Synthesis of Symmetric and Unsymmetric 1,1′-Dialkenylferrocenes via Samarium Diiodide Promoted Reactions of 1,1′-Diacetylferrocene with Halides

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Monoalkenylferrocenes were prepared from 1,1′-diacetylferrocene and appropriate benzyl bromides by the promotion of samarium diiodide. A practical method for preparation of both symmetric and unsymmetric dialkenylferrocenes was also explored. The reactions were stereoselective to give only (*E*) double bonds. The unsymmetric dialkenylferrocene bearing electron-donating substituent (e.g. methoxy group) and electron-withdrawing substituent (e.g. cyano group) on different phenyl rings likely exhibits a large nonlinear optical property.

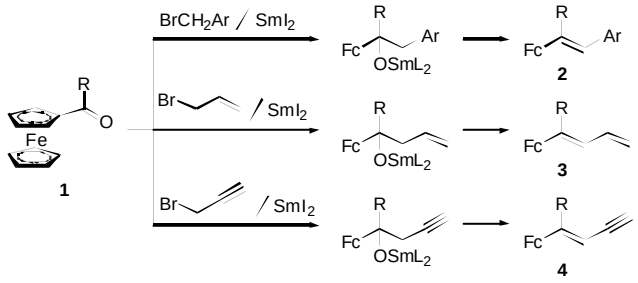
INTRODUCTION

Ferrocenyl alkenes and dienes are important substrates for applications in material science.[1-3] For example, 1-ferrocenyl-2-(4-nitrophenyl)ethene and the related ferrocenyl alkenes exhibit large optical non-linearities useful for the development of optical information processing.[1] Ferrocenyl 1,3-butadiene is an important substrate for manufacturing copolymer and homopolymer,[2] which are employed as the coating material for aerospace transportation to enhance resistance against photo degradation. Ferrocene-1,3-butadiene can also be used as an enhancement fuel in solid propellants.[2]

We have recently reported an efficient method for the preparation of ferrocenyl alkenes **2**, dienes **3** and enynes **4** by the SmI_2 promoted condensation reactions of ferrocene carbonyls with benzyl bromides, allyl bromide and propargyl bromide (Fig. 1).[4] This SmI_2 promoted one-pot reaction proceeds with a Barbier-type addition[5] followed by elimination of $HOSmL_2$ (L = I or Br)[6] to furnish the desired products in very high yields. By comparison with the previous methods using Wittig reactions,[7] organometallic addition reactions,[8] or Heck coupling reactions,[9] our method shows several advantageous features of simple operation and high yields. We describe herein an application of the SmI_2 promoted reaction to 1,1′-diacetylferrocene (**5**) for formation of symmetric and unsymmetric 1,1′-dialkenylferrocenes (Scheme I).

RESULTS AND DISCUSSION

When a THF solution of 1,1′-diacetylferrocene (1.2 mmol) and benzyl bromide (2 mmol) was treated with SmI_2 (3.6 mmol) at ambient temperature for 24 h, the product of monoalkenylferrocene **6a** was obtained in a quantitative yield. No dialkenylferrocene was formed. The similar reactions with *p*- and *m*-methylbenzyl bromide also gave monoalkenylferrocenes **6b** and **6c** in quantitative yields, but not the corresponding dialkenylferrocenes. However, a dialkenylferrocene **7d** could be obtained in 19% yield along with the



R = H, CH_3, Ph and *n*-Pr　　L = I or Br
Ar = Ph, *p*-NCC_6H_4, *m*-$MeOC_6H_4$, 2-naphthyl, *p*-$F_3CC_6H_4$

Fig. 1. Synthesis of ferrocenyl alkenes, dienes and enynes via samaruim diiodide promoted tandem addition and dehydration of ferrocenyl carbonyls with halides.

Dedicated to Professor Sheng-lieh Liu on the occasion of his nineteenth birthday.

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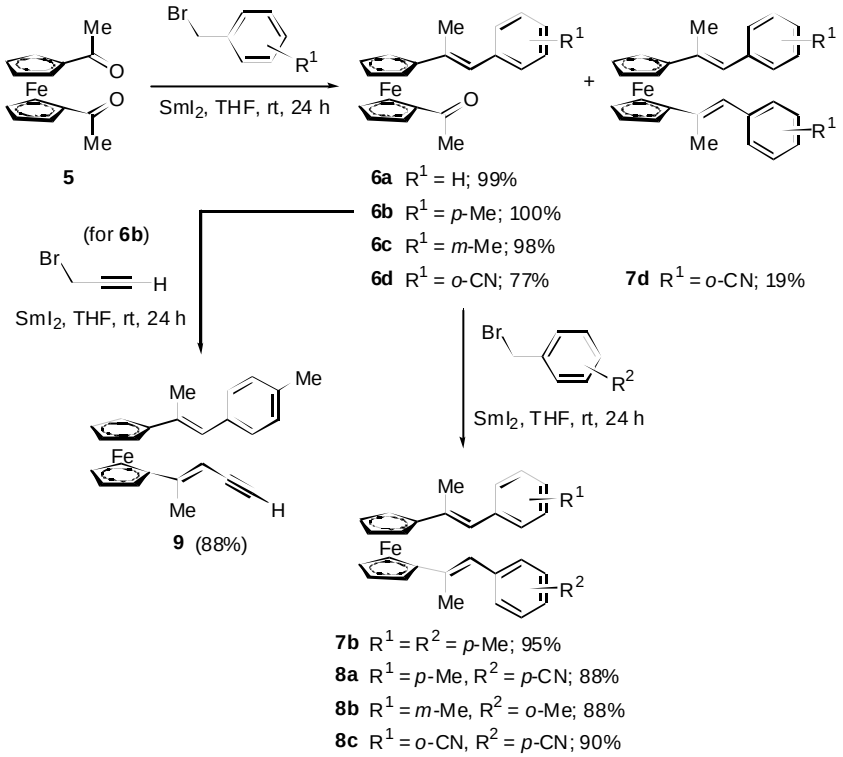
Scheme I



major monoalkenylferrocene product **6d** (77%) by the SmI_2 promoted reaction with *o*-cyanobenzyl bromide. These results might reflect the relative reluctance of the second Sm-Barbier addition to the monoalkenylferrocene.

Fortunately, the second Sm-Barbier addition to monoalkenylferrocenes was achieved by a subsequent treatment with freshly prepared SmI_2 and appropriate benzyl bromides. Thus, both symmetric and unsymmetric dialkenylferrocenes **7b** and **8a-c** were synthesized in an expedient manner. A condensation reaction of monoalkenylferrocene **6b** with propargyl bromide was also carried out by the promotion of SmI_2, giving compound **9** in 88% yield.

The detailed NMR and X-ray analyses indicated that the double bonds in the prepared mono- and dialkenyl ferrocenes **6a-9** all existed as the (*E*) configuration, presumably due to the stability of (*E*) isomers over the (*Z*) isomers.

Crystal data

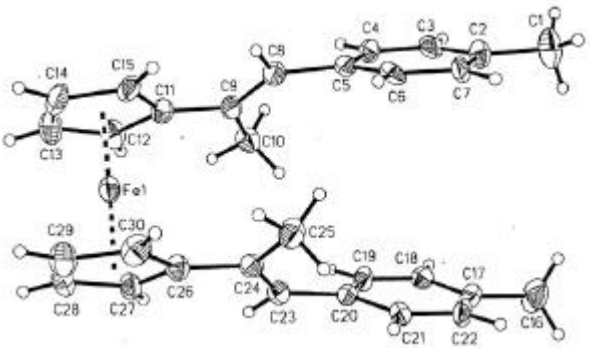
Dialkenylferrocenes **7b**, **7d**, **8a** and **8c** were recrystallized from $CHCl_3$/hexane. Essential crystal data of these compounds appear in Table 1. The solid-state structures of **7b** ($R^1 = R^2 =$ *p*-Me), **8a** ($R^1 =$ *p*-Me, $R^2 =$ *p*-CN) and **8c** ($R^1 =$ *o*-CN, $R^2 =$ *p*-CN) existed as the syn conformation, whereas that of **7d** ($R^1 = R^2 =$ *o*-CN) existed as the anti conformation. The syn conformation of **7d** might be disfavored by the steric effect from the *ortho*-substituents.

Summary

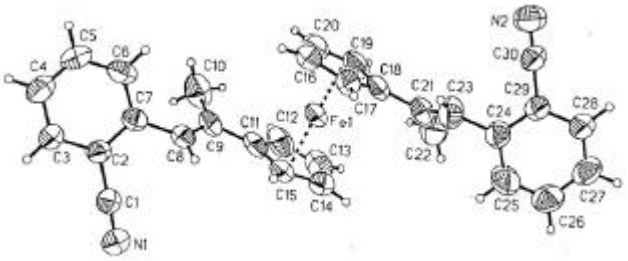
The different reactivity of 1,1′-acetylferrocene against its monoalkenylferrocene derivatives (e.g. **6a-d**) allows us to synthesize a series of unsymmetric dialkenylferrocenes (e.g. **8a-c** and **9**) with exclusive (*E*) configuration. The unsymmetric dialkenylferrocene **8a** ($R^1 =$ *p*-Me, $R^2 =$ *p*-CN) with a donor-acceptor character likely exhibits a large nonlinear optical property.[1]

EXPERIMENTAL SECTION

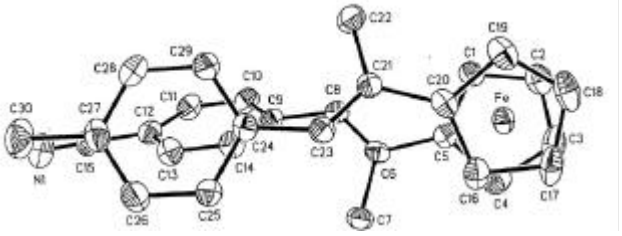
Melting points are uncorrected. Chemical shifts are reported relative to $CHCl_3$ (δ_H 7.26) and $CDCl_3$ [δ_C (central line of t) 77.0]. All reactions requiring anhydrous conditions were conducted in flame-dried apparatus under an atmosphere of nitrogen. Syringes and needles for the transfer of reagents were dried at 120 °C and allowed to cool in a desiccator over P_2O_5 before use. THF was distilled from sodium benzophenone ketyl. Column chromatography was generally carried out on Kieselgel 60 (40-63 μm) unless specified. Merck silica gel 60F sheets were used for analytical thin-layer chromatography.



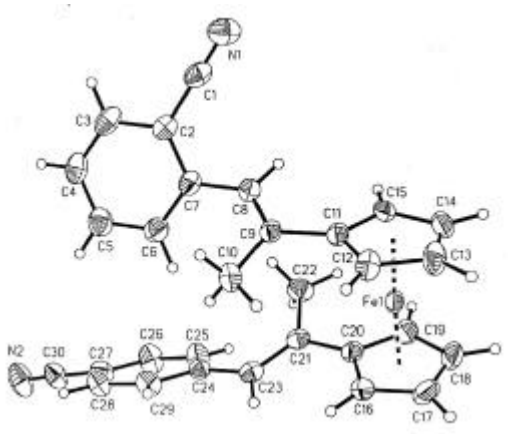
ORTEP drawing of compound **7b**



ORTEP drawing of compound **7d**



ORTEP drawing of compound **8a**



ORTEP drawing of compound **8c**

Representative Procedure for the SmI_2 Promoted Reactions of 1,1′-Diacetylferrocene with Benzyl Bromides and Propargyl Bromide

Under an atmosphere of argon, a deep blue SmI_2 solution (0.1 M) was prepared by treatment of Sm (661 mg, 4.4 mmol) with 1,2-diiodoethane (1.01 g, 3.6 mmol) in an hydrous THF (20 mL) for 1.5 h at room temperature (27 °C). To the SmI_2 solution (cooled in an ice bath) were added a THF solution (10 mL) of appropriate bromide (2.0 mmol) and 1,1′-diacetylferrocene (1.2 mmol). The ice bath was removed, and the mixture was kept stirring at 0-27 °C for 24 h. The septum was removed, and the mixture was stirred at room temperature for additional 48 h. The mixture was passed through a short silica gel column by rinse with EtOAc/hexane (1:1). The filtrate was concentrated, and chromatographed by elution with EtOAc/hexane (5:95) to give the desired condensation products.

1-Acetyl-1′-(1-methyl-2-phenyl)ethenylferrocene (6a)

According to the representative procedure, the SmI_2 promoted reaction of 1,1′-acetylferrocene (324 mg, 1.2 mmol) with benzyl bromide (342 mg, 2.0 mmol) gave the title compound (409 mg) in quantitative yield (99 %). **6a**: Red-brown solid, mp 92-94 °C; IR (KBr) 1612 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.15 (3H, d, J = 1.0 Hz), 2.32 (3H, s), 4.29 (2H, t, J = 1.7 Hz), 4.45 (2H, t, J = 1.7 Hz), 4.49 (2H, t, J = 1.7 Hz), 4.72 (2H, t. J = 1.7 Hz), 6.73 (1H, d, J = 1.0 Hz), 7.37-7.20 (5H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.8, 27.5, 67.0 (2 ×), 70.5 (4 ×), 73.3 (2 ×), 80.1, 90.7, 104.7, 126.3, 128.1 (2 ×), 129.0 (2 ×), 133.2, 137.8, 201.8; FAB-MS *m/z* 344 (M^+); HRMS Calcd for $C_{21}H_{20}FeO$: 344.0864. Found: 344.0876.

1-Acetyl-1′-[1-methyl-2-(4-methylphenyl)]ethenylferrocene (6b)

According to the representative procedure, the SmI_2 promoted reaction of 1,1′-acetylferrocene (324 mg, 1.2 mmol) with 4-methylbenzyl bromide (370 mg, 2.0 mmol) gave the title compound (409 mg) in quantitative yield (100%). **6b**: Red-brown solid; mp 60-62 °C; IR (KBr) 1658 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.15 (3H,d, J = 1.3 Hz), 2.32 (3H, s), 3.35 (3H, s), 4.28 (2H, t, J = 2.0 Hz), 4.45 (2H, t, J = 2.0 Hz), 4.49 (2H, t, J = 2.0 Hz), 4.72 (2H, t, J = 2.0 Hz), 6.71 (1H, s), 7.26-7.13 (4H, m); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 16.8, 21.1, 27.5, 66.9 (2 ×), 70.4 (4 ×), 73.2 (2 ×), 80.5, 90.9, 124.5, 128.8 (4 ×), 132.3, 134.9, 135.9, 201.8; FAB-MS *m/z* 358 (M^+); HRMS Calcd for $C_{22}H_{22}FeO$: 358.1020. Found: 358.1023.

Table 1. Crystal Data of Compounds **7b**, **7d**, **8a** and **8c**

Compound	**7b**	**7d**	**8a**	**8c**
Formula	$C_{30}H_{30}Fe$ ½ H_2O	$C_{30}H_{24}FeN_2$	$C_{30}H_{27}FeN$	$C_{30}H_{24}FeN_2$
Diffractometer	SMART CCD	SMART CCD	SMART CCD	SMART CCD
Temperature (K)	200	295(2)	295(2)	150
λ(Mo, K_α), Å	0.7107	0.7107	0.7107	0.7107
Space group	P -1	Cc	$P2_1$	$P2_1/n$
a (Å)	8.337(1)	7.966(1)	11.390(1)	15.249(1)
b (Å)	10.029(1)	18.646(1)	7.527(1)	7.743(1)
c (Å)	27.675(1)	16.333(1)	13.750(1)	19.959(1)
α (deg.)	84.82(1)	90	90	90
β (deg.)	89.53(1)	100.08(1)	102.42(1)	102.62(1)
γ (deg.)	88.81(1)	90	90	90
V ($Å^3$)	2303.74(5)	2388.4(2)	1151.30(4)	2299.7(1)
Z	4	4	2	4
D(calc), $g.cm^{-3}$	1.310	1.303	1.319	1.353
F(000)	960	976	480	976
Crystal size (mm)	0.30 × 0.20 × 0.02	0.30 × 0.25 × 0.20	0.50 × 0.10 × 0.10	0.25 × 0.25 × 0.20
θ range for data collection	0.74-25.00	2.18-27.49	1.52-27.50	1.90-25.00
No. of meas. Reflns.	22366	11728	15126	17933
No. of unique reflns, R_{int}	8091, 0.067	5302, 0.027	5278, 0.058	4049, 0.023
No. of obs. Reflns. (I>2(σ)I)	7402	5091	4856	3950
No. of refined params.	714	299	290	299
Goodness-of-fit on F^2	1.038	1.030	1.001	1.027
R_1, wR_2	0.077, 0.196	0.041, 0.102	0.050, 0.102	0.037, 0.100
Extinction coefficient	0.010(1)	0.000(1)	0.017(2)	0.000(1)

$R_{int} = \Sigma | I_i - \bar{I} | / \Sigma \bar{I}$
$R_1 = \Sigma | F_o - F_c | / \Sigma | F_o |$
$wR_2 = (\Sigma w | F_o^2 - F_c^2 |^2 / \Sigma w F_o^4)^{½}$
Compound **7b** has disorder part in the phenyl ring as rotation around C-C single bond.

1-Acetyl-1′-[1-methyl-2-(3-methylphenyl)]ethenylferrocene (6c)

According to the representative procedure, the SmI_2 promoted reaction of 1,1′-acetylferrocene (324 mg, 1.2 mmol) with 3-methylbenzyl bromide (370 mg, 2.0 mmol) gave the title compound (420 mg) in 98% yield. **6c**: Red-brown oil; IR (KBr) 1671 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.16 (3H, s), 2.33 (3H, s), 3.37 (3H, s), 4.29 (2H, t, *J* = 1.9 Hz), 4.45 (2H, t, *J* =1.9 Hz), 4.49 (2H, t, *J* = 1.9 Hz), 4.72 (2H, t, *J* = 1.9 Hz), 6.71 (1H, s), 7.29-7.03 (4H, m); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 16.8, 21.4, 27.5, 66.9 (2 ×), 70.4 (4 ×), 73.3 (2 ×), 79.9, 90.8, 124.7, 126.0, 127.0, 128.0, 129.6, 132.9, 137.6, 137.7; FAB-MS *m/z* 358 (M^+); HRMS Calcd for $C_{22}H_{22}FeO$: 358.1020. Found: 358.1028.

1-Acetyl-1′-[1-methyl-2-(2-cyanophenyl)]ethenylferrocene (6d) and 1,1′-Bis[1-methyl-2-(2-cyanophenyl)]ethenylferrocene (7d)

According to the representative procedure, the SmI_2 promoted reaction of 1,1′-acetylferrocene (324 mg, 1.2 mmol) with 2-cyanobenzyl bromide (392 mg, 2.0 mmol) gave **6d** (420 mg, 77%) and **7d** (110 mg, 19%).

6d: Red-brown oil; IR (KBr) 2217, 1669 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.06 (3H, d, *J* = 1.3 Hz), 2.32 (3H, s), 4.31 (2H, t, *J* = 3.7 Hz), 4.77-4.87 (6H, m), 6.85 (1H, m), 7.29 (1H, t, *J* = 7.5 Hz), 7.44 (1H, d, *J* = 7.5 Hz), 7.53 (1H, t, *J* = 7.5 Hz), 7.60 (1H, d, *J* = 7.5 Hz); ^{13}C NMR ($CDC1_3$, 75 MHz) δ 16.9, 27.6, 67.3 (2 ×), 70.6 (2 ×), 70.9 (2 ×), 73.7 (2 ×), 80.0, 88.6, 112.0, 118.2, 120.2, 126.6, 129.8, 131.9, 132.2, 133.7, 138.5, 141.5, 201.7; FAB-MS *m/z* 369 (M^+); HRMS Calcd for $C_{22}H_{19}FeNO$: 369.0816. Found: 369.0811.

7d: Red-brown solid; mp 122-124 °C; IR (KBr) 2227, 1620 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.14 (6H, d, *J* = 1.2 Hz), 4.35 (4H, t, *J* = 1.5 Hz), 4.54 (4H, t, *J* = 1.5 Hz), 6.88 (2H, s), 7.26 (2H, t, *J* = 7.5 Hz), 7.35 (2H, d, *J* = 7.5 Hz), 7.47 (2H, t, *J* = 7.5 Hz), 7.60 (2H, d, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.3 (2 ×), 67.4 (4 ×), 70.9 (4 ×), 88.0 (2 ×), 112.1 (2 ×), 118.4 (2 ×), 119.3 (2 ×), 126.2 (2 ×), 129.7 (2 ×), 132.1 (2 ×), 133.8 (2 ×), 139.7 (2 ×), 141.9 (2 ×); FAB-MS *m/z* 468 (M^+); HRMS Calcd for $C_{30}H_{24}FeN_2$: 468.1289. Found:

468.1290. The structure of **7d** (recrystallized from $CHCl_3$/hexane) was confirmed by an X-ray diffraction analysis.

1,1′-Bis[1-methyl-2-(4-methylphenyl)]ethenylferrocene (7b)

According to the representative procedure, the SmI_2 (0.9 mmol) promoted reaction of the substituted acetylferrocene **6b** (215 mg, 0.6 mmol) with 4-methylbenzyl bromide (185 mg, 1.0 mmol) gave the title compound (255 mg) in 95% yield. **7b**: Red-brown solid; mp 127-129 °C; IR (KBr) 1626 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.19 (3H, s), 2.20 (3H, s), 2.36 (6H, s), 4.26 (4H, t, *J* = 1.9 Hz), 4.44 (4H, t, *J* = 1.9 Hz), 6.69 (2H, s), 7.24-7.10 (8H, m); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 17.0 (2 ×), 21.2 (2 ×), 66.7 (4 ×), 69.7 (5 ×), 90.0 (2 ×), 123.3 (2 ×), 128.8 (8 ×), 133.7 (2 ×), 135.4 (2 ×), 135.5, 152.2; FAB-MS *m/z* 446 (M^+); HRMS Calcd for $C_{30}H_{30}Fe$: 446.1693, Found: 446.1697. The structure of **7b** (recrystallized from $CHCl_3$/hexane) was confirmed by an X-ray diffraction analysis.

1-[1-Methyl-2-(4-cyanophenyl)]ethenyl-1′-[1-methyl-2-(4-methylphenyl)]ethenylferrocene (8a)

By a procedure similar to that for compound **7b**, the SmI_2 promoted reaction of the substituted acetylferrocene **6b** (215 mg, 0.6 mmol) with 4-cyanobenzyl bromide (196 mg, 1.0 mmol) gave the title compound **8a** (241 mg) in 88% yield. **8a**: Red-brown solid, mp 157-159 °C; IR (KBr) 2223, 1606 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.18 (3H, d, *J* = 1.1 Hz), 2.20 (3H, d, *J* = 1.1 Hz), 2.38 (3H, s), 4.28 (2H, t, *J* = 2.0 Hz), 4.33 (2H, t, *J* = 2.0 Hz), 4.48-4.46 (4H, m), 6.64 (1H, s), 6.68 (lH, s), 7.17-7.10 (3H, m), 7.27 (2H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.0, 17.2, 21.1, 66.7 (2 ×), 66.9 (2 ×), 69.7 (2 ×), 70.2 (2 ×), 88.6, 90.3, 108.7, 119.2, 121.6, 123.6, 128.7, 128.8 (2 ×), 129.2 (2 ×), 131.7 (2 ×), 131.9, 133.1, 135.1, 135.7, 138.6, 142.8; FAB-MS *m/z* 457 (M^+); HRMS Calcd for $C_{30}H_{27}FeN$: 457.1493, Found: 457.1496. The structure of **8a** (recrystallized from $CHCl_3$/hexane) was confirmed by an X-ray diffraction analysis.

1-[1-Methyl-2-(2-methylphenyl)]ethenyl-1′-[1-methyl-2-(3-methylphenyl)]ethenylferrocene (8b)

By a procedure similar to that for compound **7b**, the SmI_2 promoted reaction of the substituted acetylferrocene **6c** (215 mg, 0.6 mmol) with 2-methylbenzyl bromide (185 mg, 1.0 mmol) gave the title compound **8b** (241 mg) in 88% yield. **8b**: Red-brown oil; IR (KBr) 1630, 1602 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.97 (3H, s), 2.14 (3H, s), 2.17 (3H, s), 2.25 (3H, s), 4.18 (4H, m), 4.36 (4H, m), 6.63 (2H, s), 7.14-6.93 (8H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.8, 17.1, 20.1, 21.5, 66.7 (2 ×), 66.8 (2 ×), 70.0 (2 ×), 70.1 (2 ×), 89.4, 89.9, 122.4, 123.6, 125.3, 126.0, 126.4, 126.7, 128.0, 129.4, 129.6, 129.8, 134.3, 134.4, 136.3. 137.5, 137.6, 138.3; FAB-MS *m/z* 446 (M^+); HRMS Calcd for $C_{30}H_{30}Fe$: 446.1697. Found: 446.1678.

1-[1-Methyl-2-(2-cyanophenyl)]ethenyl-1′-[1-methyl-2-(4-cyanophenyl)]ethenylferrocene (8c)

By a procedure similar to that for compound **7b**, the SmI_2 promoted reaction of the substituted acetylferrocene **6d** (221 mg, 0.6 mmol) with 4-cyanobenzyl bromide (196 mg, 1.0 mmol) gave the title compound **8c** (253 mg) in 90% yield. **8c**: Red-brown solid, mp 123-125 °C; IR (KBr) 2226, 1622, 1602 cm^{-1}; ^1H NMR ($CDC1_3$, 300 MHz) δ 2.10 (3H, d, *J* = 1.1 Hz), 2.20 (3H, d, *J* = 1.1 Hz), 4.30 (2H, t, *J* = 1.7 Hz), 4.35 (2H, t, *J* = 1.7 Hz), 4.50 (4H, m), 6.67 (1H, s), 6.85 (1H, s), 7.63-7.28 (8H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.1,17.3, 67.2 (5 ×), 70.4 (2 ×), 70.7 (2 ×), 88.0, 88.8, 108.7, 111.9, 118.3, 119.2, 119.3, 121.8, 126.3, 129.2 (2 ×), 129.4, 131.7 (2 ×), 132.0, 132.7, 138.4, 139.3, 141.6, 142.8; FAB-MS *m/z* 468 (M^+); HRMS Calcd for $C_{30}H_{24}FeN_2$: 468.1289. Found: 468.1304. The structure of **8c** (recrystallized from $CHCl_3$/hexane) was confirmed by an X-ray diffraction analysis.

1-[1-Methyl-2-(4-methylphenyl)]ethenyl-1′-(pent-1-yn-3-en-4-yl)ferrocene (9)

By a procedure similar to that for compound **7b**, the SmI_2 promoted reaction of the substituted acetylferrocene **6b** (430 mg, 1.2 mmol) with propargyl bromide (297 mg, 2.0 mmol) gave the title compound **9** (402 mg) in 88% yield. **9**: Red-brown oil; IR (KBr) 1625, 1604 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.22 (3H, s), 2.27 (3H, s), 2.41 (3H, s), 3.28 (1H, d, *J* = 2.3 Hz), 4.28 (2H, m), 4.31 (2H,m), 4.41 (2H, m), 4.46 (2H, m), 5.70 (1H, d, *J* = 2.3 Hz), 6.75 (1H, s), 7.22 (2H, d, *J* = 8.0 Hz), 7.31 (2H, d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.9, 18.2, 21.1, 66.8 (2 ×), 66.9 (2 ×), 70.0 (2 ×), 70.5 (2 ×), 81.3 (2 ×), 82.7, 85.8, 90.2, 101.0, 123.7, 128.8 (2 ×), 128.9 (2 ×), 133.1, 135.2, 135.6, 149.4; FAB-MS *m/z* 380 (M^+), HRMS Calcd for $C_{25}H_{24}Fe$: 380.1227. Found: 380.1224.

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Key Words

1,1'-Diacetylferrocene; 1,1'-Dialkenylferrocenes; Samaruim diiodide.

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