DOI: 10.1002/ejoc.201001394

# Electrophilic $C_{12}$ Building Blocks for Alkaloids: *1,1* Iterative Organoiron-Mediated Routes to (±)-Lycoramine and (±)-Maritidine

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**Keywords:** Asymmetric synthesis / Regioselectivity / Iron complexes / Cations / Alkaloids / Lycoramine / Maritidine

Aryllithium reagents generated from protected 6-bromoguaiacol and 2-bromo-4,5-dimethoxybenzyl alcohol derivatives were used to prepare *ortho*-substituted (1-arylcyclohexadienyl)iron(1+) electrophiles. These were treated with $Na^+[Me_3SiCH_2CH_2O_2CCHCN]^-$ to build aryl-substituted quaternary centres in new examples of *1,1* iterative $\{[\eta^4]\rightarrow[\eta^5]^+\rightarrow[\eta^4]\rightarrow[\eta^5]^+\rightarrow[\eta^4]\}$ reaction sequences, which make use of the electrophilicity of the metal complex in two key carbon–carbon bond-formation steps. MOM protection of the guaiacol was better than SEM for access to the lycoramine skeleton, and TBDPS was best for maritidine. Decomplexation, hydrolysis, and cyclisation completed formal total syntheses of the *Amaryllidaceae* alkaloids (±)-lycoramine and (±)-maridiidine, establishing the compatibility of the organoiron method with the presence of *ortho* substituents on the aryl group, and nucleophile addition *ipso* to the substituted arene.

## Introduction

The complete stereocontrol available[1] through the use of electrophilic multihapto transition metal complexes has stimulated sustained efforts to develop versatile procedures that are compatible with a wide range of nucleophiles.[2] We have recently described[3] general methods to produce aryl-substituted electrophilic tricarbonyl($\eta^5$-cyclohexadienyl)-iron complexes by exploiting nucleophile addition to simpler organoiron precursor electrophiles. By the correct placement of alkoxy substituents in the precursor complex, all four possible substitution patterns (C-1, C-2, C-3 and C-6) are accessible.[3] A second nucleophile addition can then be used to further elaborate the ligand. The regiocontrol in this step is a consequence of the nature and position of the aryl substituent and other functional groups that are present.[4] Retrosynthetic analysis that makes multiple use of metal mediated electrophilicity of this type needs to take into account the relative positions which the nucleophiles can take up in product structures, a procedure which has been the subject of a systematic analysis.[2,5] When both reactions take place at the same atom in the ligand, this is referred to as "*1,1*" (Figure 1); reactions at adjacent positions are "*1,2*", and so on.[6] The *1,1* relative regiocontrol pattern is especially attractive because it builds quaternary stereogenic centres when different nucleophiles are used in the two steps, and this is exemplified in this paper by our formal total syntheses of lycoramine (**1**) and maritidine (**2**). The *1,2* pattern is illustrated by our work towards hippeastrine,[7] and our approach to lycorine[8] corresponds to a *1,3* procedure. By demonstrating the practicality of these different patterns of reactivity in real synthetic situations, we aim to showcase the power of electrophilic $\eta^5$ multihapto complexes. Two additional factors should also be taken into account; the choice of hapticity[9] in the simple precursor structures, and the sequence of changing hapticity during the development of the synthetic route ("linear" or "iterative", or a combination of the two[10]). Defining and classifying these issues has been an important

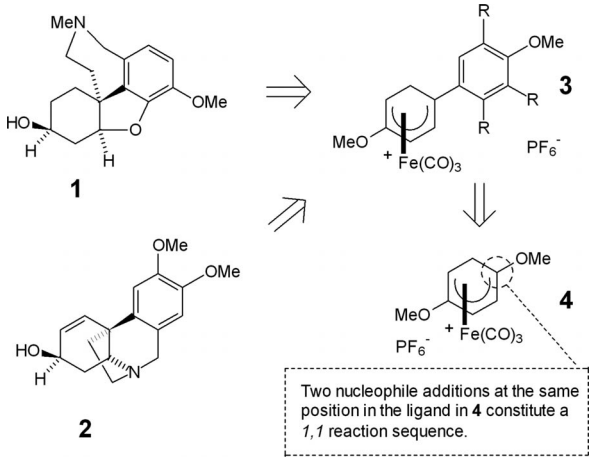


Figure 1. Illustration of the concept of *1,1* regiocontrol in the multiple iron-mediated bond formations that give access to, and then alkylate, (1-arylcyclohexadienyl)iron(1+) complexes envisaged[11,12] as intermediates for lycoramine **1** and maritidine **2**. The proposed routes each use a sequence of two ($\eta^5$-cyclohexadienyl)iron electrophiles, and so correspond to iterative reaction sequences.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201001394.

part[2] of our recent work. Our organoiron approach to lycoramine and maritidine illustrates an iterative $[\eta^4]\rightarrow[\eta^5]^+\rightarrow[\eta^4]\rightarrow[\eta^5]^+\rightarrow[\eta^4]$ multistep process with *1*,*1* relative regiocontrol. Part of this work has been the subject of preliminary communication.[11,12]

Lycoramine (**1**)[13] is an example of the galanthamine-type[14] *Amaryllidaceae* alkaloids[15] and like galanthamine has been shown to be a reversible cholinesterase inhibitor[16] and a modulator of nicotinic receptors,[17] a property important in the treatment Alzheimer's disease,[18] and a number of other conditions including Tourette's syndrome.[19] Lycoramine derivatives are active in the relief of symptoms of myasthenia gravis,[20] and have antiarrhythmic activity[21] (suppression of fast rhythms of the heart). A dimethyl carbamate of deoxydemethyl-lycoramine methiodide (MCDL) has been found[22] to produce a greater amount of muscle potentiation than neostigmine or physostigmine. Maritidine (**2**)[23] is also an *Amaryllidaceae* alkaloid. Like lycoramine (**1**), it contains a quaternary centre, but the benzylic tertiary amine is folded back differently and bonded to the cyclohexanol at the position of the C–O ether linkage in **1**. Maritidine, which has cytotoxic[24] properties, exhibits clastogenic effects,[25] and has been shown to have significant activity as an inhibitor of [3*H*]citalopram binding to the rat brain serotonin transporter.[26] Improved understanding of the physico-chemical properties relating to the binding to the serotonin re-uptake transport protein could lead to the development of new therapeutic agents.

There has been considerable attention paid to the development of synthetic routes to lycoramine[27] and galanthamine,[28] and since Martin and Garrison's short route[29] to lycoramine from *o*-vanilin, there have been significant advances[30,31,32] but only quite recently has the first enantioselective synthesis been reported.[33] Typically, the methods now preferred for the direct construction of the quaternary centre use palladium catalysed[31,34] or radical[35,36] cyclisations to alkenes, but an unusual photochemical intramolecular cyclisation of an activated arene to cyclohexenone has also provided a highly original basis for a total synthesis.[37] The Martin and Garrison approach[29] (using anions developed from enamines), and a later Robinson annellation approach,[38] however, are among the few[39] completed syntheses that use nucleophile addition to electrophilic centres to build this hindered quaternary centre at a late stage in the route. Indeed, some of the most recent and successful developments have employed rearrangement reactions (semipinacol[30] and Cope[31] rearrangements) to side-step this problem and gradually build up the steric challenge of these targets.

Initial synthetic approaches[40,41] to maritidine and oxomaritidine[42,43] were similarly inspired by phenolic coupling, including an unusual photochemical cyclisation developed by Kametani and co-workers.[44] In 1996, Kita et al.[45] made an important contribution to the syntheses of maritidine and later galanthamine-type alkaloids,[46] when they reported the use of PIFA as a suitable oxidising agent for intramolecular oxidative phenolic couplings reactions. This route was modified by Ley et al.[47] to synthesise (±)-oxomaritidine and (±)-epimaritidine using only polymer-supported reagents. Intramolecular Heck reactions show much promise to access structures of this type, as demonstrated by the Guillou group's total synthesis of (±)-maritidine (**2**).[48] The key quaternary carbon centre was achieved under $Pd^0$-catalysed conditions in the presence of thallium acetate. Stereoselective Luche reduction of the enone gave an allylic alcohol which after mesyl protection and inversion using cesium acetate and saponification gave maritidine (**2**). This efficient synthesis of (±)-maritidine was completed in ten steps with a 6% overall yield. These different routes to lycoramine and maritidine connect the main key bonds in the same order, commencing from either a norbelladine-type derivative or an aryl iodide, with the C–N bond being created by reductive amination. The C–C bond formation between the two six-membered rings (A and C) is performed by either an oxidative phenolic coupling, a photochemical intramolecular cyclisation, or a Heck coupling.

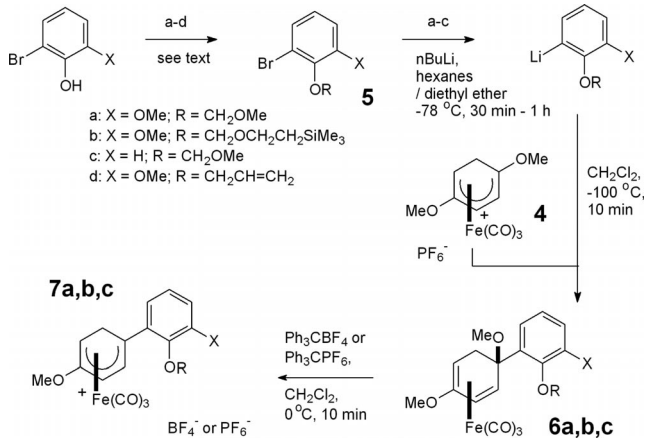
In contrast, our iterative organoiron-mediated approach[3,5,11,12] to both lycoramine and maritidine is conceptually distinct, and develops from a key electrophilic $\eta^5$ complex **4**[49,50] for which an enantioselective preparation[51] based on a novel asymmetric hydride abstraction is under development. The crucial step in our route is the introduction of a nucleophile *ipso* to the aryl substituent in a suitably functionalised (1-arylcyclohexadienyl)iron complex **3** which serves as a $C_{12}$ building[52] block to construct the required quaternary stereogenic centre in lycoramine. The corresponding intermediate for maritidine extends the (1-arylcyclohexadienyl)iron building block with a benzylic substituent adjacent to the point of attachment of the arene. Compared to our earlier *1*,*1* iterative syntheses of the simple target molecules *O*-methyljoubertiamine[50] and mesembrine,[53] the corresponding step for lycoramine is more challenging because an *ortho* oxygen substituent is present on the arene, and this may block the approach of the nucleophile by the *ipso* pathway. However, crystallographic studies[5] have shown that ether substituents can be accommodated below the plane of the dienyl system (and thus out of the path of the incoming nucleophile). This raises the possibility that in synthetic applications, the accessibility of this conformation may allow efficient nucleophile addition to proceed. The lycoramine target molecule was chosen to test this proposition, and to explore the tolerance of the reaction to bulky protecting groups on the ether. In the maritidine case, the benzylic carbon lies at this position and creates a greater steric block to the approach of the nucleophile. The only crystallographically defined conformation[5] has this methylene group lying above the plane of the dienyl ligand.

## Results and Discussion

The starting point for lycoramine was the readily available 6-bromoguaiacol[54] which was converted (Scheme 1) into the MOM, SEM and allyl derivatives **5a**, **5b** and **5d** by standard procedures.[55,56,57] The introduction of the allyl

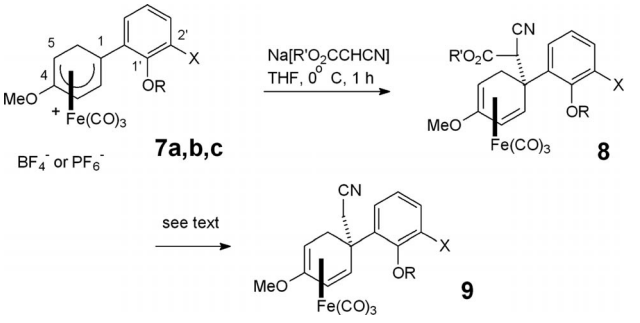
  

protecting group was significantly less straight-forward, but the easily accessible MOM and SEM ethers were converted into the aryllithium reagents by reaction with *n*-butyllithium in diethyl ether at –78 °C. Reaction with tricarbonyl($\eta^5$-1,4-dimethoxycyclohexadienyl)iron hexafluorophosphate **4** in dichloromethane[58] at –100 °C gave the *exo*[59] products **6a** and **6b** in about 50–65% yield. A simple MOM 2-bromophenol derivative[60] was also prepared and converted into the corresponding adduct **6c**, to explore the effect of the flanking OMe group in **5a** in the regiocontrol of nucleophile addition to the (1-arylcyclohexadienyl)iron complexes. Our original[61] acid-mediated demethoxylation methods would clearly be unsuitable for the acetal-protected structures, but our more recently developed[62] use of triphenylcarbenium ion reagents for demethoxylation combined with the in situ use of solid anhydrous potassium carbonate to control traces of acid, provided a better approach. The MOM-protected (1-arylcyclohexadienyl)iron complexes **7a** and **7c** were obtained in 56 and 73% yields, respectively. In the SEM case, however, the product **7b** proved unstable and difficult to isolate, and was only obtained in 11% yield.




Scheme 1. Preparation of protected 6-bromoguaiacol derivatives, and the preparation and use of aryllithium reagents in metal-mediated construction of the (1-arylcyclohexadienyl)iron(1+) electrophiles.

The regiocontrol in the second nucleophile addition step depends on the relative ω[63] directing properties of the 1-aryl and 4-methoxy substituents on the cyclohexadienyliron complex **7**. These have opposed directing effects.[64] In our work towards the alkaloid crinine,[3] we have used the sodium enolates of malononitrile esters ($MeO_2CCH_2CN$ in the model series, and $Me_3SiCH_2CH_2OCH_2CN$ to start the synthesis) to assess the prospects for regiocontrol and found that the 4-methoxy group sufficiently deactivated C-5 to promote addition of the enolate at C-1, producing the 3′,4′-methylenedioxyphenyl analogue of **8** in good yield. For lycoramine, the required oxygenation pattern on the arene is 2′,3′-, and particularly with a bulky protecting group as the C-2′ ether, it is possible that the aryl group would be too strongly ω directing. A preliminary experiment (Scheme 2) in which the monosubstituted MOM ether **7c** was treated with Na[$MeO_2CCHCN$] as a model nucleophile, however, gave encouraging results as the required *ipso* adduct **8** (R = MOM, R′ = Me, X = H) was obtained in near quantitative yield. The use of Na[$Me_3SiCH_2CH_2O_2CCHCN$] with **7c** was similarly well regiocontrolled, but the yield dropped to 66%. Fortunately, when the second substituent on the arene was included (electrophile **7a**), despite the greater bulk of the C-2′/C-3′ substituents, the yield improved to 81%.




Scheme 2. Formation of the quaternary centre [(a: R = MOM, X = OMe; b: R = SEM, X = OMe; c: R = MOM, X = H); R′ = Me or $Me_3SiCH_2CH_2$].

Because of the low yield and sensitivity of the SEM protected electrophile **7b** (Table 1), nucleophile addition in this case was not examined in detail. However, the potential advantage of the SEM group is that it would allow the concurrent deprotection of the phenol and desilylation/dealkoxylation/decarboxylation of the ester, and this was tested in an exploratory series of experiments (Scheme 3) in which **7b** was not isolated but trapped in a one-pot procedure by addition of an excess of Na[$Me_3SiCH_2CH_2O_2CCHCN$] to the reaction mixture formed by adding triphenylcarbenium hexafluorophosphate to **6b**. The crude product (36%) was separated from the excess malononitrile ester and treated with tetrabutylammonium fluoride (TBAF) in THF at reflux for 2 hours. The required phenol **10** was obtained in 18% overall yield together with 6-(4′-methoxyphenyl)guaiacol which was the major product (60%). In the MOM series

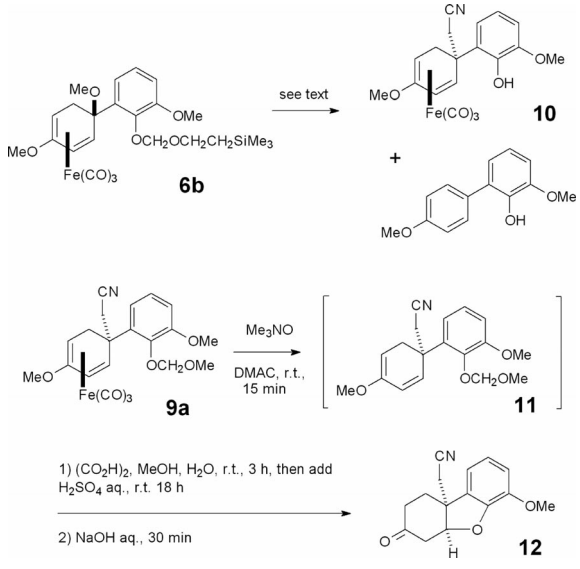
Table 1. Formation of *ortho*-ether-substituted (1-arylcyclohexadienyl)iron(1+) complexes and their reactions with nucleophiles.

| Starting material | | | Results of salt formation and nucleophile addition steps | | | | | |
|---|---|---|---|---|---|---|---|---|
| | R | X | Yield (%) of **6** | Yield (%) of **7** | Anion | Yield (%) of **8** | Yield (%) of **9** | Yield (%) of **10** |
| a | MOM | OMe | 51 | 56 | $BF_4^-$ | 81 (R′ = $CH_2CH_2SiMe_3$)[a] | 73 | – |
| b | SEM | OMe | 65 | 11 | $PF_6^-$ | – | – | 12 [b] |
| c | MOM | H | 75 | 73 | $BF_4^-$ | > 99 (R′ = Me) [a] | – | – |
| d | MOM | H | | | $BF_4^-$ | 66 (R′ = $CH_2CH_2SiMe_3$)[a] | 37 | – |

[a] Complete *ipso* selectivity relative to the aryl group. [b] Prepared from **6b** without isolation of **8b**.

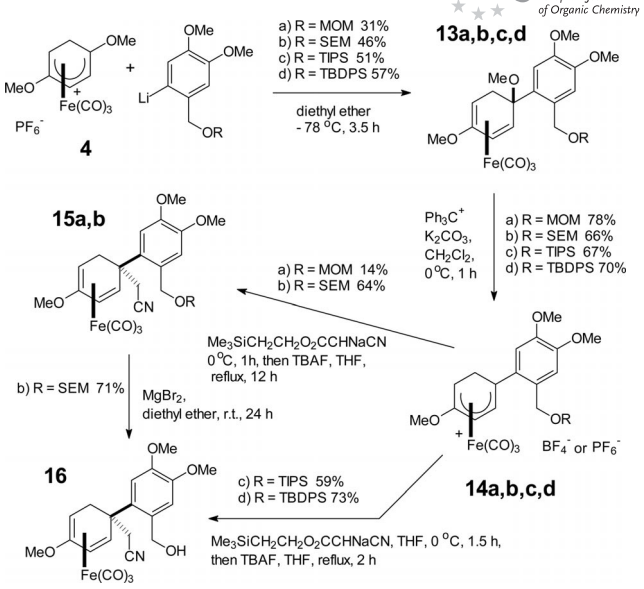
  

(electrophile **7a**), deprotection in the presence of the $Fe(CO)_3$ group proved difficult and **10** could not be formed from **8a**. These problems were solved (Scheme 3) by removing the metal (using trimethylamine *N*-oxide[65]) followed by a concurrent one-pot hydrolysis of the enol ether and detachment of the acid-sensitive MOM ether (oxalic acid/10% aq. sulfuric acid), and a basic work-up (aq. sodium hydroxide) to complete the formal total synthesis by Michael addition of the resulting phenolate anion to the enone generated from the methoxycyclohexadiene. The product had spectroscopic properties that corresponded to the reported data for the same compound in the Ackland and Pinhey[66]/Martin and Garrison[29] route to lycoramine.




Scheme 3. Decomplexation and deprotection steps to complete the formal total synthesis of lycoramine by the *1,1* iterative method.

The intermediates for lycoramine have ether substituents on the arene, *ortho* to the point of attachment to the quaternary centre, and our results demonstrate that this type of substitution is compatible with the proposed *1,1* iterative strategy. Preliminary studies[5] with benzylic *ortho* substituents, however, had shown that the ω directing effect OMe group was no longer strong enough to ensure complete *i* substitution in the nucleophile addition step (with $CH_2OMe$, a 1:4 *i*/ω ratio had been observed). In many alkaloid syntheses, this carbon is added at a relatively late stage, typically using a Pictet–Spengler reaction.[67] The inclusion of this $CH_2$ group in the aryllithium reagent used at the start of the *1,1* iterative procedure, however, is an attractive objective because the resulting synthetic route is more convergent, and so intrinsically more efficient. This extension of the $C_{12}$ building block to the $C_{13}$ benzylic series was thus chosen as a test of the generality of applicability of our approach. Maritidine is a suitable alkaloid target to explore this problem, and constitutes a more severe test of our methods than was the case with lycoramine (Scheme 4).




Scheme 4. The aryllithium reagent was generated from the corresponding aryl bromide using *n*BuLi at –78 °C in diethyl ether as follows: MOM series for 1 h; SEM series for 1 h; TIPS series: for 1 h; TBDPS series: for 15 min.

A series of protected 2-bromo-4,5-dimethoxy benzyl alcohols were prepared by standard methods for use as the precursors for the desired aryllithium reagents to start the first step of the iterative sequence. The MOM and SEM ether protecting groups used in the lycoramine work were supplemented by TBDMS, TIPS and TBDPS silyl protecting groups to provide a range of examples. A simple THP ether was also tried, but the derived aryllithium reagent performed badly in the reaction with the 1,4-dimethoxy salt **4** [the reaction was low-yielding (< 22%) and the product proved difficult to separate from other by-products of the reaction]. The use of MOM protection also gave a poor yield (31%), and SEM proved superior (46%). At first, attempts to employ the silyl protecting groups were unsuccessful, with TBDMS affording none of the expected product **13d**. Instead, a product from silyl migration[68] to the site of lithiation was isolated in 49% yield. Even with the more bulky and more stable[69] TBDPS group, this arylsilane formation could still be observed, but as expected, the silyl migration was slower. Before addressing the aryllithium addition to salt **4**, the lithiation step itself was examined in more detail using *n*BuLi at –78 °C, by varying solvent and reaction time and quenching with $D_2O$ to establish the ratio of aryllithium and silylaryl benzyl alcoholate species at the end of the time allowed for lithium–bromine exchange. The use of $Et_2O$ proved better than THF, and TIPS performed more cleanly then TBDMS. The best procedures are given in Scheme 4 (details of the optimisation of the aryllithium generation are presented in the Supporting Information). In practice, traces of arylsilane by-products can be tolerated in the reaction with **4** since they are easily separated from the product **13**, and Scheme 4 shows that TBDPS performed marginally better than TIPS and also gave a better result in the second nucleophile addition step, so giving the best

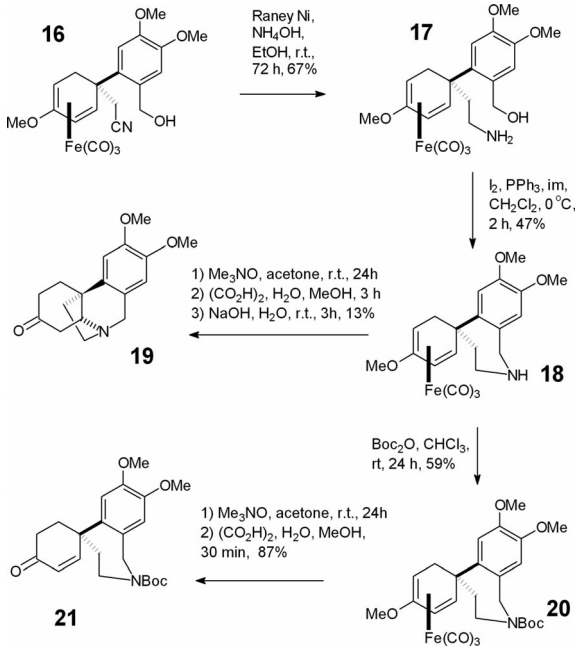
Table 2. Formation of *ortho*-benzyl ether substituted (1-arylcyclohexadienyl)iron(1+) complexes and their reactions with nucleophiles.

| | Starting material R | | Salt formation Yield of **13** (%) | Yield of **14** (%) | Anion | Cyanoacetate addition [a] Yield of **15** (%) | Yield of **16** (%) |
|---|---|---|---|---|---|---|---|
| a | MOM | $OCH_2OMe$ | 31 | 78 | $PF_6^-$ | 14 | – |
| b | SEM | $OCH_2OCH_2CH_2SiMe_3$ | 46 | 66 | $PF_6^-$ | 64 | 71 |
| c | TIPS | $OSiiPr_3$ | 51 | 67 | $BF_4^-$ | – | 59 |
| d | TBDPS | $OSitBuPh_2$ | 57 | 70 | $BF_4^-$ | – | 73 |

[a] Complete *ipso* selectivity relative to the aryl group.

overall yield to the benzyl alcohol **16** (TBDPS: 30%; TIPS: 20%). The MOM, SEM, TIPS and TBDPS-protected salts **14** were used (Table 2) in reactions with the $Na[Me_3SiCH_2CH_2O_2CCHCN]$ reagent already described for lycoramine. In the case of **14**, the use of MOM was significantly worse than SEM in this reaction. SEM was also expected to be a superior strategic choice because of the possibility that both $CH_2CH_2SiMe_3$ groups could be removed in a single procedure. It was found, however, that while simplification of the side-chain at the quaternary centre to $CH_2CN$ was straightforward, the benzyloxy-SEM group was stable to TBAF. Eventually this problem was solved by deprotection of the benzyl alcohol with $MgBr_2$ in a second step. The two silyl ether protecting groups also give the possibility of a one-pot procedure, and reaction of **4** with $Na[Me_3SiCH_2CH_2O_2CCHCN]$ followed by addition of TBAF to the reaction mixture led directly to **16**, with TBDPS giving the better yield (Scheme 4).

The final stages of the synthesis (Scheme 5) concentrated on gaining access to Guillou's intermediate **21** for maritidine, which is three steps away from the target. This structure also includes the benzo-2-azacycloheptane ring of lycoramine **1**, which was not addressed in our formal total synthesis via **12**. The nitrile was reduced in 67% yield to give primary amine. Cyclisation of **17** by the Appel procedure which uses triphenylphosphane ($PPh_3$) and carbon tetrabromide to replace the alcohol with a bromide allowing the amine to perform a nucleophilic displacement, was inefficient, but the Garegg-Samuelsson reaction, which uses iodine, triphenylphosphane and imidazole to replace the alcohol with an iodide, worked better giving **18** in 47% yield. Formation of **19** by decomplexation of **18** established the possibility of access to the fused 6,6,5-tricyclic ring system of maritidine by a Michael reaction after hydrolysis of the enol ether. Traces of the eneone of oxomaritidine were identified in the NMR spectrum of the crude product before purification. The mechanism of this unusual oxidative dehydrogenation is not known, but we have similarly observed traces of the mesembrenone in the final product of our iron-mediated synthesis of mesembine,[53] suggesting the process is general in the decomplexation of this type of tricarbonyliron complex. A more efficient route to maritidine **2**, however, was achieved by a formal total synthesis linking to the Guillou route[48] by BOC protection of the amine before removal of the $Fe(CO)_3$ group from **20**. Guillou completed maritidine by a selenium dioxide mediated conversion of the enone **21** into a dienone followed by cyclisation to the 6,6,5-fused ring. In view of the discovery of traces of oxidative dehydrogenation products in our earlier decomplexation reactions with $Me_3NO$, we looked for this dienone by-product in the NMR spectrum of crude **21** since this could substantially shorten the synthetic route. Traces of the dienone could be identified from signals at $\delta$ = 6.28 ppm (d, $J$ = 10.3 Hz) and 6.99 ppm (d, $J$ = 10.3 Hz), but we were unable to increase the yield. The expected product **21**, however, was obtained in 87% yield and easily purified. This efficient decomplexation step completed a formal total synthesis of maritidine, and established the viability of the *1,1* iterative procedure in the more difficult "$C_{13}$" benzyloxysilyl ether series of intermediates.




Scheme 5. Cyclisation and decomplexation steps to complete the formal total synthesis of maritidine **2** by the *1,1* iterative method.

The completion of these two synthetic routes has made available a representative selection of metal complexes which are typical of applications of 1-aryl-substituted cyclohexadienyliron complexes in synthesis. Selected examples were studied in detail (see Supporting Information) by 2D NMR spectroscopy to establish definitive assignments of $^1H$ chemical shifts and coupling constants, and $^{13}C$ chemical shifts. This extends the data available from our much earlier full paper[50] on the synthesis of the simple "model" alkaloid *O*-methyl joubertiamine, and crucially, the use of HSQC proton-carbon correlation has now established un-

ambiguous $^{13}C$ assignments for all except the quaternary carbon atoms. The approach used was rigorous. COSY and where necessary, NOESY spectra were used to establish the assignments of signals in the $^1H$ NMR spectra. The $^1H$ assignments then determined the majority of $^{13}C$ NMR signals. In future, new intermediates from *1,1*-iterative routes to other alkaloids will be easy to identify with certainty based on the data presented here. The same approach was applied to all the positions in the molecules, and a complete tabulation of NMR assignments of the aromatic rings, ethers, and other side-chain groups is available in the Supporting Information.

## Conclusions

The organoiron mediated formal total syntheses of lycoramine and maritidine via the (1-arylcyclohexadienyl)iron electrophiles **7a** and **14d** have established the compatibility of the *ortho* substituted aryl groups with *ipso* nucleophile addition. Despite the bulky nature of the MOM and $CH_2OTBDPS$ substituents on the arene, which could lie over the desired electrophilic centre in the dienyliron complex, the opposed regiodirecting effect of the 4-methoxy group is sufficiently powerful to give access to the quaternary centres in the Ackland and Pinhey intermediate **12**[66] and the Guillou intermediate **21**.[48] Both syntheses use *1,1*[4] iterative sequences of two iron mediated carbon–carbon bond formation steps, that introduce first the aryl group and secondly the $CH_2CN$ side chain to the 1,4-dimethoxy-substituted starting material **4**. In this work, all the key features of the natural product targets have been achieved, with examples of the benzo-2-azacycloheptane ring of lycoramine and the more compact fused 6,6,5-tricyclic ring system of maritidine being completed, as well as the fully-substituted quaternary centres of the two natural products. The examples described here establish the generality of application of our organoiron procedure for the crinine subclass of *Amaryllidaceae* alkaloids, which have important biological activities. The sequence of bond-formation steps in our routes is distinct from those typical of syntheses based on standard methods, so offering complementary strategies for analogue synthesis.

## Experimental Section

**General:** Chemicals were reagent grade and used as supplied unless otherwise stated. All chiral compounds were prepared as racemic mixtures. All reactions were carried out in oven or flame dried glassware, under dry, oxygen-free nitrogen. Diethyl ether and THF were dried by distillation from sodium and benzophenone; dichloromethane was dried by distillation from calcium hydride. Reaction temperatures: –78 °C refers to acetone/dry ice; 0 °C refers to ice/water; –100 °C refers to diethyl ether/liquid nitrogen cooling. Light petroleum refers to the fraction with b.p. 40–60 °C. Filtration refers to filtration under water-pump suction. Column chromatography was performed using Merck 7734 silica gel and BDH alumina (Brockmann 1). TLC was performed using Camlab Polygram® SIL G/$UV_{254}$ plates, visualized by UV irradiation (254 nm) or exposure to alkaline potassium permanganate solution followed by heating. IR spectra were recorded as a thin film or as a solution in the specified solvent on Avatar 360, Perkin–Elmer BX or Perkin–Elmer 1720X FTIR spectrometers. NMR spectra were recorded on Varian Unity Plus, Varian Gemini 2000, Jeol GX400, Jeol EX270, Bruker AC250 or Jeol EX90 spectrometers, and were referenced to $Me_4Si$ ($\delta$ = 0 ppm). CI, FAB and high resolution mass spectra were recorded at the EPSRC Mass Spectrometry Centre at the University of Wales, Swansea.

**Formal Total Synthesis of Lycoramine. An Organoiron-Mediated Route to the Ackland and Pinhey Intermediate 9b-Cyanomethyl-6-methoxy-1,4,4a,9b-tetrahydro-dibenzofuran-3(2*H*)-one[66] (12)**

**Tricarbonyl[(1,2,3,4-η)-2,5β-dimethoxy-5α-(2′-methoxymethoxy-3′-methoxyphenyl)-1,3-cyclohexadiene]iron(0) (6a):** The MOM-protected aryl bromide **5a** (1.1 equiv., 1.48 g, 6.01 mmol) was dissolved in dry diethyl ether (20 mL) and cooled to –78 °C under nitrogen. *n*BuLi (1.6 M in hexanes; 1.1 equiv., 6.01 mmol, 3.8 mL) was added and a white suspension formed after stirring for 30 min at –78 °C. This mixture was allowed to settle and was cooled to –100 °C. The supernatant was added via a cannula to tricarbonyl[(1,2,3,4,5-η)-1,4-dimethoxycyclohexadienyl]iron hexafluorophosphate (**4**) (1 equiv., 2 g, 5.46 mmol) dissolved in dry dichloromethane (10 mL) at –100 °C. The mixture was stirred for 10 min at –100 °C and quenched with water (25 mL) and diethyl ether (25 mL) at –100 °C and warmed to room temp. The mixture was extracted into diethyl ether (3 × 25 mL) and water (3 × 25 mL). The combined organic extracts were washed with water (3 × 25 mL), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to afford a dark green oil which was purified by column chromatography on silica (diethyl ether/petroleum ether gradient) to give **6a** as a pale brown gum (1.24 g, 51%). $^1H$ NMR (270 MHz, $CDCl_3$): $\delta$ = 7.11 [dd, $^3J$(H,H) = 7.9, 1.7 Hz, 1 H, 6′-H], 6.99 (t, $^3J_{H,H}$ = 7.9 Hz, 1 H, 5′-H), 6.85 (dd, $^3J_{H,H}$ = 7.9, 1.7 Hz, 1 H, 4′-H), 5.16 (dd, $^3J_{H,H}$ = 6.9, 2.6 Hz, 1 H, 3-H), 5.07 (d, $^3J_{H,H}$ = 4.3 Hz, 1 H, $OCH_2O$), 4.96 (d, $^3J_{H,H}$ = 4.3 Hz, 1 H, $OCH_2O$), 3.81 (s, 3 H, Ar-OMe), 3.64 (s, 3 H, 2-OMe), 3.61 (s, 3 H, OMe), 3.32 (m, 1 H, 1-H), 3.07 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, 4-H), 2.99 (s, 3 H, 5-OMe), 2.39 (m, 2 H, 6-H) ppm. IR ($CH_2C1_2$): $\tilde{\nu}_{max}$ = 2048, 1979 (CO), 1504, 1254, 1079, 855 $cm^{-1}$. MS (EI): *m*/*z* (%) = 390 (5) [$M$ – 2CO]$^+$, 362 (11) [$M$ – 3CO]$^+$, 330 (100). Elemental analysis calcd. (%) for $C_{20}H_{22}FeO_8$ (446.23): C 53.8; H 5.0; found C 54.0; H 5.1. Also obtained was tricarbonyl[(2,3,4,5-η)-4-methoxy-2,4-cyclohexadien-1-one]-iron(0)[49,50] (0.441 g, 1.67 mmol, 31%).

**Tricarbonyl[(1,2,3,4,5-η)-1-(2′-methoxymethoxy-3′-methoxyphenyl)-4-methoxy-2,4-cyclohexadienyl]iron(1+) Tetrafluoroborate(1–) (7a):** Iron(0) complex **6a** (1 equiv., 478 mg, 1.07 mmol) was added to a mixture of triphenylcarbenium tetrafluoroborate (1 equiv., 354 mg, 1.07 mmol) and potassium carbonate (140 mg) in freshly distilled dichloromethane (5 mL) at 0 °C. The reaction mixture darkened and was stirred for 10 min and then was added dropwise into dry diethyl ether (200 mL) at 0 °C. A yellow precipitate and was collected by filtration. Reprecipitation (acetone/diethyl ether) afforded **7a** as a yellow solid (0.303 g, 56%). $^1H$ NMR (270 MHz, $CD_3COCD_3$): $\delta$ = 7.41–7.12 (m, 3 H, Ar), 7.02 (dd, $^3J_{H,H}$ = 6.9, 2.3 Hz, 1 H, 3-H), 6.58 (dt, $^3J_{H,H}$ = 6.9, 1.3 Hz, 1 H, 2-H), 5.21 (s, 2 H, $OCH_2O$), 4.41 (m, 1 H, 5-H), 4.05 (s, 3 H, 4-OMe), 3.91 (s, 3 H, Ar-OMe), 3.42 (s, 3 H, OMe), 3.71 (ddd, $^3J_{H,H}$ = 15.5, 6.6, 1.3 Hz, 1 H, 6β-H), 2.96 (d, $^3J_{H,H}$ = 15.5 Hz, 1 H, 6α-H) ppm. IR (acetone): $\tilde{\nu}_{max}$ = 2104, 2044 (CO) $cm^{-1}$. MS (EI): *m*/*z* (%) = 330 (2) [M + H – CO – $BF_4$]$^+$, 274 (25) [M + H – 3CO – $BF_4$]$^+$, 242 (30), 229 (25), 199 (13). MS (FAB): *m*/*z* (%) = 415 (100) [M – $BF_4$]$^+$, 387 (8) [M – CO – $BF_4$]$^+$, 331 (64) [M – 3CO – $BF_4$]$^+$, 285

(58). HRMS (FAB): *m*/*z*: calcd. for $C_{19}H_{19}FeO_7$: 415.0481; found 415.0481 $[M - BF_4]^+$.

**Tricarbonyl{2′′-trimethylsilylethyl [(2,3,4,5-η)-1β-(2′-Methoxymethoxy-3′-methoxyphenyl)-4-methoxy-2,4-cyclohexadien-1α-yl]-cyanoethanoate}iron(0) (8) R = $CH_2OCH_3$; R′ = $CH_2CH_2SiMe_3$; X = OMe):** NaH (60% suspension in mineral oil; 1 equiv., 24 mg, 0.60 mmol) was suspended in dry THF (5 mL) at 0 °C. A solution of 2-(trimethylsilyl)ethyl cyanoethanoate[70] (1 equiv., 111 mg, 0.60 mmol) in dry THF (5 mL) was added at 0 °C and the mixture was stirred for 15 min at 0 °C to give a white suspension of 2-(trimethylsilyl)ethyl sodiocyanoethanoate. This mixture was added to a suspension of **7a** (0.93 equiv., 283 mg, 0.56 mmol) in THF (5 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, and then was quenched with water (25 mL) and diethyl ether (25 mL) and extracted into diethyl ether (3 × 25 mL). The combined organic extracts were washed with water (3 × 25 mL), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to afford a yellow oil. Column chromatography (2:3 diethyl ether/petroleum ether on silica) afforded **8** (R = $CH_2OCH_3$; R′ = $CH_2CH_2SiMe_3$; X = OMe) as a 2:1 mixture of two inseparable diastereoisomers as a pale yellow gum (274 mg, 81%). $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 7.11–6.75 (m, 3 H, Ar), 5.39 (dd, $^3J_{H,H}$ = 6.9, 2.3 Hz, 0.67 H, 3-H), 5.22–5.16 (m, 2 H, $OCH_2O$, 3-H), 4.99 (d, $^3J_{H,H}$ = 12.5 Hz, 0.33 H, $OCH_2O$), 4.82 (s, 0.67 H, CHCN), 4.77 (s, 0.33 H, CHCN), 4.31 (m, 2 H, $CO_2CH_2$), 3.88 (s, 3 H, Ar-OMe), 3.78 (s, 3 H, 4-$OCH_3$), 3.59 (s, 2 H, OMe), 3.57 (s, 1 H, OMe), 3.31 (m, 1 H, 5-H), 2.91 (d, $^3J_{H,H}$ = 6.9 Hz, 0.67 H, 2-H), 2.86 (d, $^3J_{H,H}$ = 6.9 Hz, 0.33 H, 2-H), 2.60 (dd, $^3J_{H,H}$ = 16.3, 2.6 Hz, 0.33 H, 6β-H), 2.53 (dd, $^3J_{H,H}$ = 16.3, 2.6 Hz, 0.67 H, 6β-H), 2.32 (dd, $^3J_{H,H}$ = 16.3, 3.3 Hz, 0.33 H, 6α-H), 2.26 (dd, $^3J_{H,H}$ = 16.3, 3.3 Hz, 0.67 H, 6α-H), 1.01 (m, 2 H, $CH_2Si$), 0.06 (s, 9 H, $SiMe_3$) ppm. IR (film): $\tilde{\nu}_{max}$ = 2248 (CN), 2048, 1967, 1733 (CO), 1493, 1086, 862, 625 $cm^{-1}$. MS (EI): *m*/*z* (%) = 515 (1) $[M - 3CO]^+$, 330 (5), 230 (37), 98 (100). HRMS (EI): *m*/*z*: calcd. for $C_{24}H_{33}FeNO_6Si$: 515.1427; found 515.1427 $[M - 3CO]^+$.

**Tricarbonyl[(1,2,3,4-η)-5α-cyanomethyl-2-methoxy-5β-(2′-methoxymethoxy-3′-methoxyphenyl)-1,3-cyclohexadiene]iron(0) (9a):** Tetra-*n*-butylammonium fluoride (1.2 equiv., TBAF; 1 M solution in THF; 0.4 mL, 0.4 mmol) was added to a solution of the trimethylsilylethyl {[1β-(2′-methoxymethoxy-3′-methoxyphenyl)-4-methoxy-2,4-cyclohexadien-1α-yl]cyanoethanoate}iron complex (**8**) (R = $CH_2OMe$; R′ = $CH_2CH_2SiMe_3$; X = OMe) (1.0 equiv., 196 mg, 0.33 mmol) in dry THF (10 mL). The mixture was heated at reflux for 3 h. A further portion of TBAF (2.1 equiv., 0.7 mL, 0.7 mmol) was added and heating was continued at reflux for 1 h until TLC analysis indicated that the reaction was complete. The cooled solution was quenched with sat. aqu. ammonium chloride (5 mL), water (5 mL) and diethyl ether (5 mL) and extracted into diethyl ether (3 × 25 mL). The combined organic extracts were washed with water (3 × 25 mL), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to afford a brown gum. Column chromatography (2:3 diethyl ether/petroleum ether) afforded **9a** as a pale yellow oil (109 mg, 73%). $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 7.08 (m, 2 H, Ar), 6.88 (dd, $^3J_{H,H}$ = 6.3, 3.3 Hz, lH, Ar), 5.28 (dd, $^3J_{H,H}$ = 6.9, 2.6 Hz, 1 H, 3-H), 5.19 (d, $^3J_{H,H}$ = 5.3 Hz, 1 H, $OCH_2O$), 5.13 (d, $^3J_{H,H}$ = 5.3 Hz, 1 H, $OCH_2O$), 3.82 (s, 3′-OMe), 3 H, 3.73 (s, 3 H, 4-OMe), 3.54 (s, 3 H, OMe), 3.35 (m, 1 H, 1-H), 3.25 (d, $^3J_{H,H}$ = 16.5 Hz, 1 H, $CH_2CN$), 3.00 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, 4-H), 2.70 (d, $^3J_{H,H}$ = 16.5 Hz, 1 H, $CH_2CN$), 2.40 (dd, $^3J_{H,H}$ = 15.8, 2.6 Hz, 1 H, 6β-H), 2.17 (dd, $^3J_{H,H}$ = 15.8, 3.3 Hz, 1 H, 6α-H) ppm. IR (film): $\tilde{\nu}_{max}$ = 2246 (CN), 2047, 1967, (C=O), 1581, 1089, 624 $cm^{-1}$. MS (EI): *m*/*z* (%) = 399 (20) $[M - 2CO]^+$, 371 (33) $[M - 3CO]^+$, 326 (52), 230 (22), 172 (9), 121 (78), 45 (100). HRMS (EI): *m*/*z*: calcd. for $C_{19}H_{21}FeNO_5$: 399.0769; found 399.0769 $[M - 2CO]^+$.

**9b-Cyanomethyl-6-methoxy-1,4,4a,9b-tetrahydrodibenzofuran-3(2*H*)-one (12):**[66] Anhydrous trimethylamine *N*-oxide (20 equiv., 475 mg, 6.33 mmol) was added to a solution of the iron complex **9a** (1 equiv., 144 mg, 0.32 mmol) in dimethylacetamide (10 mL) and stirred for 15 min at room temp. Water (10 mL) and diethyl ether (10 mL) were added and the product was extracted with diethyl ether (3 × 10 mL). The combined organic extracts were washed with water (3 × 25 mL), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to afford a colourless oil of pure 5-cyanomethyl-2-methoxy-5-(2′-methoxymethoxy-3′-methoxyphenyl)-1,3-cyclohexadiene (**11**) (85 mg, 85%). $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 7.15–6.97 (m, 3 H, Ar), 6.41 (d, $^3J_{H,H}$ = 10.2 Hz, 1 H, 4-H), 6.02 (dd, $^3J_{H,H}$ = 10.2, 2.3 Hz, 1 H, 3-H), 5.31 (d, $^3J_{H,H}$ = 10.9 Hz, 1 H, $OCH_2$), 5.29 (d, $^3J_{H,H}$ = 10.9 Hz, 1 H, $OCH_2$), 4.78 (m, 1 H, 1-H), 3.93 (s, 3 H, Ar-OMe), 3.70 (s, 3 H, 2-OMe), 3.62 (s, 3 H, OMe), 3.29 (s, 2 H, $CH_2CN$), 3.07 (dd, $^3J_{H,H}$ = 16.5, 4.6 Hz, 1 H, 6-H), 2.77 (dd, $^3J_{H,H}$ = 16.5, 4.6 Hz, 1 H, 6-H) ppm. This methoxycyclohexadiene was dissolved in methanol (5 mL) and a solution of oxalic acid dihydrate (68 mg, 0.54 mmol) in water (2 mL) was added. The mixture was stirred at room temp. for 3 h after which time TLC analysis indicated the disappearance of the enol ether and carbonyl bands were observed in the IR spectrum. 10% $H_2SO_4$ in methanol (1 mL) was added the mixture was stirred for 18 h at room temp. The reaction was made basic by the addition of solid NaOH, stirred for 30 min and then extracted into diethyl ether (3 × 10 mL). The combined organic extracts were washed with water (3 × 10 mL), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to give a yellow oil. Column chromatography (1:1 ethyl acetate/petroleum ether) afforded a colourless oil (24 mg, 0.093 mmol, 35%) of **12** which exhibited the same spectroscopic data as quoted in the literature.[66]

**Formal Total Synthesis of Maritidine. An Organoiron-Mediated Route to the Guillou Intermediate (±)-*tert*-Butyl-7,8-dimethoxy-1,2,3,4-tetrahydrospiro[5*H*-2-benzazepine-5,1′-(4′-oxo-2′-cyclohexene)-2-carboxylate][48] (21)**

**(±)-Tricarbonyl{(1,2,3,4-η)-2,5β-dimethoxy-5α-[2′-(*tert*-butyl-diphenyl-silanyloxymethyl)-4′,5′-dimethoxyphenyl]-1,3-cyclohexadiene}iron(0) (13d):** Diphenyl-*tert*-butylsilyl 2-bromo-4,5-dimethoxybenzyl ether (4.0 equiv., 2.73 g, 5.63 mmol) was dissolved in dry diethyl ether (35 mL) at –78 °C. *n*BuLi (2.5 M in hexanes) (2.25 mL, 5.63 mmol, 4.0 equiv.) was added and a white precipitate formed. After 15 min, tricarbonyl[(1,2,3,4,5-η)-1,4-dimethoxycyclohexadienyl]iron hexafluorophosphate (**4**) (1.0 equiv., 515 mg, 1.41 mmol) in dry DCM (10 mL) at –78 °C was added. After 3.5 h at –78 °C, water (30 mL) was added and the reaction mixture was extracted into diethyl ether (6 × 30 mL). The combined organic extracts were washed with brine (25 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure to give the crude product (3.10 g) as a brown oil. Column chromatography (gradient of 2:1 to 1:1 hexane/diethyl ether on silica) afforded **13d** (545 mg, 796 μmol, 57%) as a cream gum; $R_f$ = 0.24 (1:1 diethyl ether/hexane). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.70 (t, $^3J_{H,H}$ = 6.1 Hz, 4 H, 2′′-H), 7.47 (s, 1 H, 3′-H), 7.44–7.34 (m, 6 H, 3′′-H, 4′′-H), 6.98 (s, 1 H, 6′-H), 5.21 (dd, $^3J_{H,H}$ = 6.8, 2.2 Hz, 1 H, 3-H), 4.90 (d, $^3J_{H,H}$ = 14.4 Hz, 1 H, $CH_2O$), 4.77 (d, $^3J_{H,H}$ = 14.4 Hz, 1 H, $CH_2O$), 3.94 (s, 3 H, 5′-OMe), 3.89 (s, 3 H, 4′-OMe), 3.63 (s, 3 H, 2-OMe), 3.18 (m, 1 H, 1-H), 2.87 (d, $^3J_{H,H}$ = 6.8 Hz, 1 H, 4-H), 2.77 (s, 3 H, 5-OMe), 1.96 (dd, $^3J_{H,H}$ = 14.7, 3.8 Hz, 1 H, 6β-H), 1.86 (dd, $^3J_{H,H}$ = 14.7, 2.0 Hz, 1 H, 6α-H), 1.12 (s, 9 H, Me) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 210.5 (Fe-CO), 147.6 (4′-C or 5′-C), 145.8 (4′-C or

5′-C), 139.9 (2-C), 135.5 (2′′-C), 133.5 (1′′-C), 133.3 (1′-C or 2′-C), 133.1 (1′-C or 2′-C), 129.6 (4′′-C), 127.6 (3′′-C), 111.7 (6′-C), 110.9 (3′-C), 82.3 (5-C), 64.9 (3-C), 63.0 ($CH_2O$), 56.2 (5′-OMe), 55.7 (4′-OMe), 54.9 (4-C), 54.5 (2-OMe), 51.6 (1-C), 49.1 (5-OMe), 42.1 (6-C), 26.9 (Me), 19.3 (Si-C) ppm. IR ($CDCl_3$): $\tilde{\nu}_{max}$ = 2933 and 2857 (C–H), 2048 and 1966 (C=O), 1581 and 1507 (C=C) $cm^{-1}$. MS (FAB): *m*/*z* (%) = 683 (1) $[M - H]^+$, 653 (20), 569 (54), 568 (95), 257 (97), 226 (100). HRMS (EI): *m*/*z*: calcd. for $C_{36}H_{39}O_8{}^{28}SiFe$: 683.1758; found 683.1762 $[M - H]^+$.

**(±)-Tricarbonyl{(1,2,3,4,5-η)-1-[2′-(*tert*-butyldiphenylsilanyloxymethyl)-4′,5′-dimethoxyphenyl]-4-methoxy-2,4-cyclohexadienyl}iron(1+) Tetrafluoroborate(1–) (14d):** Complex **13d** (1.0 equiv., 366 mg, 535 μmol) dissolved in dry DCM (5 mL) was added to triphenylcarbenium tetrafluoroborate (1.0 equiv., 177 mg, 535 μmol) and potassium carbonate (1.0 equiv., 74 mg, 535 μmol) in dry DCM (5 mL) at 0 °C. After 1 h, the reaction mixture was filtered and added slowly to dry diethyl ether (125 mL) and a yellow precipitate formed which was collected by filtration and washed with dry diethyl ether to give **14d** (277 mg, 374 μmol, 70%) as a yellow powder; $R_f$ = 0.11 (1:1 hexane/ethyl acetate). $^1H$ NMR (300 MHz, [D$_6$]acetone): $\delta$ = 7.72 (dd, $^3J_{H,H}$ = 7.7, 1.7 Hz, 2 H, 2′′-H), 7.64 (dd, $^3J_{H,H}$ = 7.9, 1.6 Hz, 2 H, 2′′-H), 7.54–7.39 (m, 6 H, 3′′-H, 4′′-H), 7.31 (dd, $^3J_{H,H}$ = 6.1, 2.5 Hz, 1 H, 3-H), 7.03 (s, 1 H, 6′-H), 6.74 (s, 1 H, 3′-H), 6.28 (ddd, $^3J_{H,H}$ = 6.1, 1.3, 1.1 Hz, 1 H, 2-H), 4.79 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H, $CH_2O$), 4.70 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H, $CH_2O$), 4.40 (ddd, $^3J_{H,H}$ = 6.3, 2.5, 1.3 Hz, 1 H, 5-H), 4.03 (s, 3 H, 4-OMe), 3.92 (s, 3 H, ArOMe), 3.79 (ddd, $^3J_{H,H}$ = 16.0, 6.3, 1.1 Hz, 1 H, 6β-H), 3.72 (s, 3 H, ArOMe), 2.90 (d, $^3J_{H,H}$ = 16.0 Hz, 1 H, 6α-H), 1.05 (s, 9 H, Me) ppm. $^{13}C$ NMR (75 MHz, [D$_6$]acetone): $\delta$ = 151.5 (4-C or 4′-C or 5′-C), 150.9 (4-C or 4′-C or 5′-C), 149.7 (4-C or 4′-C or 5′-C), 136.6 (2′′-C), 134.0 (1′′-C), 133.0 (2′-C), 131.1 (4′′-C), 129.0 (3′′-C), 128.9 (3′′-C), 127.4 (1′-C), 114.9 (6′-C), 114.5 (3′-C), 99.6 (1-C), 96.5 (2-C), 71.7 (3-C), 65.0 ($CH_2O$), 58.1 (4-OMe), 56.2 (ArOMe and ArOMe), 43.1 (5-C), 34.5 (6-C), 27.3 (Me), 19.7 (Si-C); m.p. 146–148 °C (dec.) ppm. IR ($CH_2Cl_2$): $\tilde{\nu}_{max}$ = 2103 and 2051 (C≡O), 1604 and 1499 (C=C) $cm^{-1}$. MS (ES): *m*/*z* (%) = 707 (37) $[M - BF_4 + NaOMe]^+$, 653 (41) $[M - BF_4]^+$, 483 (10), 429 (6), 139 (100), 81 (81). HRMS (EI): *m*/*z*: calcd. for $C_{35}H_{37}O_7{}^{28}Si^{54}Fe$: 653.1652; found 653.1662 $[M - BF_4]^+$.

**(±)-Tricarbonyl[(1,2,3,4-η)-5α-cyanomethyl-5β-(2′-hydroxymethyl-4′,5′-dimethoxyphenyl)-2-methoxy-1,3-cyclohexadiene]iron(0) (16):** 2-Trimethylsilylethyl cyanoethanoate (2.2 equiv., 237 mg, 1.28 mmol) in dry THF (2 mL) was added to sodium hydride (60% suspension in mineral oil) (2.0 equiv., 46 mg, 1.16 mmol) in dry THF (5 mL) at 0 °C. Stirred at 0 °C for 10 min, and then the reaction mixture was added to (±)-tricarbonyl{(1,2,3,4,5-η)-1-[2′-(*tert*-butyl-diphenylsilanyloxymethyl)-4′,5′-dimethoxyphenyl]-4-methoxy-2,4-cyclohexadienyl}iron(1+) tetrafluoroborate(1–) (**14d**) (1.0 equiv., 430 mg, 581 μmol) in dry THF (5 mL) at 0 °C and stirred for 1.5 h. TBAF (1 M in THF) (5.0 equiv., 2.9 mL, 2.90 mmol) was added to the reaction and it was refluxed for 2 h. The solvent was evaporated under reduced pressure. Water (15 mL) was added to the cooled reaction mixture and it was extracted with diethyl ether (4 × 15 mL). The combined organic layers were dried ($MgSO_4$), filtered and evaporated under reduced pressure to give the crude product (446 mg) as a brown oil. Column chromatography (gradient from 2:1 to 1:3 hexane/ethyl acetate on silica) afforded **16** (194 mg, 426 μmol, 73%) as a cream gum. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.14 (s, 1 H, 6′-H), 6.90 (s, 1 H, 3′-H), 5.28 (dd, $^3J_{H,H}$ = 6.8, 2.5 Hz, 1 H, 3-H), 4.49 (s, 2 H, $CH_2O$), 3.95 (s, 3 H, 5′-OMe), 3.86 (s, 3 H, 4′-OMe), 3.73 (s, 3 H, 2-OMe), 3.33 (dt, $^3J_{H,H}$ = 3.5, 2.5 Hz, 1 H, 1-H), 3.04 (d, $^3J_{H,H}$ = 16.6 Hz, 1 H, $CH_2CN$), 2.94 (d, $^3J_{H,H}$ = 6.8 Hz, 1 H, 4-H), 2.70 (d, $^3J_{H,H}$ = 16.6 Hz, 1 H, $CH_2CN$), 2.40 (dd, $^3J_{H,H}$ = 14.6, 2.5 Hz, 1 H, 6β-H), 2.13 (dd, $^3J_{H,H}$ = 14.6, 3.5 Hz, 1 H, 6α-H), 1.89 (br. s, 1 H, OH) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 211.6 (Fe-CO), 147.9 (4′-C or 5′-C), 147.4 (4′-C or 5′-C), 140.8 (2-C), 137.1 (1′-C), 130.4 (2′-C), 118.5 (CN), 115.0 (3′-C), 112.0 (6′-C), 64.2 (3-C), 63.2 ($CH_2OH$), 57.3 (4-C), 55.8 (4′-OMe), 55.7 (5′-OMe), 54.6 (2-OMe), 52.1 (1-C), 44.1 (5-C), 42.5 (6-C), 35.9 (5-$CH_2$) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3520 (O–H), 2920 (C–H), 2044 and 1963 (C≡O), 1605 and 1514 (C=C) $cm^{-1}$. MS [CI + ($NH_3$)]: *m*/*z* (%) = 473 (100) $[M + NH_4]^+$, 335 (24), 316 (27), 170 (26), 167 (39), 150 (31). HRMS (EI): *m*/*z*: calcd. for $C_{21}H_{25}O_7N_2{}^{54}Fe$: 471.1052; found 471.1055 $(M^+ + NH_4)$.

**(±)-Tricarbonyl[(1,2,3,4-η)-5α-(2′-amino-ethyl)-5β-(2′′-hydroxymethyl-4′′,5′′-dimethoxyphenyl)-2-methoxy-1,3-cyclohexadiene]iron(0) (17):** Complex **16** (1.0 equiv., 140 mg, 308 μmol) was dissolved in 2 M ammonia in ethanol (15 mL). Raney nickel (50% dispersion in water) (3 mL) was added to the reaction mixture and it was stirred under an atmosphere of hydrogen for 48 h. 2 M ammonia in ethanol (5 mL) and Raney nickel (50% dispersion in water) (1 mL) was added and the reaction was stirred under an atmosphere of hydrogen for 24 h. The reaction mixture was filtered through celite and the solvent evaporated under reduced pressure to the give crude product (179 mg) as a pale yellow oil. Column chromatography (10:2:1 ethyl acetate/methanol/ammonia on silica) afforded **17** (95 mg, 207 μmol, 67%) as a cream gum; $R_f$ = 0.30 (10:2:1 ethyl acetate/methanol/ammonia). $^1H$ NMR (300 MHz, [D$_6$]acetone): $\delta$ = 7.08 (s, 1 H, 6′-H), 6.99 (s, 1 H, 3′-H), 5.54 (dd, $^3J_{H,H}$ = 6.9, 2.5 Hz, 1 H, 3-H), 4.61 (d, $^3J_{H,H}$ = 11.7 Hz, 1 H, $CH_2OH$), 4.31 (d, $^3J_{H,H}$ = 11.7 Hz, 1 H, $CH_2OH$), 3.86 (s, 3 H, 5′-OMe), 3.78 (s, 6 H, 2-OMe and 4′-OMe), 3.43 (m, 1 H, 1-H), 3.33 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, 4-H), 3.13 (m, 2 H, $CH_2N$), 2.67 (dt, $^3J_{H,H}$ = 13.7, 6.7 Hz, 1 H, 5-$CH_2$), 2.46 (dd, $^3J_{H,H}$ = 14.5, 2.4 Hz, 1 H, 6β-H), 2.15–2.05 (m, 1 H, 6α-H), 1.73 (dt, $^3J_{H,H}$ = 13.7, 5.7 Hz, 1 H, 5-$CH_2$), 1.58 (br. s, 2 H, $NH_2$) ppm. $^{13}C$ NMR (75 MHz, [D$_6$]-acetone): $\delta$ = 148.3 (4′-C or 5′-C), 147.8 (4′-C or 5′-C), 141.8 (2-C or 1′-C), 139.4 (2-C or 1′-C), 134.0 (2′-C), 116.8 (3′-C), 113.7 (6′-C), 66.7 (3-C), 63.1 ($CH_2OH$), 61.6 (4-C), 56.1 (5′-OMe), 56.0 (4′-OMe), 55.1 (2-OMe), 54.3 (1-C), 49.7 (5-$CH_2$), 48.1 ($CH_2NH$), 46.7 (6-C), 46.3 (5-C) ppm. IR ($CDCl_3$): $\tilde{\nu}_{max}$ = 3373 and 3312 (N–H), 3006 (Ar–H), 2938 and 2847 (C–H), 2046 and 1976 (C≡O), 1515 (C=C) $cm^{-1}$. MS (ES): *m*/*z* (%) = 919 (11) $[M + M + H]^+$, 846 (4), 460 (57) $[M + H]^+$, 442 (100) $[M + H - H_2O]^+$, 386 (13), 302 (50). HRMS (EI): *m*/*z*: calcd. for $C_{21}H_{26}O_7N^{54}Fe$: 458.1100; found 458.1106 $(M^+ + H)$.

**(±)-Tricarbonyl{(2′,3′,4′,5′-η)-7,8-dimethoxy-1,2,3,4-tetrahydrospiro[5*H*-2-benzazepine-5,1′-(4′-methoxy-2′,4′-cyclohexadiene)]}iron(0) (18):** Iodine (1.5 equiv., 72 mg, 284 μmol) was added to complex **17** (1.0 equiv., 87 mg, 189 μmol), triphenylphosphane (1.5 equiv., 75 mg, 284 μmol), and imidazole (2.0 equiv., 26 mg, 379 μmol) in dry DCM (25 mL) at 0 °C and stirred for 18 h. Saturated sodium sulfite (5 mL) was added and stirred for 5 min. Water (10 mL) was added and the reaction mixture was extracted with DCM (4 × 10 mL). The combined organics were washed with brine (10 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure to give crude product (317 mg) as a pale yellow solid. Column chromatography (gradient from 10:2:0.1 to 10:2:0.5 ethyl acetate/methanol/ammonia on silica) afforded **18** (39 mg, 88.4 μmol, 47%) as a pale yellow oil; $R_f$ = 0.29 (10:2:0.5 ethyl acetate/methanol/ammonia). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.29 (s, 1 H, 6-H), 6.60 (s, 1 H, 9-H), 5.16 (dd, $^3J_{H,H}$ = 6.8, 2.3 Hz, 1 H, 3′-H), 3.98 (s, 3 H, 7-OMe), 3.85 (s, 3 H, 8-OMe), 3.81 (d, $^3J_{H,H}$ = 14.7 Hz, 1 H, 1-H), 3.70 (s, 3 H, 4′-OMe), 3.67 (d, $^3J_{H,H}$ = 14.7 Hz,

1 H, 1-H), 3.41 (m, 1 H, 5′-H), 3.23 (d, $^3J_{H,H}$ = 13.8 Hz, 1 H, 3-H), 3.13 (dd, $^3J_{H,H}$ = 13.8, 11.6 Hz, 1 H, 3-H), 2.82–2.75 (m, 1 H, 4-H), 2.81 (d, $^3J_{H,H}$ = 6.8 Hz, 1 H, 2′-H), 2.02 (s, 1 H, NH), 1.88–1.78 (m, 1 H, 4-H), 1.82 (d, $^3J_{H,H}$ = 14.0 Hz, 1 H, 6′β-H), 1.43 (d, $^3J_{H,H}$ = 14.0 Hz, 1 H, 6′α-H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 146.4 (7-C or 8-C), 146.1 (7-C or 8-C), 141.1 (4′-C or 5a-C), 140.1 (4′-C or 5a-C), 131.8 (9a-C), 114.2 (9-C), 112.4 (6-C), 64.5 (3′-C), 63.1 (2′-C), 55.9 (8-OMe), 55.7 (7-OMe), 54.5 (4′-OMe), 53.7 (1-C), 53.3 (5′-C), 50.3 (3-C), 47.4 (6′-C), 45.7 (5-C), 37.1 (4-C) ppm. IR ($CDCl_3$): $\tilde{\nu}_{max}$ = 3417 (N–H), 3007 (Ar–H), 2935 and 2853 (C–H), 2046 and 1974 (C≡O), 1606 and 1515 (C=C) cm$^{-1}$. MS (CI): *m*/*z* (%) = 442 (11) [M + H]$^+$, 318 (16), 305 (100). HRMS (EI): *m*/*z*: calcd. for $C_{21}H_{24}O_6N^{56}Fe$: 442.0948; found 442.0947 ($M^+$+H).

**(±)-Tricarbonyl{*tert*-butyl (2′,3′,4′,5′-η)-7,8-Dimethoxy-1,2,3,4-tetrahydrospiro[5*H*-2-benzazepine-5,1′-(4′-methoxy-2′,4′-cyclohexadiene)-2-carboxylate]}iron(0) (20):** Boc anhydride (2.0 equiv., 26 μL, 115 μmol) was added to complex **18** (1.0 equiv., 25 mg, 56.7 μmol) in chloroform (3 mL) and stirred overnight at room temp. The solvent was evaporated under reduced pressure and was purified by column chromatography (2:1 diethyl ether/hexane on silica) to give **20** (18 mg, 33.2 μmol, 59%) as a cream powder; $R_f$ = 0.30 (2:1 diethyl ether/hexane). $^1$H NMR (400 MHz, $CDCl_3$) (two rotamers): $\delta$ = 7.25 and 7.22 (s, 1 H, 6-H), 6.75 and 6.66 (s, 1 H, 9-H), 5.16 (dd, $^3J_{H,H}$ = 6.7, 2.2 Hz, 1 H, 3′-H), 4.43 and 4.34 (d, $^3J_{H,H}$ = 15.3 Hz, 1 H, 1-H), 4.17 and 4.09 (d, $^3J_{H,H}$ = 15.3 Hz, 1 H, 1-H), 3.97 (s, 3 H, 7-OMe), 3.92 and 3.60 (m, 1 H, 3-H), 3.86 (s, 3 H, 8-OMe), 3.70 (s, 3 H, 2-OMe), 3.48 and 3.26 (m, 1 H, 3-H), 3.39 (m, 1 H, 5′-H), 2.80 (d, $^3J_{H,H}$ = 6.7 Hz, 1 H, 2′-H), 2.66 and 2.55 (dm, $^3J_{H,H}$ = 14.5 Hz, 1 H, 4-H), 1.94–1.73 (m, 1 H, 4-H), 1.86 (d, $^3J_{H,H}$ = 15.2 Hz, 1 H, 6′β-H), 1.52 and 1.41 (s, 9 H, $Me_{BOC}$), 1.51–1.44 (m, 1 H, 6′α-H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$) (two rotamers): $\delta$ = 154.5 (O=$C_{BOC}$), 146.4 (7-C or 8-C), 145.8 (7-C or 8-C), 140.1 (4′-C or 5a-C), 139.8 (4′-C or 5a-C), 129.4 (9a-C), 114.6 and 114.4 (9-C), 112.2 and 111.8 (6-C), 79.6 (O-$C_{BOC}$), 64.5 (3′-C), 62.9 (2′-C), 55.8 (8-OMe), 55.6 (7-OMe), 54.5 (4′-OMe), 53.3 (5-C), 51.8 and 51.3 (Ar$CH_2$N), 46.6 and 46.3 (3-C), 45.6 (6′-C), 45.2 (5-C), 37.6 and 37.5 (4-C), 28.5 and 28.3 ($Me_{BOC}$) ppm. IR ($CDCl_3$): $\tilde{\nu}_{max}$ = 3002 (Ar–H), 2937 and 2850 (C–H), 2046 and 1973 (C≡O), 1682 and 1515 (C=C) cm$^{-1}$. MS (CI): *m*/*z* (%) = 542 (1) [M + H]$^+$, 503 (10), 442 (11), 302 (100). HRMS (EI): *m*/*z*: calcd. for $C_{26}H_{32}O_8NFe$: 542.1472; found 542.1478 [M + H]$^+$.

**(±)-*tert*-Butyl 7,8-Dimethoxy-1,2,3,4-tetrahydrospiro[5*H*-2-benzazepine-5,1′-(4′-oxo-2′-cyclohexene)]-2-carboxylate (21):**[48] Anhydrous trimethylamine *N*-oxide (20 equiv., 45 mg, 592 μmol) was added to complex **20** (1.0 equiv., 16 mg, 29.6 μmol) dissolved in acetone (1 mL) and stirred at room temp. overnight. The mixture was filtered through a short silica column (eluting with acetone) and evaporated under reduced pressure to give 13 mg of crude solid which was redissolved in methanol (0.2 mL). Oxalic acid dihydrate (12 mg, 97.1 μmol, 3.0 equiv.) was dissolved in water (0.2 mL) and added to the reaction mixture and stirred for 30 min. Water (0.5 mL) was added and the reaction mixture was extracted with diethyl ether (3 × 0.5 mL). The combined organic extracts were evaporated under reduced pressure to give crude product (12 mg) as a pale yellow oil. Column chromatography (diethyl ether on silica) afforded **21**[48] (10 mg, 25.8 μmol, 87%) as a pale yellow oil; $R_f$ = 0.13 (4:1 diethyl ether/hexane). $^1$H NMR (400 MHz, $CDCl_3$) (two rotamers): $\delta$ = 6.83 (d, $^3J_{H,H}$ = 10.1 Hz, 1 H, 2′-H), 6.77 and 6.69 (s, 1 H, 6-H), 6.68 and 6.66 (s, 1 H, 9-H), 6.11 (d, $^3J_{H,H}$ = 10.1 Hz, 1 H, 3′-H), 4.57–4.41 (m, 2 H, 1-H), 3.87 (s, 3 H, 7-OMe), 3.80 (s, 3 H, 8-OMe), 3.75 (m, 2 H, 3-H), 2.49–2.15 (m, 5 H, 5′-$H_2$, 6′-$H_2$ and 4-H), 1.94 and 1.91 (m, 1 H, 4-H), 1.43 and 1.36 (s, 9 H, Me) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$) (two rotamers): $\delta$ = 199.3 (4′-C), 157.8 (2′-C), 155.0 (O = $C_{BOC}$), 147.5 (7-C or 8-C), 147.4 (7-C or 8-C), 134.5 (5a-C), 130.8 and 130.6 (9a-C), 127.3 (3′-C), 113.7 (9-C), 113.2 (6-C), 80.0 (O-$C_{BOC}$), 56.0 (8-OMe), 55.8 (7-OMe), 50.4 and 49.4 (1-C), 44.6 and 44.5 (3-H), 43.5 (5-C), 36.2 and 35.8 (4-C), 34.2 (5′-C), 33.4 and 33.1 (6′-C), 28.5 and 28.3 ($Me_{BOC}$) ppm. IR ($CDCl_3$): $\tilde{\nu}_{max}$ = 2973 and 2934 (C–H), 1686 (C=O), 1607 and 1519 (C=C) cm$^{-1}$. MS (EI): *m*/*z* (%) = 387 (6) [M]$^+$, 330 (100) [M – $C(CH_3)_3$]$^+$. HRMS (EI): *m*/*z*: calcd. for $C_{22}H_{29}O_5N$: 387.2040; found 387.2040 ($M^+$).

**General Procedures for the Preparation of (1-Aryl-4-methoxycyclohexadienyl)iron Electrophiles and Their Reactions with Malononitrile-Derived Nucleophiles in *1,1* Iterative Synthetic Routes to Alkaloids**

**General Procedure A: Formation of Ethers from Bromobenzyl Alcohols or Bromophenols:** A solution of the bromobenzyl alcohol or bromophenol (1 equiv.) in dry THF was added over 1 h to NaH (60% suspension in mineral oil; 1.0–1.55 equiv.) in dry THF at 0 °C. The reaction mixture was stirred at 0 °C for 1 h to give a pale brown solution. Allyl bromide, methoxymethyl chloride or 2-(trimethylsilyl)ethoxymethyl chloride (1.75–2.2 equiv.) was added at 0 °C. The reaction mixture was stirred at 0 °C to reflux for 2–96 h during and a white precipitate formed. The mixture was quenched with water and diethyl ether and extracted into diethyl ether. The combined organic extracts were washed with water, dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure. Column chromatography over silica gel afforded the following compounds: 1-bromo-2-(methoxymethoxy)-3-methoxybenzene, 1-bromo-3-methoxy-2-[2-(trimethylsilyl)ethoxymethoxy]benzene, 1-bromo-2-(methoxymethoxy)benzene, 1-(allyloxy)-3-bromo-2-methoxybenzene, 1-bromo-3,4-dimethoxy-6-[(methoxymethoxy)methyl]-benzene, or 1-bromo-3,4-dimethoxy-6-[2-(trimethylsilylethoxy)-methoxymethyl]benzene.

**General Procedure B. Silylation of Bromobenzyl Alcohols:** Imidazole (2.0 equiv.) and then the bromobenzyl alcohol (1.0 equiv.) were added to *tert*-butyldimethylsilyl chloride (TBDMSCl), *tert*-butyldiphenylsilyl chloride (TBDPSCl), or triisopropylsilyl chloride (TIPSCl) (1.0–1.2 equiv.) in THF or DMF (20–100 mL). The mixture was stirred at room temp. for 2 days. Water was added and the reaction mixture was extracted into diethyl ether. The combined organic extracts were washed with water, brine, dried ($MgSO_4$), filtered and evaporated under reduced pressure to give the crude product. The crude product was purified by crystallisation or column chromatography over silica gel to give [(2-bromo-4,5-dimethoxybenzyl)oxy]-*tert*-butyldiphenylsilane, [(2-bromo-4,5-dimethoxybenzyl)oxy]-*tert*-butyldimethylsilane, or [(2-bromo-4,5-dimethoxybenzyl)oxy]triisopropylsilane.

**General Procedure C: Addition of Aryllithium Reagents to Tricarbonyl[(1,2,3,4,5-η)-1,4-dimethoxy-cyclohexadienyl]iron Hexafluorophosphate (4):** The aryl bromide (2–3.5 equiv.) was dissolved in dry diethyl ether (5–50 mL) and cooled to –78 °C under nitrogen. *n*-Butyllithium (1.6–2.5 M in hexanes) (2–3.5 equiv.) was added and after stirring for 1 h at –78 °C, a white suspension formed.

**Variation 1:** This was cooled to –100 °C. The hexafluorophosphate **4** (1 equiv., 2.2 g, 6.0 mmol) was dissolved in dry dichloromethane (20 mL) and cooled to –100 °C. The slurry of the aryllithium reagent at –100 °C was added through a cannula and the mixture was stirred for 10–30 min. The reaction was quenched at –100 °C with water (25–50 mL) and diethyl ether (25–50 mL) and warmed to room temp. The mixture was extracted into diethyl ether (3 × 25–50 mL) and water (3 × 25–50 mL).

**Variation 2:** Hexafluorophosphate **4** (1.0 equiv.) in dry dichloromethane (15–40 mL) at –78 °C was added through a cannula. After stirring for 2–4 h at –78 °C, water (25–50 mL) was added and the reaction mixture was extracted into diethyl ether (1 × 100 mL, 3 × 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated under reduced pressure to give the crude product. Column chromatography over silica gel (eluting with petroleum ether or hexane/diethyl ether mixtures) afforded the (5β-methoxy-5α-aryl-1,3-cyclohexadiene)iron(0) complexes.

**General Procedure D: Preparation of 1-Aryl Salts by Demethoxylation Using Triphenylcarbenium Ion Reagents. Variation 1:** The (5α-aryl-5β-methoxy-1,3-cyclohexadiene)iron(0) complex (1.0 equiv.) dissolved in dry dichloromethane (5 mL) was added to triphenylcarbenium tetrafluoroborate (1.0 equiv.) and potassium carbonate (1.0 equiv.) in dry dichloromethane (2–5 mL) at 0 °C.

**Variation 2:** Triphenylcarbenium tetrafluoroborate (1 equiv.) dissolved in freshly distilled dichloromethane (5 mL) was added to a solution of the (5α-aryl-5β-methoxy-1,3-cyclohexadiene)iron(0) (1 equiv.) and potassium carbonate (0.2 equiv.) in freshly distilled dichloromethane (2 mL) at 0 °C.

**Variation 3:** Triphenylcarbenium tetrafluoroborate or hexafluorophosphate (1 equiv.) was dissolved in freshly distilled dichloromethane (20–30 mL) with a slurry of potassium carbonate (0.3–1.0 equiv.) and stirred at 0 °C for 5–10 min. The (5β-methoxy-5α-aryl-1,3-cyclohexadiene)iron(0) complex (1 equiv.) was dissolved in dichloromethane (5–10 mL) and was added to the solution. After stirring for 1 h at 0 °C, the reaction mixture was allowed to settle and the liquid layer was added slowly to dry diethyl ether (75–200 mL) and a yellow precipitate formed which was collected by filtration and washed with dry diethyl ether to give the (1-arylcyclohexadienyl)iron(1+) salt.

**General Procedure E. Reaction of 2-Trimethylsilylethyl Sodiocyanoethanoate with (1-Arylcyclohexadienyl)iron(1+) Complexes and TBAF-Mediated Desylylation/Dealkylation/Decarboxylation Reactions:** 2-Trimethylsilylethyl cyanoethanoate (1.6–2.0 equiv.) in dry THF (1–5 mL) was added to sodium hydride (60% suspension in mineral oil) (1.5–2.0 equiv.) in dry THF (2–5 mL) at 0 °C and stirred for 15 min at 0 °C to give a white suspension of 2-trimethylsilylethyl sodiocyanoethanoate.

**Variation 1:** The mixture was added to a suspension of the (1-arylcyclohexadienyl)iron cation (l equiv.) in THF (2–5 mL) at 0 °C and the reaction was stirred for 1 h. The reaction was quenched with 2 M HC1 (25 mL), water (25 mL) and diethyl ether (25 mL) and extracted into diethyl ether (3 × 25 mL). The combined organic extracts were washed with water (3 × 25 mL), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to afford a yellow gum of tricarbonyl{2-trimethylsilylethyl [(2,3,4,5-η)-1β-aryl-4-methoxy-2,4-cyclohexadien-1α-yl]cyanoethanoate}iron(0) which was redisolved in dry THF (10 mL). TBAF (1 M solution in THF) (0.9–2.2 equiv.) was added and the mixture was heated at reflux for 1–12 h. The cooled solution was quenched with saturated ammonium chloride solution (5 mL), water (5 mL) and diethyl ether (5 mL) and extracted into diethyl ether (3 × 25 mL). The combined organic extracts were washed with water (3 × 25 mL), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to afford a yellow gum. Column chromatography over silica gel eluted with diethyl ether/petroleum ether or hexane mixtures afforded tricarbonyl[(1,2,3,4-η)-5α-cyanomethyl-2-methoxy-5β-(2-methoxymethoxymethyl-3,4-dimethoxyphenyl)-1,3-cyclohexadiene]iron(0), tricarbonyl[(1,2,3,4-η)-5α-cyanomethyl-2-methoxy-5β-[(2-(trimethylsilylethyl)methoxymethyl]-3,4-dimethoxyphenyl)-1,3-cyclohexadiene]iron(0) or tricarbonyl[(1,2,3,4-η)-5α-cyanomethyl-5β-(2′-hydroxymethyl-4′,5′-dimethoxyphenyl)-2-methoxy-1,3-cyclohexadiene]iron(0).

**Variation 2:** The (1-arylcyclohexadienyl)iron cation (l equiv.) in THF (2–5 mL) was added and the a white suspension of 2-trimethylsilylethyl sodiocyanoethanoateand the mixture was stirred at 0 °C for a further 2 h. TBAF (1 M solution in THF) (4.0 equiv.) was added to the reaction mixture which was then heated at reflux for 1 h. Water (3 mL) was added to the cooled reaction mixture which was extracted with diethyl ether (4 × 3 mL). The combined organic layers were dried ($K_2CO_3$), and the product was isolated as described in Variation 1 to give tricarbonyl[(1,2,3,4-η)-5α-cyanomethyl-5β-(2′-hydroxy-3′-methoxyphenyl)-2-methoxy-1,3-cyclohexadiene]iron(0).

**Preparations of Protected Bromobenzyl Alcohols and Bromophenols**

**1-Bromo-3-methoxy-2-(methoxymethoxy)benzene (5a):** Following general procedure A, 2-bromo-3-methoxyphenol (l equiv., 5 g, 24.6 mmol), NaH (60% suspension in mineral oil) (1 equiv., 0.99 g, 24.6 mmol) in dry THF (20 mL) at 0 °C for 30 min gave a pale brown solution. Methoxymethyl chloride (1.1 equiv., 27 mmol, 2.2 g, 2.1 mL) was added. The reaction mixture was stirred at room temp. for 18 h then worked up as described in general procedure A. Column chromatography (1:4 diethyl ether/petroleum ether) afforded **5a** as a colourless liquid (5.18 g, 21 mmol, 85%).[71] $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 7.12 (dd, $^3J_{H,H}$ = 7.9, 1.7 Hz, 1 H, 6-H), 6.91 (t, $^3J_{H,H}$ = 7.9 Hz, 1 H, 5-H), 6.84 (dd, $^3J_{H,H}$ = 7.9, 1.7 Hz, 1 H, 4-H), 5.16 (s, 2 H, $OCH_2O$), 3.81 (s, 3 H, ArOMe), 3.65 (s, 3 H, OMe) ppm. MS (EI): *m*/*z* (%) = 248 (55) [$^{81}$Br, M]$^+$, 246 (57) [$^{79}$Br, M]$^+$, 218 (48) [$^{81}$Br, M – $2CH_3$]$^+$, 216 (49) [$^{79}$Br, M – $2CH_3$]$^+$, 167 (14), 138 (8), 94 (16), 79 (16), 45 (100). HRMS (FAB): *m*/*z*: calcd. for $C_9H_{11}O_3{}^{79}Br$: 245.9892; found 245.9892.

**1-Bromo-3-methoxy-2-[2′-(trimethylsilyl)ethoxymethoxy]benzene (5b):** 2-Bromo-3-methoxyphenol (1.0 equiv., 11.5 g, 56.9 mmol) was dissolved in dry dichloromethane (200 mL) and cooled to 0 °C. [2-(Trimethylsilyl)ethoxy]methyl chloride (1.1 equiv., 11.1 mL, 167 mmol) and then diisopropylethylamine (2.0 equiv., 20 mL, 114 mmol) were added. The reaction mixture was stirred for 1 h at 0 °C, and then evaporated under reduced pressure. Water (100 mL) was added. The reaction mixture was extracted with dichloromethane (3 × 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and evaporated under reduced pressure to give crude product as a yellow oil. Column chromatography over silica gel (eluting with a gradient of 10:1 to 4:1 hexane/diethyl ether) afforded **5b** (18.6 g, 55.8 mmol, 98%) as a colourless oil; $R_f$ = 0.39 (4:1 hexane/diethyl ether). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.12 (dd, $^3J_{H,H}$ = 8.0, 1.5 Hz, 1 H, 6-H), 6.91 (dd, $^3J_{H,H}$ = 8.0, 8.2 Hz, 1 H, 5-H), 6.83 (dd, $^3J_{H,H}$ = 8.2, 1.5 Hz, 1 H, 4-H), 5.21 (s, 2 H, $OCH_2O$), 3.96 (m, 2 H, $OCH_2$), 3.81 (s, 3 H, ArOMe), 0.98 (m, 2 H, $CH_2Si$), 0.02 (s, 9 H, $SiMe_3$) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta_C$ = 153.5 (2-C), 143.2 (3-C), 124.9 (4-C and 5-C), 117.8 (1-C), 111.5 (6-C), 96.5 ($OCH_2O$), 67.5 ($OCH_2$), 55.9 (ArOMe), 18.0 ($CH_2Si$), –1.5 ($SiMe_3$) ppm. IR ($CDCl_3$): $\tilde{\nu}_{max}$ = 2953 and 2896 (C–H), 1585 (C=C), 1098 (C–O) cm$^{-1}$. IR (neat): $\tilde{\nu}_{max}$ = 2954, 1585, 1478, 1250, 1038, 954 cm$^{-1}$. MS (EI): *m*/*z* (%) = 276 (9) [$^{81}$Br, M – $SiMe_2$]$^+$, 274 (9) [$^{79}$Br, M – $SiMe_2$]$^+$, 261 (20) [$^{81}$Br, M – $SiMe_3$]$^+$, 259 (20) [$^{79}$Br, M – $SiMe_3$]$^+$, 246 (25) [$^{81}$Br, M – $SiMe_3$ – Me]$^+$, 244 (23) [$^{79}$Br, M – $SiMe_3$ – Me]$^+$, 73 (100). HRMS (EI): *m*/*z*: calcd. for $C_{13}H_{25}O_3{}^{79}BrN^{28}Si$: 350.0787; found 350.0787 [M + $NH_4$]$^+$.

**1-Bromo-2-(methoxymethoxy)benzene (5c):**[72] Following general procedure A, 2-bromophenol (l equiv., 10 g, 58 mmol), NaH (60% suspension in mineral oil) (1 equiv., 2.3 g, 58 mmol) in dry THF (40 mL) at 0 °C for 30 min gave a pale brown solution. Methoxymethyl chloride (2 equiv., 116 mmol, 9.3 g, 8.8 mL) was added

at 0 °C. The reaction mixture was stirred at 0 °C for 2 h then worked up as described in general procedure A. Column chromatography (1:10 diethyl ether/petroleum ether) afforded **5c** as a clear liquid (6.67 g, 31 mmol, 53%).[72] $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 7.51 (dd, $^3J_{H,H}$ = 7.9, 1.7 Hz, 1 H, 3-H), 7.20 (ddd, $^3J_{H,H}$ = 8.3, 7.3, 1.7 Hz, 1 H, 5-H), 7.11 (dd, $^3J_{H,H}$ = 8.3, 1.7 Hz, 1 H, 6-H), 6.85 (ddd, $^3J_{H,H}$ = 7.9, 7.3, 1.7 Hz, 1 H, 4-H), 5.20 (s, 2 H, $OCH_2O$), 3.48 (s, 3 H, OMe) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2960, 1589, 1479, 1155, 751 cm$^{-1}$. MS (EI): *m*/*z* (%) = 218, (31) [$^{81}$Br, M]$^+$, 216, (32) [$^{79}$Br, M]$^+$, 188 (9) [$^{81}$Br, M – $OCH_3$ + H]$^+$, 186 (10) [$^{79}$Br, M – $OCH_3$ + H]$^+$, 172 (5), 157 (9) [$^{81}$Br, M – $OCH_2$-$OCH_3$]$^+$, 155 (7), [$^{79}$Br, M – $OCH_2OCH_3$]$^+$, 145 (11), 143 (11), 131 (2), 119 (4), 92 (4), 75 (7), 63 (13), 45 (100).

**2-Allyloxy-1-bromo-3-methoxybenzene (5d):** Following general procedure A, 6-bromoguaiacol (1 equiv., 1 g, 4.9 mmol) in dry THF (10 mL) was added over 10 min to NaH (60% suspension in mineral oil) (1 equiv., 0.196 g, 4.9 mmol) in dry THF (20 mL) at 0 °C for 30 min gave a pale brown solution. Allyl bromide (2 equiv., 1.2 g, 9.8 mmol) was added at 0 °C. The reaction mixture was heated at reflux for 4 days then worked up as described in general procedure A. Column chromatography (2:3 diethyl ether/petroleum ether) afforded **5d** (0.448 g, 1.8 mmol, 38%) as a pale yellow oil. $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 7.13 (dd, $^3J_{H,H}$ = 7.9, 1.7 Hz, 1 H, 6-H), 6.92 (dd, $^3J_{H,H}$ = 8.3, 7.9 Hz, 1 H, 5-H), 6.84 (dd, $^3J_{H,H}$ = 8.3, 1.7 Hz, 1 H,4-H), 6.14 (ddt, $^3J_{H,H}$ = 11.8, 10.2, 5.9 Hz, 1 H, CH), 5.38 (ddd, $^3J_{H,H}$ = 11.8, 3.0, 1.3 Hz, 1 H, =$CH_2$), 5.23 (ddd, $^3J_{H,H}$ = 10.2, 3.0, 1.0 Hz, 1 H, =$CH_2$), 4.54 (ddd, $^3J_{H,H}$ = 5.9, 1.3, 1.0 Hz, 2 H, $OCH_2$), 3.85 (s, 3 H, OMe) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2939, 1584, 1477, 1037, 769 cm$^{-1}$. MS (EI): *m*/*z* (%) = (%)244 (27) [$^{81}$Br, M]$^+$, 242 (20) [$^{79}$Br, M]$^+$, 203 (55) [$^{81}$Br, M – $CH_2CHCH_2$]$^+$, 201 (59) [$^{79}$Br, M – $CH_2CHCH_2$]$^+$, 94 (100). Elemental analysis calcd. (%) for $C_{10}H_{11}O_2Br$ (243.10): C 49.6; H 4.6; found C 49.6; H 4.6.

**1-Bromo-4,5-dimethoxy-2-(methoxymethyl)benzene (5e):**[73] Following general procedure A, sodium hydride (60% suspension in mineral oil) (1.55 equiv., 618 mg, 15.5 mmol) in dry THF (20 mL) was cooled to 0 °C. (2-Bromo-4,5-dimethoxyphenyl)methanol (1.0 equiv., 2.46 g, 9.96 mmol) dissolved in dry THF (20 mL) was added. After 30 min, methyl iodide (1.6 equiv., 0.99 mL, 16.0 mmol) was added. After 4 h at 0 °C, water (50 mL) was added and then worked up as described in general procedure A. Column chromatography (2:1 diethyl ether/hexane) afforded 1-bromo-4,5-dimethoxy-2-(methoxymethyl)benzene (2.42 g, 93%) as a colourless solid; m.p. 41–43 °C (lit.[73] 45–46 °C); $R_f$ = 0.24 (2:1 hexane/diethyl ether). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.01 (s, 1 H, 6-H), 6.98 (s, 1 H, 3-H), 4.46 (s, 2 H, $CH_2O$), 3.88 (s, 3 H, ArOMe), 3.86 (s, 3 H, ArOMe), 3.45 (s, 3 H, OMe) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 148.7 (4-C or 5-C), 148.3 (4-C or 5-C), 129.4 (1-C), 115.1 (3-C), 112.6 (2-C), 111.6 (6-C), 73.5 ($CH_2O$), 58.3 ($OMe_{MOM}$), 56.0 (4-OMe), 55.9 (5-OMe) ppm. IR ($CDCl_3$): $\tilde{\nu}_{max}$ = 2933 and 2838 (C–H), 1604 and 1506 (C=C), 1098 (C–O) cm$^{-1}$.

**2-[(2′-Bromo-4′,5′-dimethoxybenzyl)oxy]tetrahydropyran (5f):** *p*-Toluenesulfonic acid monohydrate (0.11 equiv., 92 mg, 484 μmol) was added to (2-bromo-4,5-dimethoxyphenyl)methanol (1.0 equiv., 1.05 g, 4.25 mmol) dissolved in dry DCM (20 mL) and stirred at room temp. Dihydropyran (1.5 equiv., 0.58 mL, 6.36 mmol) was added to the reaction mixture slowly. Stirred at room temp. for 1.5 h. The reaction mixture was washed with 5% aqueous potassium carbonate (20 mL), washed with brine (20 mL), dried ($K_2CO_3$), filtered and evaporated under reduced pressure to give the crude product (1.52 g) as a yellow oil. The crude product was purified by column chromatography over silica gel (eluting with a gradient from 2:1 hexane/diethyl ether to 1:1 hexane/diethyl ether) to give 2-[(2′-bromo-4′,5′-dimethoxybenzyl)oxy]tetrahydropyran (960 mg, 2.90 mmol, 66%) as a colourless oil; $R_f$ = 0.37 (1:1 diethyl ether/hexane). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.00 (s, 2 H, 3′-H and 6′-H), 4.74 (d, $^3J_{H,H}$ = 12.5 Hz, 1 H, $ArCH_2O$), 4.73 (s, 1 H, OCHO), 4.51 (d, $^3J_{H,H}$ = 12.5 Hz, 1 H, $ArCH_2O$), 3.93 (ddd, $^3J_{H,H}$ = 11.3, 8.1, 3.4 Hz, 1 H, $CH_2O$), 3.87 (s, 3 H, ArOMe), 3.85 (s, 3 H, ArOMe), 3.55 (dd, $^3J_{H,H}$ = 11.3, 4.4 Hz, 1 H, $CH_2O$), 1.90–1.80 (m, 1 H, 11-H), 1.80–1.62 (m, 2 H, 12-$H_2$), 1.62–1.48 (m, 3 H, 10-$H_2$ and 11-H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 148.7 (4′-C or 5′-C), 148.3 (4′-C or 5′-C), 129.6 (1′-C), 115.3 (3′-C), 113.0 (2′-C), 112.2 (6′-C), 98.3 (2-C), 68.5 ($CH_2O$), 62.3 (6-C), 56.1 (ArOMe), 56.0 (ArOMe), 30.5 (3-C), 25.4 (5-C), 19.5 (4-C) ppm. IR ($CDCl_3$): $\tilde{\nu}_{max}$ = 3010 (Ar–H), 2943 and 2850 (C–H), 1604 and 1507 (C=C) cm$^{-1}$. MS (EI): *m*/*z* (%) = 332 (4) [$^{81}$Br, M]$^+$, 330 (4) [$^{79}$Br, M]$^+$, 231 (64), 229 (59), 151 (100), 85 (45). HRMS (EI): *m*/*z*: calcd. for $C_{14}H_{19}O_4{}^{79}Br$: 330.0461; found 330.0466.

**1-Bromo-4,5-dimethoxy-2-[(methoxymethoxy)methyl]benzene (5g):**[74] Following general procedure A, a solution of (2-bromo-4,5-dimethoxyphenyl)methanol (1 equiv., 4.766 g, 19.3 mmol) in dry THF (50 mL) was added over 1 h to NaH (60% suspension in mineral oil) (1.1 equiv., 0.849 g, 21.2 mmol) in dry THF (20 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h to give a pale brown solution. Methoxymethyl chloride (2.2 equiv., 3.2 mL, 42.5 mmol) was added at 0 °C. The reaction mixture was stirred at room temp. for 18 h during which time a white precipitate formed. The mixture was quenched with water (50 mL) and diethyl ether (50 mL) and then worked up as described in general procedure A. Column chromatography (3:7 diethyl ether/petroleum ether) afforded 1-bromo-4,5-dimethoxy-2-[(methoxymethoxy)methyl]benzene as a clear liquid (3.42 g, 11.8 mmol, 61%). $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 7.02 (s, 1 H, 3-H or 6-H), 7.00 (s, 1 H, 3-H or 6-H), 4.75 (s, 2 H, $ArCH_2O$), 4.60 (s, 2 H, $OCH_2O$), 3.89 (s, 3 H, Ar-OMe), 3.86 (s, 3 H, Ar-OMe), 3.43 (s, 3 H, OMe); $\delta$ = 148.8 (4-C or 5-C), 148.2 (4-C or 5-C), 129.1 (1-C), 115.2 (3-C), 113.0 (2-C), 112.1 (6-C), 95.9 ($OCH_2O$), 68.6 ($ArCH_2O$), 56.0 (4-OMe or 5-OMe), 55.9 (4-OMe or 5-OMe), 55.4 ($OMe_{MOM}$) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2937, 1604, 1507, 1384, 1264, 1162, 1056, 804 cm$^{-1}$. MS (EI): *m*/*z* (%) = 292, (43) [$^{81}$Br, M]$^+$, 290 (44) [$^{79}$Br, M]$^+$, 231 (93) [M – OMe]$^+$, 229 (100) [M – OMe]$^+$. Elemental analysis calcd. (%) for $C_{11}H_{15}O_4Br$ (291.14): C 45.4; H 5.2; Br 27.5; found C 45.2; H 4.9; Br 27.5.

**1-Bromo-4,5-dimethoxy-2-[(trimethylsilyl)ethoxymethoxymethyl]-benzene (5h):** Following general procedure A, a solution of (2-bromo-4,5-dimethoxyphenyl)methanol (1 equiv., 4.23 g, 17.1 mmol) in dry THF (50 mL) was added over 1 h to NaH (60% suspension in mineral oil) (1.1 equiv., 0.754 g, 18.9 mmol) in dry THF (20 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h to give a pale brown solution. 2-Trimethylsilylethoxymethyl chloride (1.75 equiv., 5 g, 30.0 mmol) was added at 0 °C. The reaction mixture was heated at reflux for 18 h during which time a white precipitate formed. The mixture was quenched with water (50 mL) and diethyl ether (50 mL) and then worked up as described in general procedure A. Column chromatography (1:4 diethyl ether/petroleum ether) afforded 1-bromo-4,5-dimethoxy-2-[(trimethylsilyl)ethoxymethoxymethyl]benzene as a clear liquid (3.765 g, 10 mmol, 58%). $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 6.99 (s, 1 H, 3-H or 6-H), 6.96 (s, 1 H, 3-H or 6-H), 4.77 (s, 2 H, $ArCH_2O$), 4.58 (s, 2 H, $OCH_2O$), 3.85 (s, 3 H, Ar-OMe), 3.83 (s, 3 H, Ar-OMe), 3.67 (m, 2 H, $OCH_2$), 0.95 (m, 2 H, $CH_2SiMe_3$), –0.01 (s, 9 H, $SiMe_3$); $\delta$ = 148.8 (4-C or 5-C), 148.3 (4-C or 5-C), 129.3 (1-C), 115.3 (3-C), 113.1 (2-C), 112.2 (6-C), 94.3 ($OCH_2O$), 68.7 ($ArCH_2O$), 65.3 ($OCH_2$), 56.0 (4-OMe or 5-OMe), 55.9 (4-OMe or 5-

OMe), 18.0 ($CH_2Si$), –1.5 ($SiMe_3$) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2952, 1604, 1507, 1384, 1264, 1060, 838 $cm^{-1}$. MS (EI): *m*/*z* (%) = 378, (33) [$^{81}$Br, M]$^+$, 376 (42) [$^{79}$Br, M]$^+$, 298 (24) [M – $^{81}$Br]$^+$, 296 (49) [M – $^{79}$Br]$^+$, 229 (100). Elemental analysis calcd. (%) for $C_{15}H_{25}O_4BrSi$ (377.35): C 47.7; H 6.7; Br 21.2; found C 47.4; H 6.6; Br 21.2.

**[(2-Bromo-4,5-dimethoxybenzyl)oxy]-*tert*-butyldimethylsilane:**[75] Following general procedure B, (2-bromo-4,5-dimethoxyphenyl)methanol (1.0 equiv., 1.00 g, 4.05 mmol) and imidazole (2.0 equiv., 551 mg, 8.09 mmol) were added to TBDMSCl (1.2 equiv., 732 mg, 4.86 mmol) dissolved in dry THF (25 mL) and stirred for 3 h at room temp. Water (30 mL) was added and the reaction mixture was extracted into diethyl ether (3 × 25 mL) and then worked up as described in general procedure B. The combined organic extracts were passed through a short column of silica (eluting with diethyl ether). The diethyl ether was evaporated under reduced pressure to give [(2-bromo-4,5-dimethoxybenzyl)oxy]-*tert*-butyldimethylsilane (1.29 g, 88%) as a colourless oil; $R_f$ = 0.52 (1:1 diethyl ether/hexane). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.12 (s, 1 H, 3-H), 6.97 (s, 1 H, 6-H), 4.67 (s, 2 H, $OCH_2$), 3.87 (s, 3 H, Ar-OMe), 3.86 (s, 3 H, Ar-OMe), 0.96 (s, 9 H, $CMe_3$), 0.13 (s, 6 H, $SiMe_2$) ppm.

**[(2-Bromo-4,5-dimethoxybenzyl)oxy]triisopropylsilane (5i):** Following general procedure B, imidazole (2.0 equiv., 2.36 g, 34.7 mmol) and then (2-bromo-4,5-dimethoxyphenyl)methanol (1.0 equiv., 4.00 g, 16.2 mmol) were added to TIPSCl (1.2 equiv., 3.83 g, 19.9 mmol) in DMF (100 mL) and it was stirred at room temp. for 2 days. Water (100 mL) was added and then worked up as described in general procedure A. Column chromatography over silica gel (eluting with 10:1 hexane/diethyl ether) afforded [(2-bromo-4,5-dimethoxybenzyl)oxy]triisopropylsilane (6.23 g, 15.4 mmol, 95%) as a colourless oil; $R_f$ = 0.16 (10:1 hexane/diethyl ether). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.24 (s, 1 H, 3-H), 6.97 (s, 1 H, 6-H), 4.75 (s, 2 H, $OCH_2$), 3.87 (s, 3 H, Ar-OMe), 3.86 (s, 3 H, Ar-OMe), 1.27–1.16 (m, 3 H, SiCH), 1.11 (d, $^3J_{H,H}$ = 6.8 Hz, 18 H, Me) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 148.4 (4-C or 5-C), 148.0 (4-C or 5-C), 132.6 (1-C), 114.8 (6-C), 110.2 (3-C), 110.0 (2-C), 64.3 ($CH_2O$), 56.1 (Ar-OMe), 55.8 (Ar-OMe), 18.0 (2′-C), 12.0 (SiCH) ppm. IR ($CDCl_3$): $\tilde{\nu}_{max}$ = 2944 and 2866 (C–H), 1608 and 1504 (C=C) $cm^{-1}$. MS (CI): *m*/*z* (%) = 422 (21) [$^{81}$Br, M + $NH_4$]$^+$, 420 (21) [$^{79}$Br, M + $NH_4$]$^+$, 265 (15), 263 (16), 248 (100), 246 (98), 231 (18), 229 (18). HRMS (CI): *m*/*z*: calcd. for $C_{18}H_{35}O_3N^{28}Si^{79}Br$: 420.1564; found 420.1567[M + $NH_4$]$^+$.

**[(2-Bromo-4,5-dimethoxybenzyl)oxy]-*tert*-butyldiphenylsilane (5j):** Following general procedure B, imidazole (2.0 equiv., 1.65 g, 24.3 mmol) and then (2-bromo-4,5-dimethoxyphenyl)methanol (1.0 equiv., 3.00 g, 12.1 mmol) were added to TBDPSCl (1.0 equiv., 3.34 g, 12.1 mmol) in dry DMF (50 mL) and stirred for 24 h at room temp. Water (50 mL) was added and then worked up as described in general procedure B to give the crude product (5.76 g) as a colourless solid, which was crystallised from diethyl ether/hexane to give [(2-bromo-4,5-dimethoxybenzyl)oxy]-*tert*-butyldiphenylsilane (4.22 g, 8.70 mmol, 72%) as colourless flakes; m.p. 88–90 °C; $R_f$ = 0.5 (1:1 diethyl ether/hexane). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.70 (d, $^3J_{H,H}$ = 6.4 Hz, 4 H, 2′-H), 7.47–7.36 (m, 6 H, 3′-H, 4′-H), 7.27 (s, 1 H, 3-H), 6.97 (s, 1 H, 6-H), 4.75 (s, 2 H, $OCH_2$), 3.87 (s, 6 H, Ar-OMe), 1.13 (s, 9 H, $CMe_3$) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 148.3 (4-C or 5-C), 148.2 (4-C or 5-C), 135.5 (2′-C), 133.2 (1-C or 1′-C), 132.1 (1-C or 1′-C), 129.8 (4′-C), 127.8 (3′-C), 119.0 (2-C), 115.0 (6-C), 110.6 (3-C), 64.9 ($CH_2O$), 56.2 (Ar-OMe), 55.9 (Ar-OMe), 26.8 (Me), 19.3 ($CMe_3$) ppm. IR ($CDCl_3$): $\tilde{\nu}_{max}$ = 3071 and 3011 (Ar–H), 2932 and 2856 (C–H), 1604 and 1506 (C=C) $cm^{-1}$. MS (CI): *m*/*z* (%) = 504 (96) [$^{81}$Br, M + $NH_4$]$^+$, 502 (92) [$^{79}$Br, M + $NH_4$]$^+$, 487 (17) [$^{81}$Br, M + H]$^+$, 485 (17) [$^{79}$Br, M + H]$^+$, 248 (98), 246 (100). HRMS (CI): *m*/*z*: calcd. for $C_{25}H_{30}O_3{}^{28}Si^{79}Br$: 485.1142; found 485.1138[M + H]$^+$; elemental analysis calcd. (%) for $C_{25}H_{29}O_3BrSi$ (486.50): C 61.85; H 6.02; found C 62.03; H 6.05.

**Addition of Aryllithium Reagents to the Cyclohexadienyliron Complex 4**

**(±)-Tricarbonyl{(1,2,3,4-η)-2,5β-dimethoxy-5α-[3′-methoxy-2′-(2′′-trimethylsilylethoxymethoxy)phenyl]-1,3-cyclohexadiene}iron(0) (6b):** Following general procedure C (Variation 2), the aryllithium reagent formed from 1-bromo-3-methoxy-2-[(trimethylsilyl)ethoxymethoxy]benzene 5b (2.0 equiv., 910 mg, 2.73 mmol) and *n*-butyllithium (2.0 M in hexanes) (2.0 equiv., 1.37 mL, 2.73 mmol) in diethyl ether (25 mL), was treated with tricarbonyl[(1,2,3,4,5-η)-1,4-dimethoxycyclohexadienyl]iron hexafluorophosphate (**4**) (1.0 equiv., 500 mg, 1.37 mmol) in dichloromethane (15 mL) for 2 h at –78 °C. Column chromatography eluting with a gradient of 10:1 to 4:1 hexane/diethyl ether afforded **6b** (492 mg, 896 μmol, 65%) as a yellow oil; $R_f$ = 0.18 (4:1 hexane/diethyl ether). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.11 (dd, $^3J_{H,H}$ = 8.0, 1.4 Hz, 1 H, 6′-H), 6.99 (t, $^3J_{H,H}$ = 8.0 Hz, 1 H, 5′-H), 6.85 (dd, $^3J_{H,H}$ = 8.0, 1.4 Hz, 1 H, 4′-H), 5.16 (dd, $^3J_{H,H}$ = 6.8, 2.4 Hz, 1 H, 3-H), 5.13 (d, $^3J_{H,H}$ = 4.2 Hz, 1 H, $OCH_2O$), 4.98 (d, $^3J_{H,H}$ = 4.2 Hz, 1 H, $OCH_2O$), 4.01–3.84 (m, 2 H, $OCH_2$), 3.81 (s, 3 H, Ar-OMe), 3.61 (s, 3 H, 2-OMe), 3.31 (dt, $^3J_{H,H}$ = 3.8, 2.4 Hz, 1 H, 1-H), 3.08 (d, $^3J_{H,H}$ = 6.8 Hz, 1 H, 4-H), 2.95 (s, 3 H, 5-OMe), 2.42 (dd, $^3J_{H,H}$ = 15.4, 2.4 Hz, 1 H, 6β-H), 2.35 (dd, $^3J_{H,H}$ = 15.4, 3.8 Hz, 1 H, 6α-H), 1.06–1.00 (m, 2 H, $CH_2Si$), 0.05 (s, 9 H, $Me_3Si$) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 153.4 (2′-C or 3′-C), 143.9 (2′-C or 3′-C), 140.0 (2-C or 1′-C), 139.0 (2-C or 1′-C), 122.8 (5′-C), 120.8 (6′-C), 111.8 (4′-C), 96.6 ($OCH_2O$), 80.8 (5-C), 67.6 ($OCH_2$), 64.8 (3-C), 55.7 (Ar-OMe), 55.6 (4-C), 54.4 (2-OMe), 52.2 (1-C), 49.4 (5-OMe), 41.7 (6-C), 18.2 ($CH_2Si$), –1.5 ($Me_3Si$) ppm. IR ($CDCl_3$): $\tilde{\nu}_{max}$ = 3010 (Ar–H), 2955 and 2893 (C–H), 2047 and 1981 and 1965 (C≡O), 1580 (C=C) $cm^{-1}$. MS (EI): *m*/*z* (%) = 532 (0.1) [M]$^+$, 504 (0.5) [M – CO]$^+$, 476 (0.3) [M – 2CO]$^+$, 448 (1.5) [M – 3CO]$^+$, 416 (27), 358 (22), 285 (19), 272 (14), 73 (100). HRMS (EI): *m*/*z*: calcd. for $C_{21}H_{32}O_5{}^{54}Fe^{28}Si$: 488.1368; found 488.1368 [M – 3CO]$^+$.

**(±)-Tricarbonyl[(1,2,3,4-η)-2,5β-dimethoxy-5α-(2-methoxymethoxyphenyl)-1,3-cyclohexadiene]iron(0) (6c):** Following general procedure C (Variation 1), the aryllithium reagent formed from 1-bromo-2-(methoxymethoxy)benzene 5c (3.5 equiv., 1.54 g, 7 mmol) and *n*-butyllithium (1.6 M in hexanes) (3.5 equiv., 4.4 mL, 7 mmol) in diethyl ether (5 mL), was treated with tricarbonyl[(1,2,3,4,5-η)-1,4-dimethoxycyclohexadienyl]iron hexafluorophosphate (4) (1 equiv., 732 mg, 2 mmol) in dichloromethane (20 mL) for 1 h at –100 °C. Column chromatography (1:4 diethyl ether/petroleum ether) afforded **6c** (628 mg, 1.51 mmol, 75%) as a pale yellow gum. $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 7.49 (dd, $^3J_{H,H}$ = 7.7, 1.5 Hz, 1 H, 3′-H), 7.23 (dd, $^3J_{H,H}$ = 7.6, 7.3 Hz, 1 H, 6′-H), 7.15 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 5′-H), 6.96 (ddd, $^3J_{H,H}$ = 1 H, =7.7, 7.3, 1.0 Hz, 4′-H), 5.16 (s, 2 H, $OCH_2$), 5.07 (dd, $^3J_{H,H}$ = 6.9, 2.3 Hz, 1 H, 3-H), 3.63 (s, 3 H, 2-OMe), 3.48 (s, 3 H, 5-OMe), 3.34 (m, 1 H, 1-H), 2.99 (s, 3 H, OMe), 2.94 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, 4-H), 2.44 (dd, $^3J_{H,H}$ = 15.2, 2.3 Hz, 1 H, 6β-H), 2.24 (dd, $^3J_{H,H}$ = 15.2, 3.6 Hz, 1 H, 6α-H) ppm. IR ($CH_2Cl_2$): $\tilde{\nu}_{max}$ = 2048, 1967 (C=O) $cm^{-1}$. MS (EI): *m*/*z* (%) = 360 (4) [M – 2CO]$^+$, 332 (5) [M – 2CO]$^+$, 300 (41), 254 (42), 244 (100). Elemental analysis calcd. (%) for $C_{19}H_{20}FeO_7$ (416.21): C 54.8; H 4.8; found C 54.9; H 4.8.

**(±)-Tricarbonyl[(1,2,3,4-η)-2,5β-dimethoxy-5α-(2′-methoxymethoxymethyl-4′,5′-dimethoxyphenyl)-2,4-cyclohexadiene]iron(0) (13a):**

Following general procedure C (Variation 1), the aryllithium reagent formed from (2-bromo-4,5-dimethoxyphenyl) methyloxymethyl ether (2 equiv., 1.746 g, 6.0 mmol) and *n*-butyllithium (2.5 M in hexanes) (2 equiv., 6.0 mmol, 2.4 mL) in diethyl ether (40 mL), was treated with tricarbonyl[(1,2,3,4,5-η)-1,4-dimethoxycyclohexadienyl]iron hexafluorophosphate (**4**) (1 equiv., 1.1 g, 3.0 mmol) in dichloromethane (20 mL) for 1 h at –100 °C. Column chromatography (diethyl ether/petroleum ether gradient) afforded **13a** as a pale brown gum (0.460 g, 0.94 mmol, 31%). $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 7.08 (s, 1 H, 3′-C or 6′-C), 7.07 (s, 1 H, 3′-C or 6′-C), 5.31 (dd, $^3J_{H,H}$ = 6.9, 2.3 Hz, 1 H, 3-H), 4.71 (m, 4 H, $CH_2OCH_2$), 3.93 (s, 3 H, Ar-OMe), 3.88 (s, 3 H, Ar-OMe), 3.64 (s, 3 H, 2-OMe), 3.41 (s, 3 H, OMe), 3.32 (m, 1 H, 1-H), 3.01 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, 4-H), 2.93 (s, 3 H, 5-OMe), 2.34 (dd, $^3J_{H,H}$ = 14.8, 4.0 Hz, 1 H, 6β-H), 2.17 (dd, $^3J_{H,H}$ = 14.8, 2.0 Hz, 1 H, 6α-H) ppm. $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$ = 210.4 (Fe-CO), 147.6 (4′-C or 5′-C), 146.3 (4′-C or 5′-C), 139.9 (2-C), 134.5 (1′-C or 2′-C), 130.2 (1′-C or 2′-C), 112.4 (6′-C), 111.8 (3′-C), 95.9 ($OCH_2O$), 82.2 (5-C), 66.6 ($ArCH_2O$), 64.9 (3-C), 56.0 ($OMe_{MOM}$), 55.6 (5′-OMe), 55.2 (4′-OMe), 54.7 (4-C), 54.4 (2-OMe), 51.3 (1-C), 49.2 (5-OMe), 42.8 (6-C) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2938, 2048, 1980 (C=O), 1606, 1492, 1266, 1107, 1051, 798 cm$^{-1}$. MS (EI): *m*/*z* (%) = 434 (14) $[M – 2CO]^+$, 406 (6) $[M – 3CO]^+$, 374 (37), 344 (37), 318 (100), 314 (48), 257 (54), 226 (85), 211 (25), 195 (18), 166 (28), 151 (55). HRMS (EI): *m*/*z*: calcd. for $C_{20}H_{26}{}^{54}FeO_7$ (M – 2CO): 434.1028; found 434.1028, and tricarbonyl[(2,3,4,5-η)-4-methoxy-2,4-cyclohexadien-1-one]iron(0)[49,50] (0.168 g, 0.64 mmol, 21%).

**(±)-Tricarbonyl[(1,2,3,4-η)-2,5β-dimethoxy-5α-(2′-trimethylsilylethoxymethoxy-methyl-4′,5′-dimethoxyphenyl)-1,3-cyclohexadiene]iron(0) (13b):** Following general procedure C (Variation 1), the aryllithium reagent formed from *2*-bromo-4,5-dimethoxybenzyl 2-(trimethylsilyl)ethoxymethoxymethyl ether (1.2 equiv., 2.714 g, 7.2 mmol) and *n*-butyllithium (2.5 M in hexanes) (1.2 equiv., 2.9 mL, 7.2 mmol) in diethyl ether (30 mL), was treated with tricarbonyl[(1,2,3,4,5-η)-1,4-dimethoxycyclohexadienyl]iron hexafluorophosphate (4) (1 equiv., 2.2 g, 6.0 mmol) in dichloromethane (20 mL) for 1 h at –100 °C. Column chromatography (20% diethyl ether/80% petroleum ether) afforded **13b** as a pale brown gum (1.605 g, 2.79 mmol, 46%). $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 7.03 (s, 2 H, 3′-H, 6′-H), 5.26 (dd, $^3J_{H,H}$ = 6.9, 2.6 Hz, 1 H, 3-H), 4.73 (m, 2 H, $ArOCH_2$), 4.67 (s, 2 H, $OCH_2O$), 3.90 (s, 3 H, Ar-OMe), 3.85 (s, 3 H, Ar-OMe), 3.65 (m, 2 H, $OCH_2$), 3.61 (s, 3 H, 2-OMe), 3.27 (m, 1 H, 1-H), 2.97 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, 4-H), 2.89 (s, 3 H, 5-OMe), 2.31 (dd, $^3J_{H,H}$ = 14.5, 3.6 Hz, 1 H, 6β-H), 2.14 (dd, $^3J_{H,H}$ = 14.5, 2.6 Hz, 1 H, 6α-H) 0.95 (m, 2 H, $CH_2Si$), –0.03 (s, 9 H, $SiMe_3$) ppm. $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$ = 210.3 (Fe-CO), 147.6 (4′-C or 5′-C), 146.2 (4′-C or 5′-C), 139.9 (2-C), 134.4 (1′-C or 2′-C), 130.3 (1′-C or 2′-C), 112.3 (6′-C), 111.8 (3′-C), 94.2 ($OCH_2O$), 82.1 (5-C), 66.5 ($ArCH_2O$), 65.0 ($OCH_2$), 64.8 (3-C), 55.9 (5′-OMe), 55.5 (4′-OMe), 54.6 (4-C), 54.3 (2-OMe), 51.3 (1-C), 49.2 (5-OMe), 42.8 (6-C), 17.8 (Si-C), –1.7 ($SiMe_3$) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2053, 2048, 1983 (C=O), 1490, 1266, 1106, 838 cm$^{-1}$. MS (EI): *m*/*z* (%) = (%)576 (1) $[M]^+$, 520 (3) $[M – 2CO]^+$, 492 (5) $[M – 3CO]^+$, 460 (43) $[M – MeOH – 3CO]^+$, 404 (50) $[M – MeOH – Fe – 3CO]^+$, 314 (41), 258 (48), 257 (63), 226 (67), 211 (22), 73 (100); and tricarbonyl[(2,3,4,5-η)-4-methoxy-2,4-cyclohexadien-1-one]iron(0)[49,50] (0.430 g, 1.63 mmol, 27%)

**(±)-Tricarbonyl[(1,2,3,4-η)-2,5β-dimethoxy-5α-[4′,5′-dimethoxy-2′-(triisopropylsilanyloxymethyl)phenyl]-1,3-cyclohexadiene]iron(0) (13c):** Following general procedure C (Variation 2), the aryllithium reagent formed from [(2-bromo-4,5-dimethoxybenzyl)oxy]triisopropylsilane (2.67 g, 6.63 mmol, 2.0 equiv.) and *n*-butyllithium (2.0 M in hexanes) (2.0 equiv., 3.31 mL, 6.63 mmol) in diethyl ether (50 mL), was treated with hexafluorophosphate **4** (1.0 equiv., 1.21 g, 3.31 mmol) in dichloromethane (40 mL) for 4 h at –78 °C. Column chromatography eluting with a gradient of 2:1 to 1:1 hexane/diethyl ether afforded **13c** (1.02 g, 1.70 mmol, 51%) as a pale brown gum; $R_f$ = 0.28 (1:1 diethyl ether/hexane). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.40 (s, 1 H, 3′-H), 7.03 (s, 1 H, 6′-H), 5.29 (dd, $^3J_{H,H}$ = 6.8, 2.4 Hz, 1 H, 3-H), 4.91 (d, $^3J_{H,H}$ = 14.5 Hz, 1 H, $OCH_2$), 4.77 (d, $^3J_{H,H}$ = 14.5 Hz, 1 H, $OCH_2$), 3.92 (s, 3 H, 12-OMe), 3.87 (s, 3 H, 11-OMe), 3.64 (s, 3 H, 2-OMe), 3.29 (m, 1 H, 1-H), 2.98 (d, $^3J_{H,H}$ = 6.8 Hz, 1 H, 4-H), 2.91 (s, 3 H, 5-OMe), 2.23 (dd, $^3J_{H,H}$ = 14.5, 3.8 Hz, 1 H, 6β-H), 2.09 (dd, $^3J_{H,H}$ = 14.5, 2.1 Hz, 1 H, 6α-H), 1.17 (m, 3 H, CHSi), 1.09 (d, $^3J_{H,H}$ = 6.7 Hz, 18 H, Me) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 210.5 (Fe-CO), 147.7 (4′-C or 5′-C), 145.5 (4′-C or 5′-C), 139.9 (2-C), 134.0 (1′-C), 132.5 (2′-C), 111.9 (6′-C), 110.3 (3′-C), 82.5 (5-C), 65.2 (3-C), 62.3 ($ArCH_2O$), 56.2 (Ar-OMe), 55.6 (Ar-OMe), 54.9 (4-C), 54.6 (2-OMe), 51.4 (1-C), 49.2 (5-OMe), 42.3 (6-C), 18.1 (Me), 12.0 (CHSi) ppm. IR ($CDCl_3$): $\tilde{\nu}_{max}$ = 2942 and 2866 (C–H), 2049 and 1984 and 1965 (C=O), 1581 and 1506 (C=C) cm$^{-1}$. MS (CI): *m*/*z* (%) = 603 (5) $[M + H]^+$, 571 (82), 486 (66), 430 (33), 257 (100). HRMS (CI): *m*/*z*: calcd. for $C_{29}H_{43}O_8{}^{28}Si^{54}Fe$: 603.2071; found 603.2078 $[M + H]^+$.

**Preparation of (1-Arylcyclohexadienyl)iron Salts**

**(±)-Tricarbonyl{(1,2,3,4,5-η)-4-methoxy-1-[3′-methoxy-2′-[2′′-(trimethylsilyl)ethoxymethoxy]phenyl]-2,4-cyclohexadienyl}iron(1+) Hexafluorophosphate(1–) (7b):** Following general procedure D (Variation 2), triphenylcarbenium hexafluorophosphate (1 equiv., 691 mg, 1.78 mmol), tricarbonyl{(1,2,3,4-η)-2,5β-dimethoxy-5α-[3′-methoxy-2′-[(2′′-(trimethylsilyl)ethoxy]methoxyphenyl]-1,3-cyclohexadiene}iron(0) (**6b**) (1 equiv., 948 mg, 1.78 mmol) and potassium carbonate (0.98 equiv., 140 mg, 1.75 mmol) in dichloromethane (5 mL) were stirred 0 °C for 10 min and then added dropwise to dry diethyl ether (200 mL) to form a yellow precipitate. Reprecipitation (acetone/diethyl ether) afforded **7b** as an unstable yellow solid (125 mg, 0.193 mmol, 11%). H NMR (270 MHz, $CD_3COCD_3$): $\delta$ = 7.39 (dd, $^3J_{H,H}$ = 6.4, 2.3 Hz, 1 H, 3-H), 7.28–7.19 (m, 2 H, 5′-H, 6′-H), 7.02 (dd, $^3J_{H,H}$ = 7.3, 2.0 Hz, 1 H, 4′-H), 6.67 (d, $^3J_{H,H}$ = 6.4 Hz, 1 H, 2-H), 5.31 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, $OCH_2O$), 5.29 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, $OCH_2O$), 4.42 (d, $^3J_{H,H}$ = 6.3 Hz, 1 H, 5-H), 4.05 (s, 3 H, 4-OMe), 3.92 (s, 3 H, ArOMe), 3.69 (m, 3 H, $OCH_2$, 6β-H), 2.97 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H, 6α-H), 0.91 (dd, $^3J_{H,H}$ = 9.7, 7.1 Hz, 2 H, $CH_2Si$), –0.01 (s, 9 H, $SiMe_3$) ppm. IR ($CH_2Cl_2$): $\tilde{\nu}_{max}$ = 2106, 2049 (CO) cm$^{-1}$. MS (FAB): *m*/*z* (%) = 501 (100) $[M – PF_6]^+$, 417 (34) $[M – PF_6 – 3CO]^+$, 387 (8), 370 (5), 357 (20), 302 (7), 285 (29), 226 (13). HRMS (FAB): *m*/*z*: calcd. for $C_{23}H_{29}O_7{}^{54}Fe^{28}Si$: 501.1032; found 501.1032 $[M – PF_6]^+$.

**(±)-Tricarbonyl[(1,2,3,4,5-)-4-methoxy-1-(2′-methoxymethoxyphenyl)-2,4-cyclohexadienyl]iron(1+) Tetrafluoroborate(1–) (7c):** Following general procedure D (Variation 2), triphenylcarbenium tetrafluoroborate (1 equiv., 203 mg, 0.615 mmol), tricarbonyl[(1,2,3,4-η)-2,5β-dimethoxy-5α-(2′-methoxymethoxyphenyl)-5β-methoxycyclohexadiene]iron(0) (**6c**) (1 equiv., 256 mg, 0.615 mmol) and potassium carbonate (0.2 equiv., 100 mg, 1.25 mmol) in dichloromethane (7 mL) were stirred 0 °C for 10 min and then added added dropwise to dry diethyl ether (200 mL) to form a yellow precipitate. Reprecipitation (acetone/diethyl ether) afforded **7c** as a yellow solid (213 mg, 0.451 mmol, 73%). $^1$H NMR (270 MHz, $CD_3COCD_3$): $\delta$ = 7.52 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, 5′-H), 7.43 (m, 1 H, 3-H), 7.32 (m, 2 H, 3′-H, 6′-H), 7.13 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, 4′-H), 6.46 (d, $^3J_{H,H}$ = 5.9 Hz, 1 H, 2-H), 5.37 (s, 2 H, $OCH_2$), 4.36 (m, 1 H, 5-H), 4.06 (s, 3 H, 4-OMe), 3.71 (dd, $^3J_{H,H}$ = 15.5, 6.6 Hz, 1 H, 6β-H β) 3.48 (s, 3 H, OMe), 3.00 (d, $^3J_{H,H}$ = 15.5 Hz, 1 H, 6α-H) ppm. IR (ace-

tone): $\tilde{\nu}_{max}$ = 2104, 2050 (C=O) $cm^{-1}$. MS (EI): *m/z* (%) = 358 (1) $[M - BF_4 - CO + H]^+$, 333 (7) $[M - BF_4 - 2CO + H]^+$, 302 (10) $[M - BF_4 - 3CO + H]^+$, 244 (100). HRMS (FAB): *m/z*: calcd. for $C_{18}H_{17}O_6{}^{54}Fe$: 385.0375; found 385.0375 $[M - BF_4]^+$.

**(±)-Tricarbonyl[(1,2,3,4,5-η)-1-(2′-methoxymethoxymethyl-4′,5′-dimethoxyphenyl)-4-methoxy-2,4-cyclohexadienyl]iron(1+) Hexafluorophosphate(1–) (14a):** Following general procedure D (Variation 3), triphenylcarbenium hexafluorophosphate (1 equiv., 289 mg, 0.745 mmol), potassium carbonate (0.3 equiv., 20 mg, 0.25 mmol) and tricarbonyl[(1,2,3,4-η)-2,5β-dimethoxy-5α-(2′-methoxymethoxymethyl-4′,5′-dimethoxyphenyl)-1,3-cyclohexadiene]iron(0) (1 equiv., 365 mg, 0.745 mmol) in dichloromethane (35 mL) were stirred 0 °C for l h and then added added dropwise to dry diethyl ether (200 mL) to form a yellow precipitate. Reprecipitation (acetone/diethyl ether) afforded **14a** as a yellow/orange solid (352 mg, 0.583 mmol, 78%). $^1$H NMR (270 MHz, $CD_3COCD_3$): $\delta$ = 7.35 (m, 1 H, 3-H), 7.13 (s, 1 H, 6′-H), 7.05 (s, 1 H, 3′-H), 6.68 (m, 1 H, 2-H), 4.65 (s, 2 H, $CH_2O$), 4.53 (s, 2 H, $OCH_2O$), 4.42 (m, 1 H, 5-H), 4.03 (s, 3 H, 4-OMe), 3.94 (s, 3 H, Ar-OMe), 3.88 (s, 3 H, Ar-OMe), 3.82 (m, 1 H, 6β-H), 2.99 (d, $^3J_{H,H}$ = 15.2 Hz, 1 H, 6α-H) ppm. $^{13}$C NMR (67.8 MHz, $CD_3COCD_3$): $\delta$ = 206.4 (FeCO), 151.3 (4-C or 4′-C or 5′-C), 150.9 (4-C or 4′-C or 5′-C), 149.8 (4-C or 4′-C or 5′-C), 130.5 (2′-C), 128.3 (1′-C), 115.7 (6′-C), 114.9 (3′-C), 98.3 (1-C), 96.9 (2-C), 96.5 ($OCH_2O$), 72.1 (3-C), 67.8 ($ArCH_2O$), 58.0 (4-OMe), 56.3 (ArOMe or $OMe_{MOM}$), 56.2 (ArOMe or $OMe_{MOM}$), 55.8 (ArOMe or $OMe_{MOM}$), 43.5 (5-C), 34.9 (6-C) ppm. IR (acetone): $\tilde{\nu}_{max}$ = 2104, 2052 (C=O) $cm^{-1}$. MS (FAB): *m/z* (%) = 459 (100) $[M - PF_6]^+$, 431 (14), 375 (60), 345 (44), 318 (32), 257 (84), 226 (73), 211 (26). HRMS (FAB): *m/z*: calcd. for $C_{21}H_{23}O_8{}^{54}Fe$: 459.0742; found 459.0742 $[M - PF_6]^+$.

**(±)-Tricarbonyl[(1,2,3,4,5-η)-4-methoxy-1-[(2′-(trimethylsilyl)ethoxymethoxymethyl]-4′,5′-dimethoxyphenyl)-2,4-cyclohexadienyl]-iron(1+) Hexafluorophosphate(1–) (14b):** Following general procedure D (Variation 3), triphenylcarbenium hexafluorophosphate (1.00 g, 2.59 mmol), potassium carbonate (0.3 equiv., 0.050 g, 0.75 mmol) and tricarbonyl{(1,2,3,4-η)-2,5-β-dimethoxy-5α-[2-(trimethylsilyl)ethoxymethoxymethyl-4,5-dimethoxyphenyl]-1,3-cyclohexadiene}iron(0) (**13b**) (1.491 g, 2.59 mmol) in dichloromethane (30 mL) were stirred 0 °C for 30 min and then added added dropwise to dry diethyl ether (200 mL) to form a yellow precipitate. Reprecipitation (acetone/diethyl ether) afforded **14b** as a yellow solid (1.184 g, 1.72 mmol, 66%). $^1$H NMR (270 MHz, $CD_3COCD_3$): $\delta$ = 7.36 (m, 1 H, 3-H), 7.13 (s, 1 H, 6′-H), 7.03 (s, 1 H, 3′-H), 6.34 (d, $^3J_{H,H}$ = 6.3 Hz, 1 H, 2-H), 4.70 (s, 2 H, $ArCH_2O$), 4.55 (s, 2 H, $OCH_2O$), 4.46 (m, 1 H, 5-H), 4.05 (s, 3 H, 4-OMe), 3.94 (s, 3 H, ArOMe), 3.88 (s, 3 H, ArOMe), 3.80 (m, 1 H, 6β-H), 3.63 (t, $^3J_{H,H}$ = 7.9 Hz, 2 H, $OCH_2$), 2.97 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H, 6α-H), 0.94 (t, $^3J_{H,H}$ = 7.9 Hz, 2 H, $CH_2Si$), 0.00 (s, 9 H, $SiMe_3$) ppm. $^{13}$C NMR (67.8 MHz, $CD_3COCD_3$): $\delta$ = 206.0 (FeCO), 150.7 (4-C or 4′-C or 5′-C), 150.4 (4-C or 4′-C or 5′-C), 149.3 (4-C or 4′-C or 5′-C), 130.2 (2′-C), 127.8 (1′-C), 115.2 (6′-C), 114.4 (3′-C), 97.7 (1-C), 96.4 (2-C), 94.4 ($OCH_2O$), 71.6 (3-C), 67.4 ($ArCH_2O$), 65.5 ($OCH_2$), 57.5 (4-OMe), 55.8 (ArOMe and ArOMe), 43.0 (5-C), 34.4 (6-C), 18.1 ($CH_2$-Si), –1.7 ($SiMe_3$) ppm. IR (acetone): $\tilde{\nu}_{max}$ = 2105, 2054 (C=O) $cm^{-1}$. MS (FAB): *m/z* (%) = 545 (100) $[M - PF_6]^+$, 404 (16), 313 (13), 226 (48), 211 (15). HRMS (FAB): *m/z*: calcd. for $C_{25}H_{33}O_8{}^{28}Si^{54}Fe$: 545.1294; found 545.1294 $[M - PF_6]^+$.

**(±)-Tricarbonyl[(1,2,3,4,5-η)-1-[4′,5′-dimethoxy-2′-(triisopropylsilanyloxymethyl)phenyl]-4-methoxy-2,4-cyclohexadienyl]iron(1+) Tetrafluoroborate(1–) (14c):** (±)-Tricarbonyl[(1,2,3,4-η)-2,5β-dimethoxy-5α-[4′,5′-dimethoxy-2′-(triisopropylsilanyl)oxymethylphenyl]-1,3-cyclohexadiene]iron(0) (**13c**) (328 mg, 544 μmol, 1.0 equiv.), triphenylcarbenium tetrafluoroborate (180 mg, 544 μmol, 1.0 equiv.) and potassium carbonate (75 mg, 544 μmol, 1.0 equiv.) in dichloromethane (10 mL) were stirred 0 °C for 30 min and then added added dropwise to dry diethyl ether (200 mL) to form a yellow precipitate which was collected by filtration and washed with dry diethyl ether to give **14c** (241 mg, 366 μmol, 67%) as an orange powder; m.p. 79–81 °C (dec.). $^1$H NMR (400 MHz, $CD_3COCD_3$): $\delta$ = 7.36 (dd, $^3J_{H,H}$ = 6.1, 2.4 Hz, 1 H, 3-H), 7.14 (s, 1 H, 6′-H), 7.06 (s, 1 H, 3′-H), 6.35 (d, $^3J_{H,H}$ = 6.1 Hz, 1 H, 2-H), 4.80 (s, 2 H, $ArCH_2O$), 4.46 (ddd, $^3J_{H,H}$ = 6.3, 2.4, 1.4 Hz, 1 H, 5-H), 4.04 (s, 3 H, 2-OMe), 3.92 (s, 3 H, ArOMe), 3.88–3.83 (m, 1 H, 6β-H), 3.87 (s, 3 H, ArOMe), 3.04 (d, $^3J_{H,H}$ = 16.1 Hz, 1 H, 6α-H), 1.18 (sept, $^3J_{H,H}$ = 7.0 Hz, 3 H, CHSi), 1.07 (d, $^3J_{H,H}$ = 7.0 Hz, 18 H, Me) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 151.2 (4-C or 4′-C or 5′-C), 150.6 (4-C or 4′-C or 5′-C), 149.1 (4-C or 4′-C or 5′-C), 133.7 (2′-C), 126.8 (1′-C), 114.7 (3′-C or 6′-C), 113.6 (3′-C or 6′-C), 99.6 (1-C), 96.1 (2-C), 71.6 (3-C), 64.2 ($CH_2O$), 57.9 (4-OMe), 56.1 (ArOMe, ArOMe), 43.0 (5-C), 34.3 (6-C), 18.3 (Me), 12.5 (CHSi) ppm. IR ([$D_6$]acetone): $\tilde{\nu}_{max}$ = 2946 and 2868 (C–H), 2104 and 2049 (C≡O), 1609 and 1505 (C=C) $cm^{-1}$. MS (ES): *m/z* (%) = 625 (17) $[M^+ - BF_4 + NaOMe]$, 571 (66) $[M^+ - BF_4]$, 139 (100), 81 (45). HRMS (ES): *m/z*: calcd. for $C_{28}H_{39}O_7{}^{28}Si^{54}Fe$: 571.1809: found 571.1811 $[M - BF_4]^+$.

**Malononitrile Additions and TBAF One Pot Procedures**

**(±)-Tricarbonyl{[methyl (2,3,4,5-η)-1β-[2′-(Methoxymethyloxy)-phenyl]-4-methoxy-2,4-cyclohexadien-1α-yl]cyanoethanoate}iron(0) (8c):** Methyl cyanoethanoate (5 equiv., 210 mg, 2.12 mmol) was dissolved in dry THF (5 mL) and cooled to 0 °C under nitrogen. NaH (60% suspension in mineral oil) (5 equiv., 85 mg, 2.12 mmol) and 2-trimethylsilylethyl cyanoethanoate (2 equiv., 581 mg, 3.14 mmol) in THF (10 mL) was added to form a milky suspension by stirring at 0 °C for 15 min. This was added to a suspension of tricarbonyl[(1,2,3,4,5-η)-4-methoxy-1-(2′-methoxymethyloxyphenyl)-2,4-cyclohexadienyl]iron(1+) hexafluorophosphate(1–) (**7c**) (l equiv., 200 mg, 0.42 mmol) in THF (5 mL). After stirring for 1 h, the reaction was quenched with water (25 mL) and diethyl ether (25 mL) and extracted into diethyl ether (3 × 25 mL). The combined organic extracts were washed with water (3 × 25 mL), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to afford a yellow oil. Column chromatography over silica gel (2:3 diethyl ether/petroleum ether) afforded **8c** as an inseparable 1:1 mixture of two diastereoisomers as a pale yellow gum (223 mg, 0.48 mmol, > 99%). $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 7.48–6.99 (m, 4 H, Ar), 5.41 (dd, $^3J_{H,H}$ = 6.9, 2.6 Hz, 0.5 H, 3-H), 5.22 (m, 2.5 H, $OCH_2O$, 3-H), 4.83 and 4.75 (s, 1 H, CHCN), 3.85 and 3.78 (s, 3 H, 4-OMe), 3.67 (s, 1.5 H, $CO_2Me$), 3.47 (s, 3 H, $CO_2Me$, $OMe_{MOM}$), 3.39 (s, 1.5 H, $OMe_{MOM}$), 3.29 (m, 1 H, 5-H), 3.05 (d, $^3J_{H,H}$ = 6.9 Hz, 0.5 H, 2-H), 2.98 (dd, $J$ = $^3J_{H,H}$ = 16.2, 2.6 Hz, 0.5 H, 6β-H), 2.86 (d, $^3J_{H,H}$ = 6.9 Hz, 0.5 H, 2-H), 2.54 (dd, $^3J_{H,H}$ = 15.8, 2.3 Hz, 0.5 H, 6β-H), (dd, $^3J_{H,H}$ = 15.8, 3.3 Hz, 0.5 H 6α-H), 2.08 (d, $^3J_{H,H}$ = 16.2, 3.3 Hz, 0.5 H 6α-H) ppm. IR (film): $\tilde{\nu}_{max}$ = 2248 (CN), 2048, 1967 (C=O), 1742 (ester), 1489, 1081, 624 $cm^{-1}$. MS (EI): *m/z* (%) = 427 (3) $[M - 2CO]^+$, 399 (39) $[M - 3CO]^+$, 343 (1) $[M - Fe(CO)_3]^+$, 328 (2) $[M - Fe(CO)_3 - Me]^+$, 300 (88), 244 (100). Elemental analysis calcd. (%) for $C_{22}H_{21}FeNO_8$ (483.25): C 54.7; H 4.4; N 2.9; found C 54.9; H 4.5; N 3.2.

**(±)-Tricarbonyl{[2′′-trimethylsilylethyl (2,3,4,5-η)-1β-[(2′-(methoxymethyloxy)phenyl]-4-methoxy-2,4-cyclohexadien-1α-yl]cyanoethanoate}iron(0) (8d):** NaH (60% suspension in mineral oil) (1.1 equiv., 13 mg, 0.32 mmol) was suspended in dry THF (5 mL) at 0 °C. A solution of 2-trimethylsilylethyl cyanoethanoate (1.1 equiv., 59 mg, 0.32 mmol) in dry THF (5 mL) was added at

0 °C and the mixture was stirred at 0 °C for 15 min to form a milky suspension. This was added to a suspension of tricarbonyl-{(1,2,3,4,5-η)-4-methoxy-1-[2′-(methoxymethyloxy)phenyl]-2,4-cyclohexadienyl}iron(1+) hexafluorophosphate(1–) (**7c**) (1 equiv., 145 mg, 0.31 mmol) in THF (5 mL). After stirring for 1 h, the reaction was quenched with water (25 mL) and diethyl ether (25 mL) and extracted into diethyl ether (3 × 25 mL). The combined organic extracts were washed with water (3 × 25 mL), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to afford a yellow oil. Column chromatography over silica gel (2:3 diethyl ether/petroleum ether) afforded **8d** as an inseparable 1:1 mixture of two diastereoisomers as a pale yellow gum (116 mg, 0.21 mmol, 66%). $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 7.49–6.94 (m, 4 H, Ar), 5.42 (dd, $^3J_{H,H}$ = 6.9, 2.3 Hz, 0.5 H, 3-H), 5.18 (m, 2.5 H, $OCH_2O$, 3-H), 4.81 and 4.71 (s, 1 H, CHCN), 4.29 (m, 2 H, $OCH_2$), 3.78 and 3.67 (s, 3 H, 4-OMe), 3.48 and 3.47 (s, 3 H, $CO_2Me$), 3.28 (m, 2 H, 5-H), 3.06 (d, $^3J_{H,H}$ = 6.9 Hz, 0.5 H, 2-H), 3.01 (dd, $J = {}^3J_{H,H}$ = 15.8, 2.6 Hz, 0.5 H, 6β-H), 2.91 (d, $^3J_{H,H}$ = 6.9 Hz, 0.5 H, 2-H), 2.51 (dd, $^3J_{H,H}$ = 16.2, 2.6 Hz, 0.5 H, 6β-H), (dd, $^3J_{H,H}$ = 15.8, 3.3 Hz, 0.5 H 6α-H), 2.08 (d, $^3J_{H,H}$ = 16.2, 3.3 Hz, 0.5 H 6α-H), 1.05 (m, 2 h, $CH_2Si$), 0.06 (s, 9 H, $SiMe_3$) ppm. IR (film): $\tilde{\nu}_{max}$ = 2246 (CN), 2049, 1967 (C=O), 1734 (ester), 1489, 1083, 861 cm$^{-1}$. MS (EI): *m*/*z* (%) = 485 (3) [M – 3CO]$^+$, 385 (1), 341 (1) 300 (7), 144 (13), 199 (6), 98 (100). HRMS (EI): *m*/*z*: calcd. for $C_{22}H_{31}NO_5{}^{54}Fe^{28}Si$: 485.1321; found 485.1321 [M – 3CO]$^+$.

**(±)-Tricarbonyl[(1,2,3,4-η)-5α-cyanomethyl-2-methoxy-5β-(2′-methoxymethoxymethyl-4′,5′-dimethoxyphenyl)-1,3-cyclohexadiene]-iron(0) (15a):** NaH (60% suspension in mineral oil) (2 equiv., 33 mg, 0.828 mmol) and 2-trimethylsilylethyl cyanoethanoate (2 equiv., 153 mg, 0.828 mmol) in THF (10 mL) was added to a suspension of (±)-tricarbonyl[(1,2,3,4,5-η)-4-methoxy-1-(2-methoxymethoxymethyl-4,5-dimethoxyphenyl)-2,4-cyclohexadienyl] iron(1+) hexafluorophosphate(1–) (1 equiv., 250 mg, 0.414 mmol) in THF (5 mL) as described in general procedure E (variation 1). After deprotection with TBAF (0.9 equiv. 0.4 mL, 0.4 mmol), the reaction was worked up as described in general procedure E. Column chromatography (1:1 diethyl ether/petroleum ether) afforded **15a** as a pale yellow solid (28 mg, 56 μmol, 14%). $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 7.14 (s, 1 H, 6′-H), 6.92 (s, 1 H, 3′-H), 5.29 (dd, $^3J_{H,H}$ = 6.9, 2.6 Hz, 1 H, 3-H) 4.69 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, $OCH_2$), 4.66 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, $OCH_2$), 4.51 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, $OCH_2O$), 4.39 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, $OCH_2O$), 3.97 (s, 3 H, Ar-OMe), 3.88 (s, 3 H, Ar-OMe), 3.76 (s, 3 H, 2-OMe), 3.40 (s, 3 H, OMe), 3.35 (m, 1 H, 1-H), 2.93 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, 4-H), 2.93 (d, $^3J_{H,H}$ = 16.8 Hz, 1 H, $CH_2CN$), 2.76 (d, $^3J_{H,H}$ = 16.8 Hz, 1 H, $CH_2CN$), 2.45 (dd, $^3J_{H,H}$ = 14.8, 2.3 Hz, 1 H, 6β-H), 2.16 (dd, $^3J_{H,H}$ = 14.8, 3.6 Hz, 1 H, 6α-H) ppm. IR ($CH_2C1_2$): $\tilde{\nu}_{max}$ = 2308, 2051, 1980 (C=O), 1608, 1423 cm$^{-1}$. MS (FAB): *m*/*z* (%) = 443 (28) [M – 2CO]$^+$, 382 (35), 354 (54), 298 (36), 257 (54), 225 (100). MS (EI): *m*/*z* (%) = 443 (13) [M – 2CO]$^+$, 355 (38), 238 (27), 223 (31), 208 (29), 99 (28), 56 (100). HRMS (EI): *m*/*z*: calcd. for $C_{21}H_{25}NO_6{}^{54}Fe$: 443.1031; found 443.1031[M – 2CO]$^+$.

**(±)-Tricarbonyl{(1,2,3,4-η)-5α-cyanomethyl-2-methoxy-5β-[2′-(trimethylsilyl)ethylmethoxymethyl-4′,5′-dimethoxyphenyl]-1,3-cyclohexadiene}iron(0) (15b):** NaH (60% suspension in mineral oil) (2 equiv., 126 mg, 3.14 mmol) and 2-trimethylsilylethyl cyanoethanoate (2 equiv., 581 mg, 3.14 mmol) in THF (10 mL) was added to a suspension of tricarbonyl{(1,2,3,4,5-η)-4-methoxy-1-[2-(trimethylsilyl)ethoxymethoxymethyl-4,5-dimethoxyphenyl]-2,4-cyclohexadienyl}iron(1+) hexafluorophosphate(1–) (1 equiv., 1.068 g, 1.55 mmol) in THF (5 mL) as described in general procedure E (variation 1). After deprotection with TBAF (2.2 equiv., 3.4 mL, 3.4 mmol), the reaction was worked up as described in general procedure E. Column chromatography (1:1 diethyl ether/petroleum ether) afforded **15b** as a pale yellow solid (578 mg, 99 μmol, 64%). $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 7.13 (s, 1 H, Ar), 6.91 (s, 1 H, Ar), 5.29 (dd, $^3J_{H,H}$ = 6.9, 2.6 Hz, 1 H, 3-H) 4.72 (m, 2 H, $ArOCH_2$), 4.50 (d, $^3J_{H,H}$ = 11.6 Hz, 1 H, $OCH_2O$), 4.39 (d, $^3J_{H,H}$ = 11.6 Hz, 1 H, $OCH_2O$), 3.96 (s, 3 H, Ar-OMe), 3.87 (s, 3 H, Ar-OMe), 3.75 (s, 3 H, C2-OMe), 3.63 (m, 2 H, $OCH_2CH_2$), 3.33 (m, 1 H, 1-H), 2.99 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, 4-H), 2.91 (d, $^3J_{H,H}$ = 16.7 Hz, 1 H, $CH_2CN$), 2.76 (d, $^3J_{H,H}$ = 16.7 Hz, 1 H, $CH_2CN$), 2.43 (dd, $^3J_{H,H}$ = 14.5, 2.3 Hz, 1 H, 6β-H), 2.15 (dd, $^3J_{H,H}$ = 14.5, 3.6 Hz, 1 H, 6α-H), 0.95 (m, 2 H, $CH_2SiMe_3$), –0.01 (s, 9 H, $SiMe_3$) ppm. IR ($CH_2C1_2$): $\tilde{\nu}_{max}$ = 2987, 2306 (CN), 205 1, 1980 (C=O) cm$^{-1}$. MS (EI): *m*/*z* (%) = 529 (3) [M – 2CO]$^+$, 374 (9), 297 (5), 258 (80), 84 (100). Elemental analysis calcd. (%) for $C_{27}H_{35}FeNO_8Si$ (585.50): C 44.4; H 6.0; N 2.4; found C 55.4; H 6.1; N 2.2.

**(±)-Tricarbonyl[(1,2,3,4-η)-5α-cyanomethyl-5β-(2′-hydroxymethyl-4′,5′-dimethoxyphenyl)-2-methoxy-1,3-cyclohexadiene]iron(0) (16):** NaH (60% suspension in mineral oil) (1.5 equiv., 4 mg, 94 μmol) and 2-trimethylsilylethyl cyanoethanoate (1.6 equiv., 19 mg, 101 μmol) in THF (3 mL) was added to a suspension of tricarbonyl{(1,2,3,4,5-η)-1-[4′,5′-dimethoxy-2′-(triisopropylsilanyloxymethyl)phenyl]-4-methoxy-2,4-cyclohexadienyl}iron(1+) tetrafluoroborate(1–) (**14c**) (1.0 equiv., 42 mg, 63 μmol) in THF (5 mL) as described in general procedure E (variation 2). After deprotection with TBAF (4.0 equiv., 0.25 mL, 250 μmol), the reaction was worked up as described in general procedure E. Column chromatography (eluting with a gradient from 1:1 to 1:3 hexane/ethyl acetate) afforded **16** as a pale yellow oil (17 mg, 37 μmol, 59%) with identical spectroscopic data to those obtained from the product from **14d** in the TBDPS-protected series (see Exp. Sect. of main paper).

**(±)-Tricarbonyl[(1,2,3,4-η)-5α-cyanomethyl-2-methoxy-5β-(2′-hydroxy-3′-methoxyphenyl)-1,3-cyclohexadiene]iron(0) (10):** 2-Trimethylsilylethyl cyanoethanoate (2.0 equiv., 547 mg, 2.95 mmol) in dry THF (5 mL) was added to sodium hydride (60% suspension in mineral oil) (1.9 equiv., 112 mg, 2.80 mmol) in dry THF (15 mL) and stirred for 35 min at 0 °C to give a white suspension of 2-(trimethylsilyl)ethyl sodiocyanoethanoate. Tricarbonyl{(1,2,3,4-η)-2,5β-dimethoxy-5α-[3′-methoxy-2′-(2′′-(trimethylsilyl)ethoxymethoxy)phenyl]-1,3-cyclohexadiene}iron(0) (**6b**) (1.0 equiv., 786 mg, 1.48 mmol) dissolved in dry dichloromethane (4 mL) was added to triphenylcarbenium tetrafluoroborate (1.0 equiv., 487 mg, 1.48 mmol) and potassium carbonate (2.0 equiv., 408 mg, 2.95 mmol) in dry DCM (10 mL) at 0 °C. After 10 min at 0 °C, the reaction mixture was filtered and added to the 2-(trimethylsilyl)-ethyl sodiocyanoethanoate solution and stirred for 4 h. The solvent was evaporated under reduced pressure and water (20 mL) was added. The reaction mixture was extracted with diethyl ether (4 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and evaporated under reduced pressure to give the crude product (1.55 g) as a brown oil. The crude oil was partially purified by column chromatography over silica gel (eluting with a gradient from 6:1 to 2:1 hexane/diethyl ether) to give the compound **8b** (303 mg, 318 μmol, 22%) as a yellow gum, which was 69% pure by $^1$H NMR analysis. TBAF (1 M in THF) (3.0 equiv., 0.94 mL, 940 μmol) was added to the crude compound **8b** (1.0 equiv., 303 mg, 318 μmol) in dry THF (10 mL) and was refluxed for 7 h at 100 °C. After cooling to room temp., the solvent was evaporated under reduced pressure. Water (15 mL) was added to the reaction mixture and it was extracted with diethyl ether (4 × 15 mL). The combined organic layers were dried ($MgSO_4$), filtered and evapo-

rated under reduced pressure to give the crude product (282 mg) as a yellow solid. The crude solid was partially purified by column chromatography over silica gel (eluting with a gradient of 4:1 to 1:1 hexane/diethyl ether) and then it was crystallised from diethyl ether/hexane to give **10** (24 mg, 58 μmol, 18%) as cream plates; m.p. 117–119 °C (dec.); $R_f$ = 0.18 (1:1 hexane/diethyl ether). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.01 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 6′-H), 6.89 (t, $^3J_{H,H}$ = 8.0 Hz, 1 H, 5′-H), 6.82 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 4′-H), 5.93 (s, 1 H, OH), 5.30 (dd, $^3J_{H,H}$ = 6.8, 2.4 Hz, 1 H, 3-H), 3.88 (s, 3 H, 3-OMe), 3.73 (s, 3 H, 2-OMe), 3.34 (dt, $^3J_{H,H}$ = 3.2, 2.4 Hz, 1 H, 1-H), 3.18 (d, $^3J_{H,H}$ = 16.3 Hz, 1 H, 5-$CH_2$), 3.02 (d, $^3J_{H,H}$ = 6.8 Hz, 1 H, 4-H), 2.61 (d, $^3J_{H,H}$ = 16.3 Hz, 1 H, 5-$CH_2$), 2.35 (dd, $^3J_{H,H}$ = 15.9, 2.4 Hz, 1 H, 6β-H), 2.17 (dd, $^3J_{H,H}$ = 15.9, 3.2 Hz, 1 H, 6α-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 146.7 (2′-C or 3′-C), 143.0 (2′-C or 3′-C), 140.7 (2-C), 130.8 (1′-C), 119.7 (6′-C), 119.2 (5′-C and CN), 109.6 (4′-C), 64.2 (3-C), 56.0 (Ar-OMe), 55.1 (4-C), 54.5 (2-OMe), 52.9 (1-C), 42.6 (5-C), 41.3 (6-C), 32.2 (5-$CH_2$) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3458 (O–H), 2930 and 2839 (C–H), 2244 (C≡N), 2051 and 1958 (C≡O), 1615 and 1588 (C=C) cm$^{-1}$. MS (EI): *m*/*z* (%) = 383 (17) [M – CO]$^+$, 355 (38) [M – 2CO]$^+$, 327 (72) [M – 3CO]$^+$, 286 (100); 271 (24), 231 (43), 189 (51). 121 (55). HRMS (EI): *m*/*z*: calcd. for $C_{18}H_{17}NO_5{}^{54}Fe$: 383.0456; found 4838.0456 [M – CO]$^+$; elemental analysis calcd. (%) for $C_{19}H_{17}FeNO_6$ (411.19): C 55.5; H 4.2; N 3.4; found C 55.6; H 4.1; N 3.3.

**Removal of the SEM Protecting Group Using $MgBr_2$**

**(±)-Tricarbonyl[(1,2,3,4-η)-5α-cyanomethyl-5β-[2-(hydroxymethyl)-4,5-dimethoxyphenyl]-2-methoxy-1,3-cyclohexadiene]iron(0) (16):** (±)-Tricarbonyl{(1,2,3,4-η)-5α-cyanomethyl-2-methoxy-5β-[2′-(trimethylsilyl)ethylmethoxymethyl-4′,5′-dimethoxyphenyl]-1,3-cyclohexadiene}iron(0) (**15b**) (1 equiv., 100 mg, 0.171 mmol) was stirred with magnesium bromide (5 equiv., 0.86 mmol, 157 mg) in dry ether (5 mL) for 24 h. The reaction was quenched with water (5 mL) and diethyl ether (5 mL) and extracted into diethyl ether (3 × 10 mL). The combined organic layers were washed with water (3 × 10 mL), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure leaving a yellow oil. Column chromatography on silica eluting with diethyl ether afforded **16** (55 mg, 0.121 mmol, 71%) as a yellow solid. $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 7.16 (s, 1 H, 13-H), 6.91, (s, 1 H, 10-H), 5.29, (dd, $^3J_{H,H}$ = 6.9, 2.3 Hz, 1 H, 3-H), 4.52, (s, 2 H, 16-$H_2$), 3.97 (s, 3 H, 18-$H_3$), 3.88 (s, 3 H, 17-$H_3$), 3.75 (s, 3 H, 7-$H_3$), 3.35, (m, 1 H, 1-H), 3.06, (d, $^3J_{H,H}$ = 16.5, 2.3 Hz, 1 H, 14-H), 2.96 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, 4-H), 2,72 (dd, $^3J_{H,H}$ = 16.5 Hz, 1 H, 14-H), 2.43 (dd, $^3J_{H,H}$ = 14.5, 2.3 Hz, 1 H, 6β-H), 2.15 (dd, $^3J_{H,H}$ = 14.5, 3.3 Hz, 1 H, 6α-H), 1.72 (br. s, 1 H, OH) ppm. HRMS (EI): *m*/*z*: calcd. for $C_{19}H_{21}NO_5{}^{54}Fe$ (M$^+$ – 2CO): 399.0769; found 399.0769 (see Exp. Sect. of main paper).

**Preparation of Dihydrooxomaritidine**[47]

**(1,2,4,4a-Tetrahydro-8,9-dimethoxy-3*H*,6*H*-5,10b-ethanophenanthridin-3-one) (19):** Anhydrous trimethylamine *N*-oxide (20 equiv., 85 mg, 1.13 mmol) was added to (±)-tricarbonyl-{(2′,3′,4′,5′-η)-7,8-dimethoxy-1,2,3,4-tetrahydrospiro[5*H*-2-benzazepine-5,1′-(4′-methoxy-2′,4′-cyclohexadiene)]}iron(0) (**18**) (1.0 equiv., 25 mg, 57 μmol) dissolved in acetone (2 mL) and stirred overnight at room temp. The mixture was filtered and the solvents evaporated in vacuo to give 106 mg of crude solid which was redissolved in methanol (3 mL). Oxalic acid dihydrate (180 mg, 1.43 mmol, 25 equiv.) was dissolved in water (3 mL) and added to the reaction mixture and stirred for 4 h. 2 M sodium hydroxide (3.6 mL) was added and stirred for 3 h. The reaction mixture was extracted with diethyl ether (4 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and the solvents evaporated in vacuo to give crude product (7 mg) as a pale yellow oil. The crude product was purified by column chromatography over silica gel (eluting with a gradient from $CHCl_3$ to 10:1 $CHCl_3$/methanol and then 10:2:0.2 $CHCl_3$/methanol/ammonia) followed by preparatory TLC (eluting with 10:1 $CHCl_3$/methanol) to give dihydrooxomaritidine (**19**)[76] (2.1 mg, 7.3 μmol, 13%) as a pale yellow oil; $R_f$ = 0.12 (10:1 $CHCl_3$/methanol). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.72 (s, 1 H, 10-H), 6.53 (s, 1 H, 7-H), 4.44 (d, $J_{15,15}$ = 16.9 Hz, 1 H, 6-H), 3.88 (d, $J_{15,15}$ = 16.9 Hz, 1 H, 6-H), 3.87 (s, 3 H, OMe), 3.84 (s, 3 H, OMe), 3.65–2.00 (m, 11 H, 4a-H, 4-H, 2-H, 1-H, 10b-$CH_2$, $NCH_2$) ppm. *m*/*z* (EI) 287 (M$^+$, 14%), 217 (20), 149 (27), 105 (31). HRMS: found 287.1513. $C_{17}H_{21}O_3N$ (M$^+$) requires 287.1516.

**Supporting Information** (see footnote on the first page of this article): Details of optimization of lithiation procedures and full tables of NMR assignments and representative 2D NMR spectra on which the assignments are based.

## Acknowledgments

The authors thank the Engineering and Physical Sciences Research Council (EPSRC) and Glaxo Smith Kline for financial support, and the EPSRC Mass Spectrometry Centre at the University of Wales, Swansea for high resolution mass spectrometric measurements.

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Received: October 11, 2010
Published Online: February 4, 2011

  