EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201403274

Copper(II)-Promoted C–C Bond Formation by Oxidative Coupling of Two C(sp^3)–H Bonds Adjacent to Carbonyl Group to Construct 1,4-Diketones and Tetrasubstituted Furans

Shuai Mao,[a] Ya-Ru Gao,[a] Shao-Liang Zhang,[a] Dong-Dong Guo,[a] and Yong-Qiang Wang*[a]

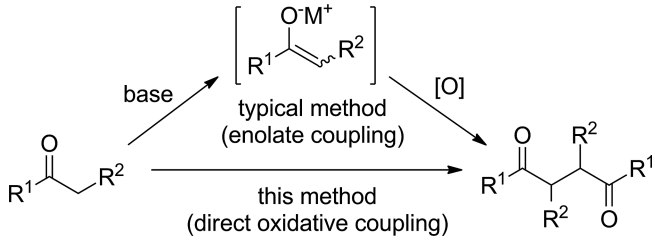
Keywords: Synthetic methods / C–C coupling / Oxidation / Copper / Oxygen heterocycles

The copper(II)-promoted C–C bond formation from the coupling of two C(sp^3)–H bonds that are adjacent to a carbonyl group was achieved. This protocol offers a simple and efficient approach to 2,3-disubstituted 1,4-diketones and tetrasubstituted furans. This method features a wide substrate scope and high functional group tolerance.

Introduction

The formation of a carbon-carbon (C–C) bond from the coupling of two simple carbon-hydrogen (C–H) bonds is of great interest because of its intrinsic advantages with regard to atom-economy and step-economy.[1] In general, this transformation proceeds under transition-metal-mediated oxidative conditions.[2] However, the coupling of two C(sp^3)–H bonds is challenging, as these bonds do not have an empty low-energy orbital or a filled high-energy orbital, and, thus, it is difficult for a metal atom to activate them through an orbital interaction.[3] Although great progress has been made with regard to C–C bond formation from the activation of C(sp^3)–H bonds,[4] the coupling of two C(sp^3)–H bonds adjacent to a carbonyl group has not yet been documented, despite the fact that the carbonyl group plays a particularly important role in organic synthesis.

2,3-Disubstituted 1,4-dicarbonyl compounds are ubiquitous substructures of natural products and pharmaceuticals[5,6] as well as highly useful synthetic building blocks of various carbocyclic and heterocyclic compounds.[7] Generally, the direct and convergent synthesis of 2,3-disubstituted-1,4-dicarbonyl compounds from two carbonyl subunits is extremely difficult. One typical method to synthesize such compounds is by using an enolate coupling reaction. However, this approach suffers from the use of a stoichiometric amount of a strong base [e.g., lithium diisopropylamide (LDA) and sodium hexamethyldisilazide (NaHMDS)] to produce the enolate followed by an oxidative coupling reaction (see Scheme 1).[8] Herein, we report an effective copper(II)-promoted direct oxidative coupling reaction of two C(sp^3)–H bonds that are adjacent to a carbonyl group to produce 2,3-disubstituted 1,4-diketones.



Scheme 1. Synthesis of 1,4-dicarbonyl compounds (M = metal).

Results and Discussion

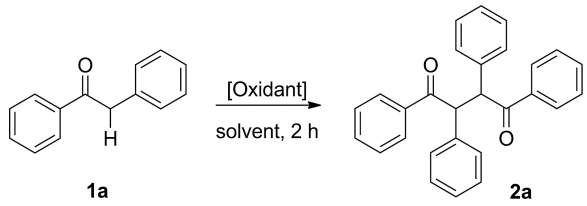
Initially, we utilized deoxybenzoin (**1a**) as a standard substrate to evaluate the coupling of two C(sp^3)–H bonds adjacent to a carbonyl group. We chose copper salts as the oxidant because they are inexpensive, readily available, and easy to handle, and they possess a distinct advantage in oxidative coupling reactions.[9] To our delight, the desired product **2a** was obtained in 35% yield when the reaction was carried out with copper chloride as the oxidant in toluene at reflux (see Table 1, Entry 1). A variety of other oxidants from copper sources were then investigated. The experiments revealed that Cu^{II} species provided better results than Cu^{I} species. $Cu(OAc)_2$ was most effective oxidant and afforded the product in 75% isolated yield (see Table 1, Entries 2–10). After a careful screening, xylene was chosen as the solvent, (see Table 1, Entries 11–15). Finally, hydrated $Cu(OAc)_2$ was as efficient an oxidant as anhydrous

[a] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Department of Chemistry & Materials Science, Northwest University, Xi'an 710069, P.R. China
E-mail: wangyq@nwu.edu.cn
http://www.nwu.edu.cn/

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201403274.

$Cu(OAc)_2$ and afforded **2a** in 90% yield (see Table 1, Entry 16). In contrast, a catalytic amount of either $Cu(OAc)_2$ or $Cu(OAc)_2{\cdot}H_2O$ (e.g., 20 mol-%) led to an incomplete reaction.

Table 1. Optimization of conditions for the oxidative coupling of **1a**.[a]

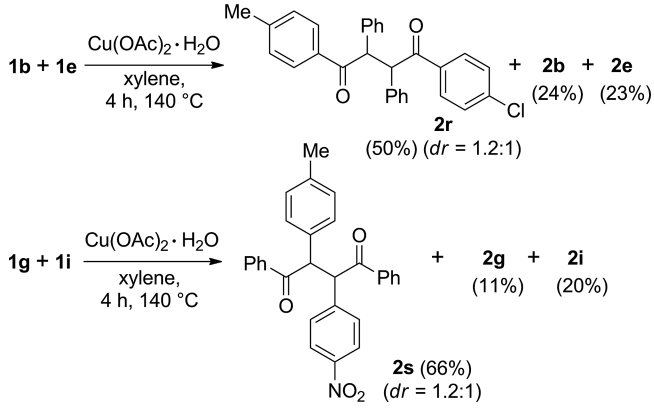


1a **2a**

Entry	Oxidant	Solvent	Yield [%][b]
1	$CuCl_2$	toluene	35
2	$CuBr_2$	toluene	30
3	$Cu(OAc)_2$	toluene	75
4	CuO	toluene	27
5	$Cu(OTf)_2$[c]	toluene	40
6	Cu_2O	toluene	18
7	CuCl	toluene	15
8	CuBr	toluene	16
9	CuI	toluene	10
10	CuOAc	toluene	5
11[d]	$Cu(OAc)_2$	xylene	92
12[d]	$Cu(OAc)_2$	DMF[c]	78
13[d]	$Cu(OAc)_2$	DMSO[c]	60
14[e]	$Cu(OAc)_2$	CH_3CN	0
15[e]	$Cu(OAc)_2$	1,4-dioxane	10
16[d]	$Cu(OAc)_2{\cdot}H_2O$	xylene	90[f]

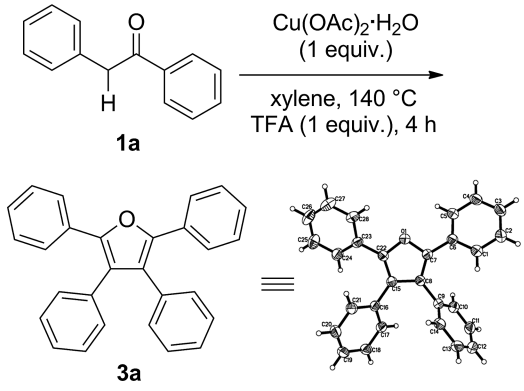
[a] Reagents and conditions: Unless otherwise noted, the reaction was carried out with **1a** (0.5 mmol), oxidant (0.5 mmol), and solvent (1.5 mL) at reflux. [b] Isolated yield. [c] OTf = trifluoromethanesulfonate, DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide. [d] At 140 °C. [e] At reflux temperature. [f] Diastereomeric ratio (*dr*, 0.75:1) was determined by ^1H NMR spectroscopic analysis.

Next, we applied the optimized reaction conditions to investigate other substrates in the copper(II)-promoted oxidative coupling reaction. Pleasingly, all of the reactions proceeded smoothly and afforded the 2,3-disubstituted-1,4-dicarbonyl compounds in good to excellent yields (see Table 2). Various substituents such as the methyl, methoxy, fluoro, chloro, bromo, and nitro group were tolerated under the reaction conditions. The steric hindrance from the substituent on the aromatic group had no effect on the reaction (see Table 2, compounds **2l**–**2n**). In addition, the deoxybenzoin derivative that contained a 4-phenyl group was also suitable for the reaction and provided the desired product in 95% yield (see Table 2, compound **2o**). The structure of the product **2j** was confirmed by single-crystal X-ray analysis.[13] Remarkably, dialkyl ketones, for example, benzyl butyl ketone (**1p**) and 2-bromophenylacetone (**1q**) also were suitable substrates and afforded the corresponding products in excellent yields (see Table 2, compounds **2p** and **2q**). However, 3-pentanone did not provide the desire product (not shown). Substrates that contained electron-withdrawing substituents on either side of the aromatic ring underwent the reaction faster than those that were substituted by electron-donating groups. This difference implies the possibility of a cross-coupling reaction. Consequently, we examined the cross-coupling reactions of **1b** with **1e** and **1g** with **1i** as typical reactions that would provide two different substitution patterns (see Scheme 2). Delightedly, the cross-coupling reactions proceeded well when the substrates with the electron-withdrawing group (i.e., **1e** and **1i**) were added slowly to their corresponding reaction system to provide cross-coupling products **2r** and **2s** in 50 and 66% isolated yield, respectively.



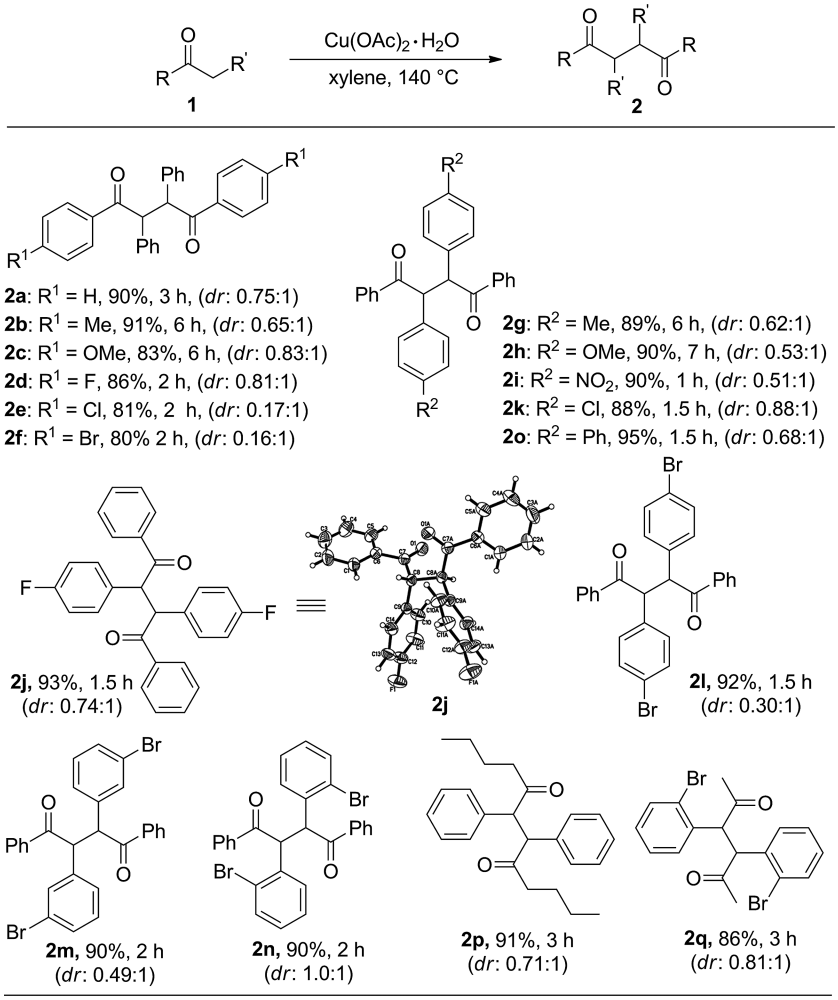
Scheme 2. Cross-coupling reactions.

Surprisingly, when 1.0 equiv. of trifluoroacetic acid (TFA) was introduced into the reaction system of deoxybenzoin (**1a**), we attained tetrasubstituted furan **3a** (confirmed by single-crystal X-ray analysis[13]) in 70% yield (see Scheme 3). Encouraged by this result, we tried to develop a direct method to synthesize polysubstituted furans from ketones in one step. It is well-known that polysubstituted furans are an important class of five-membered heterocycles that are prevalent in natural products, pharmaceuti-



Scheme 3. Synthesis of tetrasubstituted furan **3a**.

Table 2. Scope of substrates for the oxidative coupling reaction.[a–c]



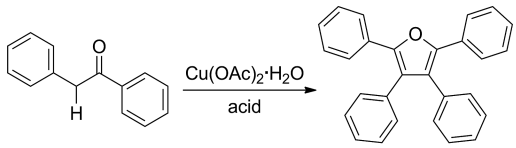
[a] Reagents and conditions: **1** (0.5 mmol), $Cu(OAc)_2·H_2O$ (0.5 mmol), and xylene (1.5 mL) at 140 °C. [b] Isolated yield. [c] Diastereomeric ratios were determined by ^{1}H NMR spectroscopic analysis.

cals, and agrochemicals. In addition, they are useful building blocks in organic synthesis.[10] Accordingly, a new and efficient process for the region-defined synthesis of polysubstituted furans is highly desirable.[11]

We then screened different acids in the reaction system as well as the amount of TFA that was employed (see Table 3, Entries 1–13). These results showed that TFA (1.6 equiv.) gave the best results and afforded **3a** in 87% yield. When the amount of $Cu(OAc)_2·H_2O$ was reduced to 0.5 equiv. and oxygen was employed as the terminal oxidant, **3a** was obtained in 65% yield (see Table 3, Entry 14). This result inspired us to explore a catalytic approach to this process. It has been reported that silver(I) species can promote the oxidation of Cu^I into Cu^{II}.[12] Therefore, a catalytic amount of a variety of silver(I) species were added to the reaction system (see Table 3, Entries 16–19). Ag_2O was shown to be the best additive. When air was used instead of oxygen as the oxidant, the reaction rate and yield decreased (see Table 3, Entry 20). After carefully screening various parameters, $Cu(OAc)_2·H_2O$ (20 mol-%), Ag_2O (10 mol-%), O_2 (1 atm), TFA (1.6 equiv.), and xylene as the solvent at 140 °C were chosen as the optimal reaction conditions.

The optimized conditions were then applied to a broad range of substrates, and the tetrasubstituted furans were efficiently obtained in all cases (see Table 4). Electron-donating and electron-withdrawing groups on both aromatic rings were compatible under the reaction conditions, and these groups were uniformly furnished in the desired products. Carbon-halogen bonds such as C–F, C–Cl, C–Br, and C–I were well-tolerated in the reaction system and provided the possibility for further functionalization of the polysubstituted furans, enabling these products to be used as core structures for polymers and functional materials. Dialkyl

Table 3. Optimization of conditions for the synthesis of tetrasubstituted furan.[a]



1a 3a

Entry	Oxidant [equiv.]	Acid [equiv.]	Additive	Yield [%][b]
1	$Cu(OAc)_2·H_2O$ (1.0)	TFA (1.0)	–	70
2	$Cu(OAc)_2·H_2O$ (1.0)	HCO_2H (1.0)	–	50
3	$Cu(OAc)_2·H_2O$ (1.0)	CH_3COOH (1.0)	–	41
4	$Cu(OAc)_2·H_2O$ (1.0)	PhCOOH (1.0)	–	13
5	$Cu(OAc)_2·H_2O$ (1.0)	TsOH (1.0)[c]	–	47
6	$Cu(OAc)_2·H_2O$ (1.0)	H_3BO_3 (1.0)	–	18
7	$Cu(OAc)_2·H_2O$ (1.0)	$CH_2(COOH)_2$ (1.0)	–	35
8	$Cu(OAc)_2·H_2O$ (1.0)	maleic acid (1.0)	–	4
9	$Cu(OAc)_2·H_2O$ (1.0)	fumaric acid (1.0)	–	6
10	$Cu(OAc)_2·H_2O$ (1.0)	TFA (0.4)	–	30
11	$Cu(OAc)_2·H_2O$ (1.0)	TFA (0.8)	–	58
12	$Cu(OAc)_2·H_2O$ (1.0)	TFA (1.6)	–	87
13	$Cu(OAc)_2·H_2O$ (1.0)	TFA (2.0)	–	85
14[d]	$Cu(OAc)_2·H_2O$ (0.5)	TFA (1.6)	–	65
15[d]	$Cu(OAc)_2·H_2O$ (0.2)	TFA (1.6)	–	40
16[d]	$Cu(OAc)_2·H_2O$ (0.2)	TFA (1.6)	Ag_2O	85
17[d]	$Cu(OAc)_2·H_2O$ (0.2)	TFA (1.6)	$AgNO_3$	58
18[d]	$Cu(OAc)_2·H_2O$ (0.2)	TFA (1.6)	Ag_2CO_3	66
19[d]	$Cu(OAc)_2·H_2O$ (0.2)	TFA (1.6)	AgOAc	78
20	$Cu(OAc)_2·H_2O$ (0.2)	TFA (1.6)	Ag_2O	70

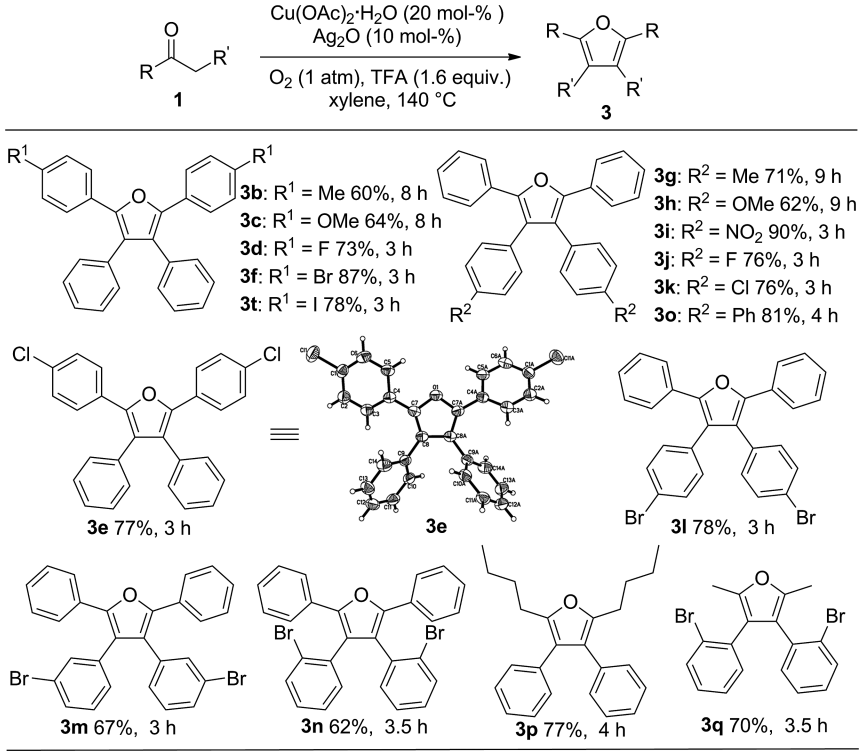
[a] Reagents and conditions: **1a** (0.5 mmol), $Cu(OAc)_2·H_2O$, acid, additive (0.05 mmol), and xylene (1.5 mL) at 140 °C under air (1 atm). [b] Isolated yield. [c] TsOH = *p*-toluenesulfonic acid. [d] Under O_2 (1 atm). [e] Under air (1 atm).

ketones also provided the desired products in good yields (see Table 4, compounds **3p** and **3q**), whereas 3-pentanone was unsuccessful. The structure of the product **3e** was confirmed by single-crystal X-ray analysis.[13]

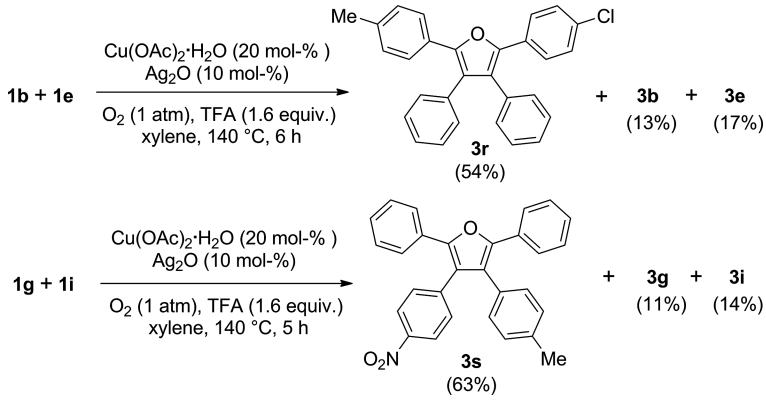
Finally, we investigated the corresponding cross-coupling reaction (see Scheme 4). Two typical reactions were examined. The substrates with an electron-withdrawing substituent, **1e** and **1i**, were added to the standard reaction systems of **1b** and **1g**, respectively, to afford the corresponding cross-coupling products in good yields.

A single-electron transfer (SET) is an obvious consideration with regard to the mechanism of the copper-promoted oxidative coupling reaction.[9] To gain insight into the mechanism, a radical-trapping experiment was carried out. The radical inhibitor TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) was introduced into the standard reaction system of deoxybenzoin (**1a**, see Scheme 5). The oxidative coupling reaction did not occur. Instead, the coupling reaction of deoxybenzoin (**1a**) with TEMPO occurred, and **4a** was produced in 40% yield. The structure of **4a** was confirmed by single-crystal X-ray analysis.[13] Thus, a possible mechanism is proposed in Scheme 6. Substrate **1** undergoes an oxidative SET by the reduction of Cu^{II} and deprotonation to generate carbonyl alkyl radical **A** followed by the coupling reaction with the other partner to give 1,4-dicarbonyl product **2**. Under acid conditions, **2** then produces tetrasubstituted furan **3**. Cu^{I} is then oxidized by Ag_2O/O_2 to regenerate Cu^{II}.[12]

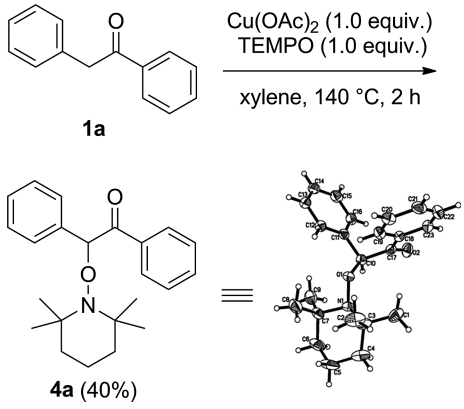
Table 4. Scope of substrates for the synthesis of tetrasubstituted furans.[a,b]



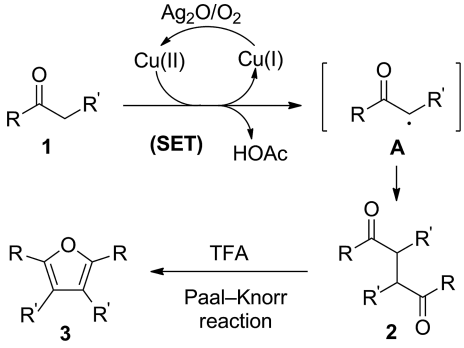
[a] Reagents and conditions: Unless otherwise noted, the reaction was carried out with **1** (0.5 mmol), $Cu(OAc)_2·H_2O$ (20 mol-%), Ag_2O (10 mol-%), O_2(1 atm), and TFA (1.6 equiv.) in xylene (1.5 mL) at 140 °C. [b] Isolated yield.



Scheme 4. Synthesis of tetrasubstituted furans by cross-coupling reactions.



Scheme 5. Radical-trapping experiment.



Scheme 6. Proposed mechanism.

Conclusions

In summary, we have developed the coupling of two C(sp^3)–H bonds that are adjacent to a carbonyl group to provide direct and efficient access to 2,3-disubstituted-1,4-dicarbonyl compounds. In addition, an unusually simple approach to produce tetrasubstituted furans directly from ketones was achieved by using the copper-catalyzed oxidative coupling reaction with oxygen as a terminal oxidant. The two economic approaches feature a wide substrate scope and a high functional group tolerance. Tentative mechanistic studies suggest that the coupling reaction is likely to proceed through a single-electron transfer (SET) process. Further mechanistic studies and applications of these approaches are in progress.

Experimental Section

General Methods: All reactions were carried out under oxygen or air. All reagents and solvents were obtained from commercial suppliers and used without further purification. The progress of the reactions was monitored by TLC with silica gel plates (GF254), and the visualization was carried out under UV light. The ^{1}H and the ^{13}C NMR spectroscopic data were recorded with a Varian Unity Inova-400 spectrometer (^{1}H and ^{13}C NMR at 400 and 100 MHz, respectively). $CDCl_3$ was used as the NMR solvent, unless otherwise noted. Infrared (IR) data were recorded as films on potassium bromide plates with a Bruker Tensor 27 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). High resolution mass spectra were acquired with a Bruker Daltonics MicroTof-Q II mass spectrometer. X-ray crystal structure analyses were measured on a Bruker Smart APEXIICCD instrument using Mo-K_α radiation. The structures were solved and refined by using the SHELXTL software package.

Typical Procedure for the Synthesis of 1,4-Diketone: A mixture of deoxybenzoin (**1a**, 1.0 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (1.0 mmol) in xylene (3 mL) was stirred at 140 °C. Upon completion of the reaction, the mixture was cooled to room temp. and filtered through a small pad of silica gel. The filtrate was concentrated in vacuo, and the residue was purified by chromatography on a silica gel column to afford product **2a**.

1,2,3,4-Tetraphenylbutane-1,4-dione (2a):[14] White solid (90% isolated yield; *dr* 0.75:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, J = 8.0 Hz, 4 H, C_6H_5), 7.43 (d, J = 8.0 Hz, 2 H, C_6H_5), 7.35 (t, J = 6.0 Hz, 4 H, C_6H_5), 7.09 (s, 6 H, C_6H_5), 7.02 (d, J = 5.3 Hz, 4 H, C_6H_5), 5.40 (s, 2 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.5, 136.4, 136.4, 133.0, 129.0, 128.9, 128.7, 128.5, 127.3, 58.5 ppm. HRMS (ESI): calcd. for $C_{28}H_{22}O_2Na$ [M + Na]$^+$ 413.1512; found 413.1517.

2,3-Diphenyl-1,4-di-*p*-tolylbutane-1,4-dione (2b):[15] White solid (91% isolated yield; *dr* 0.65:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.0 Hz, 4 H, H-Ar), 7.53 (d, J = 4.0 Hz, 4 H, H-Ar), 7.18 (d, J = 8.0 Hz, 4 H, H-Ar), 7.13–7.08 (m, 6 H, H-Ar), 5.77 (s, 2 H, CH), 2.30 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.1, 143.9, 137.2, 134.4, 129.2, 129.1, 128.8, 128.7, 127.3, 55.9, 21.6 ppm.

1,4-Bis(4-methoxyphenyl)-2,3-diphenylbutane-1,4-dione (2c):[16] White solid (83% isolated yield; *dr* 0.83:1). ^{1}H NMR (400 MHz,

$CDCl_3$): δ = 7.98 (d, J = 8.0 Hz, 4 H, H-Ar), 7.10 (d, J = 8.0 Hz, 6 H, H-Ar), 7.01 (d, J = 8.0 Hz, 4 H, H-Ar), 6.84 (d, J = 8.0 Hz, 4 H, H-Ar), 5.34 (s, 2 H, CH), 3.80 (s, 6 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.9, 163.3, 137.0, 131.3, 129.5, 128.8, 128.6, 127.1, 113.7, 58.1, 55.5 ppm.

1,4-Bis(4-fluorophenyl)-2,3-diphenylbutane-1,4-dione (2d): White solid (86% isolated yield; *dr* 0.81:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (s, 4 H, H-Ar), 7.12 (s, 6 H, H-Ar), 7.04 (t, J = 10.0 Hz, 4 H, H-Ar), 6.99 (s, 4 H, H-Ar), 5.31 (s, 2 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.0, 165.7 (d, $J_{F,C}$ = 250 Hz), 136.1, 132.8 (d, $J_{F,C}$ = 3.0 Hz), 131.6 (d, $J_{F,C}$ = 9.0 Hz), 128.84, 128.76, 127.5, 115.7 (d, $J_{F,C}$ = 22.0 Hz), 58.5 ppm. IR (KBr): $\tilde{\nu}$ = 3065, 3032, 2927, 2854, 1672, 1596, 1232, 1155, 860, 842, 738, 700 cm^{-1}. HRMS (ESI): calcd. for $C_{28}H_{20}F_2O_2Na$ $[M + Na]^+$ 449.1324; found 449.1332.

1,4-Bis(4-chlorophenyl)-2,3-diphenylbutane-1,4-dione (2e):[17] White solid (81% isolated yield; *dr* 0.17:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, J = 8.0 Hz, 4 H, H-Ar), 7.34 (d, J = 8.0 Hz, 4 H, H-Ar), 7.12 (s, 6 H, H-Ar), 6.97 (s, 4 H, H-Ar), 5.29 (s, 2 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.1, 139.7, 136.5, 135.1, 129.9, 129.0, 128.91, 127.7, 56.3 ppm.

1,4-Bis(4-bromophenyl)-2,3-diphenylbutane-1,4-dione (2f): White solid (80% isolated yield; *dr* 0.16:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, J = 8.0 Hz, 4 H, H-Ar), 7.46 (d, J = 8.0 Hz, 4 H, H-Ar), 7.10 (s, 6 H, H-Ar), 6.97 (s, 4 H, H-Ar), 5.31 (s, 2 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.4, 135.8, 135.0, 131.8, 130.4, 128.8, 128.7, 128.2, 127.5, 58.4 ppm. IR (KBr): $\tilde{\nu}$ = 3057, 3031, 2924, 2853, 1665, 1585, 1564, 1485, 1453, 1253, 1205, 1174, 1071, 1008, 850, 821, 800, 728, 705 cm^{-1}. HRMS (ESI): calcd. for $C_{28}H_{21}Br_2O_2$ $[M + H]^+$ 546.9903; found 546.9905.

1,4-Diphenyl-2,3-di-*p*-tolylbutane-1,4-dione (2g):[14] White solid (89% isolated yield; *dr* 0.62:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, J = 8.0 Hz, 4 H, H-Ar), 7.42 (d, J = 8.0 Hz, 6 H, H-Ar), 7.32 (t, J = 8.0 Hz, 4 H, H-Ar), 7.01 (d, J = 8.0 Hz, 4 H, H-Ar), 5.75 (s, 2 H, CH), 2.17 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.5, 137.0, 136.9, 134.0, 132.9, 129.6, 129.0, 128.6, 128.5, 55.7, 21.0 ppm. HRMS (ESI): calcd. for $C_{30}H_{26}O_2Na$ $[M + Na]^+$ 441.1825; found 441.1825.

2,3-Bis(4-methoxyphenyl)-1,4-diphenylbutane-1,4-dione (2h):[14] White solid (90% isolated yield; *dr* 0.53:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 4.0 Hz, 4 H, H-Ar), 7.45 (d, J = 8.0 Hz, 2 H, H-Ar), 7.36 (t, J = 6.0 Hz, 4 H, H-Ar), 6.93 (d, J = 8.0 Hz, 4 H, H-Ar), 6.67 (d, J = 8.0 Hz, 4 H, H-Ar), 5.30 (s, 2 H, CH), 3.70 (s, 6 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.9, 158.6, 136.5, 132.9, 130.2, 129.9, 128.9, 128.5, 114.1, 57.7, 55.1 ppm.

2,3-Bis(4-nitrophenyl)-1,4-diphenylbutane-1,4-dione (2i):[18] White solid (90% isolated yield; *dr* 0.51:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, J = 8.0 Hz, 2 H, H-Ar), 7.98 (d, J = 8.0 Hz, 4 H, H-Ar), 7.91 (d, J = 4.0 Hz, 4 H, H-Ar), 7.80 (d, J = 8.0 Hz, 2 H, H-Ar), 7.69 (d, J = 12.0 Hz, 2 H, H-Ar), 7.51–7.44 (m, 5 H, H-Ar), 7.39–7.31 (m, 8.2 H, H-Ar), 7.22 (s, 9 H, H-Ar), 5.84 (s, 1 H, CH), 5.56 (s, 2 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.6, 196.8, 147.4, 143.6, 143.2, 135.8, 135.5, 134.2, 133.9, 130.1, 129.6, 129.00, 128.97, 128.9, 128.6, 124.3, 124.2, 57.7, 56.0 ppm. HRMS (ESI): calcd. for $C_{28}H_{20}N_2O_6Na$ $[M + Na]^+$ 503.1214; found 503.1217.

2,3-Bis(4-fluorophenyl)-1,4-diphenylbutane-1,4-dione (2j): White solid (93% isolated yield; *dr* 0.74:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 8.0 Hz, 4 H, H-Ar), 7.86 (d, J = 8.0 Hz, 3 H, H-Ar), 7.51 (t, J = 6.0 Hz, 4 H, H-Ar), 7.45 (d, J = 8.0 Hz, 3 H, H-Ar), 7.32–7.39 (m, 7 H, H-Ar), 6.99 (t, J = 6.0 Hz, 4 H, H-Ar), 6.90 (q, J = 8.0 Hz, 3 H, H-Ar), 6.84 (t, J = 8.0 Hz, 4 H, H-Ar), 5.72 (s, 1.5 H, CH), 5.36 (s, 2 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, major isomer): δ = 199.3, 162.0 (d, $J_{F,C}$ = 245 Hz), 136.1, 133.2, 132.1 (d, $J_{F,C}$ = 3.0 Hz), 130.3 (d, $J_{F,C}$ = 8.0 Hz), 128.9, 128.6, 116.0, 57.6 ppm. ^{13}C NMR (100 MHz, $CDCl_3$, minor isomer): δ = 198.3, 162.1 (d, $J_{F,C}$ = 245 Hz), 136.6, 133.3, 132.5 (d, $J_{F,C}$ = 3.0 Hz), 130.7 (d, $J_{F,C}$ = 8.0 Hz), 128.7, 128.5, 115.8, 55.4 ppm. IR (KBr): $\tilde{\nu}$ = 3069, 2924, 1670, 1598, 1578, 1508, 1449, 1377, 1323, 1291, 1225, 1160, 1099, 1013, 938, 814, 750, 690 cm^{-1}. HRMS (ESI): calcd. for $C_{28}H_{20}F_2O_2Na$ $[M + Na]^+$ 449.1324; found 449.1338.

2,3-Bis(4-chlorophenyl)-1,4-diphenylbutane-1,4-dione (2k):[14] White solid (88% isolated yield; *dr* 0.88:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.0 Hz, 4 H, H-Ar), 7.84 (d, J = 8.0 Hz, 3.6 H, H-Ar), 7.50–7.42 (m, 7.7 H, H-Ar), 7.40–7.32 (m, 7.7 H, H-Ar), 7.18 (d, J = 8.0 Hz, 3.6 H, H-Ar), 7.12 (d, J = 8.0 Hz, 4 H, H-Ar), 6.96 (d, J = 8.0 Hz, 3.8 H, H-Ar), 5.70 (s, 1.7 H, CH), 5.34 (s, 2 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.9, 197.9, 136.5, 136.0, 135.2, 134.7, 133.6, 133.52, 133.47, 133.3, 130.4, 130.1, 129.2, 129.2, 128.9, 128.72, 128.66, 128.5, 57.6, 55.5 ppm.

2,3-Bis(4-bromophenyl)-1,4-diphenylbutane-1,4-dione (2l):[19] White solid (92% isolated yield; *dr* 0.30:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.0 Hz, 4 H, H-Ar), 7.44 (d, J = 8.0 Hz, 2 H, H-Ar), 7.34 (t, J = 8.0 Hz, 4 H, H-Ar), 7.25 (d, J = 8.0 Hz, 4 H, H-Ar), 6.89 (d, J = 8.0 Hz, 4 H, H-Ar), 5.32 (s, 2 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.8, 136.0, 135.2, 133.3, 132.1, 130.4, 128.9, 128.6, 121.7, 57.6 ppm.

2,3-Bis(3-bromophenyl)-1,4-diphenylbutane-1,4-dione (2m): White solid (90% isolated yield; *dr* 0.49:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 8.0 Hz, 4 H, H-Ar), 7.46 (t, J = 6.0 Hz, 2 H, H-Ar), 7.37 (t, J = 6.0 Hz, 4 H, H-Ar), 7.26–7.23 (m, 4 H, H-Ar), 7.01–6.97 (m, 2 H, H-Ar), 6.93 (d, J = 7.0 Hz, 2 H, H-Ar), 5.34 (s, 2 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.5, 138.3, 135.9, 133.4, 131.4, 130.7, 130.4, 128.9, 128.6, 127.6, 122.8, 57.8 ppm. IR (KBr): $\tilde{\nu}$ = 3056, 2925, 1668, 1593, 1576, 1473, 1447, 1425, 1285, 1250, 1200, 1178, 1074, 1006, 972, 780, 713, 686 cm^{-1}. HRMS (ESI): calcd. for $C_{28}H_{20}Br_2O_2Na$ $[M + Na]^+$ 568.9722; found 568.9699.

2,3-Bis(2-bromophenyl)-1,4-diphenylbutane-1,4-dione (2n): White solid (90% isolated yield; *dr* 1.0:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 8.0 Hz, 4 H, H-Ar), 7.96 (d, J = 8.0 Hz, 3 H, H-Ar), 7.62 (t, J = 10.0 Hz, 4 H, H-Ar), 7.47–7.39 (m, 10 H, H-Ar), 7.31 (t, J = 8.0 Hz, 6 H, H-Ar), 7.18–7.13 (m, 4 H, H-Ar), 6.98–6.94 (m, 4 H, H-Ar), 6.19 (s, 1.5 H, CH), 6.11 (s, 2 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.0, 198.0, 136.7, 135.9, 135.7, 134.1, 133.4, 133.3, 133.2, 133.1, 131.5, 130.4, 129.2, 129.1, 128.9, 128.8, 128.6, 128.4, 127.8, 127.6, 125.8, 125.4, 55.2, 54.3 ppm. IR (KBr): $\tilde{\nu}$ = 3060, 2958, 2851, 1673, 1595, 1469, 1445, 1285, 1249, 1202, 1023, 1003, 973, 749, 703, 687 cm^{-1}. HRMS (ESI): calcd. for $C_{28}H_{21}Br_2O_2$ $[M + H]^+$ 546.9903; found 546.9908.

2,3-Di(biphenyl-4-yl)-1,4-diphenylbutane-1,4-dione (2o): White solid (95% isolated yield; *dr* 0.68:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, J = 8.0 Hz, 4 H, H-Ar), 7.48 (s, 6.7 H, H-Ar), 7.38 (d, J = 8.0 Hz, 12.5 H, H-Ar), 7.32–7.22 (m, 3.6 H, H-Ar), 7.13 (d, J = 8.0 Hz, 4 H, H-Ar), 5.48 (s, 2 H, CH), 5.28 (s, 1.3 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.5, 140.3, 139.9, 136.4, 135.4, 133.1, 129.3, 129.0, 128.8, 128.6, 127.4, 126.9, 58.1 ppm. IR (KBr): $\tilde{\nu}$ = 3060, 3029, 2922, 2853, 1665, 1597, 1579, 1486, 1447, 1280, 1247, 1176, 1009, 842, 815, 764, 693 cm^{-1}. HRMS (ESI): calcd. for $C_{40}H_{30}NaO_2$ $[M + Na]^+$ 565.2138; found 565.2143.

6,7-Diphenyldodecane-5,8-dione (2p): White solid (91% isolated yield; *dr* 0.71:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.0 Hz, 4 H, C_6H_5), 7.31 (t, J = 8.0 Hz, 4 H, C_6H_5), 7.27–7.21 (m, 2 H, C_6H_5), 4.61 (s, 2 H, CH), 2.32–2.20 (m, 2 H, CH_2), 2.11–1.99 (m, 2 H, CH_2), 1.29–1.10 (m, 4 H, CH_2), 0.93–0.85 (m, 4 H, CH_2), 0.64 (t, J = 8.0 Hz, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.7, 136.6, 129.0, 128.8, 127.6, 60.6, 43.2, 25.3, 21.8, 13.7 ppm. IR (KBr): $\tilde{\nu}$ = 3061, 2957, 2869, 1710, 1600, 1495, 1457, 1368, 1239, 1126, 1043, 747, 702 cm^{-1}. HRMS (ESI): calcd. for $C_{24}H_{30}O_2Na$ [M + Na]$^+$ 373.2138; found 373.2134.

3,4-Bis(2-bromophenyl)hexane-2,5-dione (2q): White solid (86% isolated yield; *dr* 0.81:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, J = 8.0 Hz, 2 H, C_6H_4), 7.42 (d, J = 8.0 Hz, 2 H, C_6H_4), 7.31 (t, J = 8.0 Hz, 2 H, C_6H_4), 7.14 (t, J = 8.0 Hz, 2 H, C_6H_4), 5.31 (s, 2 H, CH), 1.96 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.9, 135.8, 133.7, 129.3, 128.8, 128.1, 126.5, 58.8, 30.5 ppm. IR (KBr): $\tilde{\nu}$ = 3053, 2917, 2850, 1702, 1555, 1463, 1415, 1350, 1262, 1214, 1145, 1018, 953, 748, 661, 627, 538, 475 cm^{-1}. HRMS (ESI): calcd. for $C_{24}H_{30}O_2Na$ [M + Na]$^+$ 444.9409; found 444.9424.

Typical Procedure for the Synthesis of 1,4-Diketone by Using a Cross-Coupling Reaction: A solution of **1b** (0.5 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (1.0 mmol) in xylene (1.5 mL) was stirred at 140 °C. A solution of **1e** (0.5 mmol) in xylene (1.5 mL) was then slowly added to the mixture. The progress of the reaction was monitored by TLC analysis. When the reaction reached completion, the crude mixture was cooled to room temperature and filtered through a small pad of silica gel. The filtrate was concentrated in vacuo, and the residue was purified by chromatography on a silica gel column to afford product **2r**.

1-(4-Chlorophenyl)-2,3-diphenyl-4-*p*-tolylbutane-1,4-dione (2r): White solid (50% isolated yield; *dr* 1.2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.87 (m, 8 H, H-Ar), 7.77 (d, J = 8.0 Hz, 2 H, H-Ar), 7.31–7.25 (m, 6 H, H-Ar), 7.19–7.16 (m, 2 H, H-Ar), 7.15–7.11 (m, 6 H, H-Ar), 7.09–7.06 (m, 6 H, H-Ar), 7.00 (s, 6 H, H-Ar), 5.35 (s, 2 H, CH), 5.33 (s, 2 H, CH), 2.31 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.9, 198.3, 143.8, 139.2, 136.5, 136.1, 134.8, 133.7, 131.4, 130.3, 129.7, 129.2, 129.1, 128.9, 128.8, 128.7, 127.4, 127.2, 58.4, 21.6 ppm. IR (KBr): $\tilde{\nu}$ = 3029, 2922, 2854, 1665, 1568, 1489, 1453, 1399, 1289, 1256, 1172, 1090, 1007, 847, 810, 737, 699 cm^{-1}. HRMS (ESI): calcd. for $C_{29}H_{24}ClO_2$ [M + H]$^+$ 439.1459; found 439.1459.

2-(4-Nitrophenyl)-1,4-diphenyl-3-*p*-tolylbutane-1,4-dione (2s): White solid (66% isolated yield; *dr* 1.2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00–7.95 (d, J = 8.0 Hz, 10 H, H-Ar), 7.50–7.44 (m, 4 H, H-Ar), 7.42–7.34 (m, 10 H, H-Ar), 7.26–7.20 (m, 4 H, H-Ar), 6.94–6.91 (m, 8 H, H-Ar), 5.54 (d, J = 8.0 Hz, 2 H, CH), 5.39 (d, J = 8.0 Hz, 2 H, CH), 2.20 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.7, 198.6, 147.1, 144.3, 137.5, 136.0, 133.5, 133.2, 132.4, 129.8, 129.7, 129.0, 128.9, 128.7, 128.6, 128.5, 128.5, 58.1, 57.8, 21.1, 21.0 ppm. IR (KBr): $\tilde{\nu}$ = 3061, 2923, 2855, 1918, 1743, 1680, 1599, 1516, 1455, 1343, 1202, 1106, 997, 583, 807, 759, 691, 569 cm^{-1}. HRMS (ESI): calcd. for $C_{29}H_{23}NO_4Na$ [M + Na]$^+$ 472.1519; found 472.1522.

Typical Procedure for the Synthesis of Tetrasubstituted Furans: Deoxybenzoin (**1a**, 1.0 mmol), Ag_2O (23.2 mg, 0.1 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (39.8 mg, 0.2 mmol) were added to a round-bottom flask (10 mL), and then xylene (3 mL) and TFA (0.12 mL, 1.6 mmol) were added to the mixture. The flask was evacuated and backfilled with O_2, and the reaction mixture was stirred at 140 °C. Upon completion of the reaction, the mixture was cooled, and the solvent was evaporated in vacuo. The residue was purified by chromatography on a silica gel column to afford product **3a**.

2,3,4,5-Tetraphenylfuran (3a):[20] White solid (85% isolated yield); m.p. 170–171 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, J = 4.0 Hz, 4 H, C_6H_5), 7.27–7.23 (m, 12 H, C_6H_5), 7.16 (s, 4 H, C_6H_5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 133.2, 130.9, 130.5, 128.4, 128.4, 127.4, 127.2, 125.9, 125.2 ppm. HRMS (ESI): calcd. for $C_{28}H_{20}ONa$ [M + Na]$^+$ 395.1406; found 395.1405.

3,4-Diphenyl-2,5-di-*p*-tolylfuran (3b):[21] White solid (60% isolated yield); m.p. 154–155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, J = 8.0 Hz, 4 H, H-Ar), 7.18 (s, 6 H, H-Ar), 7.11 (s, 4 H, H-Ar), 7.03 (d, J = 8.0 Hz, 4 H, H-Ar), 2.27 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.7, 137.1, 133.4, 130.5, 129.1, 128.4, 128.3, 127.1, 125.9, 124.4, 21.4 ppm. HRMS (ESI): calcd. for $C_{30}H_{24}ONa$ [M + Na]$^+$ 423.1719; found 423.1726.

2,5-Bis(4-methoxyphenyl)-3,4-diphenylfuran (3c):[15] White solid (64% isolated yield); m.p. 123–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, J = 8.0 Hz, 4 H, H-Ar), 7.13 (s, 6 H, H-Ar), 7.06 (s, 4 H, H-Ar), 6.71 (d, J = 8.0 Hz, 4 H, H-Ar), 3.68 (s, 6 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 147.4, 133.5, 130.5, 128.4, 127.3, 127.0, 123.9, 123.5, 113.9, 55.3 ppm.

2,5-Bis(4-fluorophenyl)-3,4-diphenylfuran (3d):[22] Red solid (73% isolated yield); m.p. 173–174 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.43 (m, 4 H, H-Ar), 7.22 (s, 6 H, H-Ar), 7.12 (s, 4 H, H-Ar), 6.96 (t, J = 8.0 Hz, 4 H, H-Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1 (d, $J_{F,C}$ = 246 Hz), 147.0, 132.9, 130.3, 128.6, 127.7 (d, $J_{F,C}$ = 8.0 Hz), 127.4, 127.1 (d, $J_{F,C}$ = 3.0 Hz), 124.7, 115.5 (d, $J_{F,C}$ = 21 Hz) ppm. HRMS (ESI): calcd. for $C_{28}H_{18}F_2ONa$ [M + Na]$^+$ 431.1218; found 431.1214.

2,5-Bis(4-chlorophenyl)-3,4-diphenylfuran (3e):[23] White solid (77% isolated yield); m.p. 155–156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, J = 12.0 Hz, 4 H, H-Ar), 7.27–7.23 (m, 10 H, H-Ar), 7.18–7.13 (m, 4 H, H-Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.0, 133.2, 132.6, 130.3, 129.2, 128.7, 128.6, 127.5, 127.0, 125.6 ppm. HRMS (ESI): calcd. for $C_{28}H_{19}Cl_2O$ [M + H]$^+$ 441.0807; found 441.0811.

2,5-Bis(4-bromophenyl)-3,4-diphenylfuran (3f):[24] White solid (87% isolated yield); m.p. 190–191 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (q, J = 8.0 Hz, 8 H, H-Ar), 7.26 (s, 6 H, H-Ar), 7.13 (d, J = 4.0 Hz, 4 H, H-Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.0, 132.6, 131.6, 130.2, 129.6, 128.6, 127.6, 127.3, 125.8, 121.5 ppm. HRMS (ESI): calcd. for $C_{28}H_{18}Br_2ONa$ [M + Na]$^+$ 550.9617; found 550.9618.

2,5-Diphenyl-3,4-di-*p*-tolylfuran (3g):[25] White solid (71% isolated yield); m.p. 174–175 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.0 Hz, 4 H, H-Ar), 7.18 (t, J = 8.0 Hz, 4 H, H-Ar), 7.12 (d, J = 4.0 Hz, 2 H, H-Ar), 6.97 (s, 8 H, H-Ar), 2.24 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.6, 136.7, 131.1, 130.3, 130.2, 129.2, 128.4, 127.2, 125.9, 125.2, 21.4 ppm. HRMS (ESI): calcd. for $C_{30}H_{24}ONa$ [M + Na]$^+$ 423.1719; found 423.1723.

3,4-Bis(4-methoxyphenyl)-2,5-diphenylfuran (3h):[26] Colorless gum (62% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, J = 8.0 Hz, 4 H, H-Ar), 7.27 (t, J = 8.0 Hz, 4 H, H-Ar), 7.21 (d, J = 4.0 Hz, 2 H, H-Ar), 7.07 (d, J = 8.0 Hz, 4 H, H-Ar), 6.80 (d, J = 8.0 Hz, 4 H, H-Ar), 3.80 (s, 6 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 147.5, 131.5, 131.1, 128.4, 127.2, 125.8, 125.4, 124.9, 113.9, 55.2 ppm.

3,4-Bis(4-nitrophenyl)-2,5-diphenylfuran (3i):[27] Yellow gum (90% isolated yield). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.40 (d, J = 12.0 Hz, 4 H, H-Ar), 8.20 (d, J = 8.0 Hz, 4 H, H-Ar), 7.99 (d, J = 8.0 Hz, 4 H, H-Ar), 7.82 (t, J = 8.0 Hz, 2 H, H-Ar), 7.64 (t, J = 8.0 Hz, 4 H, H-Ar) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ =

193.2, 192.7, 151.0, 136.7, 135.8, 131.9, 131.3, 130.0, 129.5, 124.4 ppm. HRMS (ESI): calcd. for $C_{28}H_{18}N_2O_5Na$ [M + Na]$^+$ 485.1108; found 485.1110.

3,4-Bis(4-fluorophenyl)-2,5-diphenylfuran (3j): White solid (76% isolated yield); m.p. 195–196 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, J = 8.0 Hz, 4 H, H-Ar), 7.30–7.23 (m, 6 H, H-Ar), 7.11 (t, J = 8.0 Hz, 4 H, H-Ar), 6.96 (t, J = 8.0 Hz, 4 H, H-Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2 (d, $J_{F,C}$ = 245 Hz), 148.0, 132.0 (d, $J_{F,C}$ = 8.0 Hz), 130.6, 129.0 (d, $J_{F,C}$ = 3.0 Hz), 128.5, 127.6, 125.9, 124.0, 115.7 (d, $J_{F,C}$ = 22.0 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3052, 2921, 2852, 1897, 1599, 1560, 1502, 1218, 1155, 841, 761, 686 cm^{-1}. HRMS (ESI): calcd. for $C_{28}H_{18}F_2ONa$ [M + Na]$^+$ 431.1218; found 431.1238.

3,4-Bis(4-chlorophenyl)-2,5-diphenylfuran (3k): White solid (76% isolated yield); m.p. 181–182 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, J = 4.0 Hz, 4 H, H-Ar), 7.21–7.15 (m, 10 H, H-Ar), 6.98 (d, J = 8.0 Hz, 4 H, H-Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.2, 133.4, 131.7, 131.4, 130.4, 128.9, 128.6, 127.8, 126.0, 123.5 ppm. IR (KBr): $\tilde{\nu}$ = 3052, 2920, 2851, 1897, 1593, 1484, 1391, 1083, 1011, 944, 831, 759, 691 cm^{-1}. HRMS (ESI): calcd. for $C_{28}H_{19}Cl_2O$ [M + H]$^+$ 441.0807; found 441.0791.

3,4-Bis(4-bromophenyl)-2,5-diphenylfuran (3l):[28] White solid (78% isolated yield); m.p. 209–210 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (s, 4 H, H-Ar), 7.35 (d, J = 4.0 Hz, 4 H, H-Ar), 7.24 (d, J = 8.0 Hz, 6 H, H-Ar), 6.97 (d, J = 4.0 Hz, 4 H, H-Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.1, 132.0, 131.8, 130.3, 128.5, 127.8, 126.0, 123.4, 121.6 ppm.

3,4-Bis(3-bromophenyl)-2,5-diphenylfuran (3m): White solid (67% isolated yield); m.p. 132–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 8.0 Hz, 4 H, H-Ar), 7.41 (d, J = 4.0 Hz, 2 H, H-Ar), 7.33–7.26 (m, 8 H, H-Ar), 7.16 (t, J = 8.0 Hz, 2 H, H-Ar), 7.08 (d, J = 8.0 Hz, 2 H, H-Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.3, 135.0, 133.2, 130.6, 130.3, 130.2, 129.1, 128.6, 127.9, 126.0, 123.3, 122.5 ppm. IR (KBr): $\tilde{\nu}$ = 3053, 2922, 2853, 1744, 1674, 1546, 1459, 1069, 1024, 756, 690 cm^{-1}. HRMS (ESI): calcd. for $C_{28}H_{18}Br_2ONa$ [M + Na]$^+$ 550.9617; found 550.9618.

3,4-Bis(2-bromophenyl)-2,5-diphenylfuran (3n): White solid (62% isolated yield); m.p. 136–137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (t, J = 4.0 Hz, 2 H, H-Ar), 7.46 (d, J = 8.0 Hz, 4 H, H-Ar), 7.39 (d, J = 8.0 Hz, 2 H, H-Ar), 7.26 (t, J = 8.0 Hz, 4 H, H-Ar), 7.20 (t, J = 8.0 Hz, 4 H, H-Ar), 7.10 (t, J = 4.0 Hz, 2 H, H-Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.6, 134.4, 134.0, 133.3, 132.7, 132.4, 130.9, 130.7, 129.5, 129.3, 128.6, 128.5, 127.6, 127.5, 127.1, 125.4, 125.3, 125.2, 124.8, 124.2 ppm. IR (KBr): $\tilde{\nu}$ = 3054, 2922, 2853, 1950, 1595, 1490, 1431, 1024, 755, 680 cm^{-1}. HRMS (ESI): calcd. for $C_{28}H_{18}Br_2ONa$ [M + Na]$^+$ 550.9617; found 550.9609.

3,4-Di(biphenyl-4-yl)-2,5-diphenylfuran (3o): White solid (81% isolated yield); m.p. 246–247 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.48 (m, 8 H, H-Ar), 7.44 (d, J = 8.0 Hz, 4 H, H-Ar), 7.34 (t, J = 8.0 Hz, 4 H, H-Ar), 7.28–7.11 (m, 12 H, H-Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.0, 140.6, 139.7, 132.2, 130.91, 130.86, 128.8, 128.5, 127.5, 127.4, 127.1, 127.0, 126.1, 124.6 ppm. IR (KBr): $\tilde{\nu}$ = 3028, 2922, 2853, 1885, 1592, 1481, 1439, 1393, 1109, 761, 685 cm^{-1}. HRMS (ESI): calcd. for $C_{40}H_{28}ONa$ [M + Na]$^+$ 547.2032; found 547.2030.

2,5-Dibutyl-3,4-diphenylfuran (3p): Colorless gum (77% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.15 (m, 6 H, H-Ar), 7.06 (s, 4 H, H-Ar), 2.66 (s, 4 H, CH_2), 1.67 (s, 4 H, CH_2), 1.36 (d, J = 8.0 Hz, 4 H, CH_2), 0.96–0.84 (m, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.6, 133.9, 129.8, 128.0, 126.1, 121.2, 31.1, 26.3, 22.6, 14.0 ppm. IR (KBr): $\tilde{\nu}$ = 3055, 3033, 2957, 2927, 2864, 1947, 1881, 1675, 1607, 1578, 1524, 1493, 1460, 1379, 1346, 1182, 1102, 1072, 1001, 983, 912, 763, 699 cm^{-1}. HRMS (ESI): calcd. for $C_{24}H_{28}ONa$ [M + Na]$^+$ 355.2032; found 355.2036.

3,4-Bis(2-bromophenyl)-2,5-dimethylfuran (3q): White solid (70% isolated yield); m.p. 92–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (t, J = 9.0 Hz, 3.5 H, H-Ar), 7.20–6.99 (m, 10.8 H, H-Ar), 2.24 (s, 4.5 H, CH_3), 2.20 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.9, 146.8, 134.5, 134.4, 133.0, 132.7, 132.39, 132.35, 128.7, 128.5, 127.0, 126.8, 125.0, 124.9, 121.8, 121.7, 13.0, 12.9 ppm. IR (KBr): $\tilde{\nu}$ = 3055, 2921, 2853, 1920, 1613, 1582, 1472, 1429, 1378, 1262, 1208, 1060, 1026, 996, 928, 752 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{14}Br_2ONa$ [M + Na]$^+$ 426.9304; found 426.9281.

Typical Procedure for the Synthesis of Tetrasubstituted Furans by Using a Cross-Coupling Reaction: Compound **1b** (0.50 mmol), Ag_2O (23.2 mg, 0.1 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (39.8 mg, 0.2 mmol) were added to a round-bottom flask (10 mL). The flask was then evacuated and backfilled with O_2, and the reaction mixture was stirred at 140 °C. A solution of **1e** (0.5 mmol) in xylene (1.5 mL) and TFA (0.12 mL, 1.6 mmol) was slowly added to the mixture. The progress of the reaction was monitored by TLC analysis. Upon completion, the crude mixture was cooled to room temperature and filtered through a small pad of silica gel. The filtrate was concentrated in vacuo, and the residue was purified by chromatography on a silica gel column to afford product **3r**.

2-(4-Chlorophenyl)-3,4-diphenyl-5-*p*-tolylfuran (3r): White solid (54% isolated yield); m.p. 150–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (dd, J = 12.1, 8.4 Hz, 4 H, H-Ar), 7.28–7.19 (m, 8 H, H-Ar), 7.17–7.11 (m, 4 H, H-Ar), 7.07 (d, J = 8.0 Hz, 2 H, H-Ar), 2.32 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.3, 146.4, 137.5, 133.1, 133.0, 132.9, 130.4, 130.3, 129.5, 129.2, 128.63, 128.56, 128.4, 128.0, 127.4, 127.2, 127.0, 126.0, 125.5, 124.6, 21.4 ppm. IR (KBr): $\tilde{\nu}$ = 2985, 1740, 1448, 1374, 1242, 1100, 1047, 937, 847, 738, 633 cm^{-1}. HRMS (ESI): calcd. for $C_{29}H_{21}ClONa$ [M + Na]$^+$ 443.1173; found 443.1170.

3-(4-Nitrophenyl)-2,5-diphenyl-4-*p*-tolylfuran (3s): White solid (63% isolated yield); m.p. 183–185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J = 8.0 Hz, 2 H, H-Ar), 7.51 (d, J = 8.0 Hz, 2 H, H-Ar), 7.46 (d, J = 4.0 Hz, 2 H, H-Ar), 7.33–7.21 (m, 8 H, H-Ar), 7.09 (d, J = 8.0 Hz, 2 H, H-Ar), 7.02 (d, J = 8.0 Hz, 2 H, H-Ar), 2.35 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.7, 148.5, 146.9, 140.7, 137.5, 131.3, 130.5, 130.19, 130.16, 129.6, 129.3, 128.7, 128.5, 128.2, 127.7, 126.4, 125.9, 124.3, 123.7, 123.0, 21.4 ppm. IR (KBr): $\tilde{\nu}$ = 2923, 2855, 1727, 1599, 1517, 1453, 1343, 1265, 1109, 1027, 948, 856, 820, 765, 693 cm^{-1}. HRMS (ESI): calcd. for $C_{29}H_{21}NO_3Na$ [M + Na]$^+$ 454.1414; found 454.1409.

2,5-Bis(4-iodophenyl)-3,4-diphenylfuran (3t):[29] White solid (78% isolated yield); m.p. 206–207 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 8.0 Hz, 4 H, H-Ar), 7.16 (d, J = 4.0 Hz, 6 H, H-Ar), 7.13 (d, J = 8.0 Hz, 4 H, H-Ar), 7.04 (d, J = 4.0 Hz, 4 H, H-Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.1, 137.6, 132.6, 130.2, 130.1, 128.6, 127.6, 127.5, 126.0, 93.1 ppm.

The Control Experiment for the Reaction Mechanism: A mixture of deoxybenzoin (**1a**, 1.0 mmol), $Cu(OAc)_2$ (1.0 mmol), and 2,2,6,6-tetramethylpiperidine-1-oxyl (1.0 mmol) in xylene (3 mL) was stirred at 140 °C for 0.5 h. The mixture was cooled to room temperature and filtered through a small pad of silica gel. The filtrate was concentrated in vacuo, and the crude residue was purified by chromatography on a silica gel column to afford the corresponding product **4a**.

1,2-Diphenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethanone (4a):[30] White solid (40% isolated yield); m.p. 170–171 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 4.0 Hz, 2 H, H-Ar), 7.53 (d, J = 4.0 Hz, 2 H, H-Ar), 7.48 (d, J = 8.0 Hz, 1 H, H-Ar), 7.41 (t, J = 8.0 Hz, 2 H, H-Ar), 7.30 (t, J = 8.0 Hz, 2 H, H-Ar), 7.21 (t, J = 8.0 Hz, 1 H, H-Ar), 6.03 (s, 1 H, CH), 1.47 (s, 4 H, CH_2), 1.31 (d, J = 16.0 Hz, 2 H, CH_2), 1.21 (s, 6 H, CH_3), 1.02 (s, 3 H, CH_3), 0.84 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.3, 137.8, 135.2, 132.9, 129.3, 128.4, 127.5, 127.2, 93.2, 60.0, 59.8, 40.2, 33.6, 33.3, 20.3, 20.2, 17.0 ppm. IR (KBr): $\tilde{\nu}$ = 3088, 3068, 2973, 2947, 2925, 2846, 1669, 1596, 1579, 1492, 1448, 1377, 1359, 1264, 1225, 1178, 1132, 1084, 1044, 1025, 765, 737, 697, 618 cm^{-1}. HRMS (ESI): calcd. for $C_{23}H_{29}NNaO_2$ $[M + Na]^+$ 374.2091; found 374.2102.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of the products, X-ray crystallographic data for **2j**, **3a**, **3e**, and **4a**.[13]

Acknowledgments

The authors are grateful for financial support from the National Natural Science Foundation of China (NSFC) (grant numbers NSFC-20972126 and 21272185).

[1] For reviews, see: a) W.-J. Yoo, C.-J. Li, *Top. Curr. Chem.* **2010**, *292*, 281–302; b) S.-L. You, J.-B. Xia, *Top. Curr. Chem.* **2010**, *292*, 165–194.

[2] For a review, see: C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Rev.* **2011**, *111*, 1293–1314.

[3] a) R. Jazzar, J. Hitce, A. Renaudat, J. Sofack-Kreutzer, O. Baudoin, *Chem. Eur. J.* **2010**, *16*, 2654–2672; b) B. Liu, T. Zhou, B. Li, S. Xu, H. Song, B. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 4191–4195; *Angew. Chem.* **2014**, *126*, 4275–4279.

[4] For selected recent examples, see: a) S. Lin, C.-X. Song, G.-X. Cai, W.-H. Wang, Z.-J. Shi, *J. Am. Chem. Soc.* **2008**, *130*, 12901–12903; b) Y.-X. Jia, E. P. Kündig, *Angew. Chem. Int. Ed.* **2009**, *48*, 1636–1639; *Angew. Chem.* **2009**, *121*, 1664–1667; c) K. B. Urkalan, M. S. Sigman, *J. Am. Chem. Soc.* **2009**, *131*, 18042–18043; d) F. Yang, J. Li, J. Xie, Z.-Z. Huang, *Org. Lett.* **2010**, *12*, 5214–5217; e) C. Gou, J. Song, S.-W. Luo, L.-Z. Gong, *Angew. Chem. Int. Ed.* **2010**, *49*, 5558–5562; *Angew. Chem.* **2010**, *122*, 5690–5694; f) O. Baudoin, *Chem. Soc. Rev.* **2011**, *40*, 4902–4911; g) J. Xie, H. Li, J. Zhou, Y. Cheng, C. Zhu, *Angew. Chem. Int. Ed.* **2012**, *51*, 1252–1255; *Angew. Chem.* **2012**, *124*, 1278–1281; h) C. He, S. Guo, J. Ke, J. Hao, H. Xu, H. Chen, A. Lei, *J. Am. Chem. Soc.* **2012**, *134*, 5766–5769; i) G. Zhang, Y. Ma, S. Wang, Y. Zhang, R. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 12334–12337; j) Y. Oonishi, Y. Kitano, Y. Sato, *Angew. Chem. Int. Ed.* **2012**, *51*, 7305–7308; *Angew. Chem.* **2012**, *124*, 7417–7420; k) D. Liu, C. Liu, H. Li, A. Lei, *Angew. Chem. Int. Ed.* **2013**, *52*, 4453–4456; *Angew. Chem.* **2013**, *125*, 4549–4552; l) G. Zhang, Y. Zhao, H. Ge, *Angew. Chem. Int. Ed.* **2013**, *52*, 2559–2563; *Angew. Chem.* **2013**, *125*, 2619–2623; m) C. Chen, X.-H. Xu, B. Yang, F.-L. Qing, *Org. Lett.* **2014**, *16*, 3372–3375; n) K.-J. Xiao, D. W. Lin, M. Miura, R.-Y. Zhu, W. Gong, M. Wasa, J.-Q. Yu, *J. Am. Chem. Soc.* **2014**, *136*, 8138–8142; o) S. A. Girard, T. Knauber, C.-J. Li, *Angew. Chem. Int. Ed.* **2014**, *53*, 74–100; *Angew. Chem.* **2014**, *126*, 76–103; p) V. P. Mehta, J.-A. García-López, M. F. Greaney, *Angew. Chem. Int. Ed.* **2014**, *53*, 1529–1533; *Angew. Chem.* **2014**, *126*, 1555–1559.

[5] S.-H. Li, J. Wang, X.-M. Niu, Y.-H. Shen, H.-J. Zhang, H.-D. Sun, M.-L. Li, Q.-E. Tian, Y. Lu, P. Cao, Q.-T. Zheng, *Org. Lett.* **2004**, *6*, 4327–4330.

[6] For selected recent reports describing the synthesis of 1,4-dicarbonyl compounds, see: a) M. P. DeMartino, K. Chen, P. S. Baran, *J. Am. Chem. Soc.* **2008**, *130*, 11546–11560; b) E. J. Yoo, M. Wasa, J.-Q. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 17378–17380; c) M. Fernández, U. Uria, J. L. Vicario, E. Reyes, L. Carrillo, *J. Am. Chem. Soc.* **2012**, *134*, 11872–11875; d) G. K. S. Prakash, F. Wang, Z. Zhang, C. Ni, R. Haiges, G. A. Olah, *Org. Lett.* **2012**, *14*, 3260–3263; e) W. Zhao, D. M. Fink, C. A. Labutta, A. T. Radosevich, *Org. Lett.* **2013**, *15*, 3090–3093; f) M. M. D. Wilde, M. Gravel, *Angew. Chem. Int. Ed.* **2013**, *52*, 12651–12654; *Angew. Chem.* **2013**, *125*, 12883–12886; g) B. B. Parida, P. P. Das, M. Niocel, J. K. Cha, *Org. Lett.* **2013**, *15*, 1780–1783; h) F. Zhang, P. Du, J. Chen, H. Wang, Q. Luo, X. Wan, *Org. Lett.* **2014**, *16*, 1932–1935; i) P. Mizar, T. Wirth, *Angew. Chem. Int. Ed.* **2014**, *53*, 5993–5997; *Angew. Chem.* **2014**, *126*, 6103–6107.

[7] For recent examples, see: a) C.-S. Li, Y.-H. Tsai, W.-C. Lee, W.-J. Kuo, *J. Org. Chem.* **2010**, *75*, 4004–4013; b) E. O'Reilly, C. Iglesias, D. Ghislieri, J. Hopwood, J. L. Galman, R. C. Lloyd, N. J. Turner, *Angew. Chem. Int. Ed.* **2014**, *53*, 2447–2450; *Angew. Chem.* **2014**, *126*, 2479–2482.

[8] a) P. S. Baran, M. P. DeMartino, *Angew. Chem. Int. Ed.* **2006**, *45*, 7083–7086; *Angew. Chem.* **2006**, *118*, 7241–7244; b) B. M. Casey, R. A. Flowers II, *J. Am. Chem. Soc.* **2011**, *133*, 11492–11495; c) F. Guo, L. C. Konkol, R. J. Thomson, *J. Am. Chem. Soc.* **2011**, *133*, 18–20; d) C. Liu, Y. Deng, J. Wang, Y. Yang, S. Tang, A. Lei, *Angew. Chem. Int. Ed.* **2011**, *50*, 7337–7341; *Angew. Chem.* **2011**, *123*, 7475–7479; e) F. Guo, M. D. Clift, R. J. Thomson, *Eur. J. Org. Chem.* **2012**, 4881–4896.

[9] a) A. E. Wendlandt, A. M. Suess, S. S. Stahl, *Angew. Chem. Int. Ed.* **2011**, *50*, 11062–11087; *Angew. Chem.* **2011**, *123*, 11256–11283; b) C. Zhang, C. Tang, N. Jiao, *Chem. Soc. Rev.* **2012**, *41*, 3464–3484; c) S. E. Allen, R. R. Walvoord, R. Padilla-Salinas, M. C. Kozlowski, *Chem. Rev.* **2013**, *113*, 6234–6458.

[10] a) T.-T. Kao, S.-e. Syu, Y.-W. Jhang, W. Lin, *Org. Lett.* **2010**, *12*, 3066–3069; b) S. Breyer, K. Effenberger-Neidnicht, S. Knauer, R. Schobert, *Bioorg. Med. Chem.* **2011**, *19*, 1264–1267.

[11] For selected recent examples, see: a) G.-C. Ge, D.-L. Mo, C.-H. Ding, L.-X. Dai, X.-L. Hou, *Org. Lett.* **2012**, *14*, 5756–5759; b) X. Huang, B. Peng, M. Luparia, L. F. R. Gomes, L. F. Veiros, N. Maulide, *Angew. Chem. Int. Ed.* **2012**, *51*, 8886–8890; *Angew. Chem.* **2012**, *124*, 9016–9020; c) J. Fournier, S. Arseniyadis, J. Cossy, *Angew. Chem. Int. Ed.* **2012**, *51*, 7562–7566; *Angew. Chem.* **2012**, *124*, 7680–7684; d) X. Cui, X. Xu, L. Wojtas, M. M. Kim, X. P. Zhang, *J. Am. Chem. Soc.* **2012**, *134*, 19981–19984; e) Y. Li, J. P. Brand, J. Waser, *Angew. Chem. Int. Ed.* **2013**, *52*, 6743–6747; *Angew. Chem.* **2013**, *125*, 6875–6879; f) A. N. Butkevich, L. Meerpoel, I. Stansfield, P. Angibaud, A. Corbu, J. Cossy, *Org. Lett.* **2013**, *15*, 3840–3843; g) H. Jiang, Y. Cheng, Y. Zhang, S. Yu, *Org. Lett.* **2013**, *15*, 4884–4887; h) Y. Yang, J. Yao, Y. Zhang, *Org. Lett.* **2013**, *15*, 3206–3209; i) S. Dhiman, S. S. V. Ramasastry, *J. Org. Chem.* **2013**, *78*, 10427–10436; j) J. Li, L. Liu, D. Ding, J. Sun, Y. Ji, J. Dong, *Org. Lett.* **2013**, *15*, 2884–2887; k) M. Zheng, L. Huang, W. Wu, H. Jiang, *Org. Lett.* **2013**, *15*, 1838–1841; l) Z.-L. Wang, H.-L. Li, L.-S. Ge, X.-L. An, Z.-G. Zhang, X. Luo, J. S. Fossey, W.-P. Deng, *J. Org. Chem.* **2014**, *79*, 1156–1165; m) Y. Ma, S. Zhang, S. Yang, F. Song, J. You, *Angew. Chem. Int. Ed.* **2014**, *53*, 7870–7874; *Angew. Chem.* **2014**, *126*, 8004–8008.

[12] a) M. Shang, S.-Z. Sun, H.-X. Dai, J.-Q. Yu, *Org. Lett.* **2014**, *16*, 5666–5669; b) F.-J. Chen, G. Liao, X. Li, J. Wu, B.-F. Shi, *Org. Lett.* **2014**, *16*, 5644–5647.

[13] CCDC-1011012 (for **2j**), -1011013 (for **3a**), -1011014 (for **3e**), and -1011015 (for **4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

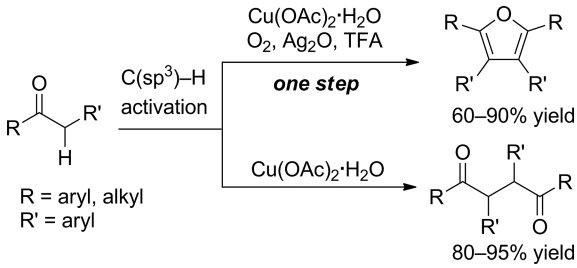
[14] M. Arisawa, G. Li, M. Yamaguchi, *Tetrahedron Lett.* **2013**, *54*, 1298–1301.

[15] D. R. Shridhar, M. Jogibhukta, P. S. Rao, V. K. Handa, *Indian J. Chem. Sect. B* **1983**, *22*, 1187–1190.

[16] H. J. Jeong, M. A. Kakimoto, Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1057–1062.
[17] G. E. Robinson, J. M. Vernon, *J. Chem. Soc. Perkin Trans. 1* **1972**, 1277–1281.
[18] H. J. Jeong, A. Kobayashi, M. Kakimoto, Y. Imai, *Polym. J.* **1994**, *26*, 99–103.
[19] W.-J. Kuo, Y.-H. Chen, R.-J. Jeng, L.-H. Chan, W.-P. Lin, Z.-M. Yang, *Tetrahedron* **2007**, *63*, 7086–7096.
[20] M. Hussain, R. A. Khera, N. T. Hunga, P. Langer, *Org. Biomol. Chem.* **2011**, *9*, 370–373.
[21] A. V. Vasil′ev, A. P. Rudenko, *Russ. J. Org. Chem.* **1997**, *33*, 1555–1584.
[22] T. A. Elwood, P. F. Rogerson, M. M. Bursey, *J. Org. Chem.* **1969**, *34*, 1138–1139.
[23] R. E. Lutz, W. J. Welstead, *J. Am. Chem. Soc.* **1963**, *85*, 755–761.
[24] C. F. Wilcox, M. P. Stevens, *J. Am. Chem. Soc.* **1962**, *84*, 1258–1262.
[25] W. Ried, R. Lantzsch, *Chem. Ber.* **1971**, *104*, 679–680.
[26] H. Fillion, A. Boucherle, D. C. Luu, *Bull. Soc. Chim. Fr.* **1974**, 734–736.
[27] H. J. Jeong, Y. Oishi, M. Kakimoto, Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 3293–3301.
[28] E. F. Pratt, S. P. Suskind, *J. Org. Chem.* **1963**, *28*, 638–642.
[29] T. Oguchi, A. Karasawa, N. Ito, *Jpn. Kokai Tokkyo Koho* JP 04224572 A 19920813, **1992**.
[30] N. Y. More, M. Jeganmohan, *Org. Lett.* **2014**, *16*, 804–807.

Received: September 28, 2014
Published Online: ■

EurJOC European Journal of Organic Chemistry



Coupling of two C–H bonds adjacent to a carbonyl group: The copper(II)-promoted coupling of two C(sp^3)–H bonds that are adjacent to a carbonyl group was carried out for the preparation of 2,3-disubstituted 1,4-diketones and tetrasubstituted furans. This economic approach features a wide substrate scope and a high functional group tolerance.

Keywords: Synthetic methods / C–C coupling / Oxidation / Copper / Oxygen heterocycles

