Supporting Information

Determination of the Absolute Configuration of 1-Arylethane-1,2-diols by a non Empirical Analysis of the CD Spectra of their 4-Biphenylboronates

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General Procedures. Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Optical rotation data were measured on a Jasco DIP-370 digital polarimeter. ^{1}H NMR (300 MHz) spectra were recorded in $CDCl_3$ or acetone-d_6. Enantiomeric excesses of the diols were determined by HPLC analysis on a Daicel Chiralcel OD or Chiralcel OJ column. $CHCl_3$ was distilled from P_2O_5 and stored over activated 4Å molecular sieves. THF was distilled over sodium immediately before use. $B(OEt)_3$ was distilled before use and stored under nitrogen. Analytical TLC were performed on 0.2 mm silica gel plates Merck 60 F-254 and column chromatography was carried out with silica gel Merck 60 (80-230 mesh). Diol (*R*)-**1a** was commercially available (Aldrich) while enantiomerically pure diols (*R*)-**1b**–**f** were obtained *via* asymmetric dihydroxylation[1] of the corresponding commercially available (Aldrich) alkenes followed by recrystallization. Absorption and CD spectra of compounds **3a**–**f** were recorded on a JASCO J600 spectropolarimeter at room temperature, in THF, using 0.1 mm cells and concentrations of about 1 $\times 10^{-3}$ M. During the measurement, the instrument was thoroughly purged with nitrogen.

(*R*)-(-)-1-(4-methoxyphenyl)-1,2-ethanediol (1b): Yield 73%; mp 94–95°C, lit.[2] mp 93–95°C; $[\alpha]^{20}_D$ = -47.1 (*c* = 1.02, MeOH), lit.[2] $[\alpha]_D$ = -35. (*c* = 1.0, EtOH); ^{1}H NMR ($CDCl_3$) δ 2.10 (br s, 1H), 2.50 (br s, 1H), 3.64 (dd, *J'* = 11.2 Hz, *J"*= 8.0 Hz, 1H), 3.72 (dd, *J'* = 11.2 Hz, *J"*= 3.8 Hz, 1H), 3.81 (s, 3H), 4.77 (dd, *J'* = 3.8 Hz, *J"*= 8.0 Hz, 1H), 6.90 (d, *J*= 8.7 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H). Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.33; H, 7.25.

[1] See. ref. 1 in the text.
[2] See ref. 18 in the text.

(*R*)-(-)-1-(4-trifluoromethylphenyl)-1,2-ethanediol (1c): Yield 82%; mp 94–95°C; $[\alpha]^{20}_D$ = -26.5 (*c* = 1.01, MeOH); ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 1H), 2.82 (s, 1H), 3.65 (dd, *J'* = 11.2 Hz, *J"*= 7.9 Hz, 1H), 3.80 (dd, *J'* = 11.2 Hz, *J"*= 3.2 Hz, 1H), 4.89 (dd, *J'* = 3.2 Hz, *J"*= 7.9 Hz, 1H), 7.49 (d, *J'*= 8.3 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H). Anal. Calcd for $C_9H_9F_3O_2$: C, 52.43; H, 4.40. Found: C, 52.27; H, 4.51.

Daicel Chiralcel OD column; λ 254 nm; *n*-hexane:*i*-PrOH 96:4; flow = 0.8 mL/min; ee>99%; first enantiomer eluted (*R*).

(*R*)-(-)-1-(4-biphenyl)-1,2-ethanediol (1d): Yield 78%; mp 151–152°C, lit.[3] mp 150–152°C; $[\alpha]^{20}_D$ = -32.6 (*c* = 1.0, MeOH), lit.[3] $[\alpha]_D$ = -38.9 (*c* = 1.03, $CHCl_3$);; ^{1}H NMR ($CDCl_3$) δ 2.10 (br s, 1H), 2.60 (br s, 1H), 3.72 (dd, *J'* = 11.2 Hz, *J"*= 8.0 Hz, 1H), 3.82 (dd, *J'* = 11.2 Hz, *J"*= 3.6 Hz, 1H), 4.89 (dd, *J'* = 3.6 Hz, *J"*= 8.0 Hz, 1H), 7.3–7.45 (m, 1H), 7.45–7.55 (m, 4H), 7.55–7.65 (m, 4H). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.27; H, 6.51.

Daicel Chiralcel OJ column; λ 220 nm; *n*-hexane:*i*-PrOH 90:10; flow = 0.8 mL/min; ee>99%; first enantiomer eluted (*R*).

(*R*)-(-)-1-(2-naphthyl)-1,2-ethanediol (1e): Yield 85%; mp 132–133°C, lit.[4] mp 134–135°C; $[\alpha]^{20}_D$ = -38.8 (*c* = 1.12, MeOH), lit.[4] $[\alpha]_D$ = -31.2 (*c* = 0.997, EtOH); ^{1}H NMR ($CDCl_3$) δ 1.80 (br s, 2H), 3.76 (dd, *J'* = 8.0 Hz, *J"*= 11.2 Hz, 1H), 3.87 (dd, *J'* = 11.2 Hz, *J"*= 3.5 Hz, 1H), 5.01 (dd, *J'* = 3.5 Hz, *J"*= 8.0 Hz, 1H), 7.4–7.6 (m, 3H), 7.8–8.0 (m, 4H). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.49; H, 6.61.

Daicel Chiralcel OD column; λ 254 nm; *n*-hexane:*i*-PrOH 90:10; flow = 1.0 mL/min; ee>99%; first enantiomer eluted (*R*).

(*R,R*)-(-)-1-(4-methoxyphenyl)-2-methyl-1,2-ethanediol (1f): Yield 83%; mp 79–81°C; $[\alpha]^{20}_D$ = -32.08 (*c* = 1.01, MeOH), lit.[5] $[\alpha]_D$ = -34.67 (*c* = 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.02 (d, *J* = 6.3 Hz, 3H), 2.69 (s, 2H), 3.80 (s, 3H), 3.81 (dq, *J'* = 6.3 Hz, *J"*= 7.7 Hz, 1H), 4.30 (d, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 1H), 7.25 (d, *J* = 8.7 Hz, 1H). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.85; H, 7.87.

Daicel Chiralcel OJ column; λ 254 nm; *n*-hexane:*i*-PrOH 90:10; flow = 0.5 mL/min; ee>99%; first enantiomer eluted (*R*).

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[3] See. ref. 21 in the text.
[4] See. ref. 22 in the text.
[5] See. ref. 25 in the text.

4-Biphenylboronic acid (2):[6] To a solution of 4-bromobiphenyl (1.5 g, 6.43 mmol) in anhydrous THF (20 mL) was slowly added at –78°C a solution of *t*-BuLi (1.5 M, 6.4 mL, 9.64 mmol). The resulting red-brown mixture was left stirring for 30 min, then $B(OEt)_3$ (3.28 mL, 19.3 mmol) was added and the resulting clear solution was left warming at r.t. stirring overnight. The mixture was then treated with 5% HCl and extracted three times with EtOAc. The collected organic phases were washed with saturated aqueous NH_4Cl, brine, and dried over anhydrous Na_2SO_4. After evaporation of solvent was recovered a white solid residue which was recrystallized from Et_2O/hexane affording 800 mg of **2** as white crystals. mp 235–237°C; ^{1}H NMR ($CDCl_3$) δ 7.3–7.6 (m, 3H), 7.6–7.9 (m, 4H), 8.38 (d, *J* = 8.1 Hz, 2H).

General Procedure for the Synthesis of Boronate Esters.

To a solution of 1-arylethane-1,2-diol (0.36 mmol) in $CHCl_3$ (5 mL) was added 4-biphenylboronic acid (0.44 mmol), activated 4 Å molecular sieves, and the mixture was left stirring at r.t. overnight. The mixture was then filtered and the solvent evaporated. The solid residue recovered was purified by column chromatography ($CHCl_3$) affording the pure boronate.

(*R*)-(-)-2-(4-Biphenyl)-4-phenyl-1,3,2-dioxaborolane (3a): Yield 89%; glassy solid; $[\alpha]^{20}_D$ = -102.1 (*c* = 1.07, THF); ^{1}H NMR ($CDCl_3$) δ 4.22 (dd, *J'* = 7.7 Hz, *J"*= 8.9 Hz, 1H), 4.77 (dd, *J'* = 8.0 Hz, *J"*= 8.9 Hz, 1H), 5.62 (dd, *J'* = 7.7 Hz, *J"*= 8.0 Hz, 1H), 7.3–7.5 (m, 8H), 7.5–7.7 (m, 4H), 7.97 (d, *J* = 8.0 Hz, 2H). Anal. Calcd for $C_{20}H_{17}O_2B$: C, 80.03; H, 5.71. Found: C, 80.19; H, 5.63.

(*R*)-(-)-2-(4-Biphenyl)-4-(4'-Methoxyphenyl)-1,3,2-dioxaborolane (3b): Yield 60%; glassy solid; $[\alpha]^{20}_D$ = -17.6 (*c* = 1.095, THF); ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 3H), 4.20 (dd, *J'* = 7.8 Hz, *J"*= 8.8 Hz, 1H), 4.70 (dd, *J'* = *J"*= 8.6 Hz, 1H), 5.55 (dd, *J'* = *J"*= 7.8 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.6–7.7 (m, 4H), 7.96 (d, *J* = 8.1 Hz, 2H). Anal. Calcd for $C_{21}H_{19}O_3B$: C, 76.39; H, 5.80. Found: C, 76.27; H, 5.92.

(*R*)-(-)-2-(4-Biphenyl)-4-(4'-Trifluoromethylphenyl)-1,3,2-dioxaborolane (3c): Yield 95%; mp 91–93°C; $[\alpha]^{20}_D$ = -113.4 (*c* = 1.07, THF); ^{1}H NMR ($CDCl_3$) δ 4.18 (dd, *J'* = 7.5 Hz, *J"*= 8.9 Hz, 1H), 4.80 (dd, *J'* = *J"*= 8.7 Hz, 1H), 5.67 (dd, *J'* = *J"*= 7.9 Hz, 1H), 7.3–7.6 (m, 5H), 7.6–7.8 (m, 6H), 7.97 (d, *J* = 8.2 Hz, 2H). Anal. Calcd for $C_{21}H_{16}O_2B$: C, 52.43; H, 4.40. Found: C, 52.37; H, 4.66.

[6] See ref. 11 in the text.

(*R*)-(-)-2-(4-Biphenyl)-4-(4'-biphenyl)-1,3,2-dioxaborolane (3d): Yield 72%; mp 159–162°C; $[\alpha]^{20}_{D}$ = -141 (*c* = 1.0, THF); ^{1}H NMR (acetone-d_6) δ 4.24 (dd, *J'* = 7.8 Hz, *J"*= 8.8 Hz, 1H), 4.87 (dd, *J'* = *J"*= 8.6 Hz, 1H), 5.78 (dd, *J'* = *J"*= 7.8 Hz, 1H), 7.3–7.8 (m, 16H), 7.97 (d, *J* = 8.1 Hz, 2H). Anal. Calcd for $C_{26}H_{21}O_2B$: C, 83.00; H, 5.63. Found: C, 82.91; H, 5.75.

(*R*)-(-)-2-(4-Biphenyl)-4-(2'-Naphthyl)-1,3,2-dioxaborolane (3e): Yield 80%; mp 158–160°C; $[\alpha]^{20}_{D}$ = -133.0 (*c* = 1.03, THF); ^{1}H NMR (acetone-d_6) δ 4.28 (dd, *J'* = 7.6 Hz, *J"*= 8.8 Hz, 1H), 4.90 (dd, *J'* = *J"*= 8.8 Hz, 1H), 5.90 (dd, *J'* = *J"*= 7.8 Hz, 1H), 7.3–7.8 (m, 10H), 7.9–8.1 (m, 6H). Anal. Calcd for $C_{24}H_{19}O_2B$: C, 82.31; H, 5.47. Found: C, 82.27; H, 5.52.

(*R,R*)-(-)-2-(4-Biphenyl)-4-(4'-Methoxyphenyl)-5-methyl-1,3,2-dioxaborolane (3f): Yield 77%; glassy solid; $[\alpha]^{20}_{D}$ = -105.8 (*c* = 1.05, THF); ^{1}H NMR ($CDCl_3$) δ 1.52 (d, *J* = 6.2 Hz, 3H), 3.81 (s, 3H), 4.47 (dd, *J'* = *J"*= 6.2 Hz, 1H), 5.00 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.36 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.65 (m, 4H), 7.96 (d, *J* = 7.9 Hz, 2H). Anal. Calcd for $C_{22}H_{21}O_3B$: C, 76.77; H, 6.15. Found: C, 76.58; H, 6.23.

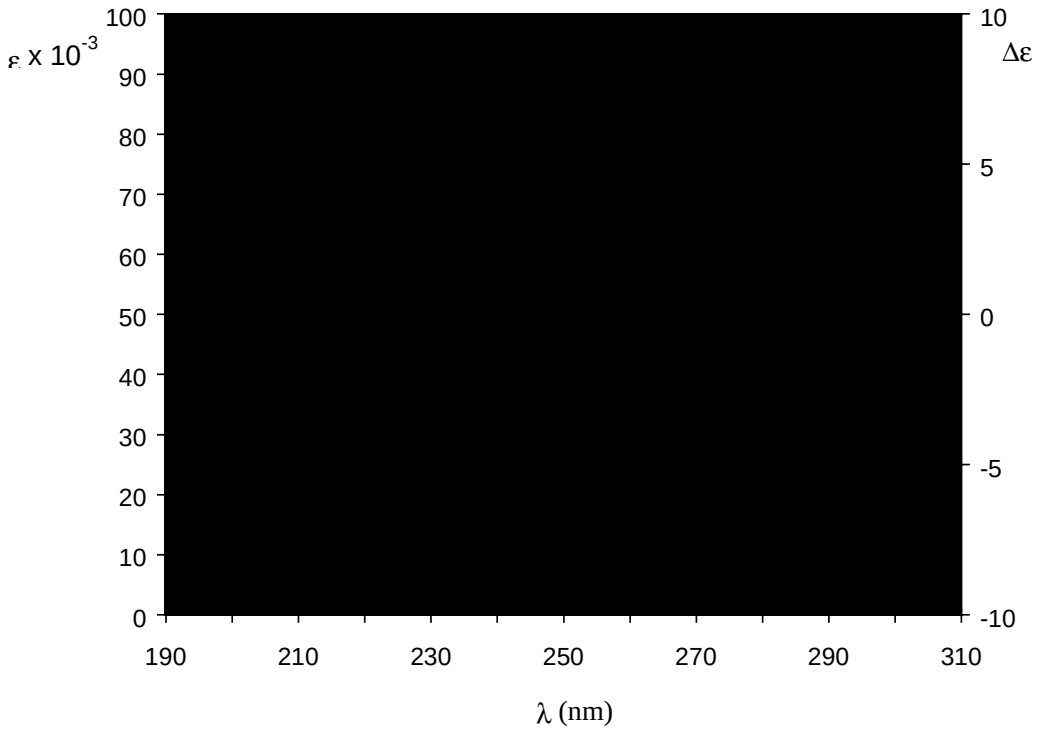

Figure. Absorption (UV) and circular dichroism (CD) spectra of (*R*)-(-)-**1e** in THF in the 190-310 nm range

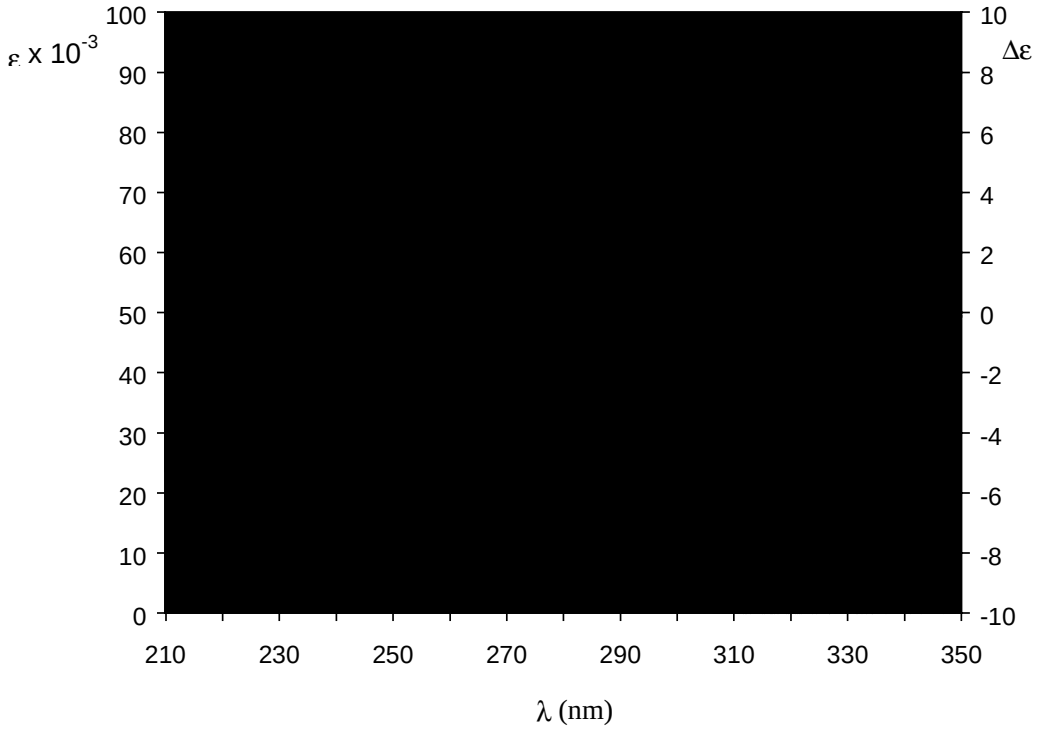

Figure. Absorption (UV) and circular dichroism (CD) spectra of (*R*)-(-)-**3a** in THF in the 210-350 nm range

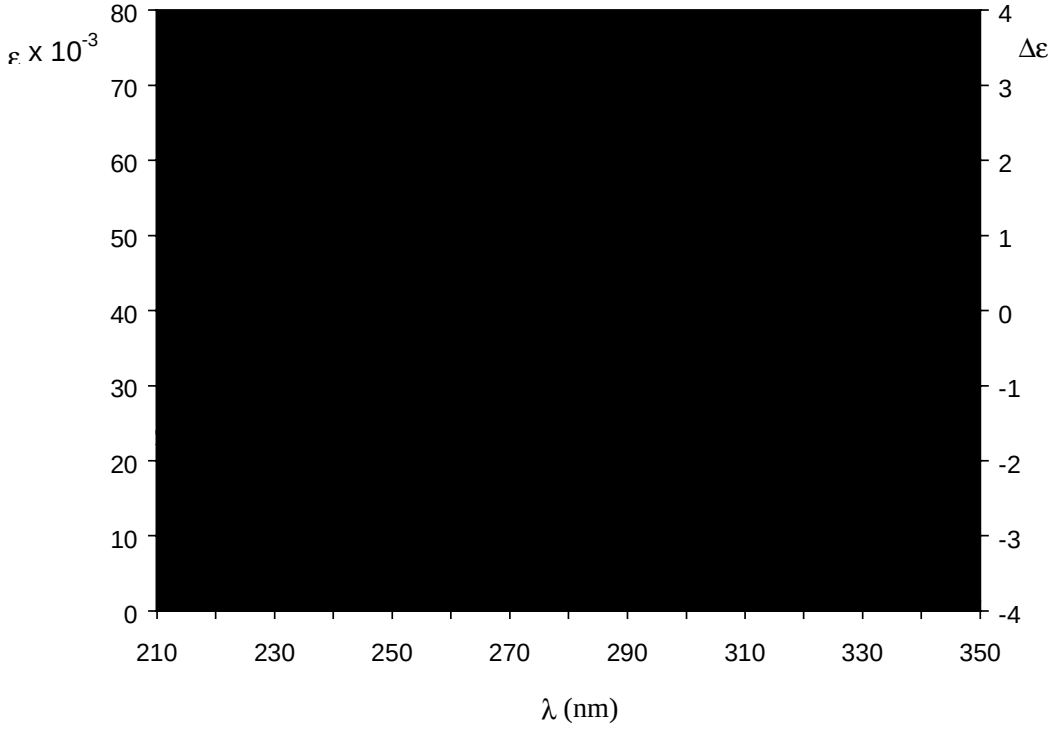

Figure. Absorption (UV) and circular dichroism (CD) spectra of (*R*)-(-)-**3c** in THF in the 210-350 nm range

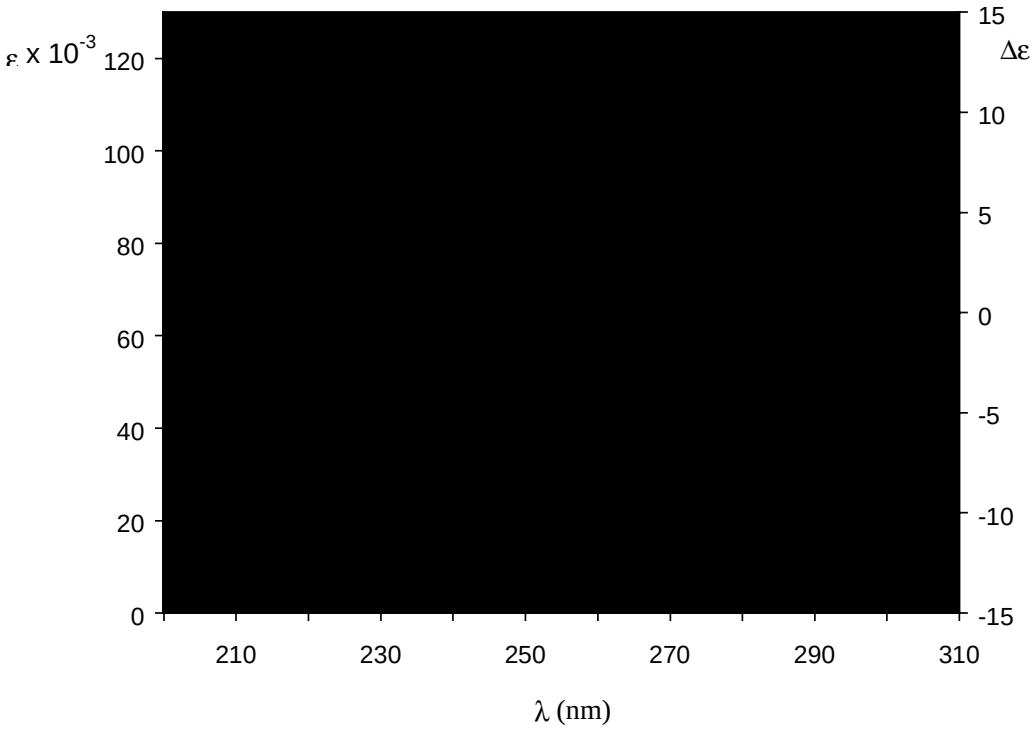

Figure. Absorption (UV) and circular dichroism (CD) spectra of (*R*)-(-)-**3e** in THF in the 200-310 nm range

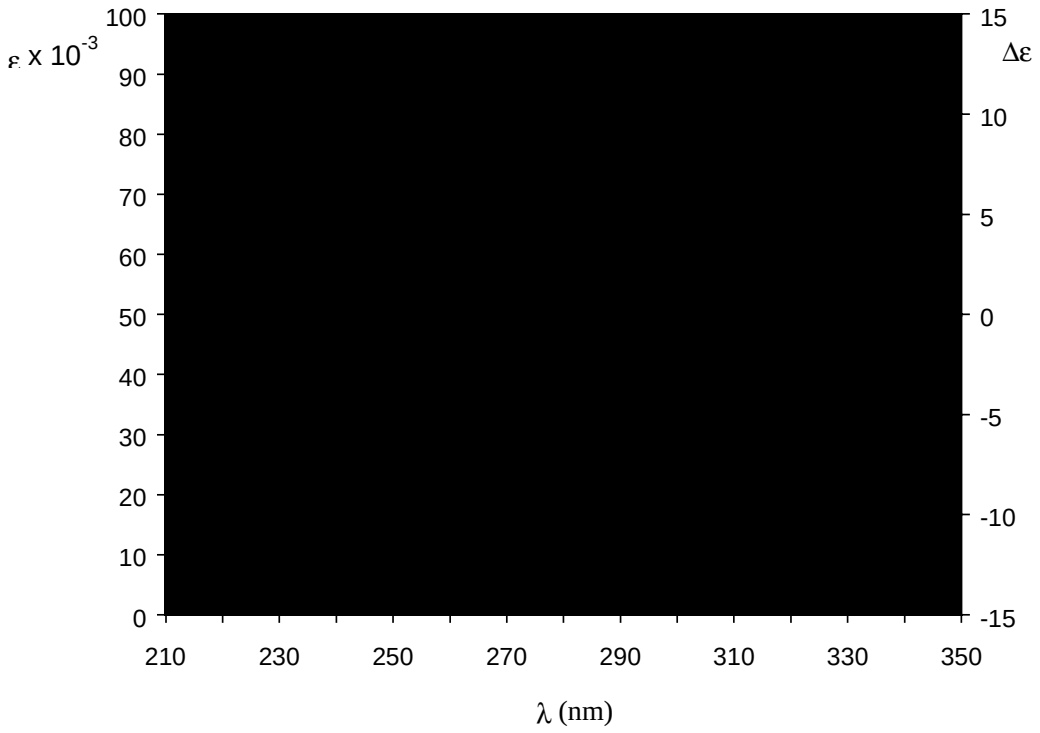

Figure. Absorption (UV) and circular dichroism (CD) spectra of (*R*)-(-)-**3f** in THF in the 210-350 nm range