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CuBr-Promoted Formal Hydroacylation of 1-Alkynes with Glyoxal Derivatives: An Unexpected Synthesis of 1,2-Dicarbonyl-3-enes

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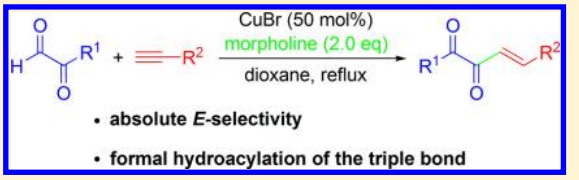
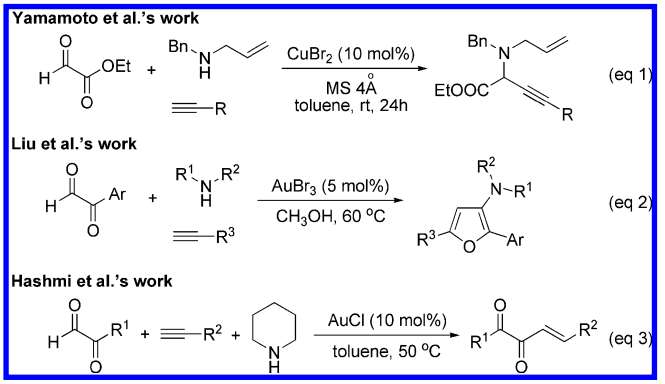
Supporting Information

ABSTRACT: An efficient and concise protocol has been developed for the highly regio- and stereoselective synthesis of *E*-1,2-dicarbonyl-3-ene derivatives by a copper-promoted reaction of 1-alkynes with α-carbonyl aldehydes in the presence of morpholine. The products obtained are believed as the formal hydroacylation of the triple bond.



During recent years, considerable interest has focused on the transition-metal-catalyzed Mannich-type three-component coupling of an aldehyde, an alkyne, and an amine (A^3-coupling), which has been established as a convenient and efficient approach toward propargylamines.[1] Moreover, the A^3-coupling as well as different tandem reactions involving A^3-coupling has found widespread application in the synthesis of various heterocycles, natural products, and biologically active compounds.[2] However, compared to the wide applications of aromatic and aliphatic aldehydes in the A^3-coupling reactions, the use of glyoxals is barely documented.[3] In 2005, Yamamoto and co-workers developed a Cu-catalyzed A^3-coupling route from ethyl glyoxalate, *N*-benzylallylamine, and 1-alkyne to alkynylglycinate (Scheme 1, eq 1).[4] More recently, Liu and co-workers reported a $AuBr_3$-catalyzed three-component coupling reaction of phenylglyoxal derivatives, secondary amines, and terminal alkynes for the synthesis of aminofurans (Scheme 1, eq 2).[5] Lately, Hashmi and co-workers disclosed a AuCl-catalyzed reaction of an α-ketoaldehyde and a terminal alkyne in the presence of piperidine to afford 1,2-dicarbonyl-3-ene, which was believed as the formal hydroacylation of the triple bond (Scheme 1, eq 3).[6]

Scheme 1



On the other hand, the A^3-coupling-based tandem reactions, followed by a 1,5-hydride shift, resulting in the formation of allene products with concomitant elimination of imine species, were first reported by Crabbé and recently modified by Ma and co-workers.[7] Our group has recently described a concise and efficient method for the synthesis of allene ferrocenes based on the modified Crabbé homologation reaction of ferrocenylacetylene with aromatic aldehydes in the presence of morpholine using ZnI_2 as the catalyst.[8] In the context of ongoing projects for the synthesis of allene derivatives, we envisioned that glyoxals might also be considered as starting materials, which can offer a series of buta-2,3-dienoates.

To test our hypothesis, we initially investigated the reaction of phenylacetylene **1a**, ethyl glyoxalate **2a**, and morpholine **3a** in the presence of ZnI_2 (Table 1, entry 1). To our surprise, no expected allene product was obtained. Instead, the *E*-1,2-dicarbonyl-3-ene **4a** was obtained in 28% yield, as the only stereoisomer under the reaction conditions. The configuration of the C=C bond in **4a** was clearly demonstrated by the olefinic coupling constant of 16.0 Hz. As we know, the 1,2-dicarbonyl-3-enes are versatile building blocks in organic synthesis;[9] we decided to investigate this unexpected transformation in detail.

In order to obtain a maximum yield of the 1,2-dicarbonyl-3-ene derivatives, different parameters were carefully screened, and the results are summarized in Table 1. Interestingly, the product **4a** was increased in 55% yield when CuBr was used as the catalyst (Table 1, entry 2). Other copper salts, such as CuI and CuCl, also worked for this reaction, albeit with lower yields (Table 1, entries 3 and 4). Notably, $Cu(OTf)_2$ and AgOTf showed no conversions (Table 1, entries 5 and 6); hence, we used CuBr for the further optimizations. Next, diverse common organic solvents were screened; dioxane was found to be the most suitable solvent for this transformation, whereas a low yield of **4a** was obtained when THF, CH_2Cl_2, or CH_3CN was used as the solvent in this reaction (Table 1, entries 7–10). Further investigation showed that polar solvent, such as CH_3NO_2, was not suitable for this reaction (Table 1, entry 11). Next, the effect of bases on this novel reaction was

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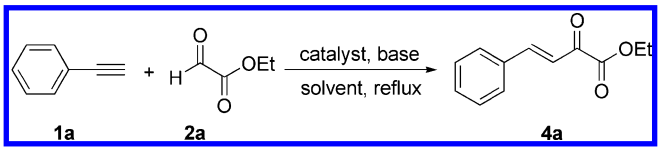
Table 1. Optimization of Reaction Conditions[a]



entry	cat. (mol %)	base	solvent	time (h)	yield (%)[b]
1	ZnI_2 (80)	morpholine	toluene	4	28
2	CuBr (80)	morpholine	toluene	7	55
3	CuI (80)	morpholine	toluene	7	48
4	CuCl (80)	morpholine	toluene	7	16
5	$Cu(OTf)_2$ (80)	morpholine	toluene	7	trace
6	AgOTf (80)	morpholine	toluene	7	trace
7	CuBr (80)	morpholine	dioxane	2	75
8	CuBr (80)	morpholine	THF	4	58
9	CuBr (80)	morpholine	CH_2Cl_2	4	30
10	CuBr (80)	morpholine	CH_3CN	4	39
11	CuBr (80)	morpholine	CH_3NO_2	2	trace
12	CuBr (80)	Et_2NH	dioxane	4	20
13	CuBr (80)	Cy_2NH	dioxane	4	30
14	CuBr (80)	*i*-Pr_2NH	dioxane	4	32
15	CuBr (80)	pyrrolidine	dioxane	4	trace
16	CuBr (50)	morpholine	dioxane	2	73
17	CuBr (10)	morpholine	dioxane	2	60
18	CuBr (100)	morpholine	dioxane	2	73
19[c]	CuBr (50)	morpholine	dioxane	2	82

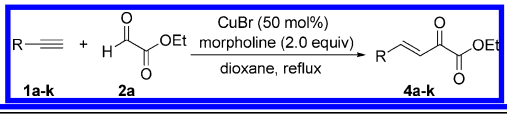
[a]All the reactions were carried out with **1a** (1.0 mmol), **2a** (1.8 mmol), and base (1.7 mmol) in 3.0 mL of solvent if not otherwise indicated. [b]Yield of isolated product after chromatography. [c]The ratio of **1a**/**2a**/morpholine is 1.0:2.0:2.0 and in 3.0 mL of dioxane.

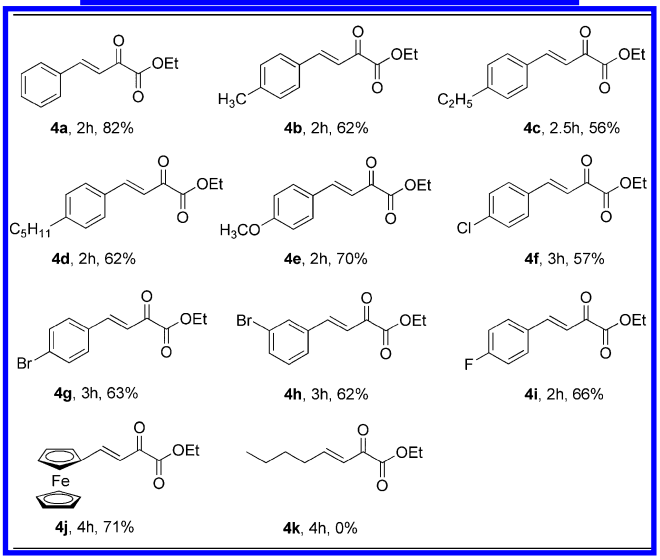
carefully examined. Among the bases tested, morpholine was still found to be the most effective for this transformation. The desired product **4a** was obtained in moderate yield when Et_2NH, Cy_2NH, or *i*-Pr_2NH was employed in this reaction (Table 1, entries 12−14). With pyrrolidine, no conversion was detected (Table 1, entry 15). Moreover, the catalyst loading of the reaction was evaluated, and 50 mol % was the best choice (Table 1, entries 16−18). Furthermore, the ratio of substrates was examined, and it was found that a **1a**/**2a**/morpholine ratio of 1.0:2.0:2.0 led to the highest yield of **4a** (Table 1, entry 19).

With the optimized reaction conditions in hand, the scope and generality of this new procedure using various terminal alkynes as the substrates were studied, and the results are summarized in Table 2. Simple ethyl glyoxalate **2a** reacted with phenylacetylene or subsitituted phenylacetylene to afford the corresponding ethyl 2-oxo-3-butenoate derivatives in good yields as well as high regio- and stereoselectivities (Table 2, **4a**−**4i**). Besides, we were pleased to discover that ferrocenylacetylene is also compatible with this transformation, and with excellent yield (Table 2, **4j**). However, when aliphatic alkyne was used instead of aromatic ones, no desired product was detected (Table 2, **4k**).

To highlight the utility of this transformation, diverse *α*-carbonyl aldehydes were subjected to the optimized reaction conditions. The results are shown in Table 3. The reaction tolerates a relatively small range of substituent on the phenylglyoxals. It was found that the substrates with a phenyl ring bearing a halogen group generally gave lower yields of the products (Table 3, **4m**−**4o**), whereas the substrates with an electron-donating substituent on the phenyl ring, such as *p*-CH_3 and *p*-OCH_3, resulted in slightly higher yields (Table 3, **4p** and **4q**). However, **4r** was obtained in only 25% yield most probably due to the strong electron-withdrawing effect of the nitro group on the phenyl ring. Notably, the high regio- and stereoselectivities were observed in all the cases, and only *E*-isomers were obtained.

Table 2. CuBr-Promoted Reaction of Various Terminal Alkynes with Ethyl Glyoxalate[a]





[a]All the reactions were carried out with 1-alkyne **1a**−**1k** (1.0 mmol), ethyl glyoxalate **2a** (2.0 mmol), morpholine **3a** (2.0 mmol), and CuBr (0.5 mmol) in 3.0 mL of dioxane, and isolated yields were reported.

The corresponding 1,2-dicarbonyl-3-ene derivatives are attractive and can be further converted in organic synthesis.[9]

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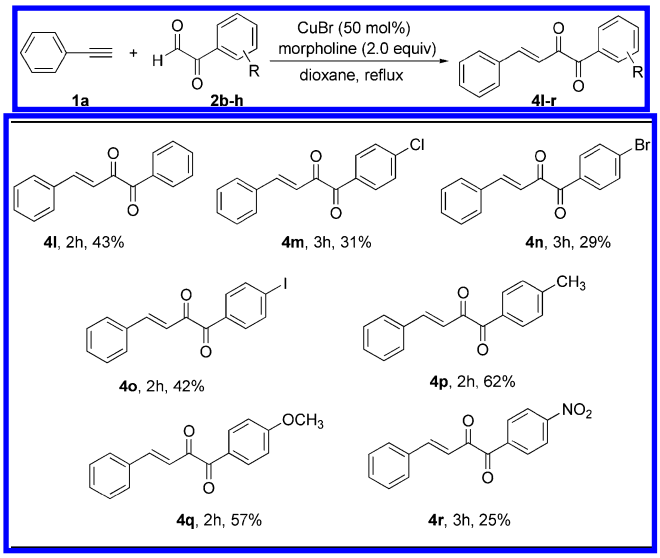
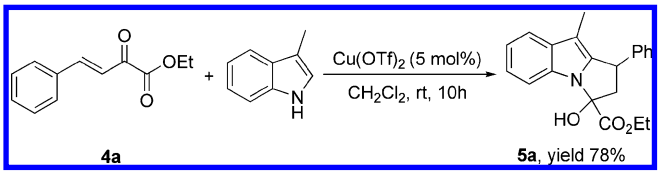
Table 3. CuBr-Promoted Reaction of Phenylacetylene 1a with Various α-Carbonyl Aldehydes[a]



[a]All the reactions were carried out with phenylacetylene **1a** (1.0 mmol), α-carbonyl aldehydes **2b−2h** (2.0 mmol), morpholine **3a** (2.0 mmol), and CuBr (0.5 mmol) in 3.0 mL of dioxane, and isolated yields were reported.

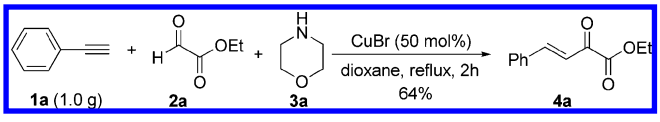
The synthetic potential of this methodology was demonstrated by the reaction of **4a**. The novel 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole **5a** was obtained in good yield when **4a** reacted with 3-methylindole in the presence of copper(II) triflate (5 mol %) in dichloromethane at room temperature for 10 h (Scheme 2).

Scheme 2. Synthetic Application of 4a



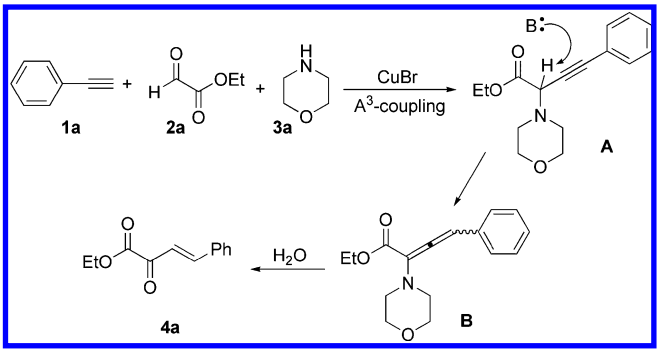
Finally, considering the general application of this formal hydroacylation reaction, we demonstrated the gram-scale progress, and an example of large-scale reaction with satisfactory yield of the product is shown in Scheme 3.

Scheme 3. Large-Scale Reaction



On the basis of the above results and related literature,[6] we proposed a plausible mechanism to account for the CuBr-promoted formal hydroacylation, as shown in Scheme 4. First, a copper-catalyzed three-component coupling of a glyoxal, an alkyne, and a morpholine occurred to afford carbonyl propargylamine intermediate **A** via an A^3-coupling reaction; the formation of intermediate **A** was further confirmed by ^1H NMR analysis of the crude product. The intermediate **A** then isomerizes to give the conjugated allenylamine intermediate **B** in the presence of morpholine. After the hydrolysis of the allenylamine intermediate **B** on silica gel, the corresponding

Scheme 4. Proposed Mechanism of the Reaction



product **4a** is afforded. The coupling constants (J = 15.5−16.5 Hz) in the ^1H NMR spectrum support the *E*-configuration of the vinyl motif.

In conclusion, we have established a convient CuBr-promoted protocol for the synthesis of 1,2-dicarbonyl-3-ene derivatives from readily available starting materials based on the reaction of 1-alkynes and α-carbonyl aldehydes in the presence of morpholine. Owing to the important applications of 1,2-dicarbonyl-3-enes in the heterocycle syntheses, this reaction will be of high interest to the scientific community.

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.[14] For chromatography, 200−300 mesh silica gel (Qingdao, China) was employed. ^1H and ^{13}C NMR spectra were recorded at 500 and 125 MHz using an FT-NMR spectrometer. Chemical shifts are reported in parts per million (ppm) using tetramethylsilane as 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 QTOF mass spectrometer. Melting points were determined with a melting points apparatus and are uncorrected.

General Procedure for the CuBr-Promoted Reaction of 1-Alkynes with α-Carbonyl Aldehydes in the Presence of Morpholine. To a solution of 1-alkynes (1.0 mmol), α-carbonyl aldehydes (2.0 mmol), and morpholine (2.0 mmol) in dioxane (3.0 mL) was added CuBr (0.5 mmol) under a N_2 atmosphere. The resulting mixture was heated at 110 °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 1,2-dicarbonyl-3-ene products **4**.

*(E)-Ethyl 2-Oxo-4-phenyl-3-butenoate (**4a**).*[10] Yellow oil; 168 mg, 82% yield; IR (KBr) 2984, 1729, 1693, 1605, 983, 745 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.40 (t, J = 7.0 Hz, 3H), 4.38 (q, J = 7.0 Hz, 2H), 7.35 (d, J = 16.0 Hz, 1H), 7.38−7.45 (m, 3H), 7.60−7.61 (m, 2H), 7.83 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 62.4, 120.6, 129.0, 129.1, 131.6, 134.0, 148.3, 162.2, 182.8.

*(E)-Ethyl 2-Oxo-4-p-tolylbut-3-enoate (**4b**).*[10] Yellow oil; 134 mg, 62% yield; IR (KBr) 2984, 1729, 1605, 983, 848 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.41 (t, J = 7.0 Hz, 3H), 2.38 (s, 3H), 4.39 (q, J = 7.0 Hz, 2H), 7.22 (d, J = 7.5 Hz, 2H), 7.31 (d, J = 16.0 Hz, 2H), 7.52 (d, J = 7.5 Hz, 2H), 7.83 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 21.6, 62.4, 119.6, 129.1, 129.9, 131.4, 142.5, 148.5, 162.4, 182.9.

*(E)-Ethyl 4-(4-Ethylphenyl)-2-oxobut-3-enoate (**4c**).* Yellow oil; 129 mg, 56% yield; IR (KBr) 2967, 1729, 1600, 986, 831 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.25 (t, J = 7.5 Hz, 3H), 1.41 (t, J = 7.0 Hz, 3H), 2.68 (q, J = 7.5 Hz, 2H), 4.39 (q, J = 7.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 16.5 Hz, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 16.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 15.2, 30.0,

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62.5, 119.6, 128.7, 129.2, 131.6, 148.6, 148.7, 162.4, 182.9; HRMS (EI) calcd for $C_{14}H_{16}O_3$ $[M]^+$ 232.1099, found 232.1101.

*(E)-Ethyl 2-Oxo-4-(4-pentylphenyl)but-3-enoate (**4d**).*[11] Yellow oil; 169 mg, 62% yield; IR (KBr) 2929, 1729, 1601, 986, 785 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H), 1.26−1.36 (m, 4H), 1.41 (t, J = 7.0 Hz, 3H), 1.62 (t, J = 7.0 Hz, 2H), 2.63 (t, J = 7.5 Hz, 2H), 4.39 (q, J = 7.0 Hz, 2H), 7.23 (t, J = 8.0 Hz 2H), 7.33 (d, J = 16.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 14.0, 22.5, 29.7, 30.8, 35.9, 62.3, 119.6, 128.4, 129.2, 131.6, 147.5, 148.6, 162.4, 182.9.

*(E)-Ethyl 4-(4-Methoxyphenyl)-2-oxobut-3-enoate (**4e**).*[10] Yellow solid; 163 mg, 70% yield; mp 46−47 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 2991, 1724, 1596, 1002, 827 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.41 (t, J = 7.0 Hz, 3H), 3.86 (s,3H), 4.39 (q, J = 7.0 Hz, 2H), 6.93 (d, J = 8.5 Hz, 1H), 7.24 (d, J = 16.0 Hz, 2H), 7.59 (d, J = 7.0 Hz, 2H), 7.83(d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 55.5, 62.4, 114.6, 118.2, 126.8, 131.1, 148.3, 162.5, 162.6, 182.7.

*(E)-Ethyl 4-(4-Chlorophenyl)-2-oxobut-3-enoate (**4f**).*[10] Yellow solid; 135 mg, 57% yield; mp 76−78 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 2925, 1720, 1690, 1607, 1004, 832 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.42 (t, J = 7.0 Hz, 3H), 4.40 (q, J = 7.0 Hz, 2H), 7.35 (d, J = 16.0 Hz, 1H), 7.40 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 16.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 62.6, 120.9, 129.4, 130.2, 132.5, 137.6, 146.8, 162.0, 182.5.

*(E)-Ethyl 4-(4-Bromophenyl)-2-oxobut-3-enoate (**4g**).*[10] Yellow solid; 177 mg, 63% yield; mp 68−70 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 2922, 1720, 1606, 1004, 829 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.42 (t, J = 7.0 Hz, 3H), 4.40 (q, J = 7.0 Hz, 2H), 7.37 (d, J = 16.5 Hz, 1H), 7.50 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 16.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 62.6, 121.0, 126.1, 130.3, 132.4, 132.9, 146.8, 162.0, 182.6.

*(E)-Ethyl 4-(3-Bromophenyl)-2-oxobut-3-enoate (**4h**).*[12] Yellow solid; 174 mg, 62% yield; mp 62−64 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 2983, 1724, 1612, 993, 863 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.42 (t, J = 7.0 Hz, 3H), 4.40 (q, J = 7.0 Hz, 2H), 7.30 (t, J = 8.0 Hz, 1H), 7.36 (d, J = 16.5 Hz, 1H), 7.54−7.57 (m, 2H), 7.74−7.78 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 62.7, 121.7, 123.2, 127.6, 130.6, 131.5, 134.3, 136.1, 146.4, 161.9, 182.4.

*(E)-Ethyl 4-(4-Fluorophenyl)-2-oxobut-3-enoate (**4i**).*[10] Yellow solid; 146 mg, 66% yield; mp 60−62 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 2989, 1723, 1592, 1004, 840 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.42 (t, J = 7.0 Hz, 3H), 4.40 (q, J = 7.0 Hz, 2H), 7.13 (t, J = 8.5 Hz, 2H), 7.31 (d, J = 16.0 Hz 1H), 7.63−7.66 (m, 2H), 7.83 (d, J = 16.0 Hz,1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 62.6, 116.3, 116.5, 120.2, 130.3, 131.1, 147.0, 162.1, 163.7, 165.7, 182.6.

*(E)-Ethyl 4-Ferrocenyl-2-oxobut-3-enoate (**4j**).* Purple solid; 221 mg, 71% yield; mp 89−90 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 2976, 1720, 1663, 1100, 1030 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.36 (t, J = 7.0 Hz, 3H), 4.23 (s, 5H), 4.31 (q, J = 7.0 Hz, 2H), 4,67 (t, J = 2.0 Hz, 2H), 4.89 (t, J = 2.0 Hz, 2H), 6.92 (d, J = 15.5 Hz, 1H), 7.48 (d, J = 15.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 61.3, 70.0, 70.4, 73.8, 79.7, 129.4, 137.3, 166.2, 191.8; HRMS (ESI) calcd for $C_{16}H_{17}FeO_3$ $[M + 1]^+$ 313.0527, found 313.0534.

*(E)-1,4-Diphenylbut-3-ene-1,2-dione (**4l**).*[6] Yellow oil; 100 mg, 43% yield; IR (KBr) 2925, 1675, 1596, 961, 863 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, J = 16.5 Hz, 1H), 7.39−7.45 (m, 3H), 7.51 (t, J = 7.0 Hz, 2H), 7.59 (d, J = 7.0 Hz, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.71 (d, J = 16.5 Hz, 1H), 8.04 (d, J = 7.0, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 122.4, 128.9, 129.1, 130.2, 131.6, 132.8, 134.0, 134.7, 148.9, 192.8, 193.3.

*(E)-1-(4-Chlorophenyl)-4-phenylbut-3-ene-1,2-dione (**4m**).* Yellow solid; 82 mg, 31% yield; mp 77−79 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 2931, 1667, 1602, 950, 837 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, J = 16.5 Hz, 1H), 7.41−7.45 (m, 3H), 7.48 (d, J = 7.5 Hz, 2H), 7.60 (d, J = 7.0 Hz, 2H), 7.73 (d, J = 16.5 Hz, 1H), 8.00 (d, J = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 121.9, 128.9, 129.1, 129.3, 131.1, 131.6, 131.7, 133.9, 141.3, 149.0, 191.6, 191.7; HRMS (EI) calcd for $C_{16}H_{11}ClO_2$ $[M]^+$ 270.0448, found 270.0451.

*(E)-1-(4-Bromophenyl)-4-phenyl-3-butene-1,2-dione (**4n**).* Yellow solid; 90 mg, 29% yield; mp 65−67 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 2925, 1670, 1602, 952, 828 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, J = 16.0 Hz, 1H), 7.41−7.47 (m, 3H), 7.60 (d, J = 6.5 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 16.5 Hz, 1H), 7.92 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 121.9, 128.9, 129.1, 130.2, 131.3, 131.5, 131.7, 132.5, 133.9, 140.9, 191.6, 191.7; HRMS (EI) calcd for $C_{16}H_{11}BrO_2$ $[M]^+$ 313.9942, found 313.9941.

*(E)-1-(4-Iodophenyl)-4-phenyl-3-butene-1,2-dione (**4o**).* Yellow solid; 151 mg, 42% yield; mp 90−92 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 2923, 1664, 1604, 951, 859 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.16 (d, J = 16.5 Hz, 1H), 7.42−7.44 (m, 3H), 7.60 (d, J = 6.5 Hz, 2H), 7.72 (d, J = 16.5 Hz, 1H), 7.75 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 103.4, 121.9, 129.0, 129.1, 131.4, 131.7, 132.1, 133.9, 138.3, 149.1, 191.7, 192.2; HRMS (ESI) calcd for $C_{16}H_{12}IO_2$ $[M + 1]^+$ 362.9882, found 362.9871.

*(E)-4-Phenyl-1-p-tolylbut-3-ene-1,2-dione (**4p**).* Yellow oil; 154 mg, 62% yield; IR (KBr) 2923, 1665, 1602, 949, 834 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.11 (d, J = 16.5 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.36−7.40 (m, 3H), 7.55 (d, J = 7.0 Hz, 2H), 7.68 (d, J = 16.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.9, 122.5, 128.8, 129.0, 129.6, 130.3, 131.5, 134.0, 145.9, 148.6, 192.9, 193.1; HRMS (EI) calcd for $C_{17}H_{14}O_2$ $[M]^+$ 250.0994, found 250.0996.

*(E)-1-(4-Methoxyphenyl)-4-phenylbut-3-ene-1,2-dione (**4q**).*[13] Yellow solid; 151 mg, 57% yield; mp 82−84 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 2947, 1649, 1598, 944, 851 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.87 (s, 3H), 6.97 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 16.0 Hz, 1H), 7.39−7.41 (m, 3H), 7.57 (d, J = 7.5 Hz, 2H), 7.69 (d, J = 16.5 Hz, 1H), 8.02 (d, J = 9.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.6, 114.2, 122.6, 125.7, 128.8, 129.0, 131.4, 132.6, 134.0, 148.5, 164.8, 191.8, 193.2.

*(E)-1-(4-Nitrophenyl)-4-phenylbut-3-ene-1,2-dione (**4r**).* Yellow solid; 70 mg, 25% yield; mp 128−130 °C (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 2925, 1675, 1600, 959, 849 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, J = 16.0 Hz, 1H), 7.42−7.48 (m, 3H), 7.63 (d, J = 7.0 Hz, 2H), 7.81 (d, J = 16.0 Hz, 1H), 8.24 (d, J = 9.0 Hz, 2H), 8.34 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 121.1, 123.9, 129.1, 129.2, 131.4, 132.0, 133.8, 137.3, 149.5, 150.9, 190.0, 190.4; HRMS (ESI) calcd for $C_{16}H_{12}NO_4$ $[M + 1]^+$ 282.0766, found 282.0755.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^1H and ^{13}C NMR spectra for all new 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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