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Regio- and Stereoselective Synthesis of Ferrocene-Containing β-Iodoallylic Esters and Ethers from the Iodofunctionalization of Ferrocenylallene with Carboxylic Acids, Phenols, and Alcohols

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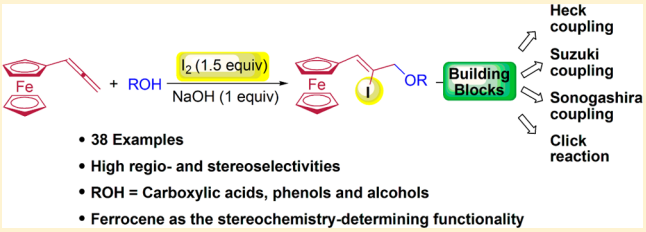
Supporting Information

ABSTRACT: The iodofunctionalization of ferrocenylallene with carboxylic acids, phenols, and alcohols is described. The reaction proceeds smoothly in the presence of molecule iodine as a halonium promoter and using various carboxylic acids, phenols, and alcohols as nucleophiles to give the corresponding ferrocene-containing β-iodoallylic ester and ether products in moderate to high yields and with high regio- and stereoselectivities. It can be envisaged that the regio- and stereoselectivity of this reaction may be controlled by the steric effect of the bulky ferrocene group. The presence of the C−I bond in the corresponding products makes these molecules highly attractive from a synthetic point of view, as it provides an opportunity for further transformations. Thus, palladium-catalyzed Heck coupling, Suzuki coupling, Sonogashira coupling, and copper-catalyzed click reactions were carried out successfully.



INTRODUCTION

Allylic ester and ether derivatives have been recognized as one of the most vital classes of compounds and are widely applied in modern organic synthesis as well as in material science as valuable intermediates and building blocks because of their versatile chemical reactivities.[1] Moreover, allylic ester and ether moieties are also broadly found in many natural products, agricultural chemicals, and pharmaceutically active molecules.[2] Ferrocene derivatives are an important class of organometallic compounds that display a wide range of biological activities, such as anti-cancer, anti-malarial, anti-proliferative, and inhibitors of enzymes.[3] Consequently, the incorporation of a ferrocene moiety into an allylic ester or ether may enhance the biological activity or create unexpected medicinal property. However, to our surprise, there is no efficient method for the construction of these novel ferrocene-containing allylic esters and ethers. The reason is most likely related to the synthetic difficulties, because it is believed that some organometallic compounds sometimes are more sensitive to certain reagents and reaction conditions.[4] More recently, we have demonstrated 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,[5] which provides an opportunity for the construction of ferrocene-containing allylic compounds under the mild reaction conditions.

During the past decade, allenes have attracted great attention from organic chemists because of their unique structural features and chemical properties related to the presence of two perpendicular π bonds.[6] Allenes can undergo diverse transformations, providing various reactivity modes to construct complex chemical architectures.[7] Among these, the electrophilic additions of allenes are synthetically attractive because two functionalities are introduced simultaneously in one operation.[7c] However, owing to the presence of two C=C bonds, it is still challenging to control the regio- and stereoselectivities of the reaction. Ma and co-workers have developed a series of halo-/seleno-promoted electrophilic addition reactions, in which a functional group, such as sulfoxide, sulfone, phosphine oxide, sulfide, or selenide, and furanone group are introduced to the allene moiety in order to obtain high regio- and stereoselectivities.[8] Moreover, we recently reported an iodine-mediated iodoamination of ferrocenylallene in moderate to high yields and with high regio- and stereoselectivities, in which the bulky ferrocene group was considered to be the stereochemistry-determining functionality.[9] As an extension of our interest in ferrocene and allene chemistry,[10] herein we show the realization of a highly selective iodofunctionalization reaction of ferrocenylallene with various carboxylic acids, phenols, and alcohols in the presence of molecular iodine, which provides a straightforward route to not readily available ferrocene-containing β-iodoallylic ester and ether compounds with excellent stereoselectivity (Scheme 1). Because of the existence of C−I bonds, different substituents can be easily introduced by the transition metal-catalyzed cross-coupling reactions.

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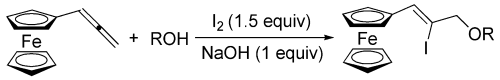
Scheme 1. Regio- and Stereoselective Iodofunctionalization of Ferrocenylallene with Carboxylic Acids, Phenols, and Alcohols



ROH = Carboxylic acids, phenols and alcohols

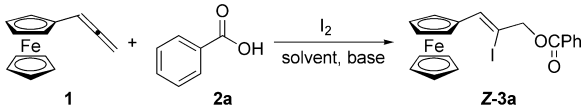
RESULTS AND DISCUSSION

At the outset of this investigation, we carried out the iodocarboxylation of ferrocenylallene **1** with benzoic acid **2a** and I_2 at room temperature in the presence of 1 equiv of NaOH in THF for 2 h; the corresponding iodocarboxylation product, *Z*-**3a**, was obtained in a yield of 18% as the only stereoisomer (Table 1, entry 1). Subsequently, various parameters were screened to optimize the reaction conditions. The experiments showed that solvents seemingly played a key role in promoting the efficiency and that dichloromethane dramatically enhanced the yield of *Z*-**3a** to 60%. When other solvents, such as DMF, CH_3CN, toluene, and dioxane, were applied instead of dichloromethane, the yield of the desired ferrocene-containing *β*-iodoallylic ester product decreased to varying degrees (entries 2−6). Similarly, $ClCH_2CH_2Cl$ was also confirmed to be suitable for this transformation, furnishing *Z*-**3a** in 56% yield (entry 7). Our recent study results showed that a mixture of solvents is very effective for this type of reaction.[9] Therefore, the effect of solvent mixtures on this iodocarboxylation reaction was next examined. To our disappointment, all of these solvent mixtures failed to improve the yield of the corresponding product (entries 8 and 9). With dichloromethane as the solvent at room temperature, the effect of base was next studied. NaOH was still found to be the most suitable base for this transformation, whereas a lower yield of *Z*-**3a** was obtained when *t*-BuOK, Cs_2CO_3, NaOAc, or Et_3N was used as the base in this reaction (entries 10−13). Only a trace amount of the product was detected when the reaction proceeded in the absence of a base (entry 14). Considering the low solubility of NaOH in organic solvents, two phase-transfer catalysts were added into the reaction system. However, no significant improvement in the yield of *Z*-**3a** was observed (entries 15 and 16). Finally, we obtained the ferrocene-containing *β*-iodoallylic ester product in acceptable yields by changing the ratio of the substrates (entries 17 and 18).

Having the optimized reaction conditions in hand, we then proceeded to study the scope and limitations of the current iodocarboxylation reaction using various carboxylic acids as the substrates (Table 2). As shown in Table 2, substrates **2a−e**, having various substituents on the aromatic ring, were compatible with the current iodocarboxylation reaction to give desired products **3a−e** in 63−88% isolated yields. Unfortunately, the substrate with a strong electron-withdrawing substituent on the phenyl ring failed to afford any product, probably due to the strong electronic effect (**3f**). Moreover, to our delight, several different aliphatic carboxylic acids, such as phenylacetic acid, propionic acid, and *n*-octanoic acid, underwent the iodocarboxylation reaction to afford **3g−i** in good yields. Notably, high regio- and stereoselectivities were achieved in all cases, and only *Z* isomers were obtained. The configuration of the C=C bonds of products *Z*-**3** was further established by NOE study of **3g** (Figure 1).

Phenols, like carboxylic acids, are often used as oxygen nucleophiles in various electrophilic addition reactions of unsaturated bonds. Thus, to expand the scope of the iodofunctionalization reaction further, diverse phenols were employed as substrates under the optimized reaction conditions

Table 1. Optimization of Reaction Conditions.[a]

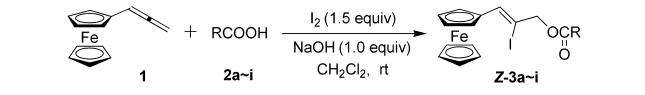


1 **2a** ***Z*-3a**

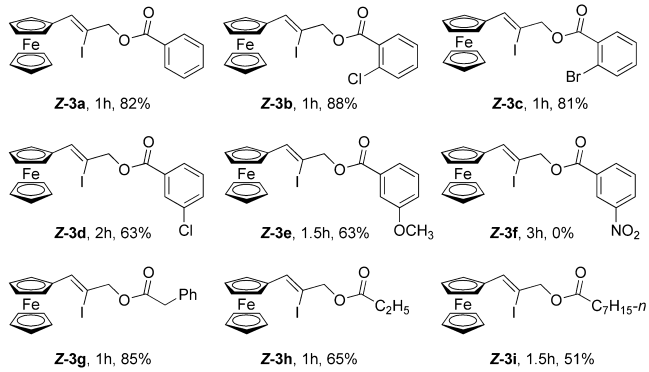
entry	solvent	base	additive (mol %)	time (h)	yield (%)[b]
1	THF	NaOH		2	18
2	CH_2Cl_2	NaOH		1	60
3	DMF	NaOH		1.5	17
4	CH_3CN	NaOH		2	43
5	toluene	NaOH		1	45
6	dioxane	NaOH		1.5	55
7	$ClCH_2CH_2Cl$	NaOH		1	56
8	CH_2Cl_2/DMF 10:1	NaOH		1.5	38
9	CH_2Cl_2/DMF 60:1	NaOH		1.5	47
10	CH_2Cl_2	*t*-BuOK		1	55
11	CH_2Cl_2	Cs_2CO_3		2	36
12	CH_2Cl_2	NaOAc		2	26
13	CH_2Cl_2	Et_3N		1.5	50
14	CH_2Cl_2			2	trace
15	CH_2Cl_2	NaOH	TBAI (20)	1	51
16	CH_2Cl_2	NaOH	TBAB (20)	1	56
17[c]	CH_2Cl_2	NaOH		1	74
18[d]	CH_2Cl_2	NaOH		1	82

[a]The reaction was carried out using 0.3 mmol of ferrocenylallene **1**, 0.3 mmol of benzoic acid **2a**, 0.3 mmol of iodine, and 0.3 mmol of base in 2.0 mL of solvent. [b]Yield of isolated product after chromatography. [c]**1**/**2a**/iodine =1.5:1.0:1.5; **2a** (0.3 mmol). [d]**1**/**2a**/iodine =2.0:1.0:1.5; **2a** (0.3 mmol).

Table 2. Synthesis of Ferrocene-Containing *β*-Iodoallylic Esters Using Ferrocenylallene and Various Carboxylic Acids[a]



1 **2a~i** ***Z*-3a~i**



***Z*-3a**, 1h, 82% ***Z*-3b**, 1h, 88% ***Z*-3c**, 1h, 81%

***Z*-3d**, 2h, 63% ***Z*-3e**, 1.5h, 63% ***Z*-3f**, 3h, 0%

***Z*-3g**, 1h, 85% ***Z*-3h**, 1h, 65% ***Z*-3i**, 1.5h, 51%

[a]Reactions were carried out with 0.60 mmol of **1**, 0.30 mmol of **2a−i**, 0.45 mmol of iodine, and 0.30 mmol of NaOH in 2.0 mL of CH_2Cl_2 at rt. Isolated yields are reported.

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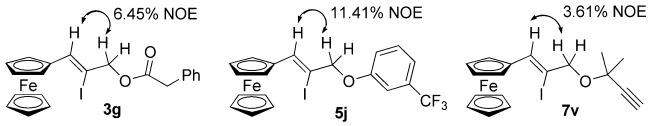
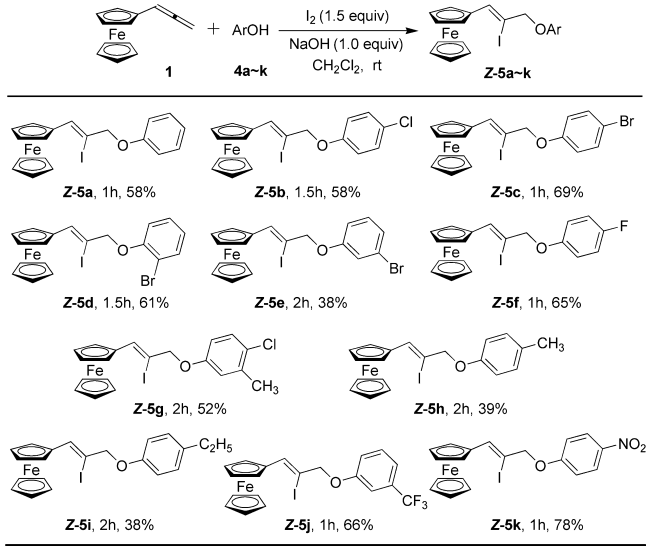


Figure 1. NOE study of **3g**, **5j**, and **7v**.

(Table 3). To our great delight, a range of substituted phenols was suitable for this iodoaryloxylation reaction and afforded *β*-

Table 3. Synthesis of Ferrocene-Containing *β*-Iodoallylic Ethers Using Ferrocenylallene and Various Phenols[a]

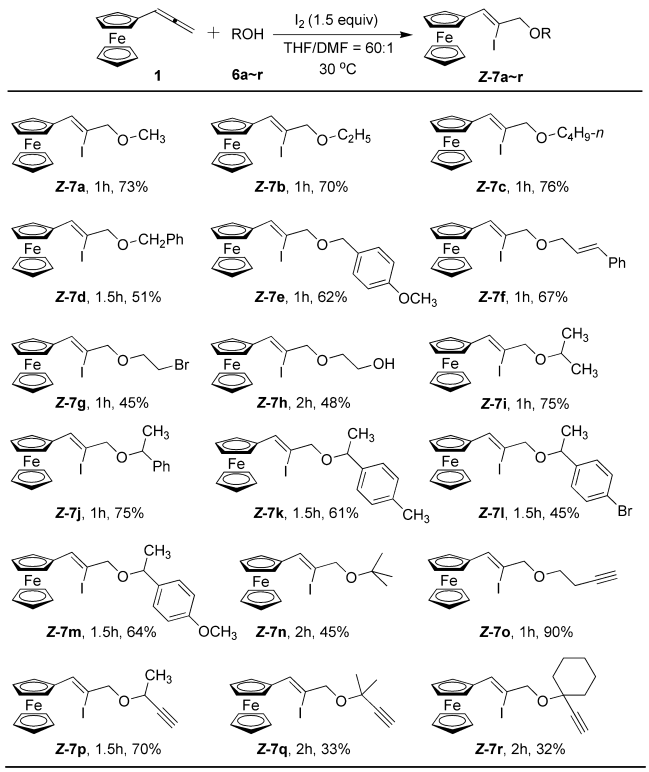


[a]Reactions were carried out with 0.60 mmol of **1**, 0.30 mmol of **4a**−**k**, 0.45 mmol of iodine, and 0.30 mmol of NaOH in 2.0 mL of CH_2Cl_2 at rt. Isolated yields are reported.

iodoallyl aryl ethers **5a**−**k** in moderate to good yields as well as high regio- and stereoselectivities. Similar to that for aromatic carboxylic acids, a series of functional groups, such as halogen, trifluoromethyl, and nitro, were tolerated under the reaction conditions. It should be noted that substrates with a phenyl ring bearing an electron-withdrawing group generally gave slightly higher yields (**5j** and **5k**), whereas substrates with an electron-donating substituent on the phenyl ring gave slightly lower yields of the corresponding products (**5h** and **5i**). This may be attributed to the stability of the oxygen anion, which was generated from phenol in the presence of NaOH. The structure of products *Z*-**5** was further established by NOE study of **5j** (Figure 1).

Inspired by the reaction of phenols, we turned our attention to expanding the substrate scope to alcohols. We found that under slightly modified reaction conditions, as shown in Table 4, the iodine-mediated iodoalkoxylation of ferrocenylallene with alcohols led to the formation of (*Z*)-*β*-iodoallyl alkyl ethers in moderate to good yields with complete stereoselectivity. It should be noted that THF/DMF (60:1) is the most effective solvent system for this iodoalkoxylation reaction, whereas CH_2Cl_2 gave the corresponding product only in moderate yield. Primary and secondary alcohols as well as methanol proved to be good substrates for the iodoalkoxylation (**7a**−**m**). Olefinic alcohol, such as chnnamyl alcohol, afforded corresponding product **7f** in good yield. In the cases of difunctional alcohols, such as 2-bromoethanol and ethane-1,2-diol, the reactions also proceeded well to give **7g** and **7h**, respectively, in 45−48%

Table 4. Highly Regio- and Stereoselective Iodoalkoxylation of Ferrocenylallene with Various Alcohols[a]



[a]Reactions were carried out with 0.30 mmol of **1**, 0.60 mmol of **6a**−**r**, and 0.45 mmol of iodine in 2.0 mL of solvent at 30 °C. Isolated yields are reported.

yields. Moreover, increasing the steric hindrance further by using a tertiary alcohol resulted in iodoalkoxylation product **7n** being isolated in a lower yield, probably due to the steric hindrance effect. Lastly, several alkynyl alcohols, **6o**−**r**, were subjected to this reaction, providing the corresponding products with satisfactory yields; significant steric effect was observed in these cases. Once again, the regiochemistry of this iodoalkoxylation reaction was established by NOE study of **7v** (Figure 1).

These ferrocene-containing *β*-iodoallyl derivatives have been demonstrated to be very attractive building blocks for further transformation in organic synthesis, as shown in Scheme 2. For example, Heck coupling of **5a**, **7a**, and **7k** with methyl acrylate successfully produced the ferrocene-containing conjugated molecules ferrocenyl butadiene **8**, **9**, and **10** in high yields. In addition, the phenyl and alkyne groups can be easily introduced into the *β*-position through the Suzuki and Sonogashira coupling protocols to afford (*Z*)-1-(1-ferrocenyl-3-methoxy-prop-1-en-2-yl)benzene **11** and (*Z*)-1-(4-ferrocenyl-3-(methoxymethyl)but-3-en-1-ynyl)benzene **12**, respectively. Moreover, **7r** could undergo the click reaction with 1-(azidomethyl)benzene by employing $CuSO_4$ as a catalyst to give ferrocene-containing triazole **13** in 63% yield without destroying the C−I bond.

The high stereoselectivity for ferrocene-containing (*Z*)-*β*-iodoallylic esters and ethers formation may be explained via the protocol shown in Scheme 3: the steric hindrance effect of the ferrocene may lead to the regioselective interaction of I_2 with the C═C bond remote from the ferrocenyl group, forming three-membered iodonium intermediate **A** or **B**. Intermediate **A**

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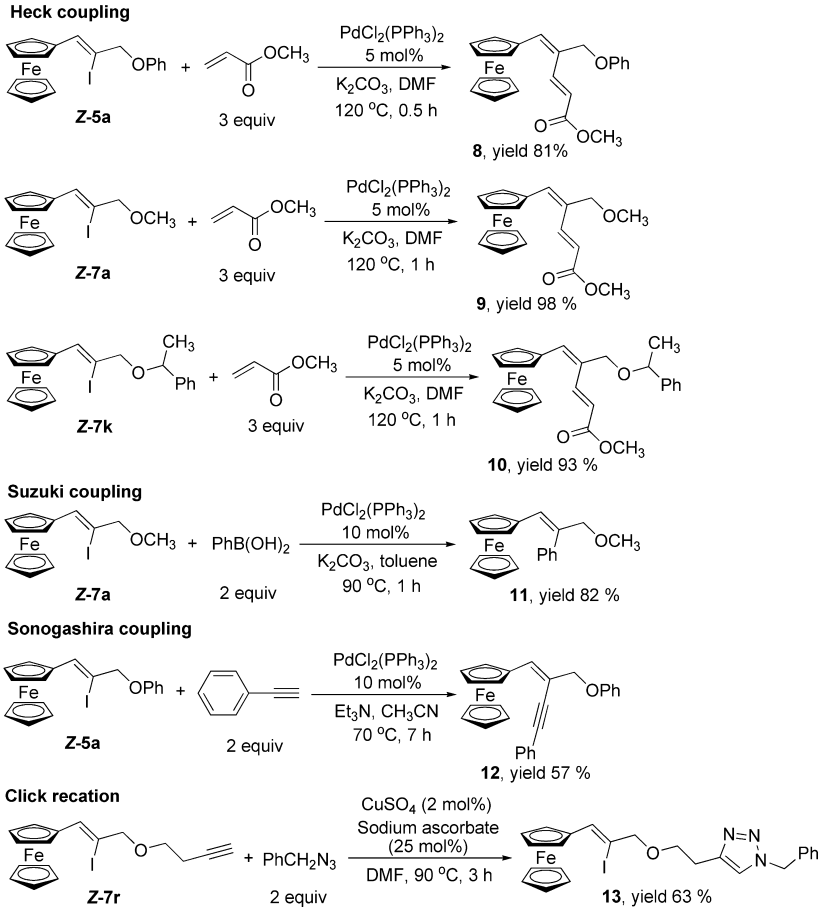
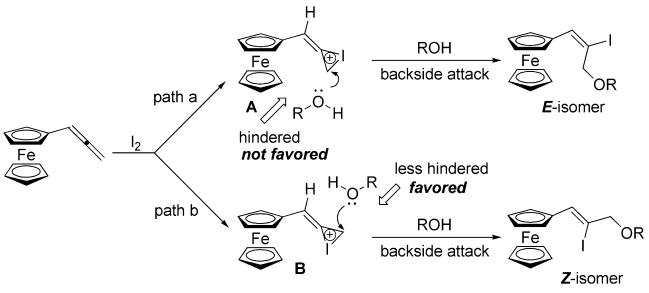
Scheme 2. Synthetic Application of Ferrocene-Containing β-Iodoallyl Derivatives



Scheme 3. Rationalization of Stereoselectivity



was attacked by the oxygen nucleophiles through path a to form *E* isomers, which may be highly unfavorable because of the steric effect. Thus, the stereoselectivity may be determined by the steric bulkiness of the ferrocenyl group, which resulted in *trans* attack by the oxygen nucleophiles at the three-membered ring in iodonium intermediate **B** through path b, affording *Z* isomers highly stereoselectively.

CONCLUSIONS

An iodine-mediated iodofunctionalization of ferrocenylallene with carboxylic acids, phenols, and alcohols has been developed, providing a series of ferrocene-containing allylic ester and ether derivatives with high regio- and stereoselectivities in moderate to excellent yields. The regio- and stereoselectivities of this reaction may be controlled by the steric effect of the bulky ferrocene group. The presence of the C−I bond in the corresponding products provides an opportunity for further transformations. Because of the increasing importance of allylic compounds and ferrocenes in the bioorganic and pharmaceutical fields, this method will be a valuable choice for organic synthesis, and it may open up new possibilities to incorporate allylic esters or ethers with ferrocene chemistry. Further studies in this area are being actively pursued in our laboratory.

EXPERIMENTAL SECTION

General Information. All reagents were used as received from commercial sources or were prepared as described in the literature. Ferrocenylallene was prepared according to our previously reported procedure.[10b] All solvents were purified following standard literature procedures. For chromatography, 200−300 mesh silica gel (Qingdao, China) was employed. ^{1}H and ^{13}C NMR spectra were recorded with 500 and 125 MHz FT-NMR spectrometers. Chemical shifts are reported in ppm using tetramethylsilane as the internal standard when $CDCl_3$ was used as solvent. IR spectra were recorded on an FT-IR instrument. The HRMS analysis was obtained on a GCTOF mass spectrometer. Melting points were determined with a melting point apparatus and are uncorrected.

General Procedure for the Iodocarboxylation of Ferrocenylallene and Carboxylic Acids. To a solution of carboxylic acid (0.3 mmol), I_2 (0.45 mmol), and NaOH (0.3 mmol) in CH_2Cl_2 (2.0 mL) was added ferrocenylallene (0.6 mmol) under an air atmosphere. The resulting mixture was heated at rt for the indicated time. After completion of the reaction, the solvent was removed in a vacuum. The resulting residue was purified on a silica gel column (EtOAc/petroleum ether) to provide the desired ferrocene-containing allylic ester products, *Z*-**3**.

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*(Z)-3-Ferrocenyl-2-iodoallyl benzoate (Z-**3a**).* Yellow solid; 116 mg, 82% yield. mp 85−86 °C (recrystallized from petroleum ether and dichloromethane at room temperature). IR (KBr) 3091, 2928, 2853, 1721, 1633, 1450, 1371, 1265, 1176, 1106, 1002, 818, 711, 684 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 4.15 (s, 5H), 4.31 (t, J = 1.5 Hz, 2H), 4.83 (t, J = 1.5 Hz, 2H), 5.08 (s, 2H), 7.00 (s, 1H), 7.45 (t, J = 8.0 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 8.11 (d, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.3, 69.5, 69.6, 74.4, 79.7, 90.8, 128.6, 129.9, 130.1, 133.3, 137.7, 165.9. HRMS (ESI) calcd for $C_{20}H_{17}FeIO_2$, 471.9623; found, 471.9624.

*(Z)-3-Ferrocenyl-2-iodoallyl 2-chlorobenzoate (Z-**3b**).* Yellow solid; 134 mg, 88% yield. mp 60−62 °C (recrystallized from petroleum ether and dichloromethane at room temperature). IR (KBr) 3017, 2934, 1729, 1637, 1400, 1244, 1106, 1039, 948, 812, 746, 608 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 4.17 (s, 5H), 4.33 (t, J = 2.0 Hz, 2H), 4.85 (t, J = 2.0 Hz, 2H), 5.11 (s, 2H), 7.05 (s, 1H), 7.35 (t, J = 6.5 Hz, 1H), 7.48 (m, 2H), 7.95 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.3, 69.5, 69.6, 75.0, 79.6, 89.8, 126.7, 129.7, 131.2, 132.8, 134.0, 138.3, 164.9. HRMS (ESI) calcd for $C_{20}H_{16}ClFeIO_2$, 505.9233; found, 505.9244.

*(Z)-3-Ferrocenyl-2-iodoallyl 2-bromobenzoate (Z-**3c**).* Yellow solid; 135 mg, 81% yield. mp 69−70 °C (recrystallized from petroleum ether and dichloromethane at room temperature). IR (KBr) 3234, 2928, 1734, 1635, 1401, 1251, 1297, 1251, 1105, 1030, 1001, 950, 867, 813, 740 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 4.17 (s, 5H), 4.33 (s, 2H), 4.85 (s, 2H), 5.12 (s, 2H), 7.06 (s, 1H), 7.34−7.42 (m, 2H), 7.68 (d, J = 7.5 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.3, 69.5, 69.6, 75.1, 79.6, 89.8, 122.0, 127.3, 131.7, 131.8, 132.9, 134.5, 138.4, 165.3. HRMS (ESI) calcd for $C_{20}H_{16}BrFeIO_2$, 549.8728; found, 549.8709.

*(Z)-3-Ferrocenyl-2-iodoallyl 2-chlorobenzoate (Z-**3d**).* Yellow solid; 96 mg, 63% yield. mp 70−71 °C (recrystallized from petroleum ether and dichloromethane at room temperature). IR (KBr) 3233, 1721, 1622, 1401, 1255, 1119, 1083, 1001, 938, 867, 819, 748 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 4.17 (s, 5H), 4.34 (s, 2H), 4.85 (s, 2H), 5.10 (s, 2H), 7.02 (s, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.0 Hz, 1H), 8.09 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.3, 69.5, 69.6, 75.0, 79.6, 89.8, 126.7, 129.7, 131.2, 132.8, 134.0, 138.3, 164.9. HRMS (ESI) calcd for $C_{20}H_{16}ClFeIO_2$, 505.9233; found, 505.9246.

*(Z)-3-Ferrocenyl-2-iodoallyl 3-methoxybenzoate (Z-**3e**).* Yellow solid; 95 mg, 63% yield. mp 114−116 °C (recrystallized from petroleum ether and dichloromethane at room temperature). IR (KBr) 2959, 2935, 2834, 1712, 1629, 1580, 1452, 1401, 1270, 1098, 1041, 1002, 951, 865, 824, 754 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 3.84 (s, 3H), 4.16 (s, 5H), 4.32 (s, 2H), 4.84 (s, 2H), 5.08 (s, 2H), 7.00 (s, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.63 (s, 1H), 7.71 (d, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4, 69.2, 69.4, 69.5, 74.3, 79.6, 90.6, 114.2, 119.6, 122.1, 129.5, 131.2, 137.6, 159.5, 165.7. HRMS (ESI) calcd for $C_{21}H_{19}FeIO_3$, 501.9728; found, 501.9733.

*(Z)-3-Ferrocenyl-2-iodoallyl 2-phenylacetate (Z-**3g**).* Yellow solid; 124 mg, 85% yield. mp 72−74 °C (recrystallized from petroleum ether and dichloromethane at room temperature). IR (KBr) 3233, 1721, 1622, 1401, 1255, 1119, 1083, 1001, 938, 867, 819, 748 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 3.70 (s, 2H), 4.10 (s, 5H), 4.29 (s, 2H), 4.76 (s, 2H), 4.85 (s, 2H), 6.78 (s, 1H), 7.26−7.30 (m, 1H), 7.34−7.35 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.5, 69.1, 69.3, 69.4, 74.0, 79.6, 90.2, 127.2, 128.6, 129.4, 133.7, 136.9, 170.7. HRMS (ESI) calcd for $C_{21}H_{19}FeIO_2$, 485.9779; found, 485.9792.

*(Z)-3-Ferrocenyl-2-iodoallyl propionate (Z-**3h**).* Yellow solid; 83 mg, 65% yield. mp 58−60 °C (recrystallized from petroleum ether and dichloromethane at room temperature). IR (KBr) 3234, 2974, 2931, 1737, 1636, 1400, 1174, 1082, 872, 817 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 1.20 (t, J = 7.5 Hz, 3H), 2.43 (q, J = 7.5 Hz, 2H), 4.16 (s, 5H), 4.32 (t, J = 2.0 Hz, 2H), 4.82 (t, J = 2.0 Hz, 2H), 4.85 (s, 2H), 6.92 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.2, 27.7, 69.2, 69.4, 69.5, 73.8, 79.7, 91.1, 137.3, 173.8. HRMS (ESI) calcd for $C_{16}H_{17}FeIO_2$, 423.9623; found, 423.9629.

*(Z)-3-Ferrocenyl-2-iodoallyl octanoate (Z-**3i**).* Yellow oil; 76 mg, 51% yield. IR (KBr) 2926, 2854, 1739, 1637, 1401, 1156, 1105, 817 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, J = 6.5 Hz, 3H), 1.25−1.35 (m, 8H), 1.65−1.71 (m, 2H), 2.39 (t, J = 7.5 Hz, 2H), 4.16 (s, 5H), 4.31 (s, 2H), 4.82 (s, 2H), 4.84 (s, 2H), 6.91 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 25.0, 29.0, 29.1, 31.7, 34.4, 69.2, 69.4, 69.5, 73.7, 79.8, 91.1, 137.3, 173.2. HRMS (ESI) calcd for $C_{21}H_{27}FeIO_2$, 494.0405; found, 494.0404.

General Procedure for the Iodoaryloxylation of Ferrocenylallene and Phenols. To a solution of phenol (0.3 mmol), I_2 (0.45 mmol), and NaOH (0.3 mmol) in CH_2Cl_2 (2.0 mL) was added ferrocenylallene (0.6 mmol) under an air atmosphere. The resulting mixture was heated at rt for the indicated time. After completion of the reaction, the solvent was removed in a vacuum. The resulting residue was purified on a silica gel column (EtOAc/petroleum ether) to provide the desired ferrocene-containing allylic ether products, *Z*-**5**.

*(Z)-1-(3-Ferrocenyl-2-iodoallyloxy)benzene (Z-**5a**).* Yellow oil; 77 mg, 58% yield. IR (KBr) 2927, 2870, 1712, 1630, 1400, 1266, 1104, 939, 865, 820, 714 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 4.07 (s, 5H), 4.28 (s, 2H), 4.74 (s, 2H), 4.78 (s, 2H), 6.93 (s, 1H), 6.98 (t, J = 4.5 Hz, 3H), 7.31 (t, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.0, 69.3, 69.5, 77.5, 80.2, 93.3, 115.6, 121.6, 129.6, 134.5, 157.9. HRMS (ESI) calcd for $C_{19}H_{17}FeIO$, 443.9674; found, 443.9660.

*(Z)-1-Chloro-4-(3-ferrocenyl-2-iodoallyloxy)benzene (Z-**5b**).* Yellow solid; 83 mg, 58% yield. mp 110−112 °C (recrystallized from petroleum ether and dichloromethane at room temperature). IR (KBr) 2918, 2851, 1636, 1592, 1501, 1401, 1255, 1107, 995, 854, 820, 750 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 4.11 (s, 5H), 4.31 (s, 2H), 4.71 (s, 2H), 4.81 (s, 2H), 6.90 (d, J = 8.5 Hz, 3H), 7.26 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.2, 69.4, 69.5, 77.9, 80.0, 92.5, 116.9, 126.9, 129.4, 135.0, 156.5. HRMS (ESI) calcd for $C_{19}H_{16}ClFeIO$, 477.9284; found, 477.9253.

*(Z)-1-Bromo-4-(3-ferrocenyl-2-iodoallyloxy)benzene (Z-**5c**).* Yellow solid; 108 mg, 69% yield. mp 70−72 °C (recrystallized from petroleum ether and dichloromethane at room temperature). IR (KBr) 2918, 2851, 1636, 1592, 1501, 1401, 1255, 1107, 995, 854, 820, 750 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 4.11 (s, 5H), 4.31 (s, 2H), 4.71 (s, 2H), 4.81 (s, 2H), 6.90 (d, J = 8.5 Hz, 3H), 7.26 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.2, 69.4, 69.5, 77.9, 80.0, 92.5, 116.9, 126.9, 129.4, 135.0, 156.5. HRMS (ESI) calcd for $C_{19}H_{16}ClFeIO$, 477.9284; found, 477.9253.

*(Z)-1-Bromo-2-(3-ferrocenyl-2-iodoallyloxy)benzene (Z-**5d**).* Yellow oil; 96 mg, 61% yield. IR (KBr) 2921, 2853, 1634, 1476, 1401, 1243, 1106, 1030, 1003, 820, 748 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 4.10 (s,5H), 4.19 (s, 2H), 4.30 (s,2H), 4.81 (s, 2H), 6.88 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 8.5 Hz, 1H), 7.02 (s, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.1, 69.4, 69.5, 69.5, 78.2, 91.6, 112.7, 114.8, 122.8, 128.5, 133.6, 134.7, 154.3. HRMS (ESI) calcd for $C_{19}H_{16}BrFeIO$, 521.8779; found, 521.8767.

*(Z)-1-Bromo-3-(3-ferrocenyl-2-iodoallyloxy)benzene (Z-**5e**).* Yellow oil; 60 mg, 38% yield. IR (KBr) 2922, 2851, 1635, 1474, 1401, 1217, 1001, 822, 771 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 4.09 (s, 5H), 4.30 (s, 2H), 4.73 (s, 2H), 4.80 (s, 2H), 6.91 (s, 2H), 6.93 (s, 1H), 7.11−7.19 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.1, 0.69.3, 69.5, 77.7, 79.9, 92.1, 114.5, 118.9, 122.8, 124.7, 130.7, 135.2, 158.7. HRMS (ESI) calcd for $C_{19}H_{16}BrFeIO$, 521.8779; found, 521.8772.

*(Z)-1-(3-Ferrocenyl-2-iodoallyloxy)-4-fluorobenzene (Z-**5f**).* Yellow solid; 90 mg, 65% yield. mp 57−58 °C (recrystallized from petroleum ether and dichloromethane at room temperature). IR (KBr) 2922, 2847, 1632, 1504, 1400, 1220, 1098, 1024, 880, 818, 770 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 4.09 (s, 5H), 4.29 (s, 2H), 4.70 (s, 2H), 4.79 (s, 2H), 6.93 (t, J = 5.0 Hz, 3H), 6.98 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.1, 69.3, 69.4, 69.5, 76.8, 80.0, 93.0, 115.8, 116.8, 134.9, 154.0. HRMS (ESI) calcd for $C_{19}H_{16}FFeIO$, 461.9579; found, 461.9582.

*(Z)-1-Chloro-4-(3-ferrocenyl-2-iodoallyloxy)-2-methylbenzene (Z-**5g**).* Yellow solid; 77 mg, 52% yield. mp 72−73 °C (recrystallized from petroleum ether and dichloromethane at room temperature). IR (KBr) 2924, 2849, 1632, 1571, 1478, 1400, 1282, 1242, 1166, 1032, 995, 869,

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807, 737 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 2.35 (s, 3H), 4.10 (s, 5H), 4.30 (s, 2H), 4.70 (s, 2H), 4.80 (s, 2H), 6.74 (d, J = 8.0 Hz, 1H), 6.85 (s, 1H), 6.91 (s, 1H), 7.24 (d, J = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.4, 69.1, 69.3, 69.5, 77.9, 80.1, 92.7, 114.1, 118.1, 126.7, 129.7, 134.8, 137.2, 156.5. HRMS (ESI) calcd for $C_{20}H_{18}ClFeIO$, 491.9440; found, 491.9438.

*(Z)-1-(3-Ferrocenyl-2-iodoallyloxy)-4-methylbenzene (Z-**5h**).* Yellow oil; 54 mg, 39% yield. IR (KBr) 2926, 2843, 1637, 1504, 1401, 1227, 1108, 989, 807 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 2.28 (s, 3H), 4.08 (s, 5H), 4.28 (s, 2H), 4.72 (s, 2H), 4.79 (s, 2H), 6.90−6.92 (m, 3H), 7.10−7.12 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.6, 69.0, 69.3, 69.4, 77.8, 80.2, 93.7, 115.5, 129.9, 130.9, 134.3, 155.8. HRMS (ESI) calcd for $C_{20}H_{19}FeIO$, 457.9830; found, 457.9847.

*(Z)-1-Ethyl-4-(3-ferrocenyl-2-iodoallyloxy)benzene (Z-**5i**).* Yellow oil; 54 mg, 38% yield. IR (KBr) 2962, 2925, 2854, 1620, 1509, 1401, 1234, 1108, 1002, 826 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 1.90 (t, J = 7.5 Hz, 3H), 2.58 (q, J = 7.5 Hz, 2H), 4.07 (s, 5H), 4.28 (s, 2H), 4.72 (s, 2H), 4.79 (s, 2H), 6.91 (d, J = 8.5 Hz, 3H), 7.13 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.9, 28.0, 69.0, 69.3, 69.4, 77.8, 80.2, 93.6, 115.5, 128.8, 134.3, 137.4, 156.0. HRMS (ESI) calcd for $C_{21}H_{21}FeIO$, 471.9987; found, 471.9986.

*(Z)-1-(3-Ferrocenyl-2-iodoallyloxy)-3-(trifluoromethyl)benzene (Z-**5j**).* Yellow oil; 100 mg, 66% yield. IR (KBr) 2919, 2854, 1635, 1452, 1401, 1327, 1218, 1169, 1127, 1011, 822, 787 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 4.08 (s, 5H), 4.31 (s, 2H), 4.78 (s, 2H), 4.80 (s, 2H), 6.96 (s, 1H), 7.15 (d, J = 7.5 Hz, 1H), 7.23 (d, J = 2.0 Hz, 2H), 7.42 (t, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.2, 69.3, 69.4, 69.5, 77.8, 79.9, 91.8, 112.4, 118.2, 118.9, 130.1, 135.5, 143.5, 158.0. HRMS (ESI) calcd for $C_{20}H_{16}F_3FeIO$, 511.9547; found, 511.9546.

*(Z)-1-(3-Ferrocenyl-2-iodoallyloxy)-4-nitrobenzene (Z-**5k**).* Yellow oil; 114 mg, 78% yield. IR (KBr) 2924, 2854, 1639, 1591, 1490, 1401, 1238, 1098, 1002, 869, 824,751 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 4.12 (s, 5H), 4.33 (s, 2H), 4.82 (s, 2H), 4.84 (s, 2H), 6.98 (s, 1H), 7.04 (d, J = 9.5 Hz, 2H), 8.23 (d, J = 9.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.4, 69.5, 78.0, 79.6, 90.4, 115.3, 125.9, 136.2, 142.0, 162.9. HRMS (ESI) calcd for $C_{20}H_{16}F_3FeIO$, 511.9547; found, 511.9546.

General Procedure for the Iodoalkoxylation of Ferrocenylallene and Alcohols. The alcohol (0.6 mmol), ferrocenylallene (0.3 mmol), I_2 (0.45 mmol), and 60:1 THF/DMF (2.0 mL) were added sequentially into a dried reaction tube in an air atmosphere. The resulting mixture was heated at 30 °C for the indicated time. The mixture was cooled to room temperature. The solvent was removed under vacuum, and the resulting residue was purified on a silica gel column (EtOAc/petroleum ether) to provide the desired ferrocene-containing allylic ether products, *Z*-7.

*(Z)-1-Ferrocenyl-2-iodo-3-methoxyprop-1-ene (Z-**7a**).* Yellow solid; 82 mg, 73% yield. mp 42−43 °C (recrystallized from petroleum ether at room temperature). IR (KBr) 3102, 1639, 1267, 1111, 1050, 818, 777 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 3.37 (s, 3H), 4.15 (s, 5H), 4.16 (s, 2H), 4.30 (s, 2H), 4.82 (s, 2H), 6.87 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 57.3, 69.0, 69.3, 69.5, 80.4, 82.2, 96.3, 134.7. HRMS (ESI) calcd for $C_{14}H_{15}FeIO$, 381.9517; found, 381.9518.

*(Z)-3-Ethoxy-1-ferrocenyl-2-iodoprop-1-ene (Z-**7b**).* Yellow oil; 83 mg, 70% yield. IR (KBr) 3088, 1634, 1267, 1109, 1002, 817 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 1.27 (t, J = 7.0 Hz, 3H), 3.52 (q, J = 7.0 Hz, 2H), 4.15 (s, 5H), 4.18 (s, 2H), 4.29 (s, 2H), 4.81 (s, 2H), 6.86 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.3, 65.1, 68.9, 69.3, 69.5, 80.3, 80.5, 97.3, 134.0. HRMS (ESI) calcd for $C_{15}H_{17}FeIO$, 395.9674; found, 395.9672.

*(Z)-1-(3-Ferrocenyl-2-iodoallyloxy)butane (Z-**7c**).* Yellow oil; 95 mg, 76% yield. IR (KBr) 2957, 1633, 1244, 1105, 1002, 819 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 0.95 (t, J = 7.5 Hz, 3H), 1.40−1.46 (m, 2H), 1.58−1.65 (m, 2H), 3.46 (t, J = 6.5 Hz, 2H), 4.15(s, 5H), 4.18 (s, 2H), 4.29 (s, 2H), 4.82 (s, 2H), 6.87 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 19.5, 29.7, 31.8, 68.9, 69.3, 69.4, 69.5, 80.5, 97.4, 133.9. HRMS (ESI) calcd for $C_{17}H_{21}FeIO$, 423.9987; found, 423.9986.

*(Z)-1-((3-Ferrocenyl-2-iodoallyloxy)methyl)benzene (Z-**7d**).* Yellow solid; 70 mg, 51% yield. mp 128−130 °C (recrystallized from petroleum ether at room temperature). IR (KBr) 3104, 1450, 1237, 1103, 1088, 822, 740 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 4.16 (s, 5H), 4.22 (s, 2H), 4.25 (s, 2H), 4.55 (s, 2H), 4.83 (s, 2H), 6.90 (s, 4H), 7.30−7.40 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.0, 69.3, 69.5, 71.3, 79.6, 80.4, 96.5, 127.8, 128.0 128.5, 134.8, 137.9. HRMS (ESI) calcd for $C_{20}H_{19}FeIO$, 457.9830; found, 457.9824.

*(Z)-1-((3-Ferrocenyl-2-iodoallyloxy)methyl)-4-methoxybenzene (Z-**7e**).* Yellow solid; 90 mg, 62% yield. mp 32−34 °C (recrystallized from petroleum ether at room temperature). IR (KBr) 3093, 2927, 1611, 1248, 1177, 1035, 820 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 3.80 (s, 3H), 4.15 (s, 5H), 4.21 (s, 2H), 4.30 (s, 2H), 4.47 (s, 2H), 4.82 (s, 2H), 6.88−6.91 (m, 3H), 7.31−7.33 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4, 69.0, 69.4, 69.5, 70.9, 79.3, 80.4, 96.8, 113.9, 129.7, 129.9, 134.7, 159.4. HRMS (ESI) calcd for $C_{21}H_{21}FeIO_2$, 487.9936; found, 487.9927.

*1-((E)-3-((Z)-3-Ferrocenyl-2-iodoallyloxy)prop-1-enyl)benzene (Z-**7f**).* Yellow oil; 96 mg, 67% yield; ^1H NMR (500 MHz, $CDCl_3$) δ 4.14−4.21 (m, 7H), 4.25 (s, 2H), 4.30 (s, 2H), 4.82 (s, 2H), 6.30−6.36 (m, 1H), 6.64 (d, J = 16.0 Hz, 1H), 6.89 (s, 1H), 7.22 (d, J = 7.0 Hz, 1H), 7.25 (d, J = 7.5 Hz, 2H), 7.39−7.30 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.0, 69.5, 69.6, 70.0, 79.6, 80.5, 96.6, 125.8, 126.6, 127.9, 128.7, 132.9, 134.6, 136.7. HRMS (ESI) calcd for $C_{22}H_{21}FeIO$, 483.9987; found, 483.9983.

*(Z)-3-(2-Bromoethoxy)-1-ferrocenyl-2-iodoprop-1-ene (Z-**7g**).* Yellow solid; 64 mg, 45% yield. mp 40−42 °C (recrystallized from petroleum ether at room temperature). IR (KBr) 3092, 2926, 1631, 1239, 1107, 1035, 817, 747 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 3.52 (t, J = 6.0 Hz, 2H), 3.78 (t, J = 6.0 Hz, 2H), 4.16 (s, 5H), 4.26 (s, 2H), 4.31 (s, 2H), 4.82 (s, 2H), 6.91 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.7, 30.4, 69.1, 69.4, 69.5, 80.2, 80.7, 95.6, 135.1. HRMS (ESI) calcd for $C_{15}H_{16}BrFeIO$, 473.8779; found, 473.8776.

*(Z)-2-(3-Ferrocenyl-2-iodoallyloxy)ethanol (Z-**7h**).* Yellow solid; 60 mg, 48% yield. mp 38−40 °C (recrystallized from petroleum ether at room temperature). IR (KBr) 3080, 1629, 1409, 1242, 1038, 819 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 2.26 (s, 1H), 3.58 (t, J = 5.0 Hz, 2H), 3.79 (s, 2H), 4.16 (s, 5H), 4.25 (s, 2H), 4.31 (s, 2H), 4.82 (s, 2H), 6.88 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 61.9, 69.1, 69.4, 69.5, 70.5, 80.1, 80.7, 96.5, 135.2. HRMS (ESI) calcd for $C_{15}H_{17}FeIO_2$, 411.9623; found, 411.9621.

*(Z)-1-Ferrocenyl-2-iodo-3-isopropoxyprop-1-ene (Z-**7i**).* Yellow oil; 91 mg, 75% yield. IR (KBr) 3092, 2967, 1633, 1492, 1295, 1084, 818 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 1.22 (d, J = 6.5 Hz, 6H), 3.67−3.72 (m, 1H), 4.14 (s, 5H), 4.18 (s, 2H), 4.28 (s, 2H), 4.80 (s, 2H), 6.87 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.3, 68.9, 69.3, 69.4, 70.6, 77.9, 80.7, 98.1, 133.4. HRMS (ESI) calcd for $C_{16}H_{19}FeIO$, 409.9830; found, 409.9824.

*(Z)-1-(1-(3-Ferrocenyl-2-iodoallyloxy)ethyl)benzene (Z-**7j**).* Yellow solid; 105 mg, 75% yield. mp 50−52 °C (recrystallized from petroleum ether at room temperature). IR (KBr) 3097, 1640, 1450, 1273, 1098, 999, 812, 766 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 1.52 (d, J = 6.5 Hz, 3H), 3.98 (d, J = 13.0 Hz, 1H), 4.09−4.15 (m, 6H), 4.29 (s, 2H), 4.52−4.55 (m, 1H), 4.80 (d, J = 7.5 Hz, 2H), 6.78 (s, 1H), 7.26−7.40 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.1, 68.8, 69.2, 69.3, 76.2, 77.7, 80.4, 97.1, 126.3, 127.6, 128.5, 134.2, 143.1. HRMS (ESI) calcd for $C_{21}H_{21}FeIO$, 471.9987; found, 471.9985.

*(Z)-1-(1-(3-Ferrocenyl-2-iodoallyloxy)ethyl)-4-methylbenzene (Z-**7k**).* Yellow solid; 90 mg, 61% yield. mp 110−112 °C (recrystallized from petroleum ether at room temperature). IR (KBr) 3089, 1654, 1480, 1245, 1098, 845 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 1.50 (d, J = 6.5 Hz, 3H), 2.37 (s, 3H), 3.97 (d, J = 13.5 Hz, 1H), 4.13 (d, J = 13.5 Hz, 1H), 4.16 (s, 5H), 4.30 (s, 2H), 4.50 (q, J = 6.5 Hz, 1H), 4.80 (s, 2H), 6.77 (s, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 24.2, 68.9, 69.4, 69.5, 76.1, 77.7, 80.7, 97.4, 126.4, 129.2 134.2, 137.3, 140.1. HRMS (ESI) calcd for $C_{22}H_{23}FeIO$, 486.0143; found, 486.0136.

*(Z)-1-Bromo-4-(1-(3-ferrocenyl-2-iodoallyloxy)ethyl)benzene (Z-**7l**).* Yellow solid; 73 mg, 45% yield. mp 106−108 °C (recrystallized from petroleum ether at room temperature). IR (KBr) 3089, 2968, 1642, 1482, 1272, 1101, 1010, 832, 775 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 1.48 (d, J = 6.5 Hz, 3H), 3.96 (d, J = 13.0 Hz, 1H), 4.12 (s,

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1H), 4.14 (s, 5H), 4.30 (s, 2H), 4.50 (q, J = 6.5 Hz, 1H), 4.79 (dd, J = 1.0, 24.0 Hz 2H), 6.76 (s, 1H), 7.24 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.1, 69.0, 69.3, 69.4, 69.5, 75.6, 78.0, 80.4, 96.7, 121.4, 128.2, 131.7, 134.7, 142.3. HRMS (ESI) calcd for $C_{21}H_{20}BrFeIO$, 549.9092; found, 549.9094.

*(Z)-1-(1-(3-Ferrocenyl-2-iodoallyloxy)ethyl)-4-methoxybenzene (Z-**7m**)*. Yellow solid; 96 mg, 64% yield. mp 89−91 °C (recrystallized from petroleum ether at room temperature). IR (KBr) 3089, 2965, 1609, 1511, 1244, 1176, 1096, 836 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.50 (d, J = 6.5 Hz, 3H), 3.82 (s, 3H), 3.93 (d, J = 13.0 Hz, 1H), 4.14 (d, J = 13.0 Hz, 1H), 4.15 (s, 5H), 4.29 (s, 2H), 4.49 (q, J = 6.5 Hz, 1H), 4.80 (d, J = 9.0 Hz, 2H), 6.77 (s, 1H), 6.91 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.1, 55.3, 68.9, 69.3, 69.4, 69.5, 75.8, 77.6, 80.6, 97.5, 113.9, 127.7, 134.2, 135.2, 159.1. HRMS (ESI) calcd for $C_{22}H_{23}FeIO_2$, 502.0092; found, 502.0094.

*(Z)-3-tert-Butoxy-1-ferrocenyl-2-iodoprop-1-ene (Z-**7n**)*. Yellow oil; 57 mg, 45% yield. IR (KBr) 2962, 1638, 1493, 1247, 1188, 967, 820 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 (s, 9H), 4.10 (d, J = 1.5 Hz, 2H), 4.16 (s, 5H), 4.27 (t, J = 1.5 Hz, 2H), 4.77 (d, J = 1.5 Hz, 2H), 6.91 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.8, 68.6, 69.2, 69.3, 72.5, 74.2, 81.2, 99.0, 132.2. HRMS (ESI) calcd for $C_{17}H_{21}FeIO$, 423.9987; found, 423.9983.

*(Z)-4-(3-Ferrocenyl-2-iodoallyloxy)but-1-yne (Z-**7o**)*. Yellow oil; 113 mg, 90% yield. IR (KBr) 3251, 3092, 2925, 1634, 1247, 1100, 820 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.02 (t, J = 2.5 Hz, 1H), 2.51−2.55 (m, 2H), 3.59 (t, J = 7.0 Hz, 2H), 4.15 (s, 5H), 4.23 (s, 2H), 4.29 (t, J = 2.0 Hz, 2H), 4.81 (t, J = 2.0 Hz, 2H), 6.90 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.0, 67.5, 69.0, 69.4, 69.5, 69.7, 80.3, 80.6, 81.2, 96.2, 134.6. HRMS (ESI) calcd for $C_{17}H_{17}FeIO$, 419.9674; found, 419.9670.

*(Z)-3-(3-Ferrocenyl-2-iodoallyloxy)but-1-yne (Z-**7p**)*. Yellow oil; 88 mg, 70% yield. IR (KBr) 3250, 3091, 2924, 1632, 1246, 1100, 817 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.51 (d, J = 7.0 Hz, 3H), 2.47 (d, J = 2.0 Hz, 2H), 4.17 (s, 5H), 4.22−4.26 (m, 1H), 4.31 (d, J = 5.5 Hz, 2H), 4.35 (d, J = 14.0 Hz, 2H), 4.82 (d, J = 13.5 Hz, 2H), 6.91 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.1, 63.2, 69.1, 69.4, 69.6, 73.5, 78.1, 80.3, 83.3, 95.7, 135.6. HRMS (ESI) calcd for $C_{17}H_{17}FeIO$, 419.9674; found, 419.9666.

*(Z)-3-(3-Ferrocenyl-2-iodoallyloxy)-3-methylbut-1-yne (Z-**7q**)*. Yellow solid; 43 mg, 33% yield. mp 56−58 °C (recrystallized from petroleum ether at room temperature). IR (KBr) 3247, 3090, 1636, 1464, 1243, 1156, 1043, 8247 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55 (s, 6H), 2.49 (s, 1H), 4.16 (s, 5H), 4.27 (t, J = 1.5 Hz, 2H), 4.32 (s, 2H), 4.78 (t, J = 2.0 Hz, 2H), 6.91 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.1, 68.8, 69.4, 69.5, 70.8, 72.8, 74.7, 81.0, 85.9, 97.1, 133.5. HRMS (ESI) calcd for $C_{18}H_{19}FeIO$, 433.9830; found, 433.9822.

*(Z)-1-Ethynyl-1-(3-ferrocenyl-2-iodoallyloxy)cyclohexane (Z-**7r**)*. Yellow solid; 40 mg, 32% yield. mp 44−46 °C (recrystallized from petroleum ether at room temperature). IR (KBr) 3265, 2931, 1634, 1454, 1250, 1145, 1045, 816 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32−1.37 (m, 1H), 1.51−1.59 (m, 3H), 1.71−1.74 (m, 4H), 1.93−1.96 (m, 2H), 2.53 (s, 1H), 4.15 (s, 5H), 4.27 (s, 2H), 4.34 (s, 2H), 4.78 (s, 2H), 6.92 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.7, 25.4, 37.4, 68.7, 69.3, 69.4, 73.7, 74.1, 74.3, 81.0, 85.0, 97.2, 133.3. HRMS (ESI) calcd for $C_{21}H_{23}FeIO$, 474.0143; found, 474.0136.

*(2E,4E)-Methyl 5-Ferrocenyl-4-(phenoxymethyl)penta-2,4-dienoate (**8**)*. Red oil; 99 mg, 81% yield. IR (KBr) 3129, 1721, 1605, 1491, 1400, 1268, 1180, 1054, 991, 815, 767 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.78 (s, 3H), 4.11 (s, 5H), 4.39 (d, J = 1.5 Hz, 2H), 4.47 (d, J = 1.5 Hz, 2H), 4.70 (s, 2H), 6.12 (s, 1H), 6.76 (s, 1H), 6.98 (t, J = 4.5 Hz, 3H), 7.31(t, J = 8.0 Hz, 2H), 8.07 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 51.6, 69.5, 69.8, 70.5, 70.7, 79.3, 115.1, 117.8, 121.3, 128.0, 129.5, 138.7, 140.7, 158.5, 168.0. HRMS (ESI) calcd for $C_{23}H_{22}FeO_3$, 402.0918; found, 402.0906.

*(2E,4E)-Methyl 5-Ferrocenyl-4-(methoxymethyl)penta-2,4-dienoate (**9**)*. Red oil; 100 mg, 98% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.37 (s, 3H), 3.77 (s, 3H), 4.11 (s, 2H), 4.16 (s, 5H), 4.37 (d, J = 2.0 Hz, 2H), 4.46 (s, 2H), 6.13 (d, J = 16.0 Hz, 1H), 6.65 (s, 1H), 8.04 (d, J = 16.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 51.6, 57.8, 69.5, 70.3, 70.6, 74.6, 79.6, 117.8, 129.4, 137.9, 140.8, 168.1. HRMS (ESI) calcd for $C_{18}H_{20}FeO_3$, 340.0762; found, 340.0765.

*(2E,4E)-Methyl 5-Ferrocenyl-4-((1-phenylethoxy)methyl)penta-2,4-dienoate (**10**)*. Red oil; 120 mg, 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (d, J = 6.5 Hz, 3H), 3.77 (s, 3H), 3.95 (d, J = 12.0 Hz, 1H), 4.09 (d, J = 12.0 Hz, 1H), 4.15 (s, 5H), 4.36 (s, 2H), 4.43 (d, J = 1.5 Hz, 2H), 4.46−4.50 (m, 1H), 6.90 (d, J = 16.0 Hz, 1H), 6.58 (s, 1H), 7.35−7.40 (m, 5H), 8.03 (d, J = 16.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.7, 51.6, 69.5, 70.2, 70.6, 77.2, 79.7, 117.8, 126.4, 127.6, 128.6, 129.8, 137.7, 141.0, 143.5, 168.2. HRMS (ESI) calcd for $C_{25}H_{26}FeO_3$, 430.1231; found, 430.1233.

*(E)-1-(1-Ferrocenyl-3-methoxyprop-1-en-2-yl)benzene (**11**)*. Orange oil; 120 mg, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.39 (s, 3H), 3.81 (t, J = 2.0 Hz, 2H), 4.03 (t, J = 2.0 Hz, 2H), 4.06 (s, 5H), 4.12 (d, J = 0.5 Hz, 2H), 6.36 (s, 1H), 7.23−7.26 (m, 2H), 7.30 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 57.8, 68.6, 69.1, 69.3, 78.4, 80.9, 126.4, 127.2, 128.5, 128.7, 135.3, 140.0. HRMS (ESI) calcd for $C_{20}H_{20}FeO$, 332.0864; found, 332.0861.

*(E)-1-(4-Ferrocenyl-3-(phenoxymethyl)but-3-en-1-ynyl)benzene (**12**)*. Red solid; 71 mg, 57% yield. mp 70−72 °C (recrystallized from petroleum ether at room temperature). IR (KBr) 3126, 1736, 1645, 1493, 1452, 1400, 1249, 1154, 1031, 998, 819, 707 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.09 (s, 5H), 4.31 (s, 2H), 4.66 (s, 2H), 4.84 (s, 2H), 6.97 (s, 1H), 6.95 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 8.0 Hz, 2H), 7.30−7.36 (m, 5H), 7.52 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.4, 69.5, 69.6, 71.4, 80.1, 88.5, 95.6, 113.7, 115.4, 121.2, 123.7, 128.3, 128.5, 129.5, 131.4, 135.8, 158.5. HRMS (ESI) calcd for $C_{27}H_{22}FeO$, 418.1020; found, 418.1027.

*(Z)-1-Benzyl-4-(2-(3-ferrocenyl-2-iodoallyloxy)ethyl)-1H-1,2,3-triazole (**13**)*. Red oil; 71 mg, 63% yield. IR (KBr) 3088, 3030, 2961, 1632, 1551, 1493, 1384, 1105, 818, 697 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.04 (t, J = 6.5 Hz, 3H), 3.69 (t, J = 6.5 Hz, 2H), 4.13 (s, 5H), 4.18 (s, 2H), 4.29 (s, 2H), 4.78 (s, 2H), 5.48 (s, 2H), 6.81 (s, 1H), 7.26−7.35 (m, 5H), 7.45 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.6, 54.1, 68.3, 69.0, 69.3, 69.5, 80.2, 80.7, 96.5, 122.1, 128.2, 128.7, 129.1, 134.9, 135.0, 145.6. HRMS (ESI) calcd for $C_{24}H_{24}FeIN_3O$, 553.0304; found, 553.0313.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for all products and NOE spectra of compound **3g**, **5j**, and **7v**. 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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