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Synthesis of ferrocenes with ene-terminus via water-promoted Barbier-like carbonyl allylation using bimetallic copper(II)/tin(II) reagent

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Abstract

Barbier-type γ-regiospecific allylation of formylferrocene (**1**) with allyl bromides in the presence of stannous chloride dihydrate and catalytic cupric chloride in dichloromethane–water (1:1) afforded corresponding ferrocenyl dienes $FcCHC(R^1)C(R^2)CH_2$ (**3**–**6**). On the other hand, similar reactions of 1,1′-bis-formylferrocene (**2**) yielded oxa-bridged [3]-ferrocenophanes having allyl pendants $Fc[CH_2C(R^2)CH(R^1)CH\text{-}\mu(O)\text{-}CHCH(R^1)C(R^2)CH_2]$ (**8**–**11**). The latter appear to result from the dehydration of intermediate homoallylic alcohols. Dehydration could be arrested in case of reaction of **1** and **2** with 1-bromo-3-methyl-but-2-ene, which results in the formation of homoallylic alcohols $FcCH(OH)C(Me_2)CHCH_2$ (**7**) and $Fc[CH(OH)C(Me_2)CHCH_2]_2$ (**12**), respectively. All the reactions completely fail in absence of water.

Keywords: Alkenylferrocene; 1,3-Butadienylferrocene; [3]-Oxa-ferrocenophane; Allyltin; Allylation

1. Introduction

Ferrocene derivatives having olefinic architecture gained prominence by virtue of their exciting structure, chemical reactivity, and potential use as molecular building blocks and in the realm of supramolecular chemistry as redox switching receptors [1–4]. Ferrocenophanes are a class of ferrocene macrocycles which, beside their bifunctional character, have drawn recent interest as building blocks for ring opening polymerization leading to soluble ferrocene-linked polymers [5–9]. Ferrocenes and ferrocenaphanes having unsaturated side chains are expected to impart physical and chemical phenomena arising from electronic communication through bond processes. The presence of donor functionalities in the bridge can further enhance the possibility of the ferrocenophane to act as potential receptor towards cation or anion recognition. The synthesis of ferrocenophanes with conjugated connecting bridges have been achieved via copper-catalyzed coupling of 1-ethynyl-1′-iodoferrocene, reductive coupling of 1,1′-bis-formylferrrocene using low-valent titanium reagents, and base-catalyzed condensation [10].

A major inspiration towards this study is the recent reports on the construction of bridged metallocenes from diallyl metallocenes via ring closing metathesis (RCM) (Scheme 1) [11]. We believe that this will promote a new focus on synthesis of ferrocenes with ene-terminus. Examples of ferrocenes with terminal-unsubstituted olefin backbone are limited to allyl, vinyl, and butadienyl ferrocenes. Capping a ferrocene unit with ene-chromophore majorly relies on Wittig protocol, McMurry coupling, and organometallic addition reactions [12]. We have recently described a Hunsdiecker–Heck methodology for the synthesis of ferrocene-capped conjugated polyenes (Scheme 2, where $Z = CO_2Me$, CO_2Et, CO_2H, $CONH_2$, 4-$NO_2C_6H_4$–) [13]. It is to be noted that due to the known limitation of Heck reaction, the method cannot be applied for the synthesis of polyenes with ene-terminus ($Z = H$). In this article, we present a water-promoted carbonyl allylation route to gain access to such building blocks from easily

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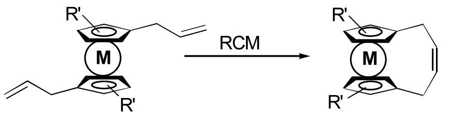
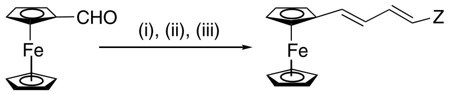


Scheme 1.

available precursors such as formylferrocene and 1,1′-bis-formylferrocene.

2. Results and discussion

Attempted allylation of **1** (in 1-mM scale) with allyl magnesium bromide, allylindium, and allyltributyltin were unsuccessful in our hand, resulting in complicated and messy product mixtures in all cases. Addition of catalysts such as $Pd_2(dba)_3$ and $PtCl_2(PPh_3)_2$, which are known to promote allylation [14], was also found to be ineffective. Henceforth, we switched to utilize a carbonyl allylation reaction under Barbier framework. The synthetic potential and operational simplicity of Barbier reactions are well recognized. Allyltin reagents can be generated in situ from allyl halides and metal or metal salts [15]. Attempted reaction of **1** with allylbromide and tin metal powder in THF led to ferrocenyl diene (**3**) in 15% yield after 24 h. Most gratifyingly we observed that a bimetallic combination comprising of catalytic copper(II) halide and stoichiometric tin(II) chloride leads to effective activation of allyl halides and promote its reaction with formylferrocenes **1** and **2** in aqueous-organic media. Thus, reaction of **1** (0.5 mmol) with 3-bromopropene (1 mmol), stannous chloride dihydrate (1 mmol), and cupric chloride dihydrate (0.05 mmol) in dichloromethane–water (1:1, v/v) afforded ferrocenyl diene **3** in 58% isolated yield after 2 h (Tables 1–3). Similar reactions of 1-bromo-2-butene, 3-bromo-2-methyl-1-propene, and 3-bromo-1-phenyl-1-propene afforded the corresponding dienes **4**–**6** in moderate yields (Table 1). Most noteworthy is the effect of water [16]. Reactions without water showed $<5\%$ conversion. Acid-catalyzed dehydration of ferrocenyl alcohols is reported earlier [17]. Therefore, we measured the pH of the aqueous part of the reaction mixture during the reaction and found it to be highly acidic (pH 2–4). The reaction can be rationalized as in Scheme 3, which involves (a) prior formation of cationic allyltin, (b) allyl transfer from allyltin to Fc–CHO, and (c) dehydration of the intermediate homoallylic alcohol to the diene **3**. Indeed, using 1-bromo-3-methyl-but-2-ene, dehydration could be arrested leading to the formation of homoallylic alcohol **7** which was isolated in 96% yield (Scheme 4). It is to be noted that the reactions are 100% γ-regioselective, affording products with terminal-unsubstituted olefin linkage.



(i) $CH(CO_2H)_2$ Py / Piperidine/105°C,

(ii) N-iodosuccinimide/$Bu_4N^+(CF_3COO)^-$ /DCE/-40°C

(iii) CH_2=CH-Z/Pd(OAc)$_2$/LiCl/(4-tolyl)$_3$As/Et_3N/MeCN

Scheme 2.

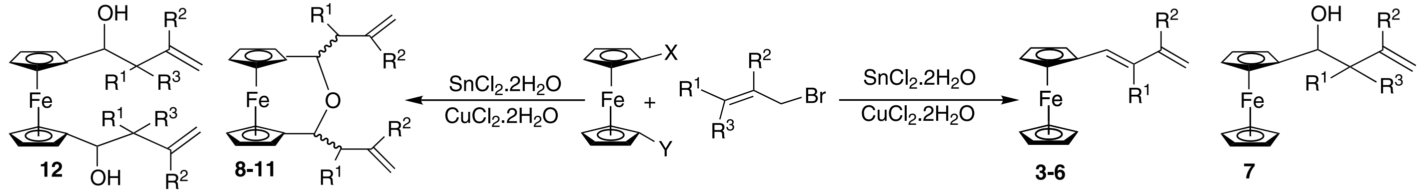
The γ-regiospecific allylation reaction was further extended to 1,1′-bis-formylferrocene (**2**). Reaction of **2** (0.25 mmol) and 3-bromopropene (2 mmol) in presence of catalytic cupric chloride (0.05 mmol) and stannous chloride (1 mmol) in dichloromethane–water (1:1) at room temperature led to the isolation of novel oxa-bridged [3]-ferrocenophane **8** bearing allyl side chains at 1,3-positions (Table 1). The reaction was easily extended to substituted allyl bromides leading to the formation of corresponding oxa-[3]-ferrocenophanes **9**–**11** in moderate yields. However, the reaction of **2** with 1-bromo-3-methyl-but-2-ene led to the isolation of homoallylic diol **12** in 72% yield (Scheme 4). We believe that the ferrocenophanes **8**–**11** result from the cooperative dehydration of respective diols under acid catalysis (Scheme 5). The formation of ferrocenophane over the other plausible dehydration product ferrocene-1,1′-bis-diene could be due to the higher thermodynamic stability of the former. Absence of linear or cyclic intermolecular dehydration products is also noteworthy. Acid catalyzed internal dehydration have been reported earlier for 1,1′-ferrocenedimethanol, 1,1′,2,2′-ferrocene-tetramethanol, and 3-phenyl[5]ferrocenophane-1,5-diol [18].

The electronic spectra of the complexes **3**–**12** show bands due to d–d transition at 440–456 nm (Table 1). The high-energy bands in the region 200–296 nm are due to side chain olefinic appendage and are characteristic of $\pi-\pi^*$ and $n-\pi^*$ transitions [19]. The electrochemical response of all the complexes shows a reversible Fc/Fc^+ couple. An increase in oxidation potential is observed in case of ferrocenophanes **8**–**11**, indicative of an enhanced electron density at the metal center due to the presence of electron-donating ether moiety in the bridgehead [20].

In summary, we have presented a facile carbonyl allylation of ferrocene aldehydes which provides an easy access to ferrocenyl building block having unsubstituted olefinic terminus. The resulting products are potential precursors towards further evaluation in RCM reaction. The ferrocenophanes having bridged oxygen along with terminal unsaturation make them interesting candidate towards the binding of metal complexes. Further, the stereospecificity of the reaction needs to be evaluated. We hope to address these issues in future.

Table 1

Products from the allylation of formylferrocene and 1,1′-bis-formylferrocene using bimetallic copper(II)/tin(II) reagent



X	Y	R^1	R^2	R^3	Product number [a]	Time (h)	Yield (%)	m.p. (°C) [b,c]	Anal. Found (Calc.) (%)		$E_{1/2}$ [d] (V)	λ_{max}(log ε) [e] assignment
CHO	H	H	H	H	**3**	2	58	80	70.28 (70.62)	5.86 (5.93)	0.48	455 (2.4), d–d 203 (4.0), 251 (3.9), 296 (3.9), π–π*
CHO	H	Me	H	H	**4**	2	60	[c]	70.99 (71.46)	6.32 (6.40)	0.47	453 (2.5), d–d 206 (4.2), 250 (4.0), 294 (4.0), π–π*
CHO	H	H	Me	H	**5**	2	55	[c]	70.91 (71.46)	6.49 (6.40)	0.43	442 (2.0), d–d 205 (4.2), 275(3.4), π–π*
CHO	H	Ph	H	H	**6**	2	47	78	76.15 (76.45)	5.70 (5.77)	0.47	454 (2.7), d–d 208 (6.3), 302(3.9), π–π*
CHO	H	Me	H	Me	**7**	2	96	49	66.94 (67.62)	6.93 (7.09)	0.43	440 (1.7), d–d 207 (4.3), π–π*
CHO	CHO	H	H	H	**8**	5	32	[c]	69.96 (70.15)	6.22 (6.54)	0.57	457 (1.9), d–d 201 (4.2), π–π*
CHO	CHO	Me	H	H	**9**	2	55	[c]	70.97 (71.44)	7.22 (7.19)	0.52	447 (1.9), d–d 200 (4.1), π–π*
CHO	CHO	H	Me	H	**10**	3	30	[c]	71.19 (71.44)	6.99 (7.19)	0.53	453 (2.0), d–d 252 (3.4), π–π*
CHO	CHO	Ph	H	H	**11**	3	49	77	77.82 (78.26)	6.01 (6.13)	0.52	456 (2.4), d–d 203 (4.3), π–π*
CHO	CHO	Me	H	Me	**12**	2	72	[c]	68.94 (69.11)	7.82 (7.91)	0.43	441 (1.9), d–d 209 (4.4), π–π*

[a] Homoallylic alcohols and dehydrated product mixtures are also formed.

[b] Uncorrected.

[c] Low-melting solid.

[d] All the potential values are with reference to Fc/Fc^+ external standard. $E_{1/2} = (Ep_a + Ep_c)/2.0$ for reversible oxidation (in volts). All the data are taken from a 50 mV s^{-1} scan rate for 0.001 M sample solutions in acetonitrile with 0.1 M tetrabutylammonium perchlorate as electrolyte.

[e] λ_{max} (in nanometer) for acetonitrile solutions (1×10^{-4} M).

Table 2

^{1}H-NMR data for the allylation products of formylferrocene $\mathrm{FcC\overset{4}{H}C\overset{3}{(R')}C\overset{2}{(R')}C\underset{2}{\overset{1}{H}}}$ (**3**–**6**), $\mathrm{FcC\overset{4}{H}(OH)C\overset{3}{(Me)}_2C\overset{2}{H}C\underset{2}{\overset{1}{H}}}$ (**7**), 1,1′-bis-formylferrocene $\mathrm{FcC\underset{2}{\overset{1}{H}}C\overset{2}{(R^2)}C\overset{3}{H}\overset{4}{(R^1)}C\underset{2}{\overset{5}{H}}-\mu-(O)-C\overset{5}{H}C\overset{3}{H}\overset{4}{(R^1)}C\overset{2}{(R^2)}C\underset{2}{\overset{1}{H}}]}$ (**8**–**11**), and $\mathrm{Fc[C\overset{5}{H}(OH)C\overset{3,4}{(Me)}_2C\overset{2}{H}C\underset{2}{\overset{1}{H}}]_2}$ (**12**)

Product number	Fc	H1	H2	H3	H4	H5	OH
3	4.12, s, 5H; 4.37, s, 2H; 4.25, s, 2H	5.09, d, 1H, $J = 10$; 5.27, d, 1H, $J = 15$	6.84–7.20, m, 1H	6.34, dd, 1H, $J = 10$, 15	6.06, d, 1H, $J = 11$		
4	4.13, s, 5H; 4.33, s, 2H; 4.22, s, 2H	5.13, d, 1H, $J = 11$; 5.27, d, 1H, $J = 17$	7.05, dd, 1H, $J = 10$, 17	1.90, s, 3H	6.13, s, 1H		
5	4.18, s, 5H; 4.38, s, 2H; 4.60, s, 2H	5.30, s, 2H	1.88, s, 3H	5.75, d, 1H, $J = 10$	5.65, d, 1H, $J = 10$		
6	4.00, s, 5H; 4.01, s, 2H; 4.18, s, 2H	5.18, d, 1H, $J = 10$; 5.29, d, 1H, $J = 16$	6.28, dd, 1H, $J = 8$, 16	7.20–7.50, m, 5H	6.02, s, 1H		
7	4.51, s, 9H	5.01, d, 1H, $J = 11$; 5.05, d, 1H, $J = 16$	5.89, dd, 1H, $J = 11$, 16	1.07, s, 6H	3.65, s, 1H		1.7, brs, 1H
8	4.23, m, 4H; 4.12, m, 2H; 4.04, m, 2H	5.01, d, 2H, $J = 10$; 5.07, d, 2H, $J = 15$	5.92–5.75, m, 2H	2.69–2.41, m, 2H	2.69–2.41, m, 2H	3.67–3.60, m, 2H	
9	4.19, m, 4H; 4.16, m, 2H; 4.03, m, 2H	4.89, d, 2H, $J = 11$; 5.01, d, 2H, $J = 16$	6.07–5.98, m, 2H	2.60–2.40, m, 2H	1.29, s, 6H	3.37–3.27, m, 2H	
10	4.23, m, 4H; 4.13, m, 2H; 4.04, m, 2H	4.72, s, 4H	1.72, s, 6H	2.67–2.57, m, 2H	2.44–2.36, m, 2H	3.78, t, 2H, $J = 7$	
11	4.16, m, 4H; 4.13, m, 2H; 4.02, m, 2H	4.98, d, 2H, $J = 11$; 5.08, d, 2H, $J = 17$; 5.04, d, 2H, $J = 11$	6.08–5.90, m, 2H	2.58–2.40, m, 2H	7.44–7.32, m, 10H	3.61–3.59, m, 2H	
12	4.50, s, 8H	5.12, d, 2H, $J = 16$	5.89, dd, 2H, $J = 10$, 17	1.05, s, 6H	1.05, s, 6H	3.75, s, 2H	1.9, brs, 2H

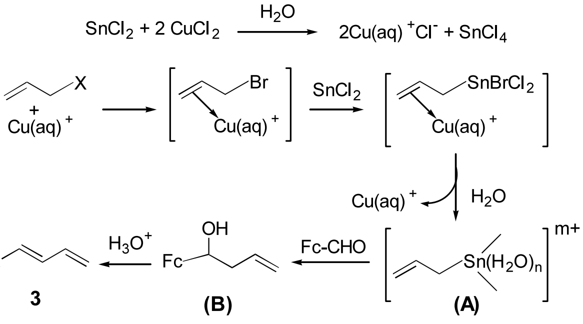
Table 3

^{13}C-NMR data for the allylation products of formylferrocene $\mathrm{Fc}\overset{4}{\mathrm{C}}\mathrm{H}\overset{3}{\mathrm{C}}(\overset{3'}{\mathrm{R}^1})\overset{2}{\mathrm{C}}(\overset{2'}{\mathrm{R}^2})\overset{1}{\mathrm{C}}\mathrm{H}^2$ (**3**–**6**), $\mathrm{Fc}\overset{4}{\mathrm{C}}\mathrm{H(OH)}\overset{3}{\mathrm{C}}(\overset{3'}{\mathrm{Me}})_2\overset{2}{\mathrm{C}}\mathrm{H}\overset{1}{\mathrm{C}}\mathrm{H}_2$ (**7**), 1,1′-bis-formylferrocene $\mathrm{Fc}\overset{1}{\mathrm{C}}\mathrm{H}_2\overset{2}{\mathrm{C}}(\overset{2'}{\mathrm{R}^2})\overset{3}{\mathrm{C}}\mathrm{H}(\overset{3'}{\mathrm{R}^1})\overset{4}{\mathrm{C}}\mathrm{H}-\mu-(\mathrm{O})-\overset{4}{\mathrm{C}}\mathrm{H}\overset{3}{\mathrm{C}}\mathrm{H}(\overset{3'}{\mathrm{R}^1})\overset{2}{\mathrm{C}}(\overset{2'}{\mathrm{R}^2})\overset{1}{\mathrm{C}}\mathrm{H}_2]$ (**8**–**11**), and $\mathrm{Fc}[\overset{4}{\mathrm{C}}\mathrm{H(OH)}\overset{3}{\mathrm{C}}(\overset{3'}{\mathrm{Me}})_2\overset{2}{\mathrm{C}}\mathrm{H}\overset{1}{\mathrm{C}}\mathrm{H}_2]_2$ (**12**)

Product number	Fc		C1	C2	C2′	C3	C3′	C4
	C_5H_5	C_5H_4						
3	69.0	66.5, 68.6, 82.5	114.4	137.2		127.1		130.9
4	69.4	68.7, 68.5, 82.3	113.8	135.5		127.3	20.1	130.0
5	68.9	66.6, 68.1, 84.3	112.4	128.2	20.3	133.8		129.1
6	69.8	69.1, 68.7, 81.9	113.9	134.9		127.0	128.9, 128.6, 128.4, 128.1	129.5
7	71.1	69.7, 70.8, 84.2	112.4	145.5		41.1	22.2, 23.9	91.8
	Cp_{unsubs}	Cp_{subs}						
8	68.3, 70.1, 71.6	88.8	116.3	135.6		40.3		65.4
9	68.3, 70.0, 72.0	88.3	114.2	140.9		42.9	17.3	65.7
10	71.5, 70.0, 68.2	89.1	112.2	125.3	22.8	43.9		65.4
11	72.1, 70.2, 68.4	87.7	113.9	141.6		55.7	129.6, 128.5, 128.4, 127.1	65.9
12	71.0, 70.4, 69.7	84.0	113.4	146.0		41.9	24.1, 21.0	92.6

3. Experimental

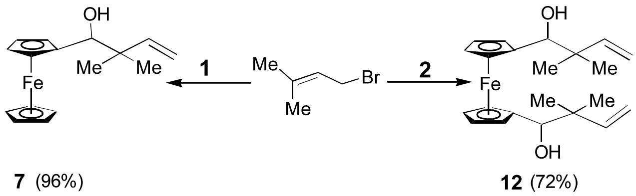
Melting points were measured using a Toshniwal melting point apparatus and are uncorrected. ^{1}H (200 MHz)- and ^{13}C (54.6 MHz)-NMR spectra were recorded in $CDCl_3$ on BRUKER-AC 200 MHz spectrometer. Me_4Si was used as the internal standard. EIMS (70 eV) spectra were recorded using Autospec-M mass spectrometer. IR spectra were obtained using a Perkin–Elmer 883 spectrophotometer. Electronic absorption spectra were recorded in HPLC grade acetonitrile using Shimadzu UV-1601 UV–vis Spectrometer. Cyclic voltammetry (CV) experiments were carried out with Model CH-600A Electrochemical Analyser at room temperature with a conventional three-electrode configuration consisting of platinum working, and auxiliary electrodes and Ag/AgCl reference electrode containing aqueous 3 M KCl. HPLC grade acetonitrile was used as solvent in all cases. The supporting electrolyte was (0.1 M) tetrabutylammonium perchlorate (Fluka) and used as-received. The redox potentials ($E_{1/2}$) were measured in volts with respect to Ag/Ag$^+$. The data were calibrated using Fc/Fc$^+$ couple ($E_{1/2} = 0.46$ V). Dichloromethane was distilled from phosphorus pentoxide. Petroleum ether refers to the fraction boiling in the range 60–80 °C. Silica gel (60–120-mesh SRL) was used for all column chromatography. For reaction monitoring, precoated silica gel 60 F_{254} TLC sheets (MERCK) were used. All reactions were performed under an inert atmosphere of argon using standard Schlenk technique. Starting materials **1** and **2** were prepared by known method [21]. Allyl bromides were prepared by the reaction of the corresponding allyl alcohols with phosphorus tribromide and pyridine in ether. Stannous chloride dihydrate and cupric chloride dihydrate are commercially available.



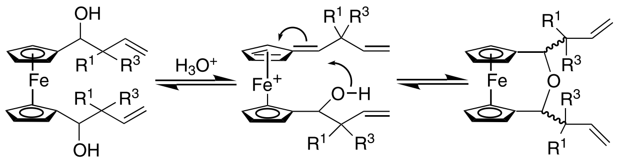
Scheme 3.

3.1. *General procedure (A) for the allylation of formylferrocene **1***

The appropriate allyl bromide (1.0 mmol) dissolved in distilled dichloromethane (0.5 ml) was added to a stirred solution of $SnCl_2 \cdot 2H_2O$ (225.6 mg, 1 mmol) and $CuCl_2 \cdot 2H_2O$ (8.50 mg, 0.05 mmol) in water (2.5 ml) at ambient temperature. Formylferrocene (107 mg, 0.5 mmol) dissolved in distilled dichloromethane (2.0 ml) was added dropwise to the clear solution and the reaction was monitored (TLC monitoring on silica gel, eluent ethyl acetate–petroleum ether, 1:9 (v/v)). Upon completion, the product was extracted with dichloromethane (3 × 15 ml). The organic layer was washed with 5% aqueous sodium bicarbonate (10 ml), water (2 × 5 ml), and brine (2 × 10 ml), dried over $MgSO_4$, and concen-



Scheme 4.



Scheme 5.

trated under reduced pressure. The pure products were obtained after column chromatography on silica gel using an ethylacetate–petroleum ether (2:98, v/v) mixture as the eluent.

*3.1.1. Synthesis of buta-1,3-dienyl-ferrocene (**3**)*

Following general procedure A, reaction of 3-bromopropene (121 mg, 1.0 mmol) and **1** (107 mg, 0.5 mmol) gave a red plate-like crystalline solid (70 mg, 58%) after 2 h. Rf = 0.8. IR ($CHCl_3$, cm^{-1}): 3440 vs, 2760 w, 1660 w, 1620 m ($\gamma_{C=C}$str), 1102 w, 769 w. HRMS Calc. for $C_{14}H_{14}Fe$, *m/z*: 238.0444; Found, *m/z*: 238.0570.

*3.1.2. Synthesis of (2-methyl-buta-1,3-dienyl)-ferrocene (**4**)*

Following general procedure A, reaction of 1-bromo-2-butene (135 mg, 1.0 mmol) and **1** (107 mg, 0.5 mmol) gave a deep orange liquid (76 mg, 60%) after 2 h. Rf = 0.8. EIMS: *m/z* (relative intensity), 252 (M^+, 100); 237 (9); 186 (49); 129 (18); 121 (30); 91 (5); 56 (27); 44 (11). IR ($CHCl_3$, cm^{-1}): 3450 m, 2930 w, 1633 w, 1220 w, 771 vs. HRMS Calc. for $C_{15}H_{16}Fe$, *m/z*: 252.0601; Found, *m/z*: 252.0595.

*3.1.3. Synthesis of (3-methyl-buta-1,3-dienyl)-ferrocene (**5**)*

Following general procedure A, reaction of 3-bromo-2-methyl-1-propene (135 mg, 1.0 mmol) and **1** (107 mg, 0.5 mmol) gave a brown low-melting solid (70 mg, 55%) after 2 h. Rf = 0.64. EIMS: *m/z* (relative intensity), 252 (M^+, 12); 237 (11); 186 (19); 121 (90); 84 (100); 69 (9); 56 (52); 49 (31). IR ($CHCl_3$, cm^{-1}): 3438 m, 1633 w, 1221 w, 771 vs. HRMS Calc. for $C_{15}H_{16}Fe$, *m/z*: 252.0601; Found, *m/z*: 252.0611.

*3.1.4. Synthesis of (2-phenyl-buta-1,3-dienyl)-ferrocene (**6**)*

Following general procedure A, reaction of 3-bromo-1-phenyl-1-propene (197 mg, 1.0 mmol) and **1** (107 mg, 0.5 mmol) gave a deep red crystalline solid (74 mg, 47%) after 2 h. Rf = 0.64. EIMS: *m/z* (relative intensity), 314 (M^+, 100); 248 (24); 192 (26); 165 (22); 121 (38); 91 (26); 56 (26). IR ($CHCl_3$, cm^{-1}): 3431 s, 2854 w, 1632 m, 1219 w, 1103 w, 770 m. HRMS Calc. for $C_{20}H_{18}Fe$, *m/z*: 314.2081; Found, *m/z*: 314.2096.

*3.1.5. Synthesis of 2,2-dimethyl-1-ferrocenyl-but-3-en-1-ol (**7**)*

Following general procedure A, reaction of 1-bromo-3-methyl-but-2-ene (149 mg, 1.0 mmol) and **1** (107 mg, 0.5 mmol) gave a yellow solid (136 mg, 96%) after 2 h. Rf = 0.58. EIMS: *m/z* (relative intensity), 284 (M^+, 26); 215 (72); 186 (100); 121 (42); 56 (14). IR ($CHCl_3$, cm^{-1}): 3450 vs, 2926 w, 1722 w, 1631 m, 1391 w, 1107 w, 770 w. HRMS Calc. for $C_{16}H_{20}FeO$, *m/z*: 284.0863; Found, *m/z*: 284.0798.

*3.2. General procedure (B) for the allylation of 1,1′-bis-formylferrocene (**2**)*

The appropriate allyl bromide (1.0 mmol) dissolved in distilled dichloromethane (0.5 ml) was added to a stirred solution of $SnCl_2 \cdot 2H_2O$ (225.6 mg, 1 mmol) and $CuCl_2 \cdot 2H_2O$ (8.50 mg, 0.05 mmol) in water (2.5 ml) at ambient temperature. 1,1′-Bis-formylferrocene (**2**) (61 mg, 0.25 mmol) dissolved in distilled dichloromethane (2.0 ml) was added dropwise to the clear solution and the reaction was monitored (TLC monitoring on silica gel, eluent ethyl acetate–petroleum ether, 2:8 (v/v)). The product was extracted with dichloromethane (3 × 15 ml). The organic layer was washed with 5% aqueous sodium bicarbonate (10 ml), water (2 × 5 ml), and brine (2 × 10 ml), dried over $MgSO_4$, and concentrated under reduced pressure. The pure products were obtained after column chromatography on silica gel using ethylacetate–petroleum ether (2:98) mixture as the eluent.

*3.2.1. Synthesis of 1,3-bis-(2-propenyl)-2-oxa-[3]-(1,1′)ferrocenophane (**8**)*

Following general procedure B, reaction of 3-bromopropene (121 mg, 1.0 mmol) and **2** (61 mg, 0.25 mmol) gave a red oil (25 mg, 32%) after 5 h. Rf = 0.86. EIMS: *m/z* (relative intensity), 308 (M^+, 100); 238 (30); 172 (34); 121 (42); 115 (30); 56 (71). IR ($CHCl_3$, cm^{-1}): 3435 m, 1634 w, 1206 m, 1180 w, 771 vs. HRMS Calc. for $C_{18}H_{20}FeO$, *m/z*: 308.0863; Found, *m/z*: 308.0858.

*3.2.2. Synthesis of 1,3-bis-(1-methyl-2-propenyl)-2-oxa-[3]-(1,1′)ferrocenophane (**9**)*

Following general procedure B, reaction of 1-bromo-2-butene (135 mg, 1.0 mmol) and **2** (61 mg, 0.25 mmol) gave a yellow low-melting solid (46 mg, 55%) after 2 h. Rf = 0.8. EIMS: *m/z* (relative intensity), 336 (M^+, 44); 252 (22); 185 (16); 135 (10); 129 (20); 121 (28); 77 (10). IR ($CHCl_3$, cm^{-1}): 3439 m, 1634 w, 1219 m, 1180 w, 1102 w, 771 vs. HRMS Calc. for $C_{20}H_{24}FeO$, *m/z*: 336.1176; Found, *m/z*: 336.1198.

*3.2.3. Synthesis of 1,3-bis-(2-methyl-2-propenyl)-2-oxa-[3]-(1,1′)ferrocenophane (**10**)*

Following general procedure B, reaction of 3-bromo-2-methyl-1-propene (135 mg, 1.0 mmol) and **2** (61 mg, 0.25 mmol) gave an orange solid (26 mg, 30%) after 3 h. Rf = 0.86. EIMS: *m*/*z* (relative intensity), 336 (M^+, 100); 316 (44); 281 (65); 252 (67); 186 (72); 121 (62); 56 (56). IR ($CHCl_3$, cm^{-1}): 3200 m, 2738 w, 1620 w, 1385 w, 1220 m, 762 vs. HRMS Calc. for $C_{20}H_{24}FeO$, *m*/*z*: 336.1176; Found, *m*/*z*: 336.1166.

*3.2.4. Synthesis of 1,3-bis-(1-phenyl-2-propenyl)-2-oxa-[3]-(1,1′)ferrocenophane (**11**)*

Following general procedure B, reaction of 3-bromo-1-phenyl-1-propene (197 mg, 1.0 mmol) and **2** (61 mg, 0.25 mmol) gave a deep red solid (56 mg, 49%) after 3 h. Rf = 0.87. EIMS: *m*/*z* (relative intensity), 460 (M^+, 91); 442 (69); 343 (20); 314 (14); 249 (100); 191 (16); 178 (10); 165 (11); 147 (10); 117 (42); 91 (24); 57 (9). IR ($CHCl_3$, cm^{-1}): 3438 vs, 2928 w, 1724 w, 1633 m, 1221 w, 1110 w, 770 s. HRMS Calc. for $C_{30}H_{28}FeO$, *m*/*z*: 460.3987; Found, *m*/*z*: 460.3992.

*3.2.5. Synthesis 1,1′-bis-2,2-dimethyl-1-ferrocenyl-but-3-en-1-ol (**12**)*

Following general procedure B, reaction of 1-bromo-3-methyl-but-2-ene (149 mg, 1.0 mmol) and **2** (61 mg, 0.25 mmol) gave a yellow solid (69 mg, 72%) after 2 h. Rf = 0.7. EIMS: *m*/*z* (relative intensity), 382 (M^+, 30); 229 (72); 215 (72); 186 (100); 129 (5); 121 (42); 56 (14); 44 (8). IR ($CHCl_3$, cm^{-1}): 3435 vs, 2938 w, 1642 m, 1219 m, 1105 w, 1060 w; 768 s; 617 w. HRMS Calc. for $C_{22}H_{30}FeO_2$, *m*/*z*: 382.1595; Found, *m*/*z*: 382.1532.

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