

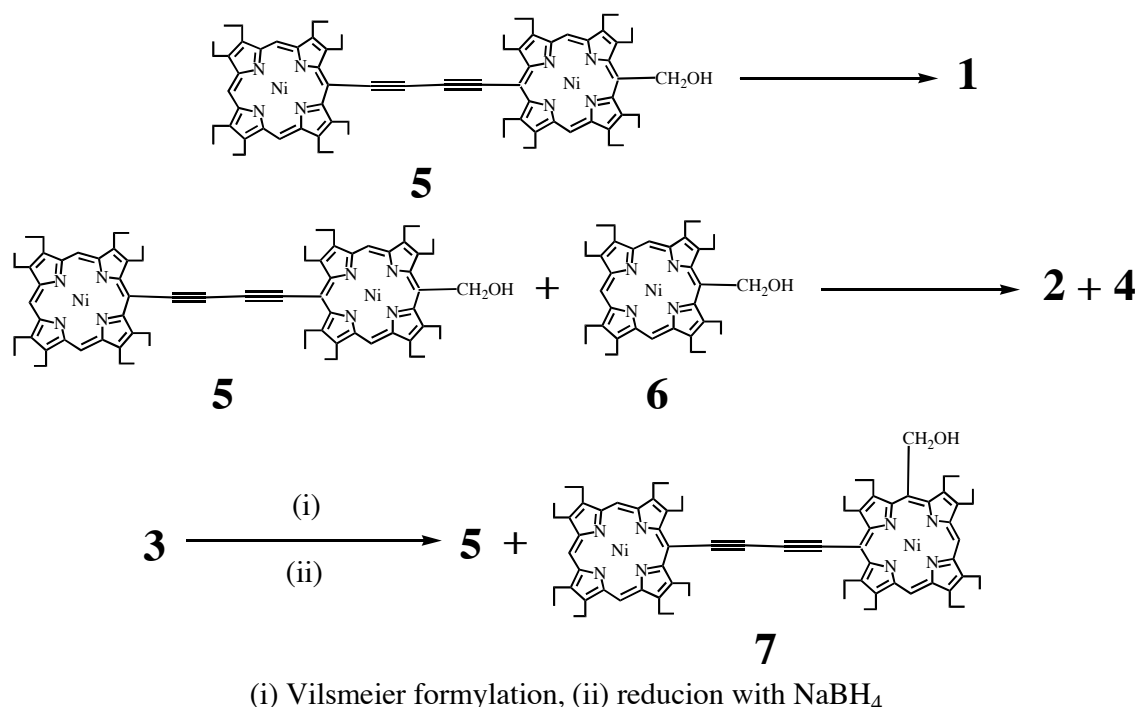
Supporting Information

Supramolecular Chirogenesis in Weakly Interacting Hosts: Role of the Temperature, Structural and Electronic Factors in Enhancement of Chiroptical Sensitivity

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Synthetic part.

Scheme S1. Syntheses of the porphyrin hosts **1**, **2** and intermediate **5**.



Preparation of 1: A solution of alcohol **5**¹ (50 mg, 0.040 mmol) in *N,N*-dimethylformamide (DMF, 15 cm³) containing conc. sulfuric acid (H₂SO₄, 0.005 cm³, 0.094 mmol) was stirred under gentle refluxing over 5 hr., then poured into water, and the reaction mixture was extracted with chloroform (CHCl₃). The extract was washed with aqueous hydrochloric acid (3M HCl), with brine, and then dried over anhydrous sodium sulfate (Na₂SO₄). The residue obtained after removal of the solvent under reduced pressure was chromatographed on alumina (Al₂O₃, ϕ3.2 x 5 cm) with hexane-CHCl₃ (4:1 in v/v) to afford **1** (4.9 mg, 10%). **1**: black purple microcrystallines (CHCl₃-MeOH); mp. > 280 °C (gradual decomp.); MS (ESI-FT-ICR) *m/z* 1241.925

(M^{2+}) for $C_{154}H_{176}N_{16}Ni_4$ (wt 2483.852); IR (KBr) ν 2963, 2926 and 2854 (C-H), 2177 and 2123 cm^{-1} (C::C); 1H NMR ($CDCl_3$, 600 MHz, 25 °C) δ 9.45 (4H, s, meso-H), 9.41 (2H, s, meso-H), 8.87 (4H, s, meso-H), 4.32 (4H, br.s, $-CH_2CH_2-$), 4.26-2.60 (64H, m, CH_2CH_3), 1.98-1.06 (96H, m, CH_2CH_3); UV-vis ($CHCl_3$, 25 °C) λ_{max} 430 (ϵ 174900), 491 (209100), 637 nm (68000); Found, C; 74.33, H; 7.30, N; 8.98%. Calcd for $C_{154}H_{176}N_{16}Ni_4$, C; 74.46, H; 7.14, N; 9.02%.

Preparation of 2: A mixture of alcohols **5**¹ (34 mg, 0.027 mmol) and **6**² (167 mg, 0.27 mmol) in DMF (30 cm^3) was added dropwise into a solution of DMF (50 cm^3) containing conc. H_2SO_4 (0.0047 cm^3 , 0.089 mmol) under gentle refluxing over 1 hr, kept for additional 4 hr, then poured into water, and the reaction mixture was extracted with $CHCl_3$. The extract was washed with aq. 3M HCl, with brine and then dried over anhydrous Na_2SO_4 . The residue obtained after removal of the solvent under reduced pressure was chromatographed on Al_2O_3 (ϕ 3.2 x 10 cm) with hexane- $CHCl_3$ (4:1 in v/v) to afford **2** (5.2 mg, 10%), together with **4**² (48 mg). **2**: deep green microcrystallines (hexane- $CHCl_3$); mp. > 265 °C (gradual decomp.); MS (FAB) m/z 1846.382 (M^+) for $C_{114}H_{132}N_{12}Ni_3$ (wt 1846.390); IR (KBr) ν 2963, 2929 and 2869 (C-H), 2178 and 2122 cm^{-1} (C::C); 1H NMR ($CDCl_3$, 600 MHz, 25 °C) δ 9.49 (1H, s, meso-H), 9.45 (2H, s, meso-H), 9.40 (1H, s, meso-H), 9.25 (2H, s, meso-H), 8.96 (2H, s, meso-H), 4.32 and 4.30 (4H, A_2B_2 t, $J=7.6$, $-CH_2CH_2-$), 4.24-2.78 (48H, m, CH_2CH_3), 1.96-1.02 (72H, m, CH_2CH_3); UV-vis ($CHCl_3$, 25 °C) λ_{max} 414 (ϵ 243000), 488 (171000), 581 (43000), 632 nm (49400); Found, C; 74.11, H; 7.38, N; 9.10%. Calcd for $C_{114}H_{132}N_{12}Ni_3$, C; 74.15, H; 7.21, N; 9.11%. **4**²: dark purple microcrystallines ($CHCl_3$ -MeOH); MS (FAB) m/z 1208.928 (M^+) for $C_{114}H_{132}N_{12}Ni_3$ (wt 1208.920); 1H NMR ($CDCl_3$, 600 MHz, 25 °C) δ 9.46 (2H, s, meso-H), 9.24 (4H, s, meso-H), 3.8-2.7 (36H, br m, CH_2CH_3 and ethylene-H), 1.84-1.05 (48H, m, CH_2CH_3); UV-vis ($CHCl_3$, 25 °C) λ_{max} 407 (ϵ 202000, sh), 423 (225000), 542 (26000), 576 nm (28900).

Preparation of 5: A solution of **3**³ (500 mg, 0.407 mmol) in 1,2-dichloroethane (100 cm^3) was added dropwise into Vilsmeier reagent ($DMF-POCl_3$, 10 mmol)⁴ at 40-45 °C over 1 hr. After being stirred for additional 3 hr, sat. aq. sodium acetate (150 cm^3) was added into the resulting mixture at 60-70 °C and stirred for additional 3 hr. The reaction mixture was poured into water and extracted with $CHCl_3$. The extract was washed with aq. 3M HCl, with brine, and then dried over anhydrous Na_2SO_4 . The residue obtained after removal of the solvent under reduced pressure was chromatographed on silica gel

(SiO₂, ϕ 3.2 x 20 cm) with hexane-CHCl₃ (3:7 in v/v) to afford a mixture (270 mg) of isomeric aldehydes, together with unreacted **3** (95 mg). The aldehyde mixture was hard to be separated by means of column chromatography. Therefore, into the above isomeric mixture dissolved in tetrahydrofuran (THF, 50 cm³) sodium borohydride (NaBH₄, 30 mg, 0.79 mmol) was added and the mixture was stirred at an ambient temperature for 3 hr. After addition of a few drops of ethyl acetate (AcOEt), the mixture was poured into water and extracted with ether. The extract was washed with brine and then dried. The residue obtained after removal of the solvent was chromatographed on Al₂O₃ (ϕ 3.2 x 6 cm) with hexane-CHCl₃ (1:2 in v/v) to afford **5** (113 mg, 22% from **3**), together with its isomer **7** (57 mg, 11% from **3**). **5**: dark green microcrystallines (CHCl₃-MeOH); MS (FAB) *m/z* 1258.936 (M⁺) for C₇₇H₈₈N₈ONi₂ (wt 1258.934); IR (KBr) ν 3445 (OH), 2960, 2925 and 2853 (C-H), 2183 and 2125 cm⁻¹ (C:::C); ¹H NMR (CDCl₃, 600 MHz, 25 °C) δ 9.42 (2H, s, meso-H), 9.40 (1H, s, meso-H), 9.18 (2H, s, meso-H), 6.23 (2H, s, -CH₂OH), 4.22-4.14 (8H, qm, CH₂CH₃), 3.83-3.70 (24H, m, CH₂CH₃), 1.87-1.67 (48H, m, CH₂CH₃), 1.28 (1H, s, OH); UV-vis (CHCl₃, 25 °C) λ_{\max} 429 (ϵ 129800), 459 (134300), 485 (154300), 631 nm (50200); Found, C; 73.25, H; 7.34, N; 8.88%. Calcd for C₇₇H₈₈N₈ONi₂, C; 73.46, H; 7.05, N; 8.90%. **7**: dark green microcrystallines (CHCl₃-MeOH); MS (FAB) *m/z* 1258.930 (M⁺) for C₇₇H₈₈N₈ONi₂ (wt 1258.934); IR (KBr) ν 3441 (OH), 2963, 2929 and 2869 (C-H), 2173 and 2123 cm⁻¹ (C:::C); ¹H NMR (CDCl₃, 600 MHz, 25 °C) δ 9.42 (2H, s, meso-H), 9.39 (1H, s, meso-H), 9.15 (1H, s, meso-H), 9.11 (1H, s, meso-H), 6.20 (2H, s, -CH₂OH), 4.20-4.10 (8H, qm, CH₂CH₃), 3.84-3.66 (24H, m, CH₂CH₃), 1.84-1.67 (48H, m, CH₂CH₃), 1.22 (1H, s, OH); UV-vis (CHCl₃, 25 °C) λ_{\max} 425 (ϵ 121600), 489 (125600), 593 (33900), 628 nm (37700); Found, C; 73.21, H; 7.28, N; 8.75%. Calcd for C₇₇H₈₈N₈ONi₂, C; 73.46, H; 7.05, N; 8.90%.

References

- (1) Hayashi, N.; Naoe, A.; Miyabayashi, K.; Yamada, M.; Miyake, M.; Higuchi, H. *Tetrahedron Lett.* **2004**, 45, 8215.
- (2) Arnold, D. P.; Johnson, A. W.; Winter, M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1643.
- (3) Arnold, D. P.; Johnson, A. W.; Mahendran, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 366.

(4) Vilsmeier, A.; Haack, A. *Ber.* **1927**, *60*, 119 and Campaigne, E.; Acher, W. L. *Org. Synth. Coll.* Vol. 4, **1963**, 331.

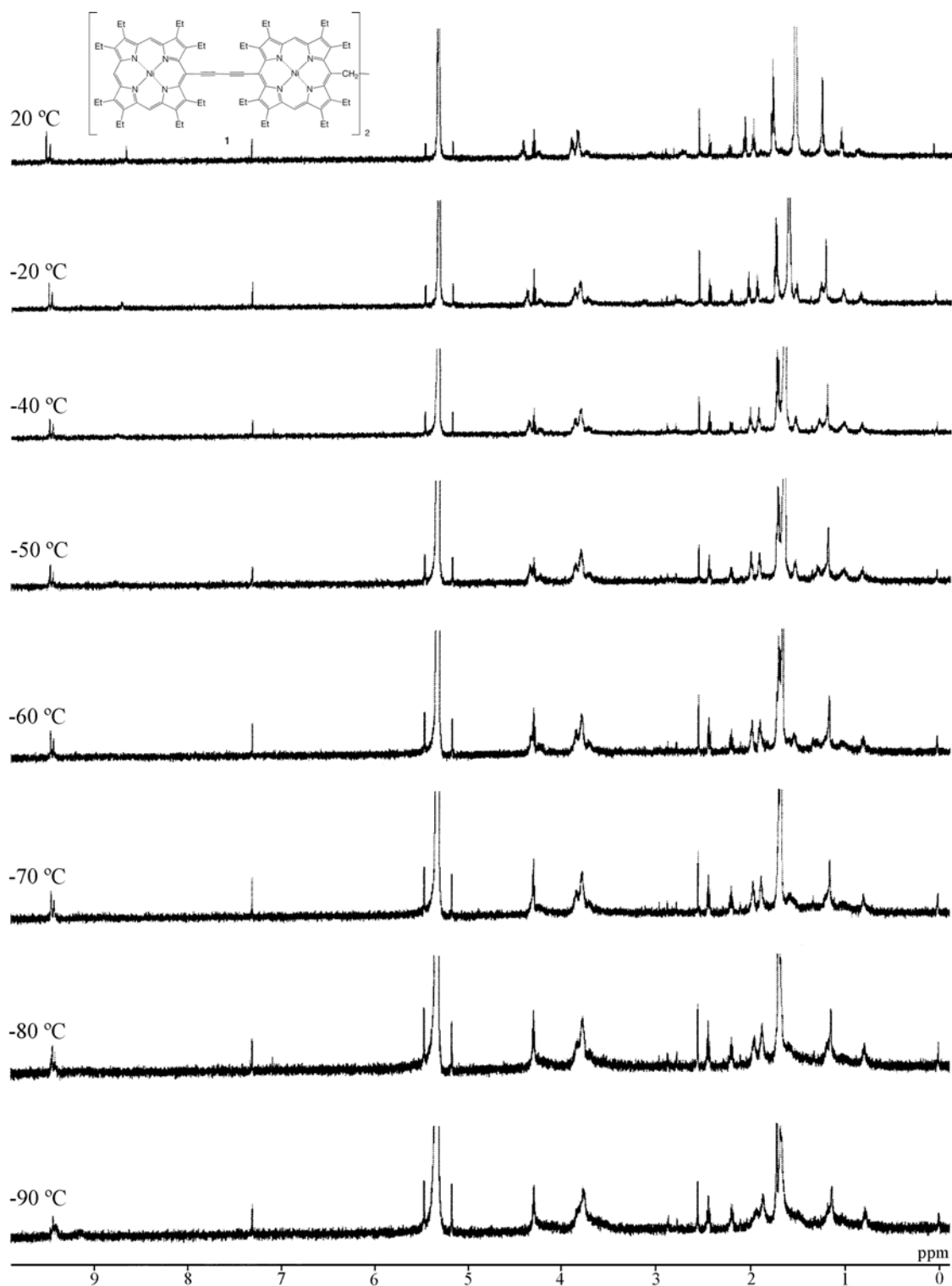


Figure S1. VT ^1H NMR spectra of **1** ($C = 0.4 \times 10^{-3}$) in CD_2Cl_2 .

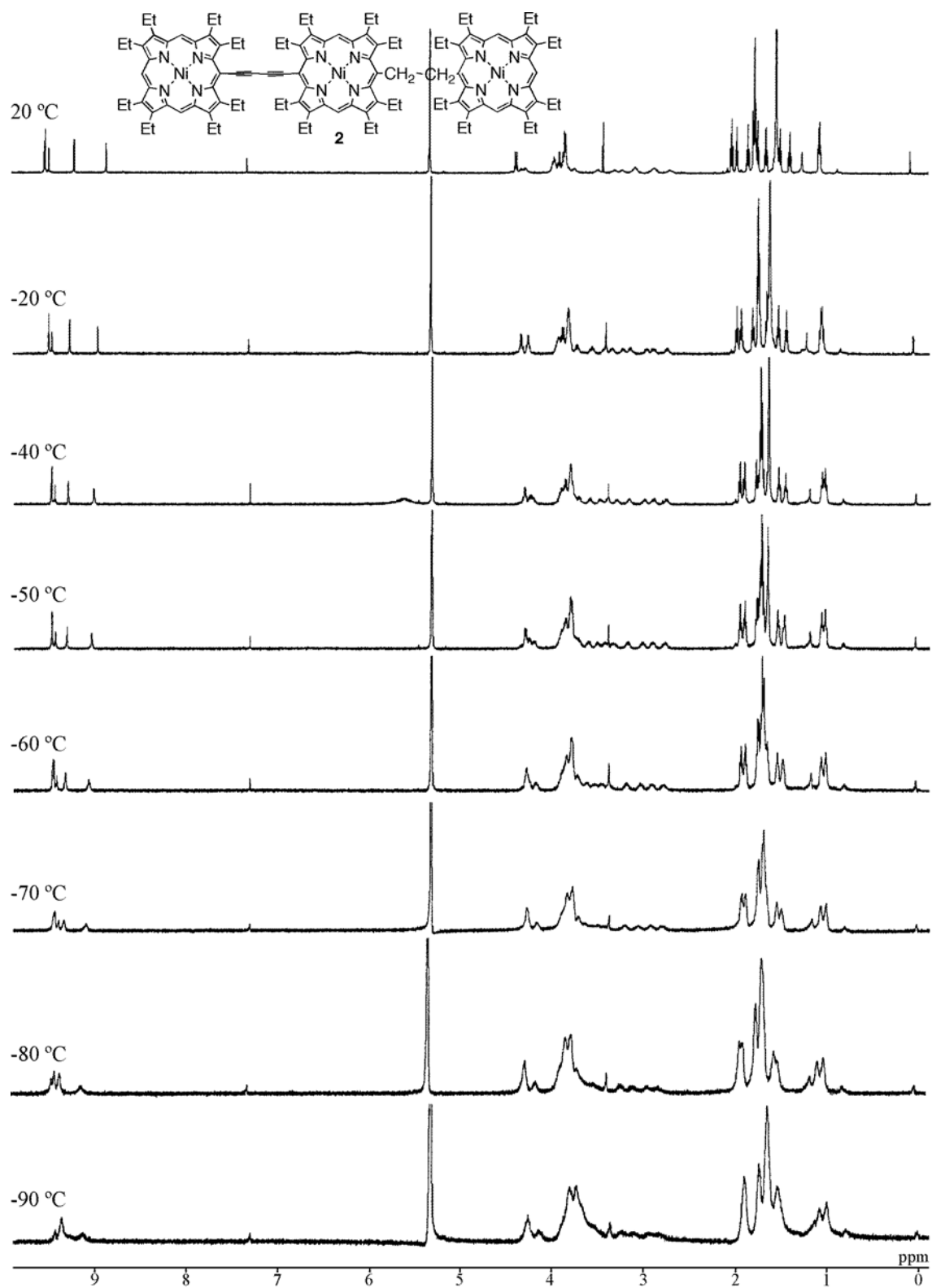


Figure S2. VT ¹H NMR spectra of **2** ($C = 0.4 \times 10^{-3}$) in CD₂Cl₂.

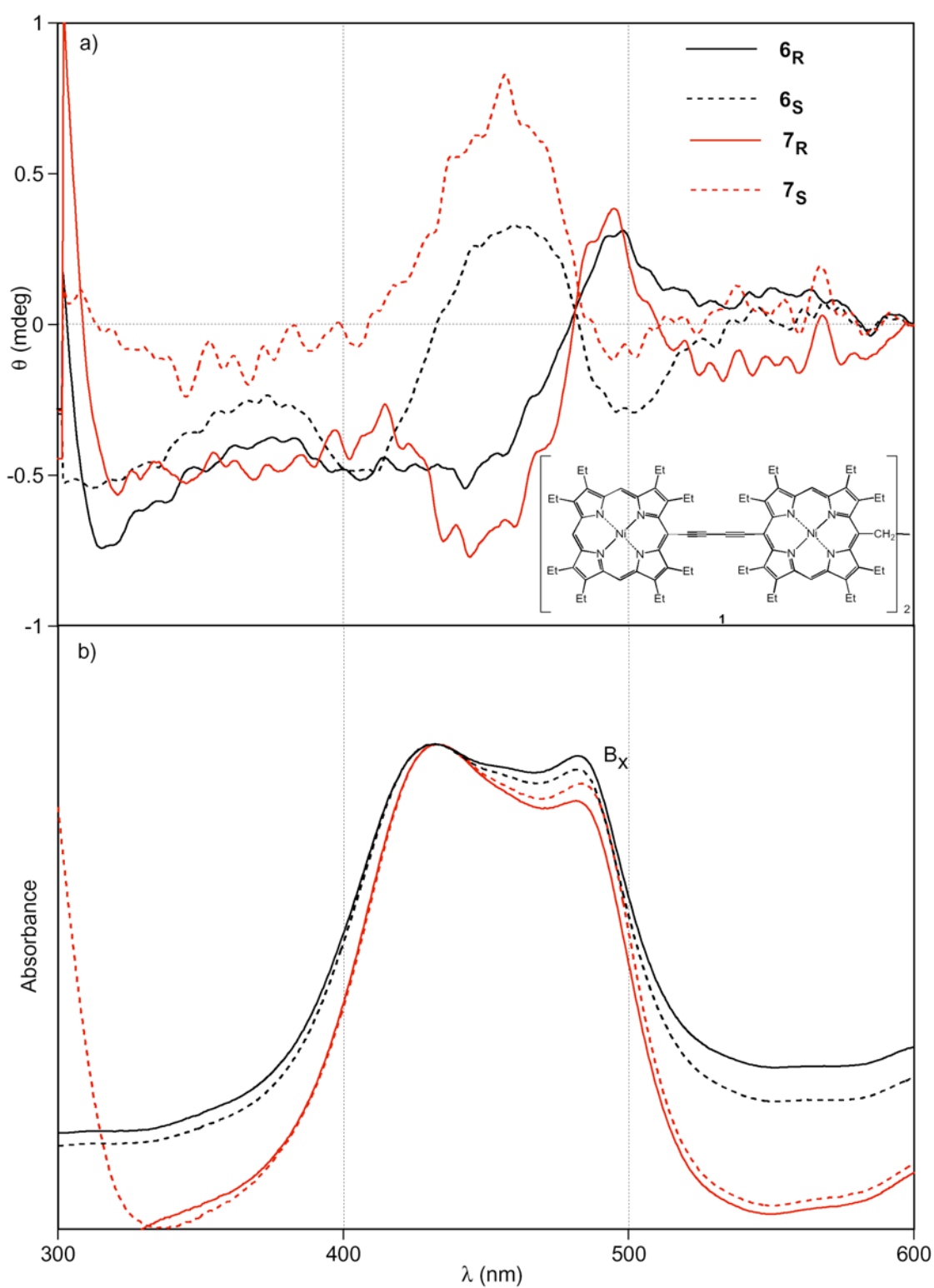


Figure S3. (a) CD and (b) UV-vis spectra of **1** in **6_R**, **6_S**, **7_R**, and **7_S** (normalized at $A = 1$ at 433 nm) at r.t.

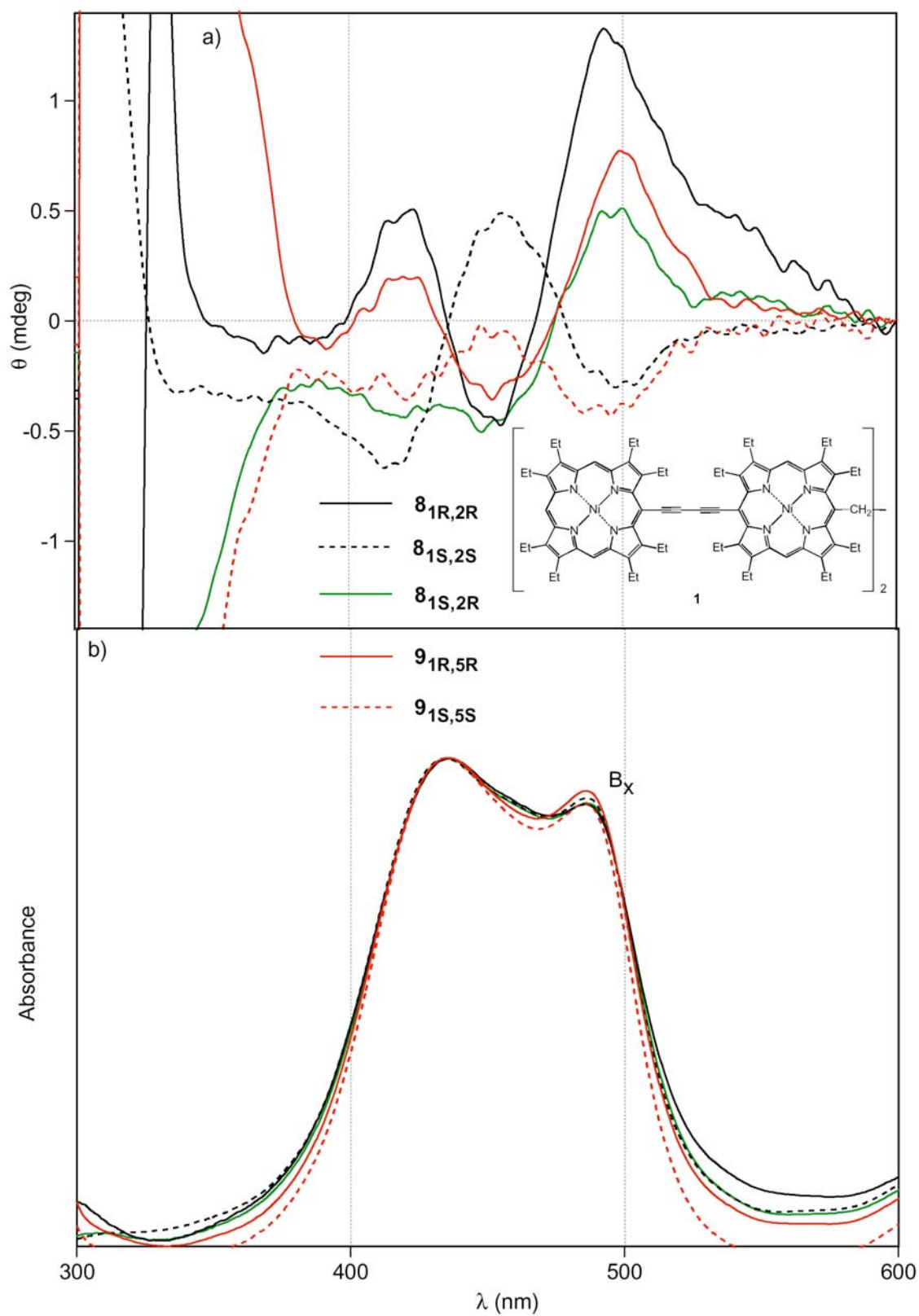


Figure S4. (a) CD and (b) UV-vis spectra of **1** in $\mathbf{8_{1R,2R}}$, $\mathbf{8_{1S,2S}}$, $\mathbf{8_{1S,2R}}$, $\mathbf{9_{1R,5R}}$, and $\mathbf{9_{1S,5S}}$ (normalized at $A = 1$ at 433 nm) at r.t.

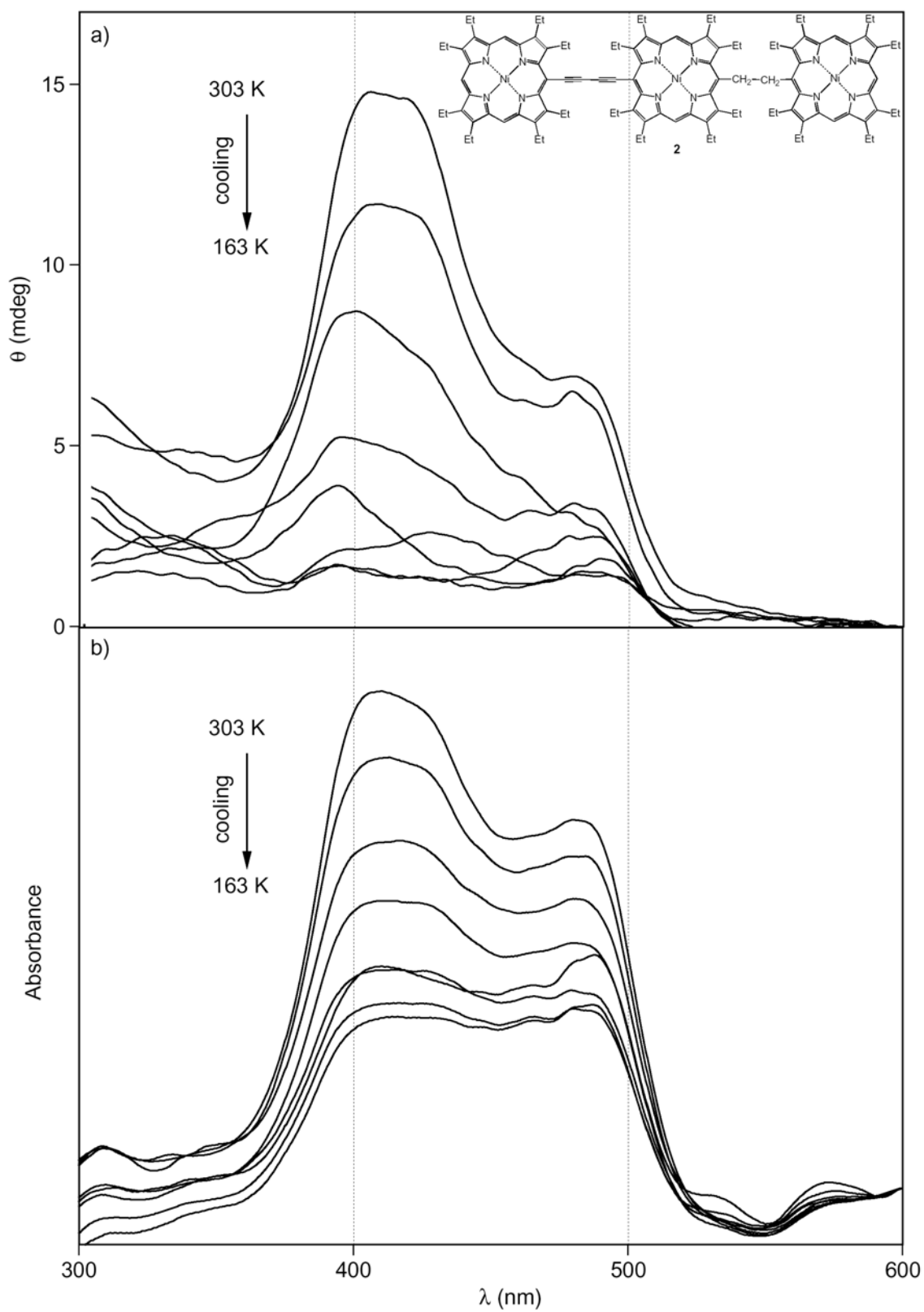


Figure S5. VT (a) CD and (b) HT spectra of **2** in **5_R** upon cooling from 303 to 163 K ($C_2 = 2.2 \times 10^{-5}$ M).

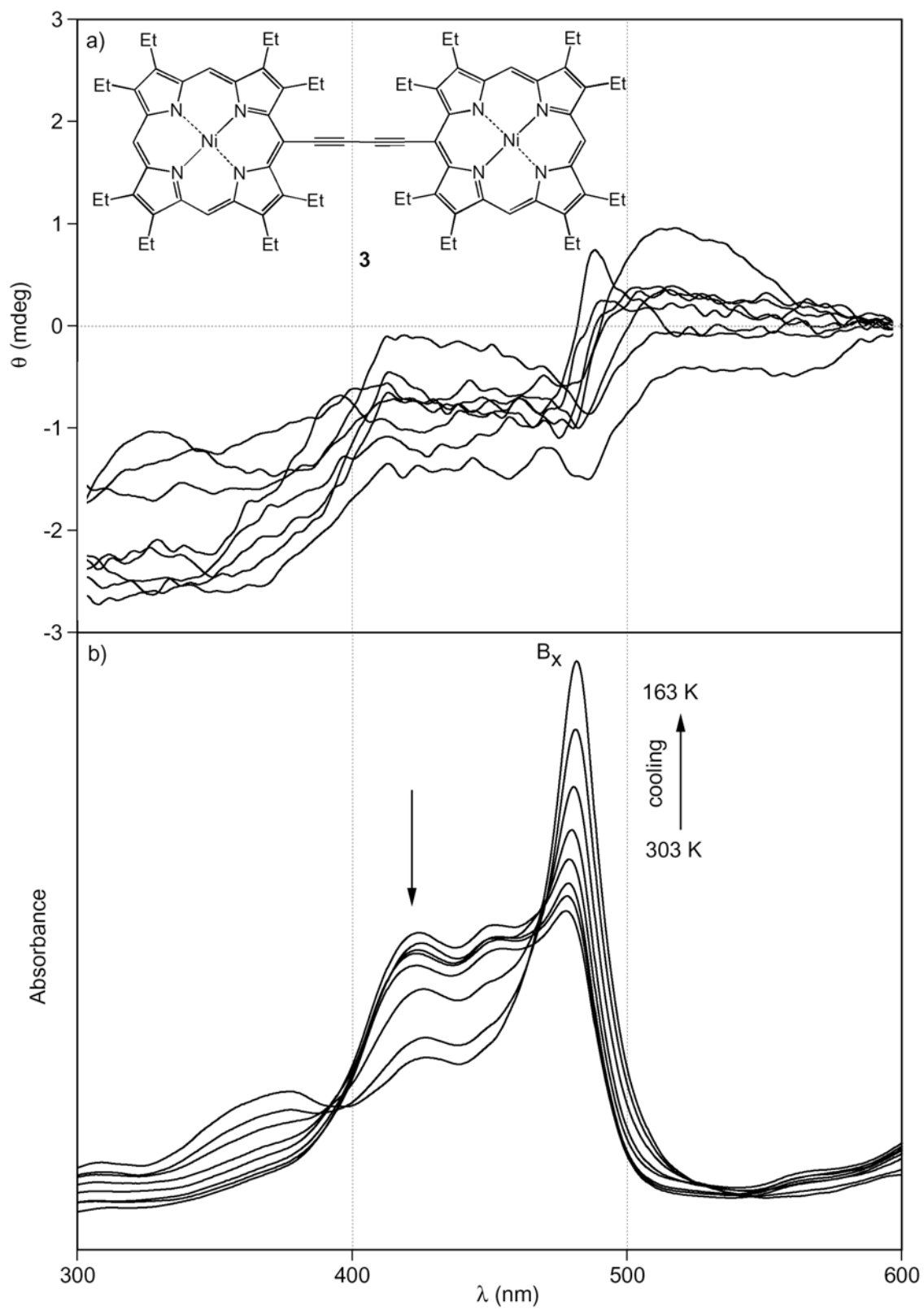


Figure S6. VT (a) CD and (b) HT spectra of **3** in **5_R** upon cooling from 303 to 163 K ($C_3 = 1.5 \times 10^{-5}$ M).

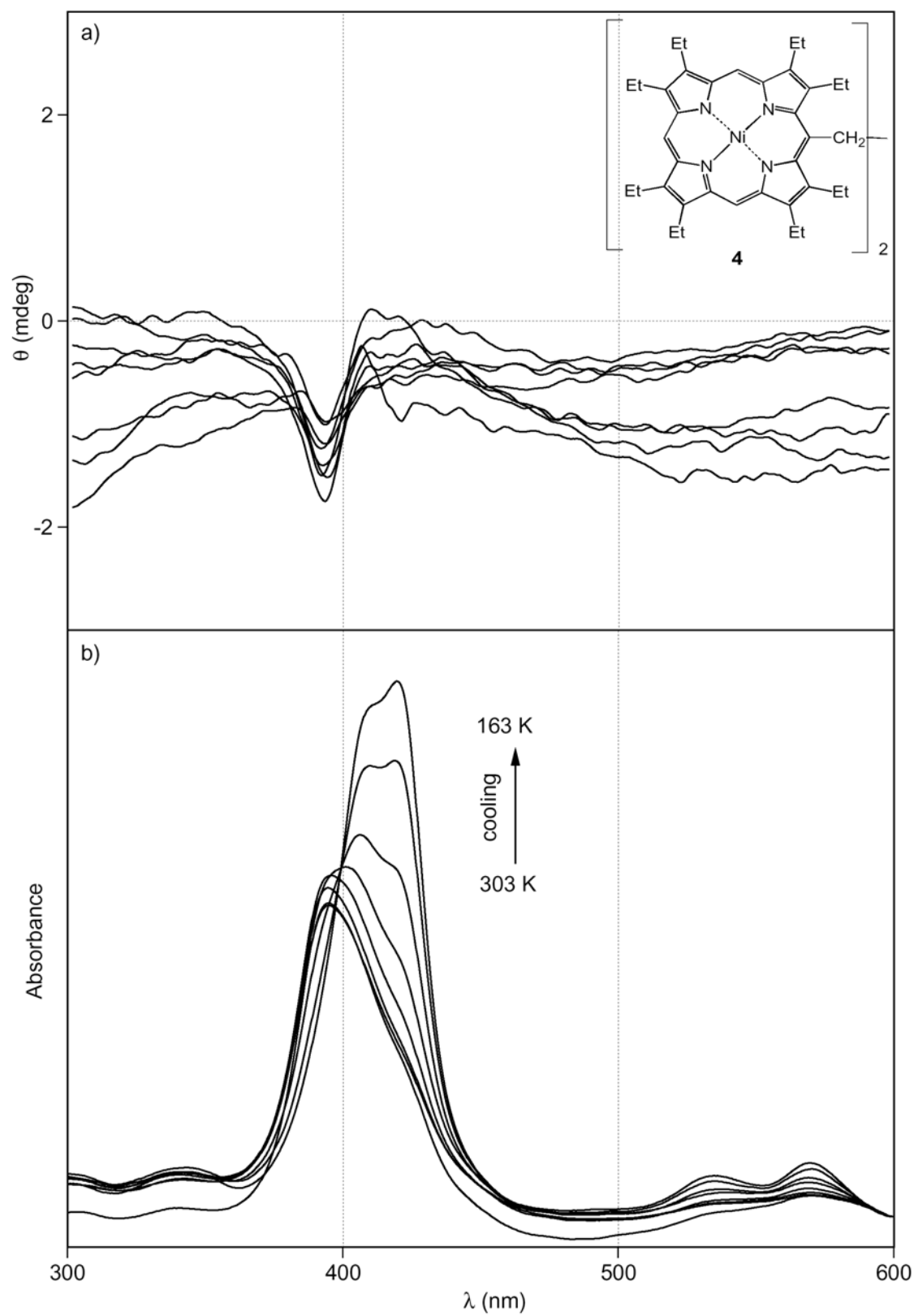


Figure S7. VT (a) CD and (b) HT spectra of **4** in **5_R** upon cooling from 303 to 163 K ($C_4 = 7.6 \times 10^{-6}$ M).