Articles

Novel Catalytic Hunsdiecker−Heck (CHH) Strategy toward All-*E* Stereocontrolled Ferrocene-Capped Conjugated Push−Pull Polyenes

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Halodecarboxylation reaction of ferrocenylacrylic acid **1** and ferrocenyldienoic acid **3d** with *N*-bromo- and *N*-iodosuccinimide in the presence of catalytic tetrabutylammonium trifluoroacetate at −40 °C and −78 °C affords the corresponding *β*-halovinylferrocenes **2a**, **2b** and *δ*-haloferrocenyldiene **4** in 37−72% yields. Heck reaction of *β*-iodovinylferrocene **2a** with vinyl substrates (CH_2═CH−Z where Z = CO_2Me, CO_2Et, COMe, CO_2H, $CONH_2$, 4′-$NO_2C_6H_4$) in the presence of tri(4-tolyl)arsine/palladium acetate/lithium chloride/triethylamine in acetonitrile at 35−80 °C affords the corresponding ferrocenyldienes **3a**−**3f** in 50−81% isolated yields. Similar reaction of *δ*-iodoferrocenyldiene **4** with vinyl substrates (CH_2═CH−Z where Z = CO_2Me, CO_2Et, CO_2H, 4′-$NO_2C_6H_4$) affords the corresponding ferrocenyltrienes **5a**−**5d** in 55−87% isolated yields. The ferrocene-capped conjugated dienes and trienes show excellent all-*E* stereoselectivity (vide NMR). The electronic, redox, and nonlinear optical properties of ferrocenylpolyenes have been evaluated. The data suggest that upon increasing the polyene chain length, (a) the absorption maxima shifts progressively to higher wavelength, (b) the oxidation potential of the Fc/Fc^+ couple ($E_{1/2}$) decreases, and (c) the HRS-derived second-order NLO response (β) increases. From the insights derived from semiempirical calculation (ZINDO/1), a mechanism for the halodecarboxylation reaction has been proposed suggesting the prior formation of tetrabutylammonium salt of ferrocenylacrylic acid **I**. Attack of the halogenium atom at the $\pi_{C=C}$ in **I** leads to the formation of intermediate **II**, and the latter triggers the elimination of carbon dioxide.

Introduction

Ferrocene-capped olefinic architecture gained prominence as a new generation molecular materials by virtue of their exciting optoelectronic properties[1,2] and in the realm of supramolecular chemistry as redox-switchable receptors.[3] Recent reports on the ROMP synthesis of soluble conjugated polymers containing a ferrocenyldiene unit in the backbone[4] and on the synthesis of bis(ferrocenyl)polymethine cations[5] and π-conjugated polymethylated biferrocenes[6] as prototype molecular wires are further noteworthy.

β-Halovinylferrocene could be regarded as a versatile

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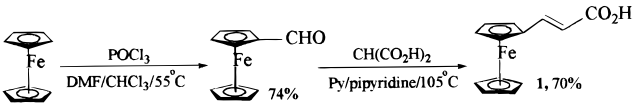
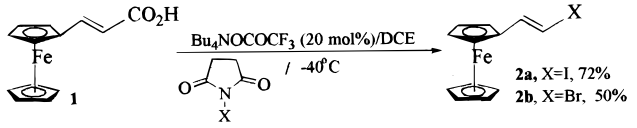
Scheme 1



Scheme 2



synthon for various oxidative addition and carbon−carbon bond forming reactions leading to novel polyene architecture. A literature search reveals that such chemistry is yet to be developed. The reported syntheses of β-halovinylferrocenes are very few, most of which are low-yielding and involve multistep synthesis.[7,8] Though olefination of ferrocene largely relies on Wittig protocol, the reactions at times are highly circuitous and nonstereoselective.[9] In our effort to devise a straightforward and convenient synthesis of β-halovinylferrocene, we sought to apply a halodecarboxylation strategy to ferrocenylacrylic acid **1**. β-Halovinylferrocene was further subjected to Heck reaction toward the formation ferrocene-capped conjugated dienes. A similar strategy on ferrocenyldienoic acid resulted in the formation of ferrocene-capped conjugated trienes.

Results and Discussion

Halodecarboxylation Reactions on Ferrocenylacrylic Acid. Ferrocenylacrylic acid **1** is prepared very easily via Vilsmeier reaction of ferrocene followed by condensation of ferrocenyl aldehyde with malonic acid (Scheme 1).[10]

Initial reaction of ferrocenylacrylic acid **1** (1 mmol) with *N*-iodosuccinimide (NIS, 1.12 mmol) and tetrabutylammonium trifluoroacetate ($Bu_4NOCOCF_3$, 0.2 mmol) in dichloroethane (DCE, 3 mL) at ambient temperature (35 °C) gives rise to β-iodovinylferrocene **2a** in 10% isolated yield. Lowering the temperature leads to an improvement in the yield of **2a**; the optimized temperature being −40 °C (Scheme 2). Similar reaction of **1** using *N*-bromosuccinimide at −40 °C for 4 h affords β-bromovinylferrocene **2b** in 50% isolated yield as a mixture of $E:Z = 9:11$.

To the best of our knowledge this is the first application of a halodecarboxylation reaction on an organometallic substrate and may involve interesting mechanistic features. Pedagogically, the synthesis bears some resemblance to the classical Hunsdiecker reaction, wherein metal carboxylates of organic acids are halodecarboxylated in the presence of molecular halogen.[11] However, unlike conventional Hunsdiecker reaction requiring a stoichiometric metal salt for halodecarboxylation, the present synthesis offers an extremely convenient, catalytic, and metal-free version, thereby conserving the atom economy of the overall process. As indicated earlier, attempts to carry out reactions at higher temperature led to significant loss in product yield due to oxidation of the ferrocene moiety.[12] Reaction of **1** with *N*-chlorosuccinimide even at −78 °C could not prevent such oxidation, resulting in negligible yield of β-chlorovinylferrocene.

Scheme 3

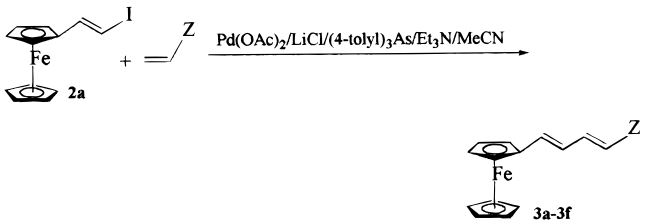


Table 1. Heck Reaction of β-Iodovinylferrocene 2a with Methylacrylate: Effect of Ligand

entry no.	Heck ligand	yield (%)[a]
1	Ph_3P	10
2	Ph_3Sb	13
3	tri(4-tolyl)$_3$P	21
4	tri(4-tolyl)$_3$As	70

[a] Isolated yield with respect to **2a**.

Heck Reaction on Halovinylferrocene for the Synthesis of Ferrocenyldienes. We foresee the potential utility of **2** as a versatile synthon in various oxidative-addition and C−C bond forming reactions, the Heck reaction presented herein being one such example. While devising the Heck strategy toward the synthesis of ferrocenyldiene **3**, β-iodovinylferrocene **2a** and tri(4-tolyl)arsine/palladium acetate/lithium chloride/triethylamine/acetonitrile were found as best reagents of choice (Scheme 3, Table 1).

Thus, reaction of **2a** with methylacrylate under the above conditions afforded the corresponding diene **3a** in 70% isolated yield and as an all-*E* isomer. Similar reactions of **2a** with ethylacrylate, methylvinyl ketone, acrylic acid, acrylamide, and 4′-nitrostyrene afforded the corresponding ferrocenyldienes **3b**−**3f** in moderate to good yields (Table 2). All the dienes show exclusive (*E*,*E*)-selectivity (vide NMR).

Hunsdiecker−Heck Strategy for the Synthesis of Ferrocenyltrienes. Ferrocenyldienoic acid **3d**

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Table 2. Synthesis of Ferrocenyldienes via Heck Reaction of 2a

entry no.	Z	temp (°C)	time (h)	product	yield (%)[a]
1	CO_2Me	70−80	2	**3a**	70
2	CO_2Et	70−80	2	**3b**	68
3	COMe	35	38	**3c**	78
4	CO_2H	70−80	5	**3d**	81
5	$CONH_2$	35	78	**3e**	60
6	4′-$NO_2C_6H_4$	70−80	2	**3f**	50

[a] Isolated yield with respect to **2a**.

Scheme 4

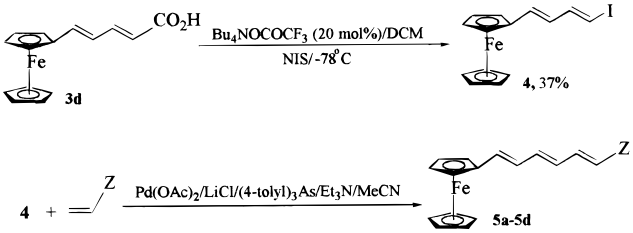


Table 3. Synthesis of Ferrocenyltrienes via Heck Reaction of 4

entry no.	Z	temp (°C)	time (h)	product	yield (%)[a]
1	CO_2Me	70−80	1	**5a**	78
2	CO_2Et	70−80	1	**5b**	87
3	CO_2H	70−80	5	**5c**	57
4	4-$NO_2C_6H_4$	70−80	3.5	**5d**	55

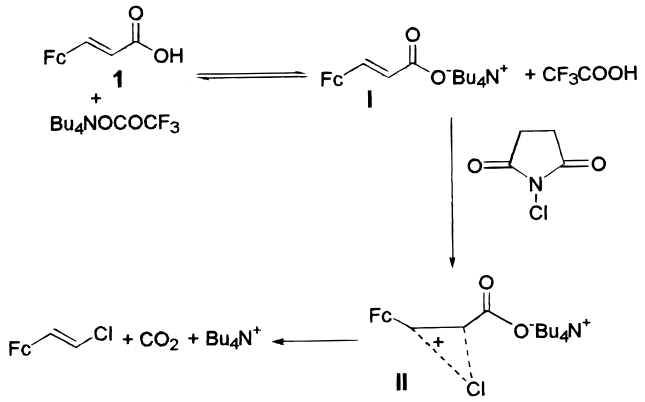
[a] Isolated yield with respect to **4**.

prompted us to test the efficacy of the halodecarboxylation protocol described for **1**. Reaction of **3d** with *N*-iodosuccinimide (NIS) and catalytic tetrabutylammonium trifluoroacetate ($Bu_4NOCOCF_3$) in dichloromethane at −78 °C gave δ-iodoferrocenyldiene **4** in 37% yield (Scheme 4). As anticipated, **4** reacted smoothly with vinyl substrates under the Heck conditions; the resulting trienes **5a**−**5d** were isolated in 55−87% yields and as all-*E* isomers (Table 3).

Though our zeal prompted us to once more subject the trienoic acid **5c** to iododecarboxylation and subsequent Heck coupling with methylacrylate, the resulting tetraene Fc[CH=CH]$_4$−CO_2Me was found highly photolabile. We believe that with innovative adjustments in bench protocol, polyenes with higher conjugation (>3) can be isolated.

Mechanism of Halodecarboxylation. Preliminary attempts have been made to understand the mechanism of the novel halodecarboxylation reaction. No significant change in reaction time and yield of **2a** was observed for the reaction of **1** in the presence of *N*-(*tert*-butyl)-α-phenyl nitrone as radical trap, thereby suggesting an ionic pathway. In-situ ^{1}H NMR monitoring in chloroform-*d* at −50 °C was inconclusive due to severe line broadening. Semiempirical calculation (ZINDO/1)[13] provided valuable insight suggesting attack of the halogenium atom at the $\pi_{C=C}$, triggering the elimination of carbon dioxide (Scheme 5). The structures of **1** and possible intermediates **I** and **II** were optimized (for X = Cl). The HOMO of **I** (at −6.86 eV) indicates a delocalized π-geometry with very large amplitude at the alkene α-carbon (bound to carboxylate), compared to the β-carbon (bound to ferrocene moiety). The LUMO, at

Scheme 5



+3.82 eV, is primarily located at the ferrocene moiety. Interestingly, the charge at the α-carbon is −0.175, compared to +0.05 at the β-carbon. Therefore, the halogenium ion will prefer the α-carbon because of its higher amplitude in HOMO and higher negative charge compared to the β-carbon. This argument gains further support from the optimized structure of **II**, where the C_α−X bond (1.75 Å, X = Cl) is significantly longer than the C_β−X bond (2.66 Å, X = Cl). A weakening of the C_α−COO bond in **II** (1.50 Å) compared to that in **I** (1.44Å) indicates the subsequent elimination of carbon dioxide.

Electronic, Redox, and Optoelectronic Properties of Ferrocenylpolyenes. There is a rich theoretical understanding of the structure versus electronic, redox, and optoelectronic properties of organic and, to some extent, organometallic push−pull polyenes.[1a,2d,14] UV−vis, CV, and NLO data (Table 4) of the ferrocenyl polyenes synthesized in the present work are in tune with the expected order. Thus, upon increasing conjugation, (a) the absorption maxima (λ_{max}, MLCT transition) shifts progressively to higher wavelength and (b) the oxidation potential of the Fc/Fc$^+$ couple ($E_{1/2}$) decreases, indicating a greater degree of charge transfer from the metal center to the polyene backbone. The outcome of the above factors is in the enhanced HRS-derived second-order NLO response (β) upon increasing the conjugation in the polyene chain. The higher β value of nitrophenyl-capped ferrocenylpolyene as compared to the carbomethoxy-capped analogue is also in tune with the concept that the greater the electronic asymmetry between donor (ferrocenyl) and acceptor groups, the larger the β response.

Conclusions and Perspectives. In summary, we have described a novel halodecarboxylation reaction on an organometallic substrate leading to the efficient synthesis of β-halovinylferrocenes from readily available ferrocenylacrylic acid. Furthermore, an iterative halodecarboxylation and carbon−carbon bond formation strategy is presented as a versatile route to all-*E* stereocontrolled ferrocene-capped push−pull polyenes. We believe that the present strategy could well be applicable to varied structural motifs. Additional experimental refinement, mechanistic exploration, and application of our strategy especially in the construction

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Table 4. UV, CV, and NLO Data of Ferrocenylpolyenes Fc−[CH=CH]$_n$−Z[a]

Z	UV (MeCN, λ_{max}, nm)			CV ($E_{1/2}$, V vs SCE)			NLO ($\beta \times 10^{-30}$, cm^5 esu^{-1})		
CO_2Me	295 (1)	320 (2)	346 (3)		0.49 (2)	0.46 (3)	35 (1)	39 (2)	42 (3)
CO_2H	295 (1)	319 (2)	346 (3)	0.52 (1)	0.48 (2)	0.45 (3)			
4′-$NO_2C_6H_4$	354 (1)	383 (2)	396 (3)		0.44 (2)	0.43 (3)	31[b] (1)	66[b] (2)	

[a] *n*-value is shown in parentheses. [b] Ref 1a.

of metallocene-(1,1′)-substituted conjugated polyene assemblies are in progress in our laboratory.

Experimental Section

General Comments. All reactions including workup were performed with minimum exposure to light. Flasks were wrapped in Al-foil. Acetonitrile (MeCN), dichloromethane (DCM), and dichloroethane (DCE) were dried over phosphorus pentoxide. Triethylamine was distilled from potassium hydroxide. Ferrocenylacrylic acid **1** was synthesized according to literature procedures.[10] Neutral alumina (Qualigens and Loba) was used for column chromatography. For reaction monitoring, precoated silica gel 60 F_{254} TLC sheets (MERCK) were used. Melting points (mp) were taken using FISHER-JOHNS apparatus and are uncorrected. Combustion analyses were performed using an Elementar Analyzer VARIO EL instrument.

^{1}H NMR spectra were recorded at 200, 250, and 400 MHz on Varian GEMINI-200, BRUKER AC-250, and Varian UNITY-400 spectrometers. *E*:*Z* isomers were characterized from *J* values in Hz. ^{13}C NMR spectra were recorded on a Bruker AC-250 (at 62.5 MHz). ^{1}H−^{1}H COSY and NOESY spectra were recorded on Bruker AC-250 and Varian UNITY-400 spectrometers, respectively. EIMS (70 eV) and HRMS spectra were recorded using VG MicroMass 70-70H and Autospec-M mass spectrometers. UV spectra were obtained using a BECKMAN DU 7400 spectrophotometer. IR spectra were obtained using a NICOLET 740 FTIR spectrometer.

Cyclic voltammetric (CV) experiments were carried out in acetonitrile with an RDK (RIKADENKI), CV-27 instrument using platinum as a *working*, as well as *auxiliary* electrode. The reference electrode chosen was a saturated calomel electrode (SCE). Tetrabutylammonium perchlorate (0.1 M) was used as the supporting electrolyte. Analysis of the CV relevant to the ferrocene-centered oxidation process with varying scan rates confirms a one-electron oxidation step. The oxidation potential ($E_{1/2}$) is measured in volts with respect to SCE.

Semiempirical calculations (ZINDO/1) were performed using the program Hyperchem 5.0 (Hypercube Inc. Ontario, Canada). Due to the lack of available parameters, the chlorine atom was chosen for geometry optimization of **II**. For simplicity in calculation, the ammonium ion was preferred instead of the tetraalkylammonium ion.

(*E*)-[1-Iodo-2-ferrocenylethylene] (2a). *N*-Iodosuccinimide (945 mg, 4.2 mmol) was added portionwise at −40 °C to a stirred solution of ferrocenylacrylic acid **1** (1.02 g, 4 mmol) and tetrabutylammonium trifluoroacetate ($Bu_4NOCOCF_3$) (20 mol %) in dichloroethane (12 mL), taken in a Schlenk flask, and wrapped with aluminum foil under a nitrogen atmosphere. After stirring for 4 h at −40 °C, water (3 mL) was added to the mixture. The solvent was evaporated under reduced pressure, and the residue was taken in ether, washed with water and brine, and dried over anhydrous magnesium sulfate. Column chromatography (neutral alumina, ethyl acetate/hexane, 1:9) afforded **2a** as a low-melting red solid (969 mg, 72%, >99% *E*). TLC (silica gel/hexane), R_f = 0.6. ^{1}H NMR ($CDCl_3$): δ 4.1 (s, 5H, Cp), 4.2 (s, 2H, Cp), 4.28 (s, 2H, Cp), 6.21 (d, 1H, J = 15 Hz); 7.13 (d, 1H, J = 15 Hz). ^{13}C NMR ($CDCl_3$): δ 66.31, 69.02, 69.29 (Cp), 137.29, 142.70 (alkenyl). IR (neat) cm^{-1}: 1035 (vs), 1694 (s), 1678 (s), 808 (s), 478 (s), 3098 (m), 2941 (m), 2926 (m), 1208 (m), 1098 (m), 957 (m), 769 (m). EIMS *m*/*z* (rel intensity): 338 (M$^+$, 100), 210 (36), 153 (25), 121 (34), 89 (33), 56 (42). UV/vis (MeCN): λ_{max} nm: 238, 282, 448. $E_{1/2}$ (Fc/Fc$^+$, V): 0.47. Anal. Calcd for $C_{12}H_{11}$FeI: C, 42.65; H, 3.28. Found: C, 42.44; H, 3.19.

(*E*/*Z*)-[1-Bromo-2-ferrocenylethylene] (2b). Following the standard procedure as above, utilizing the following amounts of reagents, *N*-bromosuccinimide (356 mg, 2 mmol), **1** (256 mg, 1 mmol), and $Bu_4NOCOCF_3$ (20 mol %) in DCE (6 mL) at −40 °C for 2 h, afforded **2b** as a low-melting red solid (145 mg, 50%, *E*:*Z* = 9:11). TLC (silica gel/hexane), R_f = 0.56. ^{1}H NMR ($CDCl_3$): *E-isomer* δ 4.08 (s, 5H, Cp), 4.16 (s, 2H, Cp), 4.22 (s, 2H, Cp), 6.17 (d, 1H, J = 14 Hz), 6.78 (d, 1H, J = 14 Hz); *Z-isomer* 4.08 (s, 5H, Cp), 4.12 (s, 2H, Cp), 4.22 (s, 2H, Cp), 6.16 (d, 1H, J = 8 Hz), 6.76 (d, 1H, J = 8 Hz). ^{13}C NMR ($CDCl_3$): *E-isomer* δ 66.47, 69.27, 69.74 (Cp), 131.07, 134.85 (alkenyl); *Z-isomer* δ 69.02, 69.27, 69.74 (Cp), 101.11, 102.67 (alkenyl). IR (neat) cm^{-1}: 816 (vs), 2926 (s), 1090 (s), 980 (s), 494 (s), 3082 (m), 1216 (m), 1035 (m), 894 (m), 737 (m), 675 (m). EIMS *m*/*z* (rel intensity): 290 (M$^+$, 100), 210 (32), 153 (42), 145 (25), 121 (24), 89 (51), 56 (40). UV/vis (MeCN): λ_{max} nm: 232, 278, 451. $E_{1/2}$ (Fc/Fc$^+$, V): 0.55. Anal. Calcd for $C_{12}H_{11}$FeBr: C, 49.54; H, 3.81. Found: C, 49.20; H, 3.75.

(*E*,*E*)-[Methyl-5-ferrocenyl-2,4-pentadienoate] (3a). β-Iodovinylferrocene **2a** (338 mg, 1 mmol), palladium acetate (10 mol %), tri(4-tolyl)arsine (30 mol %), lithium chloride (20 mol %), dry triethylamine (3 mmol), and dry acetonitrile (2 mL) were taken in a Schlenk flask equipped with a reflux condenser. The mixture was stirred for 10 min at ambient temperature under nitrogen. A solution of methylacrylate (2 mmol) in acetonitrile (1 mL) was added dropwise, and the mixture was stirred at 70−80 °C for 2 h. Following solvent removal under reduced pressure, the residue was subjected to column chromatography (neutral alumina, ethyl acetate/hexane, 1:9) to afford **3a** as a red solid (207 mg, 70%, >99% *E*). TLC (silica gel/ethyl acetate−hexane; 1:4), R_f =0.5; mp 180−181 °C. ^{1}H NMR (DMSO-d_6): δ 3.68 (s, 3H, OMe), 4.06 (s, 5H, Cp), 4.29 (brs, 2H, Cp), 4.38 (brs, 2H, Cp), 5.78 (d, 1H, J = 15 Hz), 6.39 (dd, 1H, J = 11, 16 Hz), 6.67 (d, 1H, J = 16 Hz), 7.28 (dd, 1H, J = 11, 15 Hz). ^{13}C NMR ($CDCl_3$): δ 51.45 (OMe), 67.75, 69.55, 70.23 (Cp), 117.67, 123.78, 140.94, 145.46 (alkenyl), 168.08 (C=O). IR (KBr) cm^{-1}: 1718 (vs), 1616 (s), 1239 (s), 1137 (s), 1318 (s), 1153 (s), 1004 (s), 808 (s), 455 (s), 3098 (m), 2910 (m), 1451 (m), 1412 (m), 722 (m). EIMS *m*/*z* (rel intensity): 296 (M$^+$, 100), 199 (19), 171 (11), 122 (9), 115 (42), 56 (16). UV/vis (MeCN): λ_{max} nm: 269, 320, 481. $E_{1/2}$ (Fc/Fc$^+$, V): 0.49. Anal. Calcd for $C_{16}H_{16}FeO_2$: C, 64.89; H, 5.45. Found: C, 64.80; H, 5.41.

(*E*,*E*)-[Ethyl-5-ferrocenyl-2,4-pentadienoate] (3b). Following the standard procedure for **3a**, utilizing the following amounts of reagents, β-Iodovinylferrocene **2a** (166 mg, 0.5 mmol), palladium acetate (10 mol %), tri(4-tolyl)arsine (30 mol %), lithium chloride (20 mol %), dry triethylamine (1.5 mmol), and ethylacrylate (0.1 mL, 1 mmol), afforded **3b** as a red solid (104 mg, 68%, >99% *E*). TLC (silica gel/ethyl acetate−hexane, 1:4), R_f = 0.25; mp 96−97 °C. ^{1}H NMR ($CDCl_3$): δ 1.24 (t, 3H, J = 7 Hz), 4.07 (s, 5H, Cp), 4.15 (q, 2H, J = 7 Hz), 4.29 (t, 2H, Cp, J = 1.8 Hz), 4.38 (t, 2H, Cp J = 1.8 Hz), 5.78 (d, 1H, J = 15 Hz), 6.40 (dd, 1H, J = 11, 15 Hz), 6.67 (d, 1H, J = 15 Hz), 7.28 (dd, 1H, J = 11, 15 Hz). IR (KBr) cm^{-1}: 1608 (vs), 1122 (vs), 1318 (s), 1239 (s), 1718 (s), 1004 (s), 1475 (m), 1380 (m), 1137 (m), 816 (m), 471 (m). EIMS *m*/*z* (rel intensity): 310 (M$^+$, 100), 199 (9), 115 (27). UV/vis (MeCN): λ_{max} nm: 269, 320, 478. $E_{1/2}$ (Fc/Fc$^+$, V): 0.49. Anal. Calcd for $C_{17}H_{18}FeO_2$: C, 65.83; H, 5.85. Found: C, 65.79; H, 5.83.

(*E,E*)-[6-Ferrocenyl-3,5-hexadiene-2-one] (3c). Following the standard procedure for **3a**, but under ambient condition (35 °C), utilizing the following amounts of reagents, β-Iodovinylferrocene **2a** (226 mg, 0.67 mmol), palladium acetate (10 mol %), tri(4-tolyl)arsine (30 mol %), lithium chloride (20 mol %), dry triethylamine (2 mmol), and methylvinyl ketone (0.1 mL, 1.3 mmol), afforded **3c** as a red solid (146 mg, 78%, >99% *E*). TLC (silica gel/ethyl acetate−hexane, 1:9), $R_f = 0.5$; mp 181−182 °C. ^{1}H NMR ($CDCl_3$): δ 2.22 (s, Me), 4.07 (s, 5H, Cp), 4.32 (t, 2H, Cp, $J = 1.8$ Hz), 4.40 (t, 2H, Cp, $J = 1.8$ Hz), 6.07 (d, 1H, $J = 15$ Hz), 6.41 (dd, 1H, $J = 11$ Hz, 15 Hz), 6.74 (d, 1H, $J = 15$ Hz), 7.16 (dd, 1H, $J = 11$ Hz, 15 Hz). ^{13}C NMR ($CDCl_3$): δ 27.20 (Me), 67.71, 69.46, 70.27 (Cp), 124.03, 127.58, 141.85, 144.02, 198.47. IR (KBr) cm^{-1}: 1616 (vs), 988 (s), 471 (s), 2910 (m), 1710 (m), 1639 (m), 1247 (m), 1082 (m), 808 (m). EIMS *m*/*z* (rel intensity): 280 (M^+, 100), 237 (12), 215 (11), 171 (27), 115 (30), 56 (23). UV/vis (MeCN): λ_{max} nm: 273, 327, 486. $E_{1/2}$ (Fc/Fc$^+$, V): 0.49. Anal. Calcd for $C_{16}H_{16}FeO$: C, 68.60; H, 5.76. Found: C, 68.50; H, 5.70.

(*E,E*)-[5-Ferrocenyl-2,4-pentadienoic acid] (3d). A mixture containing β-iodovinylferrocene **2a** (900 mg, 2.6 mmol), palladium acetate (10 mol %), tri(4-tolyl)arsine (30 mol %), lithium chloride (20 mol %), dry triethylamine (1.1 mL, 8 mmol), and acrylic acid (0.36 mL, 5.3 mmol) in acetonitrile (12 mL) was stirred at 80 °C for 5 h. After solvent removal, the residue was taken in dichloromethane and washed with water and sodium hydroxide (1 N) solution. The aqueous part was acidified with hydrochloric acid (4 N) at 0 °C and extracted with dichloromethane. The organic layer was washed successively with water and brine and dried over anhydrous magnesium sulfate. Solvent evaporation furnished **3d** as a red solid (608 mg, 81%, >99% *E*). TLC (silica gel/ethyl acetate−hexane, 1:4), $R_f = 0.2$; mp 210−212 °C (dec). ^{1}H NMR ($CDCl_3$): δ 4.18 (s, 5H, Cp), 4.32 (t, 2H, Cp, $J = 1.8$ Hz), 4.40 (t, 2H, Cp, $J = 1.8$ Hz), 5.79 (d, 1H, $J = 15$ Hz), 6.43 (dd, 1H, $J = 11$, 15 Hz), 6.73 (d, 1H, $J = 15$ Hz), 7.37 (dd, 1H, $J = 11$, 15 Hz). ^{13}C NMR (DMSO-d_6): δ 67.56, 69.23, 69.92 (Cp), 118.83, 123.79, 140.36, 144.84 (alkenyl), 167.89 (C═O). IR (KBr) cm^{-1}: 1616 (vs), 1675 (s), 1255 (s), 988 (s), 471 (s), 3384 (m), 2863 (m), 1467 (m), 1412 (m), 1318 (m), 1122 (m), 690 (m). EIMS *m*/*z* (rel intensity): 283 (M^+, 100), 238 (7), 200 (24), 166 (13), 121 (36), 115 (91), 86 (54), 56 (37). UV/vis (MeCN): λ_{max} nm: 269, 319, 480. $E_{1/2}$ (Fc/Fc$^+$, V): 0.48. Anal. Calcd for $C_{15}H_{14}FeO_2$: C, 63.86; H, 5.00. Found: C, 63.76; H, 4.97.

(*E,E*)-[5-Ferrocenyl-2,4-pentadienamide] (3e). Following the standard procedure for **3a**, but under ambient condition (35 °C), utilizing the following amounts of reagents, β-iodovinylferrocene **2a** (169 mg, 0.5 mmol), palladium acetate (10 mol %), tri(4-tolyl)arsine (30 mol %), lithium chloride (20 mol %), dry triethylamine (0.2 mL, 1.5 mmol), and acrylamide (71 mg, 1 mmol), afforded **3e** as a red solid (110 mg, 60%, >99% *E*). TLC (silica gel/ethyl acetate−hexane, 3:7), $R_f = 0.25$. ^{1}H NMR ($CDCl_3$): δ 4.06 (s, 5H, Cp), 4.27 (s, 2H, Cp), 4.36 (s, 2H, Cp), 5.83 (d, 1H, $J = 15$ Hz), 6.38 (dd, 1H, $J = 12$, 15 Hz), 6.64 (d, 1H, $J = 15$ Hz), 7.22 (dd, 1H, $J = 12$, 15 Hz). ^{13}C NMR ($CDCl_3$): δ 67.36, 69.25, 69.79 (Cp), 123.41, 129.71, 131.14, 139.8, 142.21. IR (KBr) cm^{-1}: 1600 (vs), 1675 (s), 800 (s), 499 (s), 3161 (m), 1377 (m), 1082 (m), 988 (m), 890 (m). EIMS *m*/*z* (rel intensity): 282 (M^+, 100), 258 (18), 217 (55), 172 (24), 121 (15), 115 (48), 71 (16), 43 (60). UV/vis (MeCN): λ_{max} nm: 265, 314, 469. $E_{1/2}$ (Fc/Fc$^+$, V): 0.45. Anal. Calcd for $C_{15}H_{15}FeNO$: C, 64.08; H, 5.38. Found: C, 63.91; H, 5.16.

(*E,E*)-[1-Ferrocenyl-4-(4′-nitrophenyl)-1,3-butadiene] (3f). Following the standard procedure for **3a**, utilizing the following amounts of reagents, β-iodovinylferrocene **2a** (83 mg, 0.25 mmol), palladium acetate (10 mol %), tri(4-tolyl)arsine (30 mol %), lithium chloride (20 mol %), dry triethylamine (0.1 mL, 0.75 mmol), and 4-nitrostyrene (75 mg, 0.5 mmol), afforded **3f** as a red solid (44 mg, 50%, >99% *E*). TLC (silica gel/hexane, fourth run), $R_f = 0.26$; mp 190−191 °C. ^{1}H NMR ($CDCl_3$): δ 4.08 (s, 5H, Cp), 4.28 (t, 2H, Cp), 4.38 (t, 2H, Cp), 6.45−6.60 (m, 3H), 6.96 (dd, 1H, $J = 10$, 14 Hz), 7.44 (d, 2H, Ar, $J = 9$ Hz), 8.1 (d, 2H, Ar, $J = 9$ Hz). ^{13}C NMR ($CDCl_3$): δ 67.27, 69.45, 69.77 (Cp), 123.90, 125.97, 134.29, 135.79 (alkenyl), 124.18, 126.19, 127.17, 127.32 (others). IR (KBr) cm^{-1}: 1341 (vs), 1584 (s), 1506 (s), 2910 (m), 1098 (m), 965 (m), 824 (m), 737 (m), 486 (m). EIMS *m*/*z* (rel intensity): 359 (M^+, 11), 329 (84), 207 (27), 186 (13), 121 (33), 115 (13), 69 (15), 43 (30). UV/vis (MeCN): λ_{max} nm: 295, 383, 496. $E_{1/2}$ (Fc/Fc$^+$, V): 0.44. Anal. Calcd for $C_{20}H_{17}FeNO_2$: C, 66.88; H, 4.77. Found: C, 66.80; H, 4.53.

(*E,E/E,Z*)-[1-Iodo-4-ferrocenyl-1,3-diene] (4). *N*-Iodosuccinimide (118 mg, 0.525 mmol) in dichloromethane (13 mL) was added dropwise at −78 °C to a stirred solution of ferrocenyldienoic acid **3d** (141 mg, 0.5 mmol) and $Bu_4NOCOCF_3$ (20 mol %) in dichloromethane (10 mL), taken in a Schlenk flask, and wrapped with aluminum foil under a nitrogen atmosphere. After stirring for 3 h at −78 °C, the mixture was brought to room temperature. The solvent was evaporated under reduced pressure, and the residue was subjected to column chromatography (neutral alumina, ethyl acetate/hexane, 1:9) to obtain the desired product **4** as a low-melting red solid (67 mg, 37%, *E,E*:*E,Z* = 7:9). TLC (silica gel/hexane), $R_f = 0.4$. ^{1}H NMR ($CDCl_3$) *E,E*: δ 4.08 (s, 5H, Cp), 4.25 (brs, 2H, Cp), 4.38 (brs, 2H, Cp), 6.22−6.30 (m, 1H), 6.45−6.55 (m, 2H), 7.01 (dd, 1H, $J = 11$, 14 Hz); *E,Z*: δ 4.06 (s, 5H, Cp), 4.22 (brs, 2H, Cp), 4.31 (brs, 2H, Cp), 6.12−6.18 (m, 2H), 6.22−6.30 (m, 1H), 6.71 (dd, 1H, $J = 8$, 9 Hz). ^{13}C NMR ($CDCl_3$): *E,E* δ 67.47, 69.64, 69.80 (Cp), 126.58, 135.98, 138.69, 145.59 (alkenyl); *E,Z* δ 67.22, 69.70, 69.80 (Cp), 126.39, 132.21 (alkenyl). IR (neat) cm^{-1}: 1545 (vs), 2910 (s), 2808 (s), 1726 (s), 1603 (s), 1070 (m), 1051 (m), 761 (m). EIMS *m*/*z* (rel intensity): 364 (M^+, 100), 254 (24), 186 (12), 171 (8), 121 (62), 115 (67), 71 (17), 43 (38). UV/vis (MeCN): λ_{max} nm: 261, 307, 460. $E_{1/2}$ (Fc/Fc$^+$, V): 0.44. Anal. Calcd for $C_{14}H_{13}FeI$: C, 46.20; H, 3.60. Found: C, 46.17; H, 3.54.

(*E,E,E*)-[Methyl-7-ferrocenyl-2,4,6-heptatrienoate] (5a). Utilizing the Heck protocol described for **3a**, with the following amounts of reagents, δ-iodoferrocenyldiene **4** (41 mg, 0.113 mmol), methylacrylate (0.02 mL, 0.23 mmol), palladium acetate (10 mol %), tri(4-tolyl)arsine (30 mol %), lithium chloride (20 mol %), and dry triethylamine (0.05 mL, 0.4 mmol) in acetonitrile (1 mL), furnished **5a** as a dark red solid (28 mg, 78%, >99% *E*). TLC (silica gel/hexane, fourth run), $R_f = 0.3$; mp 183−184 °C. ^{1}H NMR ($CDCl_3$): δ 3.69 (s, 3H, OMe), 4.06 (s, 5H, Cp), 4.26 (t, 2H, Cp, $J = 1.8$ Hz), 4.35 (t, 2H, Cp, $J = 1.8$ Hz), 5.81 (d, 1H, $J = 15$ Hz), 6.25 (dd, 1H, $J = 12$, 14 Hz), 6.38−6.60 (m, 3H), 7.28 (dd, 1H, $J = 12$, 15 Hz). ^{13}C NMR ($CDCl_3$): δ 51.37 (OMe), 67.34, 69.43, 69.82 (Cp), 118.98, 125.71, 127.41, 136.64, 141.50, 145.20, (alkenyl), 167.69 (C═O). IR (KBr) cm^{-1}: 1140 (vs), 2918 (s), 1710 (s), 1608 (s), 1004 (s), 2831 (m), 1424 (m), 1255 (m), 1153 (m), 828 (m), 486 (m). EIMS *m*/*z* (rel intensity): 322 (M^+, 100), 263 (24), 225 (28), 197 (27), 186 (25), 169 (15), 149 (58), 141 (59), 122 (15), 115 (63), 105 (9), 83 (13), 71 (31), 57 (58), 43 (61). UV/vis (MeCN): λ_{max} nm: 281, 346, 485. $E_{1/2}$ (Fc/Fc$^+$, V): 0.46. Anal. Calcd for $C_{18}H_{18}FeO_2$: C, 67.10; H, 5.63. Found: C, 66.96; H, 5.64.

(*E,E,E*)-[Ethyl-7-ferrocenyl-2,4,6-heptatrienoate] (5b). Utilizing the Heck protocol described for **3a**, with the following amounts of reagents, δ-iodoferrocenyldiene **4** (42 mg, 0.113 mmol), ethylacrylate (0.03 mL, 0.23 mmol), palladium acetate (10 mol %), tri(4-tolyl)arsine (30 mol %), lithium chloride (20 mol %), and dry triethylamine (0.05 mL, 0.4 mmol) in acetonitrile (1 mL), furnished **5b** as a dark red solid (34 mg, 87%, >99% *E*). TLC (silica gel/hexane, fourth run), $R_f = 0.35$; mp 78−79 °C. ^{1}H NMR ($CDCl_3$): δ 1.2 (t, 3H, $J = 7$ Hz), 4.06 (s, 5H, Cp), 4.17 (q, 2H, $J = 7$ Hz), 4.26 (brs, 2H, Cp), 4.35 (brs, 2H, Cp), 5.81 (d, 1H, $J = 15$ Hz), 6.24 (dd, 1H, $J = 12$, 14 Hz), 6.38−6.60 (m, 3H), 7.28 (dd, 1H, $J = 12$, 15 Hz). ^{13}C NMR ($CDCl_3$): δ 14.43, 60.27, 69.91, 69.54, 67.42, 119.59, 125.86, 127.59, 136.60, 141.46, 145.07, 168.15. IR (KBr) cm^{-1}: 2918 (vs), 1702 (s), 1608 (s), 1137 (s), 1004 (s), 2831 (m), 1456 (m),

1349 (m), 1239 (m), 1153 (m), 761 (m), 463 (m). EIMS *m*/*z* (rel intensity): 336 (M^+, 91), 312 (58), 263 (11), 214 (15), 186 (15), 141 (15), 121 (18), 41 (100). UV/vis (MeCN): λ_{max} nm: 281, 347, 484. $E_{1/2}$ (Fc/Fc^+, V): 0.43. Anal. Calcd for $C_{19}H_{20}FeO_2$: C, 67.88; H, 6.00. Found: C, 67.88; H, 5.98.

(*E*,*E*,*E*)-[7-Ferrocenyl-2,4,6-heptatrienoic acid] (5c). Utilizing the Heck protocol described for **3d**, with the following amounts of reagents, δ-iodoferrocenyldiene **4** (178 mg, 0.5 mmol), acrylic acid (0.07 mL, 1 mmol), palladium acetate (10 mol %), tri(4-tolyl)arsine (30 mol %), lithium chloride (20 mol %), and dry triethylamine (0.2 mL, 1.5 mmol) in acetonitrile (2 mL), furnished **5c** as a dark red solid (86 mg, 57%, >99% *E*). TLC (silica gel/hexane/ethyl acetate, 6:4, second run), R_f = 0.14; mp 220−223 °C (dec). ^{1}H NMR (acetone-d_6 and DMSO-d_6): δ 4.07 (s, 5H, Cp), 4.28 (s, 2H, Cp), 4.43 (s, 2H, Cp), 5.82 (d, 1H, J = 15 Hz), 6.36 (dd, 1H, J = 12, 15 Hz), 6.5−6.8 (m, 3H), 7.28 (dd, 1H, J = 12, 15 Hz). IR (KBr) cm^{-1}: 1678 (vs), 1012 (vs), 1608 (s), 1412 (s), 1280 (s), 3412 (m), 2910 (m), 1294 (m), 1098 (m), 792 (m), 470 (m). EIMS *m*/*z* (rel intensity): 308 (M^+, 69), 262 (22), 225 (16), 197 (9), 186 (18), 169 (11), 141 (31), 110 (88), 95 (11), 91 (16), 71 (28), 56 (100), 39 (78), 36 (7). UV/vis (MeCN): λ_{max} nm 283, 346, 484. $E_{1/2}$ (Fc/Fc^+, V): 0.45. Anal. Calcd for $C_{17}H_{16}FeO_2$: C, 66.26; H, 5.23. Found: C, 66.01; H, 5.19.

(*E*,*E*,*E*)-[1-Ferrocenyl-6-(4′-nitrophenyl)-1,3,5-hexatriene] (5d). Utilizing the Heck protocol described for **3a**, with the following amounts of reagents, δ-iodoferrocenyldiene **4** (92 mg, 0.253 mmol), *p*-nitrostyrene (75 mg, 0.51 mmol), palladium acetate (10 mol %), tri(4-tolyl)arsine (30 mol %), lithium chloride (20 mol %), and dry triethylamine (0.1 mL, 0.34 mmol) in acetonitrile (3 mL), furnished **5d** as a dark red solid (52 mg, 55%, >99% *E*). TLC (silica gel/hexane, third run), R_f = 0.1; mp 193−194 °C. ^{1}H NMR ($CDCl_3$): δ 4.12 (s, 5H, Cp), 4.32 (s, 2H, Cp), 4.46 (s, 2H, Cp), 6.05−6.30 (m, 2H), 6.4−6.7 (m, 3H), 6.93 (dd, 1H, J = 11, 14 Hz), 7.56 (d, 2H, Ar, J = 9 Hz), 8.2 (d, 2H, Ar, J = 9 Hz). ^{13}C NMR ($CDCl_3$): δ 67.21, 69.39, 69.67 (Cp), 121.38, 126.05, 126.30, 128.96, 129.51, 133.81 (alkenyl), 124.14, 126.60, 129.37, 129.66 (others). IR (KBr) cm^{-1}: 1333 (vs), 2902 (s), 1506 (s), 1569 (s), 996 (s), 2824 (m), 1106 (m), 808 (m), 722 (m), 463 (m). EIMS *m*/*z* (rel intensity): 385 (M^+, 56), 277 (11), 253 (18), 215 (8), 201 (21), 149 (24), 125 (32), 97 (36), 69 (60), 57 (100). UV/vis (MeCN): λ_{max} nm: 317, 396, 504. $E_{1/2}$ (Fc/Fc^+, V): 0.43. HRMS ($C_{22}H_{19}FeNO_2$) calcd, 385.076518; found, 385.076738.

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Supporting Information Available: ZINDO/1-derived orbital energy diagram of **I** and structures of intermediates **I** and **II**. This material is available free of charge via the Internet at http://pubs.acs.org.

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