Electronic Supplementary Information

Chiral tether-mediated stabilisation and helix-sense control of complementary metallo-double helices

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Table of Contents:

Experimental Section

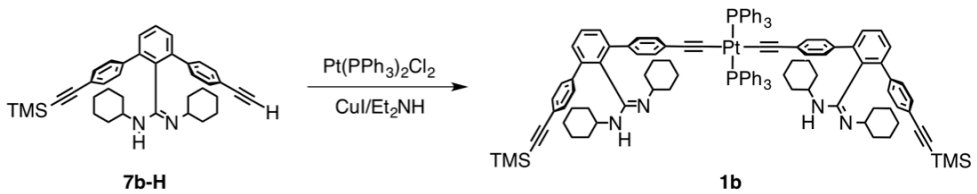
1. Materials and Instruments

Materials. All starting materials and dehydrated solvents were purchased from Aldrich Co. (Milwaukee, WI), Wako Pure Chemical Industries (Osaka, Japan), and Tokyo Kasei Kogyo (TCI) (Tokyo, Japan) unless otherwise noted. Bio-Beads SX-1 for the size exclusion column chromatography (SEC) was purchased from Bio-Rad Laboratories (Hercules, CA). Amidine monomer, **7b-H**,[S1] amidine dimers, **1a**[S2] and **1c**,[S3] carboxylic acid dimer, **2**,[S3] and the duplexes, **1a**·**2**,[S2] and **1c**·**2**[S3] were synthesized according to the reported methods.

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 Bruker Ascend 500 or a Varian UNITY INOVA 500AS spectrometer operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C and a Varian Mercury 300 spectrometer (121.5 MHz for ^{31}P). Chemical shifts are reported in parts per million (δ) downfield from tetramethysilane (TMS) as the internal standard in $CDCl_3$ (^{1}H and ^{13}C), while H_3PO_4 was used as the external standard for ^{31}P NMR measurements. The electron and cold spray ionisation mass spectra (ESI-MS and CSI-MS) 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 1.0-mm quartz cell on a JASCO V-570 spectrophotometer and a JASCO J-820 spectropolarimeter, respectively. The temperature was controlled by a JASCO PTC-423L apparatus.

2. Synthetic Procedures

Scheme S1. Synthesis of Amidine Dimer **1b**.

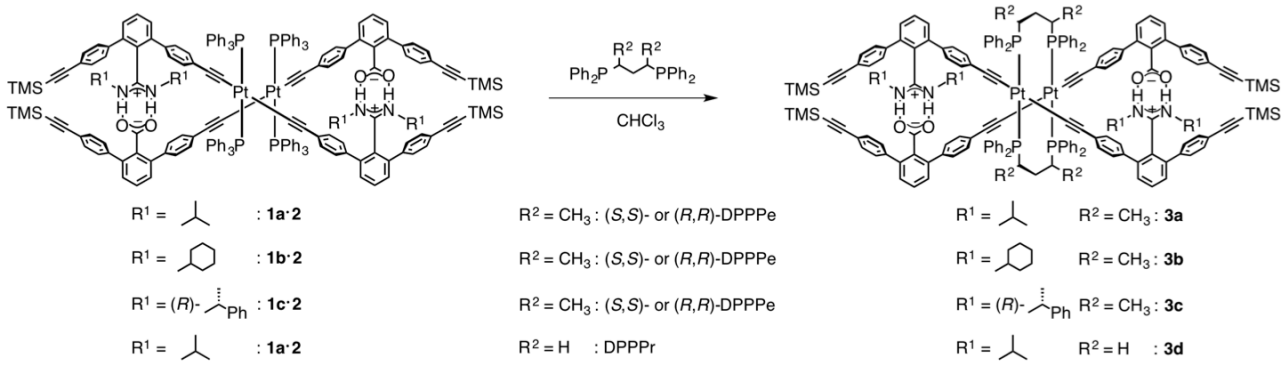


1b. To a solution of **7b-H** (111 mg, 0.200 mmol) and $Pt(PPh_3)_2Cl_2$ (79 mg, 0.10 mmol) in degassed Et_2NH (13 mL) was added CuI (2.4 mg, 0.013 mmol) at room temperature under N_2. After the mixture was stirred at reflux for 4 h under N_2, the solvent was evaporated to dryness. The residue was dissolved in $CHCl_3$ (50 mL), and the solution was washed subsequently with 0.5 M HCl (50

mL), water (50 mL), 0.5 M NaOH (3 × 50 mL), water (50 mL), and brine (50 mL), and then dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated to dryness. The residue was washed with *n*-hexane (3 × 10 mL) and dried *in vacuo*, and then purified by SEC (Bio-Beads SX-1, $CHCl_3$ as eluent) to afford **1b** (168 mg, 91.7% yield) as a pale yellow solid. Mp: 153–155 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as **1b**·$(CH_3CO_2H)_2$): δ 11.82 (br s, 4H, NH), 7.84–7.78 (m, 12H, ArH) 7.62 (t, J = 7.8 Hz, 2H, ArH), 7.54 (d, J = 8.5 Hz, 4H, ArH), 7.49–7.43 (m, 14H, ArH), 7.41–7.36 (m, 12H, ArH), 7.09 (d, J = 8.5 Hz, 4H, ArH), 6.32 (d, J = 8.4 Hz, 4H, ArH), 2.61–2.52 (m, 4H, CHN), 2.09 (s, CH_3CO_2), 1.57–1.49 (m, 4H, CH_2), 1.46–1.33 (m, 8H, CH_2), 1.29–1.13 (m, 8H, CH_2), 1.07–0.95 (m, 4H, CH_2), 0.87–0.64 (m, 16H, CH_2), 0.27 (s, 18H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as **1b**·$(CH_3CO_2H)_2$): δ 176.59, 161.56, 141.79, 140.55, 138.98, 135.23, 134.59, 132.65, 131.53, 131.51, 131.27, 131.04, 130.60, 130.56, 130.03, 129.23, 128.85, 128.70, 128.08, 127.63, 123.72, 122.32, 104.29, 96.32, 54.56, 32.41, 32.27, 25.42, 24.61, 0.06. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, as **1b**·$(CH_3CO_2H)_2$): δ 19.33 ($J_{P\text{-}Pt}$ = 2622 Hz). IR (KBr, cm^{-1}): 3433 ($\nu_{N\text{-}H}$), 2156 ($\nu_{C\equiv C}$), 2108 ($\nu_{C\equiv C}$), 1636 ($\nu_{C=N}$). HRMS(ESI-MS): *m*/*z* calcd for $[M(C_{112}H_{116}N_4P_2PtSi_2) + 2H]^{2+}$, 915.9012; found 915.8972.

1b·2. The amidine strand **1b** (55 mg, 0.030 mmol) and carboxylic acid strand **2** (45 mg, 0.030 mmol) were dissolved in $CHCl_3$ (1.0 mL). The solution was then filtered through a membrane filter (ϕ = 0.45 μm). The filtrate was evaporated *in vacuo* to afford the duplex **1b·2** (99 mg, 99% yield) as a pale yellow solid. Mp: 200 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): Most of the signals were highly broadened, suggesting that the molecular motion of the complexes is highly restricted probably due to the steric repulsion of triphenylphosphine ligands.[S3] ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 19.12 ($J_{P\text{-}Pt}$ = 2631 Hz). IR (KBr, cm^{-1}): 3448 ($\nu_{N\text{-}H}$), 2156 ($\nu_{C\equiv C}$), 2107 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). CSI-MS: *m*/*z* calcd for $[M(C_{200}H_{188}N_4O_4P_4Pt_2Si_4) + 2H]^{2+}$, 1668.61; found 1668.63. Anal. Calcd for $C_{200}H_{188}N_4O_4P_4Pt_2Si_4$: C, 71.96; H, 5.68; N, 1.68. Found: C, 71.69; H, 5.38; N, 1.59.

Scheme S2. Synthesis of **3a-d**.



(*S*,*S*)-**3a** and (*R*,*R*)-**3a.** To a solution of **1a**·**2** (31 mg, 9.6 μmol) in dry $CHCl_3$ (16 mL) was added (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane [(*S*,*S*)-DPPPe] (8.46 mg, 19.2 μmol) at room temperature under Ar. The mixture was stirred at room temperature for 2 h under Ar, and the solvent was evaporated to dryness. The residue was washed with *n*-hexane (3 × 10 mL) and dried *in vacuo,* and then purified by SEC (Bio-Beads SX-1, $CHCl_3$ as eluent) to afford (*S*,*S*)-**3a** (25 mg, 87% yield) as a pale yellow solid. In the same way, (*R*,*R*)-**3a** was also prepared using (*R*,*R*)-DPPPe in 87% yield.

(*S*,*S*)-**3a.** Mp: 245 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 12.42 (br s, 2H, NH), 12.02 (br s, 2H, NH), 8.11–8.03 (m, 4H, ArH), 7.80–7.69 (m, 8H, ArH), 7.67–7.56 (m, 10H, ArH), 7.54–7.44 (m, 12H, ArH), 7.40–7.30 (m, 20H, ArH), 7.24–7.14 (m, 16H, ArH), 7.11–7.05 (m, 2H, ArH), 6.84–6.75 (m, 4H, ArH), 6.55–6.42 (m, 4H, ArH), 6.30–6.15 (m, 4H, ArH), 3.85–3.56 (m, 4H, CHP), 3.24–3.11 (m, 2H, CH_2), 3.03–2.87 (m, 4H, CHN), 2.85–2.72 (m, 2H, CH_2), 1.48–1.33 (m, 12H, CH_3), 0.95 (d, J = 6.4 Hz, 6H, CH_3), 0.79 (d, J = 6.3 Hz, 6H, CH_3), 0.28 (s, 18H, $SiCH_3$), 0.27 (s, 18H, $SiCH_3$), 0.21–0.14 (m, 6H, CH_3), 0.08–0.04 (m, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 177.03, 161.68, 143.28, 141.06, 140.45, 140.41, 138.56, 138.53, 137.71, 137.54, 135.54, 135.22, 134.59, 132.84, 132.54, 131.68, 131.58, 131.29, 131.13, 130.42, 129.98, 129.87, 129.79, 129.67, 129.48, 128.86, 128.75, 128.44, 128.21, 128.08, 128.01, 127.82, 127.53, 127.40, 126.28, 124.15, 122.71, 121.28, 105.86, 104.47, 96.95, 93.09, 46.82, 46.80, 38.93, 29.10, 28.23, 22.88, 22.69, 22.48, 22.07, 15.62, 14.91, 0.42, 0.12. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 26.48 ($J_{P\text{-}Pt}$ = 2549 Hz), 25.72 ($J_{P\text{-}Pt}$ = 2618 Hz). IR (KBr, cm^{-1}): 3422 ($\nu_{N\text{-}H}$), 2156 ($\nu_{C\equiv C}$), 2105 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). HRMS(CSI-MS): *m*/*z* calcd for $[M(C_{174}H_{172}N_4O_4P_4Pt_2Si_4) + 2H]^{2+}$, 1504.5431; found 1504.5415.

(*R*,*R*)-**3a.** Mp: 245 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 12.44 (br s, 2H, NH), 12.03 (br s, 2H, NH), 8.11–8.04 (m, 4H, ArH), 7.80–7.69 (m, 8H, ArH), 7.66–7.56 (m, 10H, ArH), 7.54–7.44 (m, 12H, ArH), 7.40–7.30 (m, 20H, ArH), 7.24–7.14 (m, 16H, ArH), 7.11–7.05 (m, 2H, ArH), 6.83–6.76 (m, 4H, ArH), 6.54–6.42 (m, 4H, ArH), 6.30–6.15 (m, 4H, ArH), 3.85–3.57 (m, 4H, CHP), 3.25–3.11 (m, 2H, CH_2), 3.04–2.87 (m, 4H, CHN), 2.85–2.72 (m, 2H, CH_2), 1.48–1.33 (m, 12H, CH_3), 0.95 (d, J = 6.4 Hz, 6H, CH_3), 0.79 (d, J = 6.4 Hz, 6H, CH_3), 0.28 (s, 18H, $SiCH_3$), 0.27 (s, 18H, $SiCH_3$), 0.21–0.14 (m, 6H, CH_3), 0.08–0.04 (m, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 177.03, 161.69, 143.27, 141.07, 140.43, 140.41, 138.55, 138.53, 137.74, 137.56, 135.57, 135.23, 134.59, 132.84, 132.55, 131.69, 131.59, 131.30, 131.11, 130.44, 129.99, 129.89, 129.81, 129.66, 129.48, 128.86, 128.75, 128.44, 128.21, 128.08, 128.02, 127.82, 127.54, 127.41, 126.30, 124.16, 122.71, 121.30, 105.87, 104.47, 96.96, 93.10, 46.83, 46.83, 38.92, 29.14, 28.20, 22.87, 22.69, 22.48, 22.07, 15.62, 14.91, 0.42, 0.12. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 26.54 ($J_{P\text{-}Pt}$ = 2546 Hz), 25.80 ($J_{P\text{-}Pt}$ = 2615 Hz). IR (KBr, cm^{-1}): 3422 ($\nu_{N\text{-}H}$), 2155 ($\nu_{C\equiv C}$), 2104 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). HRMS(CSI-MS): *m*/*z* calcd for $[M(C_{174}H_{172}N_4O_4P_4Pt_2Si_4) + 2H]^{2+}$, 1504.5431; found 1504.5405.

(*S*,*S*)-**3b** and (*R*,*R*)-**3b.** To a solution of **1b**·**2** (32 mg, 9.6 μmol) in dry $CHCl_3$ (16 mL) was added (*S*,*S*)-DPPPe (8.46 mg, 19.2 μmol) at room temperature under Ar. After the mixture was stirred at room temperature for 2 h under Ar, the solvent was evaporated to dryness. The residue was washed with *n*-hexane (3 × 10 mL) and dried *in vacuo*, and then purified by SEC (Bio-Beads SX-1, $CHCl_3$ as eluent) to afford (*S*,*S*)-**3b** (27 mg, 88% yield) as a pale yellow solid. In the same way, (*R*,*R*)-**3b** was also prepared using (*R*,*R*)-DPPPe in 85% yield.

(*S*,*S*)-**3b.** Mp: 265 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 12.51 (br d, 2H, NH), 11.71 (br d, 2H, NH), 8.25–8.18 (m, 4H, ArH), 7.87-7.81 (m, 4H, ArH), 7.75–7.70 (m, 4H, ArH), 7.65–7.58 (m, 12H, ArH), 7.57–7.53 (m, 8H, ArH), 7.45–7.41 (m, 4H, ArH), 7.38–7.24 (m, 24H, ArH), 7.23–7.05 (m, 10H, ArH), 6.94–6.89 (m, 2H, ArH), 6.54–6.45 (m, 4H, ArH), 6.38–6.33 (m, 4H, ArH), 5.99–5.93 (m, 4H, ArH), 4.02–3.90 (m, 2H, CHP), 3.60–3.44 (m, 4H, CHP and CH_2), 2.66–2.54 (m, 4H, CH_2 and CHN), 2.52–2.42 (m, 2H, CHN), 1.79–1.70 (m, 6H, CH_3), 1.66–1.22 (m, 26H, CH_2 and CH_3), 1.15–1.03 (m, 4H, CH_2), 0.93–0.53 (m, 14H, CH_2), 0.28 (s, 18H, $SiCH_3$), 0.27 (s, 18H, $SiCH_3$), 0.17–0.09 (m, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 176.71, 161.34, 143.11, 141.43, 140.55, 140.41, 138.94, 138.86, 137.86, 137.13, 135.09, 134.80, 134.55, 133.02, 132.56, 132.39, 131.77, 131.65, 131.27, 131.16, 130.56, 130.36, 130.06, 130.03, 129.75,

129.67, 129.44, 129.37, 129.30, 128.98, 128.71, 128.60, 128.20, 128.11, 127.91, 127.80, 127.75, 127.65, 126.12, 124.23, 122.55, 121.09, 106.09, 104.51, 97.15, 93.22, 54.16, 53.92, 39.21, 32.72, 32.52, 32.33, 29.84, 29.11, 25.27, 25.14, 24.63, 16.06, 15.55, 0.41, 0.13. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 27.02 ($J_{P\text{-}Pt}$ = 2545 Hz), 25.11 ($J_{P\text{-}Pt}$ = 2650 Hz). IR (KBr, cm^{-1}): 3422 ($\nu_{N\text{-}H}$), 2156 ($\nu_{C\equiv C}$), 2105 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). HRMS(CSI-MS): *m*/*z* calcd for $[M(C_{186}H_{188}N_4O_4P_4Pt_2Si_4) + 2H]^{2+}$, 1584.6058; found 1584.6020.

(*R*,*R*)-**3b.** Mp: 270 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 12.46 (br d, 2H, NH), 11.66 (br d, 2H, NH), 8.24–8.18 (m, 4H, ArH), 7.87–7.80 (m, 4H, ArH), 7.75–7.69 (m, 4H, ArH), 7.65–7.58 (m, 12H, ArH), 7.57–7.53 (m, 8H, ArH), 7.45–7.41 (m, 4H, ArH), 7.38–7.24 (m, 24H, ArH), 7.22–7.05 (m, 10H, ArH), 6.95–6.89 (m, 2H, ArH), 6.54–6.45 (m, 4H, ArH), 6.38–6.33 (m, 4H, ArH), 5.99–5.94 (m, 4H, ArH), 4.02–3.90 (m, 2H, CHP), 3.60–3.44 (m, 4H, CHP and CH_2), 2.66–2.54 (m, 4H, CH_2 and CHN), 2.52–2.42 (m, 2H, CHN), 1.80–1.70 (m, 6H, CH_3), 1.67–1.22 (m, 26H, CH_2 and CH_3), 1.15–1.03 (m, 4H, CH_2), 0.93–0.53 (m, 14H, CH_2), 0.28 (s, 18H, $SiCH_3$), 0.27 (s, 18H, $SiCH_3$), 0.17–0.09 (m, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 176.71, 161.35, 143.13, 141.45, 140.55, 140.43, 138.94, 138.86, 137.87, 137.16, 135.14, 134.81, 134.55, 133.04, 132.57, 132.38, 131.78, 131.66, 131.27, 131.17, 130.57, 130.37, 130.06, 130.03, 129.77, 129.68, 129.44, 129.38, 129.30, 128.98, 128.72, 128.61, 128.22, 128.13, 127.93, 127.80, 127.76, 127.66, 126.13, 124.25, 122.56, 121.11, 106.09, 104.52, 97.16, 93.24, 54.18, 53.93, 39.25, 32.73, 32.53, 32.34, 29.86, 29.11, 25.28, 25.14, 24.64, 16.06, 15.55, 0.41, 0.14. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 27.02 ($J_{P\text{-}Pt}$ = 2548 Hz), 25.12 ($J_{P\text{-}Pt}$ = 2646 Hz). IR (KBr, cm^{-1}): 3423 ($\nu_{N\text{-}H}$), 2156 ($\nu_{C\equiv C}$), 2105 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). HRMS(CSI-MS): *m*/*z* calcd for $[M(C_{186}H_{188}N_4O_4P_4Pt_2Si_4) + 2H]^{2+}$, 1584.6058; found 1584.6077.

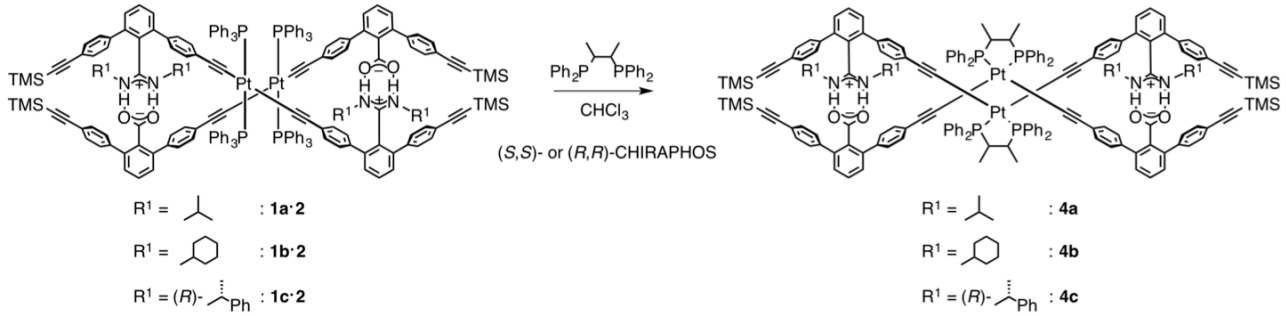
(*S*,*S*)-**3c.** To a solution of **1c**·**2** (33 mg, 9.6 μmol) in dry $CHCl_3$ (16 mL) was added (*S*,*S*)-DPPPe (8.46 mg, 19.2 μmol) at room temperature under Ar. After the mixture was stirred at room temperature for 1 h under Ar, the solvent was evaporated to dryness. The residue was washed with *n*-hexane (3 × 10 mL) and dried *in vacuo*, and then purified by SEC (Bio-Beads SX-1, $CHCl_3$ as eluent) to afford (*S*,*S*)-**3c** (28 mg, 90% yield) as a pale yellow solid. Mp: 270 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 14.04 (d, J = 8.5 Hz, 2H, NH), 12.68 (d, J = 8.9 Hz, 2H, NH), 8.46–8.38 (m, 4H, ArH), 7.94–7.88 (m, 4H, ArH), 7.76–7.69 (m, 8H, ArH), 7.67–7.60 (m, 6H, ArH), 7.58 (d, J = 8.5 Hz, 4H, ArH), 7.52–7.22 (m, 36H, ArH), 7.18–7.10 (m, 6H, ArH), 7.00–6.95 (m, 4H, ArH), 6.90–6.85 (m, 4H, ArH), 6.79–6.74 (m, 2H, ArH), 6.69–6.64 (m, 2H, ArH),

6.62–6.52 (m, 12H, ArH), 6.45 (d, J = 8.5 Hz, 4H, ArH), 6.37 (d, J = 8.3 Hz, 4H, ArH), 6.25–6.20 (m, 4H, ArH), 3.85–3.77 (m, 2H, CHN), 3.74–3.57 (m, 6H, CHN and CHP), 3.50–3.38 (m, 2H, CH_2), 2.76–2.67 (m, 2H, CH_2), 1.90–1.80 (m, 6H, CH_3), 1.30–1.22 (m, 6H, CH_3), 0.81 (d, J = 6.9 Hz, 6H, CH_3), 0.28 (s, 18H, $SiCH_3$), 0.28 (s, 18H, $SiCH_3$), 0.18 (d, J = 6.8 Hz, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 176.65, 162.82, 143.17, 143.04, 142.78, 141.90, 141.56, 140.78, 138.98, 138.69, 137.05, 136.74, 135.50, 134.32, 132.97, 132.58, 132.48, 131.55, 131.44, 131.31, 130.90, 130.70, 130.40, 130.28, 130.04, 129.72, 129.65, 129.46, 129.10, 129.04, 128.81, 128.73, 128.26, 128.13, 127.88, 127.77, 127.64, 127.56, 126.90, 126.73, 126.31, 126.24, 123.36, 122.22, 121.50, 109.20, 106.23, 104.44, 96.48, 94.83, 55.54, 55.38, 39.46, 23.85, 29.28, 22.22, 21.93, 16.02, 15.77, 0.38, 0.23. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 30.02 ($J_{P\text{-}Pt}$ = 2559 Hz), 25.25 ($J_{P\text{-}Pt}$ = 2663 Hz). IR (KBr, cm^{-1}): 3422 ($\nu_{N\text{-}H}$), 2156 ($\nu_{C\equiv C}$), 2105 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). HRMS(CSI-MS): m/z calcd for $[M(C_{194}H_{180}N_4O_4P_4Pt_2Si_4) + 2H]^{2+}$, 1628.5745; found 1628.5792.

(*R*,*R*)-**3c.** To a solution of **1c**·**2** (31 mg, 9.0 μmol) in dry $CHCl_3$ (15 mL) was added (*R*,*R*)-DPPPe (7.9 mg, 18 μmol) under Ar. After the mixture was stirred at room temperature for 16 h under Ar, the solvent was evaporated to dryness. The residue was washed with *n*-hexane (3 × 10 mL) and dried *in vacuo*, and then purified by SEC (Bio-Beads SX-1, $CHCl_3$ as eluent) to afford (*R*,*R*)-**3c** (26 mg, 87% yield) as a pale yellow solid. Mp: 250 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 13.00 (br s, 2H, NH), 12.29 (br s, 2H, NH), 8.00–7.89 (m, 4H, ArH), 7.82-7.54 (m, 14H, ArH), 7.50 (d, J = 8.5 Hz, 4H, ArH), 7.48–7.40 (m, 6H, ArH), 7.37–7.16 (m, 40H, ArH), 7.09–6.87 (m, 16H, ArH), 6.85–6.74 (m, 8H, ArH), 6.71 (d, J = 8.5 Hz, 4H, ArH), 6.35–6.28 (m, 4H, ArH), 6.24–5.99 (m, 4H, ArH), 3.97–3.45 (m, 2H, CHP and CHN), 3.26–2.99 (m, 2H, CH_2), 2.87–2.60 (m, 2H, CH_2), 1.49–1.39 (m, 6H, CH_3), 1.38–1.23 (m, 6H, CH_3), 0.44–0.29 (m, 6H, CH_3), 0.26 (s, 18H, $SiCH_3$), 0.24 (s, 18H, $SiCH_3$), 0.21 (d, J = 7.0 Hz, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 176.68, 162.84, 143.32, 142.42, 142.38, 141.59, 141.17, 140.65, 138.47, 138.41, 138.09, 137.98, 135.26, 135.01, 134.37, 132.82, 132.51, 132.15, 131.69, 131.52, 131.41, 130.90, 130.36, 130.30, 130.05, 129.75, 129.46, 129.31, 129.08, 128.79, 128.70, 128.63, 128.13, 127.96, 127.91, 127.82, 127.68, 127.51, 127.46, 127.29, 126.88, 126.72, 126.49, 123.84, 122.93, 121.29, 105.81, 104.64, 96.74, 92.85, 55.46, 55.43, 39.05, 28.97, 28.30, 22.90, 21.61, 15.73, 14.78, 0.46, 0.11. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 26.61 ($J_{Pt\text{-}P}$ = 2549 Hz), 25.44 ($J_{Pt\text{-}P}$ = 2609 Hz). IR (KBr, cm^{-1}): 3423 ($\nu_{N\text{-}H}$), 2156 ($\nu_{C\equiv C}$), 2105 ($\nu_{C\equiv C}$), 1638 ($\nu_{C=N}$). HRMS(CSI-MS): m/z calcd for $[M(C_{194}H_{180}N_4O_4P_4Pt_2Si_4) + 2H]^{2+}$, 1628.5745; found 1628.5727.

3d. To a solution of **1a·2** (11 mg, 3.6 μmol) in dry $CHCl_3$ (6 mL) was added 1,3-bis(diphenylphosphino)propane (DPPPr) (3.0 mg, 7.2 μmol) at room temperature under Ar. After the mixture was stirred at room temperature for 2 h under Ar, the solvent was evaporated to dryness. The residue was washed with *n*-hexane (3 × 5 mL) and dried *in vacuo*, and then purified by SEC (Bio-Beads SX-1, $CHCl_3$ as eluent) to afford **3d** (10 mg, 96% yield) as a pale yellow solid. Mp: 215 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 12.37 (br d, 2H, NH), 7.90–7.84 (m, 8H, ArH), 7.71–7.64 (m, 8H, ArH), 7.62–7.57 (m, 6H, ArH), 7.55 (d, J = 8.5 Hz, 4H, ArH), 7.50–7.42 (m, 10H, ArH), 7.41–7.34 (m, 8H, ArH), 7.33–7.25 (m, 16H, ArH), 7.24–7.17 (m, 6H, ArH), 7.15 (d, J = 8.4 Hz, 4H, ArH), 7.13–7.06 (m, 6H, ArH), 6.62 (d, J = 8.4 Hz, 4H, ArH), 6.40 (d, J = 8.3 Hz, 4H, ArH), 3.17–2.88 (m, 16H, CH_2 and CHN), 0.56 (d, J = 6.4 Hz, 12H, CH_3), 0.53 (d, J = 6.4 Hz, 12H, CH_3), 0.28 (s, 18H, $SiCH_3$), 0.26 (s, 18H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 177.03, 161.63, 143.20, 140.65, 140.52, 138.83, 138.52, 137.68, 137.27, 134.46, 133.45, 133.32, 133.10, 132.86, 132.57, 132.29, 132.21, 132.09, 132.07, 131.89, 131.68, 131.46, 131.39, 130.90, 130.83, 130.69, 130.53, 130.44, 129.93, 129.56, 129.02, 128.84, 128.69, 128.60, 128.53, 128.07, 127.43, 126.33, 124.02, 122.61, 121.36, 105.87, 104.39, 96.57, 93.55, 46.83, 29.85, 23.91, 22.77, 22.38, 0.34, 0.16. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 13.52 ($J_{P\text{-}Pt}$ = 2574 Hz), 13.26 ($J_{P\text{-}Pt}$ = 2616 Hz). IR (KBr, cm^{-1}): 3422 ($\nu_{N\text{-}H}$), 2156 ($\nu_{C\equiv C}$), 2104 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). HRMS(CSI-MS): *m/z* calcd for $[M(C_{170}H_{164}N_4O_4P_4Pt_2Si_4) + 2H]^{2+}$, 1476.5118; found 1476.5059.

Scheme S3. Synthesis of **4a-c**.



(*S*,*S*)-**4a** and (*R*,*R*)-**4a.** To a solution of **1a·2** (31 mg, 9.6 μmol) in dry $CHCl_3$ (10 mL) was added (2*S*,3*S*)-(–)-bis(diphenylphosphino)butane [(*S*,*S*)-CHIRAPHOS] (12 mg, 29 μmol) at room temperature under Ar. After the mixture was stirred at room temperature for 5 h under Ar, the solvent was evaporated to dryness. The residue was washed with *n*-hexane (3 × 10 mL) and dried *in vacuo*, and then purified by SEC (Bio-Beads SX-1, $CHCl_3$ as eluent) to afford (*S*,*S*)-**4a** (25 mg,

87% yield) as a pale yellow solid. In the same way, (*R*,*R*)-**4a** was also prepared using (*R*,*R*)-CHIRAPHOS in 85% yield.

(*S*,*S*)-**4a.** Mp: 205 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): Most of the signals were highly broadened probably due to its non-cross-linked duplex structure.[S3] ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 43.10 ($J_{P\text{-}Pt}$ = 2245 Hz), 43.01 ($J_{P\text{-}Pt}$ = 2249 Hz). IR (KBr, cm^{-1}): 3423 ($\nu_{N\text{-}H}$), 2155 ($\nu_{C\equiv C}$), 2111 ($\nu_{C\equiv C}$), 1638 ($\nu_{C=N}$). CSI-MS: *m*/*z* calcd for $[M(C_{172}H_{168}N_4O_4P_4Pt_2Si_4) + 2H]^{2+}$, 1490.53; found 1490.61. Anal. Calcd for $C_{172}H_{168}N_4O_4P_4Pt_2Si_4$: C, 69.29; H, 5.68; N, 1.88. Found: C, 69.29; H, 5.53; N, 1.75.

(*R*,*R*)-**4a.** Mp: 205 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): Most of the signals were highly broadened probably due to its non-cross-linked duplex structure.[S3] ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 43.24 ($J_{P\text{-}Pt}$ = 2223 Hz), 42.68 ($J_{P\text{-}Pt}$ = 2236 Hz). IR (KBr, cm^{-1}): 3423 ($\nu_{N\text{-}H}$), 2155 ($\nu_{C\equiv C}$), 2111 ($\nu_{C\equiv C}$), 1638 ($\nu_{C=N}$). CSI-MS: *m*/*z* calcd for $[M(C_{172}H_{168}N_4O_4P_4Pt_2Si_4) + 2H]^{2+}$, 1490.53; found 1490.59. Anal. Calcd for $C_{172}H_{168}N_4O_4P_4Pt_2Si_4$: C, 69.29; H, 5.68; N, 1.88. Found: C, 69.30; H, 5.73; N, 1.84.

(*S*,*S*)-**4b** and (*R*,*R*)-**4b.** To a solution of **1b**·**2** (32 mg, 9.6 μmol) in dry $CHCl_3$ (10 mL) was added (*S*,*S*)-CHIRAPHOS (12 mg, 29 μmol) at room temperature under Ar. After the mixture was stirred at room temperature for 8 h under Ar, the solvent was evaporated to dryness. The residue was washed with *n*-hexane (3 × 10 mL) and dried *in vacuo*, and then purified by SEC (Bio-Beads SX-1, $CHCl_3$ as eluent) to afford (*S*,*S*)-**4b** (26 mg, 86% yield) as a pale yellow solid. In the same way, (*R*,*R*)-**4b** was also prepared using (*R*,*R*)-CHIRAPHOS in 84% yield.

(*S*,*S*)-**4b.** Mp: 210 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): Most of the signals were highly broadened probably due to its non-cross-linked duplex structure.[S3] ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 43.16 ($J_{P\text{-}Pt}$ = 2230 Hz), 42.76 ($J_{P\text{-}Pt}$ = 2245 Hz). IR (KBr, cm^{-1}): 3422 ($\nu_{N\text{-}H}$), 2155 ($\nu_{C\equiv C}$), 2111 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). CSI-MS: *m*/*z* calcd for $[M(C_{184}H_{184}N_4O_4P_4Pt_2Si_4) + H]^{+}$, 3140.17; found 3140.24. Anal. Calcd for $C_{184}H_{184}N_4O_4P_4Pt_2Si_4$: C, 70.34; H, 5.90; N, 1.78. Found: C, 70.33; H, 6.02; N, 1.78.

(*R*,*R*)-**4b.** Mp: 215 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): Most of the signals were highly broadened probably due to its non-cross-linked duplex structure.[S3] ^{31}P NMR (121.5 MHz, $CDCl_3$,

25 °C): δ 43.03 ($J_{P\text{-}Pt}$ = 2214 Hz), 42.87 ($J_{P\text{-}Pt}$ = 2227 Hz). IR (KBr, cm^{-1}): 3422 ($\nu_{N\text{-}H}$), 2155 ($\nu_{C\equiv C}$), 2112 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). CSI-MS: *m*/*z* calcd for $[M(C_{184}H_{184}N_4O_4P_4Pt_2Si_4) + H]^+$, 3140.17; found 3140.24. Anal. Calcd for $C_{184}H_{184}N_4O_4P_4Pt_2Si_4$: C, 70.34; H, 5.90; N, 1.78. Found: C, 70.22; H, 5.98; N, 1.70.

(*S*,*S*)-**4c** and (*R*,*R*)-**4c.** To a solution of **1c**·**2** (33 mg, 9.6 μmol) in dry $CHCl_3$ (16 mL) was added (*S*,*S*)-CHIRAPHOS (12 mg, 29 μmol) at room temperature under Ar. After the mixture was stirred at room temperature for 18 h under Ar, the solvent was evaporated to dryness. The residue was washed with *n*-hexane (3 × 10 mL) and dried *in vacuo*, and then purified by SEC (Bio-Beads SX-1, $CHCl_3$ as eluent) to afford (*S*,*S*)-**4c** (23 mg, 74% yield) as a pale yellow solid. In the same way, (*R*,*R*)-**4c** was also prepared using (*R*,*R*)-CHIRAPHOS in 71% yield.

(*S*,*S*)-**4c.** Mp: 205 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): Most of the signals were highly broadened probably due to its non-cross-linked duplex structure.[S3] ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 45.30 ($J_{P\text{-}Pt}$ = 2231 Hz), 42.86 ($J_{P\text{-}Pt}$ = 2198 Hz). IR (KBr, cm^{-1}): 3423 ($\nu_{N\text{-}H}$), 2155 ($\nu_{C\equiv C}$), 2112 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). CSI-MS: *m*/*z* calcd for $[M(C_{192}H_{176}N_4O_4P_4Pt_2Si_4) + H]^+$, 3228.11; found 3228.20. Anal. Calcd for $C_{192}H_{176}N_4O_4P_4Pt_2Si_4$: C, 71.40; H, 5.49; N, 1.73. Found: C, 71.38; H, 5.65; N, 1.77.

(*R*,*R*)-**4c.** Mp: 205 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): Most of the signals were highly broadened probably due to its non-cross-linked duplex structure.[S3] ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 44.86 ($J_{P\text{-}Pt}$ = 2228 Hz), 42.86 ($J_{P\text{-}Pt}$ = 2237 Hz), 42.16 ($J_{P\text{-}Pt}$ = 2200 Hz), 41.91 ($J_{P\text{-}Pt}$ = 2213 Hz). IR (KBr, cm^{-1}): 3423 ($\nu_{N\text{-}H}$), 2155 ($\nu_{C\equiv C}$), 2112 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). CSI-MS: *m*/*z* calcd for $[M(C_{192}H_{176}N_4O_4P_4Pt_2Si_4) + H]^+$, 3228.11; found 3228.23. Anal. Calcd for $C_{192}H_{176}N_4O_4P_4Pt_2Si_4$: C, 71.40; H, 5.49; N, 1.73. Found: C, 71.40; H, 5.31; N, 1.70.

(*S*,*S*)-**5a.** To a solution of **1a** (25 mg, 0.015 mmol) in dry $CHCl_3$ (10 mL) was added (*S*,*S*)-CHIRAPHOS (6.4 mg, 0.015 mmol) at room temperature under Ar. After the mixture was stirred at room temperature for 2 h under Ar, the solvent was evaporated to dryness. The residue was washed with *n*-hexane (3 × 10 mL) and dried *in vacuo*, and then purified by SEC (Bio-Beads SX-1, $CHCl_3$ as eluent) to afford (*S*,*S*)-**5a** (21 mg, 89% yield) as a pale yellow solid. Mp: 177–178 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as (*S*,*S*)-**5a**·$(CH_3CO_2H)_2$): δ 12.04 (br s, 4H, NH), 7.88–7.78 (m, 8H, ArH), 7.62 (t, J = 7.8 Hz, 2H, ArH), 7.58–7.42 (m, 24H, ArH), 7.25 (d, J = 8.9 Hz, 4H, ArH), 7.10 (d, J = 8.5 Hz, 4H, ArH), 3.10–3.02 (m, 4H, CHN), 2.44–2.39 (m, 2H, CHP), 1.11–1.06 (m, 6H, CH_3), 0.75 (d, J = 6.5 Hz, 6H, CH_3), 0.72 (d, J = 6.8 Hz, 6H, CH_3), 0.71 (d, J = 6.8 Hz, 6H, CH_3), 0.63 (d, J = 6.4 Hz, 6H, CH_3), 0.27 (s, 18H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as (*S*,*S*)-**5a**·$(CH_3CO_2H)_2$): δ 176.58, 161.81, 141.76, 140.44, 138.72, 136.63, 134.68, 132.94, 132.73, 132.18, 131.95, 131.70, 131.20, 129.23, 128.86, 128.77, 128.53, 128.03, 123.73, 122.04, 104.25, 96.38, 47.10, 47.09, 37.53, 22.50, 22.45, 22.38, 22.12, 22.11, 14.92, 0.04. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, as (*S*,*S*)-**5a**·$(CH_3CO_2H)_2$): δ 43.16 ($J_{P\text{-}Pt}$ = 2232 Hz). IR (KBr, cm^{-1}): 3423 ($\nu_{N\text{-}H}$), 2156 ($\nu_{C\equiv C}$), 2115 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). HRMS(ESI-MS): *m*/*z* calcd for $[M(C_{92}H_{98}N_4P_2PtSi_2) + 2H]^{2+}$, 786.8307; found 786.8343.

(*S*,*S*)-**5b.** To a solution of **1b** (37 mg, 0.020 mmol) in dry $CHCl_3$ (10 mL) was added (*S*,*S*)-CHIRAPHOS (8.5 mg, 0.020 mmol) at room temperature under Ar. After the mixture was stirred at room temperature for 2 h under Ar, the solvent was evaporated to dryness. The residue was washed with *n*-hexane (3 × 10 mL) and dried *in vacuo*, and then purified by SEC (Bio-Beads SX-1, $CHCl_3$ as eluent) to afford (*S*,*S*)-**5b** (30 mg, 88% yield) as a pale yellow solid. Mp: 190–192 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as (*S*,*S*)-**5b**·$(CH_3CO_2H)_2$): δ 12.04 (br s, 4H, NH), 7.90–7.82 (m, 4H, ArH), 7.80-7.73 (m, 4H, ArH), 7.64 (t, J = 7.8 Hz, 2H, ArH), 7.58–7.41 (m, 24H, ArH), 7.25 (d, J = 7.0 Hz, 4H, ArH), 7.11 (d, J = 8.2 Hz, 4H, ArH), 2.67–2.53 (m, 4H, CHN), 2.44–2.35 (m, 2H, CHP), 1.58–1.44 (m, 6H, CH_2), 1.42–1.18 (m, 10H, CH_2), 1.15–0.91 (m, 14H, CH_2 and CH_3), 0.84–0.58 (m, 10H, CH_2), 0.27 (s, 18H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as (*S*,*S*)-**5b**·$(CH_3CO_2H)_2$): δ 176.68, 161.68, 141.89, 140.55, 138.95, 136.76, 134.90, 132.88, 132.67, 132.09, 132.04, 131.94, 131.74, 131.25, 130.86, 130.08, 129.25, 128.90, 128.70, 128.51, 127.99, 123.74, 104.29, 96.33, 54.63, 54.61, 37.34, 32.44, 32.25, 32.20, 25.32, 25.25, 24.65, 21.44, 14.86, 0.06. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, as (*S*,*S*)-**5b**·$(CH_3CO_2H)_2$): δ 42.91 ($J_{P\text{-}Pt}$ = 2232 Hz). IR (KBr, cm^{-1}): 3423 ($\nu_{N\text{-}H}$), 2156 ($\nu_{C\equiv C}$), 2115 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). HRMS(ESI-MS): *m*/*z* calcd for $[M(C_{104}H_{114}N_4P_2PtSi_2) + 2H]^{2+}$, 866.8933; found 866.8947.

(*S*,*S*)-**5c.** To a solution of **1c** (38 mg, 0.020 mmol) in dry $CHCl_3$ (10 mL) was added (*S*,*S*)-CHIRAPHOS (8.5 mg, 0.020 mmol) at room temperature under Ar. After the mixture was stirred at room temperature for 2 h under Ar, the solvent was evaporated to dryness. The residue was washed with *n*-hexane (3 × 10 mL) and dried *in vacuo*, and then purified by SEC (Bio-Beads SX-1, $CHCl_3$ as eluent) to afford (*S*,*S*)-**5c** (30 mg, 85% yield) as a pale yellow solid. Mp: 177–179 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as (*S*,*S*)-**5c**·$(CH_3CO_2H)_2$): δ 12.57 (br s, 4H, NH), 7.85–7.75 (m, 8H, ArH), 7.67 (t, J = 7.8 Hz, 2H, ArH), 7.60–7.37 (m, 18H, ArH), 7.28–7.14 (m, 14H, ArH), 7.05–6.96 (m, 8H, ArH), 6.78 (d, J = 8.3 Hz, 4H, ArH), 6.64 (d, J = 8.4 Hz, 4H, ArH), 6.41 (d, J = 8.3 Hz, 4H, ArH), 3.94–3.86 (m, 4H, CHN), 2.42–2.36 (m, 2H, CHP), 1.13–1.05 (m, 6H, CH_3), 0.69 (d, J = 6.8 Hz, 6H, CH_3), 0.62 (d, J = 6.9 Hz, 6H, CH_3), 0.25 (s, 18H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as (*S*,*S*)-**5c**·$(CH_3CO_2H)_2$): δ 177.28, 163.10, 142.63, 142.44, 141.27, 138.40, 136.54, 134.23, 133.03, 132.32, 131.92, 131.64, 131.07, 130.69, 129.93, 129.09, 128.76, 128.68, 128.58, 128.52, 128.04, 127.75, 126.75, 126.66, 123.30, 122.17, 104.37, 96.01, 55.64, 55.58, 37.54, 22.23, 22.11, 21.23, 14.85, 0.04. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, as (*S*,*S*)-**5c**·$(CH_3CO_2H)_2$): δ 42.76 ($J_{P\text{-}Pt}$ = 2229 Hz). IR (KBr, cm^{-1}): 3433 ($\nu_{N\text{-}H}$), 2155 ($\nu_{C\equiv C}$), 2114 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). HRMS(ESI-MS): *m*/*z* calcd for $[M(C_{112}H_{106}N_4P_2PtSi_2) + 2H]^{2+}$, 910.8620; found 910.8655.

(*R*,*R*)-**5c.** To a solution of **1c** (38 mg, 0.020 mmol) in dry $CHCl_3$ (10 mL) was added (*R*,*R*)-CHIRAPHOS (8.5 mg, 0.020 mmol) at room temperature under Ar. After the mixture was stirred at room temperature for 4 h under Ar, the solvent was evaporated to dryness. The residue was washed with *n*-hexane (3 × 10 mL) and dried *in vacuo*, and then purified by SEC (Bio-Beads SX-1, $CHCl_3$ as eluent) to afford (*R*,*R*)-**5c** (29 mg, 81% yield) as a pale yellow solid. Mp: 173–175 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as (*R*,*R*)-**5c**·$(CH_3CO_2H)_2$): δ 12.93 (br s, 4H, NH), 7.86–7.79 (m, 4H, ArH), 7.72–7.62 (m, 8H, ArH), 7.55–7.37 (m, 16H, ArH), 7.27–7.14 (m, 14H, ArH), 7.10–6.99 (m, 8H, ArH), 6.73 (d, J = 8.2 Hz, 4H, ArH), 6.65 (d, J = 8.3 Hz, 4H, ArH), 6.41 (d, J = 8.3 Hz, 4H, ArH), 3.95–3.84 (m, 4H, CHN), 2.39–2.30 (m, 2H, CHP), 1.15–1.03 (m, 6H, CH_3), 0.71 (d, J = 6.8 Hz, 6H, CH_3), 0.58 (d, J = 6.8 Hz, 6H, CH_3), 0.25 (s, 18H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as (*R*,*R*)-**5c**·$(CH_3CO_2H)_2$): δ 176.99, 163.12, 142.67, 142.59, 141.28, 138.52, 136.84, 134.16, 132.72, 132.30, 131.91, 131.81, 131.67, 131.08, 130.62, 129.88, 129.11, 129.05, 128.95, 128.73, 128.63, 128.55, 128.43, 128.08, 127.96, 127.66, 126.76, 126.68, 123.24, 122.26, 104.42, 95.96, 55.62, 55.58, 36.74, 22.34, 22.07, 21.97, 14.57, 0.05. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, as (*R*,*R*)-**5c**·$(CH_3CO_2H)_2$): δ 42.15 ($J_{P\text{-}Pt}$ = 2223 Hz). IR (KBr, cm^{-1}): 3433 ($\nu_{N\text{-}H}$),

2155 ($\nu_{C\equiv C}$), 2114 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). HRMS(ESI-MS): *m*/*z* calcd for $[M(C_{112}H_{106}N_4P_2PtSi_2) + 2H]^{2+}$, 910.8620; found 910.8648.

(*S*,*S*)-**6** and (*R*,*R*)-**6.** To a solution of **2** (30 mg, 0.020 mmol) in dry $CHCl_3$ (10 mL) was added (*S*,*S*)-CHIRAPHOS (8.5 mg, 0.020 mmol) at room temperature under Ar. After the mixture was stirred at room temperature for 2 h under Ar, the solvent was evaporated to dryness. The residue was washed with *n*-hexane (3 × 10 mL) and dried *in vacuo*, and then purified by SEC (Bio-Beads SX-1, $CHCl_3$ as eluent) to afford (*S*,*S*)-**6** (29 mg, 98% yield) as a pale yellow solid. In the same way, (*R*,*R*)-**6** was also prepared using (*R*,*R*)-CHIRAPHOS in 85% yield.

(*S*,*S*)-**6.** Mp: 200 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.93–7.80 (m, 8H, ArH), 7.53-7.39 (m, 20H, ArH), 7.31 (d, J = 8.2 Hz, 4H, ArH), 7.26–7.24 (m, 2H, ArH), 7.21–7.10 (m, 8H, ArH), 2.45–2.37 (m, 2H, CHP), 1.11–1.02 (m, 6H, CH_3), 0.26 (s, 18H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 173.21, 140.95, 139.81, 136.74, 136.69, 136.64, 133.01, 131.98, 131.79, 131.36, 130.90, 129.69, 129.50, 129.33, 128.83, 128.65, 128.55, 128.41, 128.07, 127.61, 122.38, 105.31, 94.86, 36.85, 14.81, 0.17. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 42.90 ($J_{P\text{-}Pt}$ = 2239 Hz). IR (KBr, cm^{-1}): 3448 ($\nu_{O\text{-}H}$), 2155 ($\nu_{C\equiv C}$), 2111 ($\nu_{C\equiv C}$), 1702 ($\nu_{C=O}$). HRMS(ESI-MS): *m*/*z* calcd for $[M(C_{80}H_{70}O_4P_2PtSi_2) - H]^-$, 1406.3862; found 1406.3851.

(*R*,*R*)-**6.** Mp: 195 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.93–7.80 (m, 8H, ArH), 7.54–7.39 (m, 20H, ArH), 7.31 (d, J = 8.2 Hz, 4H, ArH), 7.26–7.24 (m, 2H, ArH), 7.21–7.10 (m, 8H, ArH), 2.45–2.37 (m, 2H, CHP), 1.11–1.02 (m, 6H, CH_3), 0.26 (s, 18H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 172.84, 140.96, 139.67, 136.72, 136.67, 136.62, 133.04, 131.98, 131.80, 131.35, 130.92, 129.68, 129.40, 129.29, 128.84, 128.68, 128.59, 128.42, 128.00, 127.67, 122.37, 105.31, 94.85, 36.91, 14.83, 0.17. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 43.16 ($J_{P\text{-}Pt}$ = 2241 Hz). IR (KBr, cm^{-1}): 3448 ($\nu_{O\text{-}H}$), 2155 ($\nu_{C\equiv C}$), 2113 ($\nu_{C\equiv C}$), 1701 ($\nu_{C=O}$). HRMS(ESI-MS): *m*/*z* calcd for $[M(C_{80}H_{70}O_4P_2PtSi_2) - H]^-$, 1406.3862; found 1406.3912.

General Procedures for the Preparation of the Model Compounds 5a-c·6. The carboxylic acid strand **6** (5.00 μmol) was dissolved with the corresponding amidine strand (**5a-c**) (5.00 μmol) in $CHCl_3$ (0.5 mL). The solution was filtered through a membrane filter (ϕ = 0.45 μm), and the filtrate was evaporated *in vacuo* to afford the corresponding duplex as a pale yellow solid.

(*S*,*S*)-**5a**·(*S*,*S*)-**6.** Mp: 205 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): Most of the signals were highly broadened probably due to its non-cross-linked duplex structure.[S3] ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 43.33 ($J_{P\text{-}Pt}$ = 2220 Hz), 42.71 ($J_{P\text{-}Pt}$ = 2220 Hz). IR (KBr, cm^{-1}): 3423 ($\nu_{N\text{-}H}$), 2155 ($\nu_{C\equiv C}$), 2111 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). CSI-MS: *m*/*z* calcd for $[M(C_{172}H_{168}N_4O_4P_4Pt_2Si_4) + H]^+$, 2980.05; found 2979.97. Anal. Calcd for $C_{172}H_{168}N_4O_4P_4Pt_2Si_4$: C, 69.29; H, 5.68; N, 1.88. Found: C, 69.28; H, 5.66; N, 1.72.

(*S*,*S*)-**5b**·(*S*,*S*)-**6.** Mp: 210 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): Most of the signals were highly broadened probably due to its non-cross-linked duplex structure.[S3] ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 43.12 ($J_{P\text{-}Pt}$ = 2238 Hz), 42.84 ($J_{P\text{-}Pt}$ = 2230 Hz). IR (KBr, cm^{-1}): 3423 ($\nu_{N\text{-}H}$), 2155 ($\nu_{C\equiv C}$), 2111 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). CSI-MS: *m*/*z* calcd for $[M(C_{184}H_{184}N_4O_4P_4Pt_2Si_4) + H]^+$, 3140.17; found 3140.13. Anal. Calcd for $C_{184}H_{184}N_4O_4P_4Pt_2Si_4$: C, 70.34; H, 5.90; N, 1.78. Found: C, 70.23; H, 5.93; N, 1.76.

(*S*,*S*)-**5c**·(*S*,*S*)-**6.** Mp: 205 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): Most of the signals were highly broadened probably due to its non-cross-linked duplex structure.[S3] ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 45.30 ($J_{P\text{-}Pt}$ = 2222 Hz), 42.87 ($J_{P\text{-}Pt}$ = 2199 Hz). IR (KBr, cm^{-1}): 3423 ($\nu_{N\text{-}H}$), 2155 ($\nu_{C\equiv C}$), 2111 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$). CSI-MS: *m*/*z* calcd for $[M(C_{192}H_{176}N_4O_4P_4Pt_2Si_4) + H]^+$, 3228.11; found 3227.92. Anal. Calcd for $C_{192}H_{176}N_4O_4P_4Pt_2Si_4$: C, 71.40; H, 5.49; N, 1.73. Found: C, 71.37; H, 5.52; N, 1.77.

(*R*,*R*)-**5c**·(*R*,*R*)-**6.** Mp: 205 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): Most of the signals were highly broadened probably due to its non-cross-linked duplex structure.[S3] ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 44.61 ($J_{P\text{-}Pt}$ = 2232 Hz), 42.56 ($J_{P\text{-}Pt}$ = 2239 Hz), 41.86 ($J_{P\text{-}Pt}$ = 2212 Hz), 41.70 ($J_{P\text{-}Pt}$ = 2219 Hz). IR (KBr, cm^{-1}): 3423 ($\nu_{N\text{-}H}$), 2155 ($\nu_{C\equiv C}$), 2112 ($\nu_{C\equiv C}$), 1638 ($\nu_{C=N}$). CSI-MS: *m*/*z* calcd for $[M(C_{192}H_{176}N_4O_4P_4Pt_2Si_4) + H]^+$, 3228.11; found 3227.92. Anal. Calcd for $C_{192}H_{176}N_4O_4P_4Pt_2Si_4$: C, 71.40; H, 5.49; N, 1.73. Found: C, 71.42; H, 5.47; N, 1.72.

3. General Procedures for Enantioselective Ligand-exchange Reaction

Stock solutions of **1c**·**2** (1.0 mM) (solution **I**), *rac*-DPPPe (16 mM) (solution **II**), and 1,3,5-trioxane (8.0 mM, as an internal standard) (solution **III**) were prepared in degassed $CDCl_3$. Aliquots of **I** (0.40 μmol, 400 μL), **II** (1.6 μmol, 100 μL), **III** (0.40 μmol, 50 μL), and degassed

$CDCl_3$ (250 μL) were added to an NMR tube (5-mm (i.d.)) under Ar. The reaction progress was monitored by ^1H NMR spectroscopy at 25 °C to determine the yield and the diastereomeric excess (*de*) of **3c** (Fig. 4).

Supporting Data

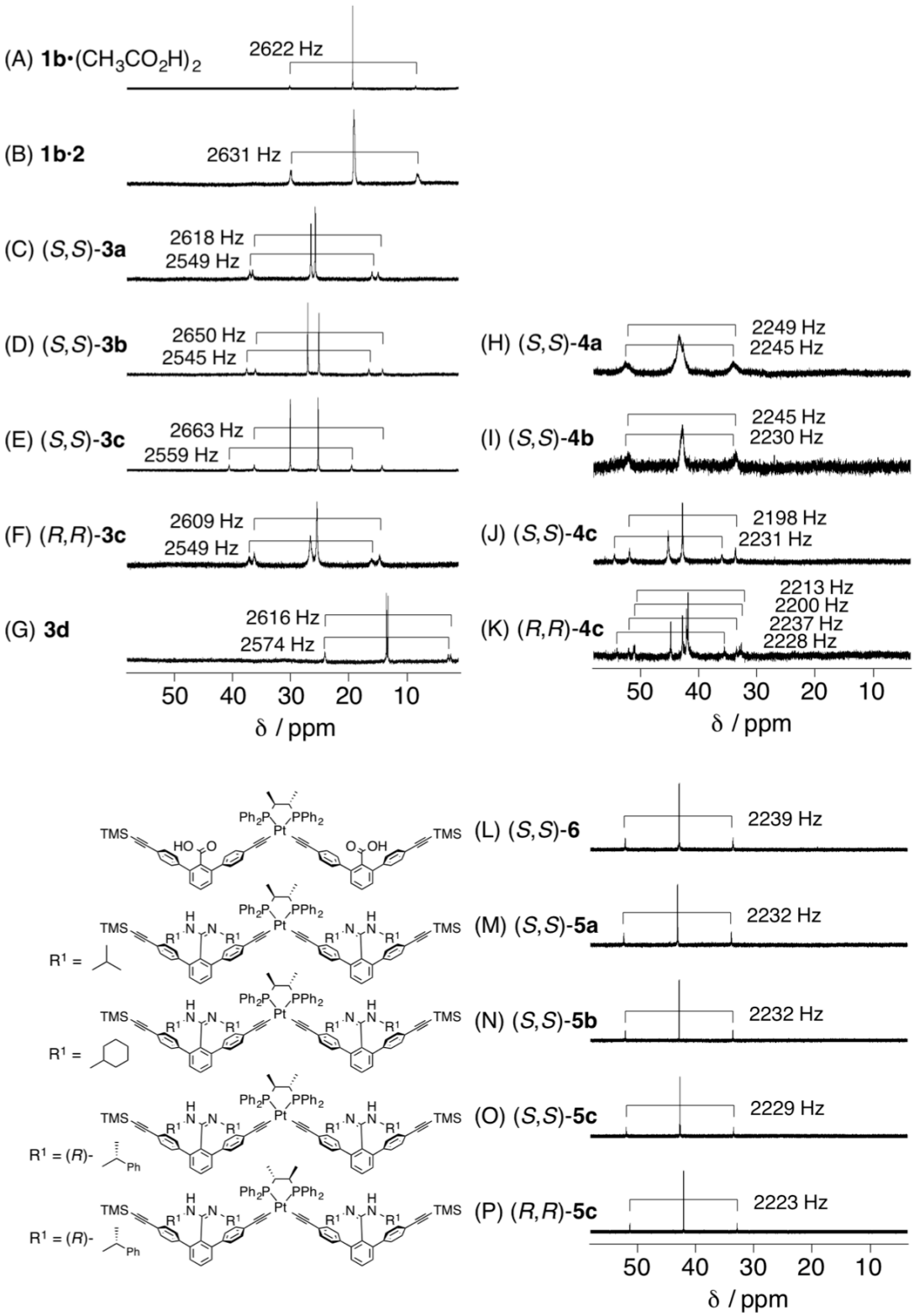


Fig. S1. Partial ^{31}P NMR (121.5 MHz) spectra of (A) **1b**·$(CH_3CO_2H)_2$, (B) **1b**·**2**, (C-G) **3a-d**, (H-K) **4a-c**, (L) (*S*,*S*)-**6**, and (M-P) **5a-c** in $CDCl_3$ at 25 °C. The coupling constants ($^1J_{P\text{-}Pt}$) are shown in each spectrum.

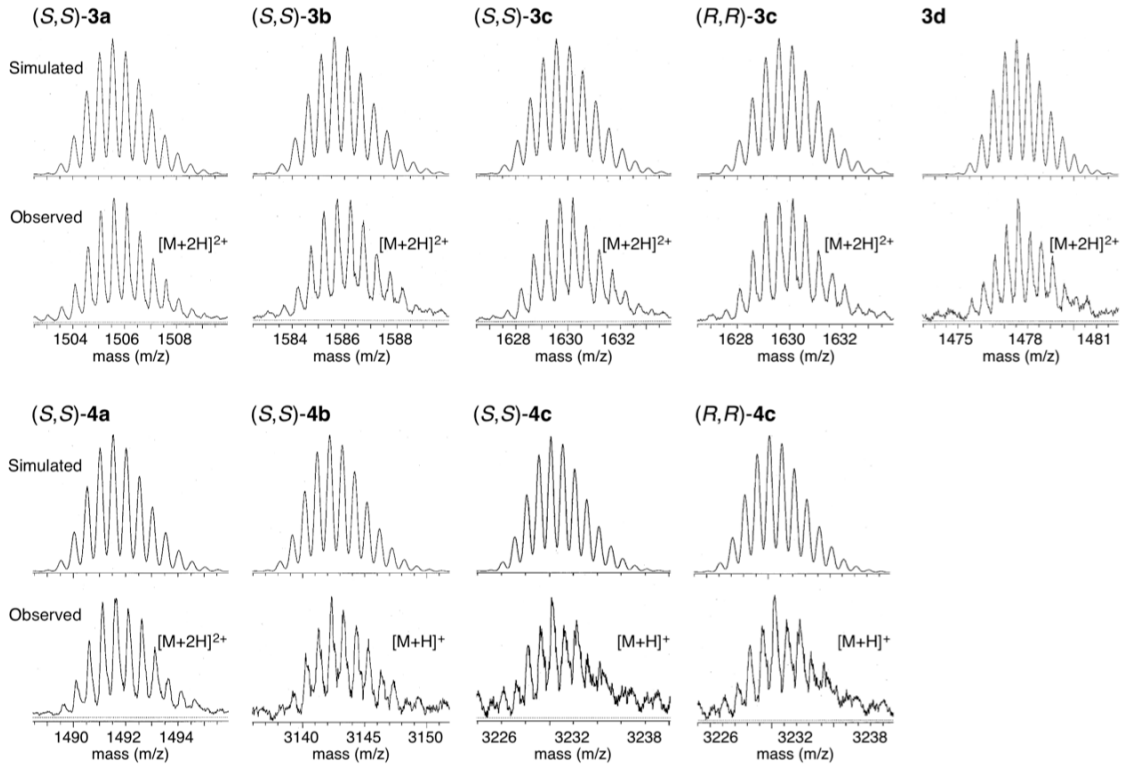


Fig. S2. Experimental (bottom) and simulated (upper) cold-spray ionisation (CSI) mass spectra of the duplexes **3a-d** and **4a-c**.

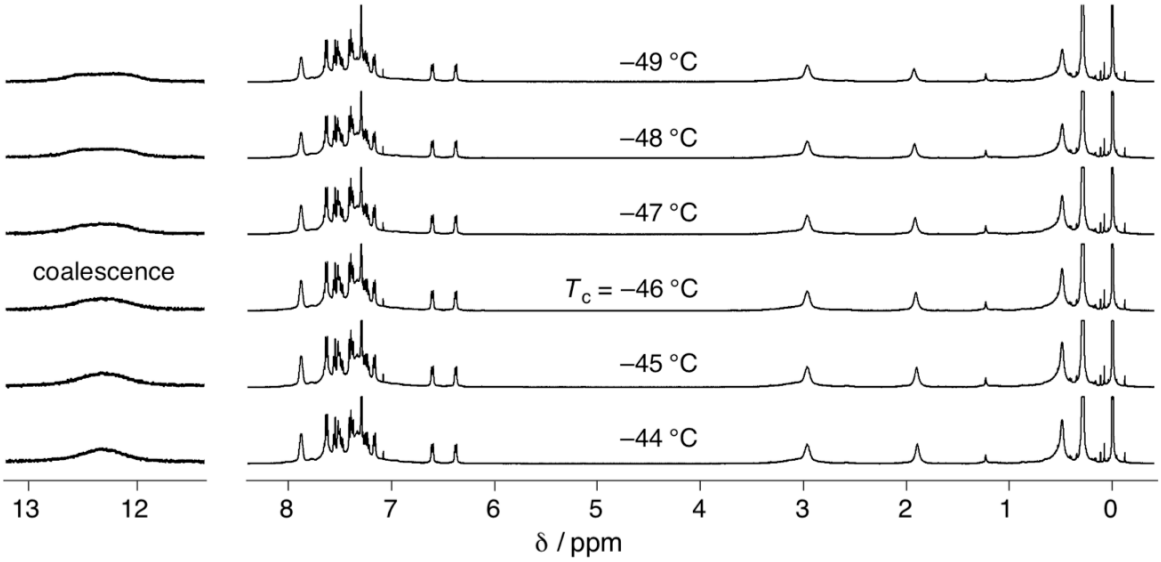


Fig. S3. Variable-temperature (from –49 to –44 °C) ^{1}H NMR (500 MHz, 2.0 mM) spectra of **3d** in $CDCl_3$.

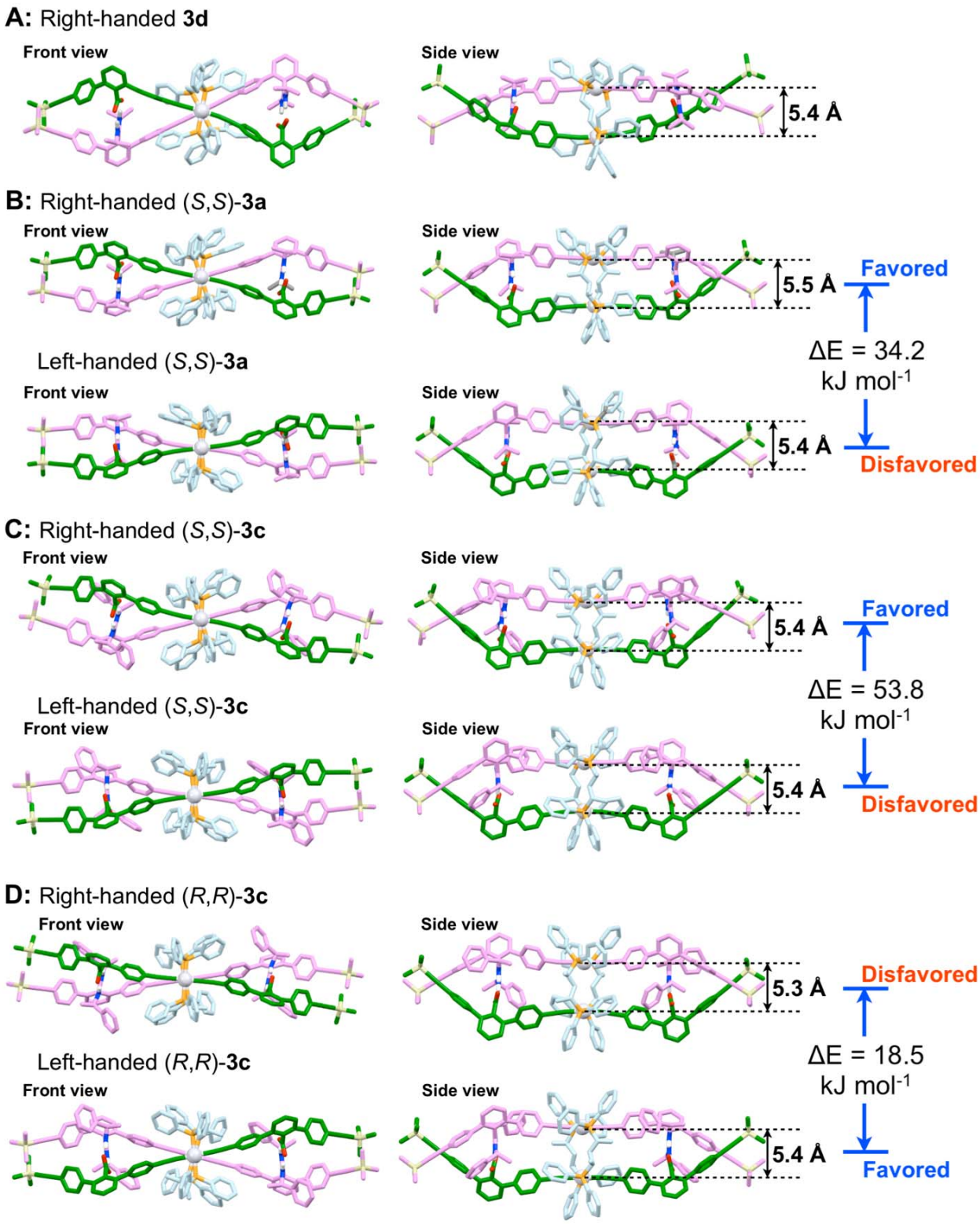


Fig. S4. The energy-minimized double helical structures of (A) **3d**, (B) (*S*,*S*)-**3a**, (C) (*S*,*S*)-**3c**, and (D) (*R*,*R*)-**3c** obtained by the semiempirical molecular orbital calculation (PM6 method[S4] in MOPAC2012[S5]). Hydrogen atoms except for the amidinium protons are omitted for clarity. The Pt-Pt distances and the energy differences (ΔE) between the right- and left-handed double helical structures are also shown.

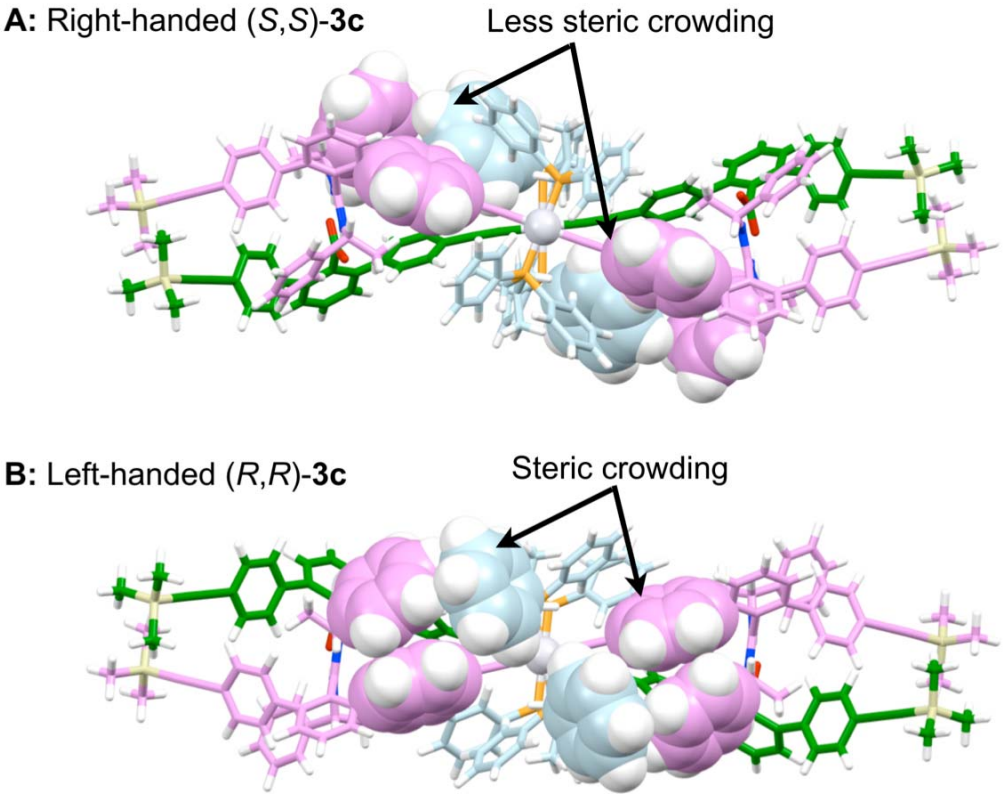


Fig. S5. The energy-minimized double helical structures of (A) right-handed (*S*,*S*)-**3c** and (B) left-handed (*R*,*R*)-**3c** obtained by the semiempirical molecular orbital calculation (PM6 method[S4] in MOPAC2012[S5]). Part of phenyl groups of the *m*-terphenyl groups (pink) and diphosphine ligands (DPPPe) (light blue) is highlighted as a space-filling model.

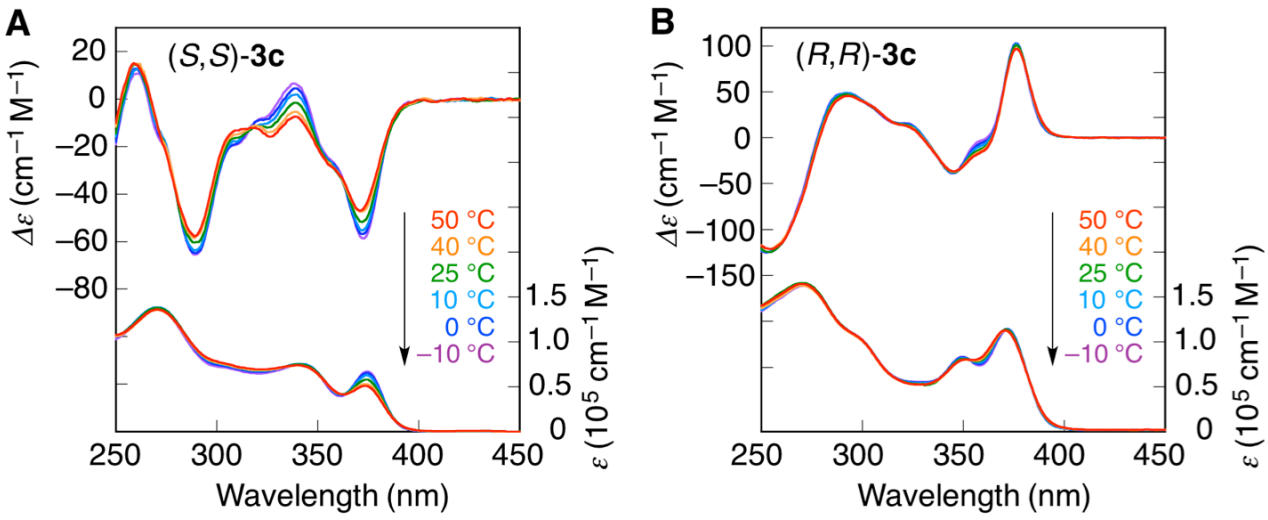


Fig. S6. Temperature-dependent CD and absorption spectral changes of (*S*,*S*)-**3c** (A) and (*R*,*R*)-**3c** (B) in $CHCl_3$. [**3c**] = 0.1 mM.

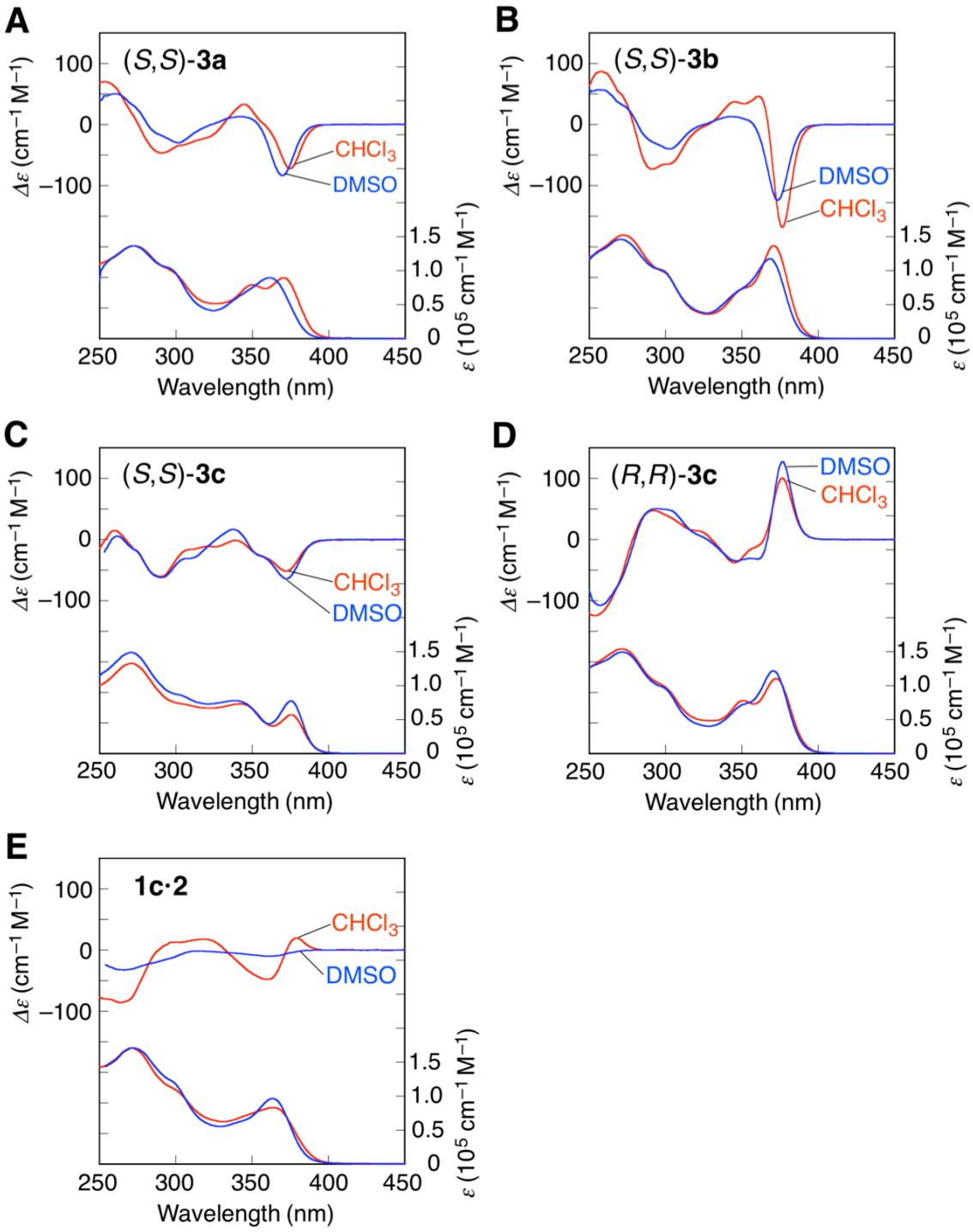


Fig. S7. (A) CD and absorption spectra of (A) (*S*,*S*)-**3a**, (B) (*S*,*S*)-**3b**, (C) (*S*,*S*)-**3c**, (D) (*R*,*R*)-**3c**, and (E) **1c**·**2** in $CHCl_3$ (red lines) and DMSO (blue lines) at 25 °C; [**3a-c**] = [**1c**·**2**] = 0.1 mM.

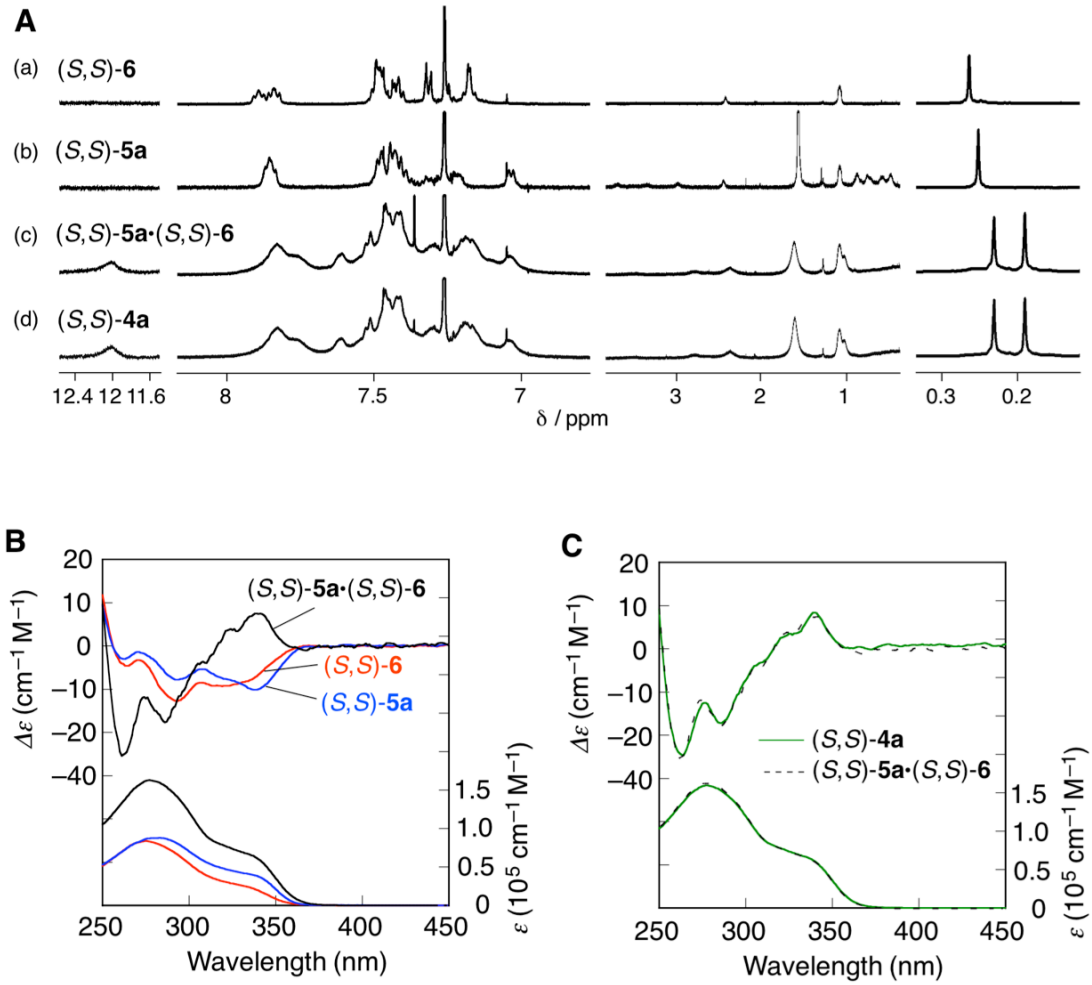


Fig. S8. (A) Partial ^{1}H NMR (500 MHz, 1.0 mM) spectra of (a) (*S*,*S*)-**6**, (b) (*S*,*S*)-**5a**, (c) (*S*,*S*)-**5a**·(*S*,*S*)-**6**, and (d) (*S*,*S*)-**4a** in $CDCl_3$ at 25 °C. (B, C) CD and absorption spectra (0.1 mM) of (B) (*S*,*S*)-**5a**, (*S*,*S*)-**6**, and (*S*,*S*)-**5a**·(*S*,*S*)-**6**, and (C) (*S*,*S*)-**4a** and (*S*,*S*)-**5a**·(*S*,*S*)-**6** in $CHCl_3$ at 25 °C.

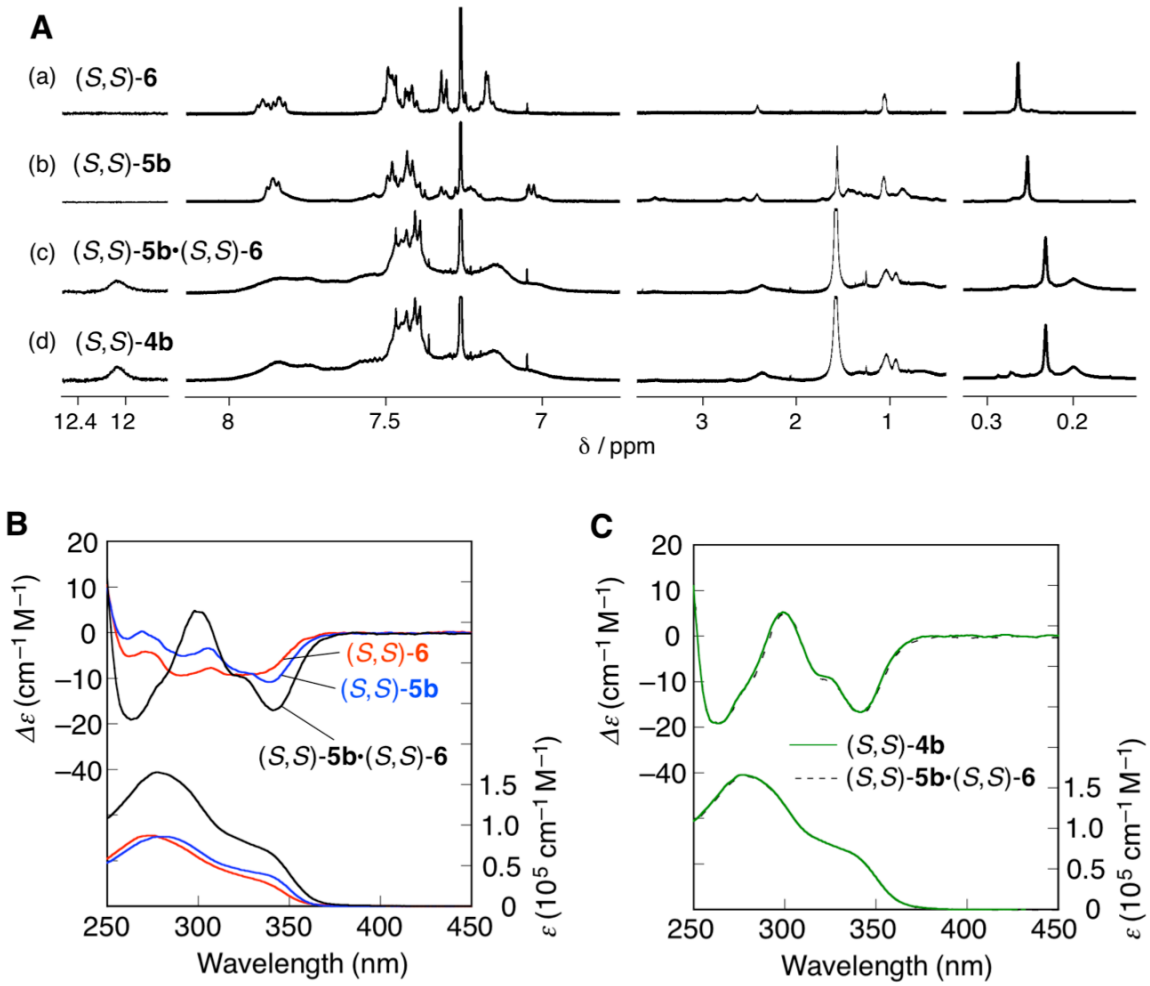


Fig. S9. (A) Partial ^{1}H NMR (500 MHz, 1.0 mM) spectra of (a) (*S*,*S*)-**6**, (b) (*S*,*S*)-**5b**, (c) (*S*,*S*)-**5b**·(*S*,*S*)-**6**, and (d) (*S*,*S*)-**4b** in $CDCl_3$ at 25 °C. (B, C) CD and absorption spectra (0.1 mM) of (B) (*S*,*S*)-**5b**, (*S*,*S*)-**6**, and (*S*,*S*)-**5b**·(*S*,*S*)-**6**, and (C) (*S*,*S*)-**4b** and (*S*,*S*)-**5b**·(*S*,*S*)-**6** in $CHCl_3$ at 25 °C.

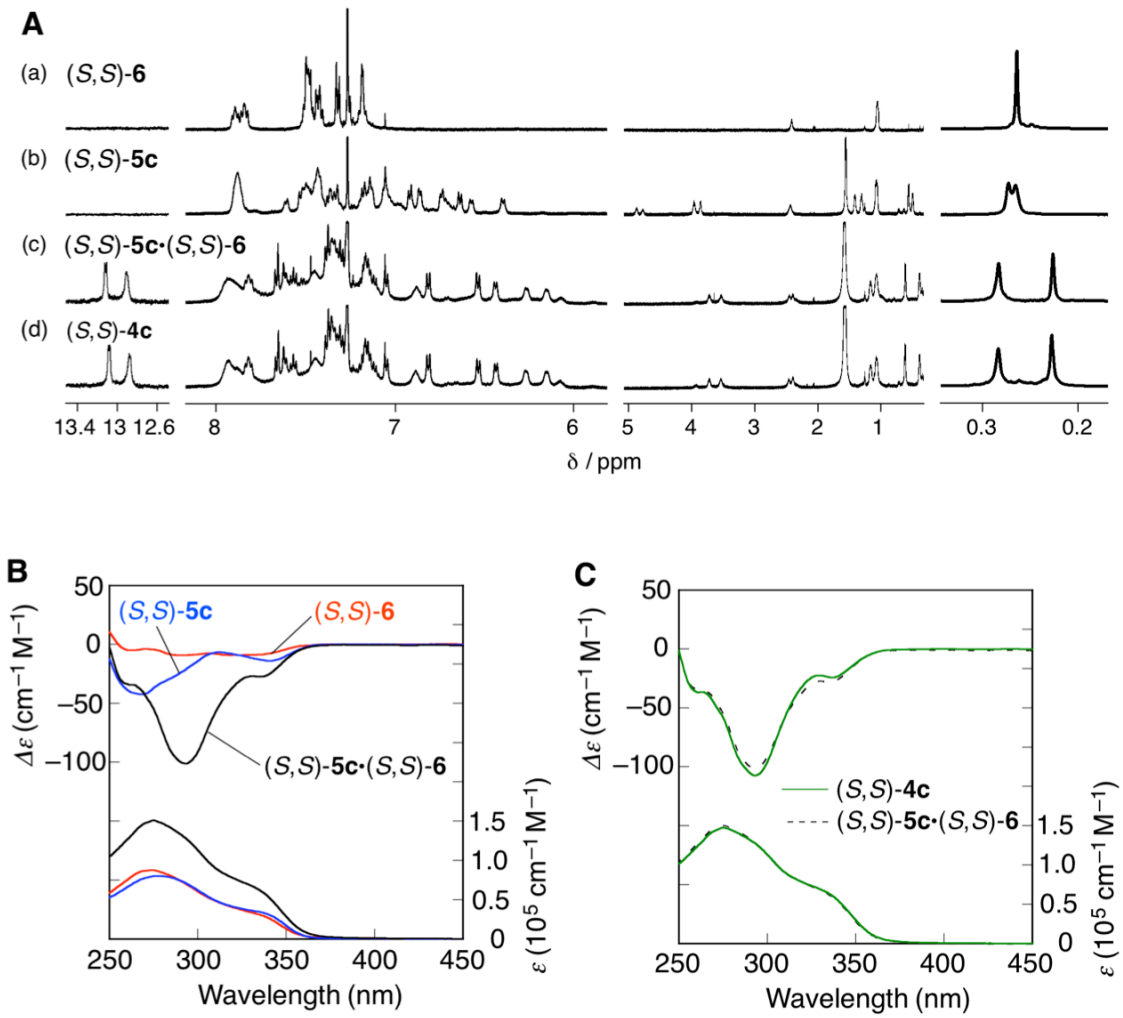


Fig. S10. (A) Partial ^{1}H NMR (500 MHz, 1.0 mM) spectra of (a) (*S*,*S*)-**6**, (b) (*S*,*S*)-**5c**, (c) (*S*,*S*)-**5c**·(*S*,*S*)-**6**, and (d) (*S*,*S*)-**4c** in $CDCl_3$ at 25 °C. (B, C) CD and absorption spectra (0.1 mM) of (B) (*S*,*S*)-**5c**, (*S*,*S*)-**6**, and (*S*,*S*)-**5c**·(*S*,*S*)-**6**, and (C) (*S*,*S*)-**4c** and (*S*,*S*)-**5c**·(*S*,*S*)-**6** in $CHCl_3$ at 25 °C.

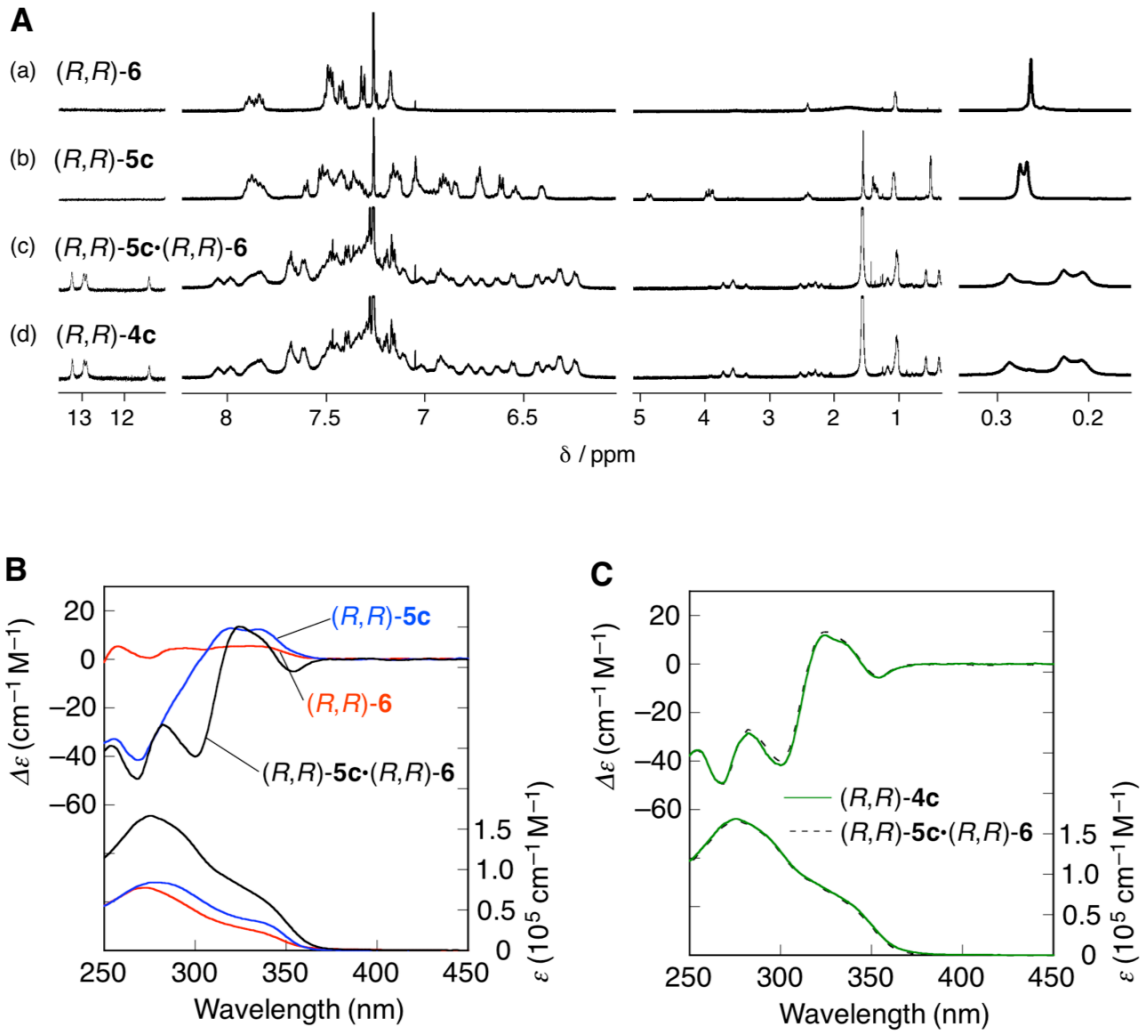


Fig. S11. (A) Partial ^{1}H NMR (500 MHz, 1.0 mM) spectra of (a) (*R*,*R*)-**6**, (b) (*R*,*R*)-**5c**, (c) (*R*,*R*)-**5c**·(*R*,*R*)-**6**, and (d) (*R*,*R*)-**4c** in $CDCl_3$ at 25 °C. (B, C) CD and absorption spectra (0.1 mM) of (B) (*R*,*R*)-**5c**, (*R*,*R*)-**6**, and (*R*,*R*)-**5c**·(*R*,*R*)-**6**, and (C) (*R*,*R*)-**4c** and (*R*,*R*)-**5c**·(*R*,*R*)-**6** in $CHCl_3$ at 25 °C.

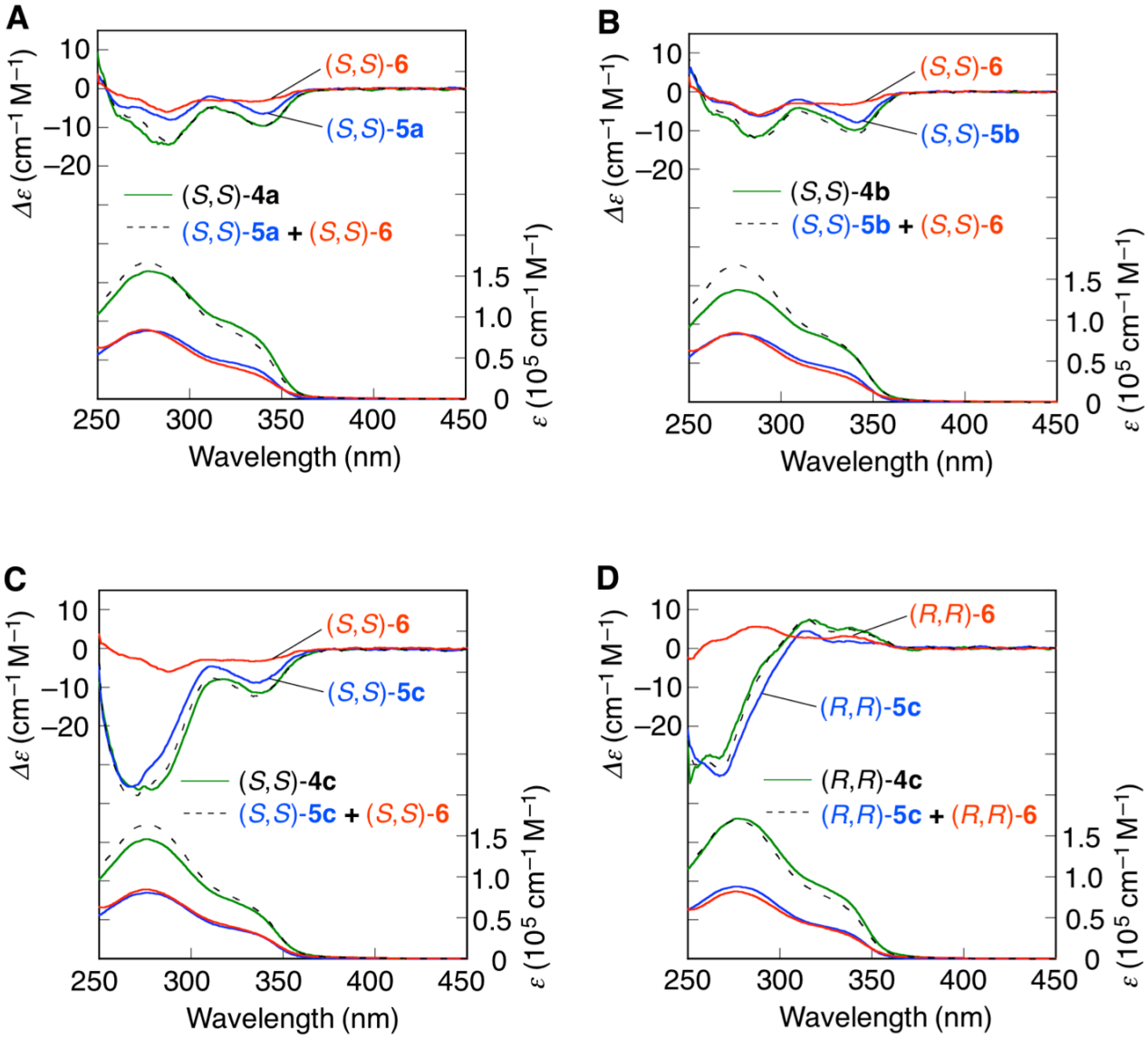


Fig. S12. (A) CD and absorption spectra of (*S*,*S*)-**4a** (green lines), (*S*,*S*)-**5a** (blue lines), and (*S*,*S*)-**6** (red lines) (0.1 mM) in DMSO at 25 °C, and the simulated CD and absorption spectra for an equimolar mixture of (*S*,*S*)-**5a** and (*S*,*S*)-**6** (dashed black lines). (B) CD and absorption spectra of (*S*,*S*)-**4b** (green lines), (*S*,*S*)-**5b** (blue lines), and (*S*,*S*)-**6** (red lines) (0.1 mM) in DMSO at 25 °C, and the simulated CD and absorption spectra for an equimolar mixture of (*S*,*S*)-**5b** and (*S*,*S*)-**6** (dashed black lines). (C) CD and absorption spectra of (*S*,*S*)-**4c** (green lines), (*S*,*S*)-**5c** (blue lines), and (*S*,*S*)-**6** (red lines) (0.1 mM) in DMSO at 25 °C, and the simulated CD and absorption spectra for an equimolar mixture of (*S*,*S*)-**5c** and (*S*,*S*)-**6** (dashed black lines). (D) CD and absorption spectra of (*R*,*R*)-**4c** (green lines), (*R*,*R*)-**5c** (blue lines), and (*R*,*R*)-**6** (red lines) (0.1 mM) in DMSO at 25 °C, and the simulated CD and absorption spectra for an equimolar mixture of (*R*,*R*)-**5c** and (*R*,*R*)-**6** (dashed black lines).

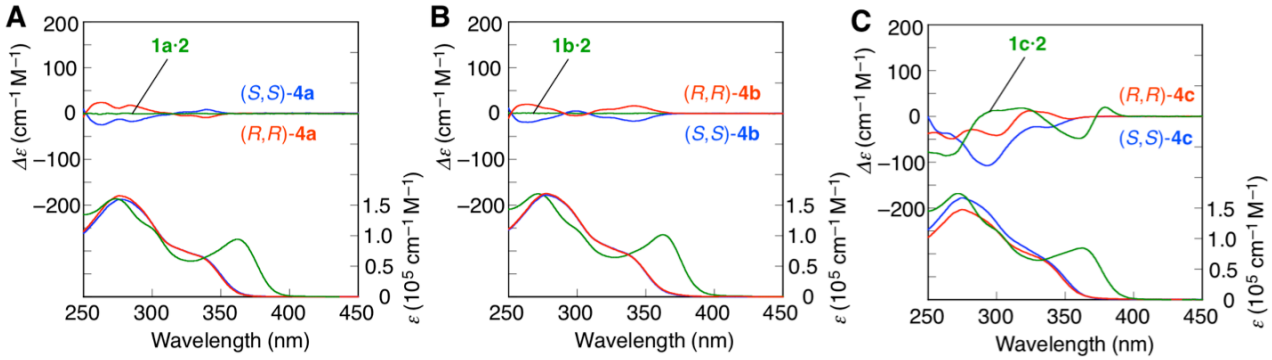


Fig. S13. CD and absorption spectra (0.1 mM) of (A) **1a**·**2**, (*S*,*S*)-**4a**, and (*R*,*R*)-**4a**, (B) **1b**·**2**, (*S*,*S*)-**4b**, and (*R*,*R*)-**4b**, and (C) **1c**·**2**, (*S*,*S*)-**4c**, and (*R*,*R*)-**4c** in $CHCl_3$ at 25 °C.

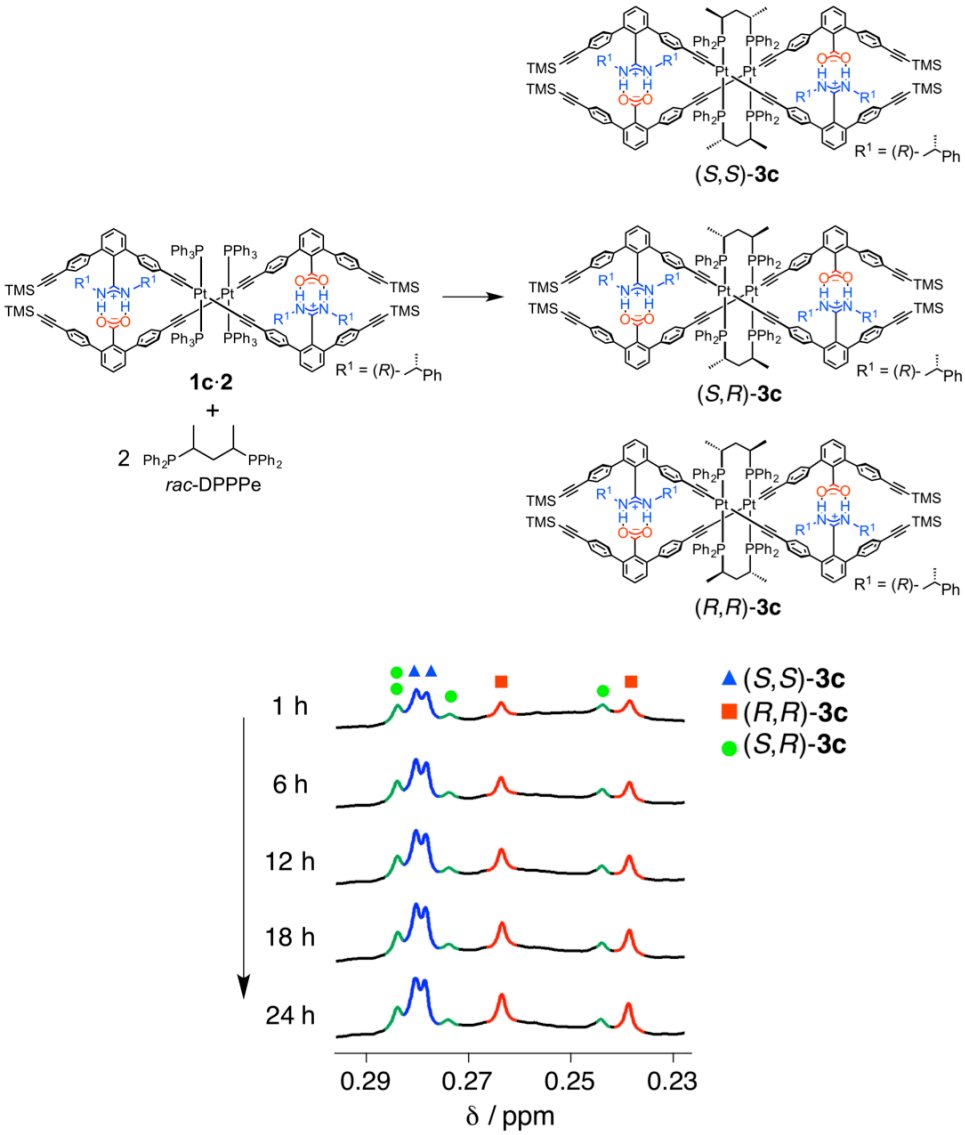


Fig. S14. Time-dependent ^{1}H NMR spectral changes of **1c**·**2** after the addition of 2 equiv *rac*-DPPPe in $CDCl_3$ at 25 °C; $[\mathbf{1c}\cdot\mathbf{2}]_0$ = 0.5 mM, $[rac\text{-DPPPe}]_0$ = 1.0 mM. In this reaction condition ($[rac\text{-DPPPe}]_0$ / $[\mathbf{1c}\cdot\mathbf{2}]_0$ = 2), the signals (marked with light-green circles) remained even after 24 h.

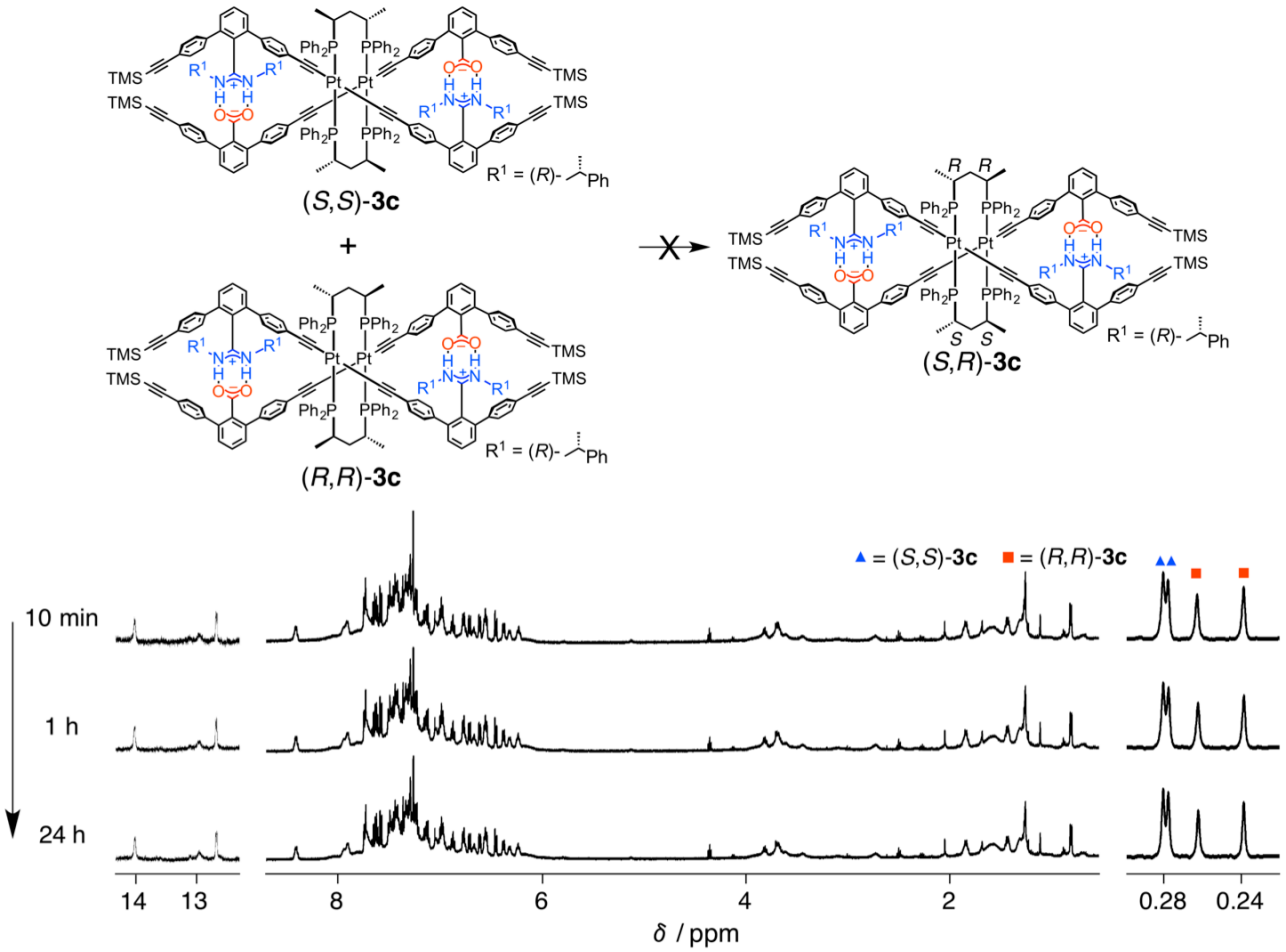


Fig. S15. Time-dependent ^{1}H NMR (500 MHz) spectral changes of (*S*,*S*)-**3c** after the addition of an equimolar (*R*,*R*)-**3c** in $CDCl_3$ at 25 °C. [(*S*,*S*)-**3c**] = [(*R*,*R*)-**3c**] = 0.5 mM.

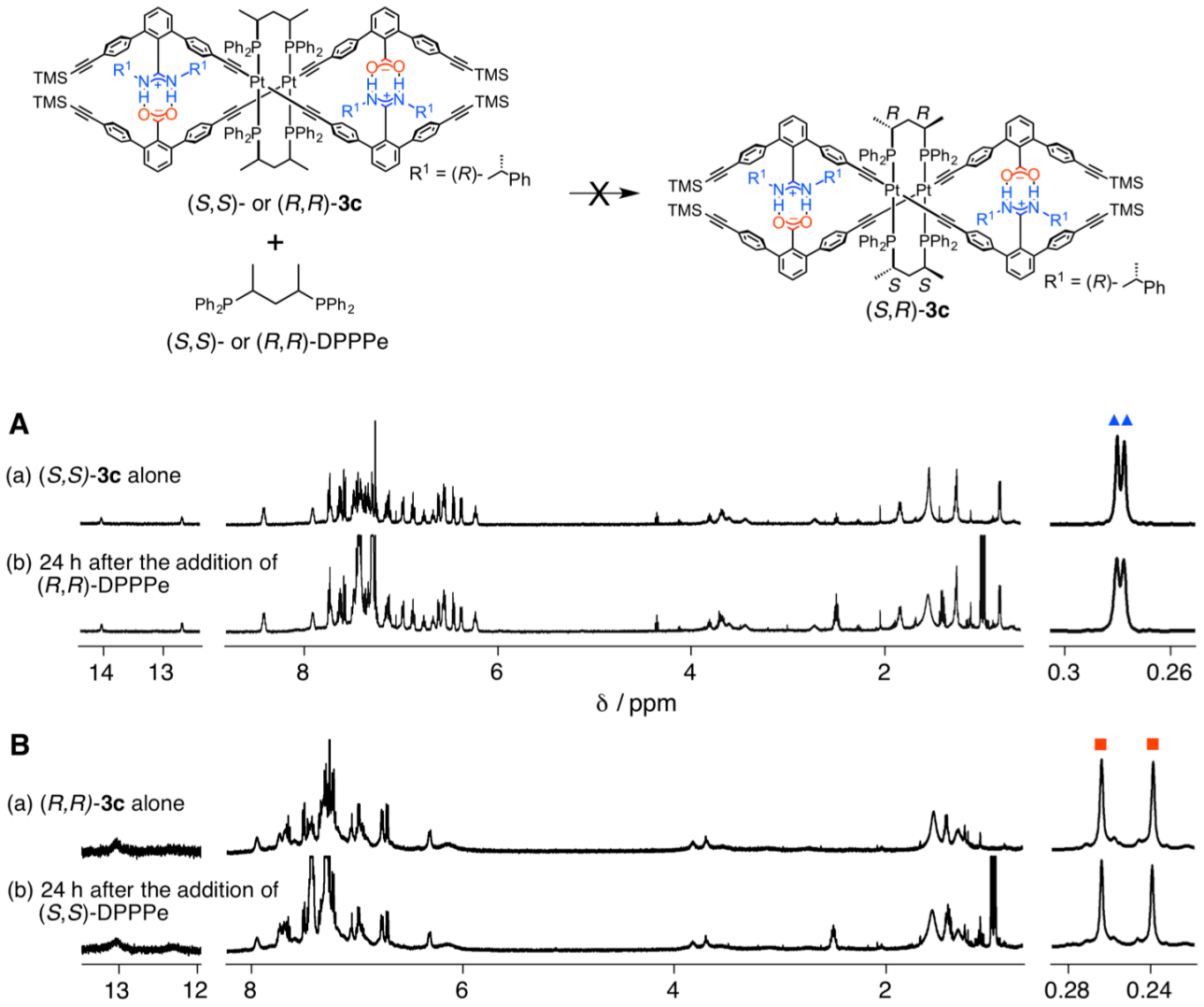


Fig. S16. (A) Time-dependent ^{1}H NMR (500 MHz) spectral changes of (*S*,*S*)-**3c** (a) before and (b) 24 h after the addition of 2 equiv (*R*,*R*)-DPPPe in $CDCl_3$ at 25 °C; [(*S*,*S*)-**3c**] = 0.5 mM, [(*R*,*R*)-DPPPe] = 1.0 mM. (B) Time-dependent ^{1}H NMR (500 MHz) spectral changes of (*R*,*R*)-**3c** (a) before and (b) 24 h after the addition of 2 equiv (*S*,*S*)-DPPPe in $CDCl_3$ at 25 °C; [(*R*,*R*)-**3c**] = 0.5 mM, [(*S*,*S*)-DPPPe] = 1.0 mM.

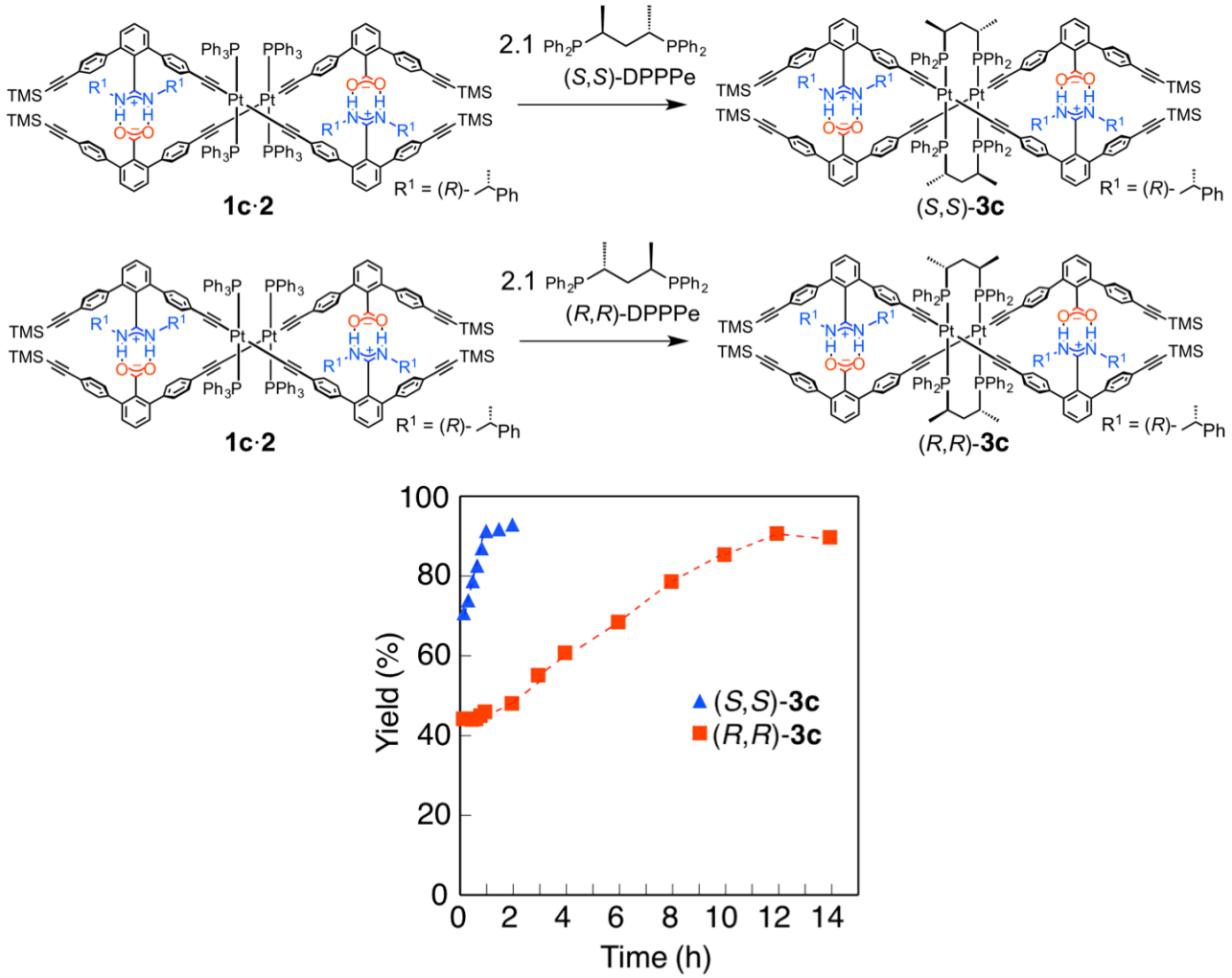


Fig. S17. Plots of yields of (*S*,*S*)- and (*R*,*R*)-**3c** from the reaction of **1c**·**2** with 2.1 equiv (*S*,*S*)- and (*R*,*R*)-DPPPe versus time, respectively (in $CDCl_3$ at 25 °C). The reaction progresses were monitored by ^{1}H NMR measurements, and the yields were estimated by using an internal standard (1,3,5-trioxane); $[\mathbf{1c}\cdot\mathbf{2}]_0 = 0.5$ mM, $[\text{DPPPe}]_0 = 1.1$ mM.

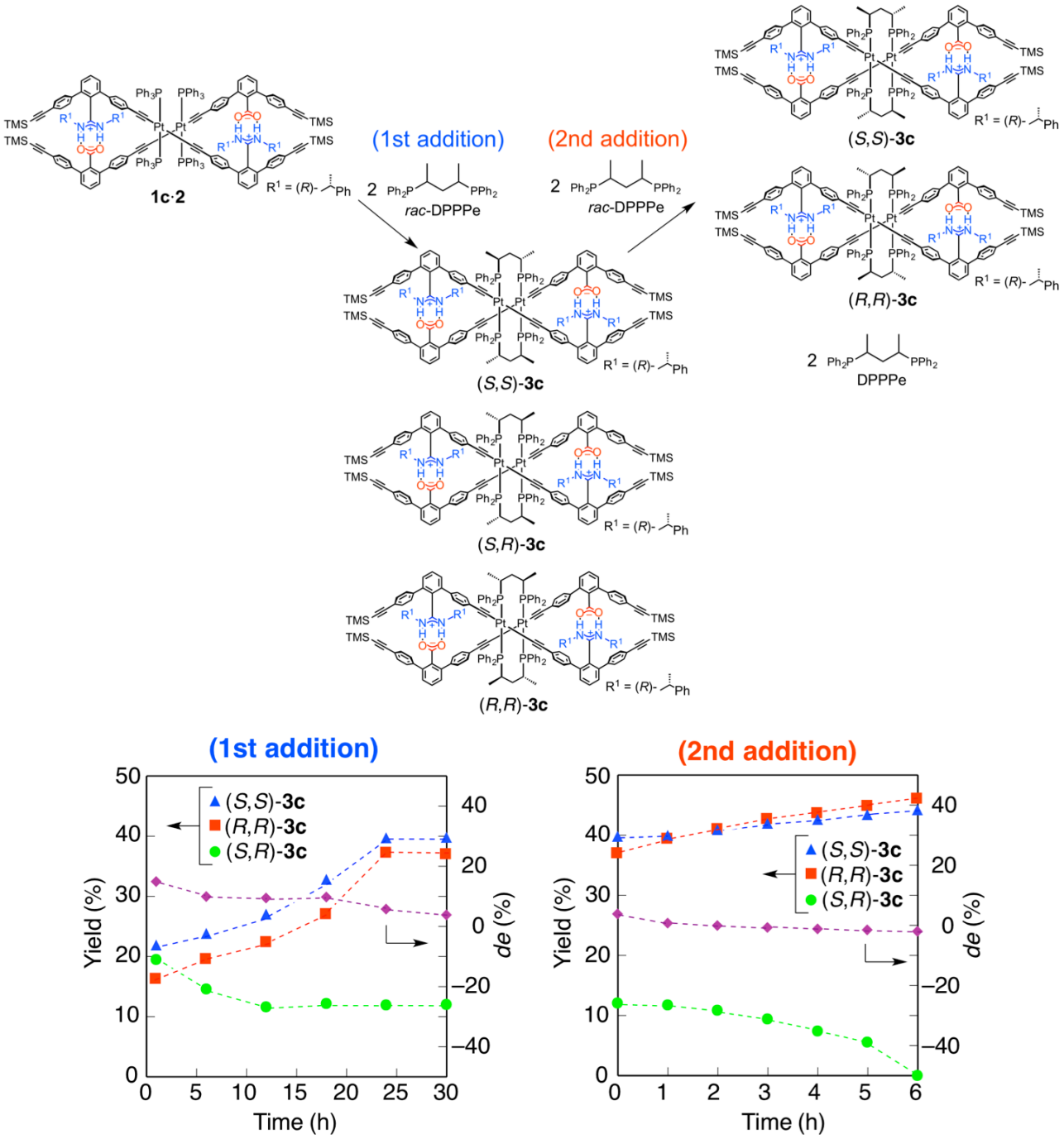


Fig. S18. (Left, 1st addition) Plots of yields of three diastereomers **3c** and diastereomeric excess (*de*) of (*S*,*S*)- and (*R*,*R*)-**3c** from the reaction of **1c**·**2** with 2 equiv *rac*-DPPPe versus time (in $CDCl_3$ at 25 °C); $[\mathbf{1c}\cdot\mathbf{2}]_0$ = 0.5 mM, $[rac\text{-DPPPe}]_0$ = 1.0 mM. (Right, 2nd addition) Plots of yields of the diastereomers **3c** and *de* of (*S*,*S*)- and (*R*,*R*)-**3c** from the reaction of the mixture of the three diastereomers **3c** with additional 2 equiv of *rac*-DPPPe versus time (in $CDCl_3$ at 25 °C). The reaction progresses were monitored by ^{1}H NMR measurements, and the yields and *de* values were estimated by using an internal standard (1,3,5-trioxane).

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