Michael Addition Reactions of the Highly Functionalized Zinc–Copper Reagents RCu(CN)ZnI to (Tropone)iron Tricarbonyl Promoted by Boron Trifluoride Etherate

Ming-Chang P. Yeh,* Chong-Chen Hwu, Chuen-Her Ueng, and Huei-Lin Lue

Department of Chemistry, National Taiwan Normal University,
88 Section 4, Ding-Jou Road, Taipei, Taiwan, 117 ROC

The zinc–copper reagents RCu(CN)ZnI, containing various functional groups such as a cyanide, ester, thio ester or benzyl, react with (tropone)iron tricarbonyl in the presence of an excess of boron trifluoride etherate to afford the Michael adducts in excellent yields. Cyano-substituted 1,4-adducts undergo an intramolecular cyclization reaction in situ, leading to highly functionalized bicyclo[5.3.0]decane and –[5.4.0]undecane derivatives, whereas treatments of an ester-substituted 1,4-adduct with lithium diisopropylamide (LDA) under an atmosphere of carbon monoxide furnishes a highly functionalized bridged bicyclo[4.2.1]nonenecarboxylic acid derivative in 88% yield.

Seven-membered carbocycles are commonly used in construction of complicated natural products.[1] Recently, tropone (1)[2] and (tropone)iron tricarbonyl (2)[3] have been shown to be versatile building blocks for the synthesis of a variety of sesquiterpenes with the bicyclo[5.3.0]decane skeleton.[4] Normally, several steps starting from 1,8-addition of a protected functionalized three-carbon chain to tropone were needed to construct the bicyclo[5.3.0]-decane or the perhydroazulene ring system.[2] Rosenblum had demonstrated that the reaction of tropyliumiron tricarbonyl cation salts with (η^1-allyl)Fp (Fp = C$_5$H$_5$Fe-(CO)$_2$) complexes gave the perhydroazulene ring system in a single step.[3a,5a] In addition, Helquist had reported the direct generation of a tricyclic cycloheptanone-containing system in a one-pot reaction sequence by the condensation of lithium cyclohexenolate with a cyclopropanone derivative.[5b] Here, we report that both fused bicyclo[5.3.0]decane and –[5.4.0]undecane skeletons can be constructed in a single step via 1,4-addition of cyano-substituted zinc–copper reagents[6] to the readily available (tropone)iron tricarbonyl complex (2) followed by in situ

addition of the resulting boron enolate to the pendant nitrile group. Moreover, the intramolecular cyclization of an ester-substituted 1,4-adduct using LDA provides a bicyclo[4.2.1]nonenecarboxylic acid derivative which cannot be obtained via intramolecular cyclization of C-5-ester-substituted (η^4-cyclohexa-1,3-diene)Fe(CO)$_3$ complexes.[7]

Results and Discussion

Conjugated Addition Reactions of Functionalized Zinc–Copper Reagents to (Tropone)iron Tricarbonyl (2). The addition of carbon nucleophiles to tropone (1) and (tropone)iron tricarbonyl (2) was reported in the literature. The addition of lithium enolates or Grignard reagents to 1 in a 1,8-fashion produced 2-substituted dihydrotropone,[2a–c,8] whereas the addition of lithium, magnesium, and hydride reagents to 2 at the C-1 position generated the corresponding alcohol complexes.[3b,9] However, only two typical Michael nucleophiles (sodium diethyl malonate and K-Selectride [KHB(*sec*-Bu)$_3$]) were known to add to 2 to provide the (dihydrotropone)iron tricarbonyl complexes.[3b] Reports of the addition of organocopper derivatives to 2 are lacking. The failure of the addition may be due to the electron-rich character of the uncomplexed double bond.[3c,10] However, with an excess of boron trifluoride etherate (BF$_3$·OEt$_2$),[11] we have successfully performed the conjugate addition reaction under mild reaction conditions. Thus, treatment of 2 with 3.0 molar equiv of functionalized zinc–copper reagents in the presence of 4.0 molar equiv of boron trifluoride etherate under nitrogen at 0 °C for 30 min gave (dihydrotropone)iron tricarbonyl complexes 3 in excellent yields (88–99%, Scheme 1). NMR (nuclear magnetic resonance) spec-

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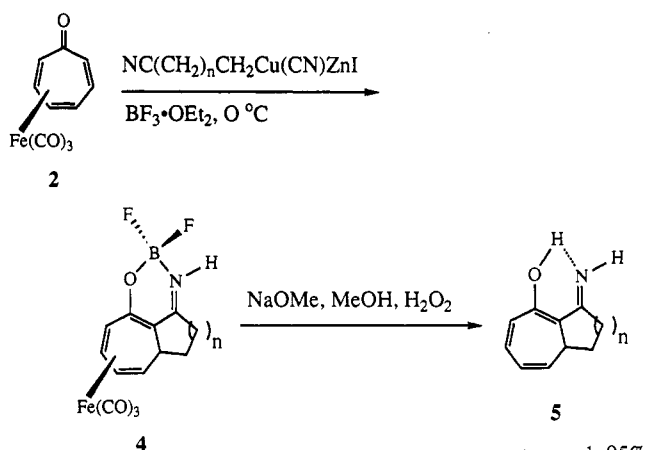
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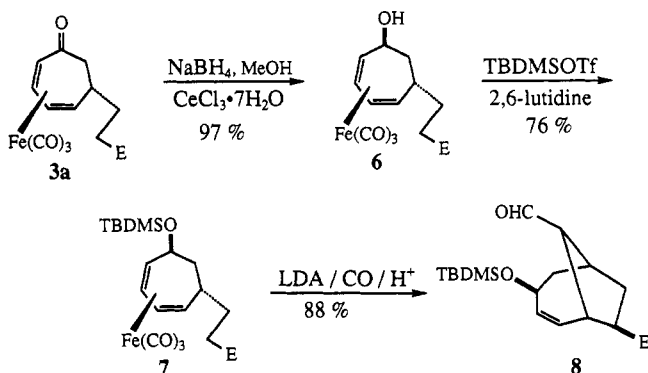
Scheme 1
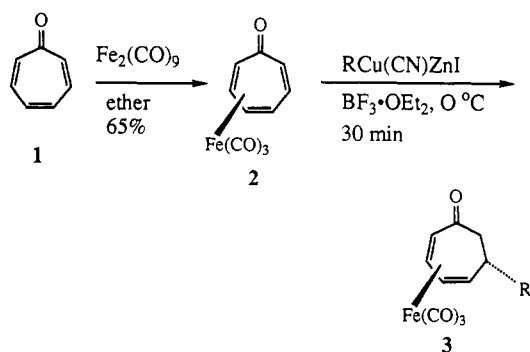
a : R = (CH₂)₂CO₂Et, 95%
b : R = (CH₂)₃CO₂Et, 99%
c : R = (CH₂)₄CO₂Et, 95%
d : R = (CH₂)₄OCOPh, 97%
e : R = (CH₂)₃SCOCH₃, 90%
f : R = CH₂Ph, 90%
g : R = (CH₂)₄CN, 88%

Scheme 2

a : n = 1, 97%
b : n = 2, 83%

5

a : n = 1, 95%
b : n = 2, 83%

Scheme 3[a]

[a] Abbreviations: E, CO_2Et; TBDMSOTf, $^tBuMe_2SiOCOCF_3$; LDA, lithium diisopropylamide.

troscopy studies provided the initial evidence for support of the structural assignments. The ^1H NMR spectrum of complex **3a** exhibited the following: a triplet, centered at δ 5.77, assigned to the vinyl H at C-3; a doublet of doublets, centered at δ 5.42, assigned to the vinyl H at C-4; a broad doublet, centered at δ 3.05, assigned to the vinyl H at C-2; a broad doublet, centered at δ 3.02, assigned to the vinyl H at C-5; two narrow quartets, centered at δ 4.04, assigned to the two diastereotopic methylene protons at C-11; a multiplet, centered at δ 2.60, assigned to the endo proton at C-6. The ^{13}C NMR spectrum of complex **3a** exhibited the following: a signal at δ 208.5 assigned to C-13 (carbonyl of the iron tricarbonyl moiety); a signal at δ 206.6 assigned to C-1 (carbonyl of the keto functionality), a signal at δ 172.8 assigned to C-10 (carbonyl of the ester functionality); two signals at δ 91.1 and 89.3 assigned to the internal vinyl carbons (C-3 and C-4); two signals at δ 63.8 and 60.5 assigned to the terminal vinyl carbons (C-2 and C-5). The conjugate-addition reaction is highly stereoselective, and only one isomer is isolated in each case. The relative stereochemistry at C-6 assigned as exo is based on the assumption that attack of the zinc–copper reagents occurs from the opposite face of the Fe(CO)₃ moiety, and the chemical shift value of δ 2.60 assigned for the proton at C-6 agrees closely with the values of the endo protons of most C-5-substituted $(\eta^4$-cyclohexa-1,3-diene)Fe(CO)₃[7] and $(\eta^4$-cyclohepta-1,3-diene)Fe(CO)₂P(OPh₃)[12] complexes. It is important to mention that these BF₃-promoted 1,4-addition reactions allow the tolerance of various oxygen- and sulfur-containing functional groups. However, 1,4-adducts containing a cyano group show the same behavior as the addition of cyano-substituted zinc–copper reagents to 2-cyclohexen-1-one.[11c] After the initial 1,4-addition, a BF₃-promoted intramolecular cyclization of boron enolates to the nitrile occurs and affords tricyclic difluoroboron enolates **4a,b**, which can be decomplexed by hydrogen peroxide in methanol to generate bicyclo-[5.3.0]decane derivative **5a** and bicyclo[5.4.0]undecane derivative **5b**, respectively. Both ring systems are characteristic of several classes of sesquiterpenes.[4,13] However, most approaches to the ring skeletons involve multistep synthesis. Thus, the Michael addition of cyano-substituted zinc–copper reagents to (tropone)iron tricarbonyl

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(2) is an effective method for use in the construction of 5,7- and 6,7-fused bicyclic systems. Attempted intramolecular cyclization using tethers longer than three methylene groups, for example complex **3g**, failed to give a bicyclo[5.5.0]dodecane derivative. The difficulty in forming the 7,7-fused bicyclic skeleton might be attributed to unfavorable formation of seven-membered rings.

Intramolecular Cyclization Reactions. As can be seen from Scheme 3, intramolecular cyclization of an ester enolate of C-6-ester-substituted complex **7** to the pendant $(\eta^4$-cycloheptadiene)Fe(CO)₃ moiety provides the bicyclo-[4.2.1]nonenecarboxylic acid derivative **8** with high stereo- and regiodirecting power. Complex **3a** was first reduced to the corresponding alcohol **6** (NaBH₄, CeCl₃·7H₂O, MeOH) in quantitative yield. The stereochemical assignment for the hydroxy group as endo was assumed to be a result of exo attack by the hydride. Protection of the hydroxy group (to give **7**) was accomplished by treatment of **6** with *tert*-butyldimethylsilyl trifluoromethanesulfonate in 2,6-lutidine in 76% yield. Intramolecular cyclization of **7** using 1.5 molar equiv of LDA at –78 °C under an atmosphere of CO produced the bicyclo[4.2.1]nonenecarboxylic acid derivative **8** as the major product in

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Scheme 4

7 $\xrightarrow{\text{LDA / H}^+}$

8
(17%)

+

9
(28%)

+

10
(37%)
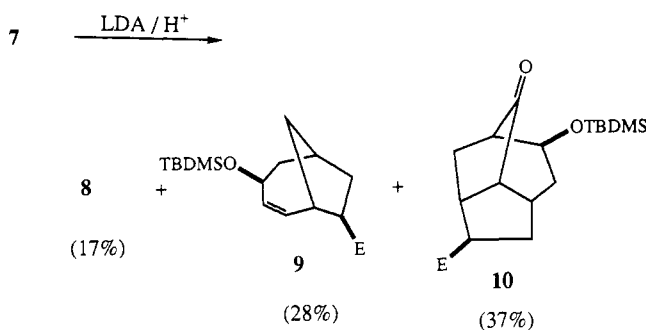
88% yield. Compound 8 results from anti addition of the kinetic ester enolate to the internal position of the diene ligand and agrees closely with the formation of bridged bicyclo[3.3.1]nonenecarboxylic acid derivatives obtained by the intramolecular cyclization of C-5-ester-functionalized (η^4-cyclohexa-1,3-diene)Fe(CO)$_3$ complexes under kinetically controlled reaction conditions.[7] It is important to note that five stereogenic centers are created in the process; however, only the single diastereomer shown is isolated.

Interestingly, the reaction undergoes different pathways without carbon monoxide. Treatment of complex 7 with 1.5 molar equiv of LDA at -78 °C under nitrogen for 2 h followed by acid quenching affords bicyclo[4.2.1]nonenecarboxylic acid derivatives 8 (17%) and 9 (28%) and tricyclo[5.2.1.0^{4,8}]decanecarboxylic acid derivative 10 (37%) (Scheme 4). However, the formation of compound 8 in Schemes 3 and 4 may result from different reaction pathways. Deprotonation of 7 using 1.5 molar equiv of LDA may remove only one of the diastereotopic protons at the α-carbon of the ester group under kinetically controlled reaction conditions. Anti addition of the ester enolate at the internal position of the diene ligand gave the putative homoallyl anion intermediate 11.[7] Carbonyl insertion was then enhanced by an external CO (Scheme 5) to generate the anionic acyliron intermediate 12. Quenching of 12 with CF$_3$COOH produced 13, which underwent reductive elimination and detachment of the iron tricarbonyl moiety from the double bond to produce 8. Iron hydride species 14, however, could be obtained upon direct quenching of 11 with CF$_3$COOH (Scheme 5). Reductive elimination of 14 followed by decomplexation of the iron tricarbonyl moiety gave 9. Complex 14 might undergo a carbonyl insertion (without an external CO) to give acyl intermediate 15, which after reductive elimination and decomplexation of the iron tricarbonyl moiety generated 8, while intramolecular alkene insertion into the iron-hydride bond of 15 would lead to the formation of acyl intermediate 16, which underwent reductive elimination to produce tricyclic compound 10. Thus, the great stereo- and regiodirecting power of complex 3a can be realized by the formation of the single diastereomer 10, which contains six stereogenic centers. Attempts to confirm the relative stereochemistry of tricyclic compound 10 using NOESY (nuclear Overhauser enhancement spectroscopy) measurements were unsuccessful. Rigorous proof of the structure of 10 was finally accomplished by X-ray diffraction analysis of the (2,4-dinitrophenyl)hydrazone derivative 17.[14] The X-ray diffraction analysis clearly proves the anti addition reactions of the zinc-copper

reagent and hydride to 2 and 3a, respectively, and regio- and stereochemical control of the intramolecular cyclization of complex 7.

E = CO$_2$Et

17
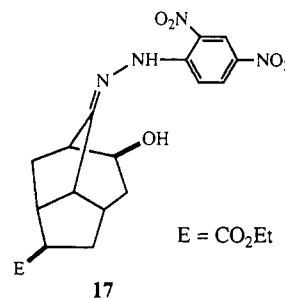
Synthesis of C-5,7-Disubstituted (η^4-cyclohepta-1,3-diene)Fe(CO)$_3$ Complexes. The C-5,7-disubstituted seven-membered ring is easily obtained by starting from 6, as can be seen from the examples in Scheme 6. Treatment of 6 with HBF$_4$ in acetic anhydride provides C-6-*exo*-substituted (η^5-cycloheptadienyl)Fe(CO)$_3$ cation 18. Anti addition of a second zinc-copper reagent to 18 at the less hindered dienyl terminus produces the C-5,7-disubstituted (η^4-cyclohepta-1,3-diene)Fe(CO)$_3$ complex 19. In principle, this chemistry could provide an alternative route to the synthesis of C-5,7-disubstituted (η^4-cyclohepta-1,3-diene)Fe(CO)$_3$P(OPh)$_3$ complexes which were generated by using expensive starting materials such as 1,3-cycloheptadiene and triphenylcarbenium hexafluorophosphate.[1b,12]

The reactions outlined herein demonstrated that (tropone)iron tricarbonyl (2) can be a good building block for the formation of fused bicyclo[5.3.0]decane and -[5.4.0]-undecane and bridged bicyclo[4.2.1]nonane and tricyclo[5.2.1.0^{4,8}]decane ring skeletons. The excellent stereocontrol of six sterogenic centers in the formation of the highly functionalized tricyclic compound 10 may have further application.

Experimental Section

All reactions were run under a nitrogen atmosphere in oven-dried glassware unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. Diethyl ether (ether) and tetrahydrofuran (THF) were distilled under nitrogen from a deep blue sodium benzophenone ketyl solution. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride. Copper cyanide (CuCN), 1,3,5-cycloheptatriene, *tert*-butyldimethylsilyl trifluoromethanesulfonate, (2,4-dinitrophenyl)hydrazine, 3-chloropropyl thiolacetate, and fluoroboric acid (48% in water) were purchased from Aldrich Chemical Co. and used as received. Zinc particles (purity >99.9%), ethyl 3-chloropropionate, ethyl 4-chlorobutyrate, 4-chlorobutyronitrile, 3-chloropropionitrile, and 5-chlorovaleronitrile were purchased from Merck Co. and used without further purification. Functionalized alkyl iodides are synthesized by refluxing the corresponding alkyl chlorides with an excess of sodium iodide in refluxing acetone. 4-Iodobutyl benzolate was synthesized by reaction of THF, sodium iodide, and benzoyl chloride.[16] (Tropone)iron tricarbonyl (2) was obtained by treatment of tropone[16] with diiron nonacarbonyl in refluxing ether for 12 h.[3a,c] Diiron nonacarbonyl was obtained by photolysis of iron pentacarbonyl in benzene and acetic acid according to the literature procedure.[17] Functionalized zinc-copper reagents were prepared according to the literature procedures.[6a,7] Flash column

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(14) Deprotection of the *tert*-butyldimethylsilyl group occurs during the preparation of (2,4-dinitrophenyl)hydrazone derivative 16.

(15) Oku, A.; Hara, T.; Kita, K. *Tetrahedron Lett.* **1982**, *23*, 681.
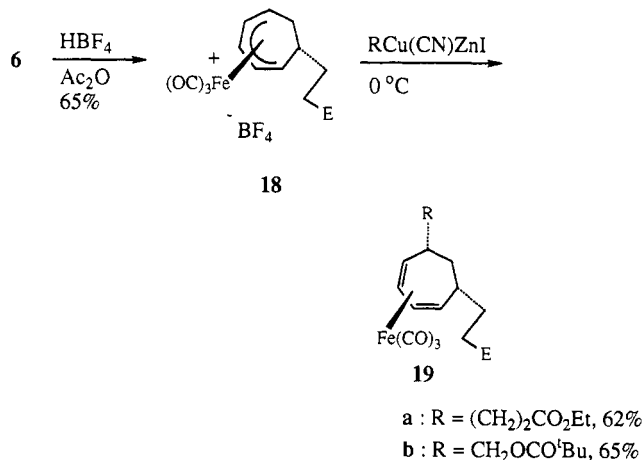(16) (a) Garfunkel, E.; Reingold, I. D. *J. Org. Chem.* **1979**, *44*, 3725. (b) Reingold, I. D.; Dinardo, L. J. *J. Org. Chem.* **1982**, *47*, 3544.

Scheme 5

Scheme 6

a : R = $(CH_2)_2CO_2Et$, 62%

b : R = CH_2OCO^tBu, 65%
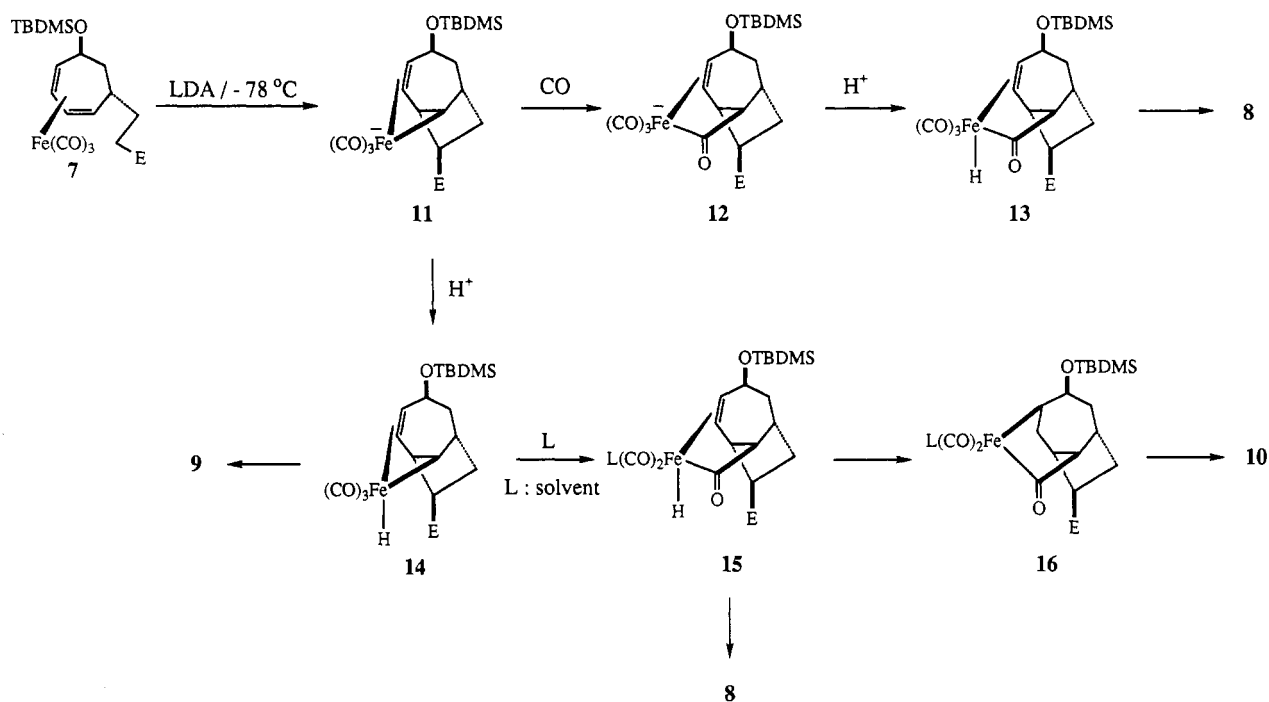
chromatography, following the method of Still,[18] was carried out with E. Merck silica gel (Kieselgel 60, 230–400 mesh) using the indicated solvents. Analytical thin-layer chromatography was performed with silica gel 60 F_{254} plastic plates of 0.2-mm thickness from E. Merck. The term "concentration" refers to the removal of solvent with an aspirator pump (Yamato Instrument Co. Model WP-15) with a Buchi Rotovapor-R. The term "under nitrogen" implies that the apparatus was evacuated (oil pump) and then filled with nitrogen three times. Melting points were determined in open capillaries with a Thomas-Hoover apparatus and are uncorrected. ¹H NMR nuclear magnetic resonance (NMR) spectra were obtained with a JEOL-EX 400 (400-MHz) spectrometer. Chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or CHCl₃ (7.26 ppm) as internal standard. ¹³C NMR spectra were recorded with a JEOL-EX 400 (100.4-MHz) spectrometer with CDCl₃ (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer. Mass spectra were measured on a JEOL JMS-D 100 spectrometer at an ionization potential of

(17) Diiron nonacarbonyl (32 g) was prepared by photolyzing iron pentacarbonyl (66 g) in acetic acid (42 mL) and benzene (150 mL): King, R. B. *Organometallics Synthesis*; Academic Press: New York, 1965; Vol. 1, p 93.

(18) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

70 eV and were reported as mass/charge (*m/e*) with percent relative abundance. High-resolution mass spectra (HRMS) were obtained with an AEI MS-9 double-focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer at the Department of Chemistry, Northern Instrument Center, Hsin Chu, Taipei, ROC. Elemental analyses were obtained from the Department of Chemistry, Northern Instrument Center, Taipei, ROC.

General Procedure for Addition of Functionalized Zinc–Copper Reagents RCu(ZnI)CN to (η^4-tropone)Fe(CO)₃ (2). A solution of the functionalized zinc–copper reagent (3.0 molar equiv) in THF (5 mL) was added to a stirred solution of 2 in THF (5 mL) at 0 °C under nitrogen followed by addition of boron trifluoride etherate (4.0 molar equiv). The reaction mixture was stirred at 0 °C for 30 min. The reaction mixture was then quenched with saturated aqueous ammonium chloride solution at 0 °C and was diluted with a solution of a mixture of ethyl acetate and hexanes (1/1, 100 mL). The resultant solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture.

[Ethyl *exo*-3-[(2-5-η)-1-oxo-2,4-cycloheptadien-6-yl]propionate]tricarbonyliron Complex (3a). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (30 mmol) to complex 2 (2.5 g, 10 mmol) in the presence of BF₃·OEt₂ (5.0 mL, 40 mmol) was purified via flash column chromatography (silica gel, 20% ethyl acetate/80% hexanes) to give complex **3a** (3.3 g, 9.5 mmol, 95%) as a yellow oil: IR (CH₂-Cl₂) 3051, 2991, 2982, 2932, 2060, 1984, 1726, 1657, 1435, 1392, 1375, 1307, 1244, 1184, 1126, 1032, 898, 869 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.77 (t, J = 5.8 Hz, 1 H), 5.42 (dd, J = 7.8, 5.4 Hz, 1 H), 4.04 (q, J = 6.8 Hz, 2 H), 3.05 (d, J = 9.8 Hz, 1 H), 3.02 (d, J = 7.3 Hz, 1 H), 2.60 (m, 1 H), 2.20 (m, 2 H), 1.92 (dd, J = 12.2, 4.2 Hz, 1 H), 1.76 (m, 1 H), 1.62 (t, J = 11.7 Hz, 1 H), 1.57 (m, 1 H), 1.17 (t, J = 6.8 Hz, 3 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 208.5, 206.6, 172.8, 91.1, 89.3, 63.8, 60.5, 56.9, 46.9, 43.5, 35.7, 30.9, 14.1; MS (30 eV) *m/e* (relative intensity) 348 (M⁺, 3), 320 (17), 292 (87), 275 (46), 264 (87), 247 (45), 234 (100), 219 (75), 208 (66), 193 (80); HRMS (EI) *m/e* calcd for C₁₅H₁₆FeO₆ (M⁺) 348.0296, found 348.0290.

[Ethyl *exo*-4-[(2-5-η)-1-oxo-2,4-cycloheptadien-6-yl]butyrate]tricarbonyliron Complex (3b). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (30 mmol) to complex 2 (2.5 g, 10 mmol) in the presence of BF₃·OEt₂ (5.0 mL, 40 mmol) was purified via flash column

chromatography (silica gel, 30% ethyl acetate/70% hexanes) to give complex **3b** (3.6 g, 9.9 mmol, 99%) as a yellow oil: IR (CH$_2$-Cl$_2$) 3053, 2988, 2062, 1996, 1728, 1655, 1421, 1373, 1277, 1269, 1253, 1182, 891, 856 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.85 (t, J = 5.8 Hz, 1 H), 5.50 (dd, J = 7.8, 5.4 Hz, 1 H), 4.14 (q, J = 7.3 Hz, 2 H), 3.17 (d, J = 7.8 Hz, 1 H), 3.11 (d, J = 6.8 Hz, 1 H), 2.67 (m, 1 H), 2.29 (t, J = 7.3 Hz, 2 H), 2.02 (dd, J = 7.3, 4.5 Hz, 1 H), 1.73 (t, J = 12.2 Hz, 1 H), 1.62 (m, 2 H), 1.51 (m, 1 H), 1.37 (m, 1 H), 1.26 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 208.5, 207.2, 173.2, 91.0, 89.4, 64.6, 60.4, 57.0, 47.6, 43.9, 40.5, 34.0, 21.5, 14.2; MS (30 eV) *m/e* (relative intensity) 362 (M$^+$, 3), 334 (2), 306 (26), 278 (32), 247 (22), 202 (32), 169 (100), 147 (40), 133 (28); HRMS (EI) *m/e* calcd for C$_{16}$H$_{18}$FeO$_6$ (M$^+$) 362.0453, found 362.0456.

[Ethyl *exo*-5-[(2-5-η)-1-oxo-2,4-cycloheptadien-6--yl]val-erate]tricarbonyliron Complex (3c). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (3 mmol) to complex **2** (0.25 g, 1 mmol) in the presence of BF$_3$·OEt$_2$ (0.5 mL, 4.0 mmol) was purified via flash column chromatography (silica gel, 20% ethyl acetate/80% hexanes) to give complex **3c** (0.36 g, 0.95 mmol, 95%) as a yellow oil: IR (CH$_2$Cl$_2$) 3065, 2991, 2982, 2939, 2864, 2060, 2002, 1728, 1653, 1439, 1373, 1307, 1182, 1126, 1032, 893, 887 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.85 (t, J = 6.1 Hz, 1 H), 5.50 (dd, J = 7.8, 5.4 Hz, 1 H), 4.12 (q, J = 7.3 Hz, 2 H), 3.17 (d, J = 7.8 Hz, 1 H), 3.10 (d, J = 6.8 Hz, 1 H), 2.65 (m, 1 H), 2.29 (t, J = 7.3 Hz, 2 H), 2.02 (dd, J = 11.7, 7.8 Hz, 1 H), 1.70 (t, J = 11.7 Hz, 1 H), 1.60 (m, 2 H), 1.46 (m, 1 H), 1.33 (m, 3 H), 1.25 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 208.6, 207.2, 173.4, 90.9, 89.4, 65.0, 60.2, 57.0, 47.7, 43.9, 40.9, 34.0, 25.7, 24.7, 14.1; MS (30 eV) *m/e* (relative intensity) 320 (M – 2 CO, 28), 292 (100), 264 (51); HRMS (EI) *m/e* calce for C$_{14}$H$_{20}$FeO$_3$ (M – 3 CO) 292.0762, found 292.0765.

[1-(Benzoyloxy)-*exo*-4-[(2-5-η)-1-oxo-2,4-cycloheptadien-6-yl]butane]tricarbonyliron Complex (3d). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (3.0 mmol) to complex **2** (0.25 g, 1.0 mmol) in the presence of BF$_3$·OEt$_2$ (0.5 mL, 4.0 mmol) was purified via flash column chromatography (silica gel, 10% ethyl acetate/90% hexanes) to give complex **3d** (0.41 g, 0.97 mmol, 97%) as a yellow oil: IR (CH$_2$Cl$_2$) 3057, 2941, 2062, 1992, 1714, 1653, 1602, 1585, 1452, 1313, 1284, 1246, 1118, 912, 887, 871 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, J = 7.3 Hz, 2 H), 7.52 (t, J = 7.3 Hz, 1 H), 7.41 (t, J = 7.3 Hz, 2 H), 5.80 (t, J = 6.3 Hz, 1 H), 5.44 (dd, J = 7.8, 6.3 Hz, 1 H), 4.27 (t, J = 6.8 Hz, 2 H), 3.13 (d, J = 7.8 Hz, 1 H), 3.06 (d, J = 6.3 Hz, 1 H), 2.63 (m, 1 H), 2.00 (brd, J = 7.3 Hz, 1 H), 1.73–1.37 (m, 7 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 208.5, 207.1, 166.4, 132.8, 130.1, 129.3, 128.2, 90.9, 89.3, 64.8, 64.3, 56.9, 47.6, 43.8, 40.6, 28.4, 22.6; MS (30 eV) *m/e* (relative intensity) 368 (M – 2 CO, 16), 340 (100), 284 (20), 234 (35), 162 (68), 113 (98); HRMS (EI) *m/e* calcd for C$_{18}$H$_{20}$FeO$_3$ (M – 3 CO) 340.0761, found 340.0759.

[1-(Acetylthio)-*exo*-3-[(2-5-η)-1-oxo-2,4-cycloheptadien-6-yl]propane]tricarbonyliron Complex (3e). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (3.0 mmol) to complex **2** (0.25 g, 1.0 mmol) in the presence of BF$_3$·OEt$_2$ (0.5 mL, 4.0 mmol) was purified via flash column chromatography (silica gel, 10% ethyl acetate/90% hexanes) to give complex **3e** (0.33 g, 0.90 mmol, 90%) as a yellow oil: IR (CH$_2$Cl$_2$) 3067, 2971, 2926, 2062, 1994, 1687, 1655, 1423, 1358, 1273, 1136, 954, 821 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.85 (t, J = 6.8 Hz, 1 H), 5.49 (dd, J = 7.8, 7.0 Hz, 1 H), 3.14 (d, J = 7.8 Hz, 1 H), 3.11 (d, J = 6.8 Hz, 1 H), 2.84 (t, J = 6.8 Hz, 2 H), 2.66 (m, 1 H), 2.34 (s, 3 H), 1.99 (dd, J = 12.2, 6.8 Hz, 1 H), 1.70 (t, J = 12.2 Hz, 1 H), 1.58–1.37 (m, 4 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 208.4, 207.1, 195.7, 91.0, 89.4, 64.5, 57.0, 47.5, 43.9, 40.1, 30.6, 28.8, 26.5; MS (30 eV) *m/e* (relative intensity) 364 (M$^+$, 1), 308 (44), 280 (100), 252 (93), 237 (61), 204 (89); HRMS (EI) *m/e* calcd for C$_{15}$H$_{18}$FeO$_5$S (M$^+$) 364.0067, found 364.0077.

[*exo*-Phenyl[(2-5-η)-1-oxo-2,4-cycloheptadien-6-yl]-methane]tricarbonyliron Complex (3f). The crude mixture obtained from the addition of the corresponding zinc-copper

reagent (3.0 mmol) to complex **2** (0.25 g, 1.0 mmol) in the presence of BF$_3$·OEt$_2$ (0.5 mL, 4.0 mmol) was purified via flash column chromatography (silica gel, 20% ethyl acetate/hexanes) to give complex **3f** (0.31 g, 0.90 mmol, 90%) as a yellow solid: mp 99–101 °C; IR (CH$_2$Cl$_2$) 3030, 2926, 2854, 2062, 1998, 1655, 1494, 1454, 1361, 1309, 1124, 991, 933 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 (m, 3 H), 7.10 (d, J = 7.3 Hz, 2 H), 5.82 (t, J = 6.1 Hz, 1 H), 5.48 (dd, J = 7.8, 5.8 Hz, 1 H), 3.23 (d, J = 7.8 Hz, 1 H), 3.10 (d, J = 6.3 Hz, 1 H), 2.94 (m, 1 H), 2.76 (dd, J = 13.5, 5.9 Hz, 1 H), 2.58 (dd, J = 13.7, 7.8 Hz, 1 H), 1.94 (dd, J = 9.8, 4.2 Hz, 1 H), 1.70 (t, J = 11.7 Hz, 1 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 208.6, 207.0, 138.0, 129.1, 128.6, 126.6, 91.0, 89.3, 64.2, 57.1, 49.4, 47.6, 44.0; MS (30 eV) *m/e* (relative intensity) 338 (M$^+$, 2), 310 (32), 282 (48), 254 (100), 198 (18), 163 (30); HRMS (EI) *m/e* calcd for C$_{17}$H$_{14}$FeO$_4$ (M$^+$) 338.0242, found 338.0247.

[*exo*-5-[(2-5-η)-1-Oxo-2,4-cycloheptadien-6-yl]valeroni-trile]tricarbonyliron Complex (3g). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (3.0 mmol) to complex **2** (0.25 g, 1.0 mmol) in the presence of BF$_3$·OEt$_2$ (0.5 mL, 4.0 mmol) was purified via flash column chromatography (silica gel, 20% ethyl acetate/80% hexanes) to give complex **3g** (0.29, 0.88 mmol, 88%) as a yellow oil: IR (CH$_2$-Cl$_2$) 3051, 2941, 2249, 2062, 1994, 1732, 1653, 1429, 1361, 1284, 1128, 908 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.87 (t, J = 5.4 Hz, 1 H), 5.49 (dd, J = 7.8, 5.4 Hz, 1 H), 3.15 (d, J = 7.8 Hz, 1 H), 3.12 (d, J = 5.4 Hz, 1 H), 2.68 (m, 1 H), 2.36 (t, J = 7.3 Hz, 2 H), 2.01 (dd, J = 7.4, 4.1 Hz, 1 H), 1.72 (t, J = 12.2 Hz, 1 H), 1.64–1.42 (m, 6 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 208.4, 206.9, 119.4, 91.0, 89.4, 64.3, 56.9, 47.5, 43.8, 40.2, 25.3, 25.2, 17.0; MS (30 eV) *m/e* (relative intensity) 329 (M$^+$, 2), 301 (5), 273 (90), 245 (100); HRMS (EI) *m/e* calcd for C$_{15}$H$_{15}$FeNO$_4$ (M$^+$) 329.0350, found 329.0347.

Tricyclic Tricarbonyliron Complex 4a. The crude mixture obtained from the addition of the corresponding zinc–copper reagent (6.0 mmol) to complex **2** (0.50 g, 2.0 mmol) in the presence of BF$_3$·OEt$_2$ (1.0 mL, 8.0 mmol) was purified via flash column chromatography (silica gel, 50% ethyl acetate/50% hexanes) to give complex **4a** (0.69 g, 1.94 mmol, 97%) as a yellow solid: mp 95–99 °C; IR (CH$_2$Cl$_2$) 3387, 3059, 2988, 2062, 1994, 1651, 1556, 1440, 1419, 1300, 1188, 1136, 1062, 1018, 991, 821 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.87 (br s, 1 H), 5.84 (dd, J = 7.8, 5.4 Hz, 1 H), 5.39 (dd, J = 7.8, 5.9 Hz, 1 H), 3.44 (m, 1 H), 3.38 (dd, J = 7.8, 2.9 Hz, 1 H), 2.86 (d, J = 7.8 Hz, 1 H), 2.68 (m, 1 H), 2.46 (dd, J = 17.6, 7.8 Hz, 1 H), 2.31 (m, 1 H), 1.41 (m, 1 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 208.7, 177.9, 173.7, 106.7, 92.2, 91.0, 62.9, 52.1, 42.8, 35.4, 33.6; MS (30 eV) *m/e* (relative intensity) 321 (M – 2 F, 16), 293 (22), 265 (53), 190 (100), 154 (28); HRMS (EI) *m/e* calcd for C$_{13}$H$_{10}$BF$_2$FeNO$_4$ (M – 2 F) 311.0052, found 311.0084. Anal. Calcd for C$_{13}$H$_{10}$BF$_2$FeNO$_4$: C, 44.76; H, 2.89; N, 4.01. Found: C, 44.98; H, 2.97; N, 3.92.

Tricyclic Tricarbonyliron Complex 4b. The crude mixture obtained from the addition of the corresponding zinc–copper reagent (3.0 mmol) to complex **2** (0.25 g, 1.0 mmol) in the presence of BF$_3$·OEt$_2$ (0.5 mL, 4.0 mmol) was purified via flash column chromatography (silica gel, 33% ethyl acetate/67% hexanes) to give complex **4b** (0.33 g, 0.90 mmol, 90%) as a yellow solid: mp 165–170 °C; IR (CH$_2$Cl$_2$) 3381, 3057, 2945, 2062, 1992, 1612, 1523, 1502, 1471, 1444, 1427, 1284, 1128, 1099, 1032, 871, 831 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.74 (br s, 1 H), 5.69 (t, J = 5.4 Hz, 1 H), 5.38 (dd, J = 7.8, 4.9 Hz, 1 H), 3.22 (dd, J = 6.8, 3.9 Hz, 1 H), 3.03 (d, J = 7.8 Hz, 1 H), 2.84 (dt, J = 12.2, 3.2 Hz, 1 H), 2.50 (m, 1 H), 2.42 (m, 1 H), 2.10 (m, 1 H), 1.82 (m, 2 H), 1.25 (m, 1 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 208.7, 175.4, 171.5, 101.8, 92.6, 89.3, 62.9, 53.5, 38.1, 34.1, 31.3, 21.2; MS (30 eV) *m/e* (relative intensity) 363 (M$^+$, 5), 335 (20), 307 (28), 279 (100), 204 (98), 185 (25); HRMS (EI) *m/e* calcd for C$_{14}$H$_{12}$BF$_2$FeNO$_4$ (M$^+$) 363.0176, found 363.0186. Anal. Calcd for C$_{14}$H$_{12}$BF$_2$FeNO$_4$: C, 46.33; H, 3.33; N, 3.86. Found: C, 46.52; H, 2.90; N, 3.89.

Bicyclic Compound 5a. Complex **4a** (60 mg, 0.17 mmol) was treated with NaOMe (39 mg of sodium in 4.0 mL of methanol) and hydrogen peroxide (0.3 mL, 35% solution in water) under nitrogen at 0 °C for 10 min. The reaction mixture was then quenched with saturated aqueous ammonium chloride solution

at 0 °C and was diluted with 50 mL of 50% ethyl acetate/50% hexanes. The resultant solution was washed with water (50 mL × 3) and brine (50 mL × 3), dried over anhydrous magnesium sulfate (5.0 g), and concentrated to give the crude mixture. The crude mixture was purified via flash chromatography (silica gel, 50% ethyl acetate/50% hexanes) to give **5a** (26 mg, 0.16 mmol, 95%) as a colorless oil: IR (CH₂Cl₂) 3479, 3258, 3055, 3024, 2986, 2962, 1618, 1589, 1502, 1431, 1398, 1381, 1329, 1207, 1095, 1014, 923 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.82 (br s, 1 H), 6.40 (dd, J = 12.2, 5.9 Hz, 1 H), 6.27 (d, J = 12.2 Hz, 1 H), 5.86 (m, 2 H), 5.26 (br s, 1 H), 3.55 (br s, 1 H), 2.67 (m, 1 H), 2.52 (m, 1 H), 2.30 (m, 1 H), 1.84 (m, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 187.4, 164.7, 141.3, 134.5, 134.1, 124.0, 109.8, 40.2, 33.3, 28.5; MS (70 eV) m/e (relative intensity) 161 (M⁺, 100), 131 (76), 117 (23), 91 (23); HRMS (EI) m/e calcd for C₁₀H₁₁NO (M⁺) 161.0841, found 161.0841.

Bicyclic Compound 5b. Complex **4b** (0.12 g, 0.33 mmol) was treated with NaOMe (77 mg of sodium in 4 mL of methanol) and hydrogen peroxide (0.8 mL, 35% solution in water) under nitrogen at 0 °C for 10 min. The reaction mixture was then quenched with saturated aqueous ammonium chloride solution at 0 °C and was diluted with 50 mL of 50% ethyl acetate/50% hexanes. The resultant solution was washed with water (50 mL × 3) and brine (50 mL × 3), dried over anhydrous magnesium sulfate (5.0 g), and concentrated to give the crude mixture. The crude mixture was purified via flash column chromatography (silica gel, 50% ethyl acetate/50% hexanes) to give **5b** (48 mg, 0.27 mmol, 82%) as a colorless oil: IR (CH₂Cl₂) 3474, 3258, 3067, 3024, 2953, 2866, 1599, 1487, 1381, 1296, 1174, 1045 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.45 (br s, 2 H), 6.00 (m, 2 H), 5.00 (br s, 1 H), 2.82 (br s, 1 H), 2.41 (m, 1 H), 2.23 (d, J = 18.6 Hz, 1 H), 1.63–1.88 (m, 5 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 190.2, 160.1, 140.9, 135.0, 133.1, 123.8, 105.5, 32.0, 30.2, 28.3, 18.1; MS (70 eV) m/e (relative intensity) 175 (M⁺, 100), 119 (21), 104 (19), 90 (13); HRMS (EI) m/e calcd for C₁₁H₁₃NO (M⁺) 175.0997, found 175.1002.

[Ethyl exo-3-[(2-5-η)-1-hydroxy-2,4-cycloheptadien-6-yl]-propionate]tricarbonyliron Complex (6). A solution of complex **3a** (2.6 g, 7.5 mmol) in 50 mL of MeOH was treated with NaBH₄ (0.42 g, 15 mmol) and CeCl₃·7H₂O (3.1 g, 8.2 mmol) under N₂ at 0 °C. The reaction mixture was stirred for 10 min at 0 °C. The reaction mixture was quenched with 10 mL of water and extracted with EtOAc (100 mL). The organic extract was washed with water (3 × 100 mL) and saturated aqueous NaCl (3 × 100 mL), dried (MgSO₄), and concentrated to give the crude mixture. The crude mixture was purified via flash column chromatography (silica gel, 17% ethyl acetate/83% hexanes) to give **6** (2.54 g, 7.26 mmol, 97%) as a yellow oil: IR (CH₂Cl₂) 3599, 3051, 2982, 2933, 2048, 1981, 1728, 1614, 1450, 1375, 1319, 1186, 1157, 1062, 1035, 912 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.40 (dd, J = 7.3, 4.9 Hz, 1 H), 5.31 (dd, J = 7.3, 4.9 Hz, 1 H), 4.18 (br s, 1 H), 4.12 (q, J = 6.8 Hz, 2 H), 2.99 (t, J = 6.8 Hz, 1 H), 2.85 (d, J = 7.3 Hz, 1 H), 2.27 (m, 3 H), 1.63 (m, 1 H), 1.53 (m, 1 H), 1.37 (d, J = 14.2 Hz, 1 H), 1.25 (t, J = 6.8 Hz, 3 H), 0.98 (td, J = 12.0, 3.0 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 210.7, 173.5, 88.9, 88.0, 66.2, 63.3, 63.0, 60.4, 36.2, 35.2, 32.3, 31.3, 14.2; MS (30 eV) m/e (relative intensity) 322 (M – CO, 2), 294 (2), 266 (97), 248 (100); HRMS (EI) m/e cald for C₁₂H₁₈FeO₃ (M – 3 CO) 266.0605, found 266.0611.

[Ethyl exo-3-[(2-5-η)-1-(tert-butyldimethylsilyloxy)-2,4-cycloheptadien-6-yl]propionate]tricarbonyliron Complex (7). A solution of complex **6** (2.5 g, 9.0 mmol) in 25 mL of dry THF was treated with tert-butyldimethylsilyl trifluoromethane-sulfonate (1.9 mL, 8.4 mmol) and 2,6-lutidine (1.6 mL, 14 mmol), and the reaction mixture was stirred for 30 min at 0 °C. The reaction mixture was poured into 100 mL of hexane. The solution was washed with water (3 × 100 mL) and saturated aqueous NaCl (3 × 100 mL), dried (MgSO₄), and concentrated to give the crude mixture. The crude mixture was purified via flash column chromatography (silica gel, 9% ethyl acetate/91% hexanes) to give **7** (2.48 g, 5.3 mmol, 76%) as a yellow oil: IR (CH₂Cl₂) 3053, 2955, 2934, 2889, 2856, 2048, 1973, 1728, 1469, 1327, 1267, 1186, 1155, 1074, 939, 804 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.32 (dd, J = 7.3, 4.4 Hz, 1 H), 5.23 (dd, J = 7.3, 3.9 Hz, 1 H), 4.14 (m, 1

H), 4.12 (q, J = 7.3 Hz, 2 H), 2.86 (t, J = 7.5 Hz, 1 H), 2.79 (d, J = 6.8 Hz, 1 H), 2.26 (m, 3 H), 1.60 (m, 1 H), 1.49 (m, 1 H), 1.25 (t, J = 7.3 Hz, 3 H), 1.23 (m, 1 H), 0.88 (m, 1 H), 0.86 (s, 9 H), 0.08 (s, 3 H), 0.03 (s, 3 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 210.9, 173.6, 88.4, 87.9, 67.1, 64.3, 63.2, 60.4, 37.0, 35.3, 32.5, 31.4, 25.9, 25.7, 18.3, 18.1, 14.2, –4.6, –4.9; MS (30 eV) m/e (relative intensity) 380 (M – 3 CO, 1), 305 (5), 263 (2), 221 (6), 189 (35), 147 (100), 133 (9), 117 (7); HRMS (EI) m/e calcd for C₁₈H₃₂FeO₃Si (M – 3 CO) 380.1470, found 380.1471.

(1S*,3S*,6R*,7R*,9R*)-3-(tert-Butyldimethylsiloxy)-7-carbethoxy-9-formylbicyclo[4.2.1]non-4-ene (8). To a solution of diisopropylamine (0.17 mL, 1.2 mmol) in 4 mL of THF under nitrogen at –78 °C was added rapidly (neat, via syringe) a solution of n-butyllithium (0.75 mL, 1.2 mmol, 1.6 M) in hexane followed by addition of HMPA (0.3 mL). The reaction mixture was stirred at –78 °C for 20 min. With the solution at –78 °C, carbon monoxide was added to the system via a syringe needle and was pressurized to ca. 2 psig (always keeping a positive pressure on the system) as measured by a regulator at the CO cylinder. The CO pressure was then released via an additional needle, and the CO was allowed to flow through the system for 20 min. A solution of complex **7** (0.47 g, 1.0 mmol) in THF (3 mL) was added dropwise via syringe, the gas exist needle was removed, and the closed system was pressurized to ca. 14 psig with CO. The mixture was stirred at –78 °C for 2 h. After this time, the CO needle was removed, and the system was depressurized via insertion of a syringe needle into the septum, which was quickly removed when gas flow could not longer be heard. The reaction mixture was quenched with trifluoroacetic acid (1.0 mL) via a syringe needle and was stirred at 25 °C for 0.5 h. After this time, the reaction mixture was diluted with a mixture of ethyl acetate and hexanes (1/2, 100 mL). The resultant solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture. The crude mixture was purified via flash column chromatography (silica gel, 9% ethyl acetate/91% hexanes) to give **8** (0.31 g, 0.88 mmol, 88%) as a colorless oil: IR (CH₂Cl₂) 3030, 2997, 2935, 2889, 2858, 2721, 1724, 1643, 1464, 1392, 1375, 1292, 1186, 1084, 970, 939 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.86 (s, 1 H), 5.97 (ddd, J = 11.7, 8.8, 2.4 Hz, 1 H), 5.65 (d, J = 11.7 Hz, 1 H), 4.57 (br d, J = 12.4 Hz, 1 H), 4.13 (q, J = 6.8 Hz, 2 H), 3.17 (t, J = 7.3 Hz, 1 H), 2.94 (m, 2 H), 2.82 (dd, J = 7.3, 6.4 Hz, 1 H), 2.16 (m, 2 H), 1.90 (t, J = 12.4 Hz, 1 H), 1.66 (m, 1 H), 1.25 (t, J = 6.8 Hz, 3 H), 0.86 (s, 9 H), 0.05 (s, 3 H), 0.04 (s, 3 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 202.6, 175.7, 140.8, 130.5, 69.5, 60.9, 60.3, 50.2, 41.8, 38.7, 35.2, 34.5, 25.8, 25.7, 18.1, 14.2, –4.7, –4.9; MS (70 eV) m/e (relative intensity) 352 (M⁺, 5), 351 (13), 337 (6), 295 (52), 221 (100), 219 (16), 203 (12), 129 (14); HRMS (EI) m/e calcd for C₁₉H₃₂O₄Si (M⁺) 352.2069, found 352.2058.

(1S*,3S*,6S*,7R*)-3-(tert-Butyldimethylsiloxy)-7-carbethoxybicyclo[4.2.1]non-4-ene (9). To a solution of diisopropylamine (0.17 mL, 1.2 mmol) in 4 mL of THF under nitrogen at –78 °C was added rapidly (neat, via syringe) a solution of n-butyllithium (0.75 mL, 1.2 mmol, 1.6 M) in hexane followed by addition of HMPA (0.3 mL). The reaction mixture was stirred at –78 °C for 20 min. A solution of complex **7** (0.47 g, 1.0 mmol) in THF (3.0 mL) was added dropwise via syringe. The mixture was stirred at –78 °C for 2 h. The reaction mixture was then quenched with trifluoroacetic acid (1.0 mL) via a syringe needle and was stirred at 25 °C for 30 min. After this time, the reaction mixture was diluted with a mixture of ethyl acetate and hexanes (1/1, 100 mL). The resultant solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture. The crude mixture was purified via flash column chromatography (silica gel, 25% ethyl acetate/75% hexanes) to give **9** (96 mg, 0.28 mmol, 28%), **8** (61 mg, 0.17 mmol, 17%), and **10** (0.13 g, 0.37 mmol, 37%) as colorless oils. **9**: IR (CH₂Cl₂) 2993, 2955, 2932, 2858, 1724, 1464, 1392, 1300, 1280, 1269, 1184, 1159, 1076, 908, 846 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.99 (ddd, J = 11.4, 6.4, 2.8 Hz, 1 H), 5.58 (d, J = 11.6 Hz, 1 H), 4.50

(m, 1 H), 4.11 (q, J = 7.0 Hz, 2 H), 2.83 (t, J = 8.0 Hz, 1 H), 2.78 (t, J = 8.0 Hz, 1 H), 2.58 (m, 1 H), 2.09 (m, 2 H), 1.85 (m, 1 H), 1.76 (m, 1 H), 1.64 (m, 1 H), 1.57 (m, 1 H), 1.25 (t, J = 7.0 Hz, 3 H), 0.89 (s, 9 H), 0.06 (s, 3 H), 0.05 (s, 3 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 176.6, 139.0, 135.0, 70.3, 60.5, 50.9, 42.3, 41.3, 40.5, 38.4, 34.8, 25.8, 18.2, 14.2, −4.7, −4.8; MS (70 eV) m/e (relative intensity) 324 (M$^+$, 34), 281 (22), 268 (24), 267 (100), 221 (38), 128 (23), 119 (98), 91 (38), 75 (87); HRMS (EI) m/e calcd for C$_{18}$H$_{32}$O$_3$-Si (M$^+$) 324.2121, found 324.2112.

(1R*,2S*,4S*,6R*,7R*,8R*)-2-(*tert*-Butyldimethylsiloxy)-6-carbethoxytricyclo[5.2.1.0^{4,8}]decan-9-one (10): IR (CH$_2$Cl$_2$) 3053, 2957, 2885, 2858, 1728, 1464, 1373, 1294, 1184, 1089, 1037, 1006, 960, 819, cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.16 (m, 1 H), 4.11 (q, J = 7.0 Hz, 2 H), 2.91 (m, 2 H), 2.87 (m, 1 H), 2.46 (t, J = 7.3 Hz, 1 H), 2.32 (m, 1 H), 2.13 (m, 2 H), 1.85 (m, 1 H), 1.60 (m, 2 H), 1.30 (dd, J = 14.0, 3.1 Hz, 1 H), 1.24 (t, J = 7.0 Hz, 3 H), 0.85 (s, 9 H), 0.03 (s, 3 H), 0.01 (s, 3 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 216.2, 175.2, 79.0, 60.7, 53.6, 53.3, 52.2, 43.1, 40.3, 38.0, 34.2, 31.3, 25.8, 25.7, 18.0, 14.2, −4.8, −4.9; MS (70 eV) m/e (relative intensity) 352 (M$^+$, 2), 337 (19), 294 (100), 249 (41), 221 (100), 205 (aq), 166 (35), 154 (55), 128 (73), 91 (38), 75 (86); HRMS (EI) m/e calcd for C$_{19}$H$_{32}$O$_4$Si (M$^+$) 352.2070, found 352.2064.

(1R*,2S*,4S*,6R*,7R*,8R*)-6-Carbethoxy-2-hydroxytricyclo[5.2.1.0^{4,8}]decan-9-one (2,4-Dinitrophenyl)hydrazone (17). The compound 10 (0.18 g, 0.5 mmol) was added to a solution of 0.16 g of (2,4-dinitrophenyl)hydrazine in 2 mL of phosphoric acid (85% in H$_2$O) and 2 mL of ethanol (95%). The reaction mixture was stirred at 25 °C for 20 min and diluted with 50 mL of ethyl acetate, and the solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture. The crude mixture was purified via flash column chromatography (silica gel, 30% ethyl acetate/70% hexanes) and recrystallization (vapr diffusion with chloroform and hexanes) to give 17 (0.11 g, 0.25 mmol, 50%) as a yellow solid: mp 173–175 °C; IR (CH$_2$Cl$_2$) 3601, 3084, 3076, 3049, 2989, 1726, 1618, 1591, 1520, 1425, 1336, 1313, 1138, 898 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 11.36 (s, 1 H), 9.08 (s, 1 H), 8.26 (d, J = 9.3 Hz, 1 H), 7.87 (d, J = 9.3 Hz, 1 H), 4.34 (m, 1 H), 4.16 (q, J = 6.8 Hz, 2 H), 3.17 (d, J = 7.3 Hz, 1 H), 3.08 (t, J = 6.8 Hz, 1 H), 2.95 (m, 2 H), 2.83 (m, 1 H), 2.41 (m, 1 H), 2.19 (m, 1 H), 1.86 (m, 1 H), 1.76 (m, 1 H), 1.60 (m, 1 H), 1.42 (dd, J = 14.2, 4.2 Hz, 1 H), 1.28 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 175.2, 169.9, 145.5, 137.3, 129.7, 128.7, 123.5, 116.0, 77.8, 60.7, 52.0, 50.8, 43.3, 42.9, 41.6, 37.1, 34.0, 33.5, 14.2; MS (70 eV) m/e (relative intensity) 418 (M$^+$, 100), 400 (37), 382 (75), 354 (62), 290 (50), 262 (63); HRMS (EI) m/e calcd for C$_{19}$H$_{22}$N$_4$O$_7$ (M$^+$) 418.1488, found 418.1484. Anal. Calcd for C$_{19}$H$_{22}$N$_4$O$_7$: C, 54.54; H, 5.30; N, 13.39. Found: C, 54.41; H, 5.20; N, 13.08.

[Ethyl *exo*-3-[(1-5-η)-cycloheptadien-6-yl]propionate]-tricarbonyliron Tetrafluoroborate (18). Fluoroboric acid (2.0 mL, 48% in water) was dissolved in acetic anhydride (5.0 mL) and cooled to 0 °C. Complex 6 (2.0 g, 5.7 mmol) in 4.0 mL of acetic anhydride was added to the solution. The reaction mixture was stirred at 25 °C for 30 min and then cooled to 0 °C. It was then diluted with 30 mL of cold ether, and the precipitate was filtered. The yellow solid was washed four times with cold ether and dried under vacuum to give cation 18 (1.72 g, 4.1 mmol, 72%); IR (CH$_2$Cl$_2$) 3063, 3051, 2988, 2116, 2062, 1730, 1423, 1377, 1192, 1161, 1062, 902, 891, 879 cm^{-1}; ^{1}H NMR (400 MHz, CD$_3$-COCD$_3$) δ 7.40 (dd, J = 7.3, 6.3 Hz, 1 H), 6.50 (t, J = 7.3 Hz, 1 H), 6.17 (dd, J = 9.7, 6.3 Hz, 1 H), 5.16 (dd, J = 7.3, 4.4 Hz, 1 H), 5.10 (m, 1 H), 4.10 (q, J = 7.3 Hz, 2 H), 3.46 (m, 1 H), 2.60 (m, 1 H), 2.34 (t, J = 6.8 Hz, 2 H), 1.73 (m, 1 H), 1.55 (m, 1 H), 1.20 (t, J = 7.3 Hz, 3 H), 1.19 (m, 1 H); ^{13}C NMR (100.4 MHz, CD$_3$COCD$_3$) δ 172.7, 103.8, 103.7, 101.3, 95.4, 90.1, 60.5, 51.9,

33.6, 32.2, 30.7, 14.2. Anal. Calcd for C$_{15}$H$_{17}$BF$_4$FeO$_5$: C, 42.90; H, 4.08. Found: C, 42.53; H, 4.18.

(5R*,7S*)-[Diethyl 3,3-[(1-4-η)-1,3-cycloheptadien-5,7-diyl]dipropionate]tricarbonyliron Complex (19a). A solution of the functionalized zinc–copper reagent [EtCO$_2$(CH$_2$)$_2$-Cu(CN)ZnI] (3.0 mmol) in THF (5.0 mL) was added to a stirred suspension of cation 18 (0.42 g, 1.0 mmol) in 5 mL of THF at 0 °C under nitrogen. A homogeneous solution was obtained after the reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was then quenched with saturated aqueous ammonium chloride solution at 0 °C and was diluted with 100 mL of 50% ethyl acetate/50% hexanes. The resultant solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture. The crude mixture was purified via flash column chromatography (silica gel, 17% ethyl acetate/83% hexanes) to give 19a (0.27 g, 0.62 mmol, 62%) as a yellow oil: IR (CH$_2$Cl$_2$) 3057, 2991, 2982, 2932, 2874, 2042, 1979, 1726, 1452, 1423, 1375, 1323, 1242, 1180, 1111, 1033, 947, 900, 889 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.25 (d, J = 7.3 Hz, 2 H), 4.12 (q, J = 7.3 Hz, 4 H), 2.80 (d, J = 7.3 Hz, 2 H), 2.30 (m, 4 H), 1.92 (m, 2 H), 1.51–1.68 (m, 4 H), 1.26 (t, J = 7.3 Hz, 6 H), 1.31 (m, 1 H), 0.54 (dd, J = 13.7, 12.2 Hz, 1 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 211.2, 173.5, 87.6, 62.8, 60.3, 38.2, 35.7, 34.6, 31.3, 14.2; MS (30 eV) m/e (relative intensity) 406 (M − CO, 1), 378 (7), 350 (100), 333 (9), 305 (11), 276 (13), 248 (36), 202 (7); HRMS (EI) m/e calcd for C$_{17}$H$_{26}$FeO$_4$ (M − 3 CO) 350.1181, found 350.1190.

(5R*,7S*)-[Ethyl 3-[(1-4-η)-7-[(pivaloyloxy)methyl]-1,3-cycloheptadien-5-yl]propionate]tricarbonyliron Complex (19b). A solution of the functionalized zinc–copper reagent [(CH$_3$)$_3$CCO$_2$CH$_2$Cu(CN)ZnI] (6.0 mmol) in 5 mL of THF was added to a stirred suspension of cation 18 (0.84 g, 2.0 mmol) in 5 mL of THF at 0 °C under nitrogen. A homogeneous solution was obtained after the reaction mixture was stirred at 0 °C for 1.5 h. The reaction mixture was then quenched with saturated aqueous ammonium chloride solution at 0 °C and was diluted with 100 mL of 50% ethyl acetate/50% hexanes. The resultant solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture. The crude mixture was purified via flash column chromatography (silica gel, 7% ethyl acetate/93% hexanes) to give 19b (0.5 g, 0.96 mmol, 48%) as a yellow oil: IR (CH$_2$Cl$_2$) 3059, 2991, 2978, 2937, 2874, 2044, 1975, 1726, 1479, 1458, 1398, 1371, 1288, 1273, 1159, 1118, 1033, 939, 898, 881 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.27 (dd, J = 8.8, 2.9 Hz, 2 H), 4.11 (q, J = 7.3 Hz, 2 H), 3.82 (dd, J = 9.8, 5.8 Hz, 1 H), 3.75 (dd, J = 9.8, 5.9 Hz, 1 H), 2.88 (dd, J = 9.3, 4.8 Hz, 2 H), 2.26 (m, 2 H), 2.21 (m, 1 H), 1.95 (m, 1 H), 1.65 (m, 1 H), 1.57 (m, 1 H), 1.33 (m, 1 H), 1.25 (t, J = 7.3 Hz, 3 H), 1.21 (s, 9 H), 0.61 (q, J = 12.7 Hz, 1 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 210.9, 178.3, 173.4, 87.9, 87.8, 70.3, 62.7, 60.4, 58.6, 38.8, 38.6, 37.7, 35.7, 31.9, 31.3, 27.2, 27.1, 27.0, 14.2; MS (30 eV) m/e (relative intensity) 420 (M − CO), 392 (8), 364 (100), 319 (16), 279 (28), 262 (46), 182 (83), 134 (60); HRMS (EI) m/e calcd for C$_{20}$H$_{28}$FeO$_6$ (M − CO) 420.1235, found 420.1239.

Supplementary Material Available: ORTEP diagram and tables of crystallographic data, positional parameters, and bond lengths and angles for 17 (5 pages). Ordering information is given on any current masthead page.