

## Detailed Experimental Section

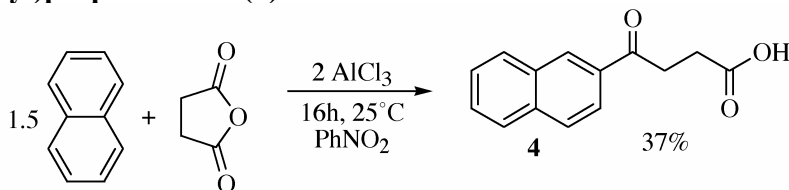
### General Methods.

All air and/or moisture sensitive compounds were manipulated using standard high-vacuum line, Schlenk, on cannula techniques, or in a glove box under a nitrogen atmosphere as described previously.<sup>i</sup> All solvents were stored under vacuum over sodium benzophenone ketyl, titanocene, or calcium hydride prior to use. Solvents used in metallation reactions were degassed before use and inert gas was purified by passing through 4Å molecular sieves and Engelhard Q5 catalyst.

Magnetic susceptibilities were measured at 296 K using a Magway Mk1 magnetic susceptibility balance. The instrument was calibrated with Hg[Co(NCS)<sub>4</sub>] standard. Magnetic susceptibilities of the iron salen complexes were corrected for metal core electrons and the diamagnetism of the free ligands. Effective magnetic moments were calculated from the corrected susceptibilities as  $\mu_{\text{eff}} = (8\chi_{\text{MT}})^{1/2}$ . NMR data were collected on a Varian Unity 400 MHz spectrometer using the residual solvent protons as an internal standard. UV-vis data were collected on a Varian Cary 500 spectrometer and CD data were collected using a JASCO 720 Spectropolarimeter. Samples for these techniques were prepared using dried spectroscopic grade tetrahydrofuran and  $2.5 \times 10^{-5}$  M solutions were loaded into a 1 cm quartz cell. UV-visible and CD data were collected at ambient temperature.

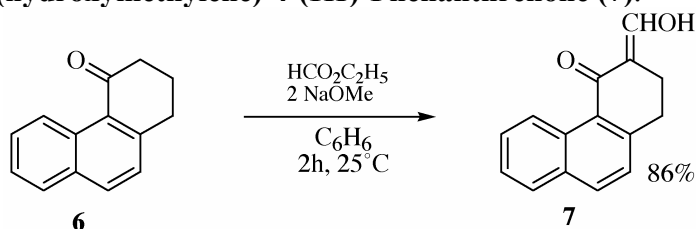
3-(2-Naphthoyl)propionic acid (**4**) was prepared by the method of Haworth<sup>ii</sup> and purified *via* a simplified workup procedure. Literature methods were used for the preparation of 4-(2-Naphthyl)butanoic acid (**5**)<sup>iii</sup> and 1,2,3,4-tetrahydrophenanthren-4-one (**6**).<sup>iv</sup> 2,3-Dihydro-3-(hydroxymethylene)-4-(*1H*)-phenanthrenone (**7**) was synthesized using a methodology described by Cagniant and Kirsch for similar compounds<sup>v</sup> and 4-hydroxy-3-phenanthrenecarboxaldehyde (**2**) was synthesized using the methods outlined by Meyer<sup>vi</sup> *et al.* and by Cagniant and Kirsch (complete procedures and characterization information were not reported and so will be detailed herein).

### 3-(2-Naphthoyl)propionic acid (**1**).



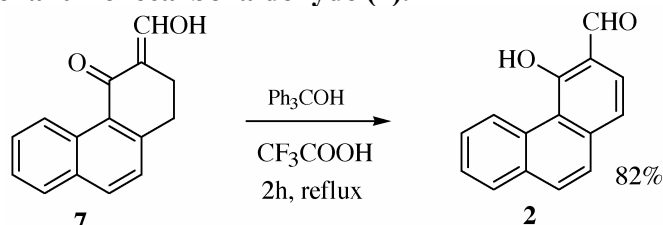
From 72 g of naphthalene. Modified workup as follows. The reaction mixture was poured into crushed ice (300 g) and acidified with 5 M HCl (200 mL). Upon vigorous stirring a brown precipitate formed. The mixture was filtered and the resultant solid washed with H<sub>2</sub>O (150 ml) and hexanes (150 mL). The solid was suspended into benzene (300 mL) at 60°C for 15 minutes, allowed to cool, and filtered to give **4** (31.81 g, 37% yield).

**2,3-Dihydro-3-(hydroxymethylene)-4-(1*H*)-Phenanthrenone (7).**



To a solution of **6** (23.53 g, 120 mmol) in benzene (350 mL) was added ethyl formate (8.88 g, 120 mmol), and sodium methoxide (12.95 g, 240 mmol). The reaction mixture was stirred for 12 h at room temperature and the resulting precipitate collected and washed with benzene (2 X 50 mL). The solid was then dissolved into 1 M NaOH (500 mL), and the aqueous solution washed with hexanes (3 X 100 mL). Acidification to pH 1 with 5 M HCl gave a precipitate that was extracted into diethyl ether (3 X 150 mL), and the extracts were combined, dried over  $\text{MgSO}_4$ , filtered, and concentrated to give **4** (23.12 g, 86% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  2.56 (t, 2 H,  $J = 7.1$  Hz,  $\text{CH}_2$ ), 3.05 (t, 2 H,  $J = 7.1$  Hz,  $\text{CH}_2$ ), 7.36 (d, 1 H,  $J = 8.2$  Hz, CH), 7.50–7.54 (m, 1 H, CH), 7.61–7.66 (m, 1 H, CH), 7.82–7.87 (m, 2 H, CH), 7.94 (d, 1 H,  $J = 8.2$  Hz, CH), 9.26 (d, 1 H,  $J = 8.7$  Hz, CH), 15.06 (d, 1 H,  $J = 8.8$  Hz, OH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  23.77, 31.30, 110.90, 126.09, 126.63, 126.72, 127.65, 128.52, 128.70, 131.39, 133.43, 134.18, 144.58, 169.32, 189.98. Anal. Calcd for  $\text{C}_{15}\text{H}_{12}\text{O}_2$ : C 80.34, H 5.39. Found: C 80.07, H 5.47.

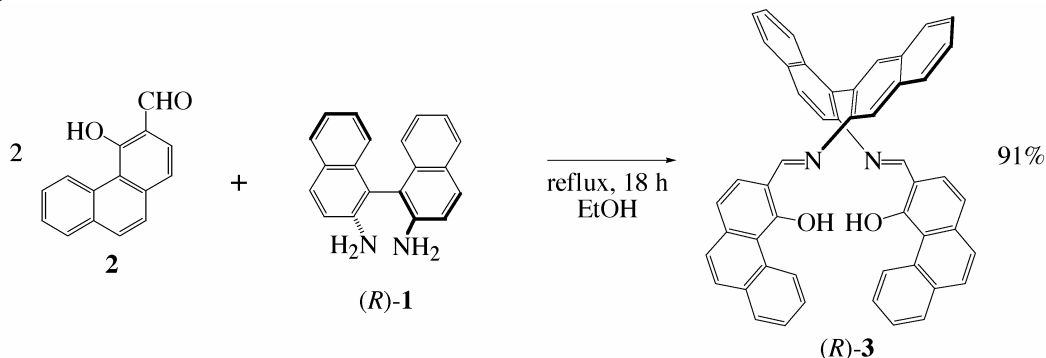
**4-Hydroxy-3-phenanthrenecarboxaldehyde (2).**



(Method A) To a solution of **7** (18.61 g, 83 mmol) in dioxane (200 mL) was added DDQ (18.84 g, 83 mmol) and acetic acid (13 mL). After stirring at room temperature for 1.5 h, the solution was filtered to remove DDQ byproduct, and the dioxane solution concentrated to a brown oil. The oil was dissolved into diethyl ether (400 mL), washed with 1 M  $\text{NaHCO}_3$  (3 X 100 mL), and with 1 M HCl (1 X 100 mL). The organic layer was dried over  $\text{MgSO}_4$ , filtered, and concentrated to give **2** (7.77 g, 42% yield) as a light brown solid. (Method B) A mixture of **7** (22.82 g, 102 mmol) and triphenylmethanol (52.98 g, 204 mmol) in trifluoroacetic acid (400 mL) was refluxed for 2 h. After allowing to cool, the solution was diluted with  $\text{H}_2\text{O}$  (800 mL). The resulting precipitate was collected and suspended into 1 M NaOH (400 mL), and after stirring for 15 minutes, filtered to remove insoluble solids. The filtrate was adjusted to pH 1 with 5 M HCl to yield a yellow precipitate that was collected, washed with  $\text{H}_2\text{O}$  (200 mL), and recrystallized from boiling ethanol to give **2** (5.68 g, 82% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.50 (d, 1 H,  $J = 8.3$  Hz, CH), 7.64–7.80 (m, 4 H, CH), 7.93–7.96 (m, 2 H, CH), 9.83 (d, 1 H,  $J = 8.2$  Hz, CH), 10.05 (s, 1 H, CH), 13.56 (s, 1 H, OH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,

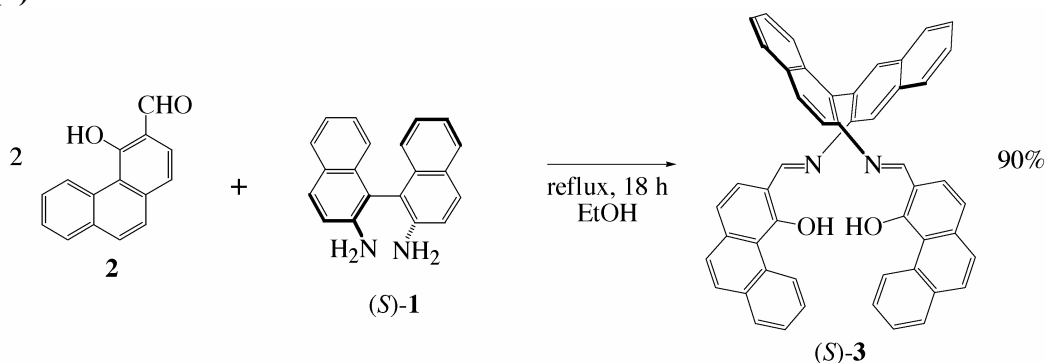
100 MHz):  $\delta$  117.10, 119.85, 120.52, 126.68, 126.83, 127.99, 128.72, 128.84, 129.39, 131.21, 132.65, 139.44, 164.16, 196.78 (one signal not observed). Anal. Calcd for  $C_{15}H_{10}O_2$ : C 81.07, H 4.54. Found: C 81.24, H 4.75.

**3,3'-[(1*R*)-[1,1'-binaphthalene]-2,2'-diylbis(nitrilomethylidene)]bis-4-Phenanthrenol, (*R*)-3.**



A mixture of **2** (2.077 g, 9.3 mmol) and (*R*)-1,1'-Binaphthyl-2,2'-diamine, (*R*)-1, (1.329 g, 4.7 mmol) in ethanol (100 mL) was brought to reflux. After 18 h the resultant suspension was hot filtered, and the precipitate washed with boiling ethanol (40 mL) to give (*R*)-3 (2.958 g, 91% yield) as a bright red solid.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  7.16 (d, 2 H,  $J = 8.2$  Hz, CH), 7.25 (d, 2 H,  $J = 8.2$  Hz, CH), 7.38–7.43 (m, 2 H, CH), 7.50–7.60 (m, 8 H, CH), 7.64–7.69 (m, 2 H, CH), 7.75 (d, 2 H,  $J = 8.6$  Hz, CH), 7.81–7.85 (m, 4 H, CH), 8.12 (d, 2 H,  $J = 8.2$  Hz, CH), 8.24 (d, 2 H,  $J = 8.8$  Hz, CH), 8.80 (s, 2 H, CH), 9.44 (d, 2 H,  $J = 8.6$  Hz, CH), 15.19 (s, 2 H, OH).  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  115.23, 116.89, 118.58, 120.37, 125.95, 126.27, 126.78, 126.91, 127.11, 117.55, 128.35, 128.54, 128.77, 129.16, 130.43, 130.78, 131.58, 132.55, 133.13, 133.78, 137.01, 142.44, 160.38, 165.71 (one signal not observed). Anal. Calcd for  $C_{50}H_{32}N_2O_2$ : C 86.68, H 4.66, N 4.04. Found: C 86.93, H 4.85, N 4.25. Crystals suitable for X-ray analysis were grown from methylene chloride over which was layered hexanes.

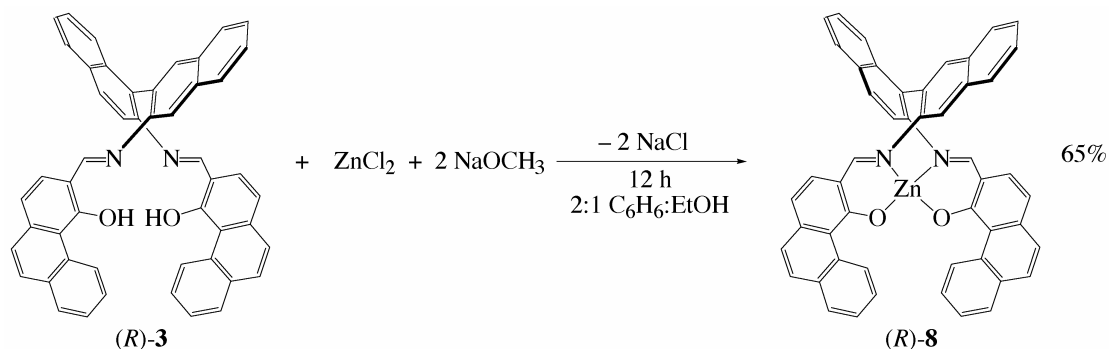
**3,3'-[(1*S*)-[1,1'-binaphthalene]-2,2'-diylbis(nitrilomethylidene)]bis-4-Phenanthrenol, (*S*)-3.**



The procedure for (*R*)-3 was followed using (*S*)-1,1'-Binaphthyl-2,2'-diamine, (*S*)-1, in place of the (*R*) enantiomer to give (*S*)-3 (1.487 g, 90% yield).  $^1H$  and  $^{13}C$  NMR spectra were identical to that of compound (*R*)-3. Anal. Calcd for  $C_{50}H_{32}N_2O_2$ : C 86.68, H 4.66,

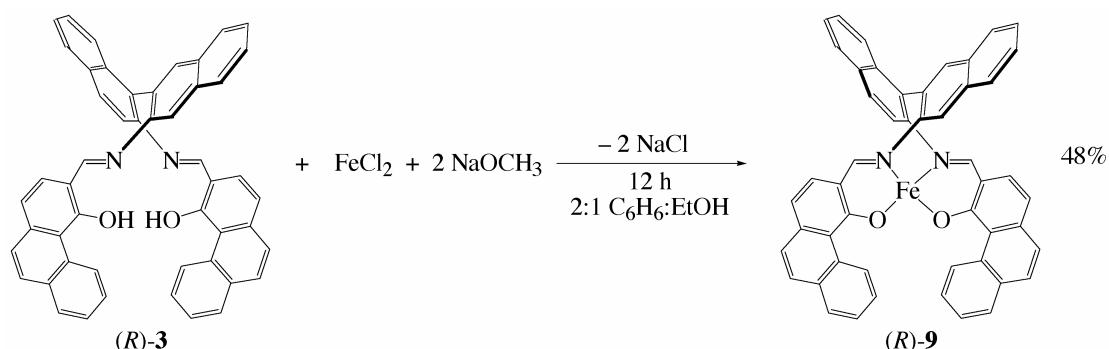
N 4.04. Found: C 86.66, H 4.88, N 4.12.

**(R)-8** (Zn(II) complex of **(R)-3**).



Zinc chloride (0.065 g, 0.48 mmol), sodium methoxide (0.070 g, 1.30 mmol) and **(R)-3** (0.300 g, 0.43 mmol) were suspended into a 2:1 mixture of benzene/ethanol (15 mL). After stirring overnight the reaction mixture was concentrated to a yellow solid that was dissolved into methylene chloride (15 mL). The solution was carefully filtered to remove fine insoluble solids, and the clear filtrate diluted with ethanol (45 mL). Upon stirring for 3 h a yellow precipitate formed that was collected to afford **(R)-8** (0.213 g, 65%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  6.97 (d, 2 H,  $J = 8.5$  Hz, CH), 7.05 (d, 2 H,  $J = 8.3$  Hz, CH), 7.18 (d, 2 H,  $J = 8.3$  Hz, CH), 7.25 (t, 2 H,  $J = 7.6$  Hz, CH), 7.41–7.53 (m, 8 H, CH), 7.58 (d, 2 H,  $J = 8.7$  Hz, CH), 7.83–7.92 (m, 6 H, CH), 8.02 (d, 2 H,  $J = 8.6$  Hz, CH), 8.52 (s, 2 H, CH), 10.57–10.62 (m, 2 H, CH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  115.40, 116.06, 122.17, 124.34, 125.67, 125.82, 126.53, 126.81, 126.87, 127.27, 127.74, 128.30, 128.57, 128.87, 131.01, 131.70, 132.32, 132.60, 132.92, 132.98, 134.25, 139.14, 145.53, 170.26, 174.26. Anal. Calcd for  $\text{C}_{50}\text{H}_{30}\text{N}_2\text{O}_2\text{Zn}$ : C 79.42, H 4.00, N 3.70. Found: C 79.06, H 3.86, N 3.77. Crystals suitable for X-ray analysis were grown from methylene chloride over which was layered methanol.

**(R)-9** (Fe(II) complex of **(R)-3**).



The procedure for **(R)-8** was followed using anhydrous iron (II) chloride, and with THF in place of methylene chloride during work-up. It was also necessary to concentrate the THF/ethanol solution to  $\frac{3}{4}$  volume for precipitation of the product to occur. The product,

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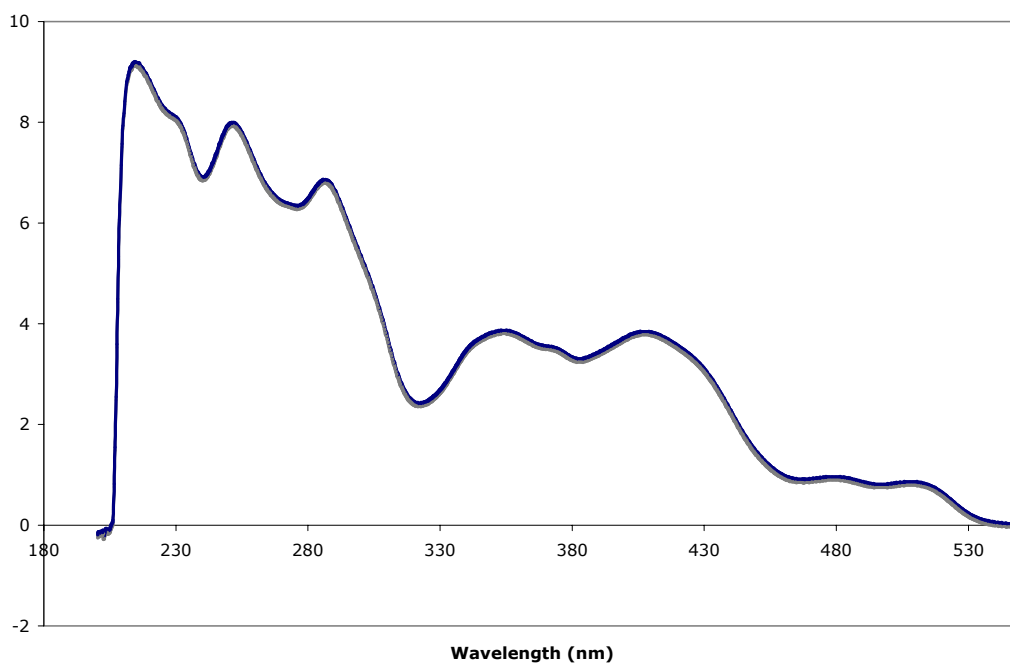
(*R*)-**9**, was afforded as a red-brown powder (0.156 g, 48% yield). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ -39.04 (br, s, 2 H, CH), -15.27 (s, 2 H, CH), -9.23 (s, 2 H, CH), -7.60 (s, 2 H, CH), 0.56 (s, 2 H, CH), 1.28 (s, 2 H, CH), 10.68 (s, 2 H, CH), 11.68 (s, 2 H, CH), 12.08 (s, 2 H, CH), 13.71 (s, 2 H, CH), 15.29 (s, 2 H, CH), 24.52 (s, 2 H, CH), 60.63 (br, s, 2 H, CH).  $\mu_{\text{eff}} = 5.05$ . Anal. calc. for C<sub>50</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>Fe: C 80.43, H 4.05, N 3.75. Found: C 80.46, H 3.84, N 3.90.

(*R/S*)-**9** (Fe(II) complex of (*R/S*)-**3**).

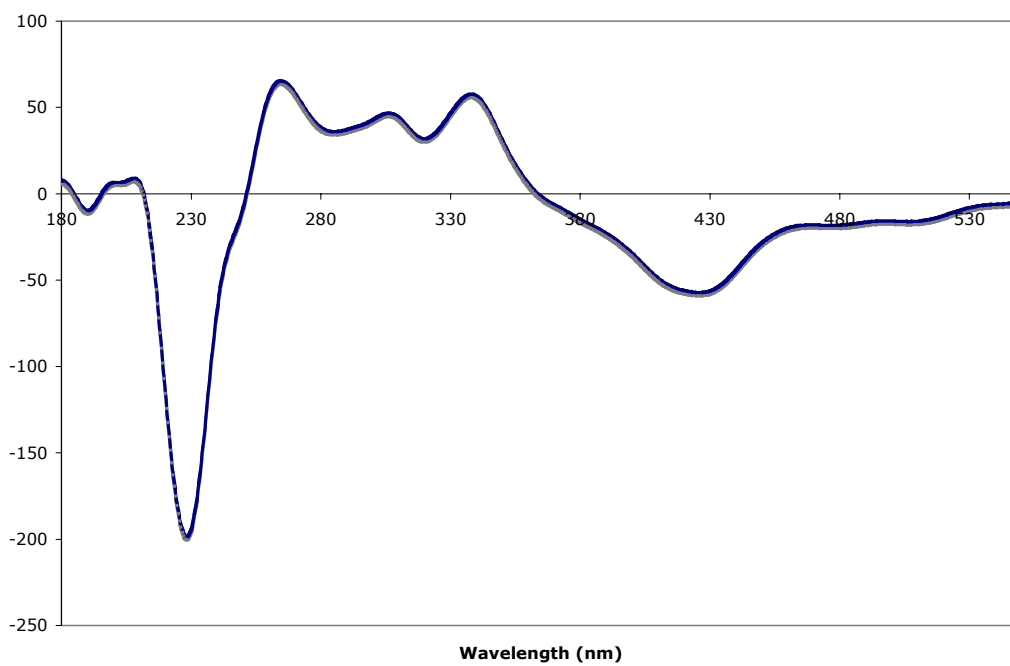
The procedure for (*R*)-**8** was followed using anhydrous iron (II) chloride, with a 1:1 mixture of (*R*)-**3** and (*S*)-**3** in place of pure (*R*)-**6**, and THF in place of methylene chloride during work-up. The racemic product, (*R/S*)-**9**, was afforded as a red-brown powder (0.206 g, 64% yield). <sup>1</sup>H NMR spectra were identical to that of compound (*R*)-**9**. Crystals suitable for X-ray analysis were grown from methylene chloride over which was layered methanol. Anal. Calcd for C<sub>50</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>Fe: C 80.43, H 4.05, N 3.75. Found: C 80.73, H 3.80, N 3.57.

### UV-Visible and CD Spectra

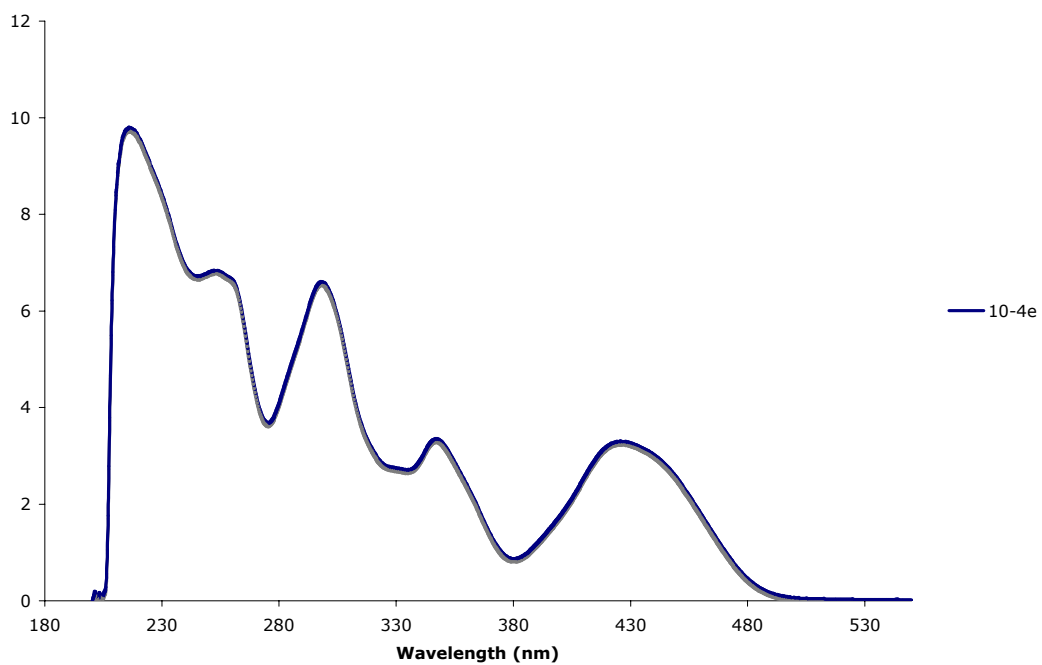
UV-Visible Spectrum of (R)-3



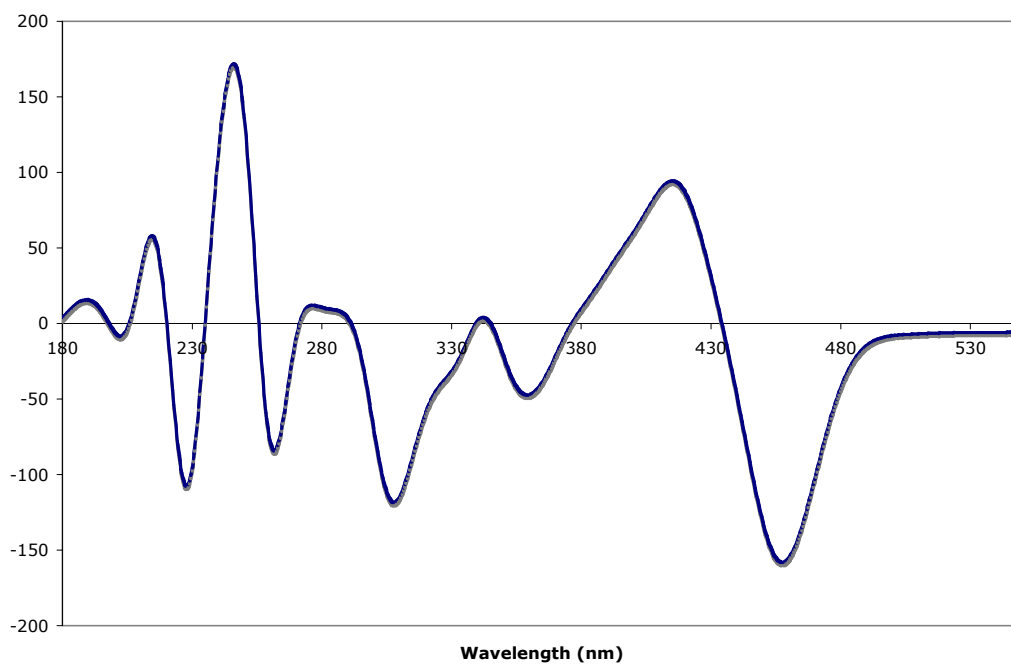
CD Spectrum of (R)-3



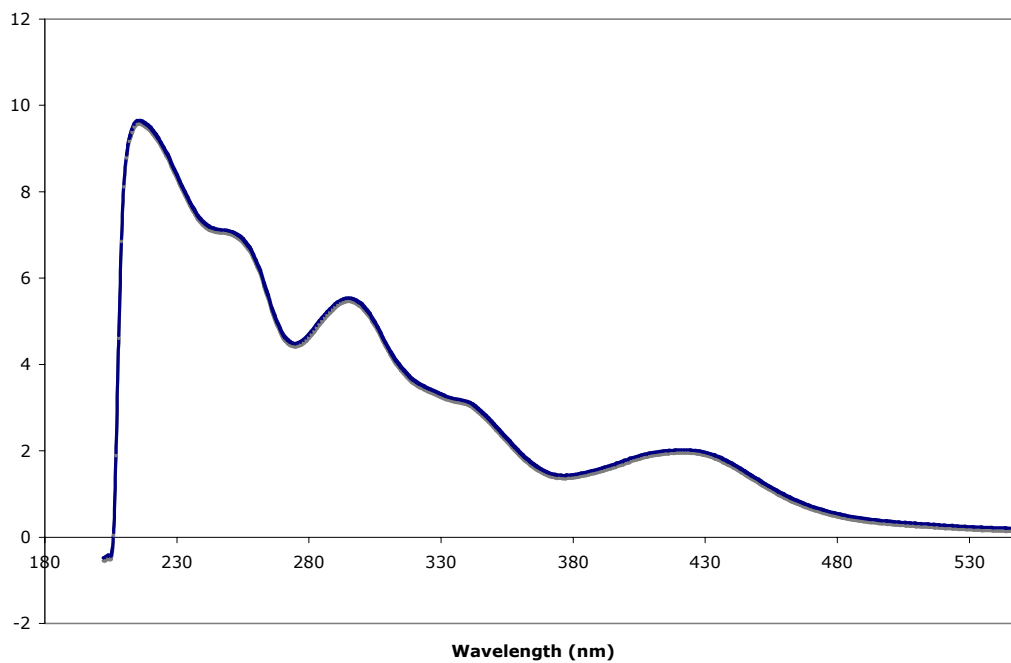
**UV-Visible Spectrum of (R)-8**



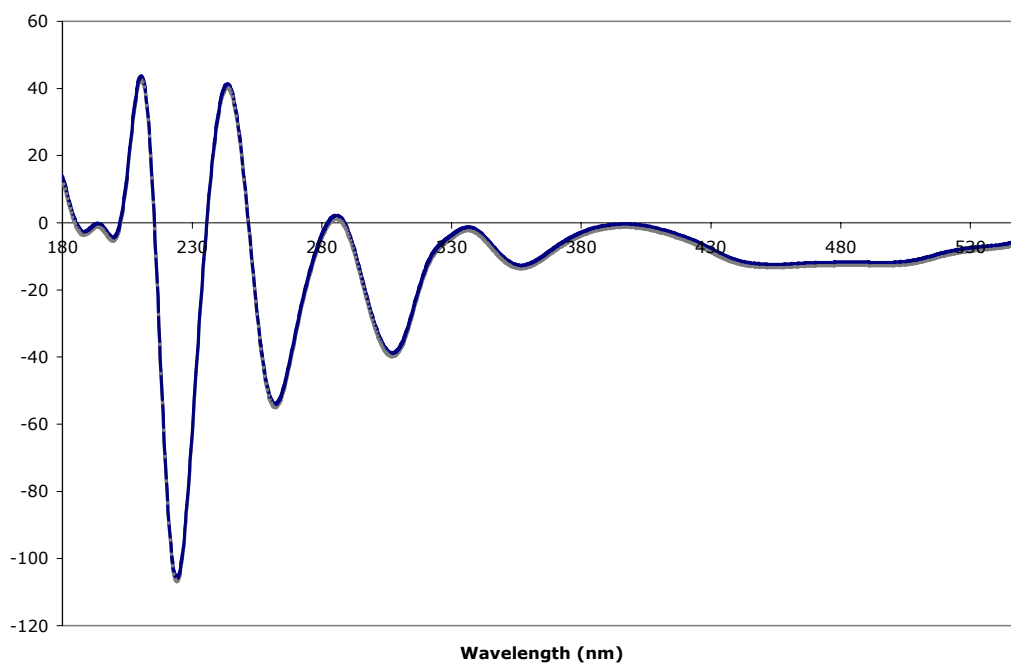
**CD Spectrum of (R)-8**



**UV-Visible Spectrum of (R)-9**



**CD Spectrum of (R)-9**





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