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Palladium-Catalyzed Regio- and Stereoselective Arylesterification of Ferrocenylallene: A Synthetic Route to Ferrocene-Containing Disubstituted *E*-Allylic Esters

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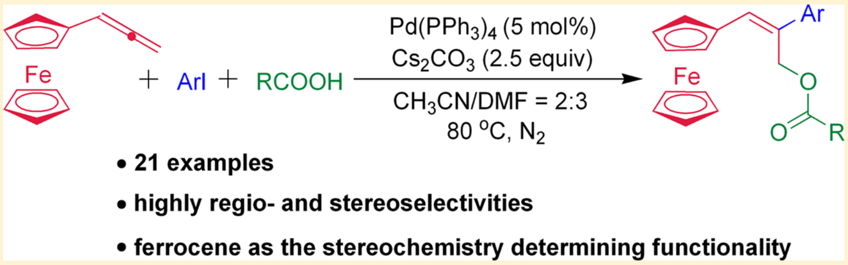
Supporting Information



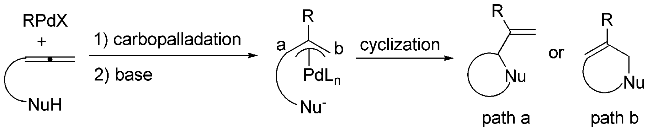
- 21 examples
- highly regio- and stereoselectivities
- ferrocene as the stereochemistry determining functionality

ABSTRACT: An efficient and concise protocol for the highly regio- and stereoselective synthesis of ferrocene-containing disubstituted *E*-allylic ester derivatives via a palladium-catalyzed intermolecular arylesterification reaction of ferrocenylallene with aryl iodides and carboxylic acids has been developed. The regio- and stereoselectivities of this reaction may be controlled by the steric effect of the bulky ferrocene group.

Since its fortuitous discovery in the 1950s,[1] ferrocene has attracted considerable attention from organic chemists because of its unique structural features, chemical and thermal stability, and electronic characteristics.[2] These properties have found widespread application in fields such as material science,[3] asymmetric catalysis,[4] and bioorganometallic chemistry.[5] Further, some specifically designed ferrocene-containing compounds are valuable candidates for antimalarial or anticancer therapies in the medicinal research area.[6] On the other hand, allylic esters are extremely important building blocks in organic synthesis[7] and are also present in many natural products and pharmaceutically active compounds.[8] Consequently, the integration of a ferrocenyl group with an allylic ester may enhance the biological activity or create a new medicinal property. However, to our surprise, there is no efficient method for the synthesis of these novel ferrocene-containing allylic esters. This is probably because of synthetic difficulties as organometallic compounds sometimes are more sensitive to certain reagents and reaction conditions. Herein, we report a highly regio- and stereoselective intermolecular three-component arylesterification reaction for the convenient synthesis of ferrocene-containing disubstituted allylic ester derivatives from ferrocenyl allene, aryl iodides, and carboxylic acids as the substrates.

Currently, the chemistry of allenes has attracted interest because of the diverse reactivities of these compounds in organic synthesis.[9] Various useful synthetic methodologies have been developed on the basis of allene chemistry. Among these, the palladium-catalyzed reactions of allenes, aryl halides, and carbon/heteroatom nucleophiles have been extensively investigated over the last few decades.[10] However, owing to the formation of a π-allyl palladium intermediate by the carbopalladation reaction of allene, it is still challenging to control the regio- and stereoselectivities of the reaction. Thus, the predesigned allenes with a carbon or heteroatom nucleophilic side chain are often used in the reactions to achieve high regio- and stereoselectivities (Scheme 1).[11]

Scheme 1. Palladium-Catalyzed Reaction of Allene with a Carbon or Heteroatom Nucleophilic Side Chain



However, compared to the wide applications of nitrogen and carbon nucleophiles in the palladium-catalyzed coupling reactions of allenes, the use of oxygen nucleophiles has rarely been reported. Such reactions using carboxylic acid nucleophiles, particularly intermolecular three-component reactions, remain an important challenge.

As an extension of our interest in ferrocene and allene chemistry,[12] we recently reported an iodine-mediated highly regio- and stereoselective iodoamination of ferrocenyl allene in which the bulky ferrocene group was believed to be the stereochemistry-determining functionality.[13] We envisioned that such high regio- and stereoselectivities can also be

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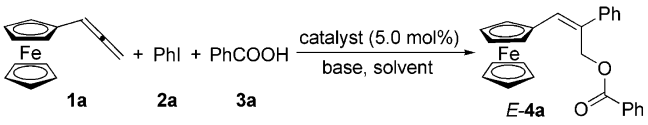
achieved in the palladium-catalyzed intermolecular three-component reactions when ferrocenylallene is used as the substrate. Herein, we report the realization of such a concept.

At the outset of this investigation, the $Pd(PPh_3)_4$-catalyzed three-component reaction of ferrocenylallene **1a**, iodobenzene **2a**, and benzoic acid **3a** was examined (Table 1). To our delight, when the reaction was carried out in DMF at 80 °C for 6 h using 2.5 equiv of Cs_2CO_3 under nitrogen atmosphere, as expected, the corresponding ferrocene-containing disubstituted allylic ester *E*-**4a** was obtained in 31% yield as the only stereoisomer (Table 1, entry 1). The configuration of the C=C bond in **4a** was determined by the NOE study.[14] To optimize the reaction conditions, the effect of bases on this three-component reaction was carefully examined. Cs_2CO_3 was found to be the most suitable base for this transformation (entry 1). Other bases, such as sodium acetate and sodium hydroxide, also worked for this reaction, albeit with lower yields (entries 2 and 3). However, *E*-**4a** was not detected when K_2CO_3 was used as the base (entry 4). Next, diverse common organic solvents were screened; DMF was still found to be the most suitable solvent for this transformation, whereas a low yield of *E*-**4a** was obtained when CH_3CN or CH_3NO_2 was used as the solvent in this reaction (entries 5 and 6). Further investigation showed that nonpolar solvents, such as $PhCH_3$ and THF, were not suitable for this reaction (entries 7 and 8). Our previous study results showed that a mixture of solvents may be effective for this type of reaction.[13] Therefore, the effect of solvent mixtures on this transformation was carefully examined (entries 9−13). As expected, the results showed that CH_3CN/DMF (2:3) is the most effective solvent system, in which the yield of *E*-**4a** was improved to 75% and the reaction time was reduced to 4 h (entry 12). Interestingly, other palladium catalysts, such as $Pd(PPh_3)_2Cl_2$, $[Pd(dba)_2]$, and $Pd(PhCN)_2Cl_2$, failed for this three-component transformation under the above reaction conditions (entries 14−16).

Table 1. Optimization of Reaction Conditions[a]

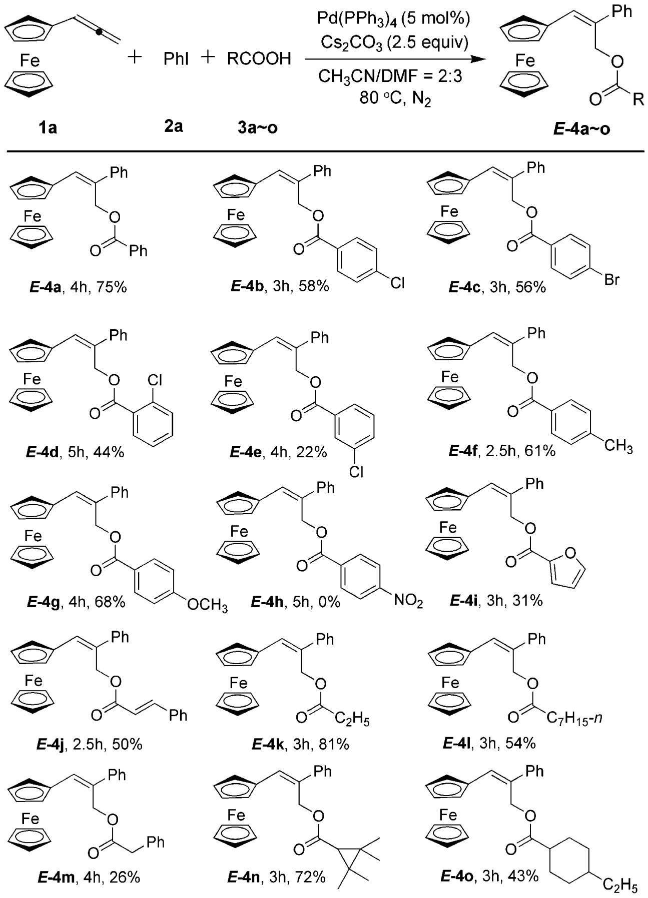


entry	cat.	base	solvent	time (h)	yield[b] (%)
1	$Pd(PPh_3)_4$	Cs_2CO_3	DMF	6	31
2	$Pd(PPh_3)_4$	CH_3COONa	DMF	10	25
3	$Pd(PPh_3)_4$	NaOH	DMF	12	12
4	$Pd(PPh_3)_4$	K_2CO_3	DMF	8	trace
5	$Pd(PPh_3)_4$	Cs_2CO_3	CH_3CN	24	21
6	$Pd(PPh_3)_4$	Cs_2CO_3	CH_3NO_2	10	17
7	$Pd(PPh_3)_4$	Cs_2CO_3	$PhCH_3$	22	NR
8	$Pd(PPh_3)_4$	Cs_2CO_3	THF	22	NR
9	$Pd(PPh_3)_4$	Cs_2CO_3	CH_3CN/DMF = 1:1	5	68
10	$Pd(PPh_3)_4$	Cs_2CO_3	CH_3CN/DMF = 5:1	20	26
11	$Pd(PPh_3)_4$	Cs_2CO_3	CH_3CN/DMF = 2:1	15	29
12	$Pd(PPh_3)_4$	Cs_2CO_3	CH_3CN/DMF = 2:3	4	75
13	$Pd(PPh_3)_4$	Cs_2CO_3	CH_3CN/DMF = 1:2	6	69
14	$Pd(PPh_3)_2Cl_2$	Cs_2CO_3	CH_3CN/DMF = 2:3	17	23
15	$[Pd(dba)_2]$	Cs_2CO_3	CH_3CN/DMF 2:3	8	trace
16	$Pd(PhCN)_2Cl_2$	Cs_2CO_3	CH_3CN/DMF = 2:3	6	8

[a] Reactions were carried out with 0.3 mmol of **1a**, 0.36 mmol of **2a**, and 0.45 mmol of **3a** in the presence of 5 mol % of catalyst and 2.5 equiv of base at 80 °C under a N_2 atmosphere. [b] Yield of isolated product after chromatography.

With the optimized reaction conditions, the substrate scope and limitation of the current $Pd(PPh_3)_4$-catalyzed intermolecular three-component arylesterification reaction using various carboxylic acids as the substrates were examined; the results are summarized in Table 2. First, different substituents on the phenyl ring of the aromatic carboxylic acids were tested, and the corresponding ferrocene-containing allylic ester products **4** were obtained in moderate to good yields as well as high regio- and stereoselectivities (Table 2, **4a−g**). It was found that substrates with a phenyl ring bearing an electron-donating group generally gave slightly higher yields (**4f** and **4g**), whereas the substrates with a strong electron-withdrawing substituent on the phenyl ring, such as a nitro group, failed to afford any product (**4h**). Moreover, the reaction was tolerant to the

Table 2. $Pd(PPh_3)_4$-Catalyzed Three-Component Reaction of Ferrocenylallene, Iodobenzene, and Various Carboxylic Acids[a]

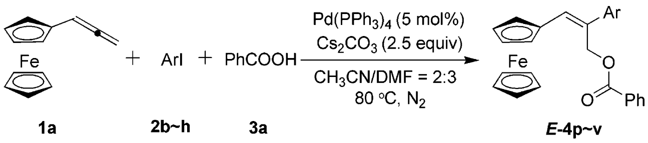


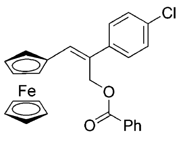
[a] Reactions were carried out with 0.3 mmol of **1a**, 0.36 mmol of **2a**, and 0.45 mmol of **3a−o** in the presence of 5 mol % of $Pd(PPh_3)_4$ and 0.75 mmol of Cs_2CO_3 at 80 °C under a N_2 atmosphere. Isolated yields were reported.

heteroaromatic carboxylic acid and afforded the corresponding allylic ester in a moderate yield (**4i**). Notably, the reaction proceeded readily and resulted in a modest yield of the corresponding product when cinnamic acid was used as the nucleophile (**4j**). In addition, to our delight, several different aliphatic carboxylic acids, such as long-chain and cyclic carboxylic acid derivatives, underwent the arylesterification reaction to afford **4k−o**.

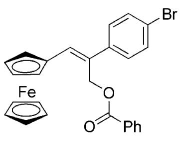
To highlight the utility of this transformation, diverse aryl iodides were subjected to the optimized reaction conditions. The results are shown in Table 3. All of them were found to be applicable in the Pd(PPh_3)$_4$-catalyzed three-component reaction with ferrocenylallene **1a** and benzoic acid **3a** to afford the corresponding ferrocene-containing allylic ester derivatives in 42−78% yields. In addition, both electron-withdrawing and electron-donating substituents on the aryl iodides were tolerated. Notably, the high regio- and stereoselectivities were observed in all cases, and only *E*-isomers were obtained.

Table 3. Pd(PPh_3)$_4$-Catalyzed Three-Component Reaction of Ferrocenylallene, Benzoic Acid, and Various Aryl Iodides[a]

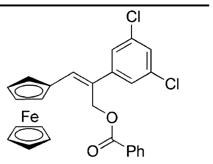




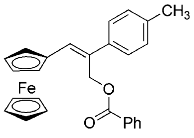
E-**4p**, 3h, 51%



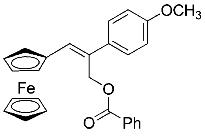
E-**4q**, 2h, 49%



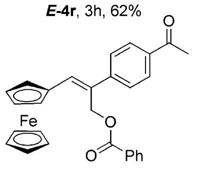
E-**4r**, 3h, 62%



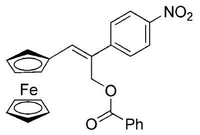
E-**4s**, 3h, 78%



E-**4t**, 5h, 60%



E-**4u**, 3h, 69%

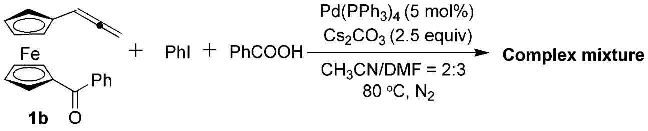


E-**4v**, 3h, 42%

[a] Reactions were carried out with 0.3 mmol of **1a**, 0.36 mmol of **2b−h**, and 0.45 mmol of **3a** in the presence of 5 mol % of Pd(PPh_3)$_4$ and 0.75 mmol of Cs_2CO_3 at 80 °C under a N_2 atmosphere. Isolated yields were reported.

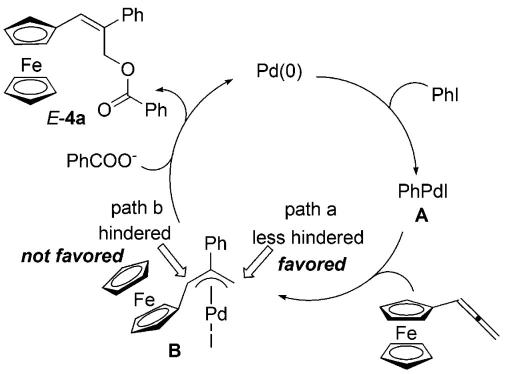
One current limitation of this method is that 1,1′-disubstituted ferrocenylallene substrates are completely inert to this Pd(PPh_3)$_4$-catalyzed arylesterification under the optimized reaction conditions. For example, when 1′-(propa-1,2-dienyl)-1-benzoylferrocene **1b** was selected as the allene partner, the reaction became very sluggish and resulted in a complex mixture (Scheme 2). This may be attributed to the steric effect of the disubstituted ferrocene group.

Scheme 2. Reaction of 1,1′-Disubstituted Ferrocenylallene



On the basis of the aforementioned results and related literature,[10,11] a plausible reaction mechanism is shown in Scheme 3, in which the bulky ferrocene group is believed to be the stereochemistry-determining functionality. The reaction is initiated by the oxidative addition of Pd(0) to aromatic iodides to afford Pd(II) intermediate **A**. The carbopalladation of **A** to the ferrocenylallene affords *π*-allyl palladium intermediate **B**.[11] The nucleophilic attack of the benzoate anion, which is generated from benzoic acid in the presence of a base, to the allyl ligand through path *a* is favored because of steric reasons and affords the ferrocene-containing allylic ester product *E*-**4a** and regenerates the Pd(0) catalyst. On the other hand, it is well-known that the *α*-carbenium center is highly stabilized by the fulvenoid resonance structure of the attached ferrocenyl moiety.[15] Therefore, the nucleophilic attack of the benzoate anion at this position through path *b* is also expected. Obviously, in this case, the steric hindrance overcomes the electronic factors.

Scheme 3. Proposed Mechanism of the Reaction



In summary, a palladium-catalyzed intermolecular three-component arylesterification of ferrocenylallene, aryl iodides, and carboxylic acids has been developed to afford a series of ferrocene-containing allylic ester derivatives in moderate-to-good yields and with high regio- and stereoselectivities. The process showed considerable synthetic advantages in terms of product diversity, simplicity of the reaction procedure, and mild reaction conditions. It is believed that the regio- and stereoselectivities may have been controlled by the steric effect of the bulky ferrocene group. Owing to the increasing importance of allylic esters and ferrocenes in bioorganic and pharmaceutical fields, this method has great potential in organic synthesis and offer new possibility to incorporate allylic esters in ferrocene chemistry.

■ EXPERIMENTAL SECTION

General Information. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. All solvents were purified following standard literature procedures. For chromatography, 200−300 mesh silica gel (Qingdao, China) was employed. ^1H and ^{13}C NMR spectra were recorded at 500 and 125 MHz FT-NMR spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard when $CDCl_3$ was used as solvent. IR spectra were recorded on a FT-IR instrument. The HRMS analysis was obtained on a QTOF mass spectrometer. Melting points were determined with a melting points apparatus and are uncorrected.

General Procedure for the Pd(PPh_3)$_4$-Catalyzed Arylesterification of Ferrocenylallene, Aryl Iodides, and Carboxylic

Acids. To a solution of carboxylic acid (0.45 mmol), aryl iodide (0.36 mmol), ferrocenylallene (0.3 mmol), and Cs_2CO_3 (0.75 mmol) in CH_3CN/DMF = 2:3 (3.0 mL) was added $Pd(PPh_3)_4$ (0.015 mmol) under a N_2 atmosphere. The resulting mixture was heated at 80 °C for the indicated time. After completion of the reaction, the mixture was cooled to room temperature. The solvent was removed in a vacuum, and the resulting residue was purified on a silica gel column (petroleum ether/EtOAc) to provide the desired ferrocene-containing allylic ester product *E*-**4**.

*(E)-3-Ferrocenyl-2-phenylallyl benzoate (E-**4a**):* red oil; 95 mg, 75% yield; IR (KBr) 3091, 2924, 1717, 1618, 1600, 1451, 1398, 1267, 1107, 948, 818, 712 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.5 Hz, 2H), 7.53−7.50 (m, 3H), 7.40−7.37 (m, 4H), 7.34 (t, *J* = 7.5 Hz, 1H), 6.87 (s, 1H), 5.40 (s, 2H), 4.47 (s, 2H), 4.28 (s, 2H), 4.13 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 141.4, 133.2, 132.3, 131.5, 130.3, 129.8, 128.7, 128.6, 127.2, 125.9, 80.8, 69.9, 69.8, 69.4, 63.4; HRMS (MALDI, positive) calcd for $C_{26}H_{22}FeO_2$ $[M^+]$ 422.0969, found 422.0961.

*(E)-3-Ferrocenyl-2-phenylallyl 4-chlorobenzoate (E-**4b**):* red solid; 79 mg, 58% yield; mp 99−100 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3125, 2850, 1707, 1617, 1400, 1268, 1102, 818, 762, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.39−7.35 (m, 4H), 7.28 (t, *J* = 7.5 Hz, 1H), 6.88 (s, 1H), 5.40 (s, 2H), 4.46 (s, 2H), 4.31 (s, 2H), 4.15 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 141.2, 139.5, 132.3, 131.4, 131.1, 128.8, 128.7, 128.6, 127.2, 125.8, 80.6, 69.9, 69.7, 69.3, 63.5; HRMS (MALDI, positive) calcd for $C_{26}H_{21}ClFeO_2$ $[M^+]$ 456.0579, found 456.0569.

*(E)-3-Ferrocenyl-2-phenylallyl 4-bromobenzoate (E-**4c**):* red solid; 84 mg, 56% yield; mp 109−110 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3120, 2925, 1716, 1617, 1396, 1265, 1098, 819, 755 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 7.5 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.28 (t, J = 7.5 Hz, 1H), 6.88 (s, 1H), 5.40 (s, 2H), 4.46 (s, 2H), 4.32 (s, 2H), 4.15 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 141.1, 132.3, 131.8, 131.3, 131.2, 129.1, 128.6, 128.2, 127.2, 125.8, 80.6, 69.8, 69.7, 69.3, 63.5; HRMS (MALDI, positive) calcd for $C_{26}H_{21}BrFeO_2$ $[M^+]$ 500.0074, found 500.0068.

*(E)-3-Ferrocenyl-2-phenylallyl 2-chlorobenzoate (E-**4d**):* red oil; 61 mg, 44% yield; IR (KBr) 3118, 2923, 1728, 1616, 1400, 1286, 1247, 1115, 1046, 818, 748 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.40−7.35 (m, 3H), 7.30−7.26 (m, 2H), 6.86 (s, 1H), 5.44 (s, 2H), 4.49 (s, 2H), 4.32 (s, 2H), 4.15 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 141.1, 133.9, 132.6, 132.4, 132.3, 131.4, 131.1, 130.1, 128.6, 127.2, 126.6, 125.9, 80.7, 69.7, 69.4, 69.2, 63.7; HRMS (MALDI, positive) calcd for $C_{26}H_{21}ClFeO_2$ $[M^+]$ 456.0579, found 456.0580.

*(E)-3-Ferrocenyl-2-phenylallyl 3-chlorobenzoate (E-**4e**):* red oil; 30 mg, 22% yield; IR (KBr) 3114, 2923, 2852, 1721, 1618, 1467, 1400, 1256, 1125, 816, 749, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.54−7.51 (m, 3H), 7.39−7.35 (m, 3H), 7.30 (d, *J* = 7.0 Hz, 1H), 6.90 (s, 1H), 5.40 (s, 2H), 4.48 (s, 2H), 4.33 (s, 2H), 4.17 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 141.1, 134.6, 133.1, 132.5, 132.0, 131.2, 129.8, 128.7, 128.6, 127.8, 127.2, 125.8, 80.6, 69.8, 69.6, 69.2, 63.6; HRMS (MALDI, positive) calcd for $C_{26}H_{21}ClFeO_2$ $[M^+]$ 456.0579, found 456.0577.

*(E)-3-Ferrocenyl-2-phenylallyl 4-methylbenzoate (E-**4f**):* red solid; 80 mg, 61% yield; mp 92−93 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3126, 2922, 1703, 1618, 1401, 1322, 1104, 820, 757 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.88 (s, 1H), 5.37 (s, 2H), 4.48 (s, 2H), 4.30 (s, 2H), 4.14 (s, 5H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 143.8, 141.4, 132.2, 131.6, 129.8, 129.2, 128.6, 127.5, 127.1, 125.8, 80.8, 69.8, 69.7, 69.3, 63.2, 21.7; HRMS (MALDI, positive) calcd for $C_{27}H_{24}FeO_2$ $[M^+]$ 436.1126, found 436.1116.

*(E)-3-Ferrocenyl-2-phenylallyl 4-methoxybenzoate (E-**4g**):* red oil; 92 mg, 68% yield; IR (KBr) 3113, 2838, 1709, 1605, 1399, 1256, 1167, 1100, 847, 769 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.87 (s, 1H), 5.36 (s, 2H), 4.47 (s, 2H), 4.28 (s, 2H), 4.13 (s, 5H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 163.5, 141.5, 132.1, 131.8, 131.7, 128.6, 127.1, 125.9, 122.7, 113.8, 80.8, 69.8, 69.7, 69.4, 63.1, 55.5; HRMS (MALDI, positive) calcd for $C_{27}H_{24}FeO_3$ $[M^+]$ 452.1075, found 452.1071.

*(E)-3-Ferrocenyl-2-phenylallyl furan-2-carboxylate (E-**4i**):* red oil; 39 mg, 31% yield; IR (KBr) 3123, 2921, 1724, 1472, 1399, 1291, 1177, 1114, 944, 819, 761 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 3.0 Hz, 1H), 6.87 (s, 1H), 6.48 (d, *J* = 3.5 Hz, 1H), 5.38 (s, 2H), 4.48 (s, 2H), 4.32 (s, 2H), 4.16 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 146.5, 144.6, 141.2, 132.6, 131.1, 128.6, 127.1, 125.8, 118.1, 111.9, 80.6, 69.8, 69.7, 69.3, 63.1; HRMS (MALDI, positive) calcd for $C_{24}H_{20}FeO_3$ $[M^+]$ 412.0762, found 412.0757.

*(E)-3-Ferrocenyl-2-phenylallyl cinnamate (E-**4j**):* red oil; 67 mg, 50% yield; IR (KBr) 3127, 3021, 1709, 1636, 1400, 1251, 1163, 979, 765, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 3.5 Hz, 2H), 7.38−7.33 (m, 5H), 7.27 (t, *J* = 7.5 Hz, 1H), 6.85 (s, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 5.30 (s, 2H), 4.46 (s, 2H), 4.30 (s, 2H), 4.16 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 145.2, 141.2, 134.4, 132.1, 131.7, 130.4, 129.0, 128.6, 128.2, 127.2, 125.9, 118.1, 80.8, 69.8, 69.8, 69.4, 62.8; HRMS (MALDI, positive) calcd for $C_{28}H_{24}FeO_2$ $[M^+]$ 448.1126, found 448.1123.

*(E)-3-Ferrocenyl-2-phenylallyl propionate (E-**4k**):* red solid; 91 mg, 81% yield; mp 66−67 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3096, 2977, 1725, 1617, 1400, 1187, 959, 820, 760, 696, 626 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 6.78 (s, 1H), 5.18 (s, 2H), 4.41 (s, 2H), 4.29 (s, 2H), 4.15 (s, 5H), 2.34 (q, *J* = 7.5 Hz, 2H), 1.12 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 141.2, 132.0, 131.7, 128.6, 127.1, 125.9, 80.8, 69.8, 69.7, 69.3, 62.5, 27.8, 9.3; HRMS (MALDI, positive) calcd for $C_{22}H_{22}FeO_2$ $[M^+]$ 374.0969, found 374.0971. Anal. Calcd for $C_{22}H_{22}FeO_2$: C, 70.60; H, 5.93. Found: C, 70.56; H, 5.85.

*(E)-3-Ferrocenyl-2-phenylallyl octanoate (E-**4l**):* red oil; 72 mg, 54% yield; IR (KBr) 3100, 2927, 2855, 1732, 1619, 1456, 1400, 1161, 1106, 1001, 818, 762, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 6.79 (s, 1H), 5.17 (s, 2H), 4.42 (s, 2H), 4.30 (s, 2H), 4.16 (s, 5H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.59 (q, *J* = 7.0 Hz, 2H), 1.30−1.26 (m, 8H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 141.1, 132.0, 131.7, 128.5, 127.1, 125.9, 80.8, 69.7, 69.6, 69.3, 62.4, 34.5, 31.7, 29.1, 29.0, 25.1, 22.7, 14.2; HRMS (MALDI, positive) calcd for $C_{27}H_{32}FeO_2$ $[M^+]$ 444.1752, found 444.1749.

*(E)-3-Ferrocenyl-2-phenylallyl 2-phenylacetate (E-**4m**):* red oil; 34 mg, 26% yield; IR (KBr) 3232, 2922, 1731, 1618, 1400, 1253, 1147, 1002, 819, 763, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.0 Hz, 2H), 7.32−7.24 (m, 8H), 6.78 (s, 1H), 5.17 (s, 2H), 4.35 (s, 2H), 4.26 (s, 2H), 4.12 (s, 5H), 3.63 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.8, 141.0, 134.0, 131.9, 131.7, 129.3, 128.6, 128.5, 127.1, 127.1, 125.9, 80.7, 69.6, 69.6, 69.3, 63.1, 41.6; HRMS (MALDI, positive) calcd for $C_{27}H_{24}FeO_2$ $[M^+]$ 436.1126, found 436.1124.

*(E)-3-Ferrocenyl-2-phenylallyl 2,2,3,3-tetramethylcyclopropanecarboxylate (E-**4n**):* red solid; 91 mg, 72% yield; mp 99−100 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 2924, 2853, 1717, 1619, 1393, 1318, 1184, 1137, 1107, 815, 765, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.0 Hz, 1H), 6.76 (s, 1H), 5.13 (s, 2H), 4.41 (s, 2H), 4.28 (s, 2H), 4.14 (s, 5H), 1.25 (s, 6H), 1.23 (s, 1H), 1.14 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 141.4, 132.4, 131.4, 128.5, 127.1, 126.0, 80.9, 69.8, 69.7, 69.4, 61.9, 36.0, 30.3, 23.7, 16.9; HRMS (MALDI, positive) calcd for $C_{27}H_{30}FeO_2$ $[M^+]$ 442.1595, found 442.1602.

*(E)-3-Ferrocenyl-2-phenylallyl 4-ethylcyclohexanecarboxylate (E-**4o**):* orange oil; 59 mg, 43% yield; IR (KBr) 2925, 2853, 1728, 1449, 1231, 1174, 1138, 1002, 817, 762, 697 cm^{-1}; ^{1}H NMR (500 MHz,

CDCl$_3$) δ 7.44 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.26 (t, J = 7.5 Hz, 1H), 6.79 (s, 1H), 5.16 (s, 2H), 4.42 (s, 2H), 4.31 (s, 2H), 4.16 (s, 5H), 2.25 (t, J = 8.0 Hz, 1H), 1.94 (d, J = 11.0 Hz, 2H), 1.79 (d, J = 13.0 Hz, 2H), 1.45−1.36 (m, 2H), 1.19 (m, 2H), 1.14−1.07 (m, 1H), 0.91−0.84 (m, 5H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 176.5, 141.1, 132.1, 131.5, 128.5, 127.1, 125.8, 80.9, 69.7, 69.3, 62.3, 43.7, 38.7, 31.9, 29.8, 29.0, 11.4; HRMS (MALDI, positive) calcd for $C_{28}H_{32}FeO_2$ [M$^+$] 456.1752, found 456.1745.

*(E)-2-(4-Chlorophenyl)-3-ferrocenylallyl benzoate (E-**4p**):* red solid; 70 mg, 51% yield; mp: 119−120 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3128, 2925, 1714, 1618, 1402, 1273, 1110, 816, 708 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.03 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.46−7.42 (m, 4H), 7.32 (d, J = 8.5 Hz, 2H), 6.85 (s, 1H), 5.37 (s, 2H), 4.48 (s, 2H), 4.32 (s, 2H), 4.15 (s, 5H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 166.7, 139.7, 133.2, 132.9, 132.7, 130.4, 130.1, 129.7, 128.7, 128.5, 127.1, 80.4, 70.0, 69.7, 69.4, 63.0; HRMS (MALDI, positive) calcd for $C_{26}H_{21}ClFeO_2$ [M$^+$] 456.0579, found 456.0571. Anal. Calcd for $C_{26}H_{21}ClFeO_2$: C, 68.37; H, 4.63. Found: C, 68.67; H, 4.91.

*(E)-2-(4-Bromophenyl)-3-ferrocenylallyl benzoate (E-**4q**):* red solid; 74 mg, 49% yield; mp 120−121 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 2922, 1714, 1621, 1401, 1273, 1109, 814, 708 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.03 (d, J = 7.0 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.49−7.38 (m, 6H), 6.86 (s, 1H), 5.37 (s, 2H), 4.48 (s, 2H), 4.33 (s, 2H), 4.16 (s, 5H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 166.7, 140.2, 133.2, 132.8, 131.6, 130.4, 130.1, 129.7, 128.5, 127.4, 121.0, 80.3, 70.0, 69.7, 69.3, 62.9; HRMS (MALDI, positive) calcd for $C_{26}H_{21}BrFeO_2$ [M$^+$] 500.0074, found 500.0077.

*(E)-2-(3,4-Dichlorophenyl)-3-ferrocenylallyl benzoate (E-**4r**):* red oil; 91 mg, 62% yield; IR (KBr) 2965, 1714, 1638, 1617, 1400, 1270, 1106, 814, 709, 617 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.05 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.39 (s, 2H), 7.27 (s, 1H), 6.88 (s, 1H), 5.32 (s, 2H), 4.49 (s, 2H), 4.36 (s, 2H), 4.16 (s, 5H); ^{13}C NMR (125 MHz, CDCl$_3$) δ166.6, 144.5, 135.1, 134.8, 133.3, 129.9, 129.7, 129.0, 128.5, 126.8, 124.4, 79.6, 70.3, 69.9, 69.4, 62.8; HRMS (MALDI, positive) calcd for $C_{26}H_{20}Cl_2FeO_2$ [M$^+$] 490.0190, found 490.0192.

*(E)-3-Ferrocenyl-2-p-tolylallyl benzoate (E-**4s**):* red solid; 102 mg, 78% yield; mp 89−90 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3197, 2935, 1716, 1622, 1400, 1274, 1110, 815, 708 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.05 (d, J = 7.0 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.44−7.40 (m, 4H), 7.17 (d, J = 8.0 Hz, 2H), 6.86 (s, 1H), 5.38 (s, 2H), 4.47 (s, 2H), 4.29 (s, 2H), 4.14 (s, 5H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 166.8, 138.4, 136.9, 133.1, 131.4, 131.4, 130.3, 129.7, 129.3, 128.5, 125.7, 80.9, 69.7, 69.6, 69.3, 63.4, 21.2; HRMS (MALDI, positive) calcd for $C_{27}H_{24}FeO_2$ [M$^+$] 436.1126, found 436.1129. Anal. Calcd for $C_{27}H_{24}FeO_2$: C, 74.32; H, 5.54. Found: C, 74.36; H, 5.84.

*(E)-3-Ferrocenyl-2-(4-methoxyphenyl)allyl benzoate (E-**4t**):* red solid; 81 mg, 60% yield; mp 127−128 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3007, 2922, 1707, 1618, 1400, 1266, 1110, 818, 716 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.05 (d, J = 7.0 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 6.80 (s, 1H), 5.38 (s, 2H), 4.46 (s, 2H), 4.28 (s, 2H), 4.14 (s, 5H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 166.8, 158.9, 133.8, 133.1, 131.1, 130.5, 130.3, 129.7, 128.5, 127.0, 114.0, 81.1, 69.6, 69.5, 69.3, 63.3, 55.4; HRMS (MALDI, positive) calcd for $C_{27}H_{24}FeO_3$ [M$^+$] 452.1075, found 452.1076. Anal. Calcd for $C_{27}H_{24}FeO_3$: C, 71.69; H, 5.35. Found: C, 71.49; H, 5.37.

*(E)-2-(4-acetylphenyl)-3-ferrocenylallyl benzoate (E-**4u**).* Red solid; 96 mg, 69% yield; mp: 155−156 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3191, 2922, 1708, 1670, 1616, 1597, 1401, 1264, 1110, 950, 828, 714 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.04 (d, J = 7.0 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 7.0 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.01 (s, 1H), 5.42 (s, 2H), 4.52 (s, 2H), 4.36 (s, 2H), 4.16 (s, 5H), 2.59 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 197.6, 166.7, 145.8, 135.5, 134.6, 133.2, 130.3, 130.0, 129.7, 128.8, 128.5, 125.8, 80.0, 70.3, 70.0, 69.4, 62.8, 26.7; HRMS (MALDI, positive) calcd for $C_{28}H_{24}FeO_3$ [M$^+$] 464.1075, found 464.1072. Anal. Calcd for $C_{28}H_{24}FeO_3$: C, 72.43; H, 5.21. Found: C, 72.16; H, 5.36.

*(E)-3-Ferrocenyl-2-(4-nitrophenyl)allyl benzoate (E-**4v**):* brownish solid; 59 mg, 42% yield; mp 124−125 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3124, 2924, 1706, 1618, 1400, 1266, 1112, 831, 714 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.22 (d, J = 9.0 Hz, 2H), 8.03 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 9.0 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 7.05 (s, 1H), 5.42 (s, 2H), 4.55 (s, 2H), 4.41 (s, 2H), 4.18 (s, 5H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 166.6, 147.7, 146.5, 136.3, 133.3, 129.8, 129.7, 129.3, 128.6, 126.3, 124.0, 79.5, 70.6, 70.1, 69.5, 62.5; HRMS (MALDI, positive) calcd for $C_{26}H_{21}FeNO_4$ [M$^+$] 467.0820, found 467.0824.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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