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Ga(OTf)$_3$-mediated synthesis of substituted benzofurans

Heui-Sin Wang, Chieh-Kai Chan, Meng-Yang Chang *

Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 807, Taiwan, ROC

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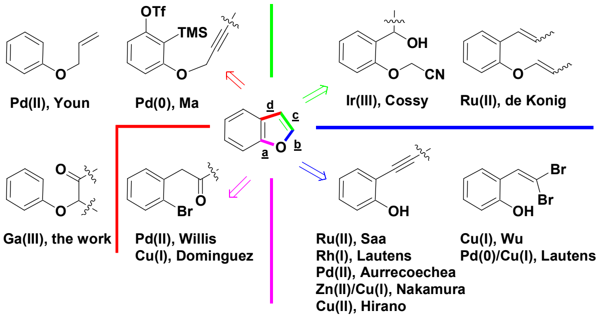
ABSTRACT

A synthetic procedure, for the synthesis of a series of functionalized benzofurans **3**–**5** and benzonaphthofurans **6**, starting from intermolecular O-alkylation of α-bromoaryl ketones **2** with potassium oxygenated phenoxides **1** followed by Ga(OTf)$_3$-catalyzed direct intramolecular cyclodehydration of the resulting α-aryloxyaryl ketones, has been developed. The use of various metal triflates was investigated for a facile approach and efficient transformation. Pentacyclic benzophenanthrofurans **7** were prepared via photolytic annulations of **5**.

1. Introduction

Substituted arene-fused furans are of great interest because of their useful biological and pharmacological activities.[1] Accordingly, there exists a wide selection of methods for the synthesis of this key benzofuran core via metal-promoted intramolecular annulation. The bond formation of a furan motif could be divided into four synthetic routes (Scheme 1),[2–5] including (1) O-arylation of enolates (Pd^{II}, Cu^{I}; a bond formation),[2] (2) cycloisomerization of *o*-functionalized phenols (Ru^{II}, Rh^{I}, Pd^{II}, Zn^{II}/Cu^{I}, Cu^{II}, Cu^{I}, Pd^{0}/Cu^{I}; b bond formation),[3a–g] (3) oxidative dehydration of a benzyl alcohol (Ir^{III})[4a] or ring-closing metathesis of a diene (Ru^{II}, c bond formation),[4b] and (4) ene reaction of alkynyl benzyne (Pd^{0})[5a] or a Claisen rearrangement/oxidative cyclization of an allyl aryl ether (Pd^{II}; d bond formation).[5b] However, intermolecular annulations are also popular routes to such benzofurans[6] among the existing methods. Development of a new, single-step route for the simultaneous bond formation and ring-construction of benzofurans from readily available starting materials still represents a continuing need in the organic synthetic field.



Scheme 1. Metal-promoted intramolecular annulations.

2. Results and discussion

As part of our efforts in the development of metal triflate-promoted robust and efficient reactions,[7,8] we have now streamlined the Ga(OTf)$_3$-mediated synthesis of substituted benzofurans (from d bond formation) via the intermolecular O-alkylation of α-bromoaryl ketones with a phenoxide followed by intramolecular cyclodehydration of the resulting α-aryloxyaryl ketones. To the best of our knowledge, for the synthesis of benzofurans, no literature on the Ga(III)-mediated intramolecular annulation has been reported. Among the many metal triflates catalysts recently studied, Ga(OTf)$_3$ is an inexpensive, oxygen-tolerant, catalytic, efficient Lewis acid.[9] Olah[10] and other researchers[11] have reported that Ga(OTf)$_3$ demonstrates high chemo- and regioselectivity, good yields, excellent stability, and recyclability in a variety of transformations. Along this line, we planned to take advantage of the intrinsically high catalytic ability of Ga(OTf)$_3$ to construct the benzofuran system.[12] Initially, we designed a route to benzofuran **3a**, starting from model materials of potassium 3,4,5-trimethoxyphenoxide (**1a**, generated from the reaction of 3,4,5-trimethoxyphenol and KOH$_{(aq)}$ and then removal of H_2O) and α-bromoacetophenone (**2a**). As shown in

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* Corresponding author. E-mail address: mychang@kmu.edu.tw (M.-Y. Chang).

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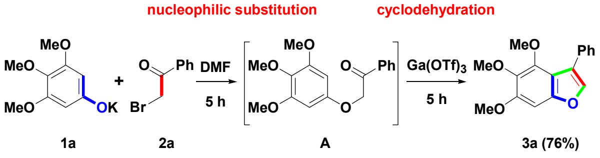
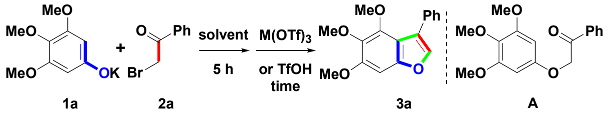
Scheme 2, an intermolecular S_N2 O-alkylation provided α-aryloxy ketone **A**. Subsequently, **3a** was obtained in a 76% yield via 2 mol % of $Ga(OTf)_3$-promoted tandem intramolecular cyclodehydration of **A** in DMF at 25 °C for 5 h under open-vessel conditions.



Scheme 2. $Ga(OTf)_3$-promoted route.

To control the reaction conditions (25 °C, DMF, 5 h), the use of various commercially available metal triflates was investigated for direct transformation. Among the screened catalysts, which included 2 mol % of AgOTf, LiOTf, $Ba(OTf)_2$, $Mg(OTf)_2$, $Ca(OTf)_2$, $Ni(OTf)_2$, $Sn(OTf)_2$, $Zn(OTf)_2$, $Cu(OTf)_2$, $Hg(OTf)_2$, $Al(OTf)_3$, $Fe(OTf)_3$, $Yb(OTf)_3$, $In(OTf)_3$, $Ce(OTf)_3$, $Sm(OTf)_3$, $Gd(OTf)_3$, $La(OTf)_3$, $Sc(OTf)_3$, $Nd(OTf)_3$, $Y(OTf)_3$, $Dy(OTf)_3$, and $Bi(OTf)_3$, only $Sn(OTf)_2$ and $Bi(OTf)_3$ provided better yields of **3a** (entries 2–3, 70% and 62%). $In(OTf)_3$ provided a 48% yield of **3a** along with an 18% yield of **A** (entry 4). In comparison with these metal triflates, $Ga(OTf)_3$ is an optimal catalyst for the generation of **3a**. Furthermore, controlling the $Ga(OTf)_3$ as the catalyst, the factors of equivalency, concentration, time and solvent were studied next. When using 5 mol % of $Ga(OTf)_3$, the isolated yield was similar to that of 2 mol % (entry 5). No obvious changes occurred when decreasing the reaction concentration (5 mL→10 mL) or extending the time (5 h→10 h), as shown in entries 6–7, respectively. After changing the solvents (from DMF to $MeNO_2$, $EtNO_2$, CH_2Cl_2, $CHCl_3$, and DMSO), different results were observed. In entries 8–9, the results showed that $MeNO_2$ and $EtNO_2$ provided **3a** in 48% and 50% yields, respectively, along with the isolation of 3,4,5-trimethoxyphenol (12% and 8%, respectively).

Table 1
Reaction conditions[a]

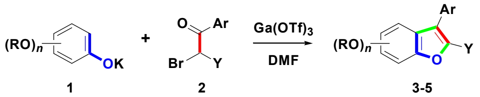


Entry	Catalysts (mol %)	Solvent (mL)	Time (h)	**3a** (%)[b]
1	$Ga(OTf)_3$ (2)	DMF (5)	5	76
2	$Sn(OTf)_3$ (2)	DMF (5)	5	70
3	$Bi(OTf)_3$(2)	DMF (5)	5	62
4	$In(OTf)_3$ (2)	DMF (5)	5	48[c] (67)[d]
5	$Ga(OTf)_3$ (5)	DMF (5)	5	76
6	$Ga(OTf)_3$ (2)	DMF (10)	5	68
7	$Ga(OTf)_3$ (2)	DMF (5)	10	70
8	$Ga(OTf)_3$ (2)	$MeNO_2$ (5)	5	48[e]
9	$Ga(OTf)_3$ (2)	$EtNO_2$ (5)	5	50[e]
10	$Ga(OTf)_3$ (2)	CH_2Cl_2 (5)	5	–[f]
11	$Ga(OTf)_3$ (2)	$CHCl_3$ (5)	5	–[f]
12	$Ga(OTf)_3$ (2)	DMSO (5)	5	–[g]
13	$Ga(OTf)_3$ (2)	DMF (5)	5	58[h]
14	$Ga(OTf)_3$ (0)	DMF (5)	5	–[i]
15	TfOH (2)	CH_2Cl_2 (5)	5	–[f]
16	TfOH (2)	DMF (5)	5	50
17	$Ga(OTf)_3$ (2)/TfOH (2)	DMF (5)	5	70

[a] The reactions were run on a 1.0 mmol scale with **1a**, **2a** (1.05 equiv), 25 °C.
[b] Isolated yields.
[c] 18% of **A** was isolated.
[d] 40 h.
[e] 3,4,5-Trimethoxyphenol was obtained (for entry 8, 12%; entry 10, 8%).
[f] No reaction.
[g] Complex mixture.
[h] 100 °C.
[i] 88% of **A** was isolated.

On the basis of an acidic α-proton of $MeNO_2$ (pK_a=17.2) or $EtNO_2$ (pK_a=16.7), the competitive deprotonation of **1a** could be a possible reason for lower yields of **3a**. Entries 10–11 show that no desired **3a** was observed due to the poor solubility of CH_2Cl_2 and $CHCl_3$. By the involvement of DMSO, a complex mixture was detected (entry 12). By elevating the reaction temperature (25 °C→100 °C, entry 13), **3a** was decreased to a 58% yield under entry 1 conditions. Without the addition of $Ga(OTf)_3$, only **A** (88%) was formed (entry 14). By the involvement of 2 mol % TfOH (entries 15–16), two solvent (CH_2Cl_2 and DMF) were examined. For the combination of 2 mol % TfOH/CH_2Cl_2, no desired **3a** was detected. And, 2 mol % TfOH/DMF provided **3a** in 50% yield.[13] In entry 17, by the combination of $Ga(OTf)_3$ (2 mol %) and TfOH (2 mol %), the yield of **3a** was maintained (70%). According to the above results, we believe that the 2 mol % $Ga(OTf)_3$/DMF system would be the optimal combination for generating **3a**. With optimal conditions (Table 1, entry 1), we further explored the substrate scope of the reaction, and the results are shown in Table 2. For R, Ar and Y substituents of **1** and **2**, the diversified, well-tolerated groups produced **3a**–**s** (70%–87%, entries 1–19), **4a**–**g** (64%–73%, entries 20–26) and **5a**–**i** (56%–67%, entries 27–36) in moderate to good yields. Different substituents of **1** (RO=MeO, CH_2O_2, n=1–3) and **2** (Ar=Ph, $3\text{-}MeOC_6H_4$, $4\text{-}MeOC_6H_4$, $4\text{-}CF_3C_6H_4$, $4\text{-}FC_6H_4$, $4\text{-}PhC_6H_4$, 2-naphthalene, $4\text{-}MeC_6H_4$, 3,4-

Table 2
Synthesis of **3**–**5**[a]

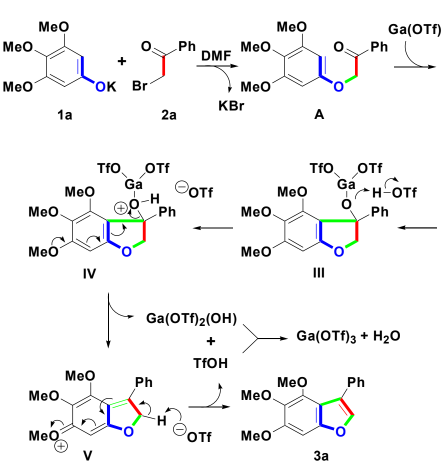


Entry	**1**, $(RO)_n$=	**2**, Ar=, Y=	Yield (%)[b]
			3, **4**, **5**
1	**1a**, 3,4,5-$(MeO)_3$	**2a**, Ph, H	**3a**, 76
2	**1b**, 3,5-$(MeO)_2$	**2b**, 3-$MeOC_6H_4$, H	**3b**, 70
3	**1a**, 3,4,5-$(MeO)_3$	**2b**, 3-$MeOC_6H_4$, H	**3c**, 73
4	**1c**, 3,4-$(MeO)_2$	**2a**, Ph, H	**3d**, 78
5	**1d**, 3,4-CH_2O_2	**2a**, Ph, H	**3e**, 77
6	**1d**, 3,4-CH_2O_2	**2b**, 3-$MeOC_6H_4$, H	**3f**, 80
7	**1d**, 3,4-CH_2O_2	**2c**, 4-$MeOC_6H_4$, H	**3g**, 87
8	**1d**, 3,4-CH_2O_2	**2d**, 4-$CF_3C_6H_4$, H	**3h**, 78
9	**1d**, 3,4-CH_2O_2	**2e**, 4-FC_6H_4, H	**3i**, 76
10	**1d**, 3,4-CH_2O_2	**2f**, 4-PhC_6H_4, H	**3j**, 78
11	**1d**, 3,4-CH_2O_2	**2g**, 2-naphthalene, H	**3k**, 82
12	**1e**, 3-MeO	**2a**, Ph, H	**3l**, 84
13	**1e**, 3-MeO	**2c**, 4-$MeOC_6H_4$, H	**3m**, 84
14	**1e**, 3-MeO	**2h**, 4-MeC_6H_4, H	**3n**, 83
15	**1e**, 3-MeO	**2f**, 4-PhC_6H_4, H	**3o**, 85
16	**1e**, 3-MeO	**2d**, 4-$CF_3C_6H_4$, H	**3p**, 80
17	**1e**, 3-MeO	**2i**, 3,4-$CH_2O_2C_6H_3$, H	**3q**, 80
18	**1e**, 3-MeO	**2j**, 3,4-$Cl_2C_6H_3$, H	**3r**, 80
19	**1e**, 3-MeO	**2g**, 2-naphthalene, H	**3s**, 84
20	**1a**, 3,4,5-$(MeO)_3$	**2k**, Ph, allyl	**4a**, 64
21	**1c**, 3,4-$(MeO)_2$	**2k**, Ph, allyl	**4b**, 66
22	**1d**, 3,4-CH_2O_2	**2k**, Ph, allyl	**4c**, 68
23	**1e**, 3-MeO	**2l**, Ph, benzyl	**4d**, 66
24	**1e**, 3-MeO	**2m**, 4-$MeOC_6H_4$, allyl	**4e**, 73
25	**1e**, 3-MeO	**2n**, 4-MeC_6H_4, allyl	**4f**, 68
26	**1e**, 3-MeO	**2o**, 4-PhC_6H_4, allyl	**4g**, 70
27	**1e**, 3-MeO	**2p**, Ph, Ph	**5a**, 63
28	**1c**, 3,4-$(MeO)_2$	**2p**, Ph, Ph	**5b**, 64
29	**1b**, 3,5-$(MeO)_2$	**2p**, Ph, Ph	**5c**, 65
30	**1d**, 3,4-CH_2O_2	**2p**, Ph, Ph	**5d**, 67
31	**1a**, 3,4,5-$(MeO)_3$	**2p**, Ph, Ph	**5e**, 62
32	**1e**, 3-MeO	**2q**, 4-FC_6H_4, Ph	**5f**, 60
33	**1e**, 3-MeO	**2r**, 4-$MeOC_6H_4$, Ph	**5g**, 63
34	**1b**, 3,5-$(MeO)_2$	**2q**, 4-FC_6H_4, Ph	**5h**, 60
35	**1d**, 3,4-CH_2O_2	**2q**, 4-FC_6H_4, Ph	**5i**, 63
36	**1a**, 3,4,5-$(MeO)_3$	**2q**, 4-FC_6H_4, Ph	**5j**, 56

[a] The reactions were run on a 1.0 mmol scale with **1**, **2** (1.05 equiv), DMF (5 mL), 25 °C, 5 h; then $Ga(OTf)_3$ (2 mol %), 25 °C, 5 h.
[b] Isolated yields.

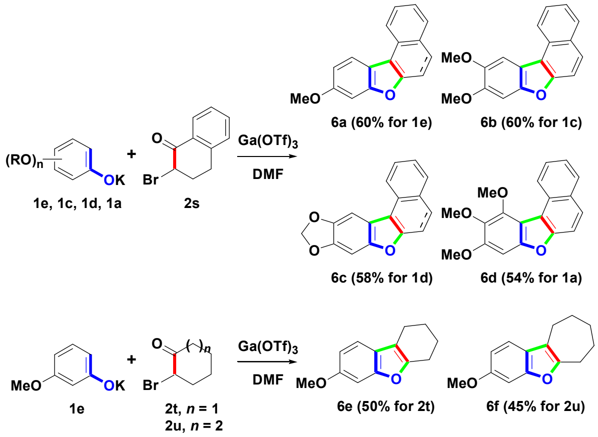
$CH_2O_2C_6H_3$, 3,4-$Cl_2C_6H_3$; Y=allyl, benzyl, Ph) did not affect the one-pot procedure. The structures of **5c**, **5d** and **5j** were determined by single-crystal X-ray crystallography.[14]

The proposed mechanism of **3a** is illustrated in Scheme 3. Beginning with **1a**, O-alkylation of **1a** with **2a** generates **A** in DMF. The initial coordination of **A** with Ga(OTf)$_3$ to the carbonyl oxygen can induce subsequent intramolecular cyclization. Through the *para*-methoxy group of aromatic moiety promoted nucleophilic attack on the intermediate **I**, **II** is formed. Following the deprotonation of **II** by in situ generated triflate ion, **III** is afforded. Then, **III** traps the proton of TfOH to lead **IV** and the resulting triflate ion. Furthermore, *para*-methoxy group promotes the removal of Ga(OTf)$_2$(OH). Finally, **3a** is produced via triflate ion mediated deprotonation of **V**. Subsequently, Ga(OTf)$_3$ is regenerated by forming Ga(OTf)$_2$(OH) and TfOH in situ.

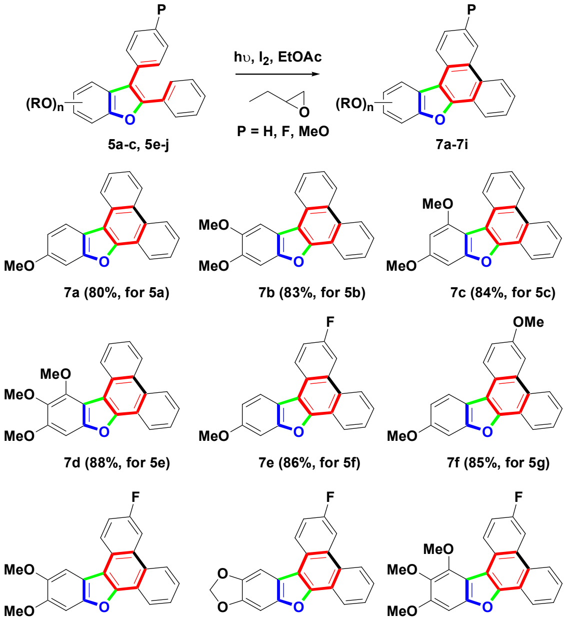


Scheme 3. Proposed mechanism.

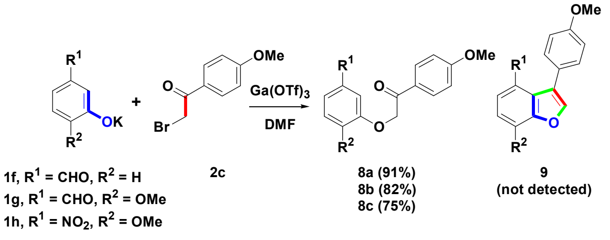
Changing skeleton **2** from acyclic α-bromoketone to bicyclic α-bromotetralone, the synthesis of benzonaphthofurans was investigated via the reaction of **1a** and **1c**–**e** with **2s**, as shown in Scheme 4. For reaction of **1e** and **2s**, an inseparated mixture of **6a** and its dihydroisomer **6a**–**1** with a ratio of 3:1 was isolated in a 60% yield. The similar result was performed for the formation of **6c** (see Supplementary data). Fully conjugated tetracycles **6b** and **6d** were generated in 60% and 54% yields, respectively via the tandem dehydrogenative process. Next, Ga(OTf)$_3$-mediated treatment of **1e** with monocyclic α-bromoketone **2t**–**u** afforded **6e** and **6f** in 50% and 45% yields, respectively. For the provided yields, **6** and **5** were similar but were accessed in lower yields than them of **3** and **4**. The structure of **6c** was determined by single-crystal X-ray crystallography.[14] To extend the application of this domino route, photolytic Scholl annulation of diarylbenzofurans **5a**–**c** and **5e**–**j** was further explored (Scheme 5).[15,16] A number of processes are available for the Scholl reaction. Of these methods used in the previous literature, the photolytic Scholl oxidative annulation provides the most convenient operation and higher yields. By the addition of molecular iodine and 1,2-epoxybutane, pentacyclic functionalized benzophenanthrofurans **7a**–**i** were isolated in 80%–88% yields by the irradiation of **5a**–**c** and **5e**–**j** in EtOAc at rt for 50 h under a 254 nm wavelength irradiation. The structural skeletons of **7f** and **7i** were determined by single-crystal X-ray crystallography.[14] To compare with **1a**–**e** with the electron-donating groups, the substrates **1f**–**h** with the electron-withdrawing group (R^1=CHO, NO_2) were examined, as shown in Scheme 6. Treatment of **1f**–**h** with **2c** furnished **8a**–**c** in 75%–91% yields with no observation of benzofuran **9**. For the generating benzofuran skeleton, the results showed that the efficiency of Ga(OTf)$_3$ was limited in the case of substrates with electron withdrawing groups. Even after increasing the catalytic amounts (10 mol %), the results were still similar. Based on the observations, the electron withdrawing nitrophenyl or carboxyphenyl group inhibit the Ga(OTf)$_3$-catalyzed direct intramolecular cyclodehydration of **1** and **2**. We envisioned that the *para*-oxygenated aryl group is a key substituent for generating the benzofuran skeleton.



Scheme 4. Synthesis of **6a**–**f**.

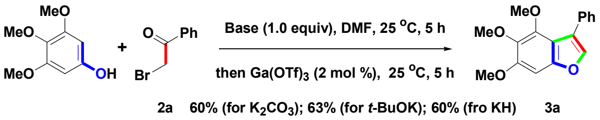


Scheme 5. Synthesis of **7a**–**f**.



Scheme 6. Synthesis of **8a**–**c**.

In further work, a one-pot synthesis of benzofuran was studied by the involvement of different potassium salts, as shown in Scheme 7. Under the above conditions, K_2CO_3, *t*-BuOK and KH provided **3a** in similar yields (60%, 63% and 60%). Although the isolated yield was low, this one-pot process by using bases/DMF was convenient.



Scheme 7. One-pot synthesis of **3a**.

3. Conclusion

In summary, we have developed a method for the synthesis of a series of functionalized benzofurans **3**–**5** and benzonaphthofurans **6** by the intermolecular O-alkylation of α-bromoaryl ketones **2** with potassium oxygenated phenoxides **1** followed by $Ga(OTf)_3$-catalyzed direct intramolecular cyclodehydration of the resulting α-aryloxyaryl ketones. The use of various metal triflates was investigated for the one-pot facile approach and efficient transformation. Pentacyclic benzophenanthrofurans **7** were prepared via photolytic annulations of **5**. The structures of the key products were confirmed by X-ray crystallography. Further investigations regarding the synthetic application of metal triflates are ongoing in our laboratory.

4. Experimental section

4.1. General

All other reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry nitrogen with magnetic stirring. Products in organic solvents were dried with anhydrous magnesium sulfate before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400 and at 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (J) are given in Hertz. High resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD).

4.2. 1-Phenyl-2-(3,4,5-trimethoxyphenoxy)-ethanone (A)

KOH (56 mg, 1.0 mmol) was added to a solution of 3,4,5-trimethoxyphenol (184 mg, 1.0 mmol) in water (5 mL) at 25 °C. The reaction mixture was stirred at 100 °C for 30 min. The reaction mixture was concentrated to afford crude potassium phenoxide **1a** under reduced pressure. Without purification, α-bromoacetophenone (**2a**, 210 mg, 1.05 mmol) was added to a solution of crude **1a** in DMF (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 5 h. The reaction mixture was concentrated and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc=50/1–10/1) afforded **A**. Yield=86% (260 mg); Colorless solid; mp=106–109 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{17}H_{19}O_5$ 303.1233, found 303.1236; ^1H NMR (400 MHz, $CDCl_3$): δ 8.01–7.99 (m, 2H), 7.64–7.60 (m, 1H), 7.52–7.48 (m, 2H), 6.21 (s, 2H), 5.22 (s, 2H), 3.81 (s, 6H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.58, 154.62, 153.73 (2×), 134.57, 133.88, 133.08, 128.83 (2×), 128.12 (2×), 92.93 (2×), 71.32, 60.95, 56.13 (2×); Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.68; H, 6.15.

4.3. A representative synthetic procedure of skeletons 3, 4, 5 and 6 is as follows

Bromides **2** (1.05 mmol) was added to a solution of crude oxygenated phenoxides **1** (1.0 mmol, prepared from phenols and aqueous KOH) in DMF (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 5 h. $Ga(OTf)_3$ (10 mg, 0.02 mmol) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at 25 °C for 5 h. The reaction mixture was concentrated and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc=4/1–1/1) afforded **3**, **4**, **5** and **6**.

*4.3.1. 4,5,6-Trimethoxy-3-phenyl-benzofuran (**3a**).* Yield=76% (216 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{17}H_{17}O_4$ 285.1127, found 285.1132; ^1H NMR (400 MHz, $CDCl_3$): δ 7.68–7.65 (m, 2H), 7.54 (s, 1H), 7.45–7.41 (m, 2H), 7.38–7.34 (m, 1H), 6.90 (s, 1H), 3.93 (s, 6H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.56, 152.27, 146.98, 140.44, 138.77, 131.81, 128.83 (2×), 127.95 (2×), 127.09, 122.61, 112.91, 91.41, 61.43, 61.32, 51.11; Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.93; H, 5.81.

*4.3.2. 4,6-Dimethoxy-3-(3-methoxyphenyl)-benzofuran (**3b**).* Yield=70% (199 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{17}H_{17}O_4$ 285.1127, found 285.1131; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 1H), 7.34 (t, J=8.0 Hz, 1H), 7.28 (t, J=0.8 Hz, 1H), 7.25 (dd, J=0.8, 8.0 Hz, 1H), 6.93 (ddd, J=0.8, 2.8, 8.4 Hz, 1H), 6.71 (d, J=2.0 Hz, 1H), 6.41 (d, J=1.6 Hz, 1H), 3.88 (s, 6H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.18, 159.10, 157.84, 154.53, 139.94, 133.58, 128.80, 122.62, 121.44, 114.75, 112.89, 109.61, 94.55, 88.29, 55.61, 55.28, 55.13.

*4.3.3. 4,5,6-Trimethoxy-3-(3-methoxyphenyl)-benzofuran (**3c**).* Yield=73% (229 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{18}H_{19}O_5$ 315.1233, found 315.1235; ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.33 (t, J=8.4 Hz, 1H), 7.27–7.22 (m, 2H), 6.91 (ddd, J=0.8, 2.4, 8.4 Hz, 1H), 6.88 (s, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.86 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.28, 152.58, 152.27, 146.95, 140.60, 138.80, 133.13, 128.91, 122.52, 121.16, 114.31, 112.87, 112.79, 91.42, 61.52, 61.32, 56.10, 55.08.

*4.3.4. 5,6-Dimethoxy-3-phenyl-benzofuran (**3d**).* Yield=78% (198 mg); Colorless solid; mp=94–96 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{16}H_{15}O_3$ 255.1021, found 255.1024; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.64–7.61 (m, 2H), 7.50–7.46 (m, 2H), 7.40–7.36 (m, 1H), 7.24 (s, 1H), 7.09 (s, 1H), 3.94 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.37, 148.11, 146.66, 140.21 (2×), 132.23, 128.85 (2×), 127.19 (2×), 122.24, 118.13, 101.51, 95.46, 56.35, 56.06.

*4.3.5. 5,6-Dioxymethylene-3-phenyl-benzofuran (**3e**).* Yield=77% (183 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{15}H_{11}O_3$ 239.0708, found 239.0712; ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.63–7.60 (m, 2H), 7.52–7.47 (m, 2H), 7.42–7.39 (m, 1H), 7.23 (s, 1H), 7.07 (s, 1H), 6.01 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.95, 146.28, 144.81, 140.69, 132.05, 128.86 (2×), 127.30, 127.25 (2×), 122.59, 119.63, 101.33, 98.70, 93.66.

*4.3.6. 5,6-Dioxymethylene-3-(3-methoxyphenyl)-benzofuran (**3f**).* Yield=80% (214 mg); Colorless solid; mp=116–117 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M$^+$+1) calcd for $C_{16}H_{13}O_4$ 269.0814, found 269.0818; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.39 (t, J=8.0 Hz, 1H), 7.21 (s, 1H), 7.19–7.14 (m, 2H), 7.04 (s, 1H), 6.93 (dd, J=2.4, 8.0 Hz, 1H), 6.00 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.95, 150.91, 146.27, 144.81, 140.81, 133.34, 129.88, 122.48, 119.69, 119.56, 112.95, 112.65, 101.34, 98.71, 93.65, 55.15.

*4.3.7. 5,6-Dioxymethylene-3-(4-methoxyphenyl)-benzofuran (**3g**).* Yield=87% (233 mg); Colorless solid; mp=127–128 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M$^+$+1) calcd for $C_{16}H_{13}O_4$ 269.0814, found 269.1812; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.50 (d, J=8.8 Hz, 2H), 7.15 (s, 1H), 7.03–6.99 (m, 3H), 6.00 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.01, 150.89, 146.23, 144.77, 140.15, 128.46 (2×), 124.44, 122.23, 119.93, 114.39 (2×), 101.35, 98.70, 93.69, 55.29; Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.76; H, 4.73.

*4.3.8. 5,6-Dioxymethylene-3-(4-trifluoromethylphenyl)-benzofuran (**3h**).* Yield=78% (239 mg); Colorless solid; mp=152–154 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M$^+$+1) calcd for $C_{16}H_{10}F_3O_3$ 307.0582, found 307.0588; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (s, 1H), 7.71 (d, J=8.4 Hz, 2H), 7.67 (d, J=8.4 Hz, 2H), 7.14 (s, 1H), 7.03 (s, 1H), 6.02 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.12, 146.65, 145.19, 141.43, 135.85, 127.36 (2×), 125.93 (d, J=3.8 Hz, 2×), 125.85 (d, J=3.8 Hz, 2×), 121.57, 119.09, 101.55, 98.42, 93.88.

*4.3.9. 5,6-Dioxymethylene-3-(4-fluorophenyl)-benzofuran (**3i**).* Yield=76% (195 mg); Colorless solid; mp=76–78 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M$^+$+1) calcd for $C_{15}H_{10}FO_3$ 257.0614, found 257.0618; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.55–7.50 (m, 2H), 7.18–7.12 (m, 2H), 7.11 (s, 1H), 7.02 (s, 1H), 6.01 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.18 (d, J=245.6 Hz), 150.92, 146.41, 144.94, 140.55, 128.89 (d, J=7.6 Hz, 2×), 128.07 (d, J=3.0 Hz), 121.74, 119.61, 115.88 (d, J=22.0 Hz, 2×), 101.43, 98.45, 93.76.

*4.3.10. 3-Biphenyl-4-yl-5,6-dioxymethylene-benzofuran (**3j**).* Yield=78% (245 mg); Colorless gum; HRMS (ESI, M$^+$+1) calcd for $C_{21}H_{15}O_3$ 315.1021, found 315.1023; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.72–7.64 (m, 6H), 7.50–7.46 (m, 2H), 7.40–7.36 (m, 1H), 7.23 (s, 1H), 7.05 (s, 1H), 6.02 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.07, 146.39, 144.94, 140.84, 140.65, 140.25, 131.09, 128.84 (2×), 127.65 (4×), 127.39 (2×), 127.00, 122.29, 119.68, 101.43, 98.82, 93.80; Anal. Calcd for $C_{21}H_{14}O_3$: C, 80.24; H, 4.49. Found: C, 80.48; H, 4.67.

*4.3.11. 5,6-Dioxymethylene-3-(2-naphthyl)-benzofuran (**3k**).* Yield=82% (236 mg); Colorless gum; HRMS (ESI, M$^+$+1) calcd for $C_{19}H_{13}O_3$ 289.0865, found 289.0871; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J=1.2 Hz, 1H), 7.93 (d, J=8.4 Hz, 1H), 7.91–7.87 (m, 2H), 7.81 (s, 1H), 7.69 (dd, J=2.0, 8.4 Hz, 1H), 7.56–7.49 (m, 2H), 7.31 (s, 1H), 7.08 (s, 1H), 6.03 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.08, 146.38, 144.93, 141.12, 133.66, 132.60, 129.51, 128.59, 127.87, 127.71, 126.41, 125.92, 125.65, 125.64, 122.60, 119.72, 101.42, 98.85, 93.80.

*4.3.12. 6-Methoxy-3-phenyl-benzofuran (**3l**).* Yield=84% (188 mg); Colorless solid; mp=45–48 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M$^+$+1) calcd for $C_{15}H_{13}O_2$ 225.0916, found 225.0921; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J=8.8 Hz, 1H), 7.74 (s, 1H), 7.69–7.65 (m, 2H), 7.52–7.48 (m, 2H), 7.42–7.37 (m, 1H), 7.12 (d, J=2.4 Hz, 1H), 6.99 (dd, J=2.4, 8.8 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.14, 156.81, 140.27, 132.17, 128.88 (2×), 127.32, 127.30 (2×), 122.06, 120.50, 119.75, 112.04, 96.13, 55.65.

*4.3.13. 6-Methoxy-3-(4-methoxyphenyl)-benzofuran (**3m**).* Yield=84% (213 mg); Colorless solid; mp=55–57 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M$^+$+1) calcd for $C_{16}H_{15}O_3$ 255.1021, found 255.1023; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J=8.8 Hz, 1H), 7.68 (s, 1H), 7.59 (d, J=8.8 Hz, 2H), 7.11 (d, J=2.0 Hz, 1H), 7.04 (d, J=8.8 Hz, 2H), 6.98 (dd, J=2.0, 8.8 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.94, 158.04, 156.69, 139.59, 128.37 (2×), 124.51, 121.58, 120.38, 119.94, 114.30 (2×), 111.86, 96.06, 55.56, 55.18; Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.68; H, 5.32.

*4.3.14. 6-Methoxy-3-(4-methylphenyl)-benzofuran (**3n**).* Yield=83% (198 mg); Colorless gum; HRMS (ESI, M$^+$+1) calcd for $C_{16}H_{15}O_2$ 239.1072, found 239.1073; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J=8.4 Hz, 1H), 7.69 (s, 1H), 7.54 (d, J=8.0 Hz, 2H), 7.28 (d, J=8.4 Hz, 2H), 7.08 (d, J=2.4 Hz, 1H), 6.95 (dd, J=2.4, 8.8 Hz, 1H), 3.88 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.10, 156.79, 140.03, 137.13, 129.60 (2×), 129.24, 127.21 (2×), 121.97, 120.54, 119.94, 111.97, 96.13, 55.71, 21.22.

*4.3.15. 3-Biphenyl-4-yl-6-methoxy-benzofuran (**3o**).* Yield=85% (255 mg); Colorless solid; mp=112–114 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M$^+$+1) calcd for $C_{21}H_{17}O_2$ 301.1229, found 301.1234; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.67 (m, 8H), 7.54–7.51 (m, 2H), 7.45–7.41 (m, 1H), 7.15 (d, J=2.0 Hz, 1H), 7.03 (dd, J=2.4, 8.8 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.16, 156.86, 140.95, 140.36, 140.08, 131.15, 128.79 (2×), 127.54 (2×), 127.33, 127.18, 126.93 (2×), 121.64, 120.53, 119.68, 112.10, 96.15, 96.15, 55.62.

*4.3.16. 6-Methoxy-3-(4-trifluoromethylphenyl)-benzofuran (**3p**).* Yield=80% (234 mg); Colorless solid; mp=85–88 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M$^+$+1) calcd for $C_{16}H_{12}F_3O_2$ 293.0789, found 293.0792; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.75–7.70 (m, 4H), 7.67 (d, J=8.8 Hz, 1H), 7.09 (d, J=2.0 Hz, 1H), 6.98 (dd, J=2.0, 8.8 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.42, 156.94, 141.06, 135.96, 129.48, 127.36 (2×), 125.90 (d, J=3.0 Hz), 125.82 (d, J=3.8 Hz), 121.04, 120.25 (2×), 119.15, 112.47, 96.26, 55.71; Anal. Calcd for $C_{16}H_{11}F_3O_2$: C, 65.76; H, 3.79. Found: C, 65.96; H, 3.61.

*4.3.17. 6-Methoxy-3-(3,4-dioxymethylenephenyl)-benzofuran (**3q**).* Yield=80% (214 mg); Colorless gum; HRMS (ESI, M$^+$+1) calcd for $C_{16}H_{13}O_4$ 269.0814, found 269.0821; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J=8.8 Hz, 1H), 7.63 (s, 1H), 7.11–7.06 (m, 3H), 6.94 (dd, J=2.4, 8.8 Hz, 1H), 6.91 (dd, J=0.8, 8.0 Hz, 1H), 6.01 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.17, 156.73, 148.11, 147.00, 139.88, 126.00, 121.89, 120.78, 120.38, 119.88, 112.01, 108.81, 107.89, 101.13, 96.17, 55.73.

*4.3.18. 6-Methoxy-3-(3,4-dichlorophenyl)-benzofuran (**3r**).* Yield=80% (234 mg); Colorless solid; mp=91–93 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M$^+$+1) calcd for $C_{15}H_{11}Cl_2O_2$ 293.0136, found 293.0141; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J=2.0 Hz, 1H), 7.57 (dd, J=2.0, 8.4 Hz, 1H), 7.44 (d, J=8.4 Hz, 1H), 7.41 (d, J=8.0 Hz, 1H), 7.02 (d, J=2.0 Hz, 1H), 6.93 (d, J=0.8 Hz, 1H), 6.85 (dd, J=2.0, 8.4 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.60, 156.09, 152.61, 133.08, 131.66, 130.75, 130.66, 126.06, 123.48, 122.14, 121.32, 112.45, 102.65, 95.82, 55.74.

*4.3.19. 6-Methoxy-3-(2-naphthyl)-benzofuran (**3s**).* Yield=84% (230 mg); Colorless solid; mp=148–149 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M$^+$+1) calcd for $C_{19}H_{15}O_2$ 275.1072, found 275.1077; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.94 (d, J=8.8 Hz, 1H), 7.90 (dt, J=1.6, 8.4 Hz, 2H), 7.84 (s, 1H), 7.83 (d, J=8.8 Hz, 1H), 7.74 (dd, J=1.6, 8.4 Hz, 1H), 7.59–7.56 (m, 2H), 7.12 (d, J=2.4 Hz, 1H), 7.00 (dd, J=2.4, 8.8 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.22, 156.93, 140.71, 133.70, 132.63, 129.64, 128.56, 127.90, 127.74, 126.40, 125.90, 125.67 (2×), 122.07, 120.63, 119.82, 112.16, 96.20, 55.71.

*4.3.20. 2-Allyl-4,5,6-trimethoxy-3-phenyl-benzofuran (**4a**).* Yield=64% (207 mg); Colorless gum; HRMS (ESI, $M^{+}+1$) calcd for $C_{20}H_{21}O_4$ 325.1440, found 325.1436; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.46 (m, 2H), 7.45–7.39 (m, 2H), 7.37–7.32 (m, 1H), 6.86 (s, 1H), 6.04–5.94 (m, 1H), 5.18–5.13 (m, 2H), 3.90 (s, 3H), 3.86 (s, 3H), 3.49 (s, 3H), 3.47 (dt, J=1.6, 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.70, 151.02 (2×), 146.66, 138.70, 134.11, 132.70, 130.03 (2×), 127.80 (2×), 127.02, 117.30, 116.87, 114.82, 91.30, 61.47, 61.36, 56.32, 30.99.

*4.3.21. 2-Allyl-5,6-dimethoxy-3-phenyl-benzofuran (**4b**).* Yield=66% (194 mg); Colorless gum; HRMS (ESI, $M^{+}+1$) calcd for $C_{19}H_{19}O_3$ 295.1334, found 295.1335; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.49 (m, 4H), 7.41–7.36 (m, 1H), 7.06 (s, 1H), 7.01 (s, 1H), 6.09–5.99 (m, 1H), 5.20–5.14 (m, 2H), 3.93 (s, 3H), 3.89 (s, 3H), 3.58 (dt, J=1.6, 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.08, 148.76, 147.61, 146.51, 134.13, 132.78, 128.81 (4x), 127.10, 120.35, 117.68, 116.88, 101.27, 95.35, 56.50, 56.28, 31.33.

*4.3.22. 2-Allyl-5,6-dioxymethylene-3-phenyl-benzofuran (**4c**).* Yield=68% (189 mg); Colorless solid; mp=72–74 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, $M^{+}+1$) calcd for $C_{18}H_{15}O_3$ 279.1021, found 279.1023; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.45 (m, 4H), 7.39–7.34 (m, 1H), 6.99 (s, 1H), 6.96 (s, 1H), 6.08–5.98 (m, 1H), 5.97 (s, 2H), 5.19–5.18 (m, 1H), 5.16–5.14 (m, 1H), 3.56 (dt, J=1.6, 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.48, 149.24, 145.67, 144.46, 134.06, 132.53, 128.80 (2×), 128.77 (2×), 127.15, 121.79, 118.02, 116.91, 101.19, 98.42, 93.41, 31.35.

*4.3.23. 2-Benzyl-6-methoxy-3-phenyl-benzofuran (**4d**).* Yield=66% (207 mg); Colorless gum; HRMS (ESI, $M^{+}+1$) calcd for $C_{22}H_{19}O_2$ 315.1385, found 315.1388; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.46 (m, 5H), 7.41–7.24 (m, 6H), 7.02 (d, J=2.0 Hz, 1H), 6.89 (dd, J=2.4, 8.8 Hz, 1H), 4.20 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.82, 155.26, 151.42, 138.13, 132.62, 128.93 (2×), 128.81 (2×), 128.59 (2×), 128.44 (2×), 127.21, 126.50, 121.99, 119.85, 118.06, 111.48, 95.97, 55.74, 32.87.

*4.3.24. 2-Allyl-6-methoxy-3-(4-methoxyphenyl)-benzofuran (**4e**).* Yield=73% (215 mg); Colorless gum; HRMS (ESI, $M^{+}+1$) calcd for $C_{19}H_{19}O_3$ 295.1334, found 295.1337; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.39 (m, 3H), 7.04–7.03 (m, 2H), 7.02 (s, 1H), 6.90 (dd, J=2.4, 8.4 Hz, 1H), 6.10–6.00 (m, 1H), 5.21–5.18 (m, 1H), 5.17–5.15 (m, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.57 (dt, J=2.0, 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.75, 157.66, 155.09, 150.59, 134.17, 129.93 (2×), 124.89, 122.20, 119.69, 116.95, 116.84, 114.21 (2×), 111.26, 95.90, 55.74, 55.29, 31.28.

*4.3.25. 2-Allyl-6-methoxy-3-(4-methylphenyl)-benzofuran (**4f**).* Yield=68% (189 mg); Colorless gum; HRMS (ESI, $M^{+}+1$) calcd for $C_{19}H_{19}O_2$ 279.1385, found 279.1389; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J=8.4 Hz, 1H), 7.39 (d, J=8.0 Hz, 2H), 7.29 (d, J=7.6 Hz, 2H), 7.04 (d, J=2.4 Hz, 1H), 6.87 (dd, J=2.4, 8.4 Hz, 1H), 6.09–5.99 (m, 1H), 5.21–5.15 (m, 2H), 3.86 (s, 3H), 3.58 (dt, J=2.0, 6.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.68, 155.14, 150.84, 136.82, 134.13, 129.62, 129.44 (2×), 128.71 (2×), 122.10, 119.78, 117.26, 116.87, 111.29, 95.93, 55.76, 31.31, 21.22.

*4.3.26. 2-Allyl-3-biphenyl-4-yl-6-methoxy-benzofuran (**4g**).* Yield=70% (238 mg); Colorless solid; mp=123–124 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, $M^{+}+1$) calcd for $C_{24}H_{21}O_2$ 341.1542, found 341.1547; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75–7.68 (m, 4H), 7.61 (d, J=8.4 Hz, 2H), 7.55–7.48 (m, 3H), 7.42–7.38 (m, 1H), 7.09 (d, J=2.0 Hz, 1H), 6.93 (dd, J=2.4, 8.4 Hz, 1H), 6.16–6.06 (m, 1H), 5.27–5.22 (m, 2H), 3.89 (s, 3H), 3.66 (dt, J=1.6, 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.75, 155.20, 151.15, 140.69, 139.87, 134.02, 131.64, 129.14 (2×), 128.81 (2×), 127.42 (2×), 127.33, 127.00 (2×), 121.85, 119.78, 117.00 (2×), 111.42, 95.93, 55.71, 31.37; Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.93; H, 6.21.

*4.3.27. 6-Methoxy-2,3-diphenyl-benzofuran (**5a**).* Yield=63% (189 mg); Colorless solid; mp=116–118 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, $M^{+}+1$) calcd for $C_{21}H_{17}O_2$ 301.1229, found 301.1234; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.64 (m, 2H), 7.54–7.26 (m, 9H), 7.13 (d, J=2.0 Hz, 1H), 6.91 (dd, J=2.0, 8.4 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.40, 154.95, 149.58, 132.93, 130.84, 129.65 (2×), 128.90 (2×), 128.36 (2×), 127.89, 127.54, 126.56 (2×), 123.68, 120.19, 117.40, 111.90, 95.66, 55.74.

*4.3.28. 5,6-Dimethoxy-2,3-diphenyl-benzofuran (**5b**).* Yield=64% (211 mg); Colorless solid; mp=162–164 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, $M^{+}+1$) calcd for $C_{22}H_{19}O_3$ 331.1334, found 331.1341; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.59 (m, 2H), 7.53–7.40 (m, 5H), 7.32–7.23 (m, 3H), 7.13 (s, 1H), 6.90 (s, 1H), 3.98 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.61, 148.64, 148.39, 146.76, 133.09, 130.88, 129.64 (2×), 129.00 (2×), 128.32 (2×), 127.71, 127.54, 126.37 (2×), 122.10, 117.69, 101.11, 95.09, 56.38, 56.27; Anal. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 80.26; H, 5.21.

*4.3.29. 5,7-Dimethoxy-2,3-diphenyl-benzofuran (**5c**).* Yield=65% (215 mg); Colorless solid; mp=129–131 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, $M^{+}+1$) calcd for $C_{22}H_{19}O_3$ 331.1334, found 331.1336; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.51 (m, 4H), 7.46–7.40 (m, 3H), 7.31–7.23 (m, 3H), 6.76 (d, J=2.0 Hz, 1H), 6.35 (d, J=2.0 Hz, 1H), 3.90 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.18, 155.79, 154.84, 148.55, 133.67, 130.92, 130.62 (2×), 128.19 (2×), 127.90 (2×), 127.42, 127.13, 126.40 (2×), 117.37, 113.07, 94.50, 87.88, 55.65, 55.33; Anal. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 80.10; H, 5.53. Single-crystal X-ray diagram: crystal of compound **5c** was grown by slow diffusion of EtOAc into a solution of compound **5c** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P–1, a=8.0579(6) Å, b=9.5536(7) Å, c=11.1123(8) Å, V=841.99(11) $Å^3$, Z=2, d_{calcd}=1.303 g/cm^3, F(000)=318, 2θ range 1.840–26.514°, R indices (all data) R1=0.0914, wR2=0.1212.

*4.3.30. 5,6-Dioxymethylene-2,3-diphenyl-benzofuran (**5d**).* Yield=67% (210 mg); Colorless solid; mp=137–138 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, $M^{+}+1$) calcd for $C_{21}H_{15}O_3$ 315.1021, found 315.1025; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.58 (m, 2H), 7.48–7.39 (m, 5H), 7.32–7.23 (m, 3H), 7.06 (s, 1H), 6.86 (s, 1H), 5.99 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.09, 149.22, 146.48, 144.75, 132.88, 130.82, 129.65 (2×), 128.96 (2×), 128.36 (2×), 127.80, 127.61, 126.37 (2×), 123.70, 118.03, 101.31, 98.47, 93.28; Anal. Calcd for $C_{21}H_{14}O_3$: C, 80.24; H, 4.49. Found: C, 80.48; H, 4.80. Single-crystal X-ray diagram: crystal of compound **5d** was grown by slow diffusion of EtOAc into a solution of compound **5d** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, a=11.1460(14) Å, b=6.0896(6) Å, c=22.939(3) Å, V=1523.2(3) $Å^3$, Z=4, d_{calcd}=1.371 g/cm^3, F(000)=656, 2θ range 1.815–26.465°, R indices (all data) R1=0.0712, wR2=0.1104.

*4.3.31. 4,5,6-Trimethoxy-2,3-diphenyl-benzofuran (**5e**).* Yield=62% (223 mg); Colorless gum; HRMS (ESI, $M^{+}+1$) calcd for $C_{23}H_{21}O_4$ 361.1440, found 361.1445; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.52

(m, 4H), 7.48–7.39 (m, 3H), 7.30–7.21 (m, 3H), 6.95 (s, 1H), 3.95 (s, 3H), 3.90 (s, 3H), 3.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.40, 150.68, 149.20, 147.04, 138.90, 133.38, 130.62, 130.31 (2×), 128.17 (2×), 128.12 (2×), 127.58, 127.33, 126.30 (2×), 117.13, 116.63, 91.08, 61.26, 61.22, 56.19; Anal. Calcd for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.87; H, 5.83.

*4.3.32. 3-(4-Fluorophenyl)-6-methoxy-2-phenyl-benzofuran (**5f**).* Yield=60% (191 mg); Colorless gum; HRMS (ESI, $M^{+}+1$) calcd for $C_{21}H_{16}FO_2$ 319.1134, found 319.1137; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.62 (m, 2H), 7.50–7.47 (m, 2H), 7.36–7.29 (m, 4H), 7.21–7.16 (m, 2H), 7.12 (d, J=2.0 Hz, 1H), 6.91 (dd, J=2.4, 8.8 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.27 (d, J=245.6 Hz), 158.45, 154.90, 149.67, 131.29 (d, J=8.3 Hz, 2×), 130.66, 128.82 (d, J=3.0 Hz), 128.42 (2×), 128.00, 126.52 (2×), 123.54, 119.94, 116.36, 115.98 (d, J=22.0 Hz, 2×), 112.01, 95.68, 55.71.

*4.3.33. 6-Methoxy-3-(4-methoxyphenyl)-2-phenyl-benzofuran (**5g**).* Yield=63% (208 mg); Colorless gum; HRMS (ESI, $M^{+}+1$) calcd for $C_{22}H_{19}O_3$ 331.1334, found 331.1341; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.68 (m, 2H), 7.40 (d, J=8.8 Hz, 2H), 7.39 (d, J=8.4 Hz, 1H), 7.36–7.25 (m, 3H), 7.13 (d, J=2.4 Hz, 1H), 7.04 (d, J=8.8 Hz, 2H), 6.92 (dd, J=2.4, 8.8 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.03, 158.32, 154.87, 149.28, 130.98, 130.72 (2×), 128.31 (2×), 127.71, 126.40 (2×), 124.95, 123.87, 120.15, 117.03, 114.36 (2×), 111.78, 95.61, 55.67, 55.18.

*4.3.34. 3-(4-Fluorophenyl)-5,6-dimethoxy-2-phenyl-benzofuran (**5h**).* Yield=60% (209 mg); Colorless solid; mp=166–168 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, $M^{+}+1$) calcd for $C_{22}H_{18}FO_3$ 349.1240, found 349.1248; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.55 (m, 2H), 7.49–7.44 (m, 2H), 7.33–7.24 (m, 3H), 7.21–7.15 (m, 2H), 7.12 (s, 1H), 6.84 (s, 1H), 3.97 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.29 (d, J=245.6 Hz), 149.72, 148.61, 148.48, 146.85, 131.31 (d, J=7.6 Hz, 2×), 130.77, 128.98 (d, J=3.0 Hz), 128.41 (2×), 127.85, 126.33 (2×), 122.04, 116.68, 116.10 (d, J=22.0 Hz, 2×), 100.86, 95.14, 56.40, 56.29; Anal. Calcd for $C_{22}H_{17}FO_3$: C, 75.85; H, 4.92. Found: C, 75.98; H, 5.18.

*4.3.35. 3-(4-Fluorophenyl)-5,6-dioxymethylene-2-phenyl-benzofuran (**5i**).* Yield=63% (209 mg); Colorless solid; mp=118–120 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, $M^{+}+1$) calcd for $C_{21}H_{14}FO_3$ 333.0927, found 333.0931; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.55 (m, 2H), 7.45–7.41 (m, 2H), 7.33–7.27 (m, 3H), 7.18–7.14 (m, 2H), 7.05 (s, 1H), 6.80 (s, 1H), 5.99 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.33 (d, J=245.6 Hz), 150.21, 149.19, 146.56, 144.84, 131.31 (d, J=7.6 Hz, 2×), 130.64, 128.77, 128.44 (2×), 127.93, 126.33 (2×), 123.59, 116.99, 116.07 (d, J=22.0 Hz, 2×), 101.37, 98.22, 93.35.

*4.3.36. 3-(4-Fluorophenyl)-4,5,6-trimethoxy-2-phenyl-benzofuran (**5j**).* Yield=56% (212 mg); Colorless solid; mp=132–134 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, $M^{+}+1$) calcd for $C_{23}H_{20}FO_4$ 379.1346, found 379.1351; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.45 (m, 4H), 7.31–7.23 (m, 3H), 7.16–7.11 (m, 2H), 6.93 (s, 1H), 3.95 (s, 3H), 3.88 (s, 3H), 3.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.28 (d, J=244.9 Hz), 152.58, 150.73, 149.49, 147.01, 138.99, 132.08 (d, J=7.6 Hz, 2×), 130.53, 129.32 (d, J=3.0 Hz), 128.34 (2×), 127.82, 126.42 (2×), 116.51, 116.12, 115.22 (d, J=21.3 Hz, 2×), 91.18, 61.35, 61.29, 56.31; Anal. Calcd for $C_{23}H_{19}FO_4$: C, 73.01; H, 5.06. Found: C, 73.32; H, 4.95. Single-crystal X-ray diagram: crystal of compound **5j** was grown by slow diffusion of EtOAc into a solution of compound **5j** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, a=10.908(7) Å, b=13.050(9) Å, c=13.425(9) Å, V=1908(2) Å^3, Z=4, d_{calcd}=1.317 g/cm^3, F(000)=792, 2θ range 1.870–25.148°, R indices (all data) $R1$=0.2231, wR2=0.3689.

*4.3.37. 9-Methoxy-benzo[b]naphtho[1,2-d]furan (**6a**).* Yield=60% (148 mg); Colorless gum; HRMS (ESI, $M^{+}+1$) calcd for $C_{17}H_{13}O_2$ 249.0916, found 249.0923; For major compound **6a**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (dd, J=8.4 Hz, 1H), 8.23 (d, J=8.8 Hz, 1H), 8.01 (dd, J=8.4 Hz, 1H), 7.85 (d, J=8.8 Hz, 1H), 7.74 (d, J=9.2 Hz, 1H), 7.69 (dt, J=1.2, 8.4 Hz, 1H), 7.54 (dt, J=1.2, 8.4 Hz, 1H), 7.22 (d, J=2.4 Hz, 1H), 7.08 (dd, J=2.4, 8.4 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.99, 157.25, 154.17, 130.50, 129.12, 128.02, 127.02, 126.84, 125.80, 124.29, 123.45, 122.51, 122.10, 112.51, 111.54, 96.63, 55.72.

*4.3.38. 9,10-Dimethoxy-benzo[b]naphtho[1,2-d]furan (**6b**).* Yield=60% (167 mg); Colorless solid; mp=160–163 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, $M^{+}+1$) calcd for $C_{18}H_{15}O_3$ 279.1021, found 279.1024; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, J=8.4 Hz, 1H), 8.00 (d, J=8.4 Hz, 1H), 7.82 (d, J=9.2 Hz, 1H), 7.74 (s, 1H), 7.70 (d, J=8.8 Hz, 1H), 7.69 (dt, J=1.2, 8.4 Hz, 1H), 7.53 (dt, J=1.2, 8.4 Hz, 1H), 7.20 (s, 1H), 4.09 (s, 3H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.07, 150.85, 148.96, 146.40, 130.39, 129.13, 128.51, 126.68, 126.65, 124.17, 123.13, 117.86, 116.44, 112.56, 103.66, 95.67, 56.69, 56.21.

*4.3.39. 9,10-Dioxymethylene-benzo[b]naphtho[1,2-d]furan (**6c**).* Yield=58% (152 mg); Colorless solid; mp=136–138 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, $M^{+}+1$) calcd for $C_{17}H_{11}O_3$ 263.0708, found 263.0713; For major compound **6c**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, J=8.4 Hz, 1H), 7.99 (d, J=8.0 Hz, 1H), 7.81 (d, J=8.8 Hz, 1H), 7.73 (s, 1H), 7.69 (d, J=8.8 Hz, 1H), 7.68 (dt, J=1.2, 8.4 Hz, 1H), 7.53 (dt, J=1.2, 8.4 Hz, 1H), 7.16 (s, 1H), 6.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.42, 151.35, 146.92, 144.75, 130.42, 129.15, 128.49, 126.80, 126.76, 124.26, 123.07, 117.87, 117.77, 112.55, 101.68, 100.61, 94.07. Single-crystal X-ray diagram: crystal of compound **6c** was grown by slow diffusion of EtOAc into a solution of compound **6c** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the orthorhombic crystal system, space group P 21 21 21, a=3.9329(11) Å, b=21.721(7) Å, c=27.730(8) Å, V=2368.9(12) Å^3, Z=8, d_{calcd}=1.471 g/cm^3, F(000)=1088, 2θ range 1.191–26.475°, R indices (all data) R1=0.1694, wR2=0.1253.

*4.3.40. 9,10,11-Trimethoxy-benzo[b]naphtho[1,2-d]furan (**6d**).* Yield=54% (166 mg); Colorless solid; mp=95–97 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, $M^{+}+1$) calcd for $C_{19}H_{17}O_4$ 309.1127, found 309.1128; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.31 (d, J=8.4 Hz, 1H), 7.98 (d, J=8.0 Hz, 1H), 7.86 (d, J=9.2 Hz, 1H), 7.70 (d, J=8.8 Hz, 1H), 7.69 (dt, J=1.2, 8.4 Hz, 1H), 7.52 (dt, J=1.2, 8.4 Hz, 1H), 7.03 (s, 1H), 4.15 (s, 3H), 4.00 (s, 3H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.87, 153.34, 152.93, 147.77, 139.14, 130.75, 128.85, 128.56, 127.55, 126.89, 126.64, 124.22, 118.56, 112.20, 112.14, 91.74, 61.92, 61.38, 56.34.

*4.3.41. 7-Methoxy-1,2,3,4-tetrahydro-dibenzofuran (**6e**).* Yield=50% (101 mg); Colorless gum; HRMS (ESI, $M^{+}+1$) calcd for $C_{13}H_{15}O_2$ 203.1072, found 203.1074; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, J=8.4 Hz, 1H), 6.98 (d, J=2.0 Hz, 1H), 6.83 (dd, J=2.0, 8.4 Hz, 1H), 3.84 (s, 3H), 2.74–2.70 (m, 2H), 2.61–2.57 (m, 2H), 1.95–1.89 (m, 2H), 1.87–1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.08, 155.15, 152.93, 122.38, 118.28, 112.51, 110.35, 96.19, 55.75, 23.37, 22.92, 22.67, 20.47.

*4.3.42. 2-Methoxy-6,7,8,9-tetrahydro-5H-10-oxa-benzo[a]azulene (**6f**).* Yield=45% (97 mg); Colorless gum; HRMS (ESI, $M^{+}+1$) calcd for $C_{14}H_{17}O_2$ 217.1229, found 217.1231; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, J=8.4 Hz, 1H), 6.95 (d, J=2.0 Hz, 1H), 6.84 (dd, J=2.0, 8.4 Hz, 1H), 3.84 (s, 3H), 2.90 (t, J=6.0 Hz, 2H), 2.67 (t, J=6.0 Hz, 2H), 1.88–1.76 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.06, 155.23, 154.04, 124.04, 118.27, 115.49, 110.35, 95.69, 55.72, 30.46, 29.02, 28.28, 26.42, 23.21.

4.4. A representative synthetic procedure of skeleton 7 is as follows

Skeleton **5** (0.3 mmol) and I_2 (100 mg, 0.4 mmol) was dissolved in EtOAc (20 mL) at 25 °C in a pyrax glass tube. Then, 1,2-epoxybutane (150 mg, 2.0 mmol) was added to the reaction mixture at 25 °C. The pyrax glass tube with the reaction mixture was irradiated under a nitrogen atmosphere with a lamp (λ=2540 Å) at 25 °C for 50 h. The solvent was evaporated to afford crude product. The residue was diluted with aqueous $Na_2S_2O_3$ (10%, 10 mL) solution, and the reaction mixture was extracted with EtOAc (2×20 mL). Purification on silica gel (hexanes/EtOAc=4/1–2/1) afforded skeleton **7**.

*4.4.1. 11-Methoxy-13-oxa-indeno[1,2-l]phenanthrene (**7a**).* Yield=80% (72 mg); Colorless solid; mp=157–159 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{21}H_{15}O_2$ 299.1072, found 299.1074; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (dd, J=1.2, 8.0 Hz, 1H), 8.76 (dd, J=1.6, 8.0 Hz, 1H), 8.60 (dd, J=1.2, 8.0 Hz, 1H), 8.47 (dd, J=1.6, 7.2 Hz, 1H), 8.24 (d, J=8.4 Hz, 1H), 7.79–7.65 (m, 4H), 7.31 (d, J=2.0 Hz, 1H), 7.10 (dd, J=2.0, 8.4 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.73, 157.15, 150.76, 129.88, 128.34, 128.15, 127.30, 127.11, 126.52, 125.01, 124.09, 123.75, 123.40, 122.26, 121.91, 121.26, 118.90, 114.60, 111.83, 96.80, 55.81; Anal. Calcd for $C_{21}H_{14}O_2$: C, 84.54; H, 4.73. Found: C, 84.69; H, 4.97.

*4.4.2. 10,11-Dimethoxy-13-oxa-indeno[1,2-l]phenanthrene (**7b**).* Yield=83% (82 mg); Colorless solid; mp=122–124 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{22}H_{17}O_3$ 329.1178, found 329.1182; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, J=8.4 Hz, 1H), 8.72 (dd, J=1.6, 8.8 Hz, 1H), 8.48 (dd, J=0.8, 8.0 Hz, 1H), 8.41 (dd, J=2.0, 8.0 Hz, 1H), 7.77–7.63 (m, 4H), 7.70 (s, 1H), 7.27 (s, 1H), 4.09 (s, 3H), 4.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.73, 150.63, 148.67, 146.52, 129.68, 129.62, 128.30, 128.05, 127.13, 127.05, 126.33, 124.86, 123.73, 123.34, 122.29, 121.10, 117.12, 114.79, 103.49, 95.82, 56.72, 56.25.

*4.4.3. 9,11-Dimethoxy-13-oxa-indeno[1,2-l]phenanthrene (**7c**).* Yield=84% (83 mg); Colorless solid; mp=167–169 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{22}H_{17}O_3$ 329.1178, found 329.1186; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.53 (dd, J=1.2, 8.4 Hz, 1H), 8.77–8.72 (m, 2H), 8.44–8.42 (m, 1H), 7.72–7.61 (m, 4H), 6.89 (d, J=2.0 Hz, 1H), 6.51 (d, J=2.0 Hz, 1H), 4.11 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.80, 158.16, 154.45, 149.58, 129.68, 128.26, 128.18, 128.05, 126.83, 126.80, 126.22, 124.80, 123.17, 123.15, 122.02, 121.13, 116.09, 109.39, 94.81, 88.81, 55.74 (2×).

*4.4.4. 9,10,11-Trimethoxy-13-oxa-indeno[1,2-l]phenanthrene (**7d**).* Yield=88% (95 mg); Colorless solid; mp=146–148 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{23}H_{19}O_4$ 359.1283, found 359.1284; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.42 (dd, J=1.2, 8.4 Hz, 1H), 8.78 (dd, J=0.4, 8.0 Hz, 1H), 8.76–8.74 (m, 1H), 8.45–8.43 (m, 1H), 7.79–7.64 (m, 4H), 6.12 (s, 1H), 4.15 (s, 3H), 4.02 (s, 3H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.02, 152.84, 150.35, 147.64, 139.40, 129.97, 128.15, 128.02, 127.59, 127.23, 126.94, 126.56, 124.93, 123.29, 123.21, 122.01, 121.26, 115.93, 112.78, 91.96, 62.02, 61.40, 56.33; Anal. Calcd for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06. Found: C, 77.29; H, 5.32.

*4.4.5. 6-Fluoro-11-methoxy-13-oxa-indeno[1,2-l]phenanthrene (**7e**).* Yield=86% (82 mg); Colorless solid; mp=176–178 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{21}H_{14}FO_2$ 317.0978, found 317.0985; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, J=8.4 Hz, 1H), 8.46 (dd, J=5.6, 8.8 Hz, 1H), 8.40 (dd, J=1.6, 8.4 Hz, 1H), 8.34 (dd, J=2.8, 11.2 Hz, 1H), 8.11 (d, J=8.8 Hz, 1H), 7.74–7.64 (m, 2H), 7.47 (dt, J=2.4, 8.4 Hz, 1H), 7.26 (d, J=2.0 Hz, 1H), 7.06 (dd, J=2.0, 8.4 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.44 (d, J=241.9 Hz), 158.82, 157.07, 129.78 (d, J=7.6 Hz), 127.65, 126.83, 126.65, 126.46, 125.70 (d, J=9.1 Hz), 124.76, 123.51, 122.49, 121.60, 121.29, 115.85 (d, J=23.5 Hz), 111.88, 105.23, 104.56, 109.08 (d, J=22.0 Hz), 96.76, 55.78.

*4.4.6. 6,11-Dimethoxy-13-oxa-indeno[1,2-l]phenanthrene (**7f**).* Yield=85% (84 mg); Colorless solid; mp=156–158 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{22}H_{17}O_3$ 329.1178, found 329.1182; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J=8.0 Hz, 1H), 8.40–8.36 (m, 2H), 8.11–8.08 (m, 2H), 7.70–7.61 (m, 2H), 7.36–7.33 (m, 1H), 7.24 (dd, J=0.8, 2.0 Hz, 1H), 7.08 (ddd, J=0.8, 2.4, 8.4 Hz, 1H), 4.02 (s, 3H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.59, 157.05, 157.01, 149.40, 129.45, 129.13, 127.05, 125.99, 125.17, 123.32, 122.49, 122.43, 121.66, 121.18, 118.78, 116.55, 114.48, 111.54, 105.81, 96.64, 55.72, 55.45. Single-crystal X-ray diagram: crystal of compound **7f** was grown by slow diffusion of EtOAc into a solution of compound **7f** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P c, a=23.874(4) Å, b=4.0071(7) Å, c=17.265(3) Å, V=1563.3(5) Å^3, Z=4, d_{calcd}=1.395 g/cm^3, F(000)=688, 2θ range 0.901–26.392°, R indices (all data) $R1$=0.0816, wR2=0.1105.

*4.4.7. 6-Fluoro-10,11-dimethoxy-13-oxa-indeno[1,2-l]phenanthrene (**7g**).* Yield=83% (86 mg); Colorless solid; mp=192–194 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{22}H_{16}FO_3$ 347.1084, found 347.1091; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, J=8.8 Hz, 1H), 8.43–8.38 (m, 2H), 8.35 (dd, J=2.4, 7.2 Hz, 1H), 7.73 (dt, J=1.2, 8.0 Hz, 1H), 7.67 (dt, J=1.2, 8.0 Hz, 1H), 7.62 (s, 1H), 7.48 (dt, J=2.4, 8.4 Hz, 1H), 7.28 (s, 1H), 4.09 (s, 3H), 4.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.36 (d, J=241.8 Hz), 150.76, 150.08, 148.86, 146.62, 129.76 (d, J=8.4 Hz), 128.84 (d, J=3.8 Hz), 127.68, 126.36, 125.40 (d, J=8.3 Hz), 124.80, 123.52, 122.59, 121.18, 116.78, 115.74 (d, J=22.7 Hz), 114.58, 109.17 (d, J=21.9 Hz), 103.21, 95.87, 56.75, 56.28; Anal. Calcd for $C_{22}H_{15}FO_3$: C, 76.29; H, 4.37. Found: C, 76.42; H, 4.58.

*4.4.8. 6-Fluoro-10,11-dioxymethylene-13-oxa-indeno[1,2-l]phenanthrene (**7h**).* Yield=83% (82 mg); Colorless solid; mp>250 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{21}H_{12}FO_3$ 331.0771, found 331.0778; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J=8.0 Hz, 1H), 8.46–8.37 (m, 3H), 7.69 (s, 1H), 7.76–7.66 (m, 2H), 7.52–7.48 (m, 1H), 7.25 (s, 1H), 6.11 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.48 (d, J=244.6 Hz), 151.35, 150.31, 146.86, 145.05, 129.95, 127.76, 126.52, 125.42 (d, J=8.4 Hz), 124.73, 123.57, 123.45, 122.61, 121.26, 118.17, 115.90 (d, J=22.8 Hz), 109.25 (d, J=22.8 Hz), 102.21, 101.77, 100.20, 94.31.

*4.4.9. 6-Fluoro-9,10,11-trimethoxy-13-oxa-indeno[1,2-l]phenanthrene (**7i**).* Yield=85% (96 mg); Colorless solid; mp=159–161 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{23}H_{18}FO_4$ 377.1189, found 377.1195; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.31 (dd, J=6.0, 9.2 Hz, 1H), 8.47 (d, J=8.0 Hz, 1H), 8.29 (dd, J=1.2, 7.6 Hz, 1H), 8.25 (dd, J=2.4, 7.6 Hz, 1H), 7.64 (dt, J=1.2, 8.0 Hz, 1H), 7.58 (dt, J=1.2, 8.0 Hz, 1H), 7.43 (ddd, J=2.4, 7.6, 8.8 Hz, 1H), 7.01 (s, 1H), 4.12 (s, 3H), 4.01 (s, 3H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.42 (d, J=242.6 Hz), 153.02, 152.65, 149.57 (d, J=2.3 Hz), 147.38, 139.18, 129.68 (d, J=7.6 Hz), 129.56 (d, J=8.4 Hz), 128.99 (d, J=3.8 Hz), 127.33, 126.36, 124.35 (d, J=1.5 Hz), 123.19, 122.04, 121.16, 115.51, 115.46 (d, J=22.0 Hz), 112.33, 108.38 (d, J=22.7 Hz), 91.81, 61.85, 61.31, 56.25; Anal. Calcd for $C_{23}H_{17}FO_4$: C, 73.40; H, 4.55. Found: C, 73.72; H, 4.61. Single-crystal X-ray diagram: crystal of compound **7i** was grown by slow diffusion of EtOAc into a solution of compound **7i** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/n, a=4.3936(2) Å, b=25.2310(12) Å, c=15.8224(7) Å, V=1744.79(14) Å^3, Z=4, d_{calcd}=1.433 g/cm^3, F(000)=784, 2θ range 1.525–26.381°, R indices (all data) $R1$=0.0998, wR2=0.1902.

4.5. A representative synthetic procedure of compounds 8a–c is as follows

2-Bromo-1-(4-methoxyphenyl)ethanone (**2c**, 240 mg, 1.05 mmol) was added to a solution of crude phenoxides **1f**–**g** (1.0 mmol, prepared from phenols and aqueous KOH) in DMF (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 5 h. Ga(OTf)$_3$ (10 mg, 0.02 mmol) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at 25 °C for 5 h. The reaction mixture was concentrated and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc=10/1–6/1) afforded **8**.

*4.5.1. 3-[2-(4-Methoxyphenyl)-2-oxo-ethoxy]-benzaldehyde (**8a**).* Yield=91% (246 mg); Colorless solid; mp=68–70 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M$^+$+1) calcd for $C_{16}H_{15}O_4$ 271.0970, found 271.0976; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 1H), 7.99 (d, J=9.2 Hz, 2H), 7.50 (dt, J=1.6, 7.6 Hz, 1H), 7.46 (t, J=7.6 Hz, 1H), 7.39 (dd, J=1.2, 2.8 Hz, 1H), 7.28–7.25 (m, 1H), 6.98 (d, J=9.2 Hz, 2H), 5.31 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.05, 191.87, 164.21, 158.72, 137.80, 130.41 (2×), 130.25, 127.36, 124.22, 122.14, 114.11 (2×), 113.04, 70.39, 55.55.

*4.5.2. 4-Methoxy-3-[2-(4-methoxyphenyl)-2-oxo-ethoxy]-benzaldehyde (**8b**).* Yield=82% (246 mg); Colorless solid; mp=93–95 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M$^+$+1) calcd for $C_{17}H_{17}O_5$ 301.1076, found 301.1081; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71 (s, 1H), 7.92 (d, J=9.2 Hz, 2H), 7.41 (dd, J=2.0, 8.4 Hz, 1H), 7.26 (d, J=2.0 Hz, 1H), 6.94 (d, J=8.4 Hz, 1H), 6.89 (d, J=9.2 Hz, 2H), 5.34 (s, 2H), 3.89 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.53, 190.46, 163.90, 154.69, 147.92, 130.08 (2×), 129.63, 127.13, 127.04, 113.86 (2×), 111.26, 110.92, 70.60, 55.98, 55.31.

*4.5.3. 2-(2-Methoxy-5-nitrophenoxy)-1-(4-methoxyphenyl)-ethanone (**8c**).* Yield=75% (234 mg); Colorless solid; mp=142–143 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M$^+$+1) calcd for $C_{16}H_{16}NO_6$ 318.0978, found 318.0981; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J=8.8 Hz, 2H), 7.91 (dd, J=2.8, 9.2 Hz, 1H), 7.64 (d, J=2.4 Hz, 1H), 6.97 (d, J=8.8 Hz, 2H), 6.93 (d, J=9.2 Hz, 1H), 5.41 (s, 2H), 3.98 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.16, 164.22, 154.93, 147.30, 141.12, 130.25 (2×), 127.12, 118.65, 114.11 (2×), 110.47, 108.62, 70.91, 56.45, 55.51.

4.6. A one-pot synthetic procedure of 3a is as follows

Base (1.0 mmol; for K_2CO_3, 140 mg; for t-BuOK, 115 mg; for KH, 35% in mineral oil, 115 mg) was added to a solution of 3,4,5-trimethoxyphenol (184 mg, 1.0 mmol) in DMF (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min α-Bromoacetophenone (**2a**, 210 mg, 1.05 mmol) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at 25 °C for 5 h. Ga(OTf)$_3$ (10 mg, 0.02 mmol) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at 25 °C for 5 h. The reaction mixture was concentrated and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc=4/1–1/1) afforded **3a**. Yield=60% (170 mg, for K_2CO_3); 63% (179 mg, for t-BuOK); 60% (170 mg, for KH).

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Supplementary data

Experimental procedure and scanned photocopies of NMR ($CDCl_3$) spectral data were supported.

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