

Supplementary information

Unprecedented formation of η^4 -(vinylketene)iron complexes from η^4 -(diene)iron complexes and aromatic compounds in the presence of a Lewis acid

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Experimental Procedures

General. All reactions were performed under a nitrogen atmosphere with magnetic stirring. Column chromatography on silica gel was performed with Fuji Silysia BW-127ZH. Preparative TLC was performed on Wakogel B-5F/TLC-cards (20×20×0.7 cm). Fe(CO)₅ was purchased from Aldrich. Organic solvents were purified and dried by standard procedures.

NMR spectra were recorded on a JEOL JNM-A500 spectrometer at 500 MHz (¹H NMR), 126 MHz (¹³C NMR) or on a Bruker Avance 400 spectrometer at 400 MHz (¹H NMR), 101 MHz (¹³C NMR).

Chemical shifts are reported in ppm relative to TMS as internal standard. FAB-MS was recorded on a JEOL JMS-SX102A system. DART-MS was recorded on JEOL AccuTOF JMS-T100 LC mass spectrometer with a DART ion source.

Infrared spectra were recorded on a JEOL JIR-WINSPEC50 spectrometer.

(1-4-η-3-tert-Butyldimethylsilyloxy-1-phenyl-1,3-butadiene)tricarbonyliron,

(1-4-η-2-tert-butyl dimethylsilyloxy-1,3-butadiene)tricarbonyliron,

(1-4-η-2-tert-butyl dimethylsilyloxy-3-methyl-1,3-butadiene)tricarbonyliron,

(1-4-η-3-tert-butyl dimethylsilyloxy-1-phenyl-1,3-pentadiene)tricarbonyliron,

(1-4-η-2-tert-butyl dimethylsilyloxy-1,1-dimethyl-4-phenyl-1,3-butadiene)tricarbonyliron, and

(1-4-η-3-tert-butyl dimethylsilyloxy-1,7-diphenyl-1,3-heptadiene)tricarbonyliron were prepared from the corresponding silyl enol ethers¹ according to the procedure described below for **1a**.²

Preparation of tricarbonyl(1-4-η-3-methansulfonyloxy-1-phenyl-1,3-butadiene)iron (**1a**)

A mixture of 3-tert-butyl dimethylsilyloxy-1-phenyl-1,3-butadiene (6.55 g, 25.2 mmol) and iron pentacarbonyl (14.8 g, 75.6 mmol) in dibutyl ether (105 mL) was refluxed for 15 h. The mixture was cooled to room temperature, filtered through Celite, concentrated under reduced pressure. The residue was purified by column chromatography with hexane as eluent to give

(1-4-η-3-tert-butyl dimethylsilyloxy-1-phenyl-1,3-butadiene)tricarbonyliron as a yellow solid (4.96 g, 60%); ¹H NMR (CDCl₃, 500 MHz) δ 7.25-7.18 (m, 4H), 7.15-7.10 (m, 1H), 5.75 (d, 1H, *J* = 7.9 Hz), 2.13 (dd, 1H, *J* = 4.2, 1.8 Hz), 1.37 (d, 1H, *J* = 8.3 Hz), 0.98 (s, 9H), 0.67 (dd, 1H, *J* = 4.2, 0.7 Hz), 0.31 (s, 3H), 0.28 (s, 3H); ¹³C NMR (CDCl₃, 126 MHz) δ 210.8, 141.2, 134.2, 128.6, 126.3, 126.0, 74.0, 52.3, 36.8, 25.6, 18.2, -4.1, -4.5; IR (KBr) 2957, 2932, 2859, 2038, 1982, 1950, 1486, 1468, 1339, 1208, 967, 841 cm⁻¹; HRMS (DART-TOF): calcd for C₁₉H₂₅FeO₄Si (M+H⁺) 401.08715, found 401.08573.

A mixture of (1-4- η -3-tert-butyltrimethylsilyloxy-1-phenyl-1,3-butadiene)tricarbonyliron (1.0 g, 2.50 mmol) and cesium fluoride (570mg, 3.75 mmol) in acetonitrile (10 mL) was stirred for 15 min at room temperature under argon. Methanesulfonyl chloride (0.23 ml, 3.00 mmol) was added to the mixture at room temperature. After being stirred for 1 h at room temperature, the reaction was quenched by addition of phosphate buffer (pH = 7). The mixture was extracted twice with ethyl acetate. The combined extracts were washed with aqueous brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by column chromatography with ethylacetate/hexane (1 : 4) as eluent to give **1a** as a yellow solid (783 mg, 86%); ¹H NMR (CDCl₃, 500 MHz) δ 7.29-7.18 (m, 5H), 6.29 (d, 1H, *J* = 8.5 Hz), 3.26 (s, 3H), 2.38 (dd, 1H, *J* = 5.0, 1.5 Hz), 1.52 (d, 1H, *J* = 8.5 Hz), 0.83 (d, 1H, *J* = 4.5 Hz); ¹³C NMR (CDCl₃, 126 MHz) δ 209.0, 138.8, 128.8, 127.0, 126.4, 126.4, 79.6, 53.4, 38.3, 36.0; IR (ATR) 2053, 1970, 1600, 1486, 1459, 1369, 1160, 1018, 970, 906, 885 cm⁻¹; HRMS (DART-TOF): calcd for C₁₄H₁₃FeO₆S (M+H⁺) 364.97823, found 364.97708; Anal. Found: C, 46.49; H, 3.64. Calcd for C₁₄H₁₂FeO₆S: C, 46.18; H, 3.32%.

Preparation of tricarbonyl(1-4- η -1-phenyl-2-*p*-toluenesulfonyloxy-1,3-butadiene)iron (1b)

Iron complex **1b** was prepared using the procedure described above for **1a** using *p*-toluenesulfonyl chloride instead of methanesulfonyl chloride.

Yellow solid; ¹H NMR (CDCl₃, 500 MHz) δ 7.88 (d, 2H, *J* = 8.0 Hz), 7.40 (d, 2H, *J* = 8.0 Hz), 7.25-7.15 (m, 5H), 6.09 (d, 1H, *J* = 8.5 Hz), 2.48 (s, 3H), 2.06 (dd, 1H, *J* = 1.8, 4.8 Hz), 1.39 (d, 1H, *J* = 9.0 Hz), 0.62 (d, 1H, *J* = 5.0 Hz); ¹³C NMR (CDCl₃, 126 MHz) δ 209.1, 145.9, 139.0, 132.3, 130.1, 129.0, 128.8, 128.7, 126.9, 126.6, 126.4, 79.6, 53.1, 36.4, 21.8; IR (ATR) 3029, 2918, 2048, 1965, 1596, 1486, 1459, 1375, 1321, 1307, 1093, 1018, 906, 883, 831, 815, 748, 694 cm⁻¹; Anal. Found: C, 54.93; H, 3.91. Calcd for C₂₀H₁₆FeO₆S: C, 54.56; H, 3.66%.

Preparation of (1-4- η -2-acetoxy-1-phenyl-1,3-butadiene)tricarbonyliron (1c)

Iron complex **1c** was prepared using the procedure described above for **1a** using acetyl chloride instead of methanesulfonyl chloride.

Yellow solid; ¹H NMR (CDCl₃, 500 MHz) δ 7.32-7.202 (m, 4H), 7.15 (t, 1H, *J* = 15.3 Hz), 6.12 (d, 1H, *J* = 8.5 Hz), 2.25 (s, 3H), 2.19 (dd, 1H, *J* = 2.0, 4.5 Hz), 1.56 (d, 1H, *J* = 8.5 Hz), 0.90 (d, 1H, *J* = 4.5 Hz); ¹³C NMR (CDCl₃, 126 MHz) δ 209.8, 170.2, 139.6, 128.7, 126.6, 126.4, 78.4, 53.2, 36.9, 21.1; IR

(ATR) 3035, 2921, 2846, 2042, 1758, 1488, 1471, 1367, 1211, 1012, 929, 854, 794, 759, 694 cm^{-1} ; Anal. Found: C, 55.26; H, 4.04. Calcd for $\text{C}_{15}\text{H}_{12}\text{FeO}_5$: C, 54.91; H, 3.69%.

Preparation of (1–4- η -2-benzoyloxy-1-phenyl-1,3-butadiene)tricarbonyliron (1d)

Iron complex **1d** was prepared using the procedure described above for **1a** using benzoyl chloride instead of methanesulfonyl chloride.

Yellow solid; ^1H NMR (CDCl_3 , 500 MHz) δ 8.12 (d, 2H, $J = 7.5$ Hz), 7.65 (t, 1H, $J = 7.3$ Hz), 7.51 (t, 2H, $J = 5.5$ Hz), 7.28–7.24 (m, 4H), 7.18 (t, 1H, $J = 6.3$ Hz), 6.27 (d, 1H, $J = 8.5$ Hz), 2.33 (dd, 1H, $J = 1.5, 4.5$ Hz), 1.65 (d, 1H, $J = 8.5$ Hz), 1.02 (d, 1H, $J = 5.0$ Hz); ^{13}C NMR (CDCl_3 , 126 MHz) δ 209.9, 166.0, 139.7, 134.0, 130.0, 128.7, 128.7, 127.0, 126.6, 126.4, 78.6, 53.3, 37.3; IR (ATR) 3031, 2917, 2846, 2360, 2044, 1974, 1731, 1600, 1486, 1452, 1257, 1176, 1060, 1025, 1014, 877, 757, 709 cm^{-1} ; Anal. Found: C, 61.61; H, 4.02. Calcd for $\text{C}_{20}\text{H}_{14}\text{FeO}_5$: C, 61.57; H, 3.62%.

Preparation of tricarbonyl(1–4- η -2-diethoxyphosphoryloxy-1-phenyl-1,3-butadiene)iron (1e)

Iron complex **1e** was prepared using the procedure described above for **1a** using diethyl chlorophosphate instead of methanesulfonyl chloride.

Yellow oil; ^1H NMR (CDCl_3 , 500 MHz) δ 7.27–7.21 (m, 4H), 7.17 (t, 1H, $J = 7.0$ Hz), 6.26 (d, 1H, $J = 8.5$ Hz), 4.26 (dq, 4H, $J = 21.0, 7.0$ Hz), 2.44 (dd, 1H, $J = 1.3, 4.8$ Hz), 1.41 (dt, 6H, $J = 6.8, 8.0$ Hz), 0.76 (d, 1H, $J = 4.5$ Hz); ^{13}C NMR (CDCl_3 , 126 MHz) δ 209.7, 128.7, 128.4 (d, $J = 3.5$ Hz), 126.6, 126.4, 76.2 (d, $J = 4.7$ Hz), 65.7 (d, $J = 5.8$ Hz), 64.9 (t, $J = 4.7$ Hz), 16.2–16.0 (m); IR (ATR) 2987, 2917, 2846, 2042, 1978, 1600, 1484, 1394, 1371, 1328, 1290, 1197, 1166, 1018, 941, 798, 757, 696 cm^{-1} ; Anal. Found: C, 48.29; H, 4.66. Calcd for $\text{C}_{17}\text{H}_{19}\text{FeO}_7\text{P}$: C, 48.37; H, 4.54%.

Preparation of tricarbonyl(1–4- η -2-methanesulfonyloxy-1,3-butadiene)iron (1f)

Iron complex **1f** was prepared from (1–4- η -2-tert-butyldimethylsilyloxy-1,3-butadiene)tricarbonyliron by the same procedure used for the synthesis of **1a**.

Pale yellow solid; ^1H NMR (CDCl_3 , 500 MHz) δ 5.80 (t, 1H, $J = 8.0$ Hz), 3.23 (s, 3H), 2.33 (d, 1H, $J = 4.8$ Hz), 1.59 (dd, 1H, $J = 7.0, 2.5$ Hz), 0.52 (d, 1H, $J = 4.5$ Hz), -0.29 (dd, 1H, $J = 8.8, 2.5$ Hz); ^{13}C NMR (CDCl_3 , 126 MHz) δ 209.0, 129.1, 38.2, 37.0, 31.5; IR (ATR) 2057, 1967, 1371, 1168, 968, 869 cm^{-1} ; Anal. Found: C, 33.44; H, 2.93. Calcd for $\text{C}_8\text{H}_8\text{FeO}_6\text{S}$: C, 33.36; H, 2.80%.

Preparation of tricarbonyl(1–4- η -2-methansulfonyloxy-3-methyl-1,3-butadiene)iron (**1g**)

Iron complex **1g** was prepared from (1–4- η -2-tert-butyldimethylsilyloxy-3-methyl-1,3-butadiene)tricarbonyliron by the same procedure used for the synthesis of **1a**.

Yellow oil; ^1H NMR (CDCl_3 , 500 MHz) δ 3.22 (s, 3H), 2.36 (s, 3H), 2.22 (d, 1H, $J = 4.5$ Hz), 1.66 (d, 1H, $J = 2.5$ Hz), 0.39 (d, 1H, $J = 4.5$ Hz), -0.18 (d, 1H, $J = 2.5$ Hz); ^{13}C NMR (CDCl_3 , 126 MHz) δ 209.2, 126.8, 98.1, 38.7, 36.7, 35.2, 18.6; IR (ATR) 2049, 1959, 1365, 1253, 1182, 1149, 970, 914 cm^{-1} ; Anal. Found: C, 35.86; H, 3.44. Calcd for $\text{C}_9\text{H}_{10}\text{FeO}_6\text{S}$: C, 35.78; H, 3.34%.

Preparation of tricarbonyl(1–4- η -3-methansulfonyloxy-1-phenyl-1,3-pentadiene)iron (**1h**)

Iron complex **1h** was prepared from (1–4- η -3-tert-butyldimethylsilyloxy-1-phenyl-1,3-pentadiene)tricarbonyliron by the same procedure used for the synthesis of **1a**.

Yellow solid; ^1H NMR (CDCl_3 , 500 MHz) δ 7.30-7.16 (m, 5H), 6.16 (d, 1H, $J = 9.0$ Hz), 3.29 (s, 3H), 1.64 (d, 3H, $J = 6.5$ Hz), 1.54 (d, 1H, $J = 9.0$ Hz), 1.50 (q, 1H, $J = 6.2$ Hz); ^{13}C NMR (CDCl_3 , 126 MHz) δ 209.6, 139.0, 128.7, 126.9, 126.5, 126.0, 76.2, 52.3, 52.1, 38.5, 14.7; IR (ATR) 2051, 1955, 1598, 1471, 1369, 1166, 964, 873, 840 cm^{-1} ; Anal. Found: C, 47.63; H, 3.92. Calcd for $\text{C}_{15}\text{H}_{14}\text{FeO}_6\text{S}$: C, 47.64; H, 3.73%.

Preparation of tricarbonyl(1–4- η -2-methansulfonyloxy-1,1-dimethyl-4-phenyl-1,3-butadiene)iron (**1i**)

Iron complex **1i** was prepared from (1–4- η -2-tert-butyldimethylsilyloxy-1,1-dimethyl-4-phenyl-1,3-butadiene)tricarbonyliron by the same procedure used for the synthesis of **1a**.

Yellow solid; ^1H NMR (CDCl_3 , 500 MHz) δ 7.33-7.18 (m, 5H), 6.14 (d, 1H, $J = 9.5$ Hz), 3.27 (s, 3H), 2.89 (d, 1H, $J = 9.0$ Hz), 1.79 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (CDCl_3 , 126 MHz) δ 209.5, 139.8, 128.7, 127.9, 126.9, 126.6, 80.9, 65.4, 51.1, 38.3, 28.7, 21.0; IR (KBr) 3028, 2840, 2049, 1966, 1600, 1485, 1364, 1177, 951 cm^{-1} ; HRMS (DART-TOF): calcd for $\text{C}_{16}\text{H}_{17}\text{FeO}_6\text{S}$ ($\text{M}+\text{H}^+$) 393.00953, found 393.01063.

Preparation of tricarbonyl(1–4- η -3-methansulfonyloxy-1,7-diphenyl-1,3-heptadiene)iron (**1j**)

Iron complex **1j** was prepared from (1–4- η -3-tert-butyldimethylsilyloxy-1,7-diphenyl-1,3-heptadiene)tricarbonyliron by the same procedure used for the synthesis of **1a**.

Yellow oil; ^1H NMR (CDCl_3 , 500 MHz) δ 7.32-7.16 (m, 10H), 6.18 (d, 1H, $J = 9.0$ Hz), 3.23 (s, 3H), 2.73 (ddt, 2H, $J = 21.5, 14.0, 7.0$ Hz), 2.12 (dq, 1H, $J = 11.5, 7.3$ Hz), 1.91 (dquin, 2H, $J = 14.5, 7.4$ Hz), 1.80 (dq, 1H, $J = 16.5, 7.7$ Hz); ^{13}C NMR (CDCl_3 , 126 MHz) δ 209.1, 141.8, 138.9, 128.7, 128.4, 126.9, 126.4, 125.9, 125.1, 76.0, 58.6, 52.3, 38.6, 35.8, 33.2, 28.8; IR (ATR) 3027, 2919, 2850, 2042, 1961, 1600, 1492, 1463, 1353, 1166, 1072, 1029, 968, 885, 790, 759, 696 cm^{-1} ; Anal. Found: C, 57.37; H, 4.84. Calcd for $\text{C}_{23}\text{H}_{22}\text{FeO}_6\text{S}$: C, 57.27; H, 4.60%.

General Procedure for the Lewis acid-promoted reaction between aromatic compound and iron complex 1a–j:

To a solution of an aromatic compound (0.7 mmol) and gallium chloride or aluminum chloride (0.7 mmol) in *o*-dichlorobenzene (1.5 mL) was added iron complex **1** (0.14 mmol) at room temperature under CO. After being stirred for 1 h at room temperature, the reaction was quenched by addition of phosphate buffer (pH = 7). The mixture was extracted twice with ethyl acetate. The combined extracts were washed with aqueous brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by TLC with ethylacetate/hexane (1:10) as eluent to give (vinylketene)iron complex **2**.

Tricarbonyl[1–4- η -4-phenyl-2-(2,3,5-trimethylphenyl)methyl-1,3-butadien-1-one]iron (2a)

Yellow solid; IR (ATR) 2917, 2051, 1976, 1766, 1608, 1450, 1373, 1029, 854 cm^{-1} ; ^1H NMR (500 MHz; CDCl_3 ; Me_4Si) δ , 7.29-7.21 (m, 5H), 6.92 (s, 2H), 6.02 (d, 1H, $J = 9.5$ Hz), 3.64 (d, 1H, $J = 16.5$ Hz), 3.43 (d, 1H, $J = 16.5$ Hz), 3.18 (d, 1H, $J = 9.0$ Hz), 2.35 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (126 MHz; CDCl_3 ; Me_4Si) δ 233.7, 208.0, 138.2, 136.9, 136.8, 130.6, 129.5, 129.1, 127.5, 126.6, 96.1, 59.1, 50.1, 27.0, 20.9, 20.3; MS (DART-TOF) m/z 417 ($\text{M}+\text{H}^+$); HRMS (DART-TOF): calcd for $\text{C}_{23}\text{H}_{21}\text{FeO}_4$ ($\text{M}+\text{H}^+$) 417.07893, found 417.07929; Anal. Found: C, 66.47; H, 5.13. Calcd for $\text{C}_{23}\text{H}_{20}\text{FeO}_4$: C, 66.37; H, 4.84%.

Tricarbonyl(1–4- η -4-phenyl-2-phenylmethyl-1,3-butadien-1-one)iron (2aa)

Yellow solid; ^1H NMR (CDCl_3 , 500 MHz) δ 7.39 (t, 2H, $J = 4.5$ Hz), 7.34-7.21 (m, 8H), 6.05 (d, 1H, $J = 9.5$ Hz), 3.61 (d, 1H, $J = 15.0$ Hz), 3.27 (d, 1H, $J = 9.5$ Hz), 3.21 (d, 1H, $J = 15.0$ Hz); ^{13}C NMR (CDCl_3 , 126 MHz) δ 233.7, 207.7, 138.0, 137.1, 129.1, 129.0, 128.9, 127.6, 127.5, 126.6, 95.5, 60.2, 50.3, 33.9;

IR (ATR) ν_{\max} 3031, 2921, 2850, 2055, 1970, 1770, 1600, 1494, 1454, 1373, 1076, 1029, 900 cm^{-1} ;
Anal. Found: C, 64.22; H, 4.07. Calcd for $\text{C}_{20}\text{H}_{14}\text{FeO}_4$: C, 64.20; H, 3.77%.

Tricarbonyl[1-4- η -2-(methoxyphenyl)methyl-4-phenyl-1,3-butadien-1-one]iron (2ab)

Obtained as a mixture of regioisomer; yellow solid; ^1H NMR (CDCl_3 , 500 MHz, mixture of regioisomers **A/B**) δ 7.31-7.07 (m, 9H), 6.05 (d, 1H, $J = 9.5$ Hz), 3.56 (dd, 1H, $J = 1.8, 15.3$ Hz), 3.26 (dd, 1H, $J = 4.5, 9.5$ Hz), 3.16 (d, 1H, $J = 15.0$ Hz), 2.37 (s, 3H, **A**), 2.36 (s, 3H, **B**); ^{13}C NMR (CDCl_3 , 126 MHz) δ 233.8 (**B**), 233.7 (**A**), 207.8, 138.7, 138.07, 137.1 (**B**), 137.1 (**A**), 134.0, 129.8(**B**), 129.7(**A**), 129.1(**A**), 129.1(**B**), 128.9, 128.8, 128.2, 127.6, 126.6, 126.0, 95.6 (**A**), 95.4 (**B**), 60.1 (**A**), 60.1 (**B**), 50.5 (**B**), 50.4 (**A**), 33.9 (**A**), 33.5 (**B**), 21.4 (**A**), 21.1 (**B**); IR (ATR) 3027, 2921, 2846, 2053, 1968, 1776, 1606, 1513, 1490, 1452, 1430, 1373, 1074, 1029, 941, 827, 759, 694 cm^{-1} ; Anal. Found: C, 65.19; H, 4.52. Calcd for $\text{C}_{21}\text{H}_{16}\text{FeO}_4$: C, 64.97; H, 4.15%.

Tricarbonyl[1-4- η -2-(2,4-dimethoxyphenyl)methyl-4-phenyl-1,3-butadien-1-one]iron (2ac)

Yellow oil, ^1H NMR (CDCl_3 , 500 MHz) δ 7.31-7.22 (m, 5H), 7.13 (d, 1H, $J=7.7$ Hz), 7.04 (d, 1H, $J=7.7$ Hz), 6.97 (s, 1H), 5.99 (d, 1H, $J=9.3$ Hz), 3.62 (d, 1H, $J=15.6$ Hz), 3.24 (d, 1H, $J=9.3$ Hz), 3.16, (d, 1H, $J=15.6$ Hz), 2.37 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (CDCl_3 , 126 MHz) δ 233.6, 138.1, 136.1, 135.2, 134.0, 133.0, 130.6, 130.5, 129.1, 128.3, 127.6, 126.5, 95.8, 59.8, 50.4, 31.0, 21.0, 19.2; IR (KBr) 3029, 2924, 2057, 1985, 1785, 1693 cm^{-1} ; MS (FAB) m/z 403 ($\text{M}+\text{H}^+$); HRMS (FAB): calcd for $\text{C}_{22}\text{H}_{19}\text{O}_4\text{Fe}$ ($\text{M}+\text{H}^+$) 403.0633, found 403.0628.

A mixture of

tricarbonyl[1-4- η -2-(2-methoxyphenyl)methyl-4-phenyl-1,3-butadien-1-one]iron(*ortho*) and tricarbonyl[1-4- η -2-(4-methoxyphenyl)methyl-4-phenyl-1,3-butadien-1-one]iron(*para*) (2ad)

Obtained as a mixture of regioisomer (*para* : *ortho* = 1 : 0.5); yellow solid; ^1H NMR (CDCl_3 , 500 MHz, *ortho*) δ 7.40-7.19 (m, 7H), 6.98-6.93 (m, 2H), 6.18 (d, 1H, $J = 9.0$ Hz), 3.87 (s, 3H), 3.63 (d, 1H, $J = 15.0$ Hz), 3.30 (d, 1H, $J = 15.0$ Hz), 3.21 (d, 1H, $J = 9.5$ Hz); ^1H NMR (CDCl_3 , 500 MHz, *para*) δ 7.34-7.17 (m, 7H), 6.92 (d, 2H, $J = 8.5$ Hz), 6.03 (d, 1H, $J = 9.0$ Hz), 3.82 (s, 3H), 3.55 (d, 1H, $J = 15.5$ Hz), 3.26 (d, 1H, $J = 9.5$ Hz), 3.15 (d, 1H, $J = 15.0$ Hz); ^{13}C NMR (CDCl_3 , 126 MHz, *ortho*) δ 234.0, 207.9, 157.3, 138.4, 129.1, 128.9, 127.4, 126.6, 126.5, 125.6, 120.9, 110.6, 96.4, 59.3, 55.2, 50.5, 28.1;

^{13}C NMR (CDCl_3 , 126 MHz, *para*) δ 233.8, 207.9, 159.0, 138.0, 130.0, 129.1, 129.0, 127.6, 126.5, 114.3, 95.3, 60.1, 55.3, 50.6, 33.1; IR (ATR) 3029, 2940, 2049, 2966, 1600, 1485, 1450, 1364, 1177, 1059, 951, 695 cm^{-1} ; HRMS (DART-TOF): calcd for $\text{C}_{21}\text{H}_{17}\text{O}_5\text{Fe}$ ($\text{M}+\text{H}^+$) 405.04254, found 405.04393.

Tricarbonyl[1–4- η –4-phenyl-2-(4-phenylphenyl)methyl-1,3-butadien-1-one]iron (2ae)

Yellow solid; ^1H NMR (CDCl_3 , 500 MHz) δ 7.64-7.60 (m, 4 H), 7.46 (t, 2H, $J = 6.0$ Hz), 7.38-7.35 (m, 3H), 7.30-7.22 (m, 5H), 6.11 (d, 1H, $J = 7.6$ Hz), 3.64 (d, 1H, $J = 12.4$ Hz), 3.30 (d, 1H, $J = 7.2$ Hz), 3.26 (d, 1H, $J = 12.0$ Hz); ^{13}C NMR (CDCl_3 , 126 MHz) δ 233.8, 140.5, 140.4, 137.9, 136.2, 129.4, 129.1, 129.0, 128.8, 127.7, 127.6, 127.5, 127.1, 126.6, 95.4, 60.2, 50.2, 33.7; IR (ATR) 3027, 2917, 2842, 2051, 1968, 1774, 1600, 1486, 1450, 1430, 1049, 1373, 1180, 1105, 1076, 1008, 910, 854, 831, 757, 736 cm^{-1} ; Anal. Found: C, 69.31; H, 4.34. Calcd for $\text{C}_{23}\text{H}_{20}\text{FeO}_4$: C, 69.35; H, 4.03%.

Tricarbonyl[1–4- η –4-phenyl-2-(naphthyl)methyl-1,3-butadien-1-one]iron (2af)

Obtained as a mixture of regioisomer; yellow solid; ^1H NMR (CDCl_3 , 500 MHz, mixture of regioisomers **A/B**) δ 8.08 (d, 1H, $J = 6.8$ Hz, **B**), 7.92-7.83 (m, 3H), 7.75 (s, 1H, **A**), 7.59-7.55 (m, 2H, **B**), 7.53-7.47 (m, 2H, **A**), 7.40 (dd, 1H, $J = 1.5, 8.5$ Hz, **A**), 7.29-7.18 (m, 5H), 6.09 (d, 1H, $J = 7.2$ Hz, **A**), 6.05 (d, 1H, $J = 7.6$ Hz, **B**), 4.16 (d, 1H, $J = 12.4$ Hz, **B**), 3.78 (d, 1H, $J = 12.4$ Hz, **A**), 3.63 (d, 1H, $J = 12.8$ Hz, **B**), 3.37 (d, 1H, $J = 12.0$ Hz, **A**), 3.30 (d, 1H, $J = 7.6$ Hz, **B**), 3.23 (d, 1H, $J = 7.6$ Hz, **A**); ^{13}C NMR (CDCl_3 , 126 MHz, **A/B**) δ 233.8, 137.9, 134.5, 133.5, 132.6, 129.1, 128.8 (**A**), 128.3 (**B**), 127.8 (**A**), 127.7 (**A**), 127.7 (**A**), 127.6, 127.6 (**B**), 126.9 (**A**), 126.7 (**B**), 126.6, 126.5 (**B**), 126.5 (**A**), 126.1 (**B**), 126.0 (**A**), 125.6 (**B**), 123.5 (**B**), 96.0 (**B**), 95.5 (**A**), 60.3 (**A**), 59.9 (**B**), 50.7 (**B**), 50.1 (**A**), 34.1; IR (ATR) 3058, 2921, 2846, 2055, 1968, 1770, 1600, 1508, 1490, 1452, 1430, 1371, 1074, 1027, 958, 896, 860, 754 cm^{-1} ; Anal. Found: C, 67.58; H, 4.18. Calcd for $\text{C}_{24}\text{H}_{16}\text{FeO}_4$: C, 67.95; H, 3.80%.

Tricarbonyl[1–4- η –2-(chlorophenyl)methyl-4-phenyl-1,3-butadien-1-one]iron (2ag)

Obtained as a mixture of regioisomer; yellow oil; ^1H NMR (CDCl_3 , 500 MHz, mixture of regioisomers **A/B**) δ 7.37-7.21 (m, 9H), 6.26 (d, 1H, $J = 9.3$ Hz, **B**), 6.06 (d, 1H, $J = 9.3$ Hz, **A**), 3.76 (d, 1H, $J = 15.1$ Hz, **B**), 3.56 (d, 1H, $J = 15.2$ Hz, **A**), 3.42 (d, 1H, $J = 15.1$, **B**), 3.29 (d, 1H, $J = 9.3$, **A**), 3.27 (d, 1H, $J = 9.1$ Hz, **B**), 3.20 (d, 1H, $J = 15.2$ Hz, **A**); ^{13}C NMR (CDCl_3 , 126 MHz, mixture of regioisomers **A/B**) δ 233.5, 208.0, 138.0 (**B**), 137.8 (**A**), 135.6 (**A**), 135.4 (**B**), 133.4 (**B**), 133.4 (**A**), 131.3 (**B**), 130.3 (**A**), 129.9 (**B**), 129.2 (**A**), 129.2 (**B**), 129.1 (**A**), 129.0 (**B**), 127.8 (**A**), 127.7 (**B**), 127.4 (**B**), 126.6 (**B**), 126.6

(B), 96.5 (B), 95.3 (A), 60.4 (A), 59.9 (B), 50.0 (B), 49.7 (A), 33.5 (A), 31.2 (B); IR (KBr) 3061, 3030, 2925, 2253, 2094, 2059, 1987, 1770 cm^{-1} ; HRMS (DART-TOF): calcd for $\text{C}_{20}\text{H}_{14}\text{O}_5\text{ClFe}$ ($\text{M}+\text{H}^+$) 408.99300, found 408.99421.

Tricarbonyl[1-4- η -2-(2,4,6-trimethylphenyl)methyl-1,3-butadien-1-one]iron (2f)

Yellow solid; ^1H NMR (CDCl_3 , 500 MHz) δ 6.90 (s, 2H), 5.52 (dd, 1H, $J = 7.0, 8.5$ Hz), 3.57 (d, 1H, $J = 16.5$ Hz), 3.36 (d, 1H, $J = 16.5$ Hz), 2.45 (dd, 1H, $J = 2.0, 7.0$ Hz), 2.31 (s, 6H), 2.28 (s, 3H), 1.34 (dd, 1H, $J = 2.0, 9.0$ Hz); ^{13}C NMR (CDCl_3 , 126 MHz) δ 234.3, 207.6, 136.8, 136.8, 130.7, 129.4, 99.6, 55.2, 37.2, 26.8, 20.9, 20.2; IR (ATR) 2913, 2059, 1982, 1764, 1448, 1033, 854 cm^{-1} ; Anal. Found: C, 60.20; H, 5.00. Calcd for $\text{C}_{17}\text{H}_{16}\text{FeO}_4$: C, 60.03; H, 4.74%.

Tricarbonyl[1-4- η -3-methyl-2-(2,4,6-trimethylphenyl)methyl-1,3-butadien-1-one]iron (2g)

Yellow solid; ^1H NMR (CDCl_3 , 500 MHz) δ 6.84 (s, 2H), 3.59 (d, 1H, $J = 16.0$ Hz), 3.48 (d, 1H, $J = 16.0$ Hz), 2.55 (s, 1H), 2.28 (m, 12H), 1.27 (s, 1H); ^{13}C NMR (CDCl_3 , 126 MHz) δ 231.6, 207.9, 136.8, 136.6, 130.2, 129.2, 115.2, 58.3, 41.5, 27.0, 20.9, 20.6, 19.0; IR (ATR) 2921, 2055, 1972, 1776, 1612, 1444, 1378, 1031, 852 cm^{-1} ; Anal. Found: C, 61.31; H, 5.31. Calcd for $\text{C}_{18}\text{H}_{18}\text{FeO}_4$: C, 61.04; H, 5.12%.

Tricarbonyl{1-4- η -2-[1-(2,4,6-trimethylphenyl)ethyl]-4-phenyl-1,3-butadien-1-one}iron (2h)

Yellow solid; ^1H NMR (CDCl_3 , 500 MHz) δ 7.28-7.20 (m, 5H), 6.88 (s, 2H), 6.14 (d, 1H, $J = 9.0$ Hz), 3.97 (q, 1H, $J = 7.3$ Hz), 3.11 (d, 1H, $J = 9.5$ Hz), 2.42 (s, 3H), 1.39 (d, 1H, $J = 7.0$ Hz); ^{13}C NMR (CDCl_3 , 126 MHz) δ 231.2, 208.0, 139.7, 137.9, 136.4, 135.8, 134.9, 131.4, 129.2, 129.0, 128.8, 127.6, 126.6, 95.4, 60.3, 55.3, 37.4, 20.7, 16.0; IR (ATR) 2921, 2055, 1968, 1776, 1610, 1450, 1378, 1029, 910, 854 cm^{-1} ; Anal. Found: C, 67.30; H, 5.47. Calcd for $\text{C}_{24}\text{H}_{22}\text{FeO}_4$: C, 66.99; H, 5.15%.

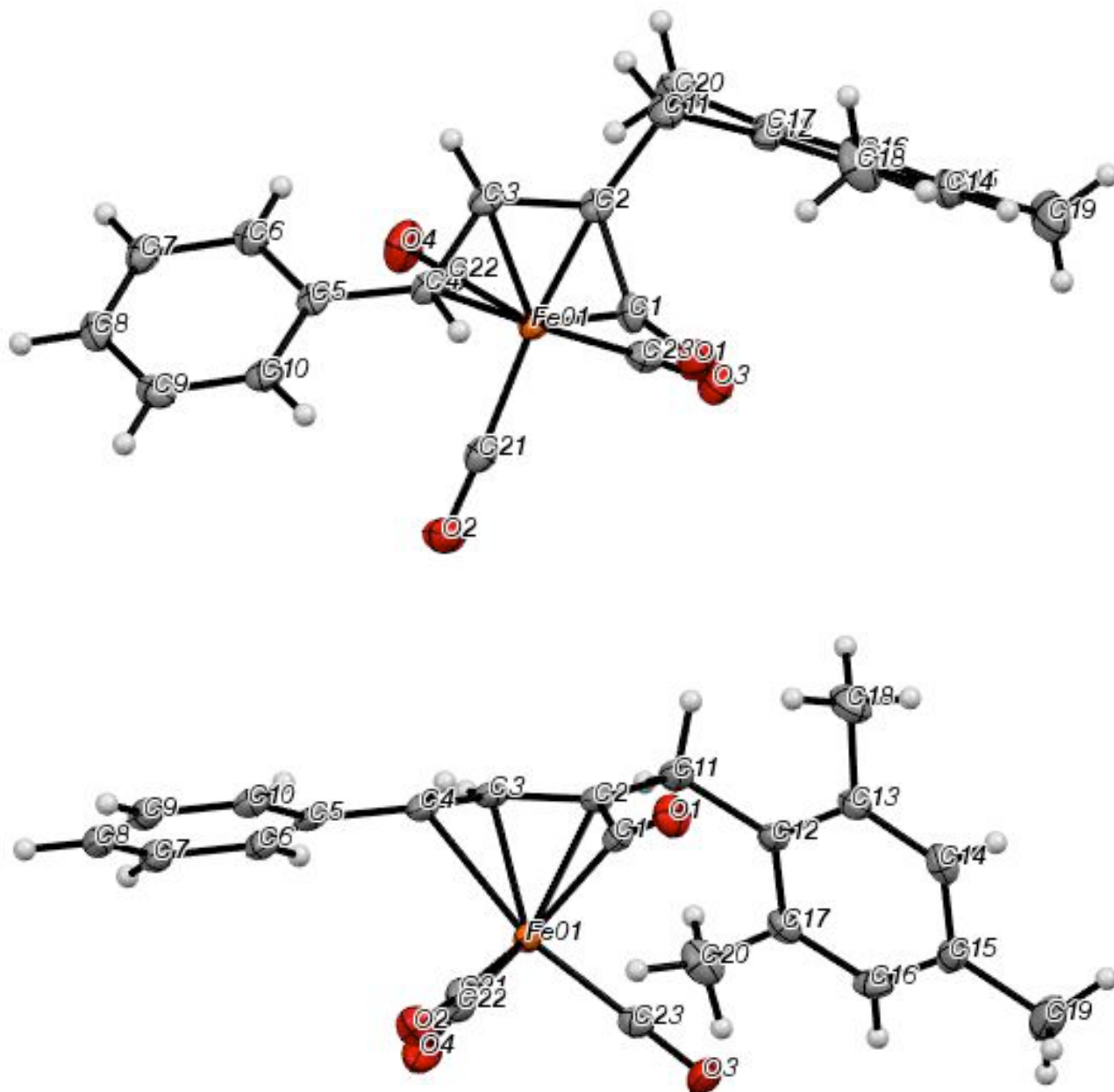
Tricarbonyl[1-4- η -2-[1-(3,5-dimethylphenyl)-1-methylethyl]-4-phenyl-1,3-butadien-1-one]iron (2i)

Yellow solid; ^1H NMR (CDCl_3 , 500 MHz) δ 7.29-7.20 (m, 5H), 7.05 (s, 2H), 6.95 (s, 1H), 5.84 (d, 1H, $J = 9.5$ Hz), 3.61 (d, 1H, $J = 15.0$ Hz), 3.17 (d, 1H, $J = 9.5$ Hz), 2.35 (s, 6H), 1.63 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (CDCl_3 , 126 MHz) δ 232.4, 208.3, 146.0, 138.0, 138.0, 129.1, 128.7, 127.6, 126.6, 123.9, 94.1, 61.9, 60.9, 36.9, 28.7, 27.3, 21.6; IR (ATR) 2917, 2053, 1978, 1756, 1598, 1463, 1365, 1211, 1027, 865, 846, 759, 696 cm^{-1} ; Anal. Found: C, 67.34; H, 5.47. Calcd for $\text{C}_{24}\text{H}_{22}\text{FeO}_4$: C, 66.99; H, 5.15%.

Tricarbonyl[1-4-η-4-phenyl-2-[1,2,3,4-tetrahydro-1-naphthyl]-1,3-butadien-1-one]iron (2j)

Yellow solid; ^1H NMR (CDCl_3 , 500 MHz) δ 7.30-7.19 (m, 6H), 7.16 (d, 2H, $J = 7.0$ Hz), 7.00 (d, 1H, $J = 7.5$ Hz), 5.39 (d, 1H, $J = 9.5$ Hz), 3.44-3.42 (m, 1H), 3.28 (d, 1H, $J = 9.5$ Hz), 2.94-2.81 (m, 2H), 2.33-2.30 (m, 1H), 2.06-1.94 (m, 2H), 1.88 (m, 1H); ^{13}C NMR (CDCl_3 , 126 MHz) δ 233.4, 211.0, 138.1, 137.7, 132.8, 129.9, 129.1, 129.0, 127.5, 127.4, 126.5, 125.6, 95.7, 60.2, 54.1, 35.8, 28.9, 26.2, 18.0; IR (ATR) 3025, 2929, 2051, 1976, 1770, 1596, 1488, 1452, 1074, 910, 815, 757, 738, 696 cm^{-1} ; Anal. Found: C, 66.81; H, 4.38. Calcd for $\text{C}_{23}\text{H}_{18}\text{FeO}_4$: C, 66.69; H, 4.38%.

Crystal Structure of 2a



X-ray data for Tricarbonyl[1-4- η -4-phenyl-2-(2,3,5-trimethylphenyl)methyl-1,3-butadien-1-one]iron (**2a**): $C_{23}H_{20}FeO_4$ Mw= 416.24; T=90.(2) K; $\lambda = 0.71073$ nm; Monoclinic; P 1 21/n 1 space group; a = 0.868790(10) nm, b = 0.641630(10) nm, c = 3.47054(5) nm; $\alpha = 90^\circ$, $\beta = 94.7760(10)^\circ$, $\gamma = 90^\circ$; V = 1.92791(5) nm³; Z = 4; D = 1.434 Mg/cm³; size = 0.20 x 0.20 x 0.40 mm; R = 0.0523, wR = 0.0728; \checkmark GoF = 2.394.

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