid 5.

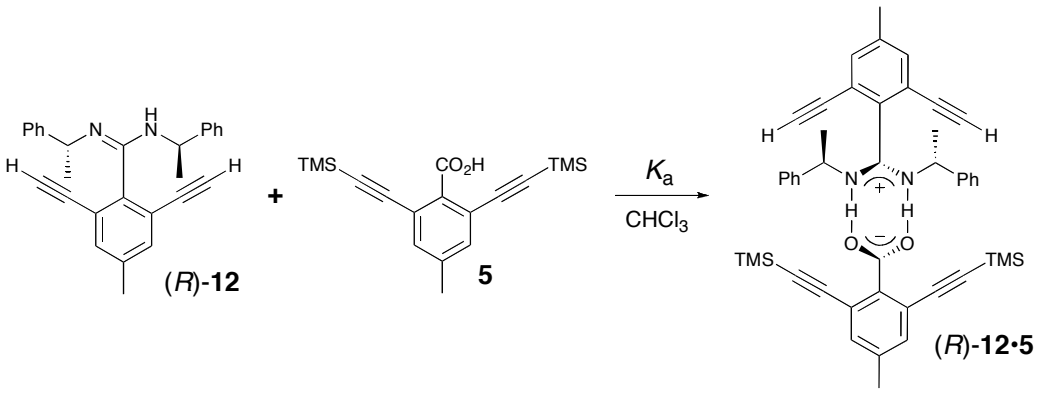
Typical Experimental Procedure for CD Titration.

Stock solutions of (*R*)-**12** (0.88 mM) and **5** (2.20 mM) in dehydrated $CHCl_3$ were prepared in two 2 mL flasks equipped with stopcocks, respectively. 50 μL of the (*R*)-**12** solution was added into a 1.0-cm cell filled with 4.0 mL dehydrated $CHCl_3$ with a stopcock, and its CD spectrum was recorded at 25 °C. Increasing amounts of the stock solution of **5** (5.0, 10, 15, 20, 30, 40, 50, and 60 μL) were then added into the cell, and the CD spectra were recorded for each addition (Fig. S6a).

Plots of the CD intensity at 261 nm of the recorded CD versus the concentration of **5** gave a binding isotherm at 25 °C, as shown in Fig. S6b. Origin 6.1 software (Origin Labs, Northampton) was used to fit the data to a 1:1 binding isotherm using the following equation (eq. 1).

$$CD = (C_{(R)\text{-}\mathbf{12}\cdot\mathbf{5}} - C_{(R)\text{-}\mathbf{12}})((([(R)\text{-}\mathbf{12}]_0 + [\mathbf{5}]_0 + 1/K_a) - (([(R)\text{-}\mathbf{12}]_0 + [\mathbf{5}]_0 + 1/K_a)^2 - 4[(R)\text{-}\mathbf{12}]_0[\mathbf{5}]_0)^{1/2}) + C_{(R)\text{-}\mathbf{12}}[(R)\text{-}\mathbf{12}]_0 \quad \text{(eq. 1)},$$

where K_a is the binding constant, $C_{(R)\text{-}\mathbf{12}}$ and $C_{(R)\text{-}\mathbf{12}\cdot\mathbf{5}}$ are CD coefficient of (*R*)-**12** and (*R*)-**12**·**5**, and $[(R)\text{-}\mathbf{12}]_0$ and $[\mathbf{5}]_0$ are the initial concentration of (*R*)-**12** and the total amount of the added **5**, respectively.



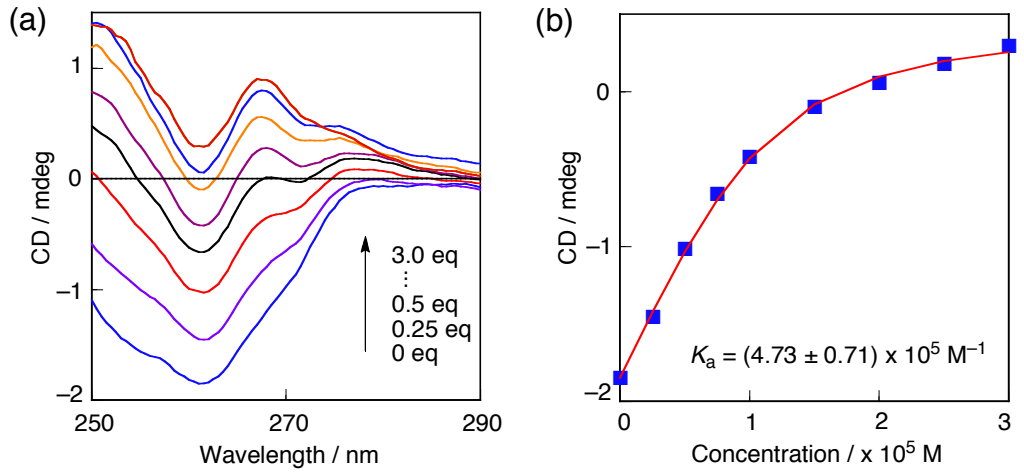


Fig. S6. (a) CD spectral changes of amidine (*R*)-**12** (c = 1.1 × 10^{-5} M, 1.0 cm cell) upon the addition of carboxylic acid **5** in $CHCl_3$ at 25 °C. (b) Plot of the CD intensity at 261 nm versus the concentration of **5**.

4-6. Association Constant of Diamindine (*R*)-1 with Dicarboxylic Acid 2.

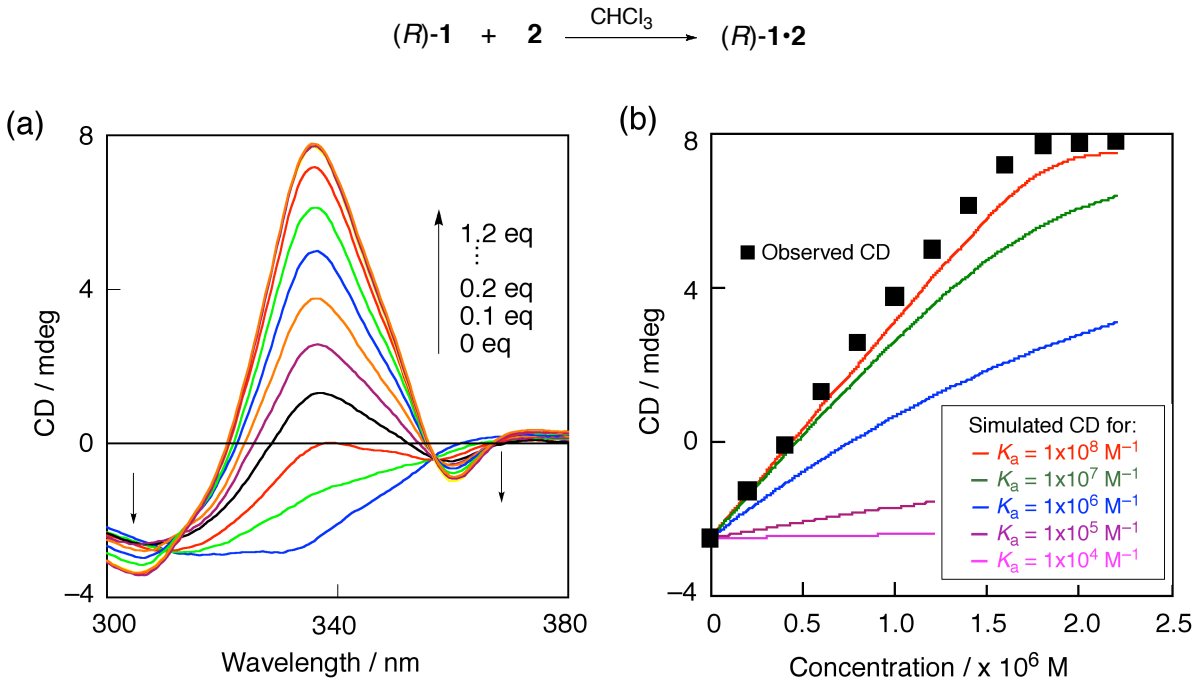


Fig. S7. (a) CD spectral changes of diamidine (*R*)-**1** ($c = 1.8 \times 10^{-6}$ M, 5.0 cm cell) upon the addition of dicarboxylic acid **2** in $CHCl_3$ at 25 °C. (b) Plot of the CD intensity at 336 nm versus the concentration of **2** (black square dots) and the simulated CD spectral changes assuming the $K_a = 1 \times 10^4$ to 1×10^8 M^{-1} (solid lines with colors).

5. DFT Calculations of Double Helical (*R*)-1·2

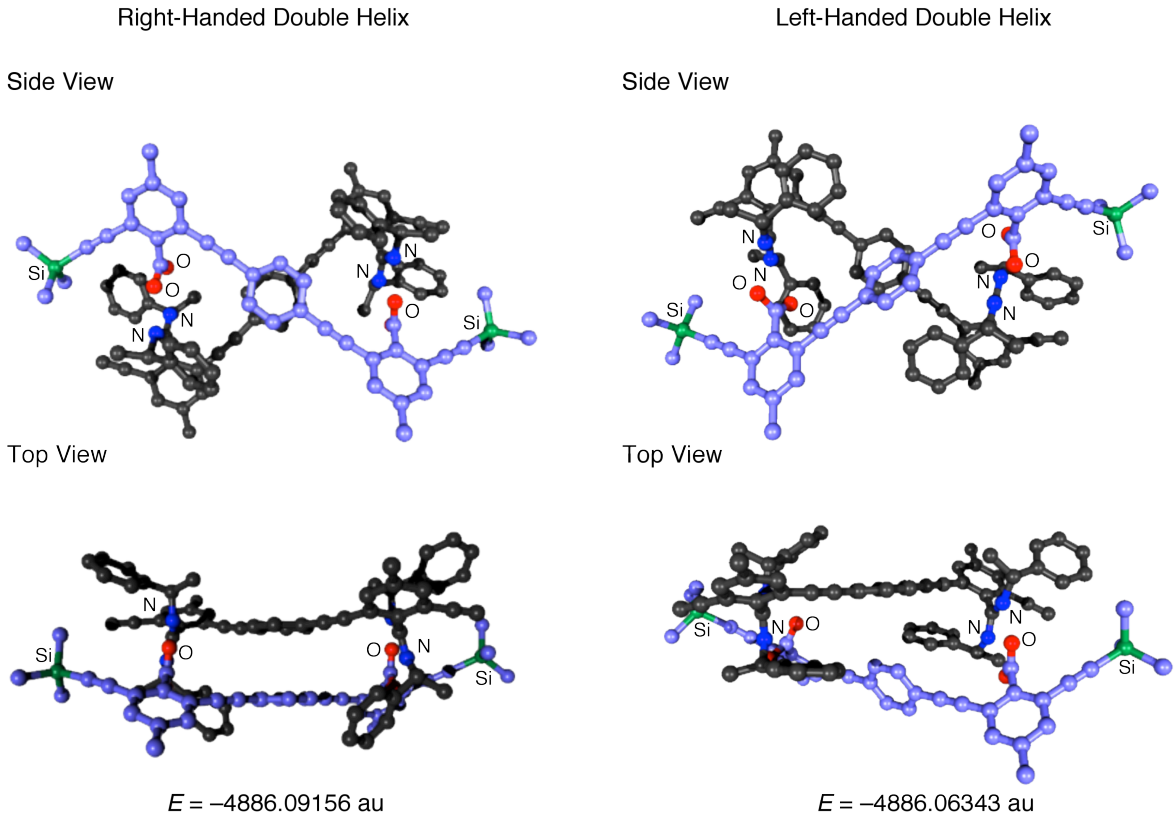


Fig. S8. Ball and stick drawings of the energy-minimized structures for the right- and left-handed double helical conformations of (*R*)-**1·2**. Hydrogen atoms are omitted for clarity. Molecular modeling and molecular mechanics calculations were performed by using Spartan 08 packages (Wavefunction, Inc., Irvine, CA, 2008). The initial structures of the right and left-handed double helices were constructed based on the crystal structure of an analogous double helical molecule bearing diacetylene linkers.[2] The geometries were further refined by using the density functional theory (DFT) calculations at the B3LYP level and the 6-31G* basis set in Gaussian 03 program (Gaussian, Inc., Pittsburgh, PA).

6. Characterization of the Lactone

Lactone 13: The lactone **13** was isolated in 20% yield as a by-product during the preparation of carboxylic acid **6** as a yellow solid: M.p. = 151.0–151.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 10 mM, 25 °C): δ 7.50 (s, 1H, aromatic), 7.49 (s, 1H, aromatic), 5.21 (AB, J_1 = 3.1 Hz, J_2 = 12.9 Hz, 2H, CH_2), 3.54 (s, 1H, CH), 2.50 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 10 mM, 25 °C): δ 165.07, 151.02, 145.56, 140.24, 136.48, 122.91, 121.23, 120.43, 91.43, 84.87, 78.49, 21.97; FT-IR (KBr, cm^{-1}): ν = 2109 (C≡C), 1775 (C=O), 1602 (C=C) cm^{-1}; Anal. Calcd for $C_{15}H_{16}Si$: C, 78.25; H, 4.38. Found: C, 78.26; H, 4.55.

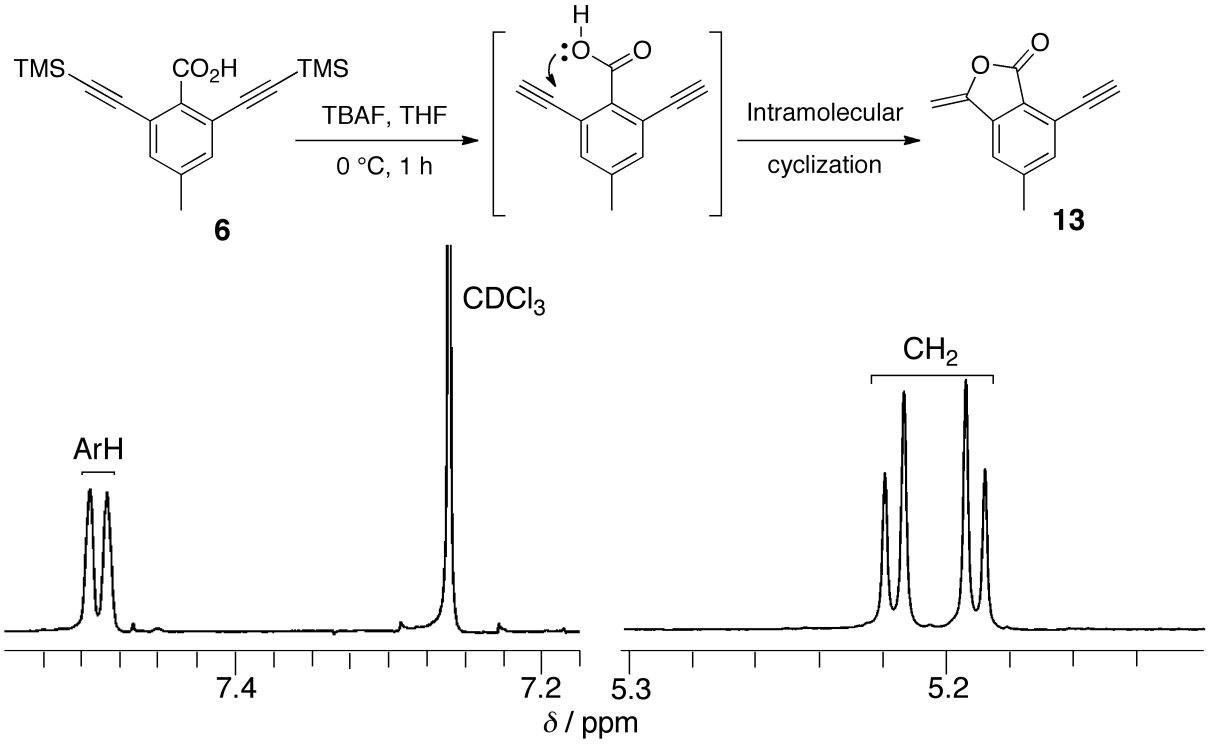


Fig. S9. Partial ^{1}H NMR (500 MHz, $CDCl_3$, 10 mM, 25 °C) spectra of **13**.

References

1. R. R. Hiatt, M.-J. Shaio and F. Georges, *J. Org. Chem.*, 2002, **44**, 3265-3266.

2. Y. Tanaka, H. Katagiri, Y. Furusho and E. Yashima, *Angew. Chem., Int. Ed.*, 2005, **44**, 3867-3870.