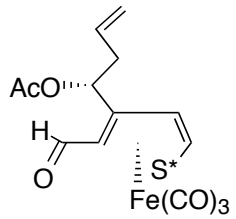
# ENANTIOPURE $\eta^4$-(1-SULFINYLDIENE)IRON(0) TRICARBONYL COMPLEXES AS TEMPLATES FOR CARBOCYCLE CONSTRUCTION VIA RING-CLOSING METATHESIS

Robert S. Paley*, Lara A. Estroff, Jean-Marc Gauguet, Diana K. Hunt, Rebecca C. Newlin

Swarthmore College, Dept. of Chemistry, Swarthmore, PA 19081, USA

## SUPPORTING INFORMATION

**General Methods**. All reactions were carried out under a positive pressure of dry argon. Reagents and solvents were handled by using standard syringe techniques. Tetrahydrofuran (THF), toluene, and ethyl ether were distilled from sodium and benzophenone; methylene chloride (DCM) and amine bases were distilled from $CaH_2$. Anhydrous dimethylformamide (DMF), anhydrous dimethylsulfoxide (DMSO), and anhydrous acetonitrile were purchased from Aldrich and stored under an argon atmosphere. All other solvents were reagent grade and were used as purchased. Flash chromatography was performed using Merck 230-400 silica gel 60. Analytical TLC was carried out on Merck silica gel 60 F-254 pre-coated glass plates, with detection by UV light and acidic vanillin solution or PMA solution in ethanol. Melting points were determined in a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra (IR) were obtained on a Perkin-Elmer 681 or 1600 Series FT-IR. $^1H$ and $^{13}C$ NMR spectra were recorded on a Brüker DRX-400 (400 MHz) spectrometer using $CDCl_3$ as solvent (unless otherwise noted) and with the residual solvent signal as internal reference ($CDCl_3$, 7.24 and 77.0 ppm). The following abbreviations are used to describe peak patterns where appropriate: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), app (apparent), br (broad). Chemical shifts are reported as $\delta$ units from tetramethylsilane as internal standard. Mass spectrometry data were obtained at the UCR Mass Spectrometry Facility, Department of Chemistry, University of California at Riverside.



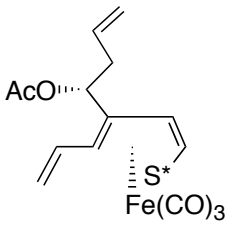

**3**

**$\eta^4$–$\alpha$–[($R_s$)-(1*Z*,3*E*)-3-[(*R*)-1-Acetoxybut-3-enyl]-1-*p*-tolylsulfinyl-1,3-pentadien-5-al]tricarbonyl iron(0) complex (3).** Alcohol **2**[1] (689.0 mg, 1.17 mmol, 1 eq) was dissolved in pyridine (11.7 mL) and treated with acetic anhydride (1.10 mL, 11.7 mmol, 10 eq). After overnight stirring at room temperature, the solution was diluted with EtOAc (120 ml), washed with 2*M* aqueous HCl (3 x 30 mL), $H_2O$ (2 x 30 mL), and brine (1 x 30 mL). After drying ($MgSO_4$), filtration, and concentration *in vacuo*, column chromatography of the residue (silica gel, hexane/EtOAc, 3:1) afforded the acetate (734.1 mg, 99.5%) as a yellow solid (mp 118.5–120 °C). $^1$H NMR (400 MHz, $CDCl_3$) δ 1.10 (m, 21H), 2.08 (s, 3H), 2.41 (s, 3H), 2.75 (m, 2H), 2.96 (m, 1H), 3.40 (d, 1H), 4.05 (ABX system, 2H, $J_{AX}$ = 8.9 Hz, $J_{BX}$ = 5.6 Hz, $J_{AB}$ = 11.6 Hz, Δ = 0.15 ppm), 5.12 (d, 1H, *J* = 7.5 Hz), 5.21 (app t, 2H, *J* = 16.7, 10.7 Hz), 5.87 (m, 2H), 7.29 (d, 2H, *J* = 8.2 Hz), 7.36 (d, 2H, *J* = 8.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 11.9, 18.0, 20.7, 21.4, 41.7, 61.8, 62.1, 69.4, 74.9, 75.8, 112.7, 119.3, 123.2, 129.9, 132.1, 140.9, 145.5, 169.1; IR ($CHCl_3$) 2944, 2866, 2065, 2007, 1742, 1463, 1370, 1216, 1047, 757, $cm^{-1}$.

The acetate (734.1 mg, 1.16 mmol, 1 eq) was dissolved in THF (11.6 mL), and treated with a 1.0 *M* THF solution of TBAF (Aldrich; 1.4 mL, 1.40 mmol, 1.2 eq). After stirring at room temperature for 1.5 h, the solution was diluted with EtOAc (120 mL) and washed with brine (30 mL). After drying ($MgSO_4$), filtration, and concentration *in vacuo*, column chromatography of the residue (silica gel, hexane/EtOAc, 1:1), gave the alcohol (552.5 mg, 100%) as a yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.07 (s, 3H), 2.39 (s, 3H), 2.75 (m, 2H), 2.92 (m, 1H), 3.38 (d, 1H, *J* = 7.4 Hz), 3.99 (ABX system, 2H, $J_{AX}$ = 8.9 Hz, $J_{BX}$ = 5.6 Hz, $J_{AB}$ = 12.0 Hz, Δ = 0.22 ppm), 5.12 (m, 3H), 5.85 (m, 2H), 7.23 (d, 2H, *J* = 8.1 Hz), 7.28 (d, 2H, *J* = 8.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 14.0, 20.7, 21.3, 41.7, 60.7, 62.3, 69.5, 74.7, 74.9,

112.9, 119.2, 123.1, 129.8, 132.1, 141.1, 144.6, 169.1; IR ($CHCl_3$) 3363 (br), 2931, 2359, 2083, 1990, 1747, 1373, 1230, 1042, 810, 617, 565, 504 $cm^{-1}$; HRMS exact mass calcd for $[MH]^+$ 475.0514, found 475.0507.

The alcohol (149.7 mg, 0.316 mmol, 1 eq) was dissolved in DCM (1.2 mL) and consecutively treated with DMSO (1.2 mL), $NEt_3$ (0.44 mL, 3.16 mmol, 10 eq) and $SO_3$•Pyr (246.4 mg, 1.58 mmol, 5 eq). After stirring at room temperature for 3 h, the solution was diluted with EtOAc (50 mL) and washed with 1*M* aq. HCl (2 x 16 mL), $H_2O$ (1 x 16 mL), and brine (1 x 16 mL). After drying ($MgSO_4$), filtration, and concentration *in vacuo*, column chromatography of the residue (silica gel, hexane/EtOAc, 2:1 to 1.5:1), aldehyde **3** (139.6 mg, 94%) was obtained as a yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 3H), 2.43 (s, 3H), 2.64 (m, 1H), 2.75 (m, 1H), 2.87 (d, 1H, *J* = 2.9 Hz), 3.67 (d, 1H, *J* = 7.6 Hz), 5.21 (m, 2H), 5.31 (d, 1H, *J* = 7.4 Hz), 5.86 (m, 1H), 6.63 (app t, 1H, *J* = 5.6, 5.5 Hz), 7.33 (d, 2H, *J* = 8.1 Hz), 7.40 (d, 2H, *J* = 8.3 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 20.7, 21.4, 41.7, 54.6, 70.2, 77.6, 112.9, 119.7, 123.2, 130.1, 131.8, 141.0, 144.6, 169.5, 194.4; IR ($CHCl_3$) 2926, 2076, 2014, 1746, 1682, 1428, 1372, 1228, 1047, 811, 612, 562 $cm^{-1}$; HRMS exact mass calcd for $[MH]^+$ 473.0357, found 473.0337.

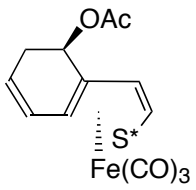



**4**

**($\eta^4$-$C_1$-$C_4$)-α-[($R_s$)-(1*Z*,3*E*)-3-[(*R*)-1-Acetoxybut-3-enyl]-1-*p*-tolylsulfinyl-1,3,5-hexatriene]-tricarbonyl iron(0) complex (4).** Aldehyde **3** (199.4 mg, 0.422 mmol, 1 eq) was dissolved in THF (4.2 mL) and the solution was cooled to –78 °C. $TMSCH_2Li$ (1.0*M* in pentane, Aldrich; 0.97 mL, 0.971 mmol, 2.3 eq) was then added dropwise. The reaction solution was stirred for 1h and then was quenched with a saturated aqueous NH4Cl solution (1 mL) and warmed to room

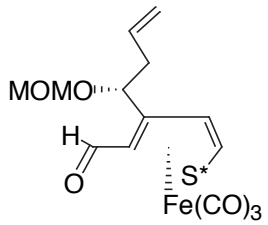
temperature. It was then diluted with EtOAc (15 mL) and washed with a saturated aqueous $NH_4Cl$ solution (2 x 10 mL). The aqueous layer was then extracted with EtOAc (10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc, 4:1 to 3:1) yielding a mixture of diastereomers (157.7 mg, 67%) as a yellow oil. A small amount of the major diastereomer could be separated: $^1$H NMR (400 MHz, $CDCl_3$) δ 0.15 (m, 9H), 1.3 (m, 2H), 2.06 (s, 3H), 2.42 (s, 3H), 2.68 (m, 2H), 2.82 (d, 1H, *J* = 9.0 Hz), 2.94 (m, 1H), 3.39 (d, 1H, *J* = 7.4 Hz), 4.01 (m, 1H), 4.98 (d, 1H, *J* = 17.0 Hz), 5.08 (m, 2H), 5.83 (m, 1H), 5.91 (app t, 1H, *J* = 5.2 Hz), 7.26 (d, 2H, *J* = 7.6 Hz), 7.30 (d, 2H, *J* = 8.2 Hz).

The mixture of diastereomeric alcohols (50.1 mg, 0.0894 mmol, 1 eq) was dissolved in DCM (0.9 mL) and treated with $BF_3$•$Et_2O$ (0.022 mL, 0.179 mmol, 2 eq). The reaction was stirred at room temperature for 2h, then was diluted with EtOAc (20 mL) and washed with a saturated aqueous $NaHCO_3$ solution (8 mL) followed by brine (8 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc, 4:1) yielding acetate **4** (33.2 mg, 79%) as a yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.12 (s, 3H), 2.42 (s, 3H), 2.65 (m, 1H), 2.74 (m, 1H), 3.41 (d, 1H, *J* = 7.5 Hz), 3.46 (d, 1H, *J* = 10.4 Hz), 5.11 (d, 1H, *J* = 7.5 Hz), 5.25 (m, 3H), 5.57 (d, 1H, *J* = 16.4 Hz), 5.86 (m, 1H), 5.95 (app t, 1H, *J* = 5.8, 5.6 Hz), 6.19 (app d of t, 1H, *J* = 16.5, 10.3 Hz), 7.30 (d, 2H, *J* = 8.1 Hz), 7.39 (d, 2H, *J* = 8.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.6, 22.2, 42.1, 63.8, 70.8, 74.5, 76.1, 110.9, 120.1, 120.4, 124.0, 130.8, 132.5, 135.1, 141.8, 146.1, 170.1; IR ($CHCl_3$) 2979, 2925, 2080, 1987, 1746, 1372, 1227, 1049, 612, 559 $cm^{-1}$; HRMS exact mass calcd for $[MH]^+$ 471.0565, found 471.0546.




**5**

**($\eta^4$-$C_1$,$C_2$,$C_1$',$C_2$')-α-{6-(*R*)-Acetoxy-1-[(*Z*)-($R_s$)-2-*p*-tolylsulfinyl-ethen-1-yl]-cyclohexa-1,3-diene}tricarbonyl iron(0) complex (5).** To a toluene (1.0 mL) solution of Grubbs' catalyst (2.8 mg, 3.0 μmol, 0.05 eq), which had been weighed in a glove box into a previously flame-dried and evacuated Schlenk flask was added a toluene (1.0 mL) solution of acetate **4** (28.6 mg, 0.0608 mmol, 1 eq) via cannula. After stirring at room temperature overnight, the Schlenk flask was then opened to air and subsequently concentrated *in vacuo*. The crude brown oil was purified via column chromatography (silica gel, hexane/EtOAc, 3:1) to afford carbocycle **5** (25.0 mg, 93%) which was obtained as a waxy yellow solid (mp: 50-52 °C). $^1$H NMR (400 MHz, $CDCl_3$) δ 2.16 (s, 3H), 2.38 (s, 3H), 2.56 (m, 2H), 3.38 (d, 1H, *J* = 7.2 Hz), 3.49 (d, 1H, *J* = 5.5 Hz), 5.40 (d, 1H, *J* = 7.3 Hz), 5.76 (d, 1H, *J* = 5.5 Hz), 5.85 (m, 1H), 6.03 (m, 1H), 7.25 (d, 2H, *J* = 8.2 Hz), 7.29 (d, 2H, *J* = 8.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 22.15, 22.2, 30.9, 57.1, 70.0, 75.3, 80.4, 104.6, 124.0, 124.5, 127.8, 130.7, 141.8, 145.7, 170.9, 208.8 (CO resonance); IR ($CHCl_3$) 2996, 2059, 1998, 1732, 1225, 1045 cm$^{-1}$; HRMS exact mass calcd for $[MH]^+$ 443.0252, found 443.0257.



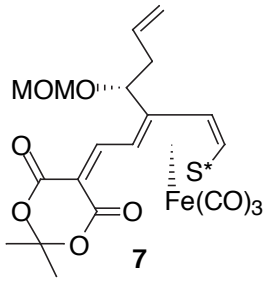

**6**

**$\eta^4$-$\alpha$-{($R_s$)-(1*Z*,3*E*)-5-Hydroxy-3-[(*R*)-1-(methoxymethyl)oxybut-3-enyl]-1-*p*-tolylsulfinyl-penta-1,3-dien-5-al}tricarbonyl iron(0) Complex (6)**. Alcohol **2**[1](1.148 g, 1.950 mmol, 1 eq) was dissolved in DCM (6.5 mL) under argon and to this solution was consecutively added diisopropylethylamine (3.06 mL, 17.55 mmol, 9 eq) and MOMCl (1.19 mL, 15.60 mmol, 8 eq) and the reaction was allowed to stir at room temperature for 93 hours. To quench the reaction, 5% aqueous $NaHCO_3$ (17 mL) was added and the mixture was allowed to stir for an additional 30 min. This solution was then diluted with EtOAc (55 mL) and the aqueous phase was extracted with EtOAc (15 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc, 4:1) to yield the MOM ether (1.185 g, 96%) as a yellow solid (mp 63.5-65 °C). $^1$H NMR (400 MHz, $CDCl_3$) δ 1.11 (m, 21H), 2.40 (s, 3H), 2.65 (m, 1H), 2.80 + 2.85 (2 m, 2H), 3.40 (s, 3H), 3.42 (obscured d, 1H), 3.98 + 4.09 (2 m, 2H), 4.60 (app t, 1H, $J$ = 4.7 Hz), 4.76 (AB system, 2H, $J$ = 7.0 Hz, Δ = 0.04 ppm), 5.23 (overlapping absorbances, 3H), 5.97 (m, 1H), 7.27 (d, 2H, $J$ = 8.0 Hz), 7.38 (d, 2H, $J$ = 8.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 11.91, 17.98, 18.01, 21.36, 41.39, 56.16, 60.16, 61.68, 74.17, 75.10, 75.84,95.98, 114.28, 118.78, 123.29, 129.77, 132.80, 140.76, 145.42; IR (neat) 2942, 2856, 2055, 1998, 1979, 1488, 1461, 1370, 1242, 1146, 1082, 1044, 916, 879, 804, 772, 681 $cm^{-1}$. HRMS exact mass calcd for $[MH]^+$ 633.2005, found 633.1988.

The MOM ether (1.185 g, 1.873 mmol, 1 eq) was dissolved in THF (18.7 mL) and treated with a 1.0 *M* THF solution of TBAF (Aldrich; 2.25 mL, 2.248 mmol, 1.2 eq. After stirring for 1.5 h at room temperature, the solution was diluted with EtOAc (205 mL). The organic layer

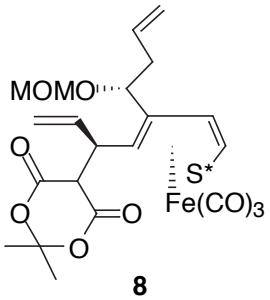
was washed with brine (70 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc, 2:1 to 1.5:1) to yield the alcohol (881.4 mg, 94%) as a yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.66 (m, 1H), 2.75 (m, 1H), 2.85 (m, 1H), 3.36 (obscured d, 1H), 3.37 (s, 3H), 3.82 (br s, 1H), 3.82 (m, 1H), 4.06 (m, 1H), 4.57 (app t, 1H, $J$ = 4.6 Hz), 4.70 (AB system, 2H, $J$ = 7.0 Hz, Δ = 0.04 ppm), 5.05 (overlapping d, 2H, $J$ = 12.1, 15.2 Hz), 5.20 (d, 1H, $J$ = 7.4 Hz), 5.90 (m, 1H), 7.20 (d, 2H, $J$ = 8.2 Hz), 7.26 (d, 2H, $J$ = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.32, 41.43, 56.11, 60.77, 60.90, 74.17, 74.17, 74.81, 74.90, 95.94, 114.89, 118.66, 123.24, 129.73, 132.79, 140.89, 144.50; IR (in $CHCl_3$) 3359 (br), 2931, 2055, 1985, 1146, 1028, 916, 804, 751, 617, 558 $cm^{-1}$. HRMS exact mass calcd for $[MH]^+$ 477.0670, found 477.0676.

The alcohol (881.4 mg, 1.850 mmol, 1 eq) was dissolved in DCM (7.2 mL) under an argon atmosphere, and was then consecutively treated with DMSO (7.2 mL), $NEt_3$ (2.58 mL, 18.50 mmol, 10 eq), and $SO_3$•pyr (1.445 g, 9.251 mmol, 5 eq. After 6 h the reaction was diluted with EtOAc (300 mL). The mixture was washed with 1*M* aqueous HCl (2 x 100 mL), $H_2O$ (1 x 100 mL) and brine (1 x 100 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting oil was purified via column chromatography (silica gel, hex/EtOAc, 1.5:1) to yield the aldehyde **6** (844.6 mg, 96%) as a yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.53 (m, 1H), 2.72 (m, 1H), 2.80 (d, 1H, $J$ = 2.6 Hz), 3.35 (s, 3H), 3.67 (d, 1H, $J$ = 7.6 Hz), 4.74 (AB system, 2H, $J$ = 6.8 Hz, Δ = 0.05 ppm), 5.17 (overlapping d, 2H, $J$ = 9.7, 17.2 Hz), 5.36 (app t, 1H, $J$ = 5.0 Hz), 5.47 (d, 1H, $J$ = 7.6 Hz), 5.89 (m, 1H), 7.28 (d, 2H, $J$ = 8.2 Hz), 7.37 (d, 2H, $J$ = 8.1 Hz), 9.61 (d, 1H, $J$ = 2.8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.41, 42.31, 53.70, 56.10, 75.24, 78.28, 96.63, 114.56, 115.84, 119.21, 123.23, 130.06, 132.61, 141.40, 144.50, 194.75; IR (neat) 3059, 2942, 2824, 2076, 2012, 1675, 1488, 1456, 1418, 1242, 1146, 1078, 1039, 916, 809, 606, 558 $cm^{-1}$. HRMS exact mass calcd for $[MH]^+$ 475.0514, found 475.0532.



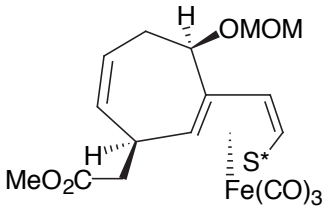

**7**

**$\eta^4$-(2-5)-$\alpha$-{5-[($R_s$)-(2*E*,4*Z*)-3-[(*R*)-1-(Methoxymethyl)oxybut-3-enyl]-5-*p*-tolylsulfinyl-2,4-pentadienylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione}tricarbonyliron(0) Complex (7).** Aldehyde **6** (844.6 mg, 1.781 mmol, 1 eq) was dissolved in pyridine (14.8 mL) under an argon atmosphere; Meldrum's acid (282 mg, 1.96 mmol, 1.1 equiv) was added and the reaction was stirred at room temperature for 23 h. The red solution was diluted EtOAc (275 mL) and washed with 1*M* aqueous HCl (2 x 75 mL). The aqueous washes were combined and extracted with EtOAc (3 x 60 mL). The combined organic layers were washed with brine (2 x 100 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc with 1% HOAc, 1.5:1 to 1:1) to yield the alkylidene malonate **7** (1.054 g, 99%) as a red-orange semi-solid. Evaporation of this solid from diethyl ether afforded a fluffy orange solid (mp: 59-75 °C, decomp). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.75 (s, 3H), 1.77 (s, 3H), 2.41 (s, 3H), 2.51 (m, 1H), 2.74 (m, 1H), 3.41 (s, 3H), 3.88 (d, 1H, $J$ = 7.6 Hz), 4.67 (d, 1H, $J$ = 12.1 Hz), 4.81 (partially obscured AB system, 2H, $J$ = 7.0, $\Delta$ = 0.07 ppm), 4.84 (obscured m, 1H), 5.16 (overlapping d, 2H, $J$ = 8.4, 15.2 Hz), 5.42 (d, 1H, $J$ = 7.6 Hz), 5.82 (m, 1H), 7.29 (d, 2H, $J$ = 8.0 Hz), 7.43 (d, 2H, $J$ = 8.0 Hz), 7.99 (d, 1H, $J$ = 12.1 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 21.39, 27.64, 42.24, 52.78, 56.26, 74.13, 78.70, 78.84, 95.97, 104.83, 111.16, 117.06, 119.94, 123.35, 129.91, 131.39, 141.20, 145.21, 159.76, 160.30, 162.61; IR ($CHCl_3$) 2985, 2931, 2066, 2012, 1717, 1573, 1434, 1376, 1279, 1173, 1034, 922, 751, 612 cm$^{-1}$. HRMS exact mass calcd for $[MH]^+$ 601.0831, found 601.0807.




**8**

**$\eta^4$-$\alpha$-{5-[($R_s$)-(2*E*,4*Z*)-1-(*S*)-Ethenyl-3-[(*R*)-1-(methoxymethyl)oxybut-3-enyl]-5-*p*-tolylsulfinyl-2,4-pentadienyl]-2,2-dimethyl-1,3-dioxane-4,6-dione}tricarbonyliron(0) Complex (8).** Alkylidene malonate **7** (251.9 mg, 0.4195 mmol, 1 eq) was dissolved in THF (3.1 mL) under an argon atmosphere and placed in a -78 ˚C acetone/dry ice bath. Vinyl magnesium bromide (1*M* in THF, Aldrich; 0.84 mL, 0.839 mmol, 2 eq) was added dropwise to the cooled. After 2 h and 40 min the solution was quenched with saturated aqueous $NH_4Cl$. After allowing the solution to warm to room temperature, the solution was diluted with EtOAc (90 mL) and washed with $H_2O$ (45 mL). The aqueous layer was extracted with EtOAc (3 x 25 mL), and the combined organic layers were washed with brine (2 x 60 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc with 1% HOAc, 2:1 to 1:1) to yield the bis-alkene **8** (225.9 mg, 85%) as a yellow semi-solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 1.77 (s, 3H), 1.88 (s, 3H), 2.40 (s, 3H), 2.59 (m, 1H), 2.85 (m, 1H), 3.40 (s, 3H), 3.51 (d, 1H, *J* = 7.7 Hz), 3.58 (m, 2H), 3.90 (s, 1H), 4.49 (app t, 1H), 4.76 (s, 2H), 5.16 (overlapping d, 2H, *J* = 9.8, 17.3 Hz), 5.25 (d, 1H, *J* = 7.6 Hz), 5.27 + 5.39 (2 d, 2H, *J* = 10.4, 17.1 Hz), 5.89 + 5.99 (2 m, 2H), 7.27 (d, 2H, *J* = 8.1 Hz), 7.39 (d, 2H, *J* = 8.1 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.32, 26.79, 28.20, 41.26, 43.76, 54.24, 56.26, 64.47, 73.68, 75.59, 77.53, 96.38, 105.29, 115.28, 118.86, 120.58, 123.40, 129.71, 132.41, 135.30, 140.84, 145.26, 162.82, 163.72; IR ($CHCl_3$) 2920, 2044, 1990, 1782, 1744, 1295, 1205, 1146, 1034, 922, 756, 620 cm$^{-1}$. HRMS exact mass calcd for $[MH]^+$ 629.1144, found 629.1122.

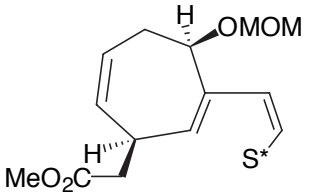



**9**

**($\eta^4$-$C_1$,$C_2$,$C_1$',$C_2$')-α-{3-(*S*)-[Carbomethoxymethyl]-7-(*R*)-[(methoxymethyl)oxy]-1-[(*Z*)-($R_s$)-2-*p*-tolylsulfinylethen-1-yl]-cyclohepta-1,4-diene}tricarbonyliron(0) Complex (9).** Bis-alkene **8** (219.7 mg, 0.3496 mmol, 1 eq) was dissolved in 3-pentanone/$H_2O$ (2:1, 3.50 mL) and the solution was stirred at reflux (bath temperature: 110 ˚C) for 20 h. The reaction was then cooled to room temperature and diluted with EtOAc (70 mL). To the organic solution $H_2O$ (36 mL) and 1*M* aqueous HCl (5 mL) were added. The layers were separated and the organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting crude carboxylic acid was dissolved in DMF (3.5 mL) under an argon atmosphere. To this solution, $K_2CO_3$ (96.6 mg, 0.6992 mmol, 2 eq) and $CH_3I$ (0.044 mL, 0.6992 mmol, 2 eq) were added consecutively. The reaction was stirred at room temperature for 5.5 hours and then diluted with EtOAc (200 mL). The organic layer was washed with $H_2O$ (2 x 36 mL), and the combined aqueous layers were extracted with EtOAc (3 x 25 mL). The combined organic layers were then washed with brine (70 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc, 3:1 to 2:1) to yield the methyl ester (128.2 mg, 66% over two steps) as a yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.56-2.93 (2 m, 4H), 2.69 (m, 1H), 2.78 (dd, 1H, *J* = 3.7, 15.0 Hz), 3.40 (s, 3H), 3.42 (d, 1H, *J* = 7.7 Hz), 3.70 (s, 3H), 4.47 (app t, 1H, *J* = 4.5 Hz), 4.74 (s, 2H), 5.17 (overlapping m, 4H), 5.22 (d, 1H, *J* = 7.8 Hz), 5.83-5.95 (overlapping m, 2H), 7.26 (d, 2H, *J* = 8.1 Hz), 7.36 (d, 2H, *J* = 8.1 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.35, 41.28, 42.03, 43.90, 51.70, 56.29, 65.20, 74.09, 74.99, 76.06, 96.32, 114.06, 116.59, 118.74, 123.29, 129.79, 132.71, 19.63, 140.87, 145.18, 171.23; IR (neat)

3070, 2953, 2923, 2852, 2055, 1986, 1737, 1683, 1488, 1434, 1360, 1285, 1253, 1210, 1151, 1039, 916, 804, 729, 617 $cm^{-1}$. HRMS exact mass calcd for $[MH]^+$ 559.1089, found 559.1081.

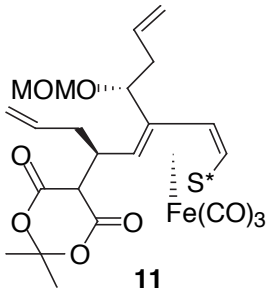
To a toluene (1.9 mL) solution of Grubbs' catalyst (15.1 mg, 18.4 μmol, 0.08 eq), which had been weighed in a glove box into a previously flame-dried and evacuated Schlenk flask, was added a toluene (5.7 mL) solution of the methyl ester (128.2 mg, 0.2296 mmol, 1 eq) via cannula. The reaction was allowed to stir at room temperature for 22 hours and then was concentrated *in vacuo*. The resulting black oil was purified via column chromatography (silica gel, hexane/EtOAc, 3:1 to 2:1) to yield carbocycle **9** (109.2 mg, 90%) as a yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.45 (m, 1H), 2.67 (ABX system, 2H, $J_{AX}$ = 9.0 Hz, $J_{BX}$ = 4.7 Hz, $J_{AB}$ = 16.0 Hz, Δ = 0.14 ppm), 2.74 (s, 1H), 2.80 (partially obscured m, 1H), 3.16 (br s, 1H), 3.36 (d, 1H, *J* = 7.4 Hz), 3.40 (s, 3H), 3.75 (s, 3H), 4.74 (AB system, 2H, *J* = 6.9 Hz, Δ = 0.08 ppm), 5.00 (dd, 1H, *J* = 4.1, 12.4 Hz), 5.47 (d, 1H, *J* = 7.5 Hz), 5.57 (m, 1H), 5.70 (m, 1H), 7.26 (d, 2H, *J* = 8.1 Hz), 7.31 (d, 2H, *J* = 8.3 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.35, 36.34, 36.42, 40.40, 51.90, 55.92, 65.08, 72.49, 73.00, 74.94, 95.45, 113.62, 123.70, 127.70, 129.86, 131.54, 140.76, 145.31, 172.01; IR ($CHCl_3$) 3006, 2942, 2354, 2044, 1985, 1734, 1434, 1146, 1098, 1078, 1034, 751, 617, 564 $cm^{-1}$. HRMS exact mass calcd for $[MH]^+$ 531.0776, found 531.0795.




**10**

**3-(*S*)-[Carbomethoxymethyl]-7-(*R*)-[(methoxymethyl)oxy]-1-[(*Z*)-(*R*$_s$)-2-*p*-tolylsulfinyl-ethen-1-yl]-cyclohepta-1,4-diene (10)**. Carbocycle **9** (109.2 mg, 0.2059 mmol, 1 eq) was dissolved in acetonitrile (2.3 mL) under an argon atmosphere and the solution was cooled to –10 °C. Ferric chloride (333.4 mg, 2.059 mmol, 10 eq) was added to the solution in three portions over a 15 minute period. After an additional 35 min the reaction was quenched with saturated $Na_2CO_3$ (74 mL) and EtOAc (74 mL). The aqueous layer was separated and brought to pH ~7

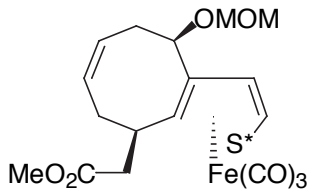
using 1*N* aqueous HCl and was then extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with brine (100 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc, 1:1 to 1:2) to yield diene **10** (65.3 mg, 81%) as a clear oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.36-2.55 (4 m, 2H), 2.59 (d, 2H,*J* = 7.6 Hz), 3.38 (s, 3H), 3.69 (s, 3H), 3.82 (br s, 1H), 4.65 (collapsed AB system, 2H, *J* = 8.9 Hz), 4.85 (dd, 1H, *J* = 3.4, 10.5 Hz), 5.43 (d, 1H, *J* = 9.5 Hz), 5.62 (m, 1H), 5.90 (d, 1H, *J* = 4.8 Hz), 6.34 (d, 1H, *J* = 10.2 Hz), 6.79 (d, 1H, *J* = 10.2 Hz), 7.32 (d, 2H, *J* = 8.2 Hz), 7.57 (d, 2H, *J* = 8.1 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.27, 32.04, 34.14, 39.93, 51.71, 55.68, 72.47, 95.12, 124.68, 127.05, 129.94, 130.65, 137.31, 137.34, 137.48, 138.30, 141.18, 141.70, 172.04; IR (neat) 3017, 2942, 2846, 2365, 1734, 1434, 1242, 1210, 1146, 1034, 911, 804, 719 $cm^{-1}$.




**11**

**$\eta^4$-α-{5-[($R_s$)-(2*E*,4*Z*)-1-(*S*)-(2-Propenyl)-3-[(*R*)-1-(methoxymethyl)oxybut-3-enyl]-5-*p*-tolyl-sulfinyl-2,4-pentadienyl]-2,2-dimethyl-1,3-dioxane-4,6-dione}tricarbonyliron(0) Complex (11).** Alkylidene malonate **7** (407.1 mg, 0.678 mmol, 1 eq) was dissolved in THF (6.8 mL) under argon. Lithium perchlorate (3.61 g, 33.90 mmol, 50 eq) was added, followed by allyl tributylstannane (0.420 mL, 1.356 mmol, 2 eq). The reaction was stirred under argon for 40 h and then was diluted with EtOAc (270 mL). The solution was washed with $H_2O$ (135 mL), and the aqueous layer was extracted with EtOAc (135 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc with 1% HOAc, 1.5:1 to 1:1) to give, upon

evaporation from $Et_2O$, **11** as a yellow solid (420.2 mg, 97%; mp 66-82 °C decomp). $^1$H NMR (400 MHz, $CDCl_3$) δ 1.75 (s, 3H), 1.84 (s, 3H), 2.41 (s, 3H), 2.49 (m, 1H), 2.65 (m, 2H), 2.98 (m, 1H), 3.24 (m, 1H), 3.41-3.45 (part. obs m, 1H), 3.43 (s, 3H), 3.76 (d, 1H, $J$ = 7.7 Hz), 4.50 (app t, 1H, $J$ = 4.4 Hz), 4.81 (AB system, 2H, $J_{AB}$ = 7.0 Hz, Δ = 0.03 ppm), 5.07 (m+m, 2H), 5.20 (m+m, 2H), 5.72 (m, 1H), 5.96 (m, 1H), 7.27 (d, 2H, $J$ = 8.1 Hz), 7.39 (d, 2H, $J$ = 8.1 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.39, 26.85, 28.15, 37.90, 38.77, 41.83, 42.44, 52.232, 56.41, 69.34, 73.68, 75.60, 77.51, 96.79, 105.20, 115.25, 119.42, 119.48, 123.51, 129.77, 132.11, 134.67, 140.94, 145.33, 163.45, 165.03; IR ($CHCl_3$) 3018, 2929, 2065, 2005, 1738, 1640, 1442, 1414, 1151, 1036, 922, 809 cm$^{-1}$; HRMS exact mass calcd for $[MH]^+$ 643.1300, found 643.1298.

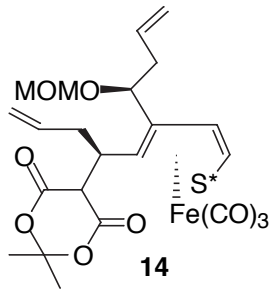



12

**($\eta^4$-$C_1$,$C_2$,$C_{1'}$,$C_{2'}$)-α-{3-(*S*)-[carbomethoxymethyl]-8-(*R*)-[(methoxymethyl)oxy]-1-[(*Z*)-($R_s$)-2-*p*-tolylsulfinylethen-1-yl]-cycloocta-1,5-diene}tricarbonyliron(0) Complex (12).** Diene **11** (84.5 mg, 0.1317 mmol) was dissolved in 3-pentanone/$H_2O$ (2:1, 1.3 mL) and the solution was stirred at reflux (bath temperature: 110 °C) for 18 h. The reaction was then diluted with EtOAc (30 mL), and the solution washed with $H_2O$ (15 mL) containing several drops of 2*M* aqueous HCl. The aqueous layer was extracted with EtOAc (15 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting crude carboxylic acid was dissolved in DMF (1.3 mL) under an argon atmosphere. To this solution $K_2CO_3$ (36.4 mg, 0.263 mmol, 2 eq) and $CH_3I$ (0.016 mL, 0.263 mmol, 2 eq) were consecutively added. The reaction was stirred for 18 hr and was then diluted with EtOAc (70 mL). The organic layer was washed with $H_2O$ (2 x 15 mL) and brine (15 mL). The combined aqueous layers were washed with EtOAc (2 x 15 mL), and then the combined organic layers were dried ($MgSO_4$), filtered,

and concentrated *in vacuo*. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc, 3:1) to give the ester (57.4 mg, 78% over two steps) as yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.42-2.96 (overlapping m+d+m+m, 8H, $J$ = 9.9 Hz), 3.39 (obs d, 1H, $J$ = 7.7 Hz), 3.41 (obs s, 3H), 3.74 (s, 3H), 4.46 (app t, 1H, $J$ = 4.4 Hz), 4.76 (app s, 2H), 5.13-5.22 (overlapping m, 5H), 5.80 (m, 1H), 5.99 (m, 1H), 7.27 (d, 2H, $J$ = 8.1 Hz), 7.35 (d, 2H, $J$ = 8.1 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.37, 35.96, 39.35, 40.89, 42.13, 51.76, 56.35, 68.83, 74.007, 74.778, 76.18, 96.61, 114.03, 118.73, 119.17, 123.31, 129.79, 132.42, 133.50, 140.89, 145.35, 172.05; IR ($CHCl_3$) 2951, 2057, 1994, 1735, 1639, 1491, 1438, 1370, 1151, 1036, 921, 809, 666, 619 cm$^{-1}$; HRMS exact mass calcd for $[MH]^+$ 587.1402, found 587.1430.

In a glove box, Grubbs' catalyst (3.4 mg, 4.13 μmol, 0.08 eq) was weighed into a flame dried and evacuated Schlenk flask. The flask was brought to the bench, and the catalyst was dissolved in toluene (0.5 mL) under an argon atmosphere. The ester (28.8 mg, 51.6 μmol, 1 eq) was dissolved in toluene (2.1 mL) under argon and transferred via cannula to the Schlenk flask. The reaction was stirred under argon for 24 h, and then opened to air and stirred for 15 min. The toluene was removed *in vacuo*, and the resulting green semi-solid was purified via column chromatography (silica gel, hexane/EtOAc, 3:1 to 2.5:1) to give the carbocycle **12** (24.4 mg, 89%) as a yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.19-2.46 (m, 3H), 2.40 (s, 3H), 2.52-2.67 (part obs d+m, 3H), 2.75 (m, 1H), 3.05 (br dt, 1H, $J$ = 4.8, 16.1 Hz), 3.34 (d, 1H, $J$ = 7.7 Hz), 3.40 (s, 3H), 3.75 (s, 3H), 4.74 (AB system, 3H, $J_{AB}$ = 7.0 Hz, Δ = 0.66 ppm), 5.29 (d, 1H, $J$ = 7.7 Hz), 5.78-5.90 (m+m, 2H), 7.26-7.32 (2 partially overlapping d, 4H, $J$ = 8.1, 8.3 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.35, 29.65, 34.74, 38.02, 38.82, 42.33, 51.83, 56.02, 67.10, 72.51, 75.40, 76.20, 95.73, 114.82, 123.00, 128.07, 129.48, 129.80, 140.73, 145.56, 172.22; IR ($CHCl_3$) 2953, 2056, 1987, 1734, 1438, 1150, 1038 cm$^{-1}$; HRMS exact mass calcd for $[MH]^+$ 545.0933, found 545.0916.




**14**

**$\eta^4$-$\alpha$-{5-[($R_s$)-(2*E*,4*Z*)-1-(*S*)-(2-Propenyl)-3-[(*S*)-1-(methoxymethyl)oxybut-3-enyl]-5-*p*-tolyl-sulfinyl-2,4-pentadienyl]-2,2-dimethyl-1,3-dioxane-4,6-dione}tricarbonyliron(0) Complex (14).** Alcohol **13**[1] (269.7 mg, 0.4581 mmol) was dissolved in DCM (1.5 mL) under an argon atmosphere and consecutively treated with diisopropylethylamine (0.878 mL, 5.04 mmol, 11 eq) and MOMCl (0.348 mL, 4.58 mmol, 10 eq). After stirring for 77 h, a solution of 5% aqueous $NaHCO_3$ (9.5 mL) was added and stirring was continued for an additional 30 min. The mixture was diluted with EtOAc (30 mL) and the aqueous layer was extracted with additional EtOAc (10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give 294.6 mg (102%) of a crude orange solid which was sufficiently pure for use in the next reaction. This material was then dissolved in THF (4.6 mL) and treated with a 1.0*M* THF solution of TBAF (Aldrich; 0.55 mL, 0.550 mmol, 1.2 eq). After stirring for 2 h, the solution was diluted with EtOAc (50 mL) and washed with brine (15 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Column chromatography of the crude material (silica gel, hexane/EtOAc, 1.5:1 to 1:1), afforded the alcohol (186.3 mg, 85% over two steps) as a waxy yellow solid (mp 64-66 °C). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.38 (s, 3H), 2.60 (m, 1H), 2.80 (m, 2H), 3.41 (d, 1H, $J$ = 7.3 Hz), 3.44 (s, 3H), 3.75 (br s, 1H), 3.98 (br d, 2H, $J$ = 7.2 Hz), 4.42 (dd, 1H, $J$ = 8.1, 5.0 Hz), 4.85 (AB system, 2H, $J$ = 7.2 Hz, $\Delta$ = 0.125 ppm), 5.04 (d, 1H, $J$ = 7.4 Hz), 5.15 + 5.20 (overlapping d, 2H, $J$ = 18.3 and 10.9 Hz), 5.91 (m, 1H), 7.25 (d, 2H, $J$ = 8.1 Hz), 7.33 (d, 2H, $J$ = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 21.32, 38.76, 55.94, 61.05, 61.78, 75.20, 75.99, 78.30, 95.29, 112.06, 118.54, 123.19, 129.90, 133.69, 140.98, 144.94. IR

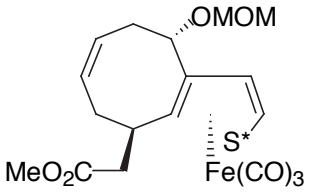
(neat) 3380, 2942, 2081, 1990, 1029. HRMS exact mass calcd for $[MH]^+$ 477.0670, found 477.0655.

The alcohol (186.3 mg, 0.3911 mmol, 1 eq) was next dissolved in DCM (1.5 mL) under an argon atmosphere and consecutively treated with DMSO (1.5 mL), $NEt_3$ (0.545 mL, 3.911 mmol, 10 eq), and $SO_3$•pyr (311 mg, 1.956 mmol, 5 eq). The solution was stirred for 6 h at room temperature, and was then diluted with EtOAc (20 mL) and washed with 1*M* aqueous HCl (2 x 8 mL), $H_2O$ (1 x 8 mL), and brine (1 x 8 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo* to afford an oil. After column chromatography (silica gel, hexane/EtOAc, 2:1 to 1.5:1) the aldehyde (169.3 mg, 90%) was obtained as a yellow solid (mp 118.5-122 °C). $^1$H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.60 (m, 1H), 2.75 (d, 1H, *J* = 6.5 Hz), 2.85 (m, 1H), 3.40 (s, 3H), 3.65 (d, 1H, *J* = 7.4 Hz), 4.70 (app t, 1H, *J* = 7.2, 6.1 Hz), 4.79 (collapsed AB system, 2H), 5.13 (d, 1H, *J* = 7.4 Hz), 5.21 (m, 2H), 5.85 (m, 1H), 7.30 (d, 2H, *J* = 8.0 Hz), 7.38 (d, 2H, *J* = 8.0 Hz), 9.82 (d, 1H, *J* = 6.5 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.22, 40.07, 55.56, 55.93, 76.54, 82.20, 96.07, 115.44, 119.12, 123.03, 129.91, 132.60, 141.28, 144.48, 196.31; IR (neat) 2073, 2008, 1669, 1150, 1037 $cm^{-1}$. HRMS exact mass calcd for $[MH]^+$ 475.0514, found 475.0493.

The aldehyde (169.3 mg, 0.3569 mmol, 1 eq) was dissolved in pyridine (3 mL) under an argon atmosphere; Meldrum's acid (56.6 mg, 0.3926 mmol, 1.1 equiv) was added and the reaction was stirred at room temperature for 18.5 h. The red solution was diluted EtOAc (50 mL) and washed with 1*M* aqueous HCl (2 x 13 mL). The aqueous washes were combined and extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine (13 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc, 2:1 with 1% HOAc to 1:1 with 1% HOAc) to yield the alkylidene malonate (168.7 mg, 80%) as an orange solid (mp 177-180 °C, decomp). $^1$H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, 3H), 1.76 (s, 3H), 2.40 (s, 3H), 2.53 (m, 1H), 2.91 (m, 1H), 3.44 (s, 3H), 3.75 (d, 1H, *J* = 7.4 Hz), 4.48 (dd, 1H, *J* = 8.3, 5.1 Hz), 4.56 (d, 1H, *J* = 11.8 Hz), 4.83 (AB system, 2H, *J* = 7.1 Hz, Δ = 0.04 ppm), 5.08 (d, 1H, *J* = 7.5 Hz), 5.17 (m, 2H), 5.77 (m, 1H), 7.28 (d, 2H, *J* = 7.8 Hz), 7.42 (d, 2H, *J* = 8.1 Hz), 8.67 (d, 1H, *J* = 11.8 Hz); $^{13}$C NMR

(100 MHz, $CDCl_3$) δ 21.36, 27.55, 27.59, 40.37, 52.42, 56.23, 77.83, 83.74, 95.97, 104.54, 110.87, 116.67, 119.48, 123.31, 129.90, 132.40, 141.19, 145.24, 160.57, 162.28, 162.57. HRMS exact mass calcd for $[MH]^+$ 601.0831, found 601.0838.

The alkylidene malonate (107.4 mg, 0.179 mmol, 1 eq) was dissolved in THF (1.8 mL) under argon. Lithium perchlorate (951.5 mg, 8.94 mmol, 50 eq) was added, followed by allyl tributylstannane (0.111 mL, 0.358 mmol, 2 eq). The reaction was stirred under argon for 29 h and then was diluted with EtOAc (80 mL). The solution was washed with $H_2O$ (40 mL), and the aqueous layer was extracted with EtOAc (40 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc containing 1% HOAc, 1.5:1 to 1:1) to give **14** (114.7 mg, 100%) as a yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 1.76 (s, 3H), 1.83 (s, 3H), 2.40 (s, 3H), 2.61-2.72 (m, 2H), 2.84-2.96 (m, 2H), 3.33 (d, 1H, *J* = 10.2 Hz), 3.45 (partially obscured d, 1H, *J* = 7.5 Hz), 3.45 (s, 3H), 3.57 (app td, 1H, *J* = 10.6, 4.7 Hz), 3.70 (d, 1H, *J* = 1.7 Hz), 4.49 (app t, 1H, *J* = 6.9 Hz), 4.82 (AB system, 2H, *J* = 7.2 Hz, Δ = 0.04 ppm), 5.01-5.22 (m, 5H), 5.73 (m, 1H), 5.87 (m, 1H), 7.28 (d, 2H, *J* = 7.8 Hz), 7.41 (d, 2H, *J* = 8.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.38, 26.91, 28.11, 29.67, 37.62, 38.70, 40.80, 51.66, 56.20, 69.91, 77.20, 77.71, 77.94, 78.63, 95.72, 105.02, 112.93, 118.73, 118.76, 123.51, 129.82, 133.56, 135.53, 141.02, 145.42, 163.77, 165.06.

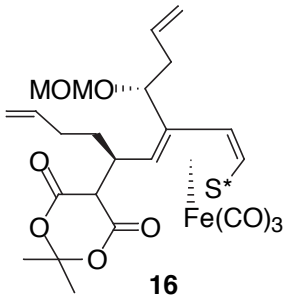



15

**($\eta^4$-$C_1$,$C_2$,$C_{1'}$,$C_{2'}$)-α-{3-(*S*)-[carbomethoxymethyl]-8-(*S*)-[(methoxymethyl)oxy]-1-[(*Z*)-(*R*$_s$)-2-*p*-tolylsulfinylethen-1-yl]-cycloocta-1,5-diene}tricarbonyliron(0) Complex (15).** Diene **14** (114.7 mg, 0.179 mmol) was dissolved in 3-pentanone/$H_2O$ (2:1, 1.8 mL) and the solution was stirred at reflux (bath temperature: 110 °C) for 20.5 h. The reaction was then cooled to room temperature and diluted with EtOAc (35 mL); the solution washed with $H_2O$ (20 mL) containing

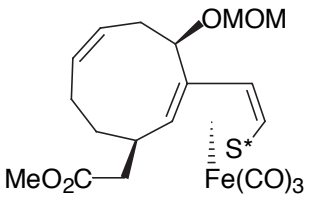
several drops of 2*M* aqueous HCl (solid NaCl was added to break up the emulsion that formed). The aqueous layer was extracted with EtOAc (10 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting crude carboxylic acid was dissolved in DMF (1.8 mL) under an argon atmosphere. To this solution $K_2CO_3$ (49.5 mg, 0.358 mmol, 2 eq) and $CH_3I$ (0.022 mL, 0.358 mmol, 2 eq) were consecutively added. The reaction was stirred for 18 hr and was then diluted with EtOAc (100 mL). The organic layer was washed with $H_2O$ (2 x 20 mL) and brine (20 mL). The combined aqueous layers were washed with EtOAc (1 x 15 mL), and then the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc, 3:1) to give the ester (64.9 mg, 65% over two steps) as yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.56-2.66 (m, 6H), 2.77-2.87 (m, 2H), 3.34 (d, 1H, *J* = 7.5 Hz), 3.43 (s, 3H), 3.73 (s, 3H), 4.44 (app t, 1H, *J* = 6.8 Hz), 4.79 (AB system, 2H, *J* = 7.1 Hz, Δ = 0.08 ppm), 5.04 (dd, 1H, *J* = 7.6, 0.7 Hz), 5.09-5.22 (m, 4H), 5.85 (m, 2H), 7.27 (d, 2H, *J* = 8.1 Hz), 7.35 (d, 2H, *J* = 8.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.35, 36.06, 39.05, 40.54, 40.60, 51.66, 56.08, 69.81, 76.32, 76.47, 78.23, 95.39, 112.72, 118.21, 118.37, 123.26, 129.84, 133.87, 134.33, 140.95, 145.42, 172.19. In a glove box, Grubbs' catalyst (7.7 mg, 9.3 μmol, 0.08 eq) was weighed into a flame dried and evacuated Schlenk flask. The flask was brought to the bench, and the catalyst was dissolved in toluene (1 mL) under an argon atmosphere. The ester (64.9 mg, 116.2 μmol, 1 eq) was dissolved in toluene (4.8 mL) under argon and transferred via cannula to the Schlenk flask. The reaction was stirred under argon for 20 h, and then opened to air and stirred for 15 min. The toluene was removed *in vacuo*, and the resulting green semi-solid was purified via column chromatography (silica gel, hexane/EtOAc, 2:1 to 1.5:1) to give the carbocycle **15** (53.8 mg, 87%) as a yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.10 (m, 1H), 2.39 (s, 3H), 2.39 (d, 1H, *J* = 11.2 Hz), 2.53 (dd, 1H, *J* = 15.6, 9.8 Hz), 2.65 (m, 1H), 2.77 (m, 2H), 2.82 (dd, 1H, *J* = 15.5, 3.5 Hz), 3.05 (m, 1H), 3.21 (d, 1H, *J* = 7.5 Hz), 3.38 (s, 3H), 3.75 (s, 3H), 4.57 (dd, 1H, *J* = 10.4, 7.2 Hz), 4.69 (AB system, 2H, *J* = 7.1 Hz, Δ = 0.10 ppm), 4.91 (d, 1H, *J* = 7.5 Hz), 5.77 (m, 2H), 7.27 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.35, 32.18, 34.90,

37.77, 44.60, 51.75, 55.86, 70.42, 74.68, 75.42, 82.52, 94.97, 115.88, 123.02, 125.48, 129.81, 132.52, 140.68, 145.64, 172.06. HRMS exact mass calcd for $[MH]^+$ 545.0933, found 545.0921.




**16**

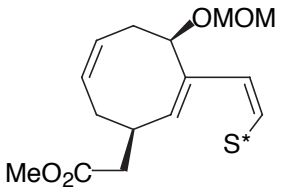
**$\eta^4$-$\alpha$-{5-[($R_s$)-(2*E*,4*Z*)-1-(*S*)-(3-butenyl)-3-[(*R*)-1-(methoxymethyl)oxybut-3-enyl]-5-*p*-tolyl-sulfinyl-2,4-pentadienyl]-2,2-dimethyl-1,3-dioxane-4,6-dione}tricarbonyl iron(0) Complex (16).** Alkylidene malonate **7** (47.3 mg, 0.0788 mmol, 1 eq) was dissolved in THF (0.79 mL) under argon and cooled to –78 °C. To this solution 3-butenylmagnesium bromide (0.5*M* in THF, Aldrich; 0.315 mL, 0.158 mmol, 2 eq) was added dropwise. The reaction was stirred at –78 °C under argon for 2.5 h, then was quenched with saturated aqueous $NH_4Cl$ (4 mL) and allowed to warm to room temperature. The solution was diluted with EtOAc (20 mL), and washed with $H_2O$ (10 mL). The aqueous layer was extracted with EtOAc (2 x 5 mL), the organic layers were combined, washed with brine (2 x 10 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting orange solid was purified via column chromatography (silica gel, hexane/EtOAc, 4:1 with 1% HOAc to 3:1 with 1% HOAc to 2:1 with 1% HOAc) to give **16** (38.5 mg, 75%) as a yellow semi-solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 1.61-1.76 (m, 2H), 1.79 (s, 3H), 1.89 (s, 3H), 2.40 (s, 3H), 2.60 (m, 1H), 2.95 (m, 1H), 3.11 (m, 1H), 3.24 (m, 1H), 3.42-3.44 (part.obs m, 1H), 3.43 (s, 3H), 3.48 (d, 1H, $J$ = 7.7 Hz), 3.89 (d, 1H, $J$ = 1.8 Hz), 4.47 (m, 1H), 4.79 (m, 2H), 5.04 (m, 2H), 5.18 (m+m, 3H), 5.74 (m, 1H), 5.98 (m, 1H), 7.28 (obs d, 2H), 7.38 (d, 2H, $J$ = 8.4 Hz).




**17**

**($\eta^4$-$C_1$,$C_2$,$C_{1'}$,$C_{2'}$)-α-{3-(*S*)-[carbomethoxymethyl]-9-(*R*)-[(methoxymethyl)oxy]-1-[(*Z*)-($R_s$)-2-*p*-tolylsulfinylethen-1-yl]-cyclonona-1,6-diene}tricarbonyliron(0) Complex (17)**. Diene **16** (32.2 mg, 0.0492 mmol) was dissolved in 3-pentanone/$H_2O$ (2:1, 0.37 mL) and the solution was stirred at reflux (bath temperature: 110°C) for 25 h. The reaction was diluted with EtOAc (20 mL), and the organic layer was washed with $H_2O$ (10 mL) containing several drops of 2*M* aqueous HCl. The aqueous layer was extracted with EtOAc (10 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting crude carboxylic acid was dissolved in DMF (0.50 mL) under argon. To this solution $K_2CO_3$ (14 mg, 0.099 mmol, 2 eq) and $CH_3I$ (6.1 μL, 0.099 mmol, 2 eq) were added consecutively. The reaction was stirred for 24 h and then diluted with EtOAc (20 mL). The organic layer was washed with $H_2O$ (2 x 5 mL) and brine (5 mL). The aqueous layers were combined and washed with EtOAc (2 x 5 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc, 3:1) to give the ester (21.7 mg, 77% in two steps) as yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 1.72 (m, 1H), 1.82 (m, 1H), 2.14 (m, 2H), 2.33 (m, 1H), 2.40 (s, 3H), 2.62 (obscured m, 1H), 2.71 (ABX system, 2H, $J_{AX}$ = 7.7 Hz, $J_{BX}$ = 4.4 Hz, $J_{AB}$ = 15.7 Hz, Δ = 0.11 ppm), 2.87 (d, 1H, *J* = 10.6 Hz), 2.93 (app dt, 1H, *J* = 14.6, 5.1 Hz), 3.40 (d, 1H, *J* = 7.7 Hz), 3.41 (s, 3H), 3.76 (s, 3H), 4.41 (app t, 1H, *J* = 4.8 Hz), 4.78 (s, 2H), 5.02 (d, 1H, *J* = 10.6 Hz), 5.07 (dd, 1H, *J* = 17.2, 1.5 Hz), 5.17 (d, 1H, *J* = 7.7 Hz), 5.22 (m, 2H), 5.79 (m, 1H), 5.97 (m, 1H), 7.28 (d, 2H, *J* = 8.4 Hz), 7.37 (d, 2H, *J* = 8.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 22.24, 30.81, 35.33, 36.79, 41.58, 43.14, 52.69, 57.20, 70.23, 72.09, 74.93, 75.61, 77.19, 97.52, 115.06, 116.39, 119.98, 124.17, 130.65, 133.39, 133.72, 138.40, 141.69, 146.257; IR ($CHCl_3$) 3018, 2932, 2359, 2061, 2003, 1730, 1439, 1152,

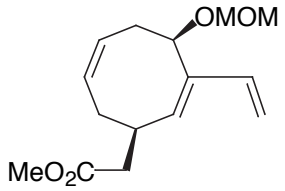
1036, 920, 668 $cm^{-1}$. In a glove box, Grubbs' catalyst (2.4 mg, 2.9 μmol, 0.08 eq) was weighed into a flame dried and evacuated Schlenk flask. The catalyst was dissolved in toluene (0.70 mL) under argon. The ester (20.7 mg, 0.0362 mmol, 1 eq) was dissolved in toluene (2.9 mL) under argon and transferred via cannula to the Schlenk flask. The reaction was stirred under argon for 24 h, and then opened to air and stirred for 15 min. The toluene was removed *in vacuo*, and the resulting green semi-solid was purified by column chromatography (silica gel, hexane/EtOAc, 3:1 to 2.5:1) to give the carbocycle **17** (17.3 mg, 88%) as a yellow solid (mp 115-117 °C). $^1$H NMR (400 MHz, $CDCl_3$) δ 1.50 (m, 1H), 1.83 (app t, 1H, $J$ = 12.8 Hz), 2.10-2.16 (m, 1H), 2.25-2.33 (m, 2H), 2.41 (s, 3H), 2.58-2.69 (m, 4H), 2.85 (d, 1H, $J$ = 12.8 Hz), 3.41 (obs d, 1H), 3.42 (s, 3H), 3.73 (s, 3H), 4.38 (br m, 1H), 4.77 (AB system, 2H, $J_{AB}$ = 7.0 Hz, Δ = 0.07 ppm), 5.22 (d, 1H, $J$ = 7.3 Hz), 5.64 (m, 1H), 5.76 (m, 1H), 7.30 (d, 2H, $J$ = 8.1 Hz), 7.37 (d, 2H, $J$ = 8.1 Hz). Note: the $^1$H NMR spectrum shows an additional doublet at δ 5.28 that is believed to be $H_{1'}$ of a minor Δ6,7-*trans* isomer of **17**. $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.40, 26.16, 34.30, 34.63, 37.16, 45.76, 51.75, 56.36, 71.13, 71.65, 75.74, 76.893, 96.13, 116.18, 123.15, 125.77, 129.93, 132.91, 140.90, 145.50, 172.07, 206.50, 207.70, 211.88; IR ($CHCl_3$) 3018, 2953, 2400, 2060, 2001, 1730, 1439, 1366, 1149, 1036, 922 $cm^{-1}$; HRMS exact mass calcd for $[MH]^+$ 559.1089, found 559.1078.




18

**3-(*S*)-[Carbomethoxymethyl]-8-(*R*)-[(methoxymethyl)oxy]-1-[(*Z*)-($R_s$)-2-*p*-tolylsulfinyl-ethen-1-yl]-cycloocta-1,5-diene (18).** Carbocycle **12** (0.913 g, 0.1721 mmol, 1 eq) was dissolved in acetonitrile (1.7 mL) under argon and cooled to –10 °C. Ferric chloride (0.2792 g, 1.721 mmol, 10 eq) was added in three portions over a 15 minute period. The reaction was stirred for 35 min, then quenched with saturated aqueous $Na_2CO_3$ (55 mL). The solution was

brought to pH ~7 by adding 1*M* aqueous HCl dropwise. The solution was washed with EtOAc (2 x 80 mL). The organic layers were combined and washed with brine (80 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting solid was purified by column chromatography (silica gel, hexane/EtOAc, 1:1 to 1:2) to give the diene **18** (0.0561 g, 98%) as a clear oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.08 (m, 1H), 2.41 (obs s, 3H), 2.44 (m, 3H), 2.63 (dd, 1H, *J* = 5.5, 18.2 Hz), 2.82 (m, 1H), 3.39 (app s, 4H), 3.69 (app s, 3H), 4.65 (app s, 2H), 5.08 (dd, 1H, *J* = 4.8, 9.1 Hz), 5.55, 5.65 (d+m, 3H, *J* = 6.6 Hz), 6.31 (dt, 1H, *J* = 2.2, 10.3 Hz), 6.80 (d, 1H, *J* = 9.9 Hz), 7.30 (d, 2H, *J* = 8.4 Hz), 7.56 (d, 2H, *J* = 8.1 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.38, 34.89, 35.19, 35.36, 41.04, 51.78, 55.86, 74.21, 95.20, 124.75, 126.32, 127.33, 130.01, 136.30, 137.08, 137.50, 138.93, 141.22, 141.99, 172.37; IR ($CHCl_3$) 3427, 3018, 1729, 1597, 1440, 1151, 1037 cm$^{-1}$. HRMS exact mass calcd for $[MH]^+$ 405.1736, found 405.1748.




19

**3-(*S*)-[Carbomethoxymethyl]-1-ethenyl-8-(*R*)-[(methoxymethyl)oxy]-cycloocta-1,5-diene (19).** To a solution of sulfinyl diene **18** (22.1 mg, 0.0528 mmol) in THF (1.6 mL) was added, via syringe, a 0.1 *M* THF solution of $SmI_2$ (1.06 mL, 0.106 mmol, 2 eq). The yellow solution was stirred for 30 min, and then anhydrous MeOH was added via syringe (4.7 μL, 0.11 mmol, 2 eq). After 4.5 h, 2 additional equiv. of $SmI_2$ in THF were added and the solution was stirred for 17 h. At that time, 2 additional equiv. each of $SmI_2$ in THF and anhydrous MeOH were added. The reaction was completed (as judged by TLC) after stirring for an additional 7 h, and the reaction was quenched with 0.1*M* aqueous HCl (8 mL) and diluted with EtOAc (20 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with $H_2O$ (25 mL), saturated aqueous $Na_2S_2O_3$ (25 mL), $H_2O$ (25 mL), and brine (25 mL), then dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (silica gel, hexane/EtOAc, 3:1) to give the diene **19** (11.8 mg, 84%) as a

clear oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.21 (m, 1H), 2.32-2.55 (m, 4H), 2.68 (m, 1H), 3.20 (m, 1H), 3.40 (s, 3H), 3.70 (s, H), 4.61 (AB system, 2H), 4.98 (d, 1H, *J* = 11.1 Hz), 5.08 (dd, 1H, *J* = 9.1, 5.2 Hz), 5.40 (d, 1H, *J* = 17.5 Hz), 5.53 (m, 2H), 5.56 (d, 1H, *J* = 6.1 Hz), 6.27 (dd, 1H, *J* = 17.6, 10.8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 34.4, 34.8, 35.3, 41.0, 51.6, 55.6, 73.1, 94.7, 113.5, 127.0, 127.3, 132.7, 136.9, 138.7, 172.8; IR (neat) 2949, 1736, 1436, 1216, 1151, 1099, 1038, 916.

**Reference:**

1) Paley, R. S.; Estroff, L. A.; McCulley, D. J.; Martînez-Cruz, L. A.; Sánchez, A. J.; Cano, F. H. *Organometallics*, **1998**, *17*, 1841.