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Synthesis of 4-Diarylamino-3-iodo-2(5H)-furanones via the Simultaneous α -Iodination and N ^{β} -Arylation by an Efficient Difunctionalizable Transfer Reagent PhI(OAc)₂

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SYNTHESIS OF 4-DIARYLAMINO-3-iodo-2(5H)-FURANONES VIA THE SIMULTANEOUS α -IODINATION AND N^{β} -ARYLATION BY AN EFFICIENT DIFUNCTIONALIZABLE TRANSFER REAGENT $\text{PhI}(\text{OAc})_2$

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GRAPHICAL ABSTRACT



Abstract During the studies on the intramolecular cyclization of 4-arylamino-2(5H)-furanones via the Pd-catalyzed C-H activation, a kind of difunctionalization reaction caused by the designed oxidant $\text{PhI}(\text{OAc})_2$ [(diacetoxyiodo)benzene, DIB] was accidentally discovered. When 1.5 eq. DIB is used as a difunctionalizable transfer reagent in the 40 h reaction at 60 °C and CH_3CN as solvent, 4-diarylamino-3-iodo-2(5H)-furanones can be obtained with the yields of 57–91% (usually more than 73%). The simultaneous α -iodination and N^{β} -arylation reaction without metal catalyst is efficient and convenient. This novel utilization with a greater atom economy provides a simple and practical conversion route for the synthesis of the potential biological 2(5H)-furanone compounds containing multifunctional groups.

Keywords (Diacetoxyiodo)benzene; difunctionalization; iodination; 2(5H)-furanone; N-arylation

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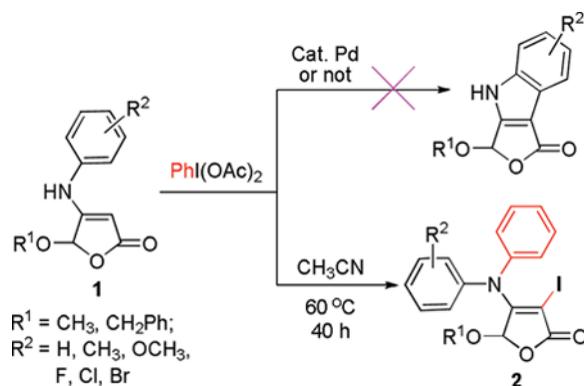
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INTRODUCTION

As a kind of efficient synthetic strategy, difunctionalization reactions,^[1–4] especially the difunctionalization reactions simultaneously yielding two different functional groups,^[5–18] have aroused great interest from organic chemists in recent years. Among them, the difunctionalization reactions with greater atom economies from the point of green chemistry are undoubtedly more promising.^[2–9,17,18] Usually, the utilization of transfer reagents, especially some hypervalent organic iodine reagents, is a simple way for the efficient difunctionalization.^[2–8,15–18] It is a pity that in some cases, there is only a functional group converted from these hypervalent iodine transfer reagents.^[15,16,19–22] Therefore, it is still a challenge for organic chemists to find a suitable hypervalent organic iodine transfer reagent for the difunctionalization simultaneously yielding two different functional groups in the synthesis of potential biological heterocyclic compounds.^[8,17,18]

Of course, many hypervalent organic iodine reagents are common oxidants in organic synthesis.^[1,23–29] For example, $\text{PhI}(\text{OAc})_2$ [(diacetoxyiodo)benzene, DIB] is an easily accessible hypervalent organic iodine reagent can be used to construct indole ring derivatives via the oxidation.^[30,31] Because of the significance of indole ring derivatives in natural products,^[32–34] pharmaceuticals,^[34–36] and materials sciences,^[37] we hoped to synthesize the fused indole ring derivatives from 4-amino-2(5H)-furanone **1** by the Pd-catalyzed C-H activation in the presence of oxidant DIB. Surprisingly, a difunctionalization reaction of hypervalent organic iodine reagent DIB as a transfer reagent was discovered even without Pd catalysts (Scheme 1).

2(5H)-Furanone is a basic structural unit in many bioactive compounds,^[38–41] and some simple 2(5H)-furanones are important intermediates.^[42–45] Therefore, among the research on 2(5H)-furanone chemistry,^[46–59] some attention has been focused on the efficient synthesis of iodo-2(5H)-furanones also for their diverse value recently.^[59–66] However, there is only a general report available for the synthesis of 3-iodo-2(5H)-furanone. Even so, some uncommon reagents are used at a strictly low temperature, and the atom economy is also lower with the yields of 54–89% (mostly more than 70%).^[59] Herein, we report an efficient and convenient synthetic method for the 4-diarylamino-3-iodo-2(5H)-furanones **2** (Scheme 1) by hypervalent iodine transfer reagent DIB with the yields of 57–91% (usually more than 73%).



Scheme 1. Unexpected difunctionalization of compound **1**.

RESULTS AND DISCUSSION

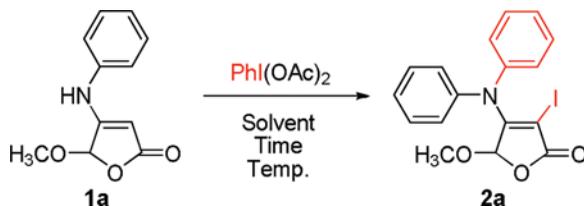
Optimization of Reaction Conditions

Because of the very useful oxidizing properties, especially their benign environmental character and commercial availability, many hypervalent organic iodine reagents, including inexpensive $\text{PhI}(\text{OAc})_2$ (DIB), have been extensively used in different oxidations.^[1,23,24,26–31] When we used DIB as an oxidant to promote the intramolecular C-C coupling in the substrate 5-methoxy-4-phenylamino-2(5*H*)-furanone **1a**, compound **2a** was unexpectedly obtained via the simultaneous α -iodination and N^β -arylation reaction even without any metal catalysts (Scheme 2).

To the best of our knowledge, only Chen et al. have reported the concurrent α -iodination and N -arylation of cyclic β -amino ketenes by DIB with the yields of 35–91% (usually more than 71%).^[67] However, using DIB as a hypervalent organic iodine transfer reagent, there is no report on the simultaneous α -iodination and N^β -arylation of β -amino-2(5*H*)-furanones before. More noticeably, β -amino-2(5*H*)-furanones as a kind of biological heterocyclic compounds,^[38,68–72] especially 5-alkoxy-4-amino-2(5*H*)-furanones **1** with lactone and acetal structures, are more sensitive than β -amino ketenes to the reaction environment, indicating that their difunctionalization simultaneously yields two different functional groups that are more important for the synthesis of potential bioactive compounds. Thus, we investigated this novel reaction of β -amino-2(5*H*)-furanones. Using 5-methoxy-4-phenylamino-2(5*H*)-furanone **1a** as typical substrate (Scheme 2), the suitable reaction conditions were optimized first (Table 1).

The evaluations on the influences of different DIB dosages show that the yield is obviously elevated with the increase of DIB dosage (Table 1, entries 1–3) and 1.5 eq. DIB is the most advantageous for the reaction with the greatest yield of 86% (entry 3). With continually increasing DIB dosage, there is a trend of lower yields (entries 4 and 5). Therefore, the suitable DIB dosage should be 1.5 eq. Reaction solvent is another important influencing factor. It can be seen that, among the different solvents (entries 3, 6–11), CH_3CN is the best (entry 3).

When the reaction temperature is decreased from 60 °C to 30 °C, the yield can be lowered (entry 12), but when increasing the temperature, the yield does not increase yet (entry 13). Thus, the suitable reaction temperature should be 60 °C (entry 3). Similarly, shortening the reaction time is not beneficial to the yield (entry 14), and extending the time cannot further improve the yield yet as anticipated (entries 15 and 16), indicating that the suitable reaction time should be 40 h (entry 3). Therefore, the optimal reaction conditions for this N^β -arylation and α -iodination reaction can be summarized as follows: 1.5 eq. $\text{PhI}(\text{OAc})_2$ in CH_3CN at 60 °C for 40 h.



Scheme 2. Synthesis of compound **2a** by the reaction of **1a** with DIB.

Table 1. Effects of different conditions on the reaction

Entry ^a	DIB dosage (eq.)	Solvent	Time (h)	Temperature (°C)	Yield ^b (%)
1	0.5	CH ₃ CN	40	60	51
2	1.0	CH ₃ CN	40	60	76
3	1.5	CH ₃ CN	40	60	86
4	2.0	CH ₃ CN	40	60	71
5	2.5	CH ₃ CN	40	60	63
6	1.5	ClCH ₂ CH ₂ Cl	40	60	73
7	1.5	CH ₂ Cl ₂	40	60	45
8	1.5	EtOAc	40	60	Trace
9	1.5	DMSO	40	60	Trace
10	1.5	DMF	40	60	Trace
11	1.5	Toluene	40	60	65
12	1.5	CH ₃ CN	40	30	36
13	1.5	CH ₃ CN	40	90	86
14	1.5	CH ₃ CN	24	60	40
15	1.5	CH ₃ CN	70	60	86
16	1.5	CH ₃ CN	96	60	87

^aReaction conditions: 5-methoxy-4-phenylamino-2(5*H*)-furanone **1a** (0.2 mmol) and solvent (totally 10 mL).

^bIsolated yield.

Influences of Different Substrates

Under the optimized conditions, the substrate scopes are examined (Table 2). Though different substrates **1** can react smoothly with the yields of 57–91% (usually more than 73%), it seems that whether methoxy or benzyloxy, or ethoxy in 5-position of 2(5*H*)-furanone **1**, the change of the yields is not regular. Similarly, whether *p*-position substituted group of benzene ring in 4-arylamino of the substrates **1** is an electron-withdrawing group or electron-donating group has no obvious effects on the reaction. In other words, different groups can be tolerated in the process.

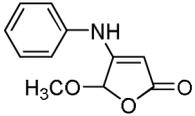
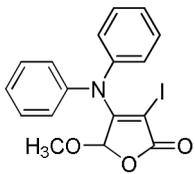
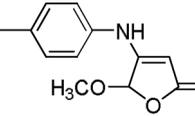
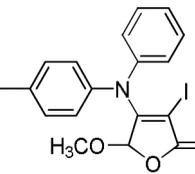
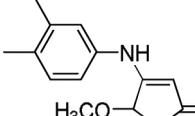
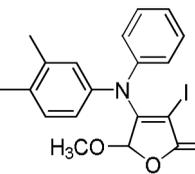
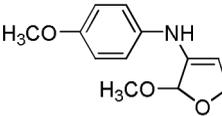
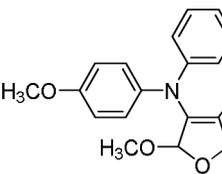
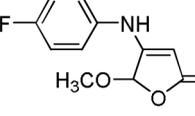
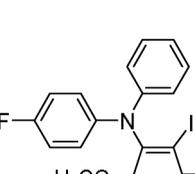
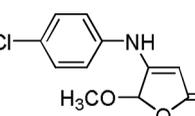
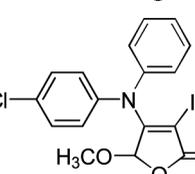
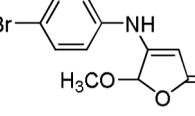
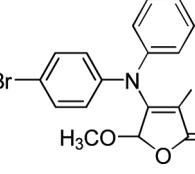
Of course, with the increase of the number of electron-donating group (e.g., methyl) in 4-arylamino, the yields have a rising trend (Table 2, entries 2 vs 3, 10 vs 11). Interestingly, if there is *p*-bromo substituted or *m*-chloro substituted (especially the latter) benzene ring in 4-arylamino of the substrates **1**, the reaction usually has a relatively greater yield than other cases (entries 7, 8, 15, and 16). However, the reasons for these phenomena are not very clear yet; they may be related to the reaction mechanism, which is further discussed in the following.

At the same time, the structures of all new products **2a–2s** are demonstrated by their Fourier-transform infrared (FTIR), ultraviolet (UV), NMR spectroscopic, mass spectrometry (MS), and elemental analysis data. Meanwhile, the structures of the products **2a** and **2e** are also confirmed by the x-ray crystallographic data, and their ORTEP structures are respectively shown in Figs. 1 and 2.

Possible Reaction Mechanism

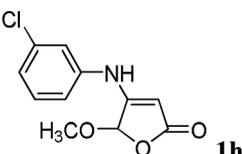
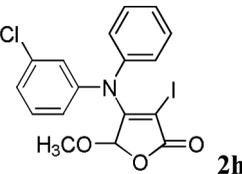
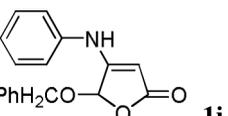
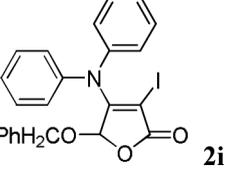
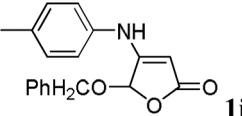
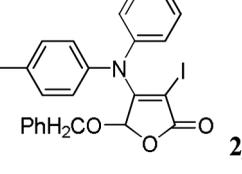
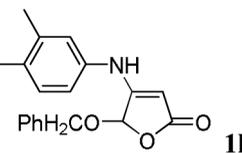
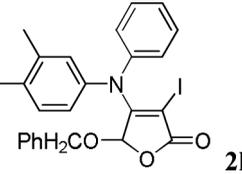
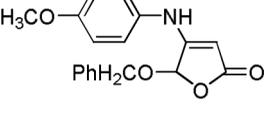
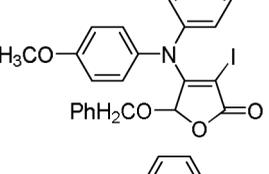
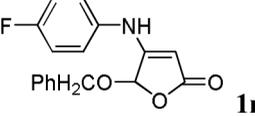
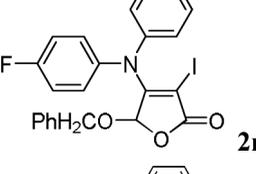
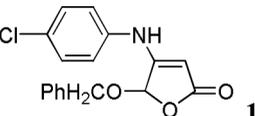
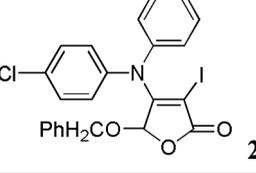
There is no report on the synthesis of 4-diarylamino-3-iodo-2(5*H*)-furanones via the difunctionalizable transfer reagent DIB. According to the literature on the

Table 2. Scope of 5-alkoxy-4-amino-2(5*H*)-furanone substrates **1** in the simultaneous α -iodination and *N*^B-arylation reaction

Entry	Substrates 1	Product 2	Isolated yield (%)
1	 1a	 2a	86
2	 1b	 2b	57
3	 1c	 2c	73
4	 1d	 2d	58
5	 1e	 2e	63
6	 1f	 2f	61
7	 1g	 2g	81

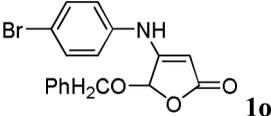
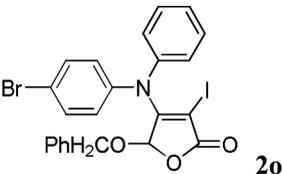
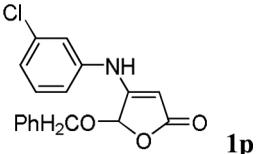
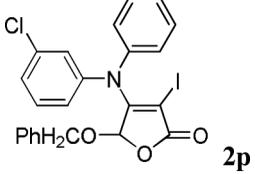
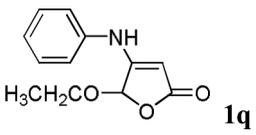
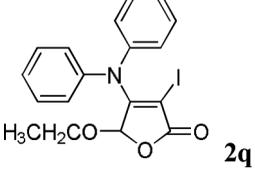
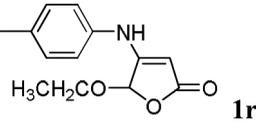
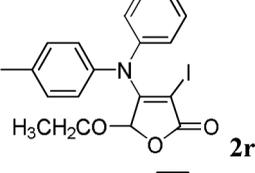
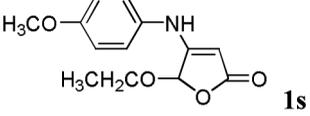
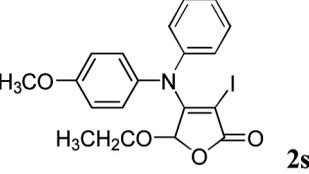
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Table 2. Continued

Entry	Substrates 1	Product 2	Isolated yield (%)
8	 1h	 2h	91
9	 1i	 2i	74
10	 1j	 2j	60
11	 1k	 2k	78
12	 1l	 2l	61
13	 1m	 2m	73
14	 1n	 2n	64

(Continued)

Table 2. Continued

Entry	Substrates 1	Product 2	Isolated yield (%)
15	 1o	 2o	82
16	 1p	 2p	89
17	 1q	 2q	83
18	 1r	 2r	79
19	 1s	 2s	66

hypervalent organic iodine reagents,^[17,18,67] a possible mechanism for the N^{β} -arylated α -iodo reaction in the presence of DIB is proposed (Scheme 3).

First, α -iodo iminium salt **A** would be formed from substrates **1** and $\text{PhI}(\text{OAc})_2$. However, intermediate **A** is greatly unstable for the presence of a lactone ring system, which would be deprotonated instantly to give the stabilized α -iodo butenolide **B**. With the leave of AcOH , intermediate **B** would be converted to iodine-nitrogen 1,4-dipoles **C**.^[5,6,67,73] Finally, the *ipso* attack of the negative nitrogen on the phenyl ring, through a five-membered cyclic intermediate **D**,^[67,74] would afford the N^{β} -arylated α -iodo butenolide **2** (Scheme 3).

It is obvious that the R^2 substituent on benzene ring in the substrates **1** is not greatly related to the stability of the important intermediate **D**. Therefore, whether R^2 substituent is electron-withdrawing or electron-donating, it has relatively less effect on the reaction (Table 2). Of course, according to the reaction mechanism,

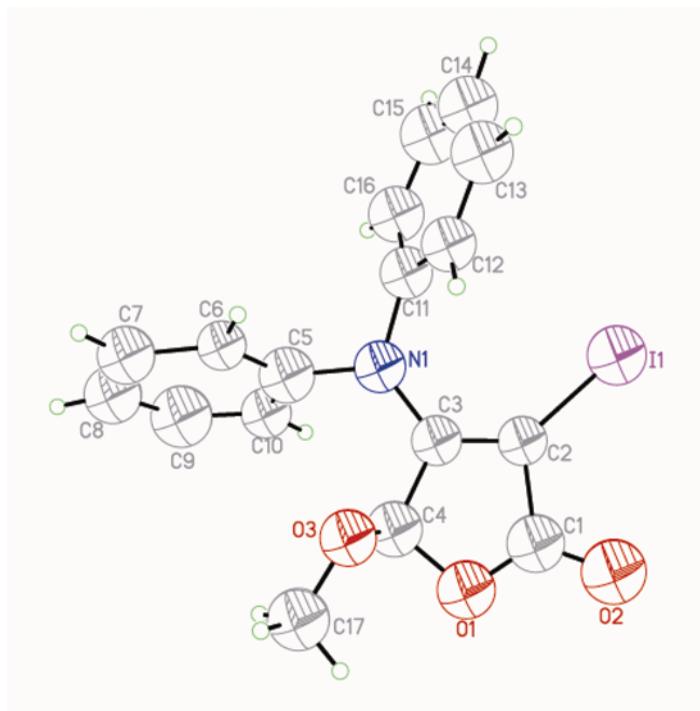


Figure 1. ORTEP structure of compound 2a.

not only the *N*-arylated substituted furanones but also the *N*-alkylated substrates are suitable for this system.^[67] Meanwhile, this is an intramolecular functional group transfer process indeed, which is confirmed by the comparative experiment. Scheme 4 is purposely designed as an intermolecular reaction, but no corresponding product was obtained or detected.

According to the reaction mechanism and the results in the literature,^[5,6,17,18,67,73,74] we can conclude that, as an important difunctionalizable transfer reagent, DIB is also suitable for the simultaneous α -iodination and O^{β} -arylation reaction of β -hydroxyl- α,β -unsaturated carbonyl compounds. Therefore, these investigations provide a simple difunctionalized conversion route with greater atom economy for β -amino(hydroxyl)- α,β -unsaturated carbonyl compounds, including 4-aryl-amino-2(5*H*)-furanones.

It is noticeable that not only 4-amino-2(5*H*)-furanones can be α -iodinated in this way, but also the product 4-diaryl-amino-3-iodo-2(5*H*)-furanones can be easily dehalogenated.^[57] Thus, further combining the different conversion of C^{sp^2} -I in organic synthesis,^[59,75-77] the simple and easy difunctionalizable reactions of simultaneous α -iodination and $N(O)^{\beta}$ -arylation can provide a good platform for more functional interconversions using iodo α,β -unsaturated carbonyl compounds as intermediates. Of course, this result also makes the intramolecular cyclization of 4-arylamino-2(5*H*)-furanones via the Pd-catalyzed C-H activation more possible, which is in progress in our laboratory.

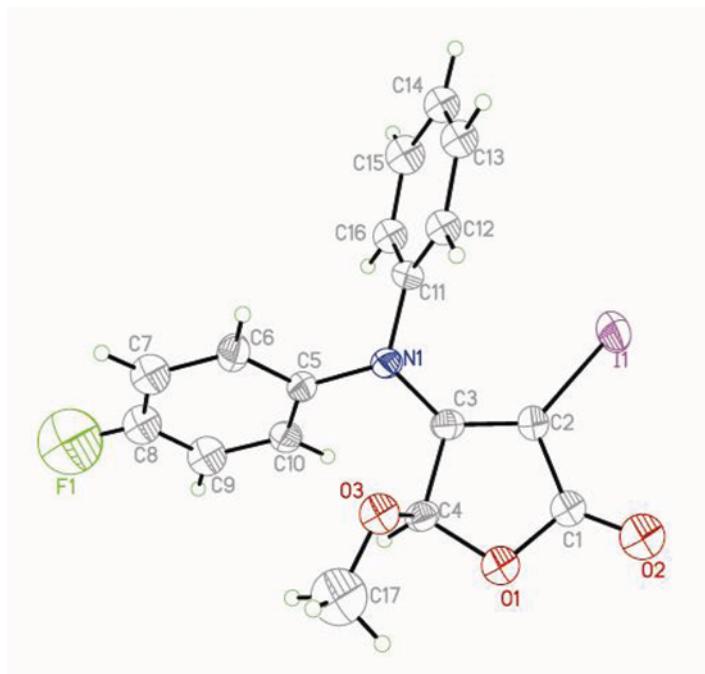
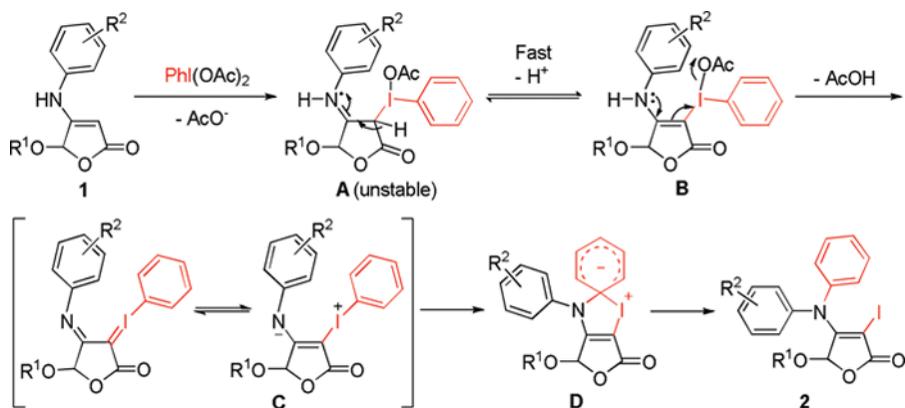
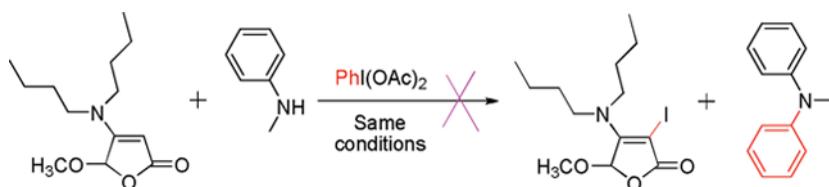


Figure 2. ORTEP structure of compound **2e**.



Scheme 3. Plausible mechanism for DIB-promoted difunctionalization.



Scheme 4. Designed intermolecular difunctionalization reaction promoted by DIB.

CONCLUSION

In summary, a series of novel 3-iodo-2(5H)-furanone derivatives containing multibenzene rings are synthesized via the green difunctionalizable transfer reagent $\text{PhI}(\text{OAc})_2$. This method is very simple, convenient, and mild with greater atom economy. It provides a practical route for the synthesis of some potential bioactive 2(5H)-furanone compounds with multifunctional groups.

EXPERIMENTAL

All melting points were determined on an X-5 digital melting-point apparatus and were uncorrected. Infrared spectra were recorded on a Bruker Vector 33 FT-IR instrument by liquid film method in the absorption range of 4000–450 cm^{-1} . ^1H and ^{13}C NMR spectra were obtained in CDCl_3 on a Varian DRX 400-MHz spectrometer, and tetramethylsilane (TMS) was used as an internal standard. The UV absorption peaks were measured by Shimadzu UV-2550 ultraviolet absorption detector with dichloromethane as a solvent. Elemental analysis was performed on a Thermo Flash EA 1112 elemental analyzer. The mass spectra (MS) were recorded on Thermo LCQ DECA XP MAX mass spectrometer.

All reagents and solvents were commercially available and used as received. The intermediates 5-alkoxy-4-arylamino-2(5H)-furanones **1** were prepared according to the literature.^[57b]

Typical Procedure

A flame-dried 25-mL round-bottomed flask was charged with 5-alkoxy-4-arylamino-2(5H)-furanones **1** (0.2 mmol) in CH_3CN (5 mL), and $\text{PhI}(\text{OAc})_2$ (1.5 eq.) in CH_3CN (5 mL) was added dropwise in 25 min. The mixture was stirred at 60 °C, and the reaction was monitored by TLC. After the completion of the reaction (about 40 h), the reaction was allowed to cool to room temperature. The reaction mixture was diluted with a saturated aqueous solution of NH_4Cl (20 mL) and extracted with ethyl acetate (3 × 20 mL). Then, the organic layer was dried over anhydrous MgSO_4 , filtered, and concentrated in vacuo. The purification of the residue by silica-gel column chromatography yielded the desired compounds **2** in 57–91% isolated yields (Table 2).

Typical Characterization Data for Compound 2a

Yellow solid, yield 86%, mp 177.9–179.2 °C; UV-vis (CH_2Cl_2) λ_{max} : 319 nm; ^1H NMR (400 MHz, CDCl_3) δ , ppm: 3.20 (s, 3H), 5.73 (s, 1H), 7.18 (d, $J = 8$ Hz, 4H), 7.29 (t, $J = 8$ Hz, 2H), 7.38–7.42 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ , ppm: 55.36, 56.86, 101.65, 126.35, 126.94, 127.10, 127.13, 129.32, 129.42, 142.60, 142.64, 162.47, 169.73; IR (film) ν , cm^{-1} : 3059, 2924, 2851, 1761, 1616, 1585, 1489, 1452, 1377, 1323, 1153, 1119, 951, 750, 698, 515; ESI-MS m/z (%): 408 ($[\text{M} + \text{H}]^+$, 100), 430 ($[\text{M} + \text{Na}]^+$, 93). Anal. calcd. for $\text{C}_{17}\text{H}_{14}\text{INO}_3$: C, 50.14; H, 3.47; N, 3.44. Found: C, 50.32; H, 3.21; N, 3.57.

X-Ray Structure Determination of Compounds **2a** and **2e**

Two suitable x-ray-quality crystals of compound **2a** and **2e** were respectively grown by slow evaporation of petroleum ether/dichloromethane solvent mixture in the temperature variation of 25 °C. Diffraction data of **2a** and **2e** were collected on a Bruker APEX II Smart CCD diffractometer equipped with graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) using the ω -scan technique. The data were corrected for absorption with the SADABS program. The structures were solved by direct methods using the SHELXS-97 program and all the nonhydrogen atoms were refined anisotropically with the full-matrix leastsquares on F^2 using the SHELX-97 program.^[78] Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. 962686 and 962687. Copies of the data can be obtained free of charge on application to the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.cam.ac.uk.

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SUPPLEMENTAL MATERIAL

Full experimental detail, characterization data for other new compounds **2b–2s**, ¹H NMR and ¹³C NMR spectra, and MS data for all new compounds **2a–2s** can be accessed on the publisher's website.

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