Construction of Bridged and Fused Bicyclic Skeletons via Intramolecular Addition of Nucleophiles to (η^4-Diene)Fe(CO)$_3$ Complexes Bearing Functionalized Side Chains

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Abstract: Reaction of lithium diisopropylamide (LDA) with (η^4-1,3-cyclohexadiene)Fe(CO)$_3$ complexes bearing functionalized side chains at C-5, under an atmosphere of carbon monoxide, gives bridged bicyclo[3.2.1]octene and bicyclo[3.3.1]nonene systems after electrophilic quenching, whereas larger rings cannot be obtained in this series. Under the same reaction conditions, intramolecular cyclization of acyclic (η^4-1,3-butadiene)Fe(CO)$_3$ complexes with functionalized side chains at the terminal position of the diene ligands furnishes fused bicyclo[3.3.0]octanone and bicyclo[4.3.0]nonanone derivatives after acid quenching. The iron-mediated intramolecular nucleophilic addition allows for the direct stereocontrol of four stereogenic centers of these fused bicyclic skeletons.

Bridged and fused bicyclic ring constructions constitute a continuing major challenge in synthetic organic chemistry. Formation of bridged bicyclic compounds normally involves intramolecular processes such as Michael addition,[1] aldol condensation,[2] free-radical cyclization,[3] and Diels–Alder reactions.[4] Among these, intramolecular Diels–Alder reactions generally result in formation of a single regio- and stereoisomer.[5] On the other hand, the rapidly growing number of structurally interesting and biologically active polycyclopentanoid natural products has prompted considerable interest in new methodology for the construction of condensed five-membered-ring systems.[6] Because the availability of functionalized bicyclo[4.3.0] and -[3.3.0] building blocks could greatly facilitate the elaboration of more complex target molecules, the design of expedient synthetic routes to such intermediates has been actively pursued.[7] Due to the high stereo- and regiochemical control, transition-metal-promoted synthesis of cyclopentanoids from unsaturated carbon–carbon bonds and carbon monoxide has attracted much attention. Of these reactions, however, formation of fused bicyclic skeletons has so far been restricted to only titanium-,[8] zirconium-,[9] cobalt-,[10] nickel-,[11] or palladium-promoted[12] cyclization of unsaturated molecules. Only limited examples of iron-mediated coupling reactions of alkyne–alkyne and alkyne–alkene to give fused bicyclic compounds have been explored.[13] Our new process has been achieved by the intramolecular cyclization of (η^4-1,3-diene)Fe(CO)$_3$ complexes. The use of diene–iron complexes has the following advantages: (i) The starting complexes are readily available at low cost.[14] (ii) They are mostly oxidatively and thermally stable. (iii) The intermolecular addition of nucleophiles to diene–iron complexes occurs with high regio- and stereochemical control.[15] In this paper, we report that bridged and fused bicyclic ring skeletons can be constructed via intramolecular cyclizations of cyclic and acyclic diene–iron complexes, respectively.

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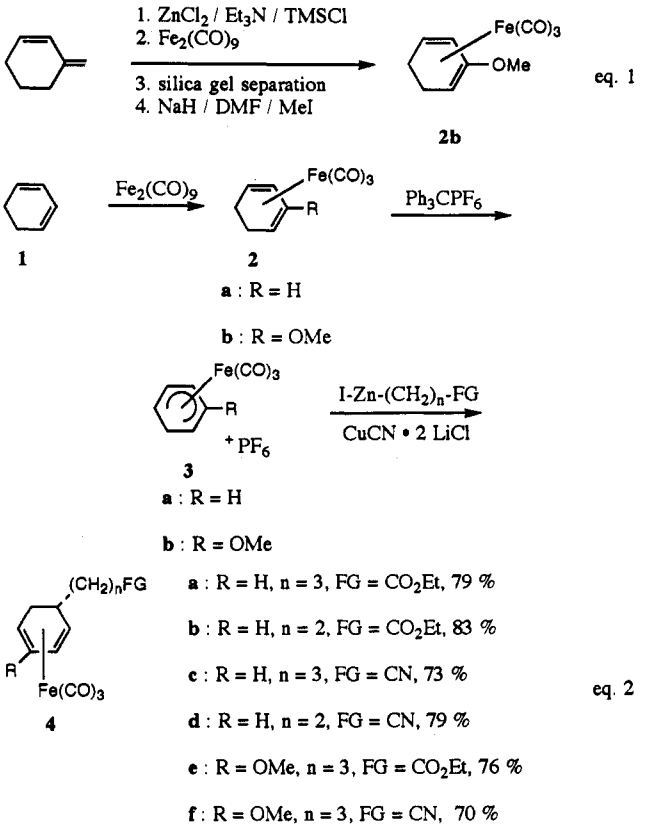
Preparation of Starting Complexes

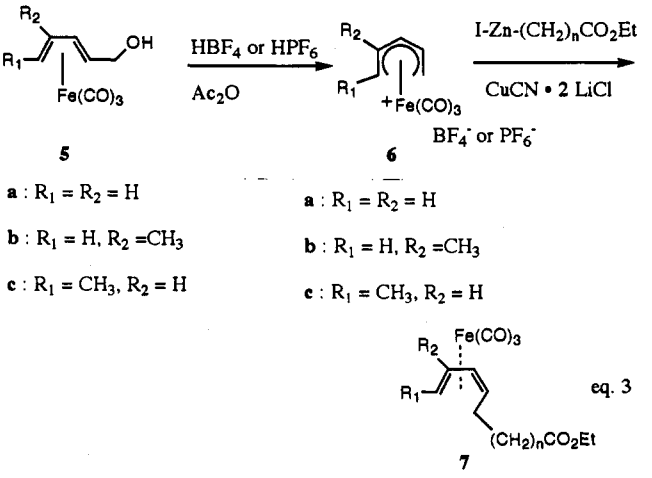
To prepare the starting (η^4-1,3-diene)$Fe(CO)_3$ complexes with functionalized side chains for intramolecular cyclizations, we adopted the well-known strategy developed by Birch and Pearson.[16] The addition of several classes of stabilized lithium nucleophiles, such as enolates,[16c] and nonstabilized lithium,[17] magnesium,[16a] cadmium,[16c,e] and zinc[16c] organometallics to (η^5-cyclohexadienyl)- and (η^5-pentadienyl)tricarbonyliron(+) salts is known to produce C-5-substituted (η^4-diene)$Fe(CO)_3$ complexes. With recently developed functionalized organometallics,[18] however, we were able to introduce a functionalized side chain at the C-5 position of the diene ligand.[19] The synthesis of the cyclic diene–iron complexes with functionalized side chains at C-5 is summarized in eq 2.

Treatment of cyclohexa-1,3-diene (**1**) with $Fe_2(CO)_9$ in refluxing ether gave complex **2a** in 64% yield. Complex **2b** could be obtained in the same way from 1-methoxycyclohexa-1,4-diene and $Fe_2(CO)_9$ in low yield.[16a] However, a large quantity of **2b** could be synthesized starting from 2-cyclohexen-1-one in 77% overall yield (eq 1).[20] Hydride abstraction of **2a** and **2b** using Ph_3CPF_6 led to cations **3a** and **3b**, respectively, each in quantitative yield. Cationic salts **3a** and **3b** were pale yellow powders and handled in air at room temperature without precautions. Finally, our synthesis of the cyclization precursors involved the addition of functionalized zinc–copper reagents [$IZn(CH_2)_nFG$, CuCN·2LiCl, 1.6–2.0 molar equiv] to a stirred suspension of cations **3a** and **3b** at 0 °C under nitrogen. The addition was carried out for 3 h at 23 °C followed by workup with saturated aqueous ammonium chloride solution and ether extraction. After purification by flash column chromatography on silica gel, complexes **4a–f** were obtained as the major products. The yields of the additions were generally high (70–83%, eq 2).

Acyclic cyclization precursors were synthesized as follows. Dienyl alcohols **5** were treated with HBF_4 or HPF_6 in the presence of acetic anhydride to give (η^5-pentadienyl)$Fe(CO)_3$ cations **6** according to the literature procedure.[21] Reaction of cations **6** with functionalized zinc–copper reagents, under the same reaction conditions as described above, afforded complexes **7** with



functionalized side chains at the terminal position of the diene ligands (eq 3).



Intramolecular Nucleophile Additions

Our cyclization study began with complex **4a**. Treatment of **4a** with 1.5 molar equiv of LDA at −78 °C under nitrogen produced a major product in 50% yield, identified as bicyclo[3.3.1]-nonenecarboxylic acid derivative **8** with an incorporated CO at the C-9 position. Thus, the addition was performed under an atmosphere of CO (14 psi), which increased the yield of

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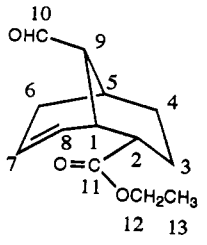
cycloadduct **8** to 82% after purification by flash column chromatography and distillation under reduced pressure. It is important to note that three new stereogenic centers of compound **8** are created; however, only the single diastereomer shown was isolated.

NMR studies provided the initial evidence for support of the structural assignments. The ^1H NMR spectrum of compound **8** exhibited a broad singlet at δ 9.59 assigned to the formyl H at C-10; a doublet of triplets, centered at δ 5.94, assigned to the vinyl H at C-7; a broad doublet of doublets, centered at δ 5.67, assigned to the vinyl H at C-8; two narrow quartets, centered at δ 4.15, assigned to the two diastereotopic methylene protons at C-12; and a triplet, centered at δ 1.28, assigned to the methyl group at C-13. The ^{13}C NMR spectrum exhibited a signal at δ 203.3 assigned to C-10 (formyl), a signal at δ 173.8 assigned to C-11 (carbonyl of the ester functionality), and two signals at δ 133.1 and 124.5 assigned to two vinyl carbons (C-7 and C-8). Attempts to confirm the relative stereochemistry of bicyclo[3.3.1] compound **8** using NOESY (nuclear Overhauser enhancement spectroscopy) measurements were unsuccessful. Rigorous proof of the structure of **8** was finally accomplished by X-ray diffraction analysis of the (2,4-dinitrophenyl)hydrazone derivative **9**.[22] The



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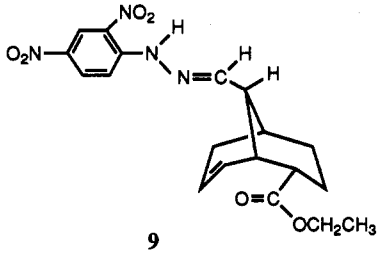

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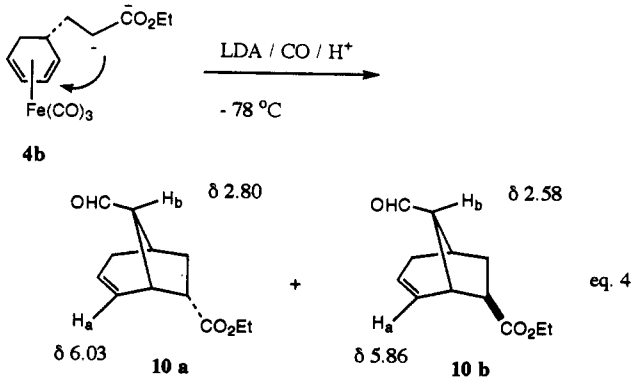
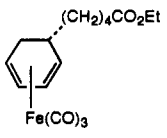
X-ray diffraction analysis clearly shows that both bulky ester and hydrazone groups occupy equatorial positions on the six-membered ring.[23] Under the same reaction conditions, however, cyclization of the starting complex **4b** gave a mixture of diastereomeric products **10a** and **10b** in a 2:1 ratio in 37% total yield (eq 4).



The structures for **10a** and **10b** were established by comparison of their ^1H and ^{13}C NMR spectral data with the corresponding data of **8**. The stereochemistry assignment for **10a** as an endo isomer was based on the downfield shift of H_a (δ 6.03), due to the deshielding effect of the carbonyl of the endo ester group, and the assignment for **10b** as the exo isomer was deduced from the upfield shift of H_b (δ 2.58), owing to the shielding effect of the carbonyl of the exo ester group. The reason for the formation of two diastereomeric products of the bicyclo[3.2.1]octenecarboxylic acid derivatives (**10a**, **10b**) and a single isomer of the bicyclo[3.3.1]nonenecarboxylic acid derivative (**8**) was not clear. It was suggested that, for complex **4a**, only one of the diastereotopic protons at the α-carbon of the ester group was removed by LDA under the kinetically controlled reaction conditions. Thus, only one diastereomer was isolated. However, with only two carbon atoms on the side chain, for example complex **4b**, deprotonation would be affected by both the ester group and the cyclohexadiene ring. Therefore, the selectivity for the removal of the diastereotopic protons at the α-carbon was poor, and the cyclization gave both diastereomers. The same reaction mixture could be coupled with carbon electrophiles such as iodomethane or benzyl bromide to give methyl and benzyl ketone, respectively, in moderate yields.[20] Results of cycloaddition/quenching processes are summarized in Table I.

Several entries in Table I deserve special mention. Intramolecular cyclization of **4c** produced a mixture of endo (**12a**) and exo (**12b**) isomers in a ratio of 1:2 (entry 4, Table I). Unlike an ester group, a cyano group is rather small. Thus, either one of the two α-protons is possibly removed by LDA. Furthermore, cycloaddition of the starting complexes with a methoxy group at C-2 of the diene ligand gave bicyclo[3.3.1]nonanone derivatives without incorporation of a carbon monoxide molecule (entries 10 and 11, Table I). Nonetheless, the product distributions of the reactions were consistent with the previous results. Cyclization of complexes with three carbon atoms and an ester group on the side chain of the starting complex, for example, cyclization of complex **4e**, gave only one isomer (**18**, entry 10, Table I). Attempted intramolecular cyclization using tethers longer than three methylene groups, for example complex **20**, gave only Claisen-condensation product **21**. However, we were able to isolate bicyclo[4.3.1]decene derivative **23** by cyclization of starting complex **22** followed by conversion of the resulting aldehyde to hydrazone derivative **23** in 5% overall yield. The difficulty in forming bicyclo[4.3.1]decene systems might be attributed to unfavorable formation of seven-membered rings.



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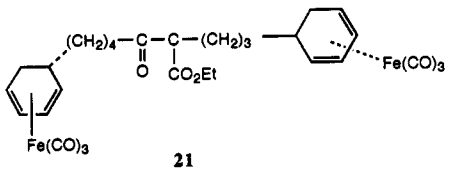

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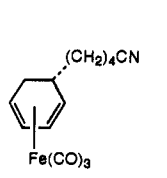

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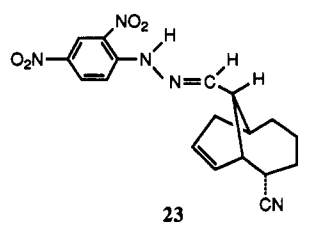

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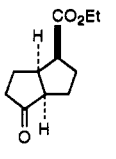

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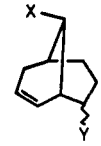
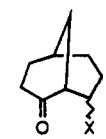
Using the same methodology, we are able to construct fused bicyclo[3.3.0]octanone and bicyclo[4.3.0]nonanone derivatives via intramolecular cyclization of acyclic (η^4-1,3-diene)$Fe(CO)_3$ complexes with functionalized side chains at the terminal positions of the diene ligands. Treatment of **7a** with LDA under an atmosphere of CO at –78 and 25 °C for 2 h, respectively, followed by quenching the reaction mixture with CF_3COOH at –78 °C, gave bicyclo[3.3.0]octanone **24** as the only diastereomeric product in 55% yield after purification via flash column chromatography and short-path distillation of the residue. None of the endo isomer **25** was obtained.

The relative stereochemistry at the ring juncture in **24** was fixed by more stable cis fusion, and ^1H NMR studies provided

(22) The hydrazone **9** was formed in the usual way: Pavia, D. L.; Lampman, G. M.; Kriz, G. S., Jr. *Introduction to Organic Laboratory Techniques*; W. B. Sanders Co.: Philadelphia, PA, 1975; p 668.

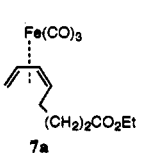
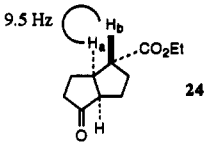
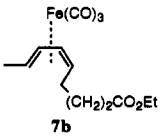
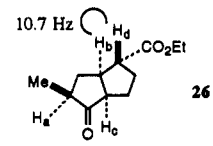
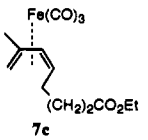
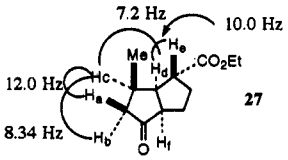
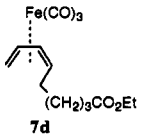
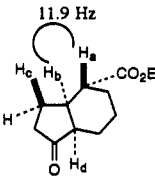
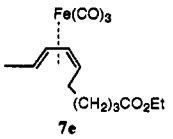
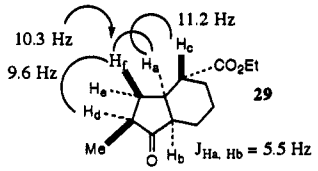
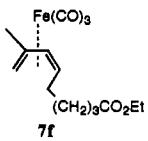
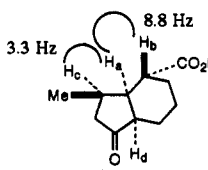
(23) The hydrazone **9** was hydrolyzed back to the original isomer **8** in order to establish that no structural change occurred during derivatization. The hydrolysis was performed according to a general procedure: McMurry, J. E.; Silvestri, M. *J. Org. Chem.* **1975**, *40*, 1502.

Table I. Intramolecular Cyclization and Electrophilic Quenching of Complexes **4a–f**

Entry	Starting Complex	Electrophile	Product	Yield (%)
1	**4a**	CF_3COOH	**8**	82 %
2	**4b**	CF_3COOH	**10 a** + **10 b** 2 : 1	37 %
3	**4a**	MeI	 **11** X = MeCO Y = endo CO_2Et	40 %
4	**4c**	CF_3COOH	**12a** + **12b** X = CHO, Y = endo CN : X = CHO, Y = exo CN 1 : 2	79 %
5	**4c**	MeI	**13a** + **13b** X = MeCO, Y = endo CN : X = MeCO, Y = exo CN 1 : 2	42 %
6	**4c**	$PhCH_2Br$	**14a** + **14b** X = $PhCH_2CO$, Y = endo CN : X = $PhCH_2CO$, Y = exo CN 1 : 2	49 %
7	**4d**	CF_3COOH	 **15a** + **15b** X = CHO, Y = endo CN : X = CHO, Y = exo CN 7 : 4	45 %
8	**4d**	MeI	**16a** + **16b** X = MeCO, Y = endo CN : X = MeCO, Y = exo CN	15 %
9	**4d**	$PhCH_2Br$	**17a** + **17b** X = $PhCH_2CO$, Y = endo CN : X = $PhCH_2CO$, Y = exo CN	14 %
10	**4e**	CF_3COOH	 **18** X = endo CO_2Et	74 %
11	**4f**	CF_3COOH	**19a** + **19b** X = endo CN : X = exo CN	42 %

the initial evidence for support of the structure assignments. The proton at δ 2.69 as a dt, J = 9.5, 4.9 Hz, was assigned to H_b. The coupling constant of H_a–H_b (J_{ab}) of 9.5 Hz agrees with the 9–10.5-Hz coupling constant for similarly disposed trans hydrogens compared to the 7–8 Hz observed when these protons are cis.[24] The excellent diastereoselectivity can also be explained by the

Table II. Intramolecular Cyclization of Complexes **7a–f**

Entry	Starting Complex	Product	Yield %
1	 **7a**	 **24**	55
2	 **7b**	 **26**	34
3	 **7c**	 **27**	30
4	 **7d**	 **28**	54
5	 **7e**	 **29**	25
6	 **7f**	 **30**	28

kinetically controlled reaction conditions and is consistent with complexes **4a** and **4e** having a long side chain and an ester functionality. Several examples of cyclization of acyclic diene–iron complexes are summarized in Table II.

Substrates with an additional methyl group at the diene ligand, **7b** and **7c** (entries 2 and 3, Table II), also underwent intramolecular cyclization to produce bicyclo[3.3.0]octanones **26** and **27**, respectively, as the only diastereomeric product in each case. It is worth noting that three carbon–carbon bonds and four stereogenic centers are created in a single step, and only one diastereomer is isolated. The relative stereochemistry of products **26** and **27** was determined by ^{1}H NMR spectroscopy, with assignments deriving from decoupling experiments. For example, coupling constants of 7.2 and 10.0 Hz for H_c–H_d and H_d–H_e of **27**, respectively, indicated a cis relationship between H_c and H_d and a trans relationship between H_d and H_e. A coupling constant of 10.7 Hz for H_b–H_d of **26** suggested a trans relationship between H_b and H_d. A cross peak for H_a and H_b in the NOESY spectrum of **26** showed the cis relationship between H_a and H_b.

Increasing the tether length by one with complex **7d** (entry 4, Table II) led to a 54% yield of bicyclo[4.3.0]nonanone derivative **28** as the only diasteromeric product isolated. The stereochemistry of the ring juncture was assigned as cis on the basis of ^{13}C NMR spectral data, which was close to that of the parent *cis*-1-hexahydroindanone reported in the literature.[25] A coupling constant of 11.9 Hz for H_a–H_b indicated a trans relationship between H_a and H_b. Additional support for this assignment came from a cross peak for H_a and H_c in the NOESY spectrum of **28**. With an additional methyl group at the C-1 position of the starting complex, for example, cyclization of complex **7e** (entry 5, Table II) gave bicyclo[4.3.0]nonanone derivative **29** as the major product under conditions identical with those used above. A small amount (<7%) of the other diastereomer was also isolated, presumably derived from epimerization at the α-carbon (C-8) of the keto group during acid quenching and aqueous workup. The relative stereochemistry of compound **29** was determined by ^{1}H NMR spectroscopy, with assignments deriving from decoupling experiments. Coupling constants of 5.5 and 11.2 Hz for H_a–H_b and H_a–H_c, respectively, in **29** indicated a cis ring juncture and a trans H_a–H_c relationship. The methyl group at C-8, assigned to be on the endo face, was determined by the peak patterns and coupling constants of H_d–H_e and H_d–H_f. Coupling constants of 9.6 and 1.0 Hz for H_d–H_f and H_d–H_e, respectively, suggested that H_d and H_f would likely to be trans. This assignment was also confirmed by the large coupling constant of H_f–H_a (10.3 Hz, trans relationship). Cyclization of complexes with a methyl group at the C-2 position of the diene ligand, for example, cyclization of complex **7f** (entry 6, Table II), gave bicyclo[4.3.0]nonanone derivative **30** in 28% yield, and only the diastereomer shown was isolated. The relative stereochemistry of compound **30** was assigned on the basis of ^{1}H NMR decoupling experiments. A coupling constant of 8.8 Hz for H_a–H_b suggested a trans relationship between H_a and H_b. A coupling constant of 3.3 Hz for H_a–H_c suggests a cis relationship between H_a and H_c. The stereochemistry of the ring juncture was assigned as cis on the basis of ^{13}C NMR spectral data, which was close to that of compound **28**. The high diastereoselectivity of these fused bicyclic compounds may be due to the formation of kinetic enolates and is consistent with cyclic precursors having a long side chain and an ester functionality, for example, complexes **4a** and **4e**.

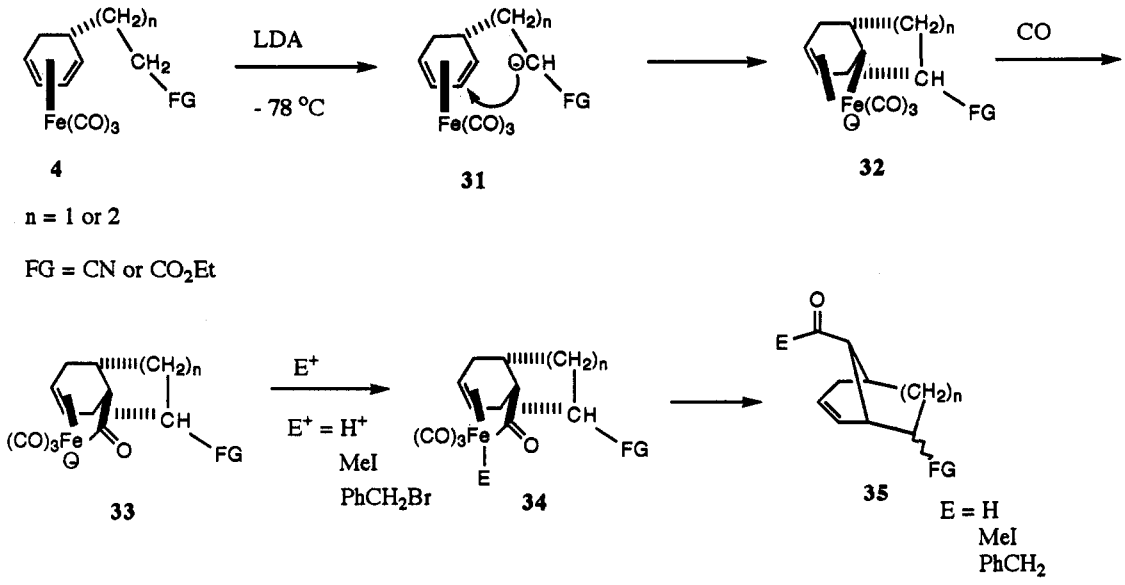
Discussion

The formation of bicyclo[3.3.1] and -[3.2.1] skeletons agrees closely with the mechanism proposed for the intermolecular addition of nucleophiles to (η^4-1,3-cyclohexadiene)Fe(CO)$_3$ complex.[15a,c] Deprotonation of **4** using LDA at –78 °C gave anion **31** (Scheme I). The stabilized secondary carbanion underwent kinetically controlled anti addition at C-3 of the diene ligand to give the putative homoallyl anion intermediate **32**. It is important to mention that secondary carbanions such as 2-lithiopropionitrile and *tert*-butyl 2-lithiopropionate do not add efficiently to (η^4-1,3-cyclohexadiene)Fe(CO)$_3$ complexes intermolecularly.[15a] Moreover, the intramolecular addition occurred exclusively at the C-3 position of the diene ligand, and none of the addition at C-2 was found. Carbonyl insertion was then enhanced by an external CO (14–18 psi) to generate acyliron anion intermediate **33**. Electrophilic quenching of **33** with trifluoroacetic acid or carbon electrophiles (iodomethane or benzyl bromide) produced **34**, which underwent reductive elimination to form bicyclo[3.3.1] and bicyclo[3.2.1] compounds **35**. In general, two diastereomeric products were generated from intramolecular nucleophile additions, whereas in the cases of **4a** and **4e**, only one isomer was isolated. It is presumed that the relative stereochemistry of bridgehead carbons and the α-carbon of the formyl group was fixed according to the mechanism proposed above. With a long side chain (three carbon atoms away from the cyclohexadiene ring and the iron carbonyl moiety) and an ester functionality, only one of the diastereotopic protons was removed under the kinetically controlled reaction conditions. It is important to mention that trifluoroacetic acid is the most

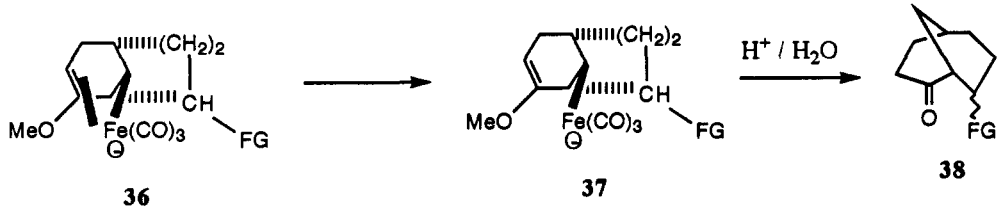
(24) Trost, B. M.; Mao, M. K.-T.; Balkovec, J. M.; Buhlmayer, P. *J. Am. Chem. Soc.* **1986**, *108*, 4965.

(25) Larock, R. C.; Oertle, K.; Potter, G. F. *J. Am. Chem. Soc.* **1980**, *102*, 190.

Scheme I



Scheme II



efficient quenching reagent for acyliron anion **33**. Iodomethane and benzyl bromide were able to couple with **33**, however, only in less than 50% isolated yields. Unlike the previous results, cyclization of complexes with a methoxy group at C-2 of the diene ligand, for example complexes **4e** and **4f** (entries 10, 11, Table I), gave the bicyclo[3.3.1] skeletons without an incorporated CO. The reason for this difference is not clear. It is suggested that the homoallyl anionic intermediate **36** was formed initially (Scheme II). Detachment of the alkene ligand (due to the electronic effect of the methoxy group at C-2) generates **37**.[15d] Reaction of anion **37** with strong acid gave bicyclo[3.3.1]nonanone derivative **38** after hydrolysis of the methyl vinyl ether during aqueous workup.

Under the same reaction conditions, intramolecular cyclizations of acyclic substrates **7a–f** led to 25–55% yields of bicyclo[3.3.0]-octanones **24** and **26–27** and bicyclo[4.3.0]nonanones **28–30** as the only diastereomeric product in each case. The highly stereocontrolled outcome is consistent with the formation of cyclopentanone derivatives by intermolecular addition of nucleophiles to acyclic diene–iron complexes under an atmosphere of carbon monoxide.[15b,e] Under kinetically controlled reaction conditions (–78 °C), the kinetic ester enolate **39** (Scheme III) could add at the internal C-3 of the diene ligand to produce the homoallyl anion intermediate **40**, followed by carbonyl insertion (to give **41**) and intramolecular alkene insertion (to give **42**). The postulated initial bicyclic intermediate **42** could rearrange rapidly to the enolate–iron derivative **43**. The rearrangement involves a stereospecific hydrogen transfer, presumably via β-hydride elimination/readdition. Protonation of **43** generates bicyclic compound **45**. It is important to mention that the endo stereochemistry of the methyl groups of **26** and **27** and of **29** and **30** as well as only cis ring fusion found for bicyclo[4.3.0]nonanones **28–30** is consistent with the reaction pathway proposed above. However, bicyclo[3.3.0]octanone derivative **26** and bicyclo[4.3.0]-nonanone derivative **29** could epimerize at C-7 and C-8, respectively, to give the more stable exo form (methyl group) when the reaction mixture is stirred in trifluoroacetic acid for 12 h.

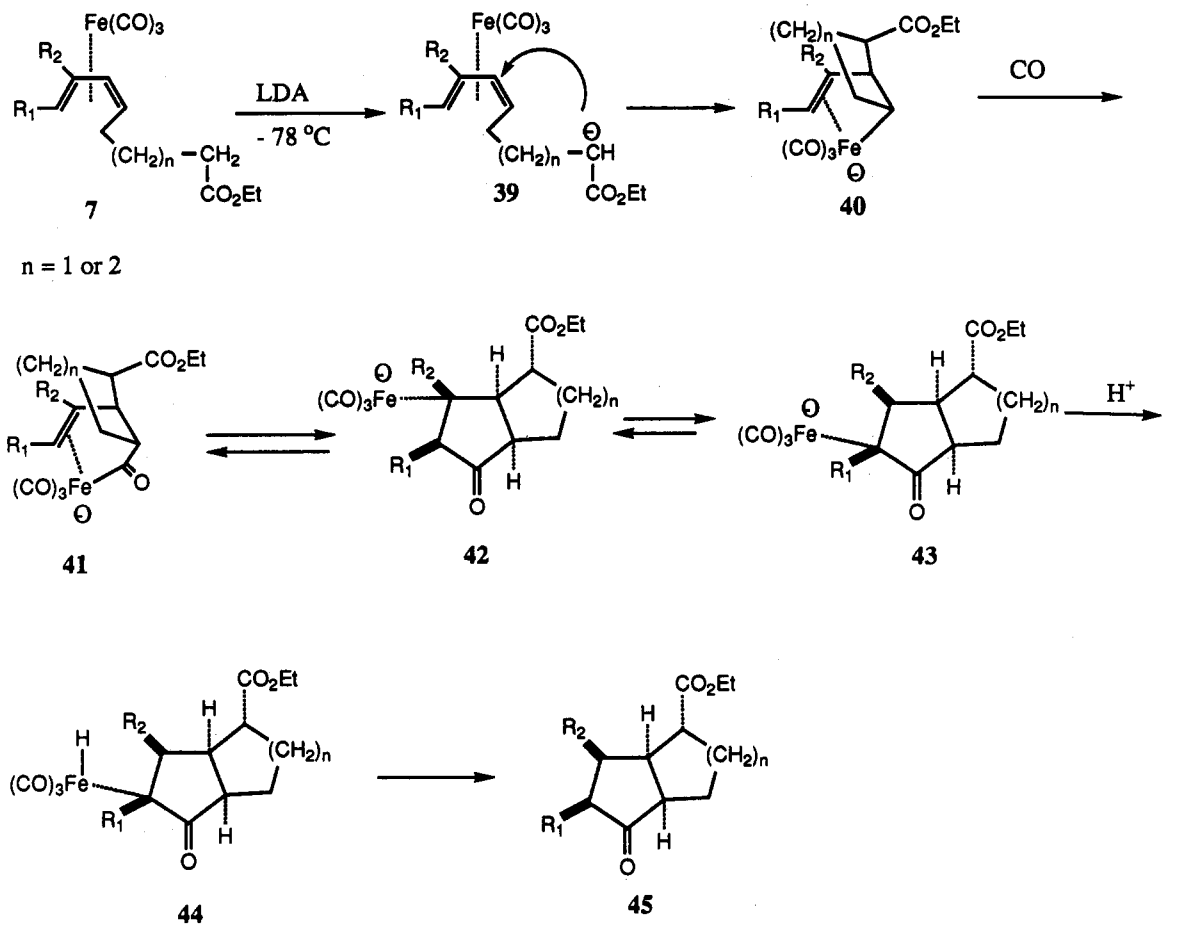
The reactions outlined herein demonstrate that the intramolecular iron-mediated cycloaddition can be an effective method for the formation of bridged and fused bicyclic compounds. The ability to achieve exclusive cis ring juncture and excellent stereocontrol of four stereogenic centers in fused bicyclic compounds in a simple reaction may have further applications. Specifically, the preparation of more highly substituted systems for natural product synthesis would be expected to demonstrate still higher levels of stereocontrol, as is often the case for the intramolecular Diels–Alder reaction.[4,5c,26]

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. Methylene chloride was distilled from calcium chloride. Copper cyanide (CuCN), 1,3-cyclohexadiene, 1-methoxy-1,4-cyclohexadiene, triphenylcarbenium hexafluorophosphate, (2,4-dinitrophenyl)hydrazine, *trans,trans*-2,4-hexadien-1-ol, fluoroboric acid (48% in water), and hexafluorophosphoric acid (60% in water) were purchased from Aldrich Chemical Co. and used as received. Zinc particles (purity >99.9%), ethyl 4-chlorobutyrate, 4-chlorobutyronitrile, 3-chloropropionitrile, and ethyl 3-chloropropionate were purchased from Merck Co. and used without further purification. (η^4-1,3-Diene)$Fe(CO)_3$ complexes **2a** and **5** were obtained by treatment of the corresponding free dienes with diiron nonacarbonyl in refluxing ether for 12 h. Complex **2b** was obtained in three steps from 2-cyclohexen-1-one according to the literature procedure.[20] Diiron nonacarbonyl was obtained by photolysis of iron pentacarbonyl in benzene and acetic acid

(26) Taber, D. F. *Intramolecular Diels-Alder and Alder Ene Reactions*; Springer-Verlag: Berlin, 1984. Roush, W. R. *Adv. Cycloaddit.* **1990**, *2*, 91.

Scheme III



according to the literature procedure.[27] Flash column chromatography, following the method of Still,[28] 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 Company 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. The term "flash distillation" refers to a vacuum distillation at 25 °C with a receiver at −78 °C. The term "short-path distillation" refers to the process in which the entire distillation apparatus (a tube closed at one end, held horizontally) with the exception of the collection bulb was slowly heated in an air bath from 25 to 150 °C under vacuum; the distillate was collected at −78 °C, and boiling points for fractions refers to the bath temperature range. Melting points were determined in open capillaries with a Thomas-Hoover apparatus and are uncorrected. ^{1}H NMR nuclear magnetic resonance (NMR) spectra were obtained with JEOL-EX 400 (400 MHz), Bruker AC-300 (300 MHz), and Bruker AC-200 (200 MHz) spectrometers. Chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or $CHCl_3$ (7.26 ppm) as internal standards. ^{13}C NMR spectra were recorded with JEOL-EX 400 (100.4 ppm) and Bruker AC-200 (50.2 ppm) spectrometers with $CDCl_3$ (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer. Mass spectra were acquired on a JEOL JMS-D 100 spectrometer at an ionization potential of 70 eV and are reported as mass/charge (*m/e*) with percent relative abundance. High-resolution mass spectra were obtained with an AEI MS-9 double-focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer in the Department of Chemistry, Northern Instrument Center, Hsin Chu.

General Procedure for the Formation of Cation 3.[16a,29] To a solution of triphenylcarbenium hexafluorophosphate (Ph_3CPF_6, 8.5 g, 22 mmol) in 60 mL of dry dichloromethane under nitrogen was added rapidly a solution of complex **2** (16.2 mmol). The reaction mixture was stirred at 25 °C for 12 h. The reaction mixture was diluted with 100 mL of cold ether, and the precipitate was filtered. The yellow solid was washed four times with ether and dried under vacuum to give cation **3** (**3a** 99%, **3b** 92%) as a pale yellow powder.

General Procedure for the Formation of Functionalized Zinc–Copper Reagents.[18a] To a solution of sodium iodide (30 g, 0.2 mol) in 90 mL of anhydrous acetone were added functionalized alkyl chlorides (0.1 mol). The reaction mixture was stirred under reflux for 16 h. After a regular aqueous process, the residue was distilled under vacuum to give the corresponding functionalized alkyl iodides (60–90%). Zinc (1.8 g, 28 mmol) was added in a dried three-neck round-bottom flask equipped with a dropping funnel, a thermometer, and a nitrogen outlet. To the reaction were added 2.5 mL of THF and 0.2 mL of 1,2-dibromoethane. The reaction mixture was heated with a heat gun for 30 s and allowed to cool to room temperature. The process was repeated two times before 0.2 mL of chlorotrimethylsilane was added via syringe. The mixture was stirred for 30 min before a THF (4 mL) solution of functionalized alkyl iodides (14 mmol) [$I(CH_2)_nFG$, FG = CO_2Et or CN] was added via the dropping funnel. Normally, the reaction was stirred at 40–50 °C for 14 h. In the case of ethyl iodopropionate and iodopropionitrile, the insertion was complete at 25 °C for 8 h. Copper cyanide (0.98 g, 10.95 mmol) was added to predried LiCl (150 °C, 3 h under vacuum, 0.93 g, 22 mmol) in a Schlenk flask under nitrogen. The reaction mixture was cooled to 0 °C before 10 mL of THF was added via syringe. The reaction mixture was stirred at 25 °C until the solid was dissolved. The above solution was cooled to −78 °C, and the functionalized alkylzinc iodide was added dropwise to the reaction mixture. The resulting light green solution was stirred at 0 °C for 30 min, and the functionalized zinc–copper reagent was ready to use.

(27) 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.

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

(29) (a) Fischer, E. O.; Fischer, R. D. *Angew. Chem.* **1960**, *72*, 919. (b) Whitesides, T. H.; Arhart, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 5296.

General Procedure for Addition of Functionalized Zinc–Copper Reagents RCu(ZnI)CN to (η^5-Cyclohexadienyl)- and (η^5-Pentadienyl)Fe(CO)$_3$ Cation Salts. A solution of functionalized zinc–copper reagents (2.0 molar equiv) in 5 mL of THF was added to a stirred suspension of a cation salt (3 or 6) in 5 mL of THF at 5 °C under nitrogen. A homogeneous solution was obtained after the reaction mixture was stirred at 25 °C for 2 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/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.

General Procedure for Intramolecular Cyclization of (η^4-Diene)Fe(CO)$_3$ Complexes Bearing Functionalized Side Chains. In a typical procedure, to a solution of diisopropylamine (0.64 mL, 4.5 mmol) in 4 mL of THF under nitrogen at −78 °C was added rapidly, neat, via syringe, a solution of *n*-butyllithium (2.8 mL, 4.5 mmol, 1.6 M) in hexane followed by addition of 0.8 mL of hexamethylphosphoramide. 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 s. A solution of a diene–iron complex (4 or 7, 2 mmol) in 3 mL of THF was added dropwise via syringe, the gas exit 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 and 25 °C for 2 h. After this time, the mixture was again cooled to −78 °C, 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 no longer be heard. The reaction mixture was quenched with electrophiles (trifluoroacetic acid, iodomethane, or benzyl bromide, 5 molar equiv, Table I) via a syringe needle and was stirred at 25 °C for 2 h. After this time, the reaction mixture was diluted with a mixture of ethyl acetate/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.

[Ethyl *exo*-4-[(1–4-η)-1,3-cyclohexadien-5-yl]butyrate]tricarbonyliron Complex (4a). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (22 mmol) to cation **3a** (4.0 g, 11 mmol) was purified via flash column chromatography (silica gel, 1:20 ethyl acetate/hexanes), followed by short-path distillation (138–142 °C, 0.02 mmHg) to give **4a** (2.9 g, 8.7 mmol, 79%) as a yellow oil: IR (CH_2Cl_2) 2987, 2849, 2465, 2043, 1964, 1734, 1628, 1539, 1455, 1373, 1241, 1186, 1030, 967, 861, 617 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.32 (dd, J = 6.3, 4.1 Hz, 1 H), 5.23 (td, J = 6.1, 1.5 Hz, 1 H), 4.07 (q, J = 7.2 Hz, 2 H), 3.08 (dd, J = 6.4, 3.0 Hz, 1 H), 3.00 (m, 1 H), 2.19 (t, J = 7.3 Hz, 2 H), 2.09 (m, 1 H), 1.92 (dd, J = 10.4, 3.7 Hz, 1 H), 1.51 (p, J = 7.5 Hz, 2 H), 1.17 (t, J = 7.2 Hz, 3 H), 1.28–1.05 (m, 3 H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 212.1, 173.4, 85.5, 84.5, 66.5, 60.2, 59.8, 39.3, 37.9, 34.2, 30.6, 23.5, 14.2; MS (70 eV) *m/e* (rel intensity) 334 (M^+, 3), 306 (7), 278 (45), 250 (100), 233 (13), 221 (40), 205 (18), 192 (41), 170 (31), 148 (88), 134 (58), 91 (25); HRMS (EI) *m/e* calcd for $C_{15}H_{18}FeO_5$ (M^+) 334.0504, found 334.0504.

[Ethyl *exo*-3-[(1–4-η)-1,3-cyclohexadien-5-yl]propionate]tricarbonyliron Complex (4b). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (11.3 mmol) to cation **3a** (2.17 g, 5.96 mmol) was purified via flash column chromatography (silica gel, 1:20 ethyl acetate/hexanes), followed by short-path distillation (112–117 °C, 0.02 mmHg) to give **4b** (1.57 g, 4.91 mmol, 83%) as a yellow oil: IR (CH_2Cl_2) 3056, 2990, 2934, 2852, 2050, 1978, 1726, 1609, 1447, 1373, 1330, 1185, 1092, 1031 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (dd, J = 6.3, 4.4 Hz, 1 H), 5.29 (td, J = 4.9, 1.5 Hz, 1 H), 4.11 (q, J = 6.8 Hz, 2 H), 3.08 (dd, J = 6.4, 4.3 Hz, 1 H), 3.03 (dd, J = 4.0, 2.0 Hz, 1 H), 2.23 (t, J = 7.8 Hz, 2 H), 2.13 (m, 1 H), 2.00 (dd, J = 14.2, 3.9 Hz, 1 H), 1.50 (m, 2 H), 1.30–1.21 (m, 4 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 211.9, 173.3, 85.6, 84.5, 65.6, 60.2, 59.5, 37.4, 34.5, 32.8, 30.4, 14.1; MS (70 eV) *m/e* (rel intensity) 320 (M^+, 2), 292 (8), 264 (47), 236 (100), 206 (53), 178 (20), 161 (95), 133 (93), 104 (21), 90 (53), 56 (83), 28 (100); HRMS (EI) *m/e* calcd for $C_{14}H_{16}FeO_5$(M^+) 320.0347, found 320.0292.

[*exo*-4-[(1–4-η)-1,3-Cyclohexadien-5-yl]butyronitrile]tricarbonyliron Complex (4c). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (10.98 mmol) to cation **3a** (2.0 g, 5.55 mmol) was purified via flash column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give **4c** (1.14 g, 3.97 mmol, 73%) as a yellow oil: IR (CH_2Cl_2) 3059, 3010, 2939, 2850, 2244, 2045, 1975, 1425, 1328, 1158, 1027, 980, 814, 547 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.35 (dd, J = 6.0, 4.1 Hz, 1 H), 5.29 (td, J = 6.0, 1.8 Hz, 1 H), 3.05 (m, 2 H), 2.25 (t, J = 6.9 Hz, 2 H), 2.05 (m, 1 H), 2.00 (dd, 10.8, 4.2 Hz, 1 H), 1.54 (m, 2 H), 1.35–1.28 (m, 3 H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 211.9, 120.0, 85.8, 84.5, 65.6, 59.5, 38.7, 37.5, 30.6, 24.0, 17.3; MS (70 eV) *m/e* (rel intensity) 287 (M^+, 5), 259 (30), 231 (94), 203 (100); HRMS (EI) *m/e* calcd for $C_{13}H_{13}FeNO_3$ (M^+) 287.0244, found 287.0233.

[*exo*-3-[(1–4-η)-1,3-Cyclohexadien-5-yl]propionitrile]tricarbonyliron Complex (4d). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (10.98 mmol) to cation **3a** (2.0 g, 5.49 mmol) was purified via flash column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give **4d** (1.18 g, 4.3 mmol, 79%) as a yellow oil: IR (CH_2Cl_2) 3032, 3000, 2942, 2847, 2468, 2250, 2049, 1962, 1424, 1350, 1165, 960 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (dd, J = 6.1, 4.0 Hz, 1 H), 5.31 (dd, J = 6.1, 3.0 Hz, 1 H), 3.04 (brs, 2 H), 2.30 (t, J = 8.4 Hz, 2 H), 2.19 (m, 1 H), 2.07 (dd, J = 14.7, 4.7 Hz, 1 H), 1.56 (m, 2 H), 1.24 (d, J = 14.7 Hz, 1 H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 211.6, 119.3, 85.9, 84.3, 63.8, 59.0, 36.9, 34.6, 30.3, 15.6; MS (70 eV) *m/e* (rel intensity) 273 (M^+, 3), 245 (7), 217 (24), 187 (100), 160 (9), 147 (13), 134 (27), 111 (10), 91 (31), 79 (11), 56 (24); HRMS (EI) *m/e* calcd for $C_9H_{11}FeN$ (M-3 CO) 189.0239, found 189.0231.

[Ethyl 5-*exo*-4-[(1–4-η)-2-methoxy-1,3-cyclohexadien-5-yl]butyrate]tricarbonyliron Complex (4e). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (12.12 mmol) to cation **3b** (2.4 g, 6.06 mmol) was purified via flash column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give **4e** (1.67 g, 4.60 mmol, 76%) as a yellow oil: IR (CH_2Cl_2) 2938, 2040, 1960, 1735, 1524, 1438, 1424, 1373, 1227, 1177, 1094, 1027, 925, 797, 614 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.05 (dd, J = 6.5, 2.2 Hz, 1 H), 4.07 (q, J = 7.2 Hz, 2 H), 3.61 (s, 3 H), 3.25 (q, J = 3.5 Hz, 1 H), 2.70 (dd, J = 6.4, 3.3 Hz, 1 H), 2.25 (t, J = 7.3 Hz, 2 H), 2.00 (dd, J = 10.8, 4.2 Hz, 1 H), 1.90 (m, 1 H), 1.55 (m, 2 H), 1.30–1.20 (m, 3 H), 1.23 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 211.3, 173.4, 139.8, 66.4, 60.2, 55.2, 54.2, 52.7, 39.4, 37.5, 34.3, 31.1, 23.6, 14.2; MS (70 eV) *m/e* (rel intensity) 364 (M^+, 2), 336 (3), 308 (8), 280 (30), 71 (100); HRMS (EI) *m/e* calcd for $C_{16}H_{20}FeO_6$ (M^+) 364.0608, found 364.0628.

[*exo*-4-[(1–4-η)-2-Methoxy-1,3-cyclohexadien-5-yl]butyronitrile]tricarbonyliron Complex (4f). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (10.98 mmol) to cation **3b** (2.0 g, 5.9 mmol) was purified via flash column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give **4f** (1.3 g, 4.13 mmol, 70%) as a yellow oil: IR (CH_2Cl_2) 3066, 3011, 2941, 2916, 2852, 2244, 2040, 1964, 1511, 1477, 1457, 1423, 1328, 1221, 1172, 1039, 967, 865, 635, 561 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.03 (dd, J = 6.5, 2.2 Hz, 1 H), 3.61 (s, 3 H), 3.25 (m, 1 H), 2.60 (dd, J = 6.5, 3.3, 1 H), 2.26 (t, J = 6.9 Hz, 2 H), 2.09 (dd, J = 9.2, 3.5 Hz, 1 H), 1.90 (m, 1 H), 1.56 (m, 2 H), 1.34–1.27 (m, 3 H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 211.1, 139.8, 119.4, 66.2, 54.3, 54.2, 52.4, 38.7, 37.1, 31.6, 24.2, 17.2; MS (70 eV) *m/e* (rel intensity) 317 (M^+, 2), 289 (12), 261 (36), 233 (100), 218 (25), 195 (32), 164 (75), 134 (21), 109 (15), 68 (55), 57 (52); HRMS (EI) *m/e* calcd for $C_{11}H_{15}FeNO$ (M-3 CO^+) 233.0503, found 233.0496.

[*exo*-5-[(1–4-η)-1,3-Cyclohexadien-5-yl[pentanenitrile]tricarbonyliron Complex (22). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (10.98 mmol) to cation **3a** (2.0 g, 6.15 mmol) was purified via flash column chromatography (silica gel, 1:20 ethyl acetate/hexane) to give **22** (1.23 g, 4.09 mmol, 66%) as a yellow oil: IR (CH_2Cl_2) 3066, 2934, 2240, 2042, 1964, 1606, 1455, 1432, 1244, 1089 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 (t, J = 5.3 Hz, 1 H), 5.27 (dd, J = 5.3, 4.9 Hz, 1 H), 3.09 (brs, 1 H), 3.04 (brs, 1 H), 2.31 (t, J = 6.8 Hz, 2 H), 2.04 (m, 1 H), 1.97 (dd, J = 10.2, 3.9 Hz, 1 H), 1.58 (m, 2 H), 1.38–1.19 (m, 5 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 212.0, 139.8, 119.6, 85.6, 84.5, 66.3, 59.7, 39.0, 37.9, 30.6, 27.2, 25.6, 17.0; MS (70 eV) *m/e* (rel intensity) 301 (M^+, 2), 273 (12), 245 (74), 271 (100); HRMS (EI) *m/e* calcd for $C_{14}H_{15}FeNO_3$ (M^+) 301.0401, found 301.0402.

[(1–5-η)-Pentadienyl]tricarbonyliron Tetrafluoroborate (6a).[30] Complex **5a** was synthesized from *trans*-2,4-pentadien-1-ol and $Fe_2(CO)_9$ according to literature procedures.[31,32] Reaction of complex **5a** with fluoroboric acid in acetic anhydride gave complex **6a** as a pale yellow powder.[31] Complex **6a** was used in the following step without further purification.

(30) Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 3955.
(31) Woodward, R. B.; Bader, F. E.; Bickel, H.; Frey, A. J.; Kierstead, R. W. *Tetrahedron* **1958**, *2*, 1.

[(1–5-η)-2-Methylpentadienyl]tricarbonyliron Hexafluorophosphate (6b).[21] Complex **6b** was synthesized from complex **5b** according to the literature procedure:[21] ^{1}H NMR (400 MHz, CD_3NO_2) δ 6.97 (d, J = 7.0 Hz, 1 H), 6.14 (ddd, J = 12.0, 10.0, 7.2 Hz, 1 H), 3.68 (dd, J = 10.0, 3.0 Hz, 1 H), 3.56 (m, 1 H), 2.40 (s, 3 H), 2.29 (dd, J = 12.0, 3.0 Hz, 1 H), 1.83 (d, J = 4.0 Hz, 1 H); ^{13}C NMR (100.4 MHz, CD_3NO_2) δ 122.2, 99.1, 94.6, 62.0, 60.2, 20.8.

[(2–5-η)-*syn*-1-Methylpentadienyl]tricarbonyl Tetrafluoroborate (6c).[34] Complex **6c** was synthesized from **5c** according to the literature procedure:[34] IR (acetone) 3020, 2993, 2114, 2065, 1973, 1676, 1491, 1477; ^{1}H NMR (400 MHz, acetone-d_6) δ 6.39 (m, 1 H), 6.23 (m, 1 H), 5.51 (m, 1 H), 5.37 (m, 1 H), 1.21 (d, J = 4.9 Hz, 3 H), 1.17 (m, 1 H), 0.48 (m, 1 H).

[(5–8-η)-Ethyl *cis*-5,7-octadienoate]tricarbonyliron Complex (7a). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (5.0 mmol) to cation **6a** (0.88 g, 3.0 mmol) was purified via flash column chromatography (silica gel, 1:20 ethyl acetate/hexane) to give **7a** (0.88 g, 95%) as a yellow oil: IR (CH_2Cl_2) 2982, 2047, 1960, 1726, 1603, 1449, 1375, 1182, 1028 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 (ddd, J = 9.8, 7.3, 4.9 Hz, 1 H), 5.30 (dd, J = 8.0, 4.9 Hz, 1 H), 4.10 (q, J = 7.3 Hz, 2 H), 2.54 (td, J = 13.1, 4.8 Hz, 1 H), 2.24 (q, J = 7.8 Hz, 2 H), 1.86 (dd, J = 7.3, 2.4 Hz, 1 H), 1.75–1.48 (m, 3 H), 1.44 (dd, J = 9.8, 2.4 Hz, 1 H), 1.24 (t, J = 7.32 Hz, 3 H), 1.06 (m, 1 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 211.2, 173.3, 90.8, 86.9, 77.0, 59.6, 40.9, 33.6, 28.0, 14.2; MS (70 eV) m/e (rel intensity) 308 (M^+, 1), 280 (6), 252 (69), 224 (100), 207 (96), 168 (74), 124 (39), 82 (78), 32 (59); HRMS (EI) m/e calcd for $C_{12}H_{16}FeO_3$ (M^+ – 2CO) 252.0449, found 252.0455.

[(5–8-η)-Ethyl *cis*-5,*trans*-7-nonadienoate]tricarbonyliron Complex (7b). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (10.0 mmol) to cation **6c** (1.77 g, 5.52 mmol) was purified via flash column chromatography (silica gel, 1:20 ethyl acetate/hexane) to give **7b** (1.77 g, 5.5 mmol, 99%) as a yellow oil: IR (CH_2Cl_2) 3059, 2982, 2040, 1967, 1728, 1452, 1377, 1277, 1261, 1186, 1030 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.21 (dd, J = 8.9, 4.9 Hz, 1 H), 5.08 (dd, J = 7.6, 5.1 Hz, 1 H), 4.08 (q, J = 7.1 Hz, 2 H), 2.44–2.17 (m, 3 H), 1.68–1.47 (m, 4 H), 1.41 (d, J = 6.2 Hz, 3 H), 1.22 (t, J = 7.1 Hz, 3 H), 1.06 (m, 1 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 211.9, 173.3, 94.6, 82.2, 60.3, 58.8, 57.7, 33.6, 28.8, 28.0, 20.2, 14.2; MS (30 eV) m/e (rel intensity) 266 (M^+ – 2CO, 20), 238 (100), 182 (19), 138 (31), 94 (27), 78 (20); HRMS (EI) m/e calcd for $C_{12}H_{18}FeO_3$ (M^+ – 2CO) 266.0605, found 266.0612.

[(5–8-η)-Ethyl 7-methyl-*cis*-5,7-octadienoate]tricarbonyliron Complex (7c). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (5.0 mmol) to cation **6b** (0.92 g, 3.0 mmol) was purified via flash column chromatography (silica gel, 1:30 ethyl acetate/hexanes) to give **7c** (0.82 g, 85%) as a yellow oil: IR (CH_2Cl_2) 3059, 2980, 2042, 1969, 1728, 1442, 1277, 1257, 1184, 1033 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.22 (d, J = 7.5 Hz, 1 H), 4.10 (q, J = 7.1 Hz, 2 H), 2.41–2.23 (m, 4 H), 2.18 (s, 3 H), 1.89–1.47 (m, 4 H), 1.24 (t, J = 7.1 Hz, 3 H), 1.10 (m, 1 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 211.3, 173.4, 108.0, 86.7, 60.3, 55.6, 43.5, 33.7, 28.0, 24.6, 17.6, 14.2; MS (30 eV) m/e (rel intensity) 322 (M^+, 6), 294 (33), 238 (100), 182 (70), 165 (96), 98 (97), 71 (52), 41 (42); HRMS (EI) m/e calcd for $C_{13}H_{18}FeO_4$ (M^+ – CO) 294.0554, found 294.0550.

[(6–9-η)-Ethyl *cis*-6,8-nonadienoate]tricarbonyliron Complex (7d). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (5.0 mmol) to cation **6a** (0.88 g, 3.0 mmol) was purified via flash column chromatography (silica gel, 1:30 ethyl acetate/hexane) to give **7d** (0.9 g, 93%): IR (CH_2Cl_2) 3051, 2988, 2935, 2860, 2046, 1973, 1728, 1658, 1448, 1375, 1275, 1182, 1141, 927 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (ddd, J = 9.8, 7.5, 4.9 Hz, 1 H), 5.28 (dd, J = 7.8, 4.9 Hz, 1 H), 4.11 (q, J = 7.3 Hz, 3 H), 2.55 (ddd, J = 13.1, 7.8, 4.9 Hz, 1 H), 2.24 (t, J = 7.3 Hz, 2 H), 1.88 (dd, J = 7.5, 2.4 Hz, 1 H), 1.55 (m, 3 H), 1.48 (dd, J = 7.6, 2.8 Hz, 1 H), 1.45 (m, 2 H), 1.25 (t, J = 7.3 Hz, 3 H), 1.07 (m, 1 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 211.3, 173.5, 90.6, 86.9, 60.2, 59.9, 40.8, 34.0, 32.34, 28.37, 24.35, 14.2; MS (30 eV) m/e (rel intensity) 266 (M^+ – 2CO, 31), 239 (29), 220 (28), 195 (65), 172 (100), 138 (42), 94 (60), 79 (32), 49 (26); HRMS (EI) m/e calcd for $C_{12}H_{18}FeO_3$ (M^+ – 2CO) 266.0605, found 266.0609.

[(6–9-η)-Ethyl *cis*-6,*trans*-8-decadienoate]tricarbonyliron Complex (7e). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (5.0 mmol) to cation **6c** (0.92 g, 3.0 mmol) was purified via flash column chromatography (silica gel, 1:30 ethyl acetate/hexane) to give **7e** (0.85 g, 82%) as a yellow oil: IR (CH_2Cl_2) 3053, 2982, 1961, 1423, 1377, 1273, 1186, 1030 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 (dd, J = 9.2, 4.9 Hz, 1 H), 5.12 (dd, J = 7.8, 5.2 Hz, 1 H), 4.12 (q, J = 6.8 Hz, 2 H), 2.44 (ddd, J = 14.2, 7.3, 6.8 Hz, 1 H), 2.33 (m, 1 H), 2.25 (t, J = 7.3 Hz, 2 H), 1.68–1.50 (m, 5 H), 1.44 (d, J = 5.9 Hz, 3 H), 1.26 (t, J = 6.8 Hz, 3 H), 1.08 (m, 1 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 212.0, 173.6, 94.5, 82.3, 60.2, 59.6, 57.6, 34.1, 32.5, 29.0, 24.4, 20.2, 14.2; MS (30 eV) m/e (rel intensity) 280 (M^+ – 2CO, 62), 252 (90), 206 (100), 196 (63), 151 (96), 79 (77), 55 (85); HRMS (EI) m/e calcd for $C_{13}H_{20}FeO_3$ (M^+ – 2CO) 280.0762, found 280.0760.

[(6–9-η)-Ethyl 8-methyl-*cis*-6,8-nonadienoate]tricarbonyliron Complex (7f). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (5.0 mmol) to cation **6b** (1.1 g, 3.6 mmol) was purified via flash column chromatography (silica gel, 1:30 ethyl acetate/hexane) to give **7f** (1.0 g, 83%) as a yellow oil: IR (CH_2Cl_2) 3061, 2932, 2042, 1977, 1728, 1440, 1377, 1263, 1184, 1032 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.17 (brd, J = 7.6 Hz, 1 H), 4.07 (q, J = 7.1 Hz, 2 H), 2.36 (td, J = 7.6, 4.0 Hz, 1 H), 2.19 (t, J = 7.2 Hz, 1 H), 2.13 (s, 3 H), 1.82 (m, 1 H), 1.57–1.32 (m, 6 H), 1.21 (t, J = 7.1 Hz, 3 H), 1.06 (m, 1 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 211.3, 173.5, 107.8, 86.8, 60.1, 56.3, 43.3, 34.0, 32.3, 28.0, 24.3, 24.2, 14.1; MS (30 eV) m/e (rel intensity) 336 (M^+, 1), 308 (5), 280 (86), 252 (100), 208 (79), 150 (66), 107 (66), 87 (91), 51 (79); HRMS (EI) m/e calcd for $C_{14}H_{20}FeO_4$ (M^+ – CO) 308.0711, found 308.0703.

(1*R,2*S**,5*S**,9*R**)-2-Carbethoxy-9-formylbicyclo[3.3.1]non-7-ene (8).** The crude mixture from intramolecular cyclization of complex **4a** (0.5 g, 1.5 mmol) followed by quenching the reaction with trifluoroacetic acid (5 molar equiv) was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **8** (0.27 g, 1.22 mmol, 82%) as a colorless liquid: IR (CH_2Cl_2) 3032, 2942, 2716, 1736, 1514, 1472, 1457, 1384, 1378, 1375, 1186, 1018, 998, 984 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.59 (s, 1 H, H_{10}), 5.94 (dt, J = 9.8, 3.3 Hz, 1 H, H_7), 5.67 (dd, J = 9.8, 2.7 Hz, 1 H, H_8), 4.15 (dq, J = 1.6, 7.2 Hz, 2 H, H_{12}), 3.23 (brs, 1 H), 2.56 (dt, J = 11.0, 3.8 Hz, 1 H), 2.49 (m, 1 H), 2.29 (m, 1 H), 1.87–1.64 (m, 6 H), 1.28 (t, J = 7.2 Hz, 3 H, H_{13}); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 203.3 (C_{10}), 173.8 (C_{11}), 133.1 (C_7), 124.5 (C_8), 60.4, 52.9, 45.5, 32.9, 32.3, 29.2, 26.9, 20.4, 14.2; MS (70 eV) m/e (rel intensity) 222 (M^+, 42), 193 (4), 177 (30), 149 (23), 119 (61), 91 (85), 79 (100); HRMS (EI) m/e calcd for $C_{13}H_{18}O_3$ (M^+) 222.1255, found 222.1238.

(1*R,2*S**,5*S**,9*R**)-2-Carbethoxy-9-formylbicyclo[3.3.1]non-7-ene (2,4-Dinitrophenyl)hydrazone (9).** The crude mixture from intramolecular cyclization of complex **4a** (0.44 g, 1.5 mmol) followed by quenching the reaction with trifluoroacetic acid (5 molar equiv) was added to a solution of 0.33 g of (2,4-dinitrophenyl)hydrazine in 9 mL of phosphoric acid (85% in H_2O) and 9 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, 20% ethyl acetate/hexanes) and recrystallization (ethanol) to give **9** (0.26 g, 0.087 mmol, 65%) as a yellow solid: mp 172–173 °C dec; IR (CH_2Cl_2) 3686, 3060, 2986, 1720, 1618, 1519, 1443, 1438, 1431, 1427, 1335, 1286, 928 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.99 (s, 1 H), 9.12 (d, J = 2.5 Hz, 1 H), 8.30 (dd, J = 9.5, 2.5 Hz, 1 H), 7.89 (d, J = 9.5 Hz, 1 H), 7.46 (d, J = 5.0 Hz, 1 H), 5.99 (dt, J = 8.8, 4.5 Hz, 1 H), 5.65 (dd, J = 8.7, 5.8 Hz, 1 H), 4.15 (2 q, J = 7.3 Hz, 2 H), 2.79 (m, 1 H), 2.62 (m, 2 H), 2.35 (m, 1 H), 1.86–1.66 (m, 6 H), 1.30 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 173.7, 154.0, 145.1, 137.8, 132.3, 129.9, 128.9, 124.3, 123.5, 116.4, 60.4, 45.7, 43.9, 34.9, 33.4, 29.5, 29.2, 20.2, 14.2; MS (70 eV) m/e (rel intensity) 402 (M^+, 15), 401 (48), 384 (56), 328 (10), 207 (20), 167 (13), 150 (68), 130 (100); HRMS (EI) m/e calcd for $C_{19}H_{22}N_4O_6$ (M^+) 402.1539, found 402.1547.

(1*R,2*S**,4*S**,8*R**)-2-Carbethoxy-8-formylbicyclo[3.2.1]oct-6-ene (10a).** The crude mixture from intramolecular cyclization of complex **4b** (0.65 g, 2.03 mmol) followed by quenching the reaction with trifluoroacetic acid (5 molar equiv) was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **10a** (110 mg, 0.5 mmol, 25%) and **10b** (55 mg, 0.25 mg, 12%), both as colorless liquids. **10a**: IR (CH_2Cl_2) 3036, 2984, 2950, 2906, 2838, 2722, 2252, 1715, 1585, 1434, 1371, 1291, 1097, 1033 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1 H), 6.03 (dd, J = 8.8, 7.3 Hz, 1 H, H_a), 5.44 (dd, J = 9.3, 3.0 Hz, 1 H), 4.12 (q, J

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= 7.3 Hz, 2 H), 3.01 (m, 2 H), 2.80 (dd, J = 4.4, 4.9 Hz, 1 H, H_b), 2.73 (brs, 1 H), 2.47 (m, 1 H), 2.33 (m, 1 H), 1.94–1.82 (m, 2 H), 1.26 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 202.5, 174.8, 130.7, 127.3, 60.7, 54.8, 52.6, 39.3, 35.7, 34.7, 33.1, 14.2; MS (70 eV) m/e (rel intensity) 208 (M^+, 21), 178 (42), 151 (28), 132 (26), 101 (100); HRMS (EI) m/e calcd for $C_{12}H_{16}O_3$ (M^+) 208.1100, found 208.1089.

(1R*,2R*,4S*,8R*)-2-Carbethoxy-8-formylbicyclo[3.2.1]oct-6-ene (10b): IR (CH_2Cl_2) 3060, 2952, 2042, 1969, 1721, 1606, 1440, 1371, 1283, 1195, 1043 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1 H), 5.86 (dd, J = 8.3, 6.4 Hz, 1 H, H_a), 5.64 (dt, J = 9.3, 3.6 Hz, 1 H), 4.12 (2 q, J = 7.3 Hz, 2 H), 3.14 (m, 2 H), 2.69 (brs, 1 H), 2.58 (brs, 1 H, H_b), 2.49 (brd, J = 18.6 Hz, 1 H), 2.32 (m, 1 H), 2.02–1.96 (m, 2 H), 1.26 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 202.6, 173.0, 128.2, 127.9, 60.5, 56.3, 52.5, 38.3, 34.6, 33.8, 33.4, 14.3; MS (70 eV) m/e (rel intensity) 208 (M^+, 9), 196 (5), 175 (10), 162 (6), 149 (11), 134 (7), 101 (100); HRMS (EI) m/e calcd for $C_{12}H_{16}O_3$ (M^+) 208.1100, found 208.1102.

(1R*,2S*,5S*,9R*)-2-Carbethoxy-9-acetylbicyclo[3.3.1]non-7-ene (11). The crude mixture from intramolecular cyclization of complex **4a** (0.58 g, 1.74 mmol) followed by quenching the reaction with iodomethane (5 molar equiv) was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **11** (0.165 g, 0.70 mmol, 40%) as a colorless liquid: IR (CH_2Cl_2) 3035, 2934, 1723, 1634, 1428, 1370, 1302, 1245, 1180, 1044, 1021 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (dt, J = 9.9, 3.3 Hz, 1 H), 5.50 (dd, J = 9.9, 6.1 Hz, 1 H), 4.02 (2 q, J = 7.1 Hz, 2 H), 3.17 (brs, 1 H), 2.43 (m, 2 H), 2.29 (m, 1 H), 2.05 (s, 3 H), 1.70–1.58 (m, 6 H), 1.18 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 208.6, 173.8, 132.0, 124.3, 60.2, 54.2, 46.0, 33.4, 33.2, 29.4, 27.5, 26.8, 20.1, 14.2; MS (70 eV) m/e (rel intensity) 236 (M^+, 58), 193 (8), 163 (20), 147 (62), 119 (100); HRMS (EI) m/e calcd for $C_{14}H_{20}O_3$ (M^+) 236.1412, found 236.1412.

(1S*,2S*,5S*,9R*)-2-Cyano-9-formylbicyclo[3.3.1]non-7-ene (12a). The crude mixture from intramolecular cyclization of complex **4c** (0.50 g, 1.73 mmol) followed by quenching the reaction with trifluoroacetic acid (5 molar equiv) was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **12a** (0.08 g, 0.4 mmol, 27%) as a light orange solid and **12b** (0.16 g, 0.8 mmol, 52%) as a red liquid. **12a**: mp 105.0–105.5 °C (hexane/ethyl acetate): IR (CH_2Cl_2) 3066, 3036, 2938, 2236, 1710, 1637, 1449, 1428, 1374, 1286, 1140, 1097, 927, 920 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, J = 2.9 Hz, 1 H), 5.92 (dt, J = 9.8, 3.4 Hz, 1 H), 5.59 (dd, J = 9.8, 6.4 Hz, 1 H), 3.08 (brs, 1 H), 2.78 (m, 1 H), 2.74 (brs, 1 H), 2.60 (brs, 1 H), 2.40 (dd, J = 19.5, 6.8 Hz, 1 H), 1.96–1.73 (m, 5 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 201.7, 134.3, 124.5, 121.3, 48.7, 32.3, 29.9, 29.5, 28.8, 26.5, 20.8; MS (70 eV) m/e (rel intensity) 175 (M^+, 9), 146 (14), 92 (53), 79 (35), 32 (100); HRMS (EI) m/e calcd for $C_{11}H_{13}NO$ (M^+) 175.0997, found 175.0986.

(1S*,2R*,5S*,9R*)-2-Cyano-9-formylbicyclo[3.3.1]non-7-ene (12b): IR (CH_2Cl_2) 3064, 3046, 2940, 2240, 1725, 1607, 1447, 1425, 1374, 1287, 1153, 1090, 1023, 951, 932 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (brs, 1 H), 6.10 (dt, J = 9.8, 3.4 Hz, 1 H), 5.9 (dd, J = 9.8, 6.3 Hz, 1 H), 3.13 (brs, 1 H), 2.71 (dt, J = 11.2, 3.9 Hz, 1 H), 2.52 (brs, 1 H), 2.40 (dd, J = 19.5, 6.8 Hz, 1 H), 2.24 (brs, 1 H), 1.90–1.83 (m, 4 H), 1.60 (m, 1 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 201.4, 134.6, 123.1, 121.0, 51.4, 32.3, 31.8, 31.1, 28.9, 26.1, 22.2; MS (70 eV) m/e (rel intensity) 175 (M^+, 36), 146 (45), 119 (36), 92 (76), 79 (100); HRMS (EI) m/e calcd for $C_{11}H_{13}NO$ (M^+) 175.0997, found 175.1001.

(1S*,2S*,5S*,9R*)-2-Cyano-9-acetylbicyclo[3.3.1]non-7-ene (13a). The crude mixture from intramolecular cyclization of complex **4c** (0.53 g, 1.83 mmol) followed by quenching the reaction with iodomethane (5 molar equiv) was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **13a** (0.05 g, 0.26 mmol, 14%) as a yellow liquid and **13b** (0.10 g, 0.52 mmol, 28%) as a colorless solid. **13a**: IR (CH_2Cl_2) 3392, 3048, 3030, 2930, 2252, 1707, 1424, 1354, 1285, 1243, 1178 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (dd, J = 9.3, 6.8 Hz, 1 H), 5.61 (dt, 9.3, 3.2 Hz, 1 H), 3.07 (m, 1 H), 2.99 (m, 1 H), 2.77 (brs, 1 H), 2.59 (brd, J = 18.3 Hz, 1 H), 2.41 (m, 1 H), 2.16 (s, 3 H), 2.03 (dd, J = 9.28, 4.39 Hz, 2 H), 1.82 (dd, J = 18.5, 1.9 Hz, 1 H), 1.20 (m, 2 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 207.5, 133.3, 124.6, 121.6, 50.0, 33.4, 33.0, 30.7, 29.6, 27.7, 26.5, 20.5; MS (70 eV) m/e (rel intensity) 189 (M^+, 89), 174 (11), 146 (73), 121 (54), 92 (100); HRMS (EI) m/e calcd for $C_{12}H_{15}NO$ (M^+) 189.1153, found 189.1145.

(1S*,2R*,5S*,9R*)-2-Cyano-9-acetylbicyclo[3.3.1]non-7-ene (13b): mp 112.0–112.5 °C (hexane/ethyl acetate); IR (CH_2Cl_2) 3064, 2988, 2934, 2308, 1723, 1634, 1442, 1428, 1370, 1302, 1245, 1220, 1180, 1092, 1021, 937 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (dt, J = 9.8, 3.4 Hz, 1 H), 5.88 (dd, J = 9.8, 6.2 Hz, 1 H), 3.15 (brs, 1 H), 2.69 (brd, J = 11.0 Hz, 1 H), 2.52 (brs, 1 H), 2.43 (dd, J = 19.5, 6.8 Hz, 1 H), 2.25 (brs, 1 H), 2.11 (s, 3 H), 1.86–1.72 (m, 4 H), 1.58 (m, 1 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 207.0, 133.8, 123.1, 121.2, 52.9, 33.0, 32.0, 31.8, 29.2, 27.0, 26.6, 21.9; MS (70 eV) m/e (rel intensity) 189 (M^+, 100), 174 (6), 146 (72), 121 (43), 92 (58); HRMS (EI) m/e calcd for $C_{12}H_{15}NO$ (M^+) 189.1153, found 189.1147.

(1S*,2S*,5S*,9R*)-2-Cyano-9-(2-phenyl-1-oxoethyl)bicyclo[3.3.1]-non-7-ene (14a). The crude mixture from intramolecular cyclization of complex **4c** (0.20 g, 0.69 mmol) followed by quenching the reaction with benzyl bromide (5 molar equiv) was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **14a** (0.03 g, 0.11 mmol, 16%) as a yellow liquid and **14b** (0.065 g, 0.23 mmol, 33%) as a colorless solid. **14a**: IR (CH_2Cl_2) 3682, 3032, 2934, 2236, 1709, 1604, 1494, 1452, 1422, 1335, 1103, 922 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, J = 7.3 Hz, 2 H), 7.26 (d, J = 7.0 Hz, 1 H), 7.16 (d, J = 7.4 Hz, 2 H), 5.92 (dt, J = 9.8, 3.4 Hz, 1 H), 5.59 (dd, J = 7.1, 6.4 Hz, 1 H), 3.77 (s, 2 H), 3.12 (brs, 1 H), 2.93 (d, J = 11.2 Hz, 1 H), 2.78 (brs, 1 H), 2.60 (brs, 1 H), 2.42 (m, 1 H), 1.92–1.72 (m, 5 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 206.3, 133.9, 133.4, 129.4, 128.7, 128.6, 128.0, 126.9, 124.3, 121.0, 49.2, 46.0, 33.3, 30.7, 30.2, 29.3, 27.6, 20.5; MS (70 eV) m/e (rel intensity) 265 (M^+, 12), 174 (26), 146 (67), 91 (49), 84 (100); HRMS (EI) m/e calcd for $C_{18}H_{19}NO$ (M^+) 256.1466, found 156.1446.

(1S*,2R*,5S*,9R*)-2-Cyano-9-(2-phenyl-1-oxoethyl)bicyclo[3.3.1]-non-7-ene (14b): mp 122.0–122.5 °C; IR (CH_2Cl_2) 3680, 3060, 3032, 2936, 2238, 1710, 1605, 1495, 1451, 1422, 1342, 1283, 1124, 1090, 924 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, J = 6.8 Hz, 2 H), 2.76 (d, J = 7.3 Hz, 1 H), 7.16 (d, J = 7.4 Hz, 1 H), 6.03 (dt, J = 9.8, 3.4 Hz, 1 H), 5.85 (dd, J = 10.0, 6.4 Hz, 1 H), 3.75 (s, 2 H), 3.19 (brs, 1 H), 2.67 (d, J = 11.2 Hz, 1 H), 2.64 (brs, 1 H), 2.42 (dd, J = 19.5, 6.8 Hz, 1 H), 2.42 (brs, 1 H), 1.84–1.78 (m, 4 H), 1.57 (m, 1 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 206.3, 133.9, 133.7, 129.2, 128.6, 126.9, 122.9, 121.0, 51.7, 46.0, 33.0, 32.8, 31.8, 29.3, 27.0, 21.8; MS (70 eV) m/e (rel intensity) 265 (M^+, 48), 174 (71), 147 (24), 91 (100); HRMS (EI) m/e calcd for $C_{18}H_{19}NO$ (M^+) 256.1466, found 156.1448.

(1S*,2S*,4S*,8R*)-2-Cyano-8-formylbicyclo[3.2.1]oct-6-ene (15a). The crude mixture from intramolecular cyclization of complex **4d** (0.29 g, 1.1 mmol) followed by quenching the reaction with trifluoroacetic acid (5 molar equiv) was purified via flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **15a** (0.055 g, 0.30 mmol, 28%) as a yellow oil and **15b** (0.032 g, 0.18 mmol, 17%) as a colorless solid. Compound **15b** slowly decomposed in the air. Further identification of **15b** was not successful. **15a**: IR (CH_2Cl_2) 3484, 3054, 2928, 2852, 2238, 1709, 1607, 1433, 1378, 1306, 1289, 1148, 1086, 1042, 1007, 963, 931, 905 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1 H), 5.96 (brdd, J = 9.0, 6.9 Hz, 1 H), 5.63 (dt, J = 9.3, 2.4 Hz, 1 H), 3.08 (m, 1 H), 3.03 (dd, J = 9.3, 3.4 Hz, 1 H), 2.92 (brs, 1 H), 2.85 (brs, 1 H), 2.50 (d, J = 19.0 Hz, 1 H), 2.36 (m, 1 H), 2.05 (dd, J = 13.7, 9.3 Hz, 1 H), 1.94 (td, J = 19.1, 2.0 Hz, 1 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 200.4, 128.5, 128.4, 122.2, 54.7, 40.3, 37.8, 35.5, 34.1, 33.0; MS (70 eV) m/e (rel intensity) 161 (M^+, 16), 108 (26), 105 (20), 80 (19), 79 (48), 77 (19), 54 (16), 39 (18), 32 (25), 28 (100); 175 (M^+, 10), 107 (13), 105 (11), 79 (14), 43 (64), 32 (32), 28 (100); HRMS (EI) m/e calcd for $C_{10}H_{11}NO$ (M^+) 161.0840, found 161.0855.

(1S*,2S*,4S*,8R*)-2-Cyano-8-acetylbicyclo[3.2.1]oct-6-ene (16a). The crude mixture from intramolecular cyclization of complex **4d** (0.26 g, 1.05 mmol) followed by quenching the reaction with iodomethane (5 molar equiv) was purified via flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **16a** (0.015 g, 0.09 mmol, 9%) as a yellow oil and **16b** (0.010 g, 0.06 mmol, 6%) as a colorless liquid. **16a**: IR (CH_2Cl_2) 3040, 2959, 2236, 1707, 1605, 1426, 1360, 1247, 1180, 1092 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (dd, J = 9.4, 6.9 Hz, 1 H), 5.56 (dt, J = 9.3, 3.2 Hz, 1 H), 3.03 (m, 1 H), 2.97 (d, J = 7.8, 3.9 Hz, 2 H), 2.81 (brs, 1 H), 2.58 (d, J = 18.6 Hz, 1 H), 2.33 (m, 1 H), 2.22 (s, 3 H), 2.04 (dd, J = 9.3, 6.9 Hz, 1 H), 1.84 (dd, J = 18.6, 1.9 Hz, 1 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 206.2, 128.6, 127.9, 122.6, 56.2, 41.2, 37.2, 35.5, 34.2, 33.1, 28.4; MS (70 eV) m/e (rel intensity) 175 (M^+, 10), 107 (13), 105 (11), 79 (14), 43 (64), 32 (32), 28 (100); HRMS (EI) m/e calcd for $C_{11}H_{13}NO$ (M^+) 175.0997, found 175.0986.

(1S*,2R*,4S*,8R*)-2-Cyano-8-acetylbicyclo[3.2.1]oct-6-ene (16b): IR (CH_2Cl_2) 3030, 2960, 2240, 1706, 1608, 1451, 1360, 1255, 1183 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (dd, J = 9.8, 6.4 Hz, 1 H), 5.72 (dt, J = 9.8, 3.2 Hz, 1 H), 3.06 (dd, J = 8.8, 5.4 Hz, 1 H), 3.01 (dd, J = 11.2, 5.4 Hz, 1 H), 2.71 (brs, 1 H), 2.60 (d, J = 19.1 Hz, 1 H), 2.57

(brs, 1 H), 2.48 (m, 1 H), 2.18 (s, 3 H), 1.92 (dd, J = 19.1, 3.2 Hz, 1 H), 1.82 (dd, J = 14.2, 6.3 Hz, 1 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 206.0, 128.8, 127.6, 121.2, 57.5, 38.7, 36.4, 36.4, 34.1, 33.7, 28.4; MS (70 eV) m/e (rel intensity) 175 (M^+, 5), 105 (7), 79 (5), 43 (55), 32 (25), 28 (100); HRMS (EI) m/e calcd for $C_{11}H_{13}NO$ (M^+) 175.0997, found 175.0977.

(1*S,2*R**,4*S**,8*R**)-8-(2-Phenyl-1-oxoethyl)bicyclo[3.2.1]oct-6-ene (17b).** The crude mixture from intramolecular cyclization of complex **4d** (0.26 g, 1.05 mmol) followed by quenching the reaction with benzyl bromide (5 molar equiv) was purified via flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **17a** (5 mg, 2%) and **17b** (43 mg, 14%). Only **17b** was isolated as a colorless and analytically pure compound: IR (CH_2Cl_2) 3044, 2956, 2240, 1708, 1638, 1600, 1495, 1451, 1350, 1232, 1185, 1108, 1075, 1031, 919 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, J = 6.8 Hz, 2 H), 7.23 (d, J = 6.8 Hz, 1 H), 7.16 (d, J = 6.8 Hz, 2 H), 6.01 (dd, J = 9.3, 6.4 Hz, 1 H), 5.74 (dd, J = 9.6, 3.9 Hz, 1 H), 3.78 (s, 2 H), 3.06 (m, 1 H), 3.0 (ddd, J = 17.0, 11.7, 5.4 Hz, 1 H), 2.74 (brs, 1 H), 2.66 (brs, 1 H), 2.63 (d, J = 19.0 Hz, 1 H), 2.46 (ddd, J = 11.2, 7.3, 1.9 Hz, 1 H), 1.94 (dd, J = 17.5, 2.0 Hz, 1 H), 1.81 (dd, J = 14.2, 6.3 Hz, 1 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 205.5, 133.9, 129.3, 128.9, 128.7, 127.5, 127.1, 121.2, 55.6, 47.9, 38.5, 36.4, 36.3, 34.2, 33.8; MS (70 eV) m/e (rel intensity) 251 (M^+, 23), 160 (89), 132 (30), 105 (28), 91 (58), 79 (42), 32 (100); HRMS (EI) m/e calcd for $C_{17}H_{17}NO$ (M^+) 251.1310, found 251.1308.

(1*R,2*S**,5*S**)-2-Carbethoxy-8-oxobicyclo[3.3.1]nonane (18).** The crude mixture from intramolecular cyclization of complex **4e** (0.33 g, 0.90 mmol) followed by quenching the reaction with trifluoroacetic acid (5 molar equiv) was purified via flash column chromatography (silica gel, 7% ethyl acetate/hexanes) to give **18** (0.14 g, 0.66 mmol, 74%) as a colorless oil: IR (CH_2Cl_2) 2978, 2931, 2860, 2360, 2341, 2040, 1967, 1762, 1635, 1546, 1516 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (2 q, J = 6.8 Hz, 2 H), 2.87 (brs, 1 H), 2.69 (m, 1 H), 2.53 (dd, J = 13.2, 8.8 Hz, 2 H), 2.40 (m, 2 H), 2.09 (m, 2 H), 1.91–1.75 (m, 5 H), 1.30 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 231.7, 173.6, 60.7, 47.7, 45.4, 39.7, 33.2, 31.0, 28.9, 25.7, 22.6, 14.0; MS (70 eV) m/e (rel intensity) 210 (M^+, 27), 163 (22), 137 (13), 73 (5), 28 (100); HRMS (EI) m/e calcd for $C_{12}H_{18}O_3$ (M^+) 210.1255, found 210.1252.

(1*R,2*S**,5*S**)-2-Cyano-8-oxobicyclo[3.3.1]nonane (19a).** The crude mixture from intramolecular cyclization of complex **4f** (0.28 g, 0.88 mmol) followed by quenching the reaction with trifluoroacetic acid (5 molar equiv) was purified via flash column chromatography (silica gel, 7% ethyl acetate/hexanes) to give **19a** (0.03 g, 0.18 mmol, 21%) as a white solid and **19b** (0.03 g, 0.18 mmol, 21%) as a colorless liquid. **19a**: mp 103.0–103.5 °C; IR (CH_2Cl_2) 3686, 3048, 2936, 2308, 2238, 1708, 1606, 1456, 1431, 1426, 1292, 1284, 1111, 935, 923 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (brs, 1 H), 2.57 (dd, J = 17.7, 8.4 Hz, 2 H), 2.38 (m, 2 H), 2.16 (dt, J = 18.0, 3.6 Hz, 2 H), 1.92–1.54 (m, 6 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 206.9, 121.3, 46.8, 46.2, 32.8, 32.4, 29.2, 28.6, 28.0, 20.6; MS (70 eV) m/e (rel intensity) 163 (M^+, 47), 136 (29), 119 (40), 81 (84), 45 (9), 29 (100); HRMS (EI) m/e calcd for $C_{10}H_{13}NO$ (M^+) 163.0997, found 163.0996.

(1*R,2*R**,5*S**)-2-Cyano-8-oxobicyclo[3.3.1]nonane (19b)**: IR (CH_2Cl_2) 3686, 3070, 2989, 2306, 2242, 1708, 1607, 1443, 1428, 1286, 1283, 1079, 942, 923 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.81 (brd, J = 15.3 Hz, 1 H), 2.77 (brs, 1 H), 2.53 (dd, J = 19.0, 8.2 Hz, 1 H), 2.49 (dd, J = 19.0, 7.8 Hz, 1 H), 2.16 (m, 3 H), 1.87–1.78 (m, 6 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 209.9, 119.9, 46.2, 39.1, 31.7, 31.0, 30.8, 27.7, 24.9, 24.6; MS (70 eV) m/e (rel intensity) 163 (M^+, 78), 135 (56), 117 (34), 81 (31), 45 (6), 32 (100); HRMS (EI) m/e calcd for $C_{10}H_{13}NO$ (M^+) 163.0997, found 163.1004.

(1*R,2*S**,6*S**,10*R**)-2-Cyano-10-formylbicyclo[4.3.1]dec-8-ene (2,4-Dinitrophenyl)hydrazone (23).** The crude mixture from intramolecular cyclization of complex **22** (0.44 g, 1.46 mmol) followed by quenching the reaction with trifluoroacetic acid (5 molar equiv) was added to a solution of 0.33 g of (2,4-dinitrophenyl)hydrazine in 9 mL of phosphoric acid (85% in H_2O) and 9 mL of ethanol (95%). The reaction mixture was 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, 20% ethyl acetate/hexanes) to give **23** (0.03 g, 0.08 mmol, 5%) as a yellow solid: mp 155–156 °C dec; IR (CH_2Cl_2) 3682, 3306, 3060, 2984, 2932, 2238, 2042, 1617, 1594, 1517, 1425, 1334, 1284, 1139, 1086 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.98 (s, 1 H), 9.04 (d, J = 2.44 Hz, 1 H), 8.23 (dd, J = 9.28, 2.44 Hz, 1 H), 7.83 (d, J = 9.28 Hz, 1 H), 7.44 (d, J = 3.91 Hz, 1 H), 5.94 (dd, J = 8.0, 4.8 Hz, 1 H), 5.55 (dt, J = 8.0, 3.1 Hz, 1 H), 3.15 (brs, 1 H), 2.96 (brd, J = 12.7 Hz, 2 H), 2.36 (m, 2 H), 1.78–1.66 (m, 3 H), 1.54 (m, 4 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 153.1, 145.0, 138.0, 130.1, 130.0, 129.5, 129.0, 126.2, 123.4, 116.6, 39.2, 37.4, 35.2, 33.4, 30.8, 30.4, 29.7, 21.6; MS (70 eV) m/e (rel intensity) 369 (M^+, 14), 285 (18), 227 (18), 187 (37), 145 (37), 91 (100); HRMS (EI) m/e calcd for $C_{18}H_{19}N_5O_4$ (M^+) 369.1437, found 369.1445.

(1*R,2*R**,5*R**)-2-Carbethoxy-6-oxobicyclo[3.3.0]octane (24).** The crude mixture from intramolecular cyclization of complex **7a** (0.68 g, 2.2 mmol) followed by quenching the reaction with trifluoroacetic acid (5 molar equiv) was purified via flash column chromatography (silica gel, 7% ethyl acetate/hexanes) and short-path distillation (0.02 mmHg, 40–50 °C) to give **24** (0.236 g, 1.39 mmol, 55%) as a colorless liquid: IR (CH_2Cl_2) 3074, 2964, 1724, 1458, 1376, 1253, 1194, 1039 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (q, J = 7.1 Hz, 2 H), 3.03 (dq, J = 9.5, 3.8 Hz, 1 H, H_a), 2.69 (td, J = 9.5, 4.9 Hz, 1 H, H_b), 2.52 (q, J = 7.3 Hz, 1 H), 2.32 (dd, J = 8.8, 7.3 Hz, 2 H), 2.17 (dt, J = 13.2, 7.8 Hz, 1 H), 2.08 (m, 1 H), 1.92 (q, J = 8.0 Hz, 2 H), 1.82 (m, 2 H), 1.28 (t, J = 5.0 Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 221.7, 174.7, 60.4, 52.0, 50.2, 45.3, 36.8, 30.5, 28.1, 25.0, 14.1; MS (70 eV) m/e (rel intensity) 196 (M^+, 54), 167 (29), 149 (65), 138 (42), 122 (66), 95 (98), 79 (62), 67 (100), 55 (58), 41 (49); HRMS (EI) m/e calcd for $C_{11}H_{16}O_3$ (M^+) 169.1099, found 169.1106.

(1*R,2*R**,5*R**,7*S**)-2-Carbethoxy-7-methyl-6-oxobicyclo[3.3.0]octane (26).** The crude mixture from intramolecular cyclization of complex **7b** (0.96 g, 3.00 mmol) followed by quenching the reaction with trifluoroacetic acid (5 molar equiv) was purified via flash column chromatography (silica gel, 7% ethyl acetate/hexanes) and short-path distillation (0.02 mmHg, 50–60 °C) to give **26** (0.214 g, 1.02 mmol, 34%) as a colorless liquid: IR (CH_2Cl_2) 2970, 1729, 1454, 1375, 1185, 1039 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.14 (dq, J = 4.3, 7.1 Hz, 2 H), 3.00 (dt, J = 10.5, 7.7 Hz, 1 H, H_b), 2.86 (dt, J = 10.7, 7.0 Hz, 1 H, H_d), 2.73 (td, J = 7.7, 1.2 Hz, 1 H, H_c), 2.31 (qd, J = 13.8, 6.8 Hz, 1 H, H_a), 2.16 (dd, J = 19.4, 7.4 Hz, 1 H), 1.94 (dd, J = 10.2, 2.4 Hz, 1 H), 1.79 (m, 1 H), 1.67 (m, 1 H), 1.61 (m, 1 H), 1.25 (t, J = 7.1 Hz, 3 H), 1.01 (d, J = 6.7 Hz, 3 H), 1.03 (m, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 220.8, 173.1, 60.3, 50.4, 48.8, 44.7, 39.9, 31.9, 27.6, 26.32, 14.3, 12.8; MS (70 eV) m/e (rel intensity) 210 (M^+, 47), 164 (100), 136 (86), 119 (90), 96 (43), 81 (53), 73 (76), 55 (92), 41 (44), 32 (33), 29 (43); HRMS (EI) m/e calcd for $C_{12}H_{18}O_3$ (M^+) 210.1255, found 210.1249.

(1*R,2*R**,5*R**,8*R**)-2-Carbethoxy-8-methyl-6-oxobicyclo[3.3.0]octane (27).** The crude mixture from intramolecular cyclization of complex **7c** (0.40 g, 1.24 mmol) followed by quenching the reaction with trifluoroacetic acid (5 molar equiv) was purified via flash column chromatography (silica gel, 7% ethyl acetate/hexanes) and short-path distillation (0.02 mmHg, 50–60 °C) to give **27** (0.067 g, 0.31 mmol, 30%) as a colorless liquid: IR (CH_2Cl_2) 2968, 1728, 1454, 1378, 1252, 1192, 1035 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (m, 2 H), 3.06 (dd, J = 10.0, 7.2 Hz, 1 H, H_d), 2.71 (ddd, J = 10.0, 7.3, 3.2 Hz, 1 H, H_e), 2.50 (m, 2 H, H_c, H_f), 2.34 (dd, J = 18.6, 8.1 Hz, 1 H, H_b), 2.08 (m, 1 H), 1.94 (m, 1 H, H_a), 1.83 (m, 3 H), 1.25 (t, J = 7.1 Hz, 3 H), 1.09 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 221.9, 175.4, 60.5, 54.7, 50.5, 44.5, 43.6, 32.4, 30.7, 28.2, 16.4, 14.1; MS (70 eV) m/e (rel intensity) 210 (M^+, 87), 165 (86), 136 (82), 119 (37), 108 (100), 93 (100), 84 (44), 69 (63), 55 (77), 42 (63), 28 (100); HRMS (EI) m/e calcd for $C_{12}H_{18}O_3$ (M^+) 210.1255, found 210.1240.

(1*R,2*R**,6*R**)-2-Carbethoxy-7-oxobicyclo[4.3.0]nonane (28).** The crude mixture from intramolecular cyclization of complex **7d** (0.86 g, 2.70 mmol) followed by quenching the reaction with trifluoroacetic acid (5 molar equiv) was purified via flash column chromatography (silica gel, 7% ethyl acetate/hexanes) and short-path distillation (0.02 mmHg, 50–60 °C) to give **28** (0.367 g, 1.75 mmol, 54%) as a colorless liquid: IR (CH_2Cl_2) 2944, 1731, 1446, 1237, 1201, 1174, 1029 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 (q, J = 7.3 Hz, 2 H), 2.62 (m, 2 H, H_b, H_d), 2.36 (dd, J = 19.0, 8.0 Hz, 1 H), 2.20 (dt, J = 11.9, 6.0 Hz, 1 H, H_a), 2.13 (dd, J = 19.0, 6.0 Hz, 1 H), 1.80 (m, 4 H, H_a and others), 1.54 (m, 2 H), 1.20 (t, J = 7.0 Hz, 3 H), 1.13 (m, 2 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 220.0, 174.0, 60.2, 48.4, 42.1, 37.3, 36.8, 23.6, 22.2, 20.5, 14.2; MS (70 eV) m/e (rel intensity) 210 (M^+, 37), 164 (24), 136 (90), 119 (61), 95 (37), 81 (38), 67 (35), 55 (32), 41 (41), 32 (100), 29 (44); HRMS (EI) m/e calcd for $C_{12}H_{18}O_3$ (M^+) 210.1255, found 210.1261.

(1*R,2*R**,6*R**,8*S**)-2-Carbethoxy-8-methyl-7-oxobicyclo[4.3.0]nonane (29).** The crude mixture from intramolecular cyclization of complex **7e** (0.92 g, 2.70 mmol) followed by quenching the reaction with trifluoroacetic acid (5 molar equiv) was purified via flash column

chromatography (silica gel, 7% ethyl acetate/hexanes) and short-path distillation (0.02 mmHg, 65–75 °C) to give **29** (0.151 g, 0.674 mmol, 25%) as a colorless liquid: IR (CH_2Cl_2) 2974, 1730, 1423, 1284, 1195, 1172 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.18 (2 q, J = 6.9 Hz, 2 H), 2.78 (ddd, J = 11.2, 10.3, 5.5 Hz, 1 H, H_a), 2.71 (ddd, J = 11.7, 5.5, 3.1 Hz, 1 H, H_b), 2.49 (dq, J = 9.6, 7.6 Hz, 1 H, H_d), 2.29 (td, J = 11.0, 4.8 Hz, 1 H, H_c), 2.20 (ddd, J = 12.0, 10.3, 9.6 Hz, 1 H, H_f), 1.84 (m, 2 H), 1.68 (m, 2 H), 1.47 (dd, J = 12.0, 6.9 Hz, 1 H, H_e), 1.27 (t, J = 6.8 Hz, 3 H), 1.22 (m, 2 H), 1.11 (d, J = 7.8 Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 220.0, 172.1, 60.2, 49.0, 41.8, 40.0, 34.5, 29.3, 24.6, 22.6, 22.0, 16.8, 14.2; MS (70 eV) m/e (rel intensity) 224 (M^+, 42), 178 (12), 150 (100), 133 (29), 109 (16), 81 (68), 67 (26), 29 (52); HRMS (EI) m/e calcd for $C_{13}H_{20}O_3$ (M^+) 224.1412, found 224.1410.

(1*R,2*R**,6*R**,9*S**)-2-Carbethoxy-9-methyl-7-oxobicyclo[4.3.0]-nonane (30).** The crude mixture from intramolecular cyclization of complex **7f** (1.30 g, 3.90 mmol) followed by quenching the reaction with trifluoroacetic acid (5 molar equiv) was purified via flash column chromatography (silica gel, 7% ethyl acetate/hexanes) and short-path distillation (0.02 mmHg, 60–75 °C) to give **30** (0.24 g, 28%) as a colorless liquid: IR (CH_2Cl_2) 2943, 1732, 1631, 1448, 1377, 1286, 1269, 1182, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.18 (2 q, J = 6.9 Hz, 2 H), 2.76 (m, 2 H, H_a, H_d), 2.60 (8 lines, J = 8.8, 7.0, 3.3 Hz, 1 H, H_c), 2.46 (dd, J = 18.0, 8.3 Hz, 1 H), 2.26 (dd, J = 8.8, 7.8 Hz, 1 H, H_b), 2.08 (dd, J = 18.0, 3.4 Hz, 1 H), 1.80 (m, 2 H), 1.68 (m, 1 H), 1.50 (m, 1 H), 1.46 (m, 1 H), 1.29 (t, J = 7.0 Hz, 3 H), 1.22 (m, 1 H), 1.09 (d, J = 7.3 Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 220.0, 174.5, 60.3, 47.3, 46.6, 41.5, 39.5, 32.0, 25.2, 24.4, 22.3, 19.0, 14.2; MS (70 eV) m/e (rel intensity) 224 (M^+, 99), 209 (56), 178 (96), 150 (63), 132 (78), 108 (100), 80 (78), 54 (76); HRMS (EI) m/e calcd for $C_{13}H_{20}O_3$ (M^+) 224.1412, found 224.1410.

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Supplementary Material Available: ORTEP diagram showing the atom-numbering scheme and tables of crystallographic data and bond lengths and angles for **9** (3 pages). Ordering information is given on any current masthead page.