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1′-Trimethylsilylethynyl-, 1′-ethenyl- and 1′-formyl-1-ethynylferrocenes: syntheses and electrochemical properties

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ABSTRACT

Efficient syntheses of 1′-trimethylsilylethynyl-, 1′-ethenyl-, and 1′-formyl-1-ethynylferrocenes are reported. The majority of these compounds exhibit chemically reversible ferrocene-based oxidation processes from cyclic voltammetry and thereby constitute key synthons for the development of redox-switchable molecular systems.

1. Introduction

Since its discovery in the early 1950s,[1] ferrocene has attracted considerable attention in diverse areas, such as catalysis, materials science, and bio-organometallic chemistry.[2] Much of this interest has been driven by the great structural diversity attainable from this redox-active scaffold, with a large variety of ferrocene-containing synthons already reported or directly available from commercial suppliers, a feature that results from the versatility of chemical reactions undergone by this simple molecule. An additional interest is the remarkable stability of this particular organometallic moiety in the Fe(II) and Fe(III) redox states[2a] compared to other redox couples with similar synthetic flexibility. These properties have made ferrocene a very popular building block for developing redox-switchable functional molecules.[3] More specifically, in the field of nonlinear optics (NLO), ferrocene was utilized as early as the mid 1980s as an organometallic donor group in dipolar architectures by Green, Marder, and co-workers.[4] Following these seminal studies, a plethora of ferrocene-containing compounds were developed and studied for their second- and third-order NLO properties by various techniques. These were often shown to exhibit significant NLO responses,[5] which can be modulated upon oxidation of the ferrocenyl unit, as experimentally demonstrated more recently.[6] In this context, we have also tried to develop redox-switchable NLO-active group 8 metal–alkynyl complexes incorporating this particular fragment and demonstrated their grafting on hydrogenated silicon surfaces.[7,8]

During these investigations the difunctional 1′-trialkylsilylethynyl-1-ethynylferrocene derivative **1** was required (Scheme 1). Considering the large scope of reactions undergone by alkynes in organic and organometallic chemistry,[9] **1** is a strategic building block for accessing differently functionalized 1,1′-bisalkynylferrocenes and their derivatives. We now report a reliable and selective synthesis of **1** in a few steps from the known 1-iodo-1′-formylferrocene (**8**)[10] along with syntheses of the related synthons 1-ethynyl-1′-ethenylferrocene (**6**) and 1-ethynyl-1′-formyl-ferrocene (**7**), which also afford possibilities for grafting on hydrogenated silicon.[11]

2. Results and discussion

In spite of the fact that various syntheses have been reported for ethynylferrocene (**2**),[12–18] an efficient synthetic route to **1** has not been reported to date, despite the numerous reactions available for the introduction of alkynyl functionalities on ferrocene moieties.[16–22] Note that 1,1′-diethynylferrocene (**3**) is not a kinetically stable molecule (Scheme 1); unlike its 1,2-isomer,[19] **3** has never been isolated,[23] since it spontaneously polymerizes in solution unless trimethylsilyl[14,15] or dimethylcarbinol[14] protecting groups are present on both alkynes (e.g., **4**). Thus, attempts to selectively remove one of the two trimethylsilyl groups of **4** never led to the selective and quantitative formation of the mono-deprotected compound **1**.[15,18,20,23] For example, when a source of

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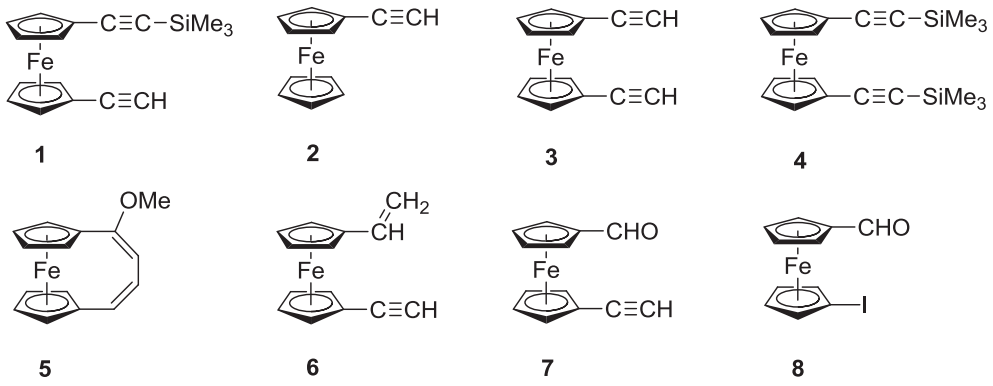


Scheme 1. Selected ferrocene derivatives.

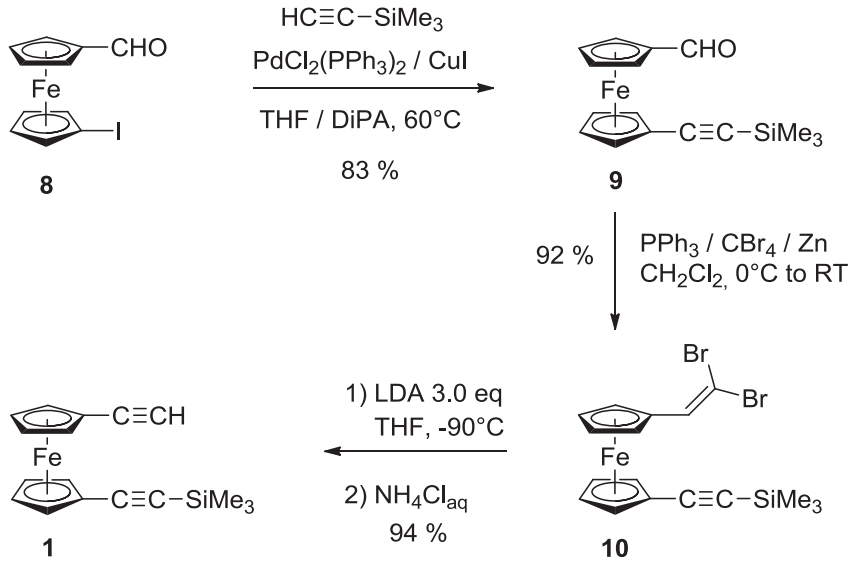
potentially nucleophilic methoxide anions was used for the deprotection, such as with methanolic KOH, the [4]-ferrocenophane compound **5** was formed.[18,20] This reaction, which is akin to the synthesis of functional [4]-ferrocenophanes from various 1,1′-bis(alkynyl)-ferrocenes and phenol or acetic acid, demonstrates that *trans*-annular addition is a reaction easily undergone by 1,1′-bisalkynyl derivatives in the presence of various nucleophiles.[24]

In order to limit any undesirable *trans*-annular addition when attempting to synthesize **1**, it was decided to introduce the terminal alkyne at the latest possible stage in the absence of strong nucleophiles. This was done by mimicking the synthesis of various (ethynylphenyl)ethynyl-trimethylsilanes from the corresponding bromobenzaldehydes[25] using a Sonogashira coupling[26]/Corey–Fuchs[27] reaction sequence. These reactions and related ones have ample precedence in ferrocene chemistry.[16–22,28] The protected alkyne moiety was first introduced by palladium-catalyzed cross-coupling of **8** with trimethyl-ethynylsilane and the expected 1-trimethylsilylethynyl-1′-formylferrocene **9** was obtained in 83% yield. Note that with the bromo analogue of **8**, **9** was not obtained, even when the more active P(*t*-Bu)$_3$/[PdCl$_2$(PhCN)$_2$] catalytic system was used,[29,30] and regardless of the reaction being carried out at higher temperatures (80 °C) and/or over extended reaction times (up to 72 h). This result is consistent with previous reports of poor reactivity of 1′-bromo-1-ethynylferrocene when used as the organic halide in Sonogashira couplings.[22] In the second step, the formyl group in **9** was converted into a terminal alkyne by first reacting **9** with CBr$_4$/PPh$_3$/Zn in CH$_2$Cl$_2$ to afford the dibromo-alkene **10** in 92% yield, and then treating **10** with excess LDA in THF at low temperature, followed by quenching with aqueous NH$_4$Cl. By this route, **1** was obtained in 72% overall yield from **8** as an isolable compound (Scheme 2).

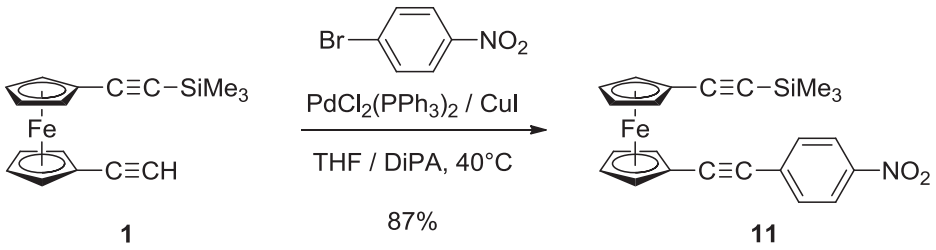
In spite of a slow decomposition taking place over prolonged periods of time, which has thus far precluded characterization of this compound by elemental analysis, **1**, when employed immediately after its synthesis, is nevertheless sufficiently stable to be further functionalized. Thus, Sonogashira coupling with *p*-bromonitrobenzene afforded the expected cross-coupled product **11** in good yield after chromatographic purification and recrystallization (Scheme 3). Under the reaction conditions used, no degradation of **1** occurred, as only **11** and excess of unreacted **1** or traces of its homo-coupling product were observed in the crude reaction mixture (TLC).

The next target, **6**, was obtained from the alkenyl analogue of **1** (**12**), which can itself be obtained by Wittig olefination[31] of **9** using methylidenetriphenylphosphorane, generated from *n*-BuLi and methyltriphenylphosphonium bromide in THF at 0 °C (Scheme 4). Alkene derivative **12** was isolated in 95% yield, 79% overall yield from **8**.

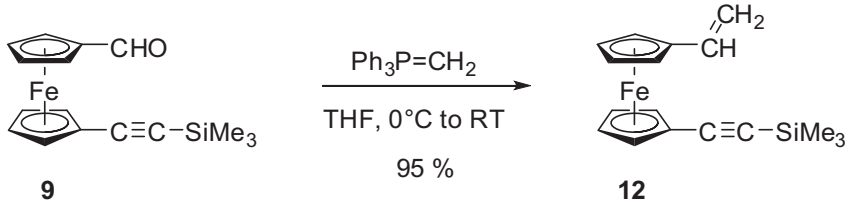
Aware of the possibility of [4]-ferrocenophane formation in the presence of alkoxide, especially methoxide anions, the



Scheme 2. Synthesis of **1** from **8**.



Scheme 3. Synthesis of **11** from **1**.

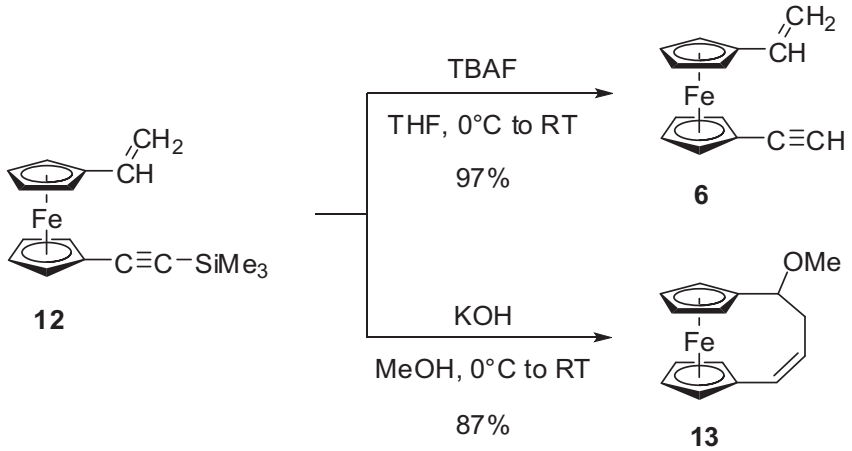


Scheme 4. Synthesis of **12** from **9**.

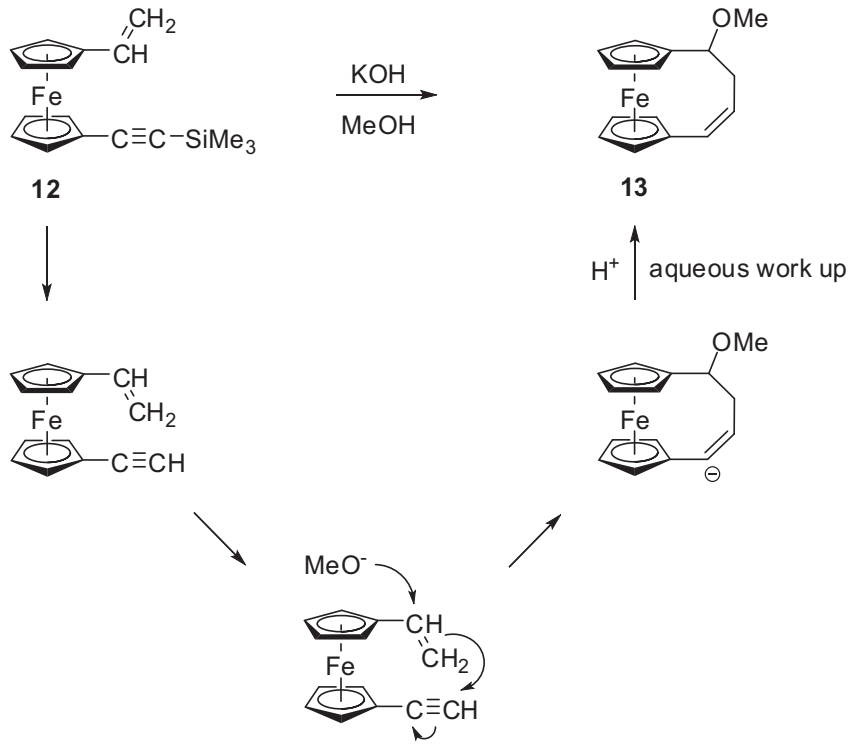
deprotection of **12** was investigated under two different sets of conditions: (i) with methanolic KOH and (ii) with fluoride ion (TBAF) in THF. In the first case, the reaction resulted in the formation of the [4]-ferrocenophane **13** in good yield and its structure was confirmed by 2D NMR (cf. Supplementary data). In contrast, when the weaker fluoride nucleophile was used to desilylate **12**, the desired terminal acetylene **6** was obtained nearly quantitatively as a stable compound (Scheme 5). However, this compound could only be isolated in at most 95% purity (by NMR, cf. Supplementary data), as extensive decomposition on both silica and alumina supports precluded further purification by chromatography. Nevertheless, its fair chemical stability remains quite surprising, especially considering the instability toward air and/or moisture reported for the 1,1′-diethenyl-[32] and 1,1′-diethynylferrocenes,[23] and to a lesser extent for 1-ethenyl-2-ethynylferrocene.[19]

A tentative mechanism can be proposed for the formation of the [4]-ferrocenophane **13** based on the formation of **5** from **4** (Scheme 6).[18,20] It involves desilylation of **12** followed by attack of the methoxide anion on the α-carbon atom of the ethenyl group. However, some questions remain regarding the actual step during which desilylation takes place; the intermediacy of a trimethylsilyl-substituted alkyne undergoing the transannular addition cannot be totally ruled out at this stage. The coexistence of several reaction pathways leading to **13** is also plausible. The formation of **13** is regiospecific: no products resulting from methoxide addition at the α-carbon atom of the ethynyl was detected in the crude reaction mixture by ^{1}H NMR. This difference in reactivity between the ethenyl and the ethynyl groups is readily explained by the difference in electrophilicity of their respective α-carbon atoms: that of the ethenyl group in **12**/**13** is much more electrophilic due to the lower π electron density relative to that of an ethynyl group. This type of methoxide addition at the α-carbon seems to be a general feature of 1-alkynylferrocenes bearing another unsaturated substituent (alkene or alkyne) at the 1′ position, since treatment of ethenylferrocene under similar conditions does not lead to the formation of 1-(methoxyethyl)ferrocene, ethenylferrocene being quantitatively recovered after the aqueous work up. Similarly, trimethylsilylethynylferrocene only gives ethynylferrocene (**2**) and not the corresponding ethenyl methyl ether when reacted with KOH in MeOH.[20]

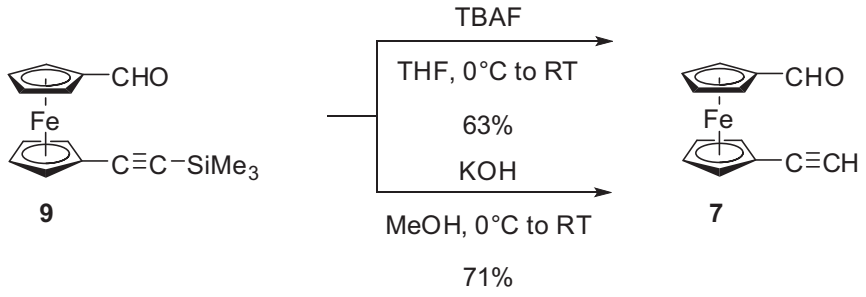
The last target, the known 1-ethynyl-1′-formylferrocene (**7**)[33] was readily obtained in either 61% or 71% yields from the formyl precursor **9** under the deprotection conditions previously employed for **12** (Scheme 7), affording **7** in a good overall yield of 59% in two steps from **8**. Note that **7**, similar to **1**, slowly decomposes when stored over prolonged periods of time.



Scheme 5. Reactivity of **12** toward TBAF in THF or methanolic KOH.



Scheme 6. Proposed mechanism for the methoxide-induced cyclization of **12**.



Scheme 7. Reactivity of **9** toward TBAF in THF or methanolic KOH.

Because the redox chemistry of these derivatives is often central to their use as electro-active synthons, these compounds have been characterized by cyclic voltammetry at a platinum electrode to confirm that aspect (Table 1). As is often observed with ferrocene derivatives, the values of the oxidation potential correlate with the electronic properties of the substitutents.[34,35] When **1**, **12**, and **9** are compared with ethynyl (**2**), ethenyl, and formylferrocene, respectively, the introduction of a trimethylsilylethynyl substituent on the 1′ position induces an increase in the oxidation potential value of 110 mV (**1**), 70 mV (**12**), and 60 mV (**9**). The same effect is observed for ethenylferrocene and **6** and formylferrocene and **7** (+130 mV). These anodic shifts of the $E_{1/2}$ values are readily explained by the electron-withdrawing nature of these alkynyl substituents relative to ferrocene,[36] rendering the Fe(II) center more difficult to oxidize.[37] In the case of **11**, in addition to this metal-centered oxidation, a very cathodic and pseudo-reversible process is found at −1.08 V, which most likely corresponds to the reduction of the nitro group, its value being very close to that reported for (*p*-nitrophenyl)-ethynyltrimethylsilane (−1.01 V) and nitrobenzene (−1.19 V) under similar conditions.[38] Compared to **5**, the more negative value found for **13** is consistent with the presence of only one alkenyl substituent on the annular bridge. Within experimental uncertainty, this value is comparable to that reported

Table 1
Electrochemical data for the Fe(III)/Fe(II) oxidation in **1**–**2**, **5**–**7**, **9**–**13** and related mono-substituted ferrocene derivatives[a]

Compound	$E_{1/2}$[b]	ΔE_p[c]	i_{Pa}/i_{Pc}	Ref
1	0.74	126	1	This work
2	0.63	128	1	This work
11	0.74	78	0.9	This work
	−1.08	110	1	
Fc−CH=CH$_2$	0.46	116	0.9	This work
1,1′-Diethenylferrocene	0.47	—	irrev.[d]	18
12	0.53	122	1	This work
6	0.59	107	0.7	This work
Fc−C(O)H	0.77	113	1	This work
9	0.83	76	1	This work
10	0.68	72	1	This work
7	0.90	105	1	This work
13	0.48	106	1	This work
5	0.55	—	1	18
1,1′-(4-Hydroxy-1-butenylene)ferrocene	0.47	—	1	18

[a] Conditions: CH_2Cl_2 solvent, 0.1 M [nBu$_4$N][PF$_6$] supporting electrolyte, 20 °C, Pt electrode, sweep rate 0.10 V s^{-1}.
[b] $E_{1/2}$ values are in V vs SCE, FcH/FcH$^+$ as internal calibrant (0.46 V vs SCE).
[c] Peak-to-peak separation (mV).
[d] Chemically irreversible oxidation.

for the closely related hydroxyl ferrocenophane 1,1′-(4-hydroxy-L-butenylene)ferrocene.[20] Except for the 1-ethynyl-1′-ethenylferrocene **6**, and perhaps the nitro derivative **11**, an apparent chemical reversibility of the metal-centered oxidation process is observed at the electrode for all the new compounds synthesized in these studies.[39]

3. Conclusions

We have described a practical and efficient synthesis of 1′-trimethylsilylethynyl-1-ethynylferrocene (**1**) and of its related ethenyl (**12**) and formyl (**9**) analogues. These compounds are quite stable under standard laboratory conditions, as are their desilylated parents **6**/**7** featuring a pendant ethynyl group. Further functionalization of these derivatives by cross-coupling chemistry can easily be effected, as demonstrated by the straightforward preparation of **11** from **1**. In the field of metal alkynyl complexes, compounds such as **1** should provide simple access to a wealth of unsymmetrical 1,1′-bismetalla-alkynylferrocenyl trinuclear complexes, which have thus far proven problematic to obtain.[9d] We have also shown that KOH/MeOH or related alkoxy-containing mixtures should be avoided for cleavage of the trimethylsilyl protecting groups in compounds such as **12**, as this leads to the selective formation of ferrocenophane derivatives as in the case of **4** and **1**. Finally, we have observed that, in almost all cases, the iron-centered oxidation processes are chemically reversible at the electrode. These synthons should find considerable utility in extended redox-active assemblies and new ferrocene-based materials.[41]

4. Experimental section

4.1. General

All air and/or moisture sensitive manipulations were performed under an atmosphere of argon in distilled and deoxygenated solvents using standard Schlenk techniques. 1′-Iodo-1-formylferrocene (**8**)[10] and $[PdCl_2(PPh_3)_2]$[42] were prepared according to the literature methods, while other chemicals were obtained commercially and used without further purification. Standard work up consists of extraction of the reaction mixtures/solid residues with Et_2O (with filtration if necessary), washing of the organic extracts with water and saturated aqueous NaCl, drying over $MgSO_4$, filtration, and removal of the solvent under reduced pressure. Flash column chromatography was performed using silica gel (Merck Kieselgel 60, 230–400 mesh) in glass columns of various sizes (indicated as diameter×length). Unless otherwise stated R_f values were measured on silica plates. Preparative thin-layer chromatography was carried out on glass plates (20×20 cm) coated with silica (Merck 60 GF_{254}, 0.5 mm thick). ^1H and ^{13}C NMR spectra were recorded on Bruker DPX200, Bruker Ascend 400 MHz NMR or Bruker AVANCE 500 spectrometers, respectively, chemical shifts being referenced to the residual chloroform signal (δ 7.26 ppm for ^1H, 77.0 ppm for ^{13}C). High resolution mass spectra were obtained on a double quadrupole Waters Q-tof 2 equipped with an orthogonal time of flight analyzer and an electrospray source. Cyclic voltammograms were recorded using a PAR 263 instrument in dichloromethane solvent at 20 °C (0.1 M $[n\text{-}Bu_4N][PF_6]$) with 100 mV/s scan rate at a platinum disk (1 mm diameter) using an SCE reference electrode and ferrocene as internal calibrant (0.46 V).[43]

*4.1.1. 1′-Trimethylsilylethynyl-1-formylferrocene (**9**).* Trimethylsilylacetylene (1.55 mL, 10.88 mmol) was added to 1′-iodo-1-formyl-ferrocene (**8**; 2.46 g, 7.25 mmol), $[PdCl_2(PPh_3)_2]$ (0.255 g, 0.36 mmol), and CuI (0.138 g, 0.73 mmol) in THF/diisopropylamine (1:1, 50 mL) at 0 °C. The reaction mixture was warmed to room temperature and heated at 60 °C for 36 h. After removal of solvents and volatiles under vacuum and following standard work up, the crude oil was adsorbed onto silica and subjected to column chromatography (silica gel, 4.5×20 cm), eluting with hexanes/Et_2O (2:1). Removal of solvents from the combined fractions gave a red oil that was subjected to vacuum (30 mbar, 40 °C) to give **9** as a dark red solid (1.87 g, 83%). R_f (hexanes/Et_2O 2:1): 0.35. Mp: 64 °C. Elemental Analysis Calcd for $C_{16}H_{18}FeOSi$: C: 61.94; H: 5.85; found: C: 62.02, H: 5.91. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{18}FeNaOSi$ $[M+Na]^+$: 333.0374, found: 333.0373. IR (KBr, cm^{-1}): 2829 (m, $\nu_{C(O)-H}$), 2148 (s, $\nu_{C\equiv C}$), 1691 (s, $\nu_{C=O}$), 1245 (s, ν_{Si-C}). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 9.93 (s, 1H, CHO), 4.80, 4.60, 4.52, and 4.27 (4× t, 4× 2H, $^3J_{H,H}$=2 Hz, C_5H_4), 0.23 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 193.6 (s, CHO), 102.0 (s, **C**≡C–$SiMe_3$), 92.8 (s, C≡**C**–$SiMe_3$), 80.1 (s, C_{quat} C_5H_4–CHO), 75.2, 73.1, 71.2, and 70.2 (4× s, C_5H_4), 67.2 (s, C_{quat} C_5H_4–C≡C($SiMe_3$)), 0.1 (s, $SiMe_3$).

*4.1.2. 1′-Trimethylsilylethynyl-1-(gem-dibromoethenyl)ferrocene (**10**).* Carbon tetrabromide (1.66 g, 5.0 mmol) was added in small portions to triphenylphosphine (1.31 g, 5.0 mmol) and zinc dust (0.327 g, 5.0 mmol) in CH_2Cl_2 (10 mL) at 0 °C. After 24 h of stirring at room temperature, the resulting suspension was cooled to 0 °C and a solution of 1′-trimethylsilylethynyl-1-formylferrocene (**9**; 0.62 g, 2.0 mmol) in CH_2Cl_2 (5 mL) was added dropwise over 5 min. The cold bath was removed, and the reaction mixture stirred for 6 h at room temperature and then filtered through a small pad of silica gel (4×5 cm). The pad was washed with CH_2Cl_2 (150 mL) to elute all the orange materials and the solvents were removed from the combined filtrates under reduced pressure. The crude oil was purified by column chromatography (silica gel, 4×20 cm). An orange band was eluted with hexanes/Et_2O (95:5), collected and taken to dryness. The orange oil was dissolved in CH_2Cl_2 (5 mL) and MeOH (10 mL), and the volume of the resultant solution was reduced to ≈5 mL and then cooled to −90 °C in an EtOH/N_2 bath. After 30 min at −90 °C, the flask was removed from the cooling bath and the solvents were removed from the solid mass by cannula filtration upon warming to room temperature. Drying of the orange solid in vacuo afforded **10** (0.86 g, 92%). R_f (hexanes/Et_2O [99:1]): 0.51. Elemental Analysis Calcd for $C_{17}H_{18}Br_2FeSi$: C: 43.81, H: 3.89, found: C: 44.05, H: 3.90. HRMS (ESI): calcd for $C_{17}H_{18}Br_2FeSi$ $[M]^+$: 463.8894, found: 463.8896. IR (KBr, cm^{-1}): 3103 and 3099 (w, $\nu_{=C-H}$), 2146 (s, $\nu_{C\equiv C}$), 1656 (w, $\nu_{C=C}$), 1245 (s, ν_{Si-C}), 845 (s, $\delta_{=C-H}$), 679 (m, δ_{C-Br}). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 7.16 (s, 1H, −CH= CBr_2), 4.65, 4.45, 4.34, and 4.23 (4× m, 4× 2H, C_5H_4), 0.24 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 134.6 (s, =CBr_2), 103.1 (s, **C**≡C($SiMe_3$)), 91.8 (s, C≡**C**($SiMe_3$)), 84.6 (s, −CH=), 80.9 (s, C_{quat} C_5H_4), 73.0, 71.3, 70.8, and 70.1 (4× s, C_5H_4), 66.4 (s, C_{quat} C_5H_4), 0.2 (s, $SiMe_3$).

*4.1.3. 1′-Trimethylsilylethynyl-1-ethynylferrocene (**1**).* A solution of lithium diisopropylamide, prepared from diisopropylamine (0.76 mL, 5.40 mmol) and *n*-BuLi (3.10 mL of a 1.60 M solution in hexanes, 4.95 mmol) in THF (5 mL) at 0 °C, was added dropwise over 10 min to 1′-trimethylsilylethynyl-1-(*gem*-dibromoethenyl) ferrocene (**10**; 0.70 g, 1.50 mmol) in THF (15 mL) at −90 °C. After 1.5 h of stirring at −90 °C, the reaction mixture was hydrolyzed with saturated aqueous NH_4Cl (10 mL), warmed to room temperature and then subjected to a standard work up. The crude oil was quickly chromatographed (silica gel, 4×15 cm) using hexanes/Et_2O (95:5) as the eluent. The orange band was collected and the solvent evaporated under reduced pressure. The resulting orange oil crystallized upon standing at −20 °C for 16 h to give **1** as a low-melting orange solid (0.43 g, 94%). R_f (hexanes/Et_2O [99:1]): 0.65. Mp: <45 °C. HRMS (ESI) Calcd for $C_{17}H_{18}FeSi$ $[M]^+$: 306.0527, found: 306.0526. IR (KBr, cm^{-1}): 3304 (s, $\nu_{\equiv C-H}$), 2148 (s, $\nu_{C\equiv C(SiMe_3)}$), 2110 (m, $\nu_{C\equiv C(H)}$), 1248 (s, ν_{Si-C}), 652 (s, $\delta_{\equiv C-H}$). ^1H NMR (300 MHz,

$CDCl_3$, ppm): δ 4.45 (t, $^3J_{H,H}$=2 Hz, 4H, C_5H_4), 4.23 (dt, $^3J_{H,H}$=2 and 3 Hz, 4H, C_5H_4), 2.77 (s, 1H, ≡CH), 0.24 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 102.8 (s, **C**≡C($SiMe_3$)), 91.5 (s, C≡**C**($SiMe_3$)), 81.5 (s, **C**≡C(H)), 74.2 (s, C≡C(H)), 73.5, 73.4, 71.3, and 71.1 (4× s, C_5H_4), 66.5 and 65.4 (2× s, C_{quat} C_5H_4), 0.3 (s, $SiMe_3$). No accurate elemental analysis of **1** could be obtained due to its slow decomposition.

*4.1.4. 1′-Trimethylsilylethynyl-1-(p-nitrophenyl)ethynylferrocene (**11**).* 1′-Trimethylsilylethynyl-1-ethynylferrocene (**1**; 0.336 g, 1.10 mmol), *p*-bromonitrobenzene (0.202 g, 1.0 mmol), [$PdCl_2(PPh_3)_2$] (0.0175 g, 0.025 mmol), and CuI (0.0095 g, 0.050 mmol) in THF/diisopropylamine (1:1, 20 mL) were heated at 40 °C for 16 h. The solvents were removed, and the crude solid obtained following standard work up of the residue was adsorbed onto silica and placed on the top of a chromatographic column (silica gel, 3.5×20 cm). Elution with hexanes/CH_2Cl_2 (3:1) gave two bands: the first orange band comprised homocoupled alkyne and the unreacted starting acetylene, while the second burgundy-red band contained the title compound. After evaporation of solvents and recrystallization of the residue from hexanes at −18 °C, red crystals of **11** were collected on a sintered glass funnel, washed with cold hexanes (5 mL) and dried in vacuo (0.372 g, 87%). R_f (hexanes/CH_2Cl_2 [3:1]): 0.37. Elemental Analysis Calcd for $C_{23}H_{21}FeNO_2Si$: C: 64.64, H: 4.95, N: 3.28; found: C: 64.57, H: 5.32, N: 3.13. HRMS (ESI): Calcd for $C_{23}H_{21}FeNO_2Si$ $[M]^+$: 427.0691, found: 427.0692. IR (KBr, cm^{-1}): 2203 (s, $\nu_{C\equiv C(Ar)}$), 2144 (s, $\nu_{C\equiv C(SiMe_3)}$), 1508 and 1342 (s, ν_{NO_2}), 1250 (m, ν_{Si-C}), 850 (vs, δ_{Ar} para substituted). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 8.22 (d, 2H, $^3J_{H,H}$=6 Hz, C_6H_4), 7.62 (d, 2H, $^3J_{H,H}$=6 Hz, C_6H_4), 4.53, 4.48, 4.35, and 4.28 (4× s, 8H, C_5H_4), 0.20 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 146.5 (s, C_{ipso} $C_6H_4NO_2$), 131.9 (s, C_{ortho} $C_6H_4NO_2$), 131.0 (s, C_{para} $C_6H_4NO_2$), 123.6 (s, C_{meta} $C_6H_4NO_2$), 102.9 (s, −**C**≡C($SiMe_3$)), 94.2 (s, (Ar)**C**≡C−), 91.8 (s, −C≡**C**($SiMe_3$)), 84.9 (s, −C≡C(Ar)), 73.7, 73.6, 72.1, and 71.1 (4× s, C_5H_4), 66.7 (s, C_{quat} C_5H_4), 65.0 (s, C_{quat} C_5H_4), 0.2 (s, $SiMe_3$).

*4.1.5. 1′-Trimethylsilylethynyl-1-ethenylferrocene (**12**).* Methyltriphenylphosphonium bromide (1.50 g, 4.20 mmol) was suspended in THF (25 mL), cooled to 0 °C and treated with *n*-BuLi (2.50 mL, 4.0 mmol, 1.60 M solution in hexanes) at a rate of approximately 0.5 mL per minute. After 30 min of stirring at 0 °C, a solution of 1′-trimethylsilylethynyl-1-formylferrocene (**9**; 0.620 g, 2.0 mmol) in THF (5 mL) was added dropwise over 10 min, the cooling bath was removed and the reaction mixture stirred for 16 h at room temperature. Hydrolysis with water (25 mL) and standard work up furnished an orange oil, which was chromatographed (silica gel, 4×20 cm) using a gradient elution from pure hexanes to hexanes/Et_2O (98:2). The orange band was collected and solvent removed by rotary evaporation to give **12** as an orange solid (0.587 g, 95%), which was dried in vacuo after being solidified by standing at −20 °C for 16 h. R_f (hexanes): 0.27. Mp: <45 °C. Elemental Analysis Calcd for $C_{17}H_{20}FeSi$: C: 66.23, H: 6.54; found: C: 66.47, H: 6.15. HRMS (ESI): Calcd for $C_{17}H_{20}FeSi$ $[M]^+$: 308.0683, found: 308.0682. IR (KBr, cm^{-1}): 3088 and 3005 (m, $\nu_{=C-H}$), 2147 (s, $\nu_{C\equiv C}$), 1630 (m, $\nu_{C=C}$), 1246 (s, ν_{Si-C}), 926 and 842 (s, $\delta_{=C-H}$). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 6.42 (dd, 1H, $^3J_{H,H}$=12 and 18 Hz, −**H**C=CH_2), 5.36 (dd, 1H, $^3J_{H,H}$=18 Hz and $^2J_{H,H}$=1 Hz, −HC=C**H**$_2$ *trans*), 5.13 (dd, 1H, $^3J_{H,H}$=12 Hz and $^2J_{H,H}$=1 Hz, −HC=C**H**$_2$ *cis*), 4.35 (m, 4H, C_5H_4), 4.24 and 4.13 (2× t, 2× 2H, $^3J_{H,H}$=2 Hz, C_5H_4), 0.23 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 133.4 (s, =CH_2), 112.0 (s, −C=), 103.6 (s, **C**≡C($SiMe_3$)), 90.9 (s, C≡**C**($SiMe_3$)), 84.8 (s, C_{quat} C_5H_4), 72.9, 70.7, 69.9, and 68.6 (4× s, C_5H_4), 65.9 (s, C_{quat} C_5H_4), 0.3 (s, $SiMe_3$).

*4.1.6. 1′-Ethenyl-1-ethynylferrocene (**6**).* TBAF (0.75 mL of a 1.0 M solution in THF, 0.75 mmol) was added dropwise to 1′-trimethylsilylethynyl-1-ethenylferrocene (**12**) in THF (5 mL) at 0 °C. The cooling bath was removed, the reaction mixture was stirred for 1 h at room temperature, quenched with water (0.50 mL) and then concentrated under reduced pressure. The orange oil (0.115 g, 97%, approx. 95% pure by NMR) obtained after standard work up was freed of traces of solvent by prolonged drying under moderate vacuum (25 mbar). Extensive decomposition on both silica and alumina prevented further purification of **6** by chromatography. R_f (alumina, hexanes): 0.64. HRMS (ESI): Calcd for $C_{14}H_{13}Fe$ $[M+H]^+$: 237.0367, found: 237.0365. IR (liquid film, cm^{-1}): 3303 (vs, $\nu_{\equiv C-H}$), 3087 and 3004 (m, $\nu_{=C-H}$), 2140 (s, $\nu_{C\equiv C}$), 1629 (s, $\nu_{C=C}$), 984 and 897 (m and s, $\delta_{=C-H}$), 647 (s, $\delta_{\equiv C-H}$). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 6.44 (dd, 1H, $^3J_{H,H}$=10 and 18 Hz, −**H**C=CH_2), 5.39 (dd, 1H, $^3J_{H,H}$=18 Hz and $^2J_{H,H}$=1 Hz, −HC=C**H**$_2$ *trans*), 5.15 (dd, 1H, $^3J_{H,H}$=10 Hz and $^2J_{H,H}$=1 Hz, −HC=C**H**$_2$ *cis*), 4.37 (m, 4H, C_5H_4), 4.28 and 4.16 (2× t, 2× 2H, $^3J_{H,H}$=2 Hz, C_5H_4), 2.77 (s, 1H, ≡CH). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 133.4 (s, =CH_2), 112.1 (s, −C=), 84.8 (s, C_{quat} C_5H_4), 82.1 (s, **C**≡CH), 73.9 (s, C≡**C**H), 72.9, 71.3, 70.8 and 68.6 (4× s, C_5H_4), 64.8 (s, C_{quat} C_5H_4).

*4.1.7. 1′-Ethynyl-1-formylferrocene (**7**).*[33]

4.1.7.1. With TBAF. 1′-Trimethylsilylethynyl-1-formylferrocene (**9**; 0.155 g, 0.50 mmol) was dissolved in THF (5 mL), cooled to 0 °C and TBAF (0.75 mL of a 1.0 M solution in THF, 0.75 mmol) was added dropwise. After 1 h of stirring at room temperature, the reaction mixture was quenched with water (0.50 mL), concentrated under reduced pressure and worked up as usual. The resulting oil was adsorbed onto silica and chromatographed (silica gel, 2.5×20 cm). The orange band containing **7** eluted with hexanes/Et_2O (2:1) was collected. Solvents were removed by rotary evaporation and the dark red oil dried in vacuo to give a red wax (0.075 g, 63%).

4.1.7.2. With methanolic KOH. Aqueous KOH (0.4 mL of a 2.50 M solution, 1.0 mmol) was added dropwise to a cooled (0 °C) solution of 1′-trimethylsilylethynyl-1-formylferrocene (0.155 g, 0.50 mmol) in MeOH (25 mL). The reaction mixture was allowed to warm to room temperature slowly with the cold bath in place, and then stirred 24 h at room temperature, and poured into water (50 mL). After a standard work up and purification as described above, 0.085 g (71%) of the title compound was obtained. R_f (hexanes/Et_2O [2:1]): 0.36.

HRMS (EI) calcd. for $C_{13}H_{10}FeO$ $[M]^+$: 238.0081, found: 238.0078. IR (liquid film, cm^{-1}): 3283 (s, $\delta_{\equiv C-H}$), 2854 (m, $\nu_{C(O)-H}$), 2109 (m, $\nu_{C\equiv C}$), 1683 (s, $\nu_{C=O}$), 654 (m, $\delta_{\equiv C-H}$). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 9.96 (s, 1H, CHO), 4.84, 4.64, 4.56, and 4.31 (4× s, 4× 2H, C_5H_4), 2.82 (s, 1H, ≡CH). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 193.6 (s, CHO), 80.7 (s, **C**≡CH), 80.2 (s, C_{quat} C_5H_4), 75.6 (s, C≡**C**H), 75.2, 73.2, 71.3, and 60.3 (4× s, C_5H_4), 66.3 (s, C_{quat} C_5H_4). No accurate elemental analysis of **7** could be obtained due its slow decomposition.

*4.1.8. 1,1′-(4-Methoxy-1-butenylene)ferrocene (**13**).* 1-Trimethylsilylethynyl-1′-ethenylferrocene (**12**; 0.154 g, 0.50 mmol) was dissolved in MeOH (25 mL), cooled to 0 °C, and aqueous KOH (0.40 mL of a 2.50 M solution, 1.0 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature slowly with the cold bath in place, and then stirred for 24 h and poured into water (50 mL). After a standard work up, the yellow oil was purified by preparative TLC (silica, hexanes/Et_2O [95:5]). The yellow band, R_f: 0.26, was collected, taken-up into Et_2O and evaporated to dryness. Recrystallization of the residue from aqueous ethanol yielded **13** (0.127 g, 87%) as yellow needles. R_f (hexanes/Et_2O [95:5]): 0.18. Mp: 76 °C. Elemental Analysis Calcd for $C_{15}H_{16}FeO\cdot\frac{1}{4}H_2O$: C: 66.08, H: 6.10; found: C: 66.37, H: 5.93. HRMS (ESI): Calcd for $C_{15}H_{16}FeO$ $[M]^+$: 268.0550, found: 268.0548. IR (KBr, cm^{-1}): 3078 and 3006 (m, $\nu_{H-C=}$), 2808 (m, ν_{H-C} OMe), 1646 (m, $\nu_{C=C}$), 1088 (s, ν_{C-O}). ^1H NMR

(300 MHz, $CDCl_3$, ppm): δ 6.18 (d, 1H, $^3J_{H,H}$=12 Hz, C_5H_4–C**H**=CH–), 5.89 (td, 1H, $^3J_{H,H}$=9 and 12 Hz, C_5H_4–CH=C**H**–), 4.36 (m, 1H, C_5H_4), 4.28–4.18 (m, 5H, C_5H_4), 4.12 (m, 1H, C_5H_4), 4.01 (m, 1H C_5H_4), 3.55 (d, 1H, $^3J_{H,H}$=6 Hz, C_5H_4–C**H**(OMe)), 3.16 (s, 3H, OMe), 2.91 (td, $^3J_{H,H}$=9 and 12 Hz, 1H, H CH_2), 2.50 (t, 1H, $^3J_{H,H}$=10 Hz, H CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 129.1 (s, C_5H_4–**C**H=CH–), 127.5 (s, C_5H_4–CH=**C**H–), 84.0 and 81.9 (2× s, C_{quat} C_5H_4), 76.1 (s, C_5H_4–**C**H(OMe)–), 70.3, 70.2, 70.0, 69.3, 68.9, 68.7, 68.5 and 66.9 (8× s, C_5H_4), 56.1 (s, OMe), 35.0 (s, CH_2).

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Supplementary data

Copies of ^1H NMR and ^{13}C NMR spectroscopic data of **1**, **6**, **7** **9**, **10**, **11**, **12**, and **13**, $^1H/^1H$ COSY of **13**, CV trace for **1**, **6**, **7**, **9**, **11**, **12**, and **13** can be found, in the online version. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.01.093.

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