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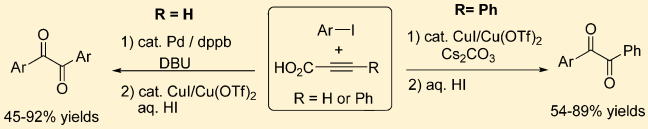
Copper-Catalyzed Direct Synthesis of Diaryl 1,2-Diketones from Aryl Iodides and Propiolic Acids

Hongkeun Min, Thiruvengadam Palani, Kyungho Park, Jinil Hwang, and Sunwoo Lee*

Department of Chemistry, Chonnam National University, Gwangju 500-757, Republic of Korea

Supporting Information

ABSTRACT: Benzil derivatives such as diaryl 1,2-diketones are synthesized via the direct decarboxylative coupling reaction of aryl propiolic acids and their oxidation. The optimized conditions are that the reaction of aryl propiolic acids and aryl iodides is conducted at 140 °C for 6 h in the presence of 10 mol % CuI/Cu(OTf)$_2$ and Cs_2CO_3, after which HI (aq) is added and further reacted. The method shows good functional group tolerance toward ester, aldehyde, cyano, and nitro groups. In addition, symmetrical diaryl 1,2-diketones are obtained from aryl iodides and propiolic acid in the presence of palladium and copper catalysts.

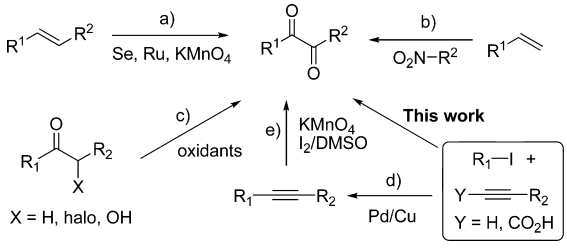


INTRODUCTION

1,2-Diketones are one of the most important skeletons in biologically active molecules[1] and are very useful building blocks that can easily be transformed into a variety of other chemicals, especially heterocyclic compounds.[2] Among 1,2-diketones, benzil derivatives also exhibit bioactivities in antitumor applications.[3] A number of methods for the preparation of 1,2-diketones have been developed, and they mostly involve the oxidation of various substrates such as olefins, methylene ketones, and alkynes.

The oxidation of olefins with selenium dioxide, potassium permanganate, and a ruthenium catalyst has been reported (Scheme 1a).[4] In addition, it has been reported that the intermolecular coupling of terminal alkenes and nitroalkanes provides diketones (Scheme 1b).[5] Methylene ketone derivatives, including α-halo and α-hydroxy ketones have been oxidized to the 1,2-diketones with iodine, oxygen, Al_2O_3/$CuBr_2$, oxothiazoline vinyl bromide, pyridine *N*-oxide, sodium hypobromite, bismuth nitrate/copper acetate, and trichlorooxovanadium (Scheme 1c).[6]

Scheme 1. Syntheses of 1,2-Diketones



However, these methods have some drawbacks such as vigorous reaction conditions, the discharge of large amounts of metal or organic wastes, and the preparation of starting materials. Since some of them were synthesized from alkynes, the direct oxidation of internal alkynes may be one of the most widely used and most straightforward methods to synthesize 1,2-diketones.[7] Furthermore, internal alkynes are easily prepared via the Sonogashira coupling reaction (Scheme 1d).[8] Recently, a number of transition-metal-catalyzed oxidations of internal alkynes have been reported, employing iron, palladium, copper, gold, silver, or ruthenium as catalysts and/or cocatalysts with oxidants (Scheme 1e).[9]

Although these methods have been attractive in the synthetic aspect, they have several drawbacks: (1) the preparation process of the internal alkynes is still needed; (2) the metal catalysts used are expensive in most cases; (3) most of the oxidation reactions require toxic or expensive reagents; and (4) there is no report of the direct synthesis of 1,2-diketones from aryl halides.

Alkynyl carboxylic acids have been intensively used as terminal alkyne surrogates in Sonogashira-type decarboxylative coupling reactions[10] because they are much simpler and easier to prepare than terminal alkynes.[11] As part of our ongoing research to expand the decarboxylative coupling of alkynyl carboxylic acids,[12] we found that benzil was formed when iodobenzene and phenylpropiolic acid were allowed to react with a copper catalyst in the absence of base. Inspired by this result, we investigated the development of a one-pot synthesis of 1,2-diketones from aryl iodides and arylalkynyl carboxylic acids using a copper catalyst without the need to isolate diarylalkynes. To the best of our knowledge, there has been no previous report of the direct synthesis of 1,2-diketones from aryl halides and alkynes.

RESULTS AND DISCUSSION

To study the direct one-pot synthesis of 1,2-diketones, iodobenzene (**1a**) and phenylpropiolic acid (**2**) were reacted under a variety of reaction conditions, and the results are summarized in Table 1. When copper(I) or copper(II) was

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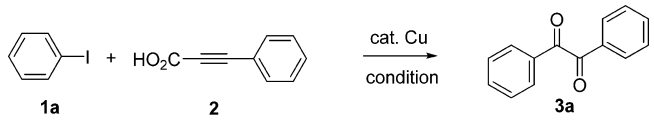
Table 1. Optimization of the Conditions for the Synthesis of 1,2-Diketones[a]



1a 2 3a

entry	1a/2 ratio	catalyst	additive (equiv)	solvent	yield of 3a (%)
1	1/1	CuI	–	DMSO	<1
2	1/1	CuCl	–	DMSO	<1
3	1/1	$Cu(OAc)_2$	–	DMSO	<1
4	1/1	$Cu(OTf)_2$	–	DMSO	<1
5	1/1	CuI/$Cu(OTf)_2$	–	DMSO	25
6	1/1	CuI/$Cu(OTf)_2$	DBU (1.0)	DMSO	– (68)[e]
7	1/1	CuI/$Cu(OTf)_2$	Cs_2CO_3 (1.0)	DMSO	– (88)[e]
8	1/1	CuI/$Cu(OTf)_2$	Cs_2CO_3 (0.5)	DMSO	– (91)[e]
9	1/1	CuI/$Cu(OTf)_2$	Cs_2CO_3/HI[b] (0.5/0.25)	DMSO	38
10	1/1.5	CuI/$Cu(OTf)_2$	Cs_2CO_3/HI[b] (0.5/0.25)	DMSO	51
11	1/2	CuI/$Cu(OTf)_2$	Cs_2CO_3/HI[b] (0.5/0.5)	DMSO	92
12	1/2	CuI/$Cu(OTf)_2$	Cs_2CO_3/HI[b] (0.5/0.5)	DMF	–
13	1/2	CuI/$Cu(OTf)_2$	Cs_2CO_3/HI[b] (0.5/0.5)	toluene	–
14	1/2	CuI/$Cu(OTf)_2$	Cs_2CO_3/HI[b] (0.5/0.5)	diglyme	–
15[c]	1/2	CuI/$Cu(OTf)_2$	Cs_2CO_3/HI[b] (0.5/0.5)	DMSO	71
16[d]	1/2	CuI/$Cu(OTf)_2$	Cs_2CO_3/HI[b] (0.5/0.5)	DMSO	35
17[f]	1/2	CuI/$Cu(OTf)_2$	Cs_2CO_3/HI[b] (0.5/0.5)	DMSO	87

[a]Reaction conditions: **1a** (0.3 mmol), **2a**, Cu catalyst (0.3 mmol), and additive were reacted at 140 °C for 6 h. [b]HI(aq) was added after the coupling reaction in the presence of base. [c]The reaction was conducted under a nitrogen atmosphere. [d]The reaction temperature was 120 °C. [e]The yield of diphenylacetylene is given in parentheses. [f]Phenylacetylene was used instead of phenylpropiolic acid.

used as a catalyst, a trace amount of the diketone, benzil (**3a**), was formed (entries 1–4). The use of both CuI and $Cu(OTf)_2$ afforded benzil in 25% yield (entry 5). When the reaction was carried out in the presence of a base such as 1,8-diazabicylo[5.4.0]undec-7-ene (DBU) or Cs_2CO_3, only the decarboxylative coupling product, diphenylacetylene, was obtained in good yield without any formation of benzil (entries 6 and 7). The 1,2-diketone product was not formed when the amount of Cs_2CO_3 was decreased to 0.5 equiv (entry 8). We envisioned that HI, which was formed in the decarboxylative coupling of iodobenzene and phenylpropiolic acid in the absence of base, might accelerate production of the 1,2-diketone. On the basis of our assumption, the reaction was conducted sequentially: the reaction was carried out in the presence of base for 12 h, and then HI was added to the reaction mixture (entries 9–11). The best conditions were found to be a 0.5/0.5 ratio of base to HI with 2.0 equiv of phenylpropiolic acid (entry 11). The desired product was not formed in other solvents such as DMF, toluene, and diglyme (entries 12–14). When the reaction was run under a nitrogen atmosphere, the product yield was 71% (entry 15). Decreasing the reaction temperature to 120 °C afforded a low product yield (entry 16). When phenylacetylene was used instead of phenylpropiolic acid, the desired product was obtained in 87% yield (entry 17). The optimized reaction conditions that we found from the screening data are the following: aryl iodide (1.0 equiv), arylalkynyl carboxylic acid (2.0 equiv), CuI (10 mol %), $Cu(OTf)_2$ (10 mol %), and Cs_2CO_3 (0.5 equiv) are reacted at 140 °C for 12 h, and then HI (0.5 equiv) is added and further reacted at 140 °C for 6 h.

To expand the substrate scope, a variety of aryl iodides were evaluated in the reaction with phenylpropiolic acid under the optimized conditions (Table 2). As expected, benzil **3a** was obtained in 89% yield from the reaction with phenyl iodide. Alkyl-substituted aryl iodides such as **1b–e** led to the desired 1,2-diketones in moderate to good yields (entries 2–5). Also, *o*-, *m*-, and *p*-iodoanisole afforded the corresponding 1,2-diketones in good yields (entries 6–8). Halo-substituted aryl iodides such as **1i** and **1j** showed good yields (entries 9 and 10). In the case of 1,4-diiodobenzene, the monosubstituted product was obtained as the major product (entry 9). Aryl iodides bearing an ester, aldehyde, cyano, or nitro group at the para position provided the corresponding 1,2-diketones **3k–n** in yields of 60%, 59%, 66%, and 54%, respectively (entries 11–14). 4-Iodobiphenyl and 1-iodonaphthalene coupled with phenylpropiolic acid to give the desired 1,2-diketones in good yields (entries 15 and 16). 2-Iodothiophene provided the corresponding 1,2-diketone **3q** in 65% yield (entry 17). When phenyl bromide (**1r**) was allowed to react with phenylpropiolic acid under the optimized conditions, benzil was formed in 15% yield (entry 18). However, phenyl chloride (**1s**) and phenyl triflate (**1t**) did not give the desired product (entries 19 and 20). Attempts to employ alkyl alkynyl carboxylic acids such as 2-butynoic, 2-hexynoic, and 2-octynoic acid did not give the desired diketones.

These results prompted us to develop the one-pot synthesis of symmetrical diaryl 1,2-diketones from aryl iodides and propiolic acid. As shown in Table 3, when phenyl iodide and propiolic acid were allowed to react under our optimized conditions [CuI/$Cu(OTf)_2$, base and then addition of HI], neither the desired 1,2-diketone nor diphenylacetylene were formed (entry 1). As a sequential reaction, a palladium catalytic system was first employed to form diphenylacetylene, and then the copper catalytic system with HI was used. When Cs_2CO_3 was used in the first step, benzil was formed 30% yield (entry 2). Changing the base to DBU increased the product yield to 78% yield (entry 3). When the reaction was conducted without copper catalyst in step 2, the desired product was formed, although its yield decreased to 53% (entry 4).

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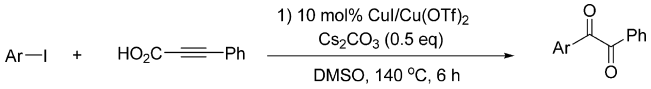
Table 2. Synthesis of 1,2-Diketones from the Coupling of Aryl Iodides and Phenylpropiolic Acid[a]



Entry	Ar-X		Product	Yield (%)
1		**1a**	**3a**	89
2		**1b**	**3b**	65
3		**1c**	**3c**	56
4		**1d**	**3d**	67
5		**1e**	**3e**	75
6		**1f**	**3f**	77
7		**1g**	**3g**	78
8		**1h**	**3h**	86
9		**1i**	**3i**	60(5)[b]
10		**1j**	**3j**	80
11		**1k**	**3k**	60
12		**1l**	**3l**	59
13		**1m**	**3m**	66
14		**1n**	**3n**	54
15		**1o**	**3o**	77
16		**1p**	**3p**	70
17		**1q**	**3q**	65
18		**1r**	**3a**	15
19		**1s**	**3a**	0
20		**1t**	**3a**	0

[a]Reaction conditions: Aryl iodide (3.0 mmol), phenylpropiolic acid (6.0 mmol), CuI (0.3 mmo), $Cu(OTf)_2$ (0.3 mmol), and Cs_2CO_3 (1.5 mmol) were reacted in DMSO (15.0 mL) at 140 °C for 6 h, and then HI (aq) (1.5 mmol) was added and reacted at 140 °C for 6 h. [b]The disubsitututed product was detected by GC–MS.

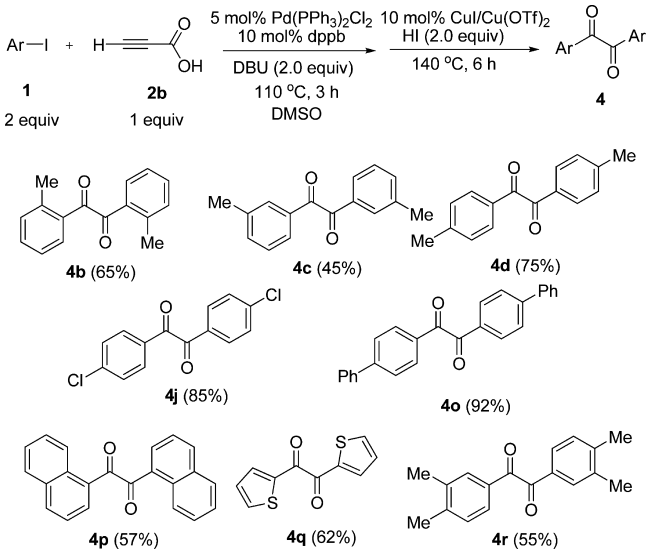
Table 3. Optimization of the Synthesis of Symmetrical Diaryl 1,2-Diketones[a]

entry	step 1	step 2	yield (%)
1	catalyst **A**, Cs_2CO_3, 140 °C, 14 h	HI	–
2	catalyst **B**, Cs_2CO_3, 110 °C, 3 h	catalyst **A**, HI	30
3	catalyst **B**, DBU, 110 °C, 3 h	catalyst **A**, HI	78
4	catalyst **B**, DBU, 110 °C, 3 h	HI	53

[a]Reaction conditions: catalyst **A** = 10 mol % CuI, 10 mol % $Cu(OTf)_2$; catalyst **B** = 5 mol % $Pd(PPh_3)_2Cl_2$, 10 mol % dppb.

To obtain symmetrical diaryl 1,2-diketones, a number of aryl iodides were evaluated under these optimized conditions. As shown in Scheme 2, *o*-, *m*-, and *p*-iodobenzene afforded the corresponding symmetric 1,2-diketones **4b–d** in yields of 65%, 45%, and 75%, respectively. 4-Iodochlorobenzene gave the desired product **4j** in 85% yield. 4-Iodobiphenyl provided 1,2-diketone **4o** in 92% yield. 1-Iodonaphthalene, 2-iodothiophene, and 4-iodo-1,2-dimethylbenzene gave the desired 1,2-diketones in moderate yields. In addition, when a mixture of phenyl iodide and 1-iodo-4-methylbenzene was allowed to react with propiolic acid, symmetrical diketones **3a** and **4d** and unsymmetrical diketone **3d** were formed in yields of 18%, 12%, and 28%, respectively. In addition, when a mixture of phenyl iodide (1.0 equiv) and 1-iodo-4-methylbenzene (1.0 equiv) was allowed to react with propiolic acid (1.0 equiv), symmetrical diketones **3a** and **4d** and unsymmetrical diketone **3d** were formed in yields of 18%, 12% and 28%, respectively.

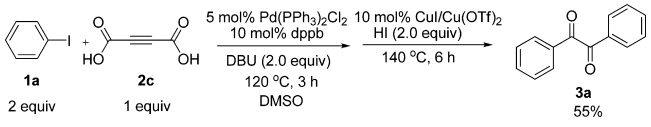
Scheme 2. Synthesis of Symmetrical Diaryl 1,2-Diketones[a]



[a]Reaction conditions: Aryl iodide (6.0 mmol), propiolic acid (3.0 mmol), $Pd(PPh_3)_2Cl_2$, dppb (0.3 mmol), and DBU (6.0 mmol) were reacted in DMSO (10 mL) at 110 °C for 3 h, and then HI (6.0 mmol), CuI (0.3 mmol), and $Cu(OTf)_2$ (0.3 mmol) were added to the reaction mixture and allowed to react at 140 °C for 6 h.

It has been reported that acetylene dicarboxylic acid (**2c**) can be employed as an alkyne source in the decarboxylative coupling reaction.[12b] As shown in Scheme 3, when it was allowed to react with iodobenzene at 120 °C, the desired benzil was obtained in 55% yield.

Scheme 3. Synthesis of Benzil from 2c



To study the reaction pathway and the role of the catalyst and additive, two possible intermediates, diphenylacetylene (**5**) and deoxybenzoin (**6**), were independently tested under a variety of conditions. The results are summarized in Table 4. When only CuI or $Cu(OTf)_2$ was used as a catalyst, **5** led to the oxidized product in 95% yield and **6** afforded a 45% yield of benzil (entries 1 and 2). Neither **5** nor **6** produced the desired product in the presence of base (entries 3 and 4). These results pinpoint that base might inhibit the oxidation process. However, the addition of HI in much greater amounts than

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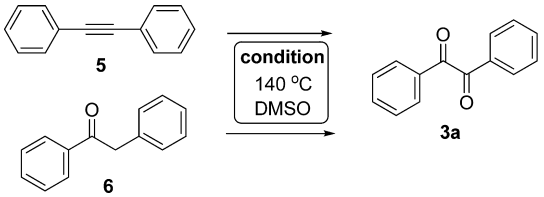
Table 4. Studies of the Synthesis of Benzil from Diphenylacetylene and Deoxybenzoin[a]



entry	substrate	catalyst	additive	yield (%)
1	**5**	CuI/Cu(OTf)$_2$	–	95
2	**6**	CuI/Cu(OTf)$_2$	–	45
3	**5**	CuI/Cu(OTf)$_2$	Cs_2CO_3 (0.5)	–
4	**6**	CuI/Cu(OTf)$_2$	Cs_2CO_3 (0.5)	–
5	**5**	CuI/Cu(OTf)$_2$	Cs_2CO_3/HI(0.5/1.0)	65
6	**6**	CuI/Cu(OTf)$_2$	Cs_2CO_3/HI(0.5/1.0)	83
7	**5**	–	Cs_2CO_3/HI(0.5/1.0)	–
8	**6**	–	Cs_2CO_3/HI(0.5/1.0)	80

[a]Reaction conditions: **4** or **5** (2.0 mmol), CuI (0.2 mmol), Cu(OTf)$_2$ (0.2 mmol), Cs_2CO_3 (0.5 mmol) and/or HI (2.0 mmol) were used. The reaction was conducted in DMSO at 140 °C for 6 h.

the base gave the desired product from both **5** and **6** (entries 5 and 6). Interestingly, **5** did not give benzil in the absence of copper catalyst (entry 7). Without copper catalyst, **6** was oxidized to give the desired product in 80% yield (entry 8).

On the basis of these results, we propose the reaction mechanism shown in Scheme 4. The copper-catalyzed decarboxylative coupling reaction of the aryl iodide and the arylalkynyl carboxylic acid produces the diarylalkyne. Copper reacts with the arylalkynyl carboxylic acid to produce an arylalkynylcopper complex through decarboxylation. A base may accelerate the decarboxlative coupling step. The resulting alkynylcopper complex reacts with aryl iodide to give an arylalkynylcopper complex.[13] After the reductive elimination of the copper complex, the oxidation process proceeds. DMSO works as a solvent and an oxidizing agent.[9e,f] The additional HI may quench the property of base that is an inhibitor in the oxidation step. Two oxidation pathways might be possible: one is the pathway through the deoxybenzoin (path **A**), and the other is the direct oxidation (path **B**). In the direct oxidation pathway, copper works as a catalyst to accelerate the oxidation process. Although we failed to find deoxybenzoin in the reaction mixture, we suggest that both pathways are possible because it has been reported that deoxybenzoin was formed from diphenylacetylene under aqueous acidic conditions at high temperature.[14] In addition, deoxybenzoin was converted to benzil under these optimized conditions.

CONCLUSION

In summary, we have developed an efficient method for the synthesis of diaryl 1,2-diketones from aryl iodides and arylalkynyl carboxylic acids using CuI/Cu(OTf)$_2$ as the catalyst. This methodology does not require an expensive metal catalyst such as palladium. In addition, this is the first example of the direct preparation of benzil from aryl iodides and arylalkynyl carboxylic acids. We suggest that this methodology consists of decarboxylative coupling and subsequent oxidation, both activated by the copper catalyst. The desired diaryl 1,2-diketones were obtained in good yields through sequential addition of base and acid without any need to isolate the intermediate. It was found that the ratio of base to acid is a crucial factor for the sequential reaction and that DMSO works as an oxidant. In addition, we have developed a direct method for the synthesis of symmetrical diaryl 1,2-diketones from aryl iodides and propiolic acid.

EXPERIMENTAL SECTION

General Procedure for the Synthesis of Unsymmetrical Diaryl 1,2-Diketones. Aryl iodide (3.0 mmol), phenylpropiolic acid (877 mg, 6.0 mmol), CuI (58 mg, 0.3 mmol), Cu(OTf)$_2$ (108 mg, 0.3 mmol), Cs_2CO_3 (488 mg, 1.5 mmol), and DMSO (6 mL) were added into a one-neck flask. The flask was sealed, and the mixture was allowed to stir at 140 °C for 15 h. A solution of HI (337 mg, 1.5 mmol, aq. 57 wt %) in DMSO (5 mL) was added to the reaction result cooled to room temperature. The solution was allowed to stir at 140 °C for 6 h. The reaction mixture was poured into ethyl acetate (50.0 mL) and extracted with water saturated with $NaHCO_3$. The organic layer was dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure, and the resulting crude product was purified by flash chromatography on silica gel (eluent = hexane).

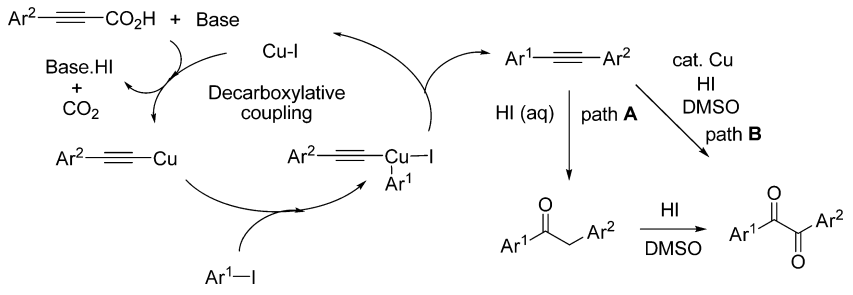
Benzil[15] ***(3a)***. Iodobenzene (612 mg) (**1a**) afforded the product **3a** (561 mg, 2.7 mmol, 89%) as a yellow solid; mp 94–95 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, J = 7.1 Hz, 4H), 7.67 (t, J = 7.4 Hz, 2H), 7.52 (t, J = 7.6 Hz, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.6, 134.9, 132.9, 129.9, 129.0; MS (m/z) 210 (M^+).

1-Phenyl-2-o-tolylethane-1,2-dione[15] ***(3b)***. 1-Iodo-2-methylbenzene (654 mg) (**1b**) afforded the product **3b** (437 mg, 2.0 mmol, 65%) as a yellow solid; mp 55–56 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 7.1 Hz, 2H), 7.68–7.63 (m, 2H), 7.54–7.46 (m, 3H), 7.34 (d, J = 7.7 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 2.71 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 196.7, 194.8, 141.3, 134.7, 133.8, 133.1, 133.0, 132.5, 131.7, 129.9, 129.0, 126.0, 21.9; MS (m/z) 224 (M^+).

1-Phenyl-2-m-tolylethane-1,2-dione[15] ***(3c)***. 1-Iodo-3-methylbenzene (654 mg) (**1c**) afforded the product **3c** (377 mg, 1.7 mmol, 56%) as a yellow solid; mp 56–57 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 7.1 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.54–7.45 (m, 3H), 7.40 (t, J = 7.2 Hz, 1H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.8, 194.7, 139.0, 135.7, 134.8, 133.0, 132.9, 130.2, 129.9, 129.0, 128.9, 127.2, 21.3; MS (m/z) 224 (M^+).

1-Phenyl-2-p-tolylethane-1,2-dione[15] ***(3d)***. 1-Iodo-4-methylbenzene (654 mg) (**1d**) afforded the product **3d** (451 mg, 2.0 mmol,

Scheme 4. Proposed Reaction Pathways



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67%) as a yellow solid; mp 94−95 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.3 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.7, 194.3, 146.2, 134.8, 133.1, 130.6, 130.0, 129.9, 129.7, 129.0, 21.9; MS (m/z) 224 (M^+).

1-(4-tert-Butylphenyl)-2-phenylethane-1,2-dione[16] ***(3e)***. 1-*tert*-Butyl-4-iodobenzene (780 mg) (**1e**) afforded the product **3e** (599 mg, 2.3 mmol, 75%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.3 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 2.44 (s, 9H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.8, 194.3, 159.0, 134.7, 133.1, 130.4, 129.9, 128.9, 129.0, 126.0, 35.4, 31.0; MS (m/z) 266 (M^+).

1-(2-Methoxyphenyl)-2-phenylethane-1,2-dione[9] ***(3f)***. 1-Iodo-2-methoxybenzene (702 mg) (**1f**) afforded the product **3f** (555 mg, 2.3 mmol, 77%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (dd, J = 7.8, 1.5 Hz, 1H), 7.92 (dd, J = 8.4, 1.4 Hz, 2H), 7.64−7.58 (m, 2H), 7.49 (t, J = 7.8 Hz, 2H), 7.13 (ddd, J = 7.8, 7.4, 0.9 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 3.56 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.6, 193.5, 160.4, 136.5, 133.7, 132.8, 130.5, 129.3, 128.7, 123.8, 121.5, 112.3, 55.6; MS (m/z) 240 (M^+).

1-(3-Methoxyphenyl)-2-phenylethane-1,2-dione[9] ***(3g)***. 1-Iodo-3-methoxybenzene (702 mg) (**1g**) afforded the product **3g** (562 mg, 2.3 mmol, 78%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, J = 7.7 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.55−7.46 (m, 4H), 7.39 (t, J = 7.9 Hz, 1H), 7.20 (dd, J = 8.1, 1.6 Hz, 1H), 3.86 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.43, 194.41, 160.0, 134.8, 134.2, 132.9, 130.0, 129.8, 129.0, 123.2, 121.8, 112.8, 55.5; MS (m/z) 240 (M^+).

1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione[9] ***(3h)***. 1-Iodo-4-methoxybenzene (702 mg) (**1h**) afforded the product **3h** (620 mg, 2.6 mmol, 86%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00−7.93 (m, 4H), 7.65 (t, J = 8.1 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.8, 193.1, 165.0, 134.7, 133.2, 132.4, 129.9, 128.9, 126.1, 114.3, 55.6; MS (m/z) 240 (M^+).

1-(4-Iodophenyl)-2-phenylethane-1,2-dione[15] ***(3i)***. 1,4-Diiodobenzene (990 mg) (**1i**) afforded the product **3i** (605 mg, 1.8 mmol, 60%) as a yellow solid; mp 84−85 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, J = 8.6 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H), 7.70−7.65 (m, 3H), 7.52 (t, J = 7.6 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 193.8, 193.6, 138.4, 135.0, 132.7, 132.2 130.9, 129.9, 129.0, 103.6; MS (m/z) 335 (M^+).

1-(4-Chlorophenyl)-2-phenylethane-1,2-dione[15] ***(3j)***. 1-Chloro-4-iodobenzene (715 mg) (**1j**) afforded the product **3j** (587 mg, 2.4 mmol, 80%) as a yellow solid; mp 71−72 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.7 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.48−7.54 (m, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 193.9, 193.1, 141.6, 135.1, 132.7, 131.3, 131.2, 129.9, 129.4, 129.1; MS (m/z) 244 (M^+).

Methyl 4-(2-Oxo-2-phenylacetyl)benzoate[4] ***(3k)***. Methyl 4-iodobenzoate (786 mg) (**1k**) afforded the product **3k** (482 mg, 1.8 mmol, 60%) as a yellow solid; mp 102−103 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 8.8 Hz, 2H), 8.05 (d, J = 8.8 Hz, 2H), 7.98 (d, J = 8.5 Hz, 2H), 7.69 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 8.0 Hz, 2H), 3.96 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 193.8, 193.6, 165.9, 136.0, 135.3, 135.1, 132.7, 130.1, 130.0, 129.8, 129.1, 52.6; MS (m/z) 268 (M^+).

4-(2-Oxo-2-phenylacetyl)benzaldehyde[9] ***(3l)***. 4-Iodobenzaldehyde (696 mg) (**1l**) afforded the product **3l** (422 mg, 1.8 mmol, 59%) as a yellow solid; mp 186−187 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.15 (d, J = 8.2 Hz, 2H), 8.04−7.97 (m, 4H), 7.70 (t, J = 7.4 Hz 1H), 7.54 (t, J = 7.6 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 193.5, 193.4, 191.3, 140.0, 137.0, 135.2, 132.6, 130.4, 129.98, 129.96, 129.1; MS (m/z) 238 (M^+).

4-(2-Oxo-2-phenylacetyl)benzonitrile[9] ***(3m)***. 4-Iodobenzonitrile (687 mg) (**1m**) afforded the product **3m** (466 mg, 2.0 mmol, 66%) as a yellow solid; mp 98−99 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, J = 8.7 Hz, 2H), 7.98 (d, J = 8.5 Hz, 2H), 7.82 (d, J = 8.7 Hz, 2H), 7.71 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)δ 193.0, 192.4, 135.8, 135.4, 132.7, 132.4, 130.2, 130.0, 129.2, 117.9, 117.6; MS (m/z) 235 (M^+).

1-(4-Nitrophenyl)-2-phenylethane-1,2-dione[9] ***(3n)***. 1-Iodo-4-nitrobenzene (747 mg) (**1n**) afforded the product **3n** (413 mg, 1.6 mmol, 54%) as a yellow solid; mp 138−139 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, J = 9.1 Hz, 2H), 8.17 (d, J = 9.1 Hz, 2H), 8.00 (d, J = 8.4 Hz, 2H), 7.72 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 192.8, 192.0, 151.1, 137.3, 135.4, 132.3, 130.9, 130.0, 129.2, 124.1; MS (m/z) 255 (M^+).

1-(Biphenyl-4-yl)-2-phenylethane-1,2-dione[17] ***(3o)***. 4-Iodobiphenyl (840 mg) (**1o**) afforded the product **3o** (661 mg, 2.3 mmol, 77%) as a yellow solid; mp 104−105 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 8.7 Hz, 2H), 8.01 (d, J = 7.8 Hz, 2H), 7.73 (d, J = 8.7 Hz, 2H), 7.68−7.61 (m, 3H), 7.56−7.42 (m, 5H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.5, 194.1, 147.6, 139.5, 134.9, 133.0, 131.7, 130.5, 129.9, 129.0, 128.6, 127.6, 127.3; MS (m/z) 286 (M^+).

1-(Naphthalen-1-yl)-2-phenylethane-1,2-dione[15] ***(3p)***. 1-Iodonaphthalene (762 mg) (**1p**) afforded the product **3p** (547 mg, 2.1 mmol, 70%) as a yellow solid; mp 101−102 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.31 (d, J = 7.9 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 8.03 (d, J = 7.1 Hz, 2H), 7.93 (t, J = 8.1 Hz, 2H), 7.75 (t, J = 7.8 Hz, 1H), 7.69−7.60 (m, 2H), 7.51 (t, J = 7.7 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.1, 194.5, 135.9, 135.0, 134.7, 134.0, 133.3, 130.9, 130.0, 129.4, 129.0, 128.8, 128.6, 127.1, 125.9, 124.4; MS (m/z) 260 (M^+).

1-Phenyl-2-(thiophen-2-yl)ethane-1,2-dione[15] ***(3q)***. 2-Iodothiophene (630 mg) (**1q**) afforded the product **3q** (422 mg, 1.9 mmol, 65%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 7.1 Hz, 2H), 7.84 (dd, J = 4.9, 1.1 Hz, 1H), 7.81 (dd, J = 3.9, 1.1 Hz, 1H), 7.67 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.19 (dd, J = 4.9, 3.9 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 192.0, 185.6, 139.8, 136.9, 136.7, 134.8, 132.6, 130.2, 128.9, 128.8; MS (m/z) 216 (M^+).

General Procedure for the Synthesis of Symmetrical Diaryl 1,2-Diketones. Aryl iodide (6.0 mmol), propiolic acid (210 mg, 3.0 mmol), $Pd(PPh_3)_2Cl_2$ (105 mg, 0.15 mmol), 1,4-bis-(diphenylphosphino)butane (128 mg, 0.3 mmol), DBU (913 mg, 6.0 mmol), and DMSO (10.0 mL) were added into one-neck flask. The flask was sealed, and the mixture was allowed to stir at 110 °C for 3 h. A solution of HI (1348 mg, 6.0 mmol, aq. 57 wt %) in DMSO (5.0 mL), CuI (58 mg, 0.3 mmol), and $Cu(OTf)_2$ (108 mg, 0.3 mmol) were added and then allowed to react at 140 °C for 6 h. The reaction mixture was poured into ethyl ether (50.0 mL), and the resulting mixture was extracted with water saturated with $NaHCO_3$. The organic layer was dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure, and the resulting crude product was purified by flash chromatography on silica gel (eluent = hexane).

1,2-Di-o-tolylethane-1,2-dione[18] ***(4b)***. 1-Iodo-2-methylbenzene (1.31 g) (**1b**) afforded the product **4b** (465 mg, 1.9 mmol, 65%) as a yellow solid; mp 80−81 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (dd, J = 7.8, 1.4 Hz, 2H), 7.48 (td, J = 7.5, 1.4 Hz, 2H), 7.34 (d, J = 7.7 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 2.70 (s, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 196.9, 141.5, 133.6, 133.0, 132.5, 131.7, 126.0, 21.9; MS (m/z) 238 (M^+).

1,2-Di-m-tolylethane-1,2-dione[18] ***(4c)***. 1-Iodo-3-methylbenzene (1.31 g) (**1c**) afforded the product **4c** (322 mg, 1.4 mmol, 45%) as a yellow solid; mp 88−89 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78−7.74 (m, 4H), 7.47 (d, J = 7.9 Hz, 2H), 7.40 (t, J = 7.8 Hz, 2H), 2.41 (s, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 195.0, 139.0, 135.7, 133.0, 130.2, 128.9, 127.2, 21.3; MS (m/z) 238 (M^+).

1,2-Di-p-tolylethane-1,2-dione[18] ***(4d)***. 1-Iodo-4-methylbenzene (1.43 g) (**1d**) afforded the product **4d** (536 mg, 2.3 mmol, 75%) as a yellow solid; mp 103−104 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 8.2 Hz, 4H), 7.30 (d, J = 8.0 Hz, 4H), 2.43 (s, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.5, 146.0, 130.7, 130.0, 129.7, 21.9; MS (m/z) 238 (M^+).

1,2-Bis(4-chlorophenyl)ethane-1,2-dione[18] ***(4j)***. 1-Chloro-4-iodobenzene (1.43 g) (**1j**) afforded the product **4j** (712 mg, 2.6 mmol, 85%) as a yellow solid; mp 196−197 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J = 8.5 Hz, 4H), 7.50 (d, J = 8.5 Hz, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 192.3, 141.8, 131.2, 131.1, 129.5; MS (m/z) 278 (M^+).

1,2-Bis(biphenyl-4-yl)ethane-1,2-dione[19] ***(4o)***. 4-Iodobiphenyl (1.68 g) (**1o**) afforded the product **4o** (1000 mg, 2.8 mmol, 92%)

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as a yellow solid; mp 131−132 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J = 8.7 Hz, 4H), 7.74 (d, J = 8.7 Hz, 4H), 7.63 (d, J = 8.1 Hz, 4H), 7.51−7.40 (m, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.1, 147.6, 139.5, 131.7, 130.5, 129.0, 128.6, 127.7, 127.4; MS (m/z) 362 (M^+).

1,2-Bis(naphthalen-1-yl)ethane-1,2-dione[20] ***(4p)***. 1-Iodonaphthalene (1.52 g) (**1p**) afforded the product **4p** (531 mg, 1.7 mmol, 57%) as a yellow solid; mp 190−191 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.36 (d, J = 8.3 Hz, 2H), 8.13 (d, J = 8.2 Hz, 2H), 8.03 (dd, J = 7.3, 1.1 Hz, 2H), 7.96 (d, J = 8.2 Hz, 2H), 7.76 (ddd, J = 8.5, 6.9, 1.4 Hz, 2H), 7.64 (ddd, J = 8.1, 6.9, 1.1 Hz, 2H), 7.49 (dd, J = 8.1, 7.4 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 196.9, 135.8, 135.1, 134.1, 131.1, 129.4, 128.9, 128.8, 127.1, 126.0. 124.5; MS (m/z) 310 (M^+).

1,2-Bis(thiophen-2-yl)ethane-1,2-dione[15] ***(4q)***. 2-Iodothiophene (1.26 g) (**1q**) afforded the product **4q** (413 mg, 1.9 mmol, 62%) as an orange solid; mp 82−83 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, J = 3.9, 1.2 Hz, 2H), 7.85 (dd, J = 4.9, 1.2 Hz, 2H), 7.21 (dd, J = 4.9, 3.9 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 182.4, 138.6, 137.5, 137.3, 128.6; MS (m/z) 222 (M^+).

1,2-Bis(3,4-dimethylphenyl)ethane-1,2-dione[21] ***(4r)***. 4-Iodo-1,2-dimethylbenzene (1.39 g) (**1r**) afforded the product **4r** (439 mg, 1.6 mmol, 55%) as a yellow solid; mp 115−116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (s, 2H), 7.69 (dd, J = 7.9, 1.8 Hz, 2H), 7.25 (d, J = 7.4 Hz, 2H), 2.34 (s, 6H), 2.30 (s, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.9, 144.8, 137.5, 131.1, 130.8, 130.2, 127.7, 20.3, 19.7; MS (m/z) 266 (M^+).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sunwoo@chonnam.ac.kr.

Notes

The authors declare no competing financial interest.

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