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Copper-Catalyzed One-Pot Synthesis of Dibenzofurans, Xanthenes, and Xanthones from Cyclic Diphenyl Iodoniums

Daqian Zhu,*[a,c] Min Li,[b] Zhouming Wu,[c] Yongliang Du,[c] Bingling Luo,[c] Peng Huang,[c] Shijun Wen*[c]

Abstract: Oxygenation of cyclic diphenyl iodoniums (CDPIs) with varied medium-ring sizes has been fully investigated. This practical copper-catalyzed tandem reaction of CDPIs with water as the oxygen source enables the construction of derivatised dibenzofurans and xanthenes at moderate to good yields. Moreover, structurally important xanthones are also successfully accessed under the oxygenation conditions with additional TEMPO.

Introduction

Cyclic heteroatom containing compounds are commonly found in pharmaceuticals, and a variety of methods have been established to obtain these important structures. Among these heterocyclic compounds, oxygenated heterocyclic dibenzofurans and xanthones are privileged scaffolds in many pharmaceutically active compounds,[1] such as eriobofuran, vialinin B,[2] griseoxanthone C,[3] and α-mangostin (Figure 1).[4] Xanthene derivatives are another special class of oxygen-incorporating tricyclic compounds, demonstrating impressive photophysical property arising from their π-conjugation systems, used as common building blocks of dyes and fluorescent materials.[5] Included are fluorescein and rhodamine based fluorescent probes to sense biologically and environmentally important species.[6]

The frequent occurrence of dibenzofurans, xanthenes, and xanthones in natural sources, medicinal chemistry as well as biological imaging demands efficient synthetic protocols to assemble these functionalized oxygen-incorporated chemicals. Classical representative approaches to dibenzofuran motifs include intramolecular C-C bond formation of functionalized diaryl ethers and intramolecular C-O bond formation of 2-arylphenols (Scheme 1a).[7] Generally, xanthenes are constructed while xanthones are treated with reductants. Alternatively, Lewis acids-catalyzed one-pot reaction of salicylaldehydes and cyclohexenones is reported to afford xanthene derivatives (Scheme 1b).[8] To produce the xanthone skeletons, intramolecular electrophilic acylation of 2-aryloxybenzoic acids is the most representative method. Besides, catalytic cross-coupling reactions of 2-substituted benzaldehydes and phenols opened up a new path to generate xanthones (Scheme 1c).[9] In spite of efficiency, these methods still suffer from drawbacks, such as high cost, narrow substrate scope, and unsatisfactory regioselectivity. Therefore, the development of an efficient and universal synthetic route to dibenzofurans, xanthenes, and xanthones is still of high importance.

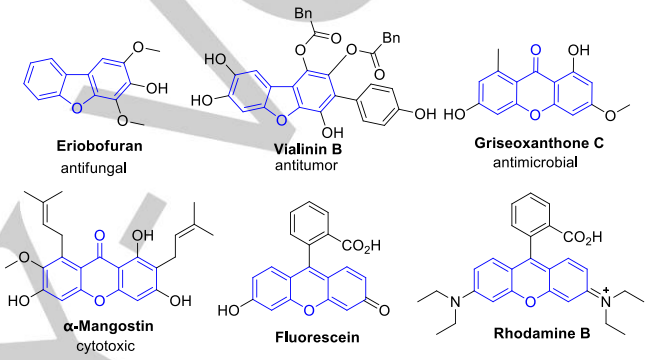

Figure 1. Selected examples of dibenzofuran, xanthene and xanthone derivatives.

One-pot tandem reactions provide a powerful tool for the construction of molecules with diversity and complexity from simple and easily available starting materials.[10] Compared with common sequential stepwise conversions, cascade reactions feature multiple-bond cleavages and formations while avoid tedious purification of intermediates. The application of non-toxic, air- and moisture-stable either linear or cyclic diphenyl iodoniums (CDPIs) in the construction of useful polycyclic aromatics is one of the fastest growing research areas.[11] Previous work has demonstrated that annulations of CDPIs with carbon, nitrogen, and sulfur sources prove valuable to deliver diverse polycyclic compounds, including substituted fluorenes,[12] phenanthrenes,[13] carbazoles,[14] acridines,[15] and dibenzothiophenes.[16] More recently, we have successfully completed the oxygenation of heterocyclic iodoniums (HCIs) with water as an oxygen source, enabling the assembly of oxygen-bridged polycyclic heteroarenes.[17] Herein, we are fully exploring the oxygenation strategy as a practical and concise method to rapidly synthesize dibenzofurans, xanthenes, and xanthones from CDPIs with medium-ring sizes. (Scheme 1d).

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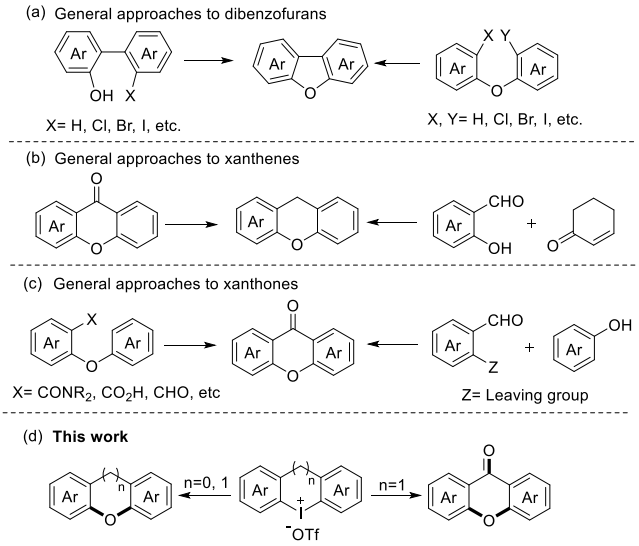
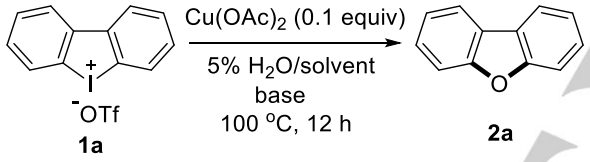


Scheme 1. Synthesis of dibenzofurans, xanthenes and xanthones. (a-c) general approaches and (d) this work.

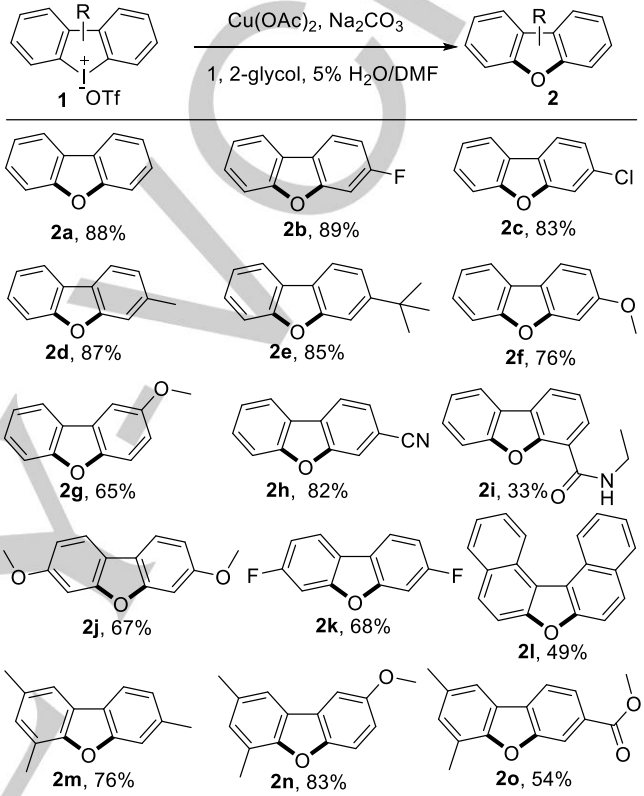
Results and Discussion



Entry	Base (3 equiv)	Solvent	Yield(%)[a]
1	Na_2CO_3	EtOH	25
2	Na_2CO_3	*i*-PrOH	73
3	Na_2CO_3	*t*-BuOH	79
4	Na_2CO_3	MeCN	34
5	Na_2CO_3	toluene	23
6	Na_2CO_3	DMSO	17
7	Na_2CO_3	DMF	88
8	K_2CO_3	DMF	74
9	K_3PO_4	DMF	51
10	Cs_2CO_3	DMF	38
11	TEA	DMF	43

Table 1. Optimization for synthesis of dibenzofuran. Reaction conditions: **1a** (0.2 mmol), $Cu(OAc)_2$ (10 mol %), 1, 2-glycol (3 equiv), base (3 equiv), 5%H_2O/solvent (1.0 mL, 0.2 M), Ar, 100 °C, 12 h. [a]Isolated yield.

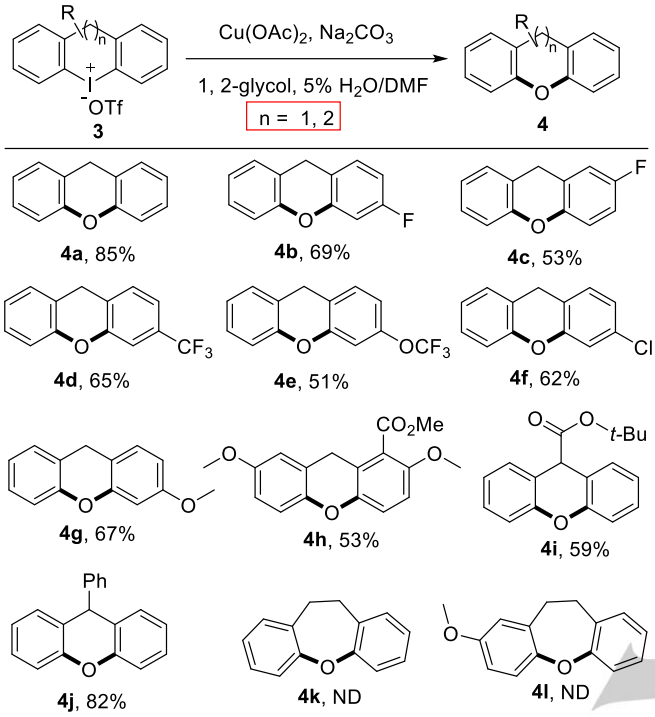
Following our previous study, a thorough screening of solvents and additional bases was carried out with $Cu(OAc)_2$ as the catalyst.[17] At the outset of this investigation, the reaction of diphenyliodonium triflate (**1a**) and water was used as a model, performed in the presence of EtOH heated at 100 °C for 12h. Simple dibenzofuran **2a** was obtained albeit at a low yield (25%, Table 1, entry 1). Surprisingly, secondary and tertiary alcohols substantially improved the reaction yields (entries 2-3). However, MeCN, toluene and DMSO were not appropriate solvents (entries 4-6), indicating that solvents have a pronounced effect on the reaction efficiency. Finally, DMF was proved to be the best choice (entry 7). In the screening of bases, various inorganic and organic bases were tested. In comparison with Na_2CO_3, bases such as K_2CO_3, K_3PO_4, Cs_2CO_3 and triethylamine (TEA) were detrimental to this transformation (entries 7-11).



Scheme 2. Substrate scope for synthesis of dibenzofuran derivatives. Reaction conditions: **1** (0.2 mmol), $Cu(OAc)_2$ (10 mol %), 1, 2-glycol (3 equiv), Na_2CO_3 (3 equiv), 5 % H_2O/DMF (1.0 mL, 0.2 M), Ar, 100 °C, 12 h.

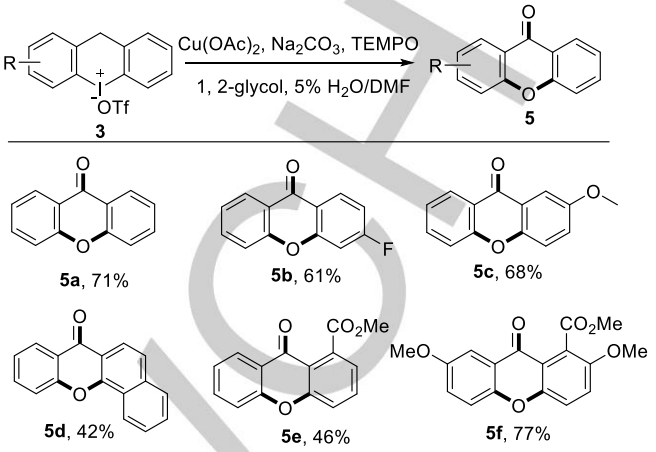
After the optimization of reaction conditions, we initially investigated the scope of 5-membered CDPIs (**1**). Advantageously, the expected dibenzofuran derivatives were obtained in moderate to good yields regardless of the chemical properties of substituted groups (scheme 2). It is important to note that substituents fluorine and chlorine were tolerated (**2a**, **2b**), offering further potential synthetic functionalization. CDPIs with both electron-donating and electron-withdrawing substituents afforded the corresponding products smoothly (**2d**-**2i**). Besides, substrates with a same substituent locating at different positions led to similar yields (**2f** *vs* **2g**), confirming the reaction efficiency was not noticeably altered by substituent positions. The CDPIs possessing disubstituent on both aryls were also applicable to give desired products (**2j** and **2k**). It is notable that hypervalent iodoniums consisting of two naphthyl moieties also worked smoothly (**2l**). The robustness of this protocol was further demonstrated when more congested substrates were successfully transformed into trisubstituted

benzofurans (**2m**-**2o**). Recently, a similar strategy with five-membered CDPIs was also reported by Li group,[18] further confirming that our previous reported oxygenation of five-membered HCIs could be expanded to CDPIs.[17]



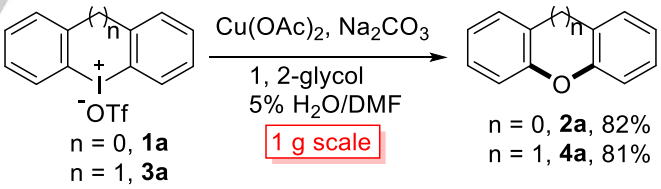
Scheme 3. Substrate scope for synthesis of xanthene derivatives. Reaction conditions: **3** (0.2 mmol), $Cu(OAc)_2$ (10 mol %), 1, 2-glycol (3 equiv), Na_2CO_3 (3 equiv), 5% H_2O/DMF (1.0 mL, 0.2 M), Ar, 100 °C, 12 h. Note: ND means not detected.

Since the oxygenation of five-membered CDPIs was realized, we wondered whether such strategy could be explored in CDPIs with other ring sizes. Thus, a range of functionalized 6-membered CDPIs were prepared and subjected to the above copper catalytic systems. As shown in scheme 3, under the reaction conditions, substrate **3a** was converted to 9H-xanthene (**4a**). It is well known that, in the drug design and discovery area, the introduction of fluorine generally increases metabolic stability and improves bioavailability of the non-fluorinated parent small molecules. Therefore, substrates fluorinated diversely (-F, -CF_3, -OCF_3) were prepared and then underwent the desired annulation to furnish xanthenes derivatives (**4b**-**4e**). Other halogen such as chlorine was also found intact in generation of **4f**. Additionally, electron-rich substrate was compatible with the method to give **4g**. Moreover, it was observed that both electron donating and electron withdrawing functionalities could be combined into one molecule to form more complex xanthene derivative **4h**. Another attractive feature of this methodology was that the methylene part in six-membered iodonium ring could be pre-installed with ester and benzene ring, diversifying xanthene structures (**4i** and **4j**). In general, the oxygenation of six-membered CDPIs worked smoothly in our current method. However, CDPIs with a seven-membered iodonium ring failed the oxygenation to give the expected compounds (**4k** and **4l**) while the sulfur insertion was successful in our previous work.[16a]



Scheme 4. Substrate scope for synthesis of xanthone derivatives. Reaction conditions: **3** (0.2 mmol), $Cu(OAc)_2$ (10 mol %), 1, 2-glycol (3 equiv), Na_2CO_3 (3 equiv), TEMPO (1.2 equiv), 5% H_2O/DMF (1.0 mL, 0.2 M), Ar, 100 °C, 12 h.

During our investigation of the oxygenation of CDPIs with water, possible radical pathways were first examined. After addition of TEMPO, a typical radical scavenger, the oxygenation was not terminated. Moreover, xanthones were obtained at reasonable yields (Scheme 4). This finding further excluded a radical pathway although hypervalent iodoniums could enable the generation of radical intermediates.[19] In this case, TEMPO likely acted as an oxidant to oxidize the above in-situ produced xanthenes during the new reaction conditions.[20] The reaction scope was extended to generate xanthones containing a variety of useful functionality including fluorine (**5b**), methoxy (**5c**), benzene ring (**5d**), and methoxycarbonyl (**5e** and **5f**) groups.



Scheme 5. Scale-up reactions. Reaction conditions: CDPIs (0.2 mmol), $Cu(OAc)_2$ (10 mol %), 1, 2-glycol (3 equiv), Na_2CO_3 (3 equiv), 5% H_2O/DMF (1.0 mL, 0.2 M), Ar, 100 °C, 12 h.

To highlight the robustness and practicality of this method, two scale-up reactions were performed using **1a** and **3a** at 1 gram scale to furnish the corresponding products **2a** and **4a** without compromised yields, indicating that the present protocol could be readily adapted for a larger-scale preparation (scheme 5).

Conclusions

In conclusion, we have fully investigated an effective copper-catalyzed oxygenation of five- and six-membered CDPIs with

H_2O to construct a library of dibenzofurans and xanthenes derivatives. Of note, seven-membered CDPIs do not work with this approach. The methodology can provide structurally diverse xanthones in presence of additional TEMPO. Our oxygenation approach may prove valuable to obtain biologically and pharmaceutically important oxygenated heterocyclic structures.

Experimental Section

General Information. All solvents were commercially available and were used without further purification unless stated. The chemicals used were either purchased from commercial sources or prepared according to literature procedures for CDPIs.[16a] The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance spectrometer 400 at 400 MHz, 100 MHz respectively. Chemical shifts are given in ppm (δ) referenced to $CDCl_3$ with 7.26 for ^{1}H and 77.10 for ^{13}C, and to d_6-DMSO with 2.50 for ^{1}H and 39.5 for ^{13}C. In the case of multiplet, the signals are reported as intervals. Signals are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants are expressed in hertz. High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer (ESI mode), Orbitrap LC-MS (APCI mode) and Agilent 7250 Accurate Mass Q-TOF GC/MS (EI mode). Melting point was measured by BUCHI Melting Point B-540.The progress of the reactions was monitored by thin-layer chromatography on a glass plate coated with silica gel with fluorescent indicator (GF254). Column chromatography was performed on silica gel (200-300 mesh).

General procedure to synthesize dibenzofuran (2) and xanthene derivatives (4). To a tube was added CDPIs (0.2 mmol, 1.0 equiv), Na_2CO_3 (3.0 equiv), $Cu(OAc)_2$ (0.1 equiv), 1,2-glycol (3.0 equiv), 5 % H_2O/DMF (1.0 mL, 0.2 M). Then the tube was sealed, degassed and recharged with argon. The reaction proceeded at 100 °C for 12 h under argon atmosphere. The remained mixture was extracted with EtOAc, the combined organic layers were washed with H_2O and brine and dried over anhydrous Na_2SO_4, evaporated in vacuo. The residue was purified by column chromatography on a silica gel (PE/EtOAc) to provide compounds **2** and **4**.

Dibenzo[*b,d*]furan (**2a**): The product was isolated as a white solid (29 mg, 88%), mp 82-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.7, 0.6 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.43 (m, 2H), 7.35 (td, J = 7.6, 0.9 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 127.3, 124.4, 122.8, 120.8, 111.8 ppm. HRMS (APCI) m/z calcd for $C_{12}H_9O$ $[M+H]^+$: 169.0649, found: 169.0648.

3-Fluorodibenzo[*b,d*]furan (**2b**): The product was isolated as a white solid (33 mg, 89%), mp 89-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.8 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.56 (d, J = 8.2 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.28 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.09 (td, *J* = 9.0, 2.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 161.3, 157.0, 126.9, 123.8, 123.2, 121.3, 121.2, 120.7, 120.5, 111.8, 111.0, 110.8, 100.1, 99.9, 99.7 ppm. HRMS (EI) m/z calcd for $C_{12}H_7FO$ $[M]^+$: 186.0475, found: 186.0481.

3-Chlorodibenzo[*b,d*]furan (**2c**): The product was isolated as a white solid (33 mg, 83%), mp 99-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.39 – 7.30 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 156.5, 132.8, 127.6, 123.6, 123.5, 123.2, 123.1, 121.3, 120.7, 112.4, 111.9 ppm. HRMS (APCI) m/z calcd for $C_{12}H_8ClO$ $[M+H]^+$: 203.0258, found: 203.0258.

3-Methyldibenzo[*b,d*]furan (**2d**): The product was isolated as a white solid (31 mg, 87%), mp 62-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.39 (s, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 156.3, 137.8, 126.7, 124.5, 124.1, 122.7, 121.8, 120.4, 120.3, 112.1, 111.7, 22.1 ppm. HRMS (APCI) m/z calcd for $C_{13}H_{11}O$ $[M+H]^+$: 183.0804, found: 183.0805.

3-(*tert*-Butyl)dibenzo[*b,d*]furan (**2e**): The product was isolated as a white solid (38 mg, 85%), mp 68-69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.60 (s, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 8.1 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 1.42 (s, 9H) ppm. HRMS (EI) m/z calcd for $C_{16}H_{16}O$ $[M]^+$: 224.1196, found: 224.1201.

3-Methoxydibenzo[*b, d*]furan (**2f**): The product was isolated as a white solid (30 mg, 76%), mp 43-44 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.4 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.35 (m, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 2.2 Hz, 1H), 6.95 (dd, *J* = 8.5, 2.2 Hz, 1H), 3.91 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 157.7, 156.5, 125.8, 124.6, 122.9, 121.1, 119.9, 117.5, 111.5, 111.1, 96.6, 55.9 ppm. HRMS (APCI) m/z calcd for $C_{13}H_{11}O_2$ $[M+H]^+$: 199.0754, found: 199.0754.

2-Methoxydibenzo[*b,d*]furan (**2g**): The product was isolated as a white solid (26 mg, 65%), mp 46-47 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.46 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.42 (d, *J* = 2.5 Hz, 1H), 7.33 (dd, *J* = 11.0, 4.0 Hz, 1H), 7.05 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.92 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 156.0, 151.1, 127.3, 124.9, 124.6, 122.6, 120.7, 115.3, 112.3, 111.9, 104.0, 56.2 ppm. HRMS (APCI) m/z calcd for $C_{13}H_{11}O_2$ $[M+H]^+$: 199.0754, found: 199.0754.

Dibenzo[*b,d*]furan-3-carbonitrile (**2h**): The product was isolated as a white solid (32 mg, 82%), mp 133-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.93 (m, 2H), 7.86 (s, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 155.1, 129.4, 128.8, 126.7, 123.8, 122.9, 121.7, 121.6, 119.2, 115.9, 112.3, 109.9 ppm. HRMS (APCI) m/z calcd for $C_{13}H_8NO$ $[M+H]^+$: 194.0600, found: 194.0601.

***N*-Ethyldibenzo[*b,d*]furan-4-carboxamide** (**2i**): The product was isolated as a white solid (16 mg, 33%), mp 96-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.7 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.55 – 7.37 (m, 3H), 3.72 – 3.63 (m, 2H), 1.38 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 155.7, 153.1, 129.2, 127.9, 125.0, 124.0, 123.8, 123.6, 123.4, 121.0, 118.3, 111.8, 35.1, 15.2 ppm. HRMS (ESI) m/z calcd for $C_{15}H_{14}NO_2$ $[M+H]^+$: 240.1019, found: 240.1013.

3,7-Dimethoxydibenzo[*b,d*]furan (**2j**): The product was isolated as a white solid (30 mg, 67%), mp 91-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 1.5 Hz, 2H), 6.91 (dd, *J* = 8.5, 1.5 Hz, 2H), 3.89 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 157.7, 120.2, 117.7, 110.8, 96.8, 55.9 ppm. HRMS (ESI) m/z calcd for $C_{14}H_{13}O_3$ $[M+H]^+$: 229.0859, found: 229.0855.

3,7-Difluorodibenzo[*b,d*]furan (**2k**): The product was isolated as a white solid (28 mg, 68%), mp 82-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.5, 5.3 Hz, 2H), 7.31 – 7.23 (m, 2H), 7.16 – 7.00 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 161.0, 157.4, 157.2, 121.0, 120.9, 120.2, 111.3, 111.1, 100.2, 100.1, 99.8 ppm. HRMS (EI) m/z calcd for $C_{12}H_6F_2O$ $[M]^+$: 204.0381, found: 204.0383.

Dinaphtho[2,1-*b*:1',2'-*d*]furan (**2l**): The product was isolated as a white solid (27 mg, 49%), mp 102-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (d, J = 8.5 Hz, 2H), 8.08 (d, J = 8.0 Hz, 2H), 7.97 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.9 Hz, 2H), 7.80 – 7.70 (m, 2H), 7.60 (t, J = 7.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 131.4, 129.7, 128.8, 128.5, 126.3, 125.8, 124.6, 119.6, 112.9 ppm. HRMS (APCI) m/z calcd for $C_{20}H_{13}O$ $[M+H]^+$: 269.0961, found: 269.0961.

2,4,7-Trimethyldibenzo[*b,d*]furan (**2m**): The product was isolated as a white solid (32 mg, 76%), mp 71-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.8 Hz, 1H), 7.53 (s, 1H), 7.37 (s, 1H), 7.13 (d, J = 7.8 Hz, 1H), 7.05 (s, 1H), 2.55 (s, 3H), 2.52 (s, 3H), 2.47 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 153.5, 137.3, 132.1, 128.9, 123.9, 123.8, 122.2, 121.3, 120.3, 117.8, 112.0, 22.1, 21.4, 15.3 ppm. HRMS (ESI) m/z calcd for $C_{15}H_{15}O$ $[M+H]^+$: 211.1117, found: 211.1120.

8-Methoxy-2,4-dimethyldibenzo[*b,d*]furan (**2n**): The product was isolated as a white solid (38 mg, 83%), mp 82-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.45 (d, J = 8.9 Hz, 1H), 7.37 (d, J = 2.6 Hz, 1H), 7.07 (s, 1H), 7.02 (dd, J = 8.9, 2.7 Hz, 1H), 3.91 (s, 3H), 2.55 (s, 3H), 2.47 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 154.4, 151.3, 132.0, 129.5, 125.3, 124.0, 121.5, 118.0, 114.9, 112.2, 104.0, 56.2, 21.4, 15.3 ppm. HRMS (ESI) m/z calcd for $C_{15}H_{15}O_2$ $[M+H]^+$: 227.1067, found: 227.1061.

Methyl 6,8-dimethyldibenzo[*b,d*]furan-3-carboxylate (**2o**): The product was isolated as a white solid (27 mg, 54%), mp 98-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.03 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.60 (s, 1H), 7.15 (s, 1H), 3.97 (s, 3H), 2.57 (s, 3H), 2.48 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 155.9, 154.9, 132.8, 130.9, 129.1, 128.6, 124.0, 122.9, 121.8, 120.3, 118.7, 113.3, 52.4, 21.4, 15.3 ppm. HRMS (ESI) m/z calcd for $C_{16}H_{15}O_3$ $[M+H]^+$: 255.1016, found: 255.1011.

9*H*-Xanthene (**4a**): The product was isolated as a white solid (31 mg, 85%), mp 101-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, J = 13.7, 7.2 Hz, 4H), 7.09 – 7.04 (m, 4H), 4.06 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 129.1, 127.8, 123.1, 120.7, 116.6, 28.0 ppm. HRMS (EI) m/z calcd for $C_{13}H_{10}O$ $[M+H]^+$: 182.0726, found: 182.0730.

3-Fluoro-9*H*-xanthene (**4b**): The product was isolated as a white solid (28 mg, 69%), mp 113-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, J = 18.0, 8.3 Hz, 2H), 7.14 – 7.08 (m, 1H), 7.07 – 7.00 (m, 2H), 6.76 (dd, J = 13.0, 9.0 Hz, 2H), 4.01 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 160.9, 152.7, 152.6, 151.6, 129.8, 129.8, 129.1, 127.9, 123.5, 120.4, 116.6, 116.3, 110.3, 110.0, 104.2, 103.9, 27.4 ppm. HRMS (EI) m/z calcd for $C_{13}H_9FO$ $[M+H]^+$: 200.0632, found: 200.0636.

2-Fluoro-9*H*-xanthene (**4c**): The product was isolated as a white solid (21 mg, 53%), mp 117-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.12 (m, 2H), 7.03 (dd, J = 7.8, 4.7 Hz, 2H), 7.01 – 6.96 (m, 1H), 6.90 (dd, J = 14.0, 5.7 Hz, 2H), 4.04 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 157.3, 152.0, 148.2, 128.9, 129.0, 123.3, 122.2, 122.1, 119.7, 117.7, 117.6, 116.6, 115.1, 114.9, 114.6, 114.4, 28.3 ppm. HRMS (EI) m/z calcd for $C_{13}H_9FO$ $[M]^+$: 200.0632, found: 200.0633.

3-(Trifluoromethyl)-9*H*-xanthene (**4d**): The product was isolated as a white solid (32 mg, 65%), mp 124-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 1H), 7.25 (d, J = 5.9 Hz, 2H), 7.23 – 7.14 (m, 2H), 7.05 (dd, J = 7.4, 3.7 Hz, 2H), 4.08 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 151.6, 130.5, 130.2, 129.6, 129.0, 128.2, 125.3, 124.7, 123.7, 122.6, 119.8, 119.7, 119.6, 116.7, 114.0, 113.9 ppm. HRMS (APCI) m/z calcd for $C_{14}H_8F_3O$ $[M-H]^-$: 249.0533, found: 249.0536.

3-(Trifluoromethoxy)-9*H*-xanthene (**4e**): The product was isolated as a white solid (27 mg, 51%), mp 142-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, J = 20.3, 7.9 Hz, 3H), 7.06 (t, J = 6.8 Hz, 2H), 6.94 (s, 1H), 6.90 (d, J = 8.4 Hz, 1H), 4.04 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 151.5, 148.5, 130.4, 129.8, 129.1, 128.7, 128.0, 123.6, 121.9, 121.1, 120.1, 119.4, 119.3, 116.6, 115.6, 109.7, 27.5 ppm. HRMS (EI) m/z calcd for $C_{14}H_9F_3O_2$ $[M]^+$: 266.0549, found: 266.0555.

3-Chloro-9*H*-xanthene (**4f**): The product was isolated as a white solid (27 mg, 62%), mp 129-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.13 (m, 2H), 7.09 (d, J = 8.1 Hz, 1H), 7.07 – 6.97 (m, 4H), 4.01 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 151.6, 132.8, 129.9, 129.1, 128.0, 123.5, 123.2, 120.2, 119.2, 116.9, 116.7, 27.6 ppm. HRMS (EI) m/z calcd for $C_{13}H_9ClO$ $[M]^+$: 216.0336, found: 216.0340.

3-Methoxy-9*H*-xanthene (**4g**): The product was isolated as a white solid (28 mg, 67%), mp 82-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 7.9 Hz, 1H), 8.26 (d, J = 8.9 Hz, 1H), 7.69 (t, J = 7.7 Hz, 1H), 7.46 (d, J = 8.3 Hz, 1H), 7.37 (t, J = 7.2 Hz, 1H), 6.95 (d, J = 8.9 Hz, 1H), 6.89 (s, 1H), 3.94 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 165.2, 158.2, 156.3, 134.4, 128.4, 126.8, 124.0, 122.1, 117.8, 115.9, 113.4, 100.3, 100.1, 56.0 ppm. HRMS (EI) m/z calcd for $C_{14}H_{12}O_2$ $[M]^+$: 212.0832, found: 212.0836.

Methyl 2,7-dimethoxy-9*H*-xanthene-1-carboxylate (**4h**): The product was isolated as a white solid (32 mg, 53%), mp 116-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 9.0 Hz, 1H), 6.94 (d, J = 8.9 Hz, 1H), 6.81 (d, J = 9.0 Hz, 1H), 6.75 (dd, J = 8.9, 3.0 Hz, 1H), 6.66 (d, J = 2.9 Hz, 1H), 3.97 (s, 5H), 3.82 (s, 3H), 3.77 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 155.4, 152.2, 146.2, 145.7, 122.6, 119.9, 119.1, 118.5, 117.1, 113.9, 113.2, 111.2, 56.7, 55.8, 52.6, 26.6 ppm. HRMS (ESI) m/z calcd for $C_{17}H_{17}O_5$ $[M+H]^+$: 301.1071, found: 301.1072.

***tert*-Butyl 9*H*-xanthene-9-carboxylate** (**4i**): The product was isolated as a white solid (33 mg, 59%), mp 132-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 4H), 7.16 – 7.11 (m, 2H), 7.08 (td, J = 7.4, 1.2 Hz, 2H), 4.87 (s, 1H), 1.35 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 151.5, 128.9, 123.2, 119.1, 117.0, 81.8, 46.6, 27.9 ppm. ^{13}C NMR (100 MHz, dept135, $CDCl_3$) δ 128.9, 128.8, 123.1, 116.9, 46.4, 27.8 ppm. HRMS (ESI) m/z calcd for $C_{18}H_{19}O_3$ $[M+H]^+$: 283.1329, found: 283.1330.

9-Phenyl-9*H*-xanthene (**4j**): The product was isolated as a yellow solid (42 mg, 82%), mp 136-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 1H), 7.35 – 7.20 (m, 7H), 7.11 – 7.05 (m, 3H), 6.94 (d, J = 7.5 Hz, 2H), 5.85 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 142.8, 140.1, 131.2, 129.9, 128.5, 128.4, 128.2, 128.1, 126.6, 60.9 ppm. ^{13}C NMR (100 MHz, dept135, $CDCl_3$) δ 140.0, 131.0, 129.8, 128.4, 128.3, 128.1, 126.5, 60.8 ppm. HRMS (EI) m/z calcd for $C_{19}H_{14}O$ $[M]^+$: 258.1039, found: 258.1040.

General procedure to synthesize xanthone derivatives (5). To a tube was added 6-membered CDPIs (0.2 mmol, 1.0 equiv), TEMPO (1.2 equiv), Na_2CO_3 (3.0 equiv), $Cu(OAc)_2$ (0.1 equiv), 1,2-glycol (3.0 equiv), 5 % H_2O/DMF (1.0 mL, 0.2 M). Then the tube was sealed, degassed and recharged with argon. The reaction proceeded at 100 °C for 12 h under argon atmosphere. The remained mixture was extracted with EtOAc, the combined organic layers were washed with H_2O and brine and dried over anhydrous Na_2SO_4, evaporated in vacuo. The residue was purified by column chromatography on a silica gel (PE/EtOAc) to provide compounds **5**.

9*H*-Xanthen-9-one (**5a**): The product was isolated as a white solid (28 mg, 71%), mp 171-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 7.6

Hz, 2H), 7.91 (t, *J* = 7.0 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.56 (t, *J* = 7.1 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 176.3, 155.3, 134.0, 125.9, 123.1, 121.0, 117.1 ppm. HRMS (ESI) m/z calcd for $C_{13}H_9O_2$ $[M+H]^+$: 197.0597, found: 197.0609.

3-Fluoro-9*H*-xanthen-9-one (**5b**): The product was isolated as a white solid (26 mg, 61%), mp 163-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.42 – 8.29 (m, 2H), 7.78 – 7.66 (m, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.18 (dd, *J* = 9.3, 2.2 Hz, 1H), 7.11 (td, *J* = 8.6, 2.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 176.3, 167.9, 165.4, 157.6, 156.4, 135.1, 129.6, 129.5, 126.9, 124.5, 121.9, 119.0, 118.0, 113.0, 112.8, 104.9, 104.6 ppm. HRMS (ESI) m/z calcd for $C_{13}H_8FO_2$ $[M+H]^+$: 215.0503, found: 215.0507.

2-Methoxy-9*H*-xanthen-9-one (**5c**): The product was isolated as a white solid (31 mg, 68%), mp 132-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.35 (d, *J* = 7.8 Hz, 1H), 7.72 (t, *J* = 5.4 Hz, 2H), 7.47 (dd, *J* = 18.1, 8.8 Hz, 2H), 7.41 – 7.31 (m, 2H), 3.92 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 177.3, 156.3, 156.1, 151.2, 134.7, 126.8, 125.1, 123.9, 122.3, 121.4, 119.6, 118.1, 106.0, 56.1 ppm. HRMS (ESI) m/z calcd for $C_{14}H_{11}O_3$ $[M+H]^+$: 227.0703, found: 227.0705.

7*H*-Benzo[*c*]xanthen-7-one (**5d**): The product was isolated as a white solid (21 mg, 42%), mp 155-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.68 (d, *J* = 7.4 Hz, 1H), 8.41 (dd, *J* = 7.9, 1.1 Hz, 1H), 8.28 (d, *J* = 8.7 Hz, 1H), 7.99 – 7.89 (m, 1H), 7.82 – 7.64 (m, 5H), 7.45 (t, *J* = 7.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 177.0, 155.9, 153.8, 136.7, 134.5, 129.7, 128.2, 127.0, 126.7, 124.6, 124.2, 124.2, 123.0, 122.6, 121.6, 118.2, 117.8 ppm. HRMS (ESI) m/z calcd for $C_{17}H_{11}O_2$ $[M+H]^+$: 247.0754, found: 247.0753.

Methyl 9-oxo-9*H*-xanthene-1-carboxylate (**5e**): The product was isolated as a white solid (23 mg, 46%), mp 144-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.29 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.58 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.32 (dd, *J* = 7.3, 1.0 Hz, 1H), 4.05 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 176.1, 170.1, 156.1, 155.8, 135.3, 134.4, 134.2, 126.8, 124.4, 122.6, 121.8, 119.7, 118.8, 117.9, 53.6, 53.2 ppm. HRMS (ESI) m/z calcd for $C_{15}H_{11}O_4$ $[M+H]^+$: 255.0652, found: 255.0648.

Methyl 2,7-dimethoxy-9-oxo-9*H*-xanthene-1-carboxylate (**5f**): The product was isolated as a white solid (48 mg, 77%), mp 167-168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.64 (d, *J* = 3.1 Hz, 1H), 7.56 (d, *J* = 9.2 Hz, 1H), 7.41 (dd, *J* = 9.2, 4.9 Hz, 2H), 7.33 (dd, *J* = 9.2, 3.1 Hz, 1H), 4.08 (s, 3H), 3.92 (s, 3H), 3.88 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 176.1, 167.9, 156.0, 152.3, 150.7, 150.1, 125.4, 121.3, 120.8, 120.1, 119.3, 119.3, 118.7, 105.5, 57.0, 55.9, 52.9 ppm. HRMS (ESI) m/z calcd for $C_{17}H_{15}O_6$ $[M+H]^+$: 315.0863, found: 315.0863.

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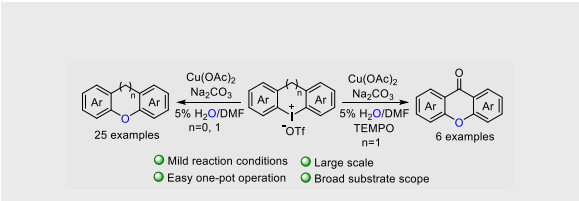

Oxygenation of cyclic diphenyl iodoniums (CDPIs) with varied medium-ring sizes has been fully investigated. This practical copper-catalyzed tandem reaction of CDPIs with water as the oxygen source enables the construction of derivatised dibenzofurans and xanthenes at moderate to good yields. Moreover, structurally important xanthones are also successfully accessed under the oxygenation conditions with additional TEMPO.

Oxygen Heterocycles*

*Daqian Zhu, Min Li, Zhouming Wu, Yongliang Du, Bingling Luo, Peng Huang, Shijun Wen**

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Copper-Catalyzed One-Pot Synthesis of Dibenzofurans, Xanthenes, and Xanthones from Cyclic Diphenyl Iodoniums