Supporting Information

General information: The following section provides general information. Immediately following this information are general and/or specific reaction conditions and spectral data for compounds along with a representative ^{1}H NMR spectrum.

Reactions were monitored by analytical thin-layer chromatography on EM-Science hard layer silica gel-60^{F-250} plates cut into 1x2.5^{cm} sections. Visualization was effected by ultraviolet light (254 nm), followed by dipping the plate into the appropriate stain and charring on a *Fisher*® micro-hot plate. The primary stain was made with [25 g of phosphoromolybdic acid and 10 g of cerium sulfate and 60 mL H_2SO_4 and 940 mL of H_2O]. Distillations were accomplished with a short-path condenser configured with multiple receiving flasks. A specific low pressure (760-1 mm Hg) was obtained and monitored with a *Buchi*®-vacuum controller model number B-721 in combination with a *Welch*® direct drive pump model number 8915A. Lower pressures were achieved using a vacuum manifold connected to an oil-diffusion pump and backed by a *Welch*® direct drive vacuum pump model number 8910A. Chromatography was performed following the method prescribed by W. C. Still.[1] In reactions, where water was <u>*not*</u> present as a solvent, reagent or by-product, vessels were flame-dried under a slow nitrogen flow. A slight positive pressure of dry nitrogen was maintained via rubber septa seal during the course of the reaction. The nitrogen stream originated from a high pressure 55 L *(l)* N_2 tank and was further dried by passing through a Drierite® tube. Reagents were purified according to the procedures describe in the *Perrin & Perrin* laboratory manual. All reactions were stirred with Teflon-coated magnetic stir bars via *Thomas*® magnetic stirrers. Removal of solvents was normally accomplished using a *Buchi*® rotary evaporator model number R-114 connected to a KNF®-vacuum pump model number UN820-3 from Fisher. The condener was cooled to 30 ^oC by a Fisher® chiller circulator bath model number 1013S. Trace solvents were removed by a *Labconco*® freeze dryer system at a pressure of approximately 0.01 mm Hg. The following solvents were distilled before use, under a slight positive pressure of nitrogen. Diethyl ether was distilled from sodium benzophenone ketyl. Methylene chloride, di-*n*-butyl ether and acetone were distilled from calcium hydride. The chloroform, isopropyl alcohol and hexanes used for infrared spectra and HPLC analyses. Acetonitrile was distilled over CaH_2 for circular dichroism spectra. Melting points were determined on a *Fisher-Johns*® melting point apparatus and are uncorrected. ^{1}H-NMR were recorded at 400 MHz or 500 MHz on a *Varian*® spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance of $CDCl_3$ (7.27 ppm) as the internal standard. Chemical ^{13}C NMR spectra were recorded at (100 MHz) with a solvent resonance of $CDCl_3$ (77.23 ppm) as the internal standard. Infrared spectra were recorded on a *Shimadzu*® Fourier transform infrared spectrometer with 2 cm resolution in a solution cell (CH_2Cl_2). Infrared frequencies are reported in reciprocal centimeters (cm^{-1}). HPLC analyses for enantiomer excess were performed isochratically using a *Shimadzu*® HPLC system (10 mL/min pump and dual channel UV detector) with a Chiracel OF column with a flow rate of 10 mL/min at 35 ^oC using 9:1 hexanes/isopropanol as the solvent system. Columns for nonchiral HPLC were supplied by *Jones*® Chromatography 25 cm long and contained 5 μ spherisorb. Circular dichroism spectra were recorded on an Aviv CD spectrophotometer model 202 at 25 ^oC. Optical rotations were recorded on a Perkin Elmer Polarimeter model 341 at 20 ^oC. Mass spectra were recorded on a VG-7035 mass spectrometer at an ionizing voltage of either 70 or 20 eV.

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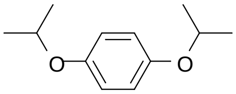
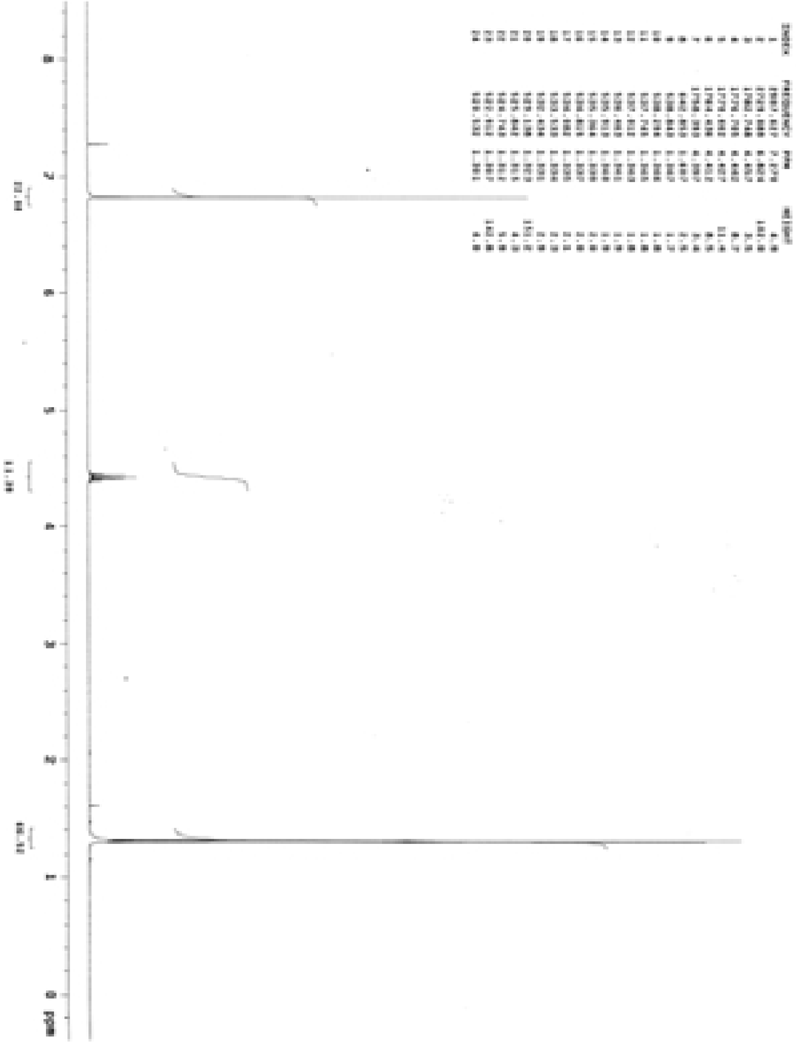
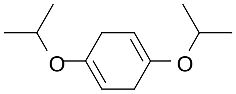
[1] Still, W. C.; Kahn, K.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2924.

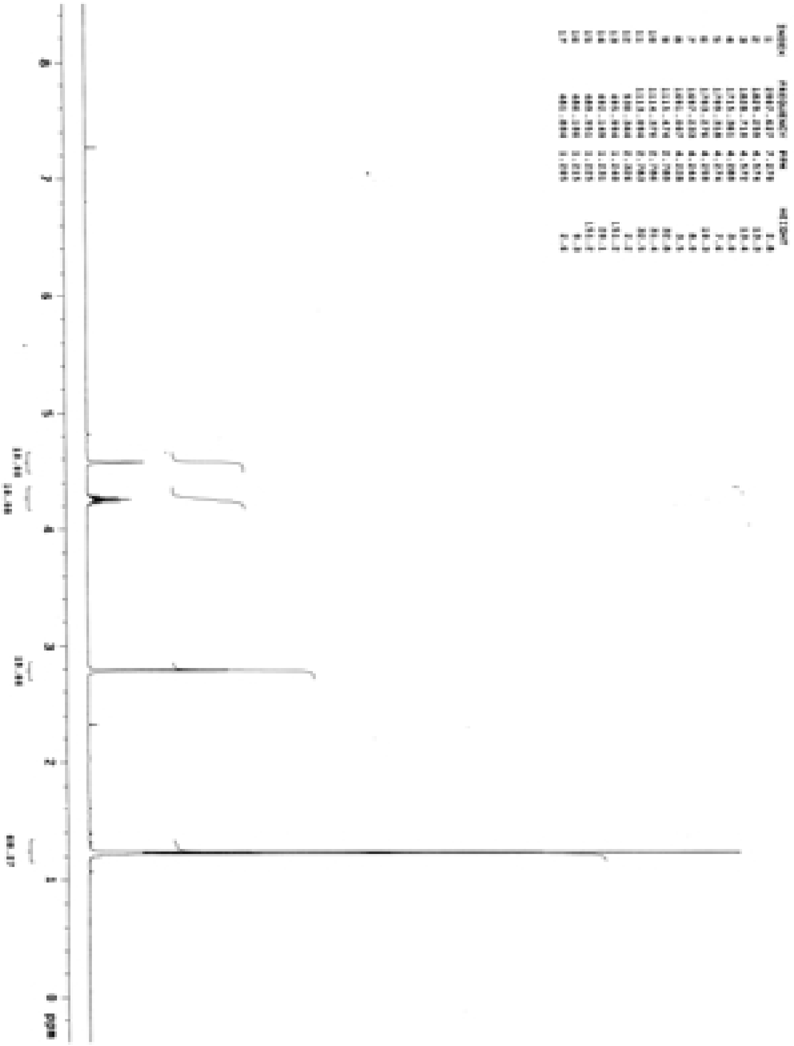
1,4-Diisopropoxybenzene. This compound is also commercially available from Wako BioProducts. A mixture of hydroquinone (1.5 g, 14 mmol), K_2CO_3 (7.5 g, 54 mmol) and tetrabutylammonium iodide (500 mg, 1.37 mmol) in acetone was permitted to stir at room temperature. 2-Bromopropane (5.0 g, 40.7 mmol) was added and the solution was allowed to reflux for one day. The resulting cooled mixture was filtered and concentrated to give a crude dark brown liquid. Chromatography on silica gel employing 95:5 petroleum ether/EtOAc yielded 2.4 g (91%) of the product as a clear yellow liquid. ^{1}H NMR [$CDCl_3$, 400 MHz] δ 6.82 (s, 2H), 4.43 (septet, 1H, J=6.0 Hz), 1.31 (d, 6H, J=6.2 Hz); ^{13}C NMR [$CDCl_3$, 100.6 MHz] δ152.1, 117.5, 71.0, 22.3; IR [CH_2Cl_2 solution, ν_{max}cm^{-1}] 3051, 2980, 2935, 1504, 1383, 1373, 1218, 1116.



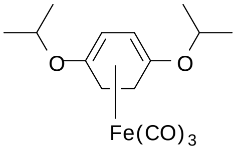


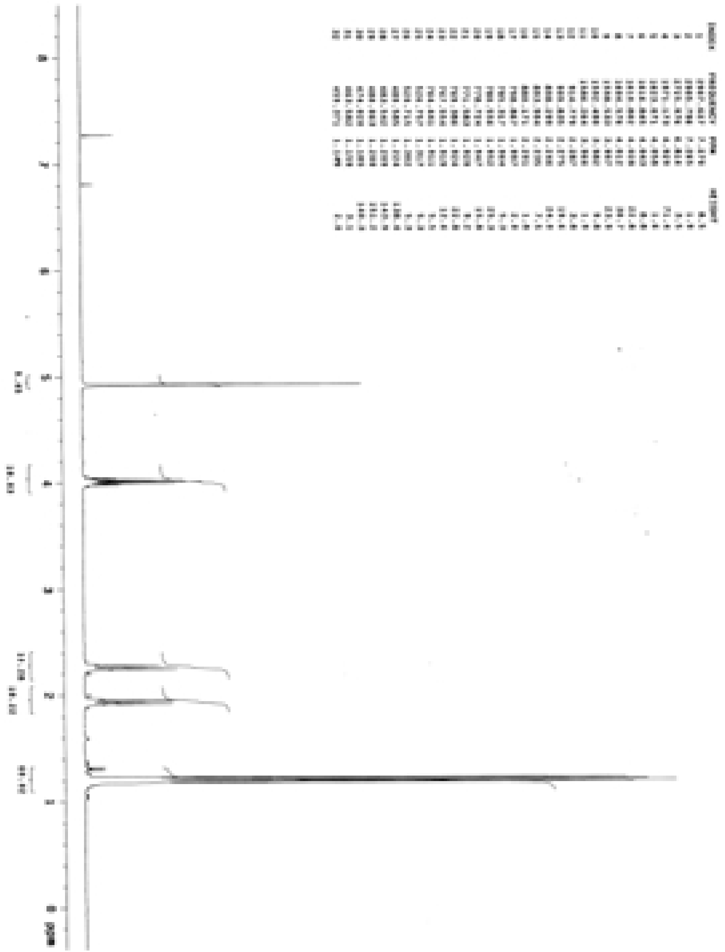
1,4-Diisopropoxy-1,4-cyclohexadiene (18). 1,4-Diisopropoxybenzene (2.4 g, 12 mmol) was dissolved in 100 mL of diethyl ether and cooled to -78 °C. Anhydrous NH_3 (~250 mL) was condensed utilizing a CO_2 condensor. Li metal (0.5 g, 74 mmol) was added followed by *t*-BuOH (3.3 g, 4.51 mmol). The resulting mixture was allowed to stir at -78 °C for 6 hours. Solid NH_4Cl was added to quench the reaction. The ammonia was allowed to evaporate overnight. Washing the resulting white solid with Et_2O and filtering generated 2.2 g of a crude yellow solid. Chromatography on silica gel using 20:1 hexanes/Et_2O yields the product (1.5 g, 60%) as a white solid: mp = 57-59 °C ^{1}H NMR [$CDCl_3$, 400 MHz] δ 4.57 (br s, 1H), 4.26 (septet, 1H, J=6.0 Hz), 2.79 (m, 2H), 1.23, (d, 6H, J=6.0 Hz); ^{13}C NMR [$CDCl_3$, 100.6 MHz] δ150.6, 91.4, 67.8, 29.1, 22.1; IR [CH_2Cl_2 solution, ν_{max}cm^{-1}] 3043, 2980, 2834, 1665, 1382, 1196; HRMS (EI) *m/z* (M^+) calcd for $C_{12}H_{20}O_2$ 196.146330, found 196.1466230.





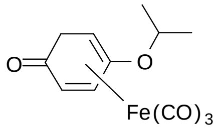
Tricarbonyl[η^4-1,4-diisopropoxy-1,3-cyclohexadiene]iron(0) (1b). $Fe(CO)_5$ 1.46 g, (7.45 mmol) was dissolved in 5 mL of di-*n*-butyl ether (freshly filtered through basic alumina). This mixture was then added to **18** (504 mg, 2.57 mmol). The reaction mixture was allowed to reflux for 18 hours under argon. The black liquid was then filtered through a pad of celite and concentrated to give 344.3 mg of crude. Chromatography on silica gel using 20:1 hexanes/Et_2O yielded 172.7 mg (20%) of a clear yellow liquid. ^{1}H NMR [$CDCl_3$, 400 MHz] δ4.93 (s, 1H), 4.01 (septet, 1H, J=6.2 Hz), 2.26 (m, 1H), 1.93 (m, 1H), 1.21 (d, 3H, J=6.0 Hz), 1.19 (d, 3H, J=6.0 Hz); ^{13}C NMR [$CDCl_3$, 100.6 MHz] δ 214.6, 111.9, 70.9, 69.2, 27.0, 23.9, 22.1; IR [CH_2Cl_2 solution, ν_{max}cm^{-1}] 2978, 2936, 2027, 1948, 1263, 1181; HRMS (EI) *m/z* (M^+-CO) found 308.069926.

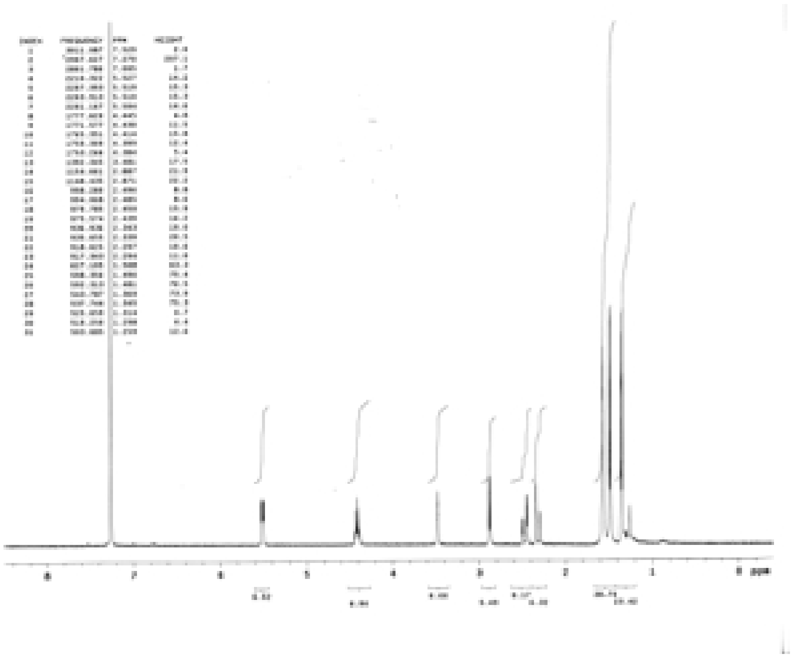




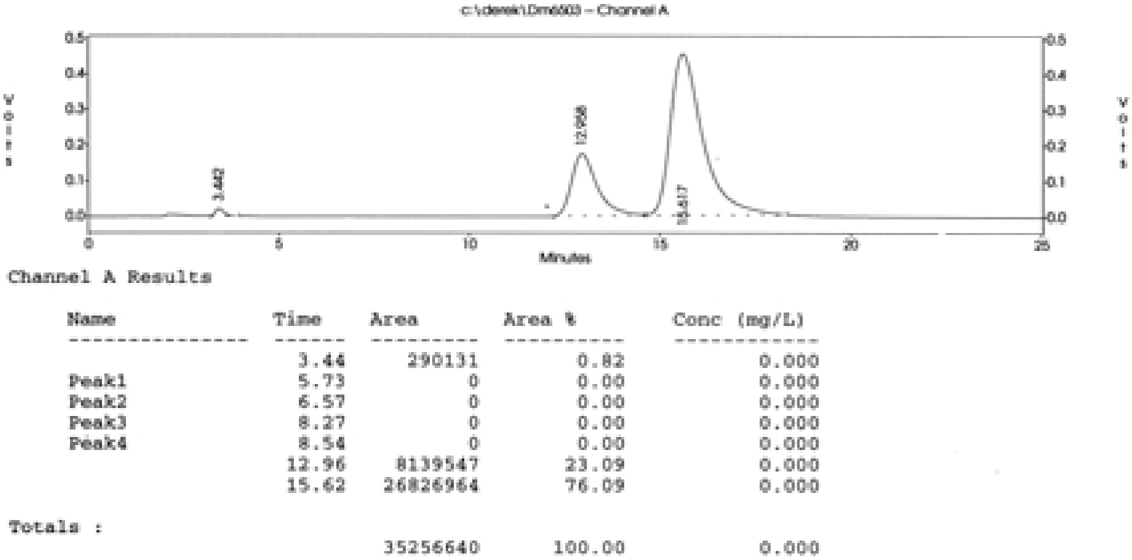
Conversion of 10 to 3. Compound **10** (71.1 mg, 0.208 mmol) was dissolved in propionic anhydride (0.6 mL) and placed in a water bath at room temperature. HPF_6 (78.8 mg, 0.540 mmol) was added dropwise. The flask was swirled after each drop in the water bath in order to maintain room temperature. After the addition of the acid, the resulting red cation usually crystallized out of the solution at room temperature. The flask was cooled to 0 °C and allowed to sit for 1 hour. Dry diethyl ether (10 mL / rinse for 10 times) chilled to 0 °C was added in order to crystallize out any remaining cation in solution and to rinse out the acid plus the anhydride. The resulting red solid cation was placed on a vacuum pump for 6 hours at 0 °C to assure that no trace acid was present to generate **3** (77.6 mg, 79%). The cation was used immediately following this procedure for hydride abstraction.

(2R)-Tricarbonyl[η^4-4S-4-methoxy-2,4-cyclohexadienone]iron(0) (5b). Carbocation **3** (21.8 mg, 0.0527 mmol) was dissolved in CH_2Cl_2 (0.18 mL). A solution of **1b** (17.7 mg, 0.0527 mmol) dissolved in 0.30 mL CH_2Cl_2 was added and the resulting red solution was stirred at room temperature for 10 hours. The reaction mixture was quenched with 1 M $NaHCO_3$ and allowed to stir for five minutes. The mixture was extracted with CH_2Cl_2, washed with brine and dried (Na_2SO_4). Evaporation of solvent gave 24.4 mg of crude residue. Chromatography on silica gel employing 85/15 petroleum ether/EtOAc resulted in 9.4 mg (65 %) of a yellow residue. ^{1}H NMR [$CDCl_3$, 400 MHz] δ5.52 (m, 1H), 4.41(septet, 1H, J=6.0 Hz), 3.48 (m, 1H), 2.88 (d, 1H, J=6.59 Hz), 2.47 (dd, 1H, J_1=18.3, J_2=4.4 Hz), 2.34 (dd, 1H, J_1=18.1 Hz, J_2=1.7 Hz), 1.49 (d, 3H, J=6.0 Hz), 1.35 (d, 3H, J=6.0 Hz); [$CDCl_3$, 100.6 MHz] δ197.8, 139.8, 72.2, 68.3, 53.7, 46.0, 35.0, 22.7, 22.3; ; IR [CH_2Cl_2 solution, $\nu_{max}cm^{-1}$] 2986, 2061, 1992, 1667, 1479, 1223; HRMS (EI) *m/z* (M^+) calcd for $C_{12}H_{12}FeO_{5}$,, 292.003413, found 292.003653; $[\alpha]^{20}_D$ = +40.6, c = 0.76 in CH_3CN.





HPLC Trace of 5b: The HPLC trace was recorded at a flow rate of 10 mL/min at 35 ºC with 9:1 hexanes/isopropanol as the solvent.



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Channel A Results

     Name              Time     Area        Area %        Conc (mg/L)
     ---------------   ------   ---------   ----------    ------------
                        3.44      290131          0.82           0.000
     Peak1              5.73           0          0.00           0.000
     Peak2              6.57           0          0.00           0.000
     Peak3              8.27           0          0.00           0.000
     Peak4              8.54           0          0.00           0.000
                       12.96     8139547         23.09           0.000
                       15.62    26826964         76.09           0.000

Totals :
                                35256640        100.00           0.000
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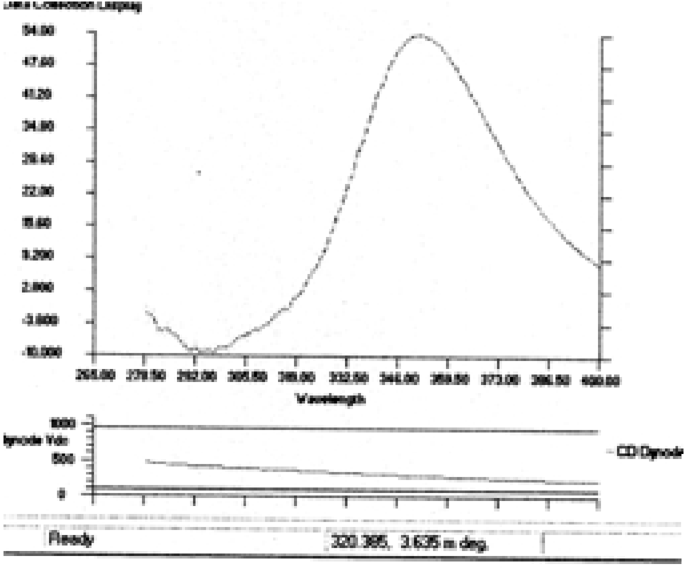
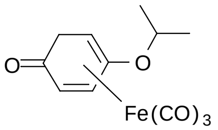
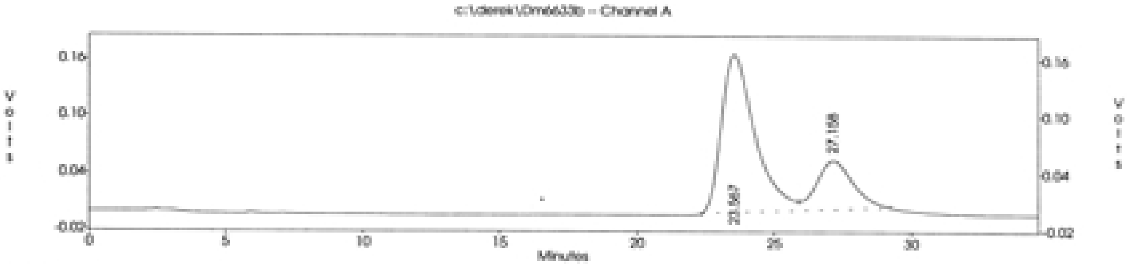
CD Spectra: The CD spectrum was recorded in MeCN (0.0013 M)



Ready 320.385, 3.635 m deg.



HPLC Trace of 5a: The HPLC trace was recorded at a flow rate of 10 mL/min at 35 °C with 9:1 hexanes/isopropanol as the solvent.



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Channel A Results

     Name              Time    Area       Area %        Conc (mg/L)
     ----------------  ------  ---------  ----------    ------------
     Peak1               5.73          0        0.00           0.000
     Peak2               6.57          0        0.00           0.000
     Peak3               8.27          0        0.00           0.000
     Peak4               8.54          0        0.00           0.000
                        23.57   14090163       74.70           0.000
                        27.16    4771775       25.30           0.000

Totals :
                                18861938      100.00           0.000
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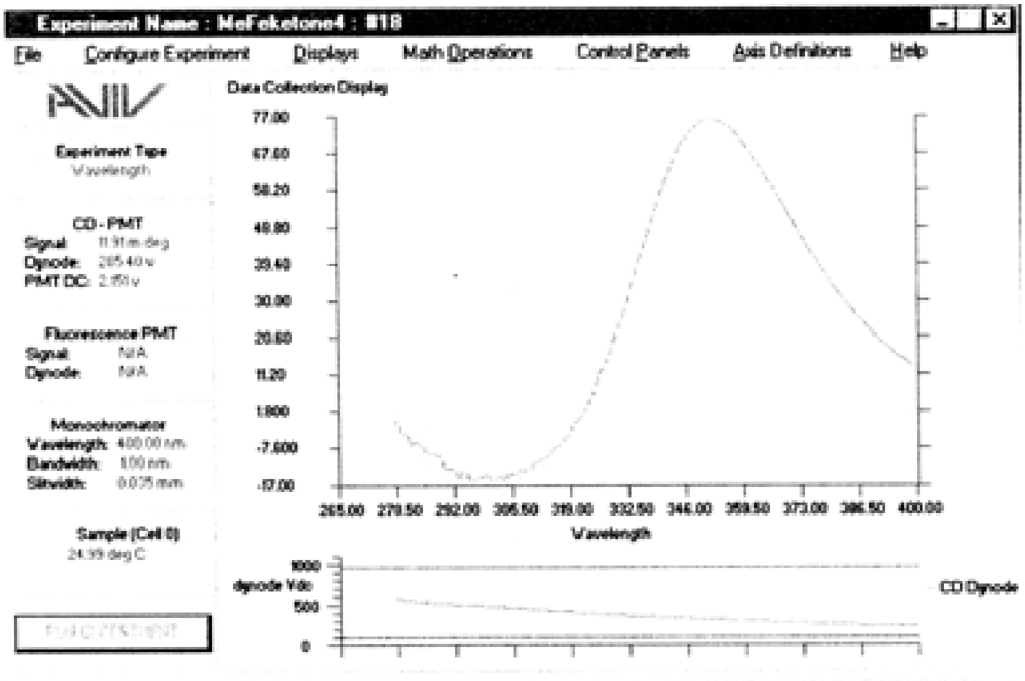
CD Spectra: The CD spectrum was recorded in MeCN (0.0016 M)



Experiment Type
Wavelength

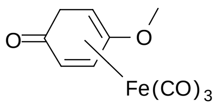
CD - PMT
Signal: 11.91 m deg
Dynode: 285.40 v
PMT DC: 2.65 v

Fluorescence PMT
Signal: N/A
Dynode: N/A

Monochromator
Wavelength: 400.00 nm
Bandwidth: 1.00 nm
Slitwidth: 0.035 mm

Sample (Cell 0)
24.99 deg C

$[\alpha]^{20}_{D}$ = +40.0, c = 0.34 in CH_3CN.



(10R,11R)-10,11-Diethyl-10,11-dihydro-5-phenyl-5*H*-dibenzo[*a,d*]cycloheptene ^{1}H NMR [$CDCl_3$, 400 MHz] δ7.30-7.15 (m, 11H), 7.03 (dd, 2H J_1=7.14 Hz, J_2=1.1 Hz), 5.36 (s, 1H), 2.97 (m, 1H), 2.74 (m, 1H), 1.54 (m, 4H), 0.76 (t, 3H, J=7.33 Hz), 0.51 (t, 3H, J=7.5 Hz); [$CDCl_3$, 100.6 MHz] δ145.8, 142.0, 141.6, 140.8, 140.5, 133.2, 132.8, 131.8, 129.9, 128.2, 127.8, 126.9, 126.7, 125.9, 125.8, 58.6, 50.8, 46.6, 30.9, 28.4, 26.4, 20.7, 12.8, 11.3; IR [CH_2Cl_2 solution, $\nu_{max}cm^{-1}$] 3016, 29.32, 29.65, 1492, 1453; HRMS (EI) *m/z* (M^+) calcd for $C_{25}H_{26}$ 326.203451, found 326.204117; $[\alpha]_D$ at 20 °C = +13, c = 2.1 in CH_2Cl_2.