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ONE-POT PREPARATION OF 2-ARYLBENZOFURANS FROM OXIMES WITH DIARYLIODONIUM TRIFLATE

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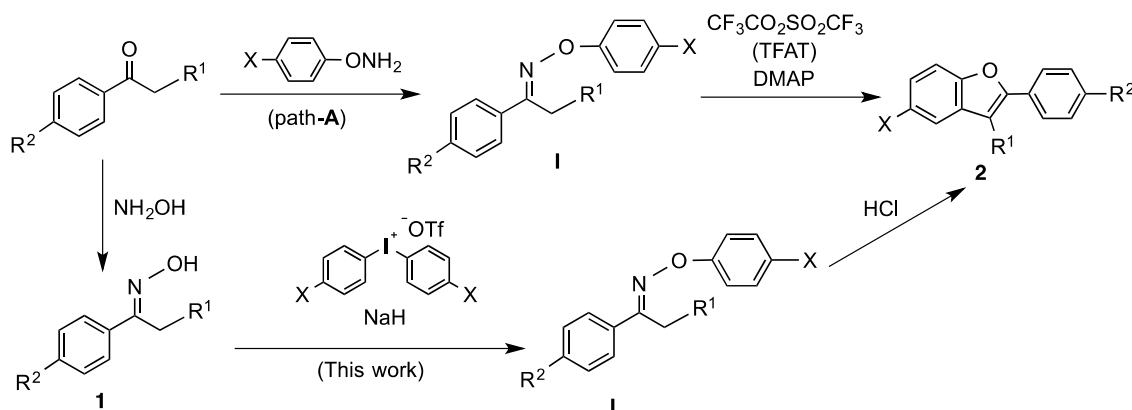
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Abstract – A variety of 2-arylbenzofurans were obtained in good yields by the *O*-arylation of oximes with diaryliodonium triflates, followed by the treatment with HCl in dioxane under warming conditions through the [3,3]-sigmatropic reaction. The present reaction is one-pot transition metal-free method for the preparation of various 2-arylbenzofurans from oximes, which are easily available from the reaction of alkyl aryl ketones with hydroxylamine.

INTRODUCTION

Benzofurans are very important core and building units for biologically active natural products and pharmaceuticals.¹ One example is Khellin, which is isolated from *Ammi visnaga* (a perennial herbaceous plant). Khellin possesses lipid-altering activity and acts as a coronary vasodilator, *i.e.*, it lowers the atherogenic VLDL+LDL-cholesterol fraction.^{1d} Some natural products containing a benzofuran core show high anti-inflammatory activities.^{1e} Therefore, the construction of benzofuran units has been actively pursued and many synthetic studies have been carried out.² Recent studies of the transition metal-catalyzed or transition metal-mediated construction of benzofurans are as follows: the reaction of titanium-benzylidene bearing a masked oxygen at *o*-position with esters,^{3a} the 5-*endo-dig* cyclization of 2-alkynylphenols with ⁿBuLi and ZnCl₂,^{3b} the PtCl₂-catalyzed cyclization of acetals derived from *o*-alkynylphenols,^{3c} the Pd/Cu-catalyzed coupling/cyclization of propargyl bromides, secondary amines, and *o*-iodophenol,^{3d} the Ir-catalyzed cyclization/dehydration of α -aryloxyketones,^{3e} the Rh-catalyzed cyclization of *o*-alkynylphenols followed by intermolecular conjugate addition to electron-deficient alkenes,^{3f} the Rh-catalyzed cyclization of *o*-alkynylphenols,^{3g} the Pd(OAc)₂-catalyzed intramolecular Heck-Masuda cyclization of *o*-allyloxy-benzenediazonium salts,^{3h} the CuBr-catalyzed coupling/cyclization of terminal alkynes with *N*-tosylhydrazones derived from *o*-hydroxybenzaldehydes,³ⁱ and others.^{3j~3q} As regards the transition metal-free construction of benzofurans, the I₂- or ICl-mediated cyclization of *o*-methoxyalkynylbenzenes,^{4a} the reaction of 1-(2'-hydroxyphenyl)-2-chloroethanones with

RMgX,^{4b} the intramolecular Wittig reaction of 2-(*o*-acyloxyphenyl)vinyl ketones with Bu₃P and acyl halides,^{4c} the reaction of *o*-hydroxyacetophenones and 1,1-dichloroethylene with *t*-BuOK, and then H₂SO₄,^{4d} and the reaction of *o*-alkynylphenyl propargyl ethers with *t*-BuOK^{4e} are reported. However, those methods have drawbacks, such as the requirement of toxic (*i.e.* Cu species) or rare metals (*i.e.* Pd species), and troublesome preparation of the starting materials. In contrast, the preparation of benzofurans **2** by the reaction of *O*-aryl oximes **1**, which can be prepared from the reaction of *O*-aryl hydroxylamines with ketones, with trifluoroacetic trifluoromethanesulfonic anhydride (TFAT)^{5a} or methanesulfonic acid^{5b} through the [3,3]-sigmatropic rearrangement is very attractive, because the reaction can be carried out under transition metal-free conditions, as shown in path-A of Scheme 1. However, *O*-aryl hydroxylamines must be prepared carefully with *N*-hydroxyphthalimide and *O*-arylation reagents, such as arylboronic acids with CuCl. On the other hand, oximes **1** are easily obtained by reacting various commercially available ketones with hydroxylamine. Diaryliodonium salts⁶ can be also easily prepared from the reaction of iodoarenes with arenes in the presence of oxidants, such as Oxone[®] and *m*CPBA, in acidic conditions, and can be used for the *O*-arylation of phenols or carboxylic acids.⁷ Recently, *O*-aryl hydroxylamines were efficiently prepared by the reaction of *N*-hydroxyphthalimide or *N*-hydroxysuccinimide with diaryliodonium salts in the presence of *t*-BuOK in DMF at 60 °C, followed by the reaction with ammonia or hydroxylamine in methanol.⁸ Based on those results, here, we would like to report a simple one-pot preparation of 2-arylbenzofurans **2** by the *O*-arylation of oximes **1** derived from alkyl aryl ketones, with diaryliodonium salts, followed by the treatment with HCl in dioxane under warming conditions.



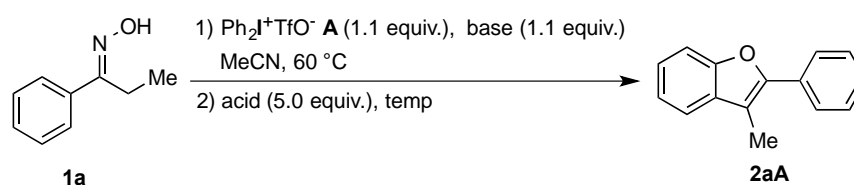
Scheme 1. Preparation of Benzofurans from Ketones

RESULTS AND DISCUSSION

Propiophenone oxime **1a**, which was formed from the reaction of propiophenone with hydroxylamine, was treated with diphenyliodonium triflate **A** in the presence of bases, such as K₂CO₃, *t*-BuONa, *t*-BuOK, NaH, and DBU, in acetonitrile at 60 °C to form *O*-phenyl oxime **1aA**, and it was found that the use of

NaH as the base gave the corresponding *O*-phenyl propiophenone oxime **1aA** in high yield (91%). Based on this preliminary study, the one-pot transformation of propiophenone oxime **1a** into 3-methyl-2-phenylbenzofuran **2aA** with diphenyliodonium triflate **A** in the presence of NaH in acetonitrile, followed by the treatment with acid (5.0 equiv.) at refluxing conditions was carried out, as shown in Table 1. For the second reaction step, pyridinium *p*-toluenesulfonate (PPTS) was not effective (entry 6) and camphorsulfonic acid (CSA) showed poor reactivity (entry 5) for the [3.3]-sigmatropic reaction. In contrast, *p*-toluenesulfonic acid monohydrate, *p*-toluenesulfonic acid, and methanesulfonic acid showed moderate reactivity to form 3-methyl-2-phenylbenzofuran **2aA** in moderate yields (entries

Table 1. Optimal Examination for One-Pot Transformation of Propiophenone Oxime **1a** into 3-Methyl-2-phenylbenzofuran **2aA**



Entry	First step		Second step			Yield (%)
	Base	Time (h)	Acid	Temp (°C)	Time (h)	
1 ^a	K ₂ CO ₃	2	TsOH·H ₂ O	reflux	2	40
2	K ₂ CO ₃	3	TsOH	reflux	2	59
3	K ₂ CO ₃	3	MeSO ₃ H	reflux	13	54
4 ^b	K ₂ CO ₃	3	MeSO ₃ H	reflux	13	56
5	K ₂ CO ₃	3	CSA	reflux	2	12
6	K ₂ CO ₃	3	PPTS	reflux	2	0
7 ^c	K ₂ CO ₃	3	HCl	reflux	3	67
8 ^d	K ₂ CO ₃	3	HCl	reflux	2	65
9 ^d	K ₂ CO ₃	2	HCl	60	2	65
10 ^d	NaOBu ^t	2	HCl	60	2	55
11 ^d	KOBu ^t	2	HCl	60	4	68
12 ^{d,e}	NaH	2	HCl	60	4	79
13 ^d	DBU	2	HCl	60	4	71

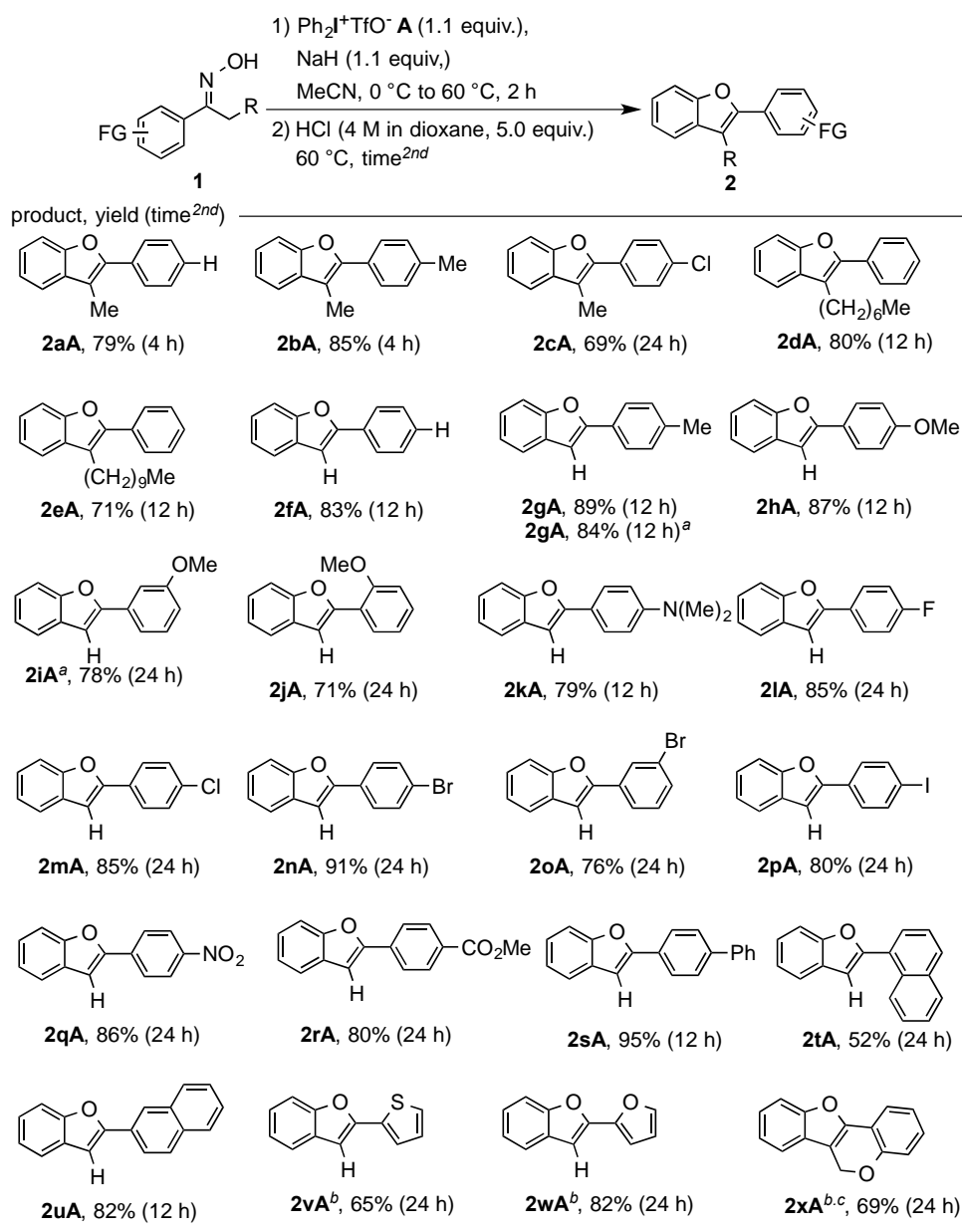
^a The 1st reaction step was carried out at refluxing temperature. ^b MeSO₃H (10.0 equiv.) was used at the 2nd reaction step. ^c Conc. aq. HCl was used at the 2nd reaction step. ^d HCl (4 M in dioxane) was used at the 2nd reaction step. ^e The 1st reaction step was carried out at 0 °C to 60 °C.

1~4), and *p*-toluenesulfonic acid showed the highest reactivity. Moreover, HCl (4 M in dioxane, 5.0 equiv.) showed the best reactivity to give 3-methyl-2-phenylbenzofuran **2aA** in good yields (entries 7~13). Thus, the first reaction step involving the treatment of propiophenone oxime **1a** with diphenyliodonium triflate **A** and NaH in acetonitrile, and the subsequent treatment with HCl (4 M in dioxane, 5.0 equiv.) at 60 °C gave 3-methyl-2-phenylbenzofuran **2aA** in 79% yield (entry 12). Using the optimum reaction

conditions, treatment of *p*-methylpropiophenone oxime **1b** and *p*-chloropropiophenone oxime **1c** with diphenyliodonium triflate **A** and NaH in acetonitrile at 60 °C for 2 h, followed by the treatment with HCl (4 M in dioxane, 5.0 equiv.) at 60 °C for 4 h and 24 h gave the corresponding 3-methyl-2-(4'-methylphenyl)benzofuran **2bA** and 3-methyl-2-(4'-chlorophenyl)benzofuran **2cA** in good yields, respectively, as shown in Table 2. When nonanophenone oxime **1d** and dodecanophenone oxime **1e** were used under the same procedure and conditions, 3-heptyl-2-phenylbenzofuran **2dA** and 3-decyl-2-phenylbenzofuran **2eA** were obtained in good yields, respectively, again. Furthermore, treatment of acetophenone oximes **1f~1u** bearing a substituent on the aromatic ring with diphenyliodonium triflate **A** and NaH in acetonitrile at 60 °C for 2 h, followed by the treatment with HCl (4 M in dioxane, 5.0 equiv.) at 60 °C for 12 h or 24 h gave the corresponding 2-arylbenzofurans **2fA~2uA** in good yields, respectively, as shown in Table 2. The *O*-phenylation reactivity of oximes **1** by diphenyliodonium salt **A** (the first reaction step) was almost the same for various oximes **1**. However, the formation of benzofurans from *O*-phenyl oximes **I** bearing an electron-donating group on the aromatic ring, which were derived from alkyl aryl ketones, proceeded more smoothly than that from *O*-phenyl oximes **I** bearing an electron-withdrawing group on the aromatic ring (from 12 h to 24 h). The same treatment of oximes **1v** and **1w** bearing heteroaromatic groups, which were derived from 2-acetylthiophene and 2-acetylfuran, gave also the corresponding benzofurans **2vA** and **2wA** bearing heteroaromatic groups at 2-position in good yields, respectively. On the other hand, the treatment of *p*-methylacetophenone oxime **1g** with diaryliodonium triflates, such as bis(*p*-chlorophenyl)iodonium triflate **B**, bis(*p*-bromophenyl)iodonium triflate **C**, and bis(*p*-methylphenyl)iodonium triflate **D**, in the presence of NaH in acetonitrile at 60 °C for 2 h, followed by the treatment with HCl (4 M in dioxane 5.0 equiv.) under refluxing conditions for 24 h provided 5-chloro-2-(4'-methylphenyl)benzofuran **2gB**, 5-bromo-2-(4'-methylphenyl)benzofuran **2gC**, and 5-methyl-2-(4'-methylphenyl)benzofuran **2gD** in good yields, respectively, as shown in Table 3. Here, again, the *O*-arylation reactivity of oxime **1g** by diaryliodonium salts **B~D** (the first reaction step) was almost the same.

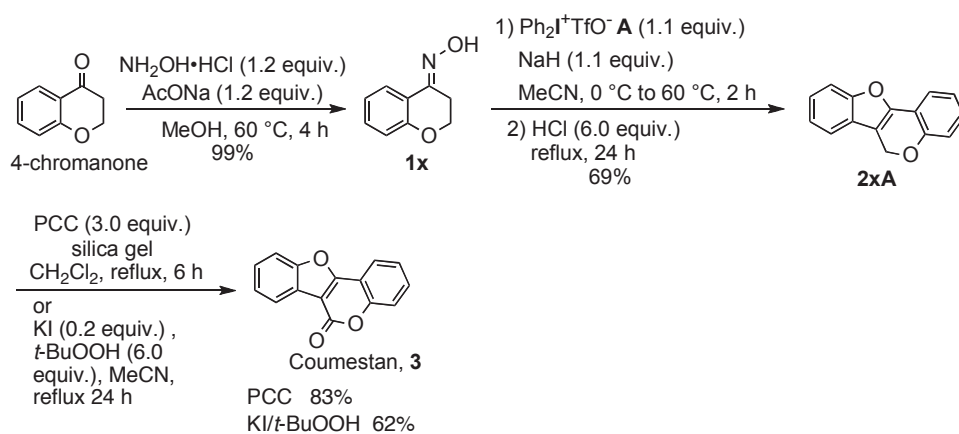
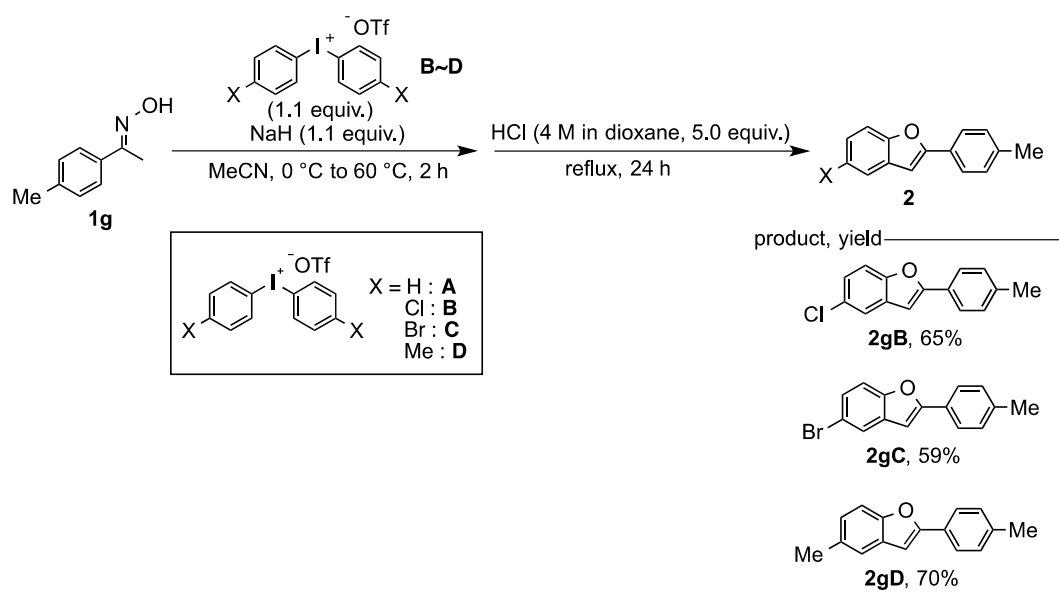
For the gram-scale reaction, treatment of *p*-methylacetophenone oxime **1g** (1.044g, 7 mmol) with diphenyliodonium triflate **A** in the presence of NaH in acetonitrile for 2 h at 60 °C, followed by the treatment with HCl (4 M in dioxane, 5.0 equiv.) provided 2-(4'-methylphenyl)benzofuran **2gA** in 84% (1.230g) yield, as shown in Table 2. Thus, the present method can be used for the gram-scale preparation of 2-arylbenzofurans.

Coumestan **3** is a basic pharmacophore, having a benzofuran structure and exhibiting estrogenic activity.⁹ Compound **3** was prepared from *O*-phenyl hydroxylamine and 4-chromanone recently.^{5a} Therefore, as a synthetic application of the present method, Coumestan **3** was prepared from 4-chromanone, as shown in

Table 2. One-Pot Transformation of Oximes **1** into 2-Arylbenzofurans **2** with Diphenyliodonium Triflate**A**^a Oxime **1g** (7.0 mmol) was used. ^b The 2nd reaction step was refluxed.^c HCl (4 M in dioxane 6.0 equiv.) was added.

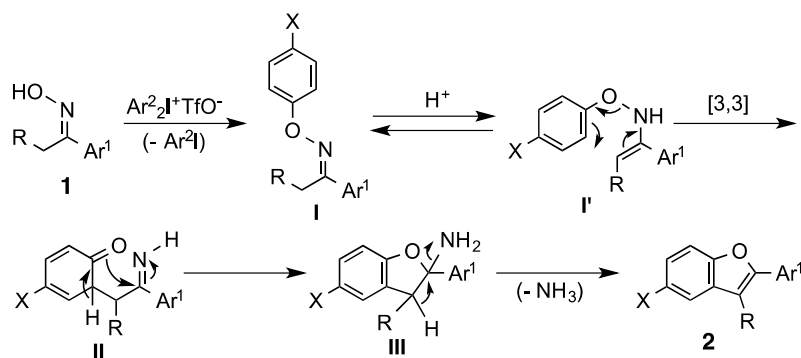
Scheme 2. 4-Chromanone was treated with hydroxylamine in methanol to form the corresponding oxime **1x** in 99% yield. Treatment of oxime **1x** with diphenyliodonium triflate **A** in the presence of NaH in acetonitrile for 2 h at 60 °C, followed by the treatment with HCl (4 M in dioxane, 6.0 equiv.) for 24 h under refluxing conditions gave benzofuran derivative **2xA** in 69% yield. Oxidation of benzofuran **2xA** with PCC^{5a} in dichloromethane or KI/*t*-BuOOH in acetonitrile¹⁰ gave coumestan **3** in 83% and 62% yields, respectively.

Table 3. One-Pot Transformation of *p*-Methylacetophenone Oxime **1g** into 5-Substituted 2-(4'-Methylphenyl)benzofurans **2** with Diaryliodonium Triflates **B~D**



Scheme 2. Preparation of Coumestan

A possible reaction mechanism of the present reaction is shown in Scheme 3. Acetophenone oximes **1** react with diaryliodonium triflates **A~D** via the $\text{S}_{\text{N}}\text{Ar}$ reaction pathway to form *O*-aryl acetophenone oximes **I**. Practically, treatment of propiophenone oxime **1a** with diphenyliodonium triflate **A** in the presence of NaH, generated the corresponding *O*-phenyl propiophenone oxime **Ia** in high yield. Then, the [3,3]-sigmatropic rearrangement of *O*-aryl acetophenone oximes **I** under acidic and warming conditions takes place to generate intermediates **III** through the cyclization of intermediate **II**, and the subsequent elimination of ammonia from intermediate **III** provides benzofurans **2**.



Scheme 3. Possible Reaction Mechanism

During our study, the two methods for the preparation of benzofurans: the reaction of ketoximes with diaryliodonium salts and ^tBuOK, followed by the treatment with HCl in dioxane,^{11a} and the reaction of ethyl acetohydroxamate with diaryliodonium salts and ^tBuONa, followed by the treatment with ketones and aq. HCl,^{11b} were reported very recently. Especially, the former reaction is essentially same to the present preparation of 2-arylbenzofurans. However, 1.5 equiv. of diaryliodonium salts were required for *O*-arylation of oximes with ^tBuOK and one-pot preparation of benzofurans from oximes was limited to two examples. In our present method, only 1.1 equiv. of diaryliodonium salts for the effective *O*-arylation of oximes with NaH were used, and the wide synthetic utility for the one-pot preparation of 2-arylbenzofurans with 27 examples is shown.

In conclusion, treatment of oximes derived from alkyl aryl ketones with diaryliodonium triflate in the presence of NaH, followed by the treatment with HCl in dioxane under warming conditions gave 2-arylbenzofurans, and 3-substituted and 3,5-disubstituted 2-arylbenzofurans in good yields in a one-pot manner under transition metal-free conditions. We believe the present method should be useful for the preparation of various 2-arylbenzofurans, as the oximes can be obtained easily from ketones.

EXPERIMENTAL

General: ¹H-NMR and ¹³C-NMR spectra were obtained with JEOL-JNM-ECX400, JEOL-JNM-ECS400, and JEOL-JNM-ECA500 spectrometers. Chemical shifts are expressed in ppm downfield from TMS in δ units. Mass spectra were recorded on JMS-T100GCV, JMS-HX110, and Thermo LTQ Orbitrap XL spectrometers. IR spectra were measured with a JASCO FT/IR-4100 spectrometer. Melting points were determined with a Yamato Melting Point Apparatus Model MP-21. Merck silica gel 60F₂₅₄ was used for TLC. Silica gel 60 (Kanto Kagaku Co.) was used for short column chromatography.

Typical Procedure for One-pot Conversion of Oximes 1 into Benzofurans 2: Propiophenone oxime (**1a**) (74.6 mg, 0.5 mmol), NaH (55% dispersion in paraffin liquid, 24.0 mg, 0.55 mmol), and diphenyliodonium trifluoromethanesulfonate **A** (236.6 mg, 0.55 mmol) were dried by vacuum pump for

30 min at room temperature. Under an argon atmosphere, MeCN (3.0 mL) was added to a flask at 0 °C. The obtained mixture was stirred for 2 h at 60 °C. Then, HCl (4 M in dioxane, 0.63 mL, 2.5 mmol) was added at 60 °C and the mixture was stirred for 4 h at 60 °C. Saturated NaHCO₃ aqueous solution (10 mL) was added to the reaction mixture, and the product was extracted with CHCl₃ (15 mL × 3). The organic layer was dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: hexane : CHCl₃ = 30:1) to give 3-methyl-2-phenylbenzofuran (**2aA**) (82.3 mg, 79% yield).

3-Methyl-2-phenylbenzofuran (2aA)¹²: Yield: 82.3 mg (79%); white solid; Mp 35-37 °C (lit.¹², colorless oil); IR (ATR) 1455, 1259, 1212, 1102, 1066, 741, 696 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ = 2.49 (s, 3H), 7.23-7.33 (m, 2H), 7.36 (t, 1H, *J* = 7.4 Hz), 7.48 (m, 3 H), 7.55 (d, 1H, *J* = 7.5 Hz), 7.82 (d, 2H, *J* = 7.2 Hz) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ = 9.46, 110.91, 111.25, 119.26, 122.31, 124.30, 126.69, 127.84, 128.60, 131.15, 131.41, 150.66, 153.77 ppm.

2-(4'-Methylphenyl)-3-methylbenzofuran (2bA)¹³: Yield: 94.5 mg (85%); white solid; Mp 64-65 °C; IR (ATR) 2918, 1454, 1257, 1092, 816, 745, 736 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ = 2.41 (s, 3H), 2.46 (s, 3H), 7.21-7.32 (m, 4H), 7.47 (d, 1H, *J* = 8.1 Hz), 7.52 (d, 1H, *J* = 7.0 Hz), 7.71 (d, 2H, *J* = 8.1 Hz) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ = 9.44, 21.33, 110.53, 110.84, 119.11, 122.24, 124.05, 126.62, 128.60, 129.31, 131.24, 137.81, 150.91, 153.67 ppm; HRMS (APCI) Calcd for C₁₆H₁₅O [M+H]⁺ = 223.1117, Found = 223.1123.

2-(4'-Chlorophenyl)-3-methylbenzofuran (2cA): Yield: 83.7 mg (69%); white solid; Mp 67-68 °C; IR (ATR) 1490, 1453, 1093, 827, 731 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ = 2.46 (s, 3H), 7.23-7.33 (m, 2H), 7.42-7.49 (m, 3H), 7.53 (d, 2H, *J* = 8.1 Hz), 7.74 (d, 2H, *J* = 8.5 Hz) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ = 9.49, 110.94, 111.75, 119.35, 122.47, 124.59, 127.80, 128.86, 129.9, 130.98, 133.66, 149.55, 153.74 ppm; HRMS (APCI) Calcd for C₁₅H₁₂OCl [M+H]⁺ = 243.0571, Found = 243.0575.

3-Heptyl-2-phenylbenzofuran (2dA): Yield: 117.0 mg (80%); colorless oil; IR (ATR) 2925, 2855, 1456, 1442, 1259, 761, 741, 691 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ = 0.87 (t, 3H, *J* = 6.5 Hz), 1.20-1.49 (m, 8H), 1.75 (quin, 2H, *J* = 7.8 Hz), 2.90 (t, 2H, *J* = 7.8 Hz), 7.20-7.30 (m, 2H), 7.34 (t, 1H, *J* = 7.4 Hz), 7.43-7.49 (m, 3H), 7.56 (d, 1H, *J* = 6.9 Hz), 7.78 (d, 2H, *J* = 7.4 Hz) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ = 14.09, 22.65, 24.24, 29.12, 29.72, 29.79, 31.80, 111.00, 116.53, 119.60, 122.23, 124.19, 126.79, 127.94, 128.61, 130.59, 131.41, 150.51, 153.89 ppm; HRMS (APCI) Calcd for C₂₁H₂₄O [M]⁺ = 292.1822, Found = 292.1817.

3-Decyl-2-phenylbenzofuran (2eA): Yield: 118.7 mg (71%); colorless oil; IR (ATR) 2923, 2853, 1456, 1259, 762, 741, 692 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ = 0.88 (t, 3H, *J* = 6.3 Hz), 1.20-1.51 (m, 14H), 1.76 (quin, 2H, *J* = 7.7 Hz), 2.90 (t, 2H, *J* = 7.7 Hz), 7.21-7.31 (m, 2H), 7.36 (t, 1H, *J* = 7.5 Hz), 7.47 (m, 3H), 7.56 (d, 1H, *J* = 7.7 Hz), 7.78 (d, 2H, *J* = 7.9 Hz) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ = 14.11,

22.67, 24.26, 29.33, 29.39, 29.46, 29.61, 29.72, 29.84, 31.90, 111.01, 116.56, 119.62, 122.25, 124.20, 126.81, 127.96, 128.62, 130.60, 131.44, 150.54, 153.91 ppm; HRMS (APCI) Calcd for C₂₄H₃₀O [M]⁺ = 334.2291, Found = 334.2287.

2-Phenylbenzofuran (2fA)^{5a}: Yield: 80.6 mg (83%); white solid; Mp 116 °C (lit.^{5a}, 118-120 °C); IR (ATR) 1455, 1020, 906, 741, 688 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ = 7.03 (s, 1H), 7.20-7.31 (m, 2H), 7.35 (t, 1H, *J* = 7.4 Hz), 7.45 (t, 2H, *J* = 7.7 Hz), 7.53 (d, 1H, *J* = 7.9 Hz), 7.57 (d, 1H, *J* = 7.2 Hz), 7.76 (d, 2H, *J* = 8.0 Hz) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ = 101.29, 111.16, 120.89, 122.92, 124.24, 124.92, 128.53, 128.77, 129.20, 130.47, 154.87, 155.90 ppm; HRMS (APCI) Calcd for C₁₄H₁₀O [M]⁺ = 194.0726, Found = 194.0723.

2-(4'-Methylphenyl)benzofuran (2gA)¹⁴: Yield: 92.7 mg (89%); white solid; Mp 125-126 °C (lit.¹⁴, 128-129 °C); IR (ATR) 2912, 1504, 1449, 1256, 1032, 799, 736 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ = 2.39 (s, 3H), 6.96 (s, 1H), 7.22 (t, 1H, *J* = 7.5 Hz), 7.28-7.24 (m, 3 H), 7.51 (d, 1H, *J* = 7.8 Hz), 7.57 (d, 1H, *J* = 7.2 Hz), 7.76 (d, 2H, *J* = 8.0 Hz) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ = 21.49, 100.64, 111.18, 120.83, 122.94, 124.08, 124.98, 127.84, 129.44, 129.58, 138.69, 154.86, 156.27 ppm.

2-(4'-Methoxyphenyl)benzofuran (2hA)^{5a}: Yield: 97.6 mg (87%); white solid; Mp 147 °C (lit.^{5a}, 148-149 °C); IR (ATR) 1607, 1503, 1246, 1022, 799, 742 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ = 3.86 (s, 3H), 6.89 (s, 1H), 6.98 (d, 2H, *J* = 9.0 Hz), 7.19-7.26 (m, 2H), 7.50 (d, 1H, *J* = 7.0 Hz), 7.55 (d, 1H, *J* = 7.5 Hz), 7.80 (d, 2H, *J* = 9.0 Hz) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ = 55.46, 99.76, 111.07, 114.34, 120.66, 122.92, 123.43, 123.83, 126.51, 129.57, 154.78, 156.14, 160.07 ppm; HRMS (APCI) Calcd for C₁₅H₁₂O₂ [M]⁺ = 224.0832, Found = 224.0829.

2-(3'-Methoxyphenyl)benzofuran (2iA)^{5a}: Yield: 87.5 mg (78%); white solid; Mp 50-51 °C (lit.^{5a}, 48-49 °C); IR (ATR) 1568, 1489, 1233, 1048, 806, 736 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ = 3.89 (s, 3H), 6.91 (d, 1H, *J* = 8.2 Hz), 7.02 (s, 1H), 7.20-7.32 (m, 2H), 7.36 (t, 1H, *J* = 8.1 Hz), 7.41 (t, 1H, 1.6 Hz), 7.46 (d, 1H, *J* = 7.6 Hz), 7.53 (d, 1H, *J* = 8.1 Hz), 7.58 (d, 1H, *J* = 7.4 Hz) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ = 55.36, 101.61, 110.10, 111.16, 114.45, 117.51, 120.91, 122.93, 124.31, 129.14, 129.84, 131.75, 154.83, 155.71, 159.92 ppm.

2-(2'-Methoxyphenyl)benzofuran (2jA)^{5a}: Yield: 79.6 mg (71%); white solid; Mp 77-78 °C (lit.^{5a}, 78-79 °C); IR (ATR) 1492, 1443, 1249, 1014, 819, 741 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ = 4.00 (s, 3H), 7.01 (d, 1H, *J* = 8.3 Hz), 7.08 (t, 1H, *J* = 7.5 Hz), 7.19-7.35 (m, 3H), 7.36 (s, 1H), 7.51 (d, 1H, *J* = 8.1 Hz), 7.59 (d, 1H, *J* = 7.4 Hz), 8.07 (d, 1H, *J* = 7.8 Hz) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ = 55.45, 106.30, 110.81, 111.00, 119.35, 120.76, 121.02, 122.61, 124.08, 127.03, 129.23, 129.77, 152.14, 153.85, 156.47 ppm.

2-(4'-N,N-Dimethylaminophenyl)benzofuran (2kA): Yield: 93.7 mg (79%); white solid; Mp 178 °C; IR (ATR) 1608, 1512, 1450, 1357, 1173, 819, 789, 742 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ = 3.02 (s,

6H), 6.74-6.82 (m, 3H), 7.15-7.24 (m, 2H), 7.48 (d, 1H, $J = 8.4$ Hz), 7.52 (d, 1H, $J = 7.8$ Hz), 7.74 (d, 2H, $J = 9.1$ Hz) ppm; ^{13}C -NMR (100 MHz, CDCl_3): $\delta = 40.40, 98.13, 110.76, 112.25, 120.15, 122.62, 123.09, 125.55, 126.13, 129.81, 150.41, 154.51, 156.95$ ppm; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{16}\text{ON}$ $[\text{M}+\text{H}]^+ = 238.1226$, Found = 238.1223.

2-(4'-Fluorophenyl)benzofuran (2IA): Yield: 90.2 mg (85%); white solid; Mp 128 °C; IR (ATR) 1498, 1450, 1224, 1098, 839, 801, 741 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3): $\delta = 6.95$ (s, 1H), 7.10-7.17 (m, 2H), 7.20-7.31 (m, 2H), 7.51 (d, 1H, $J = 7.5$ Hz), 7.57 (d, 1H, $J = 7.7$ Hz), 7.81-7.86 (m, 2H) ppm; ^{13}C -NMR (100 MHz, CDCl_3): $\delta = 101.00, 111.13, 115.88$ (d, $J_{\text{C-F}} = 21.9$ Hz), 120.88, 123.01, 124.28, 126.76 (d, $J_{\text{C-F}} = 8.6$ Hz) 129.17, 154.84, 155.01, 162.87 (d, $J_{\text{C-F}} = 248.9$ Hz) ppm; HRMS (APCI) Calcd for $\text{C}_{14}\text{H}_{10}\text{OF}$ $[\text{M}+\text{H}]^+ = 213.0710$, Found = 213.0715.

2-(4'-Chlorophenyl)benzofuran (2mA)¹⁵: Yield: 97.2 mg (85%); white solid; Mp 149-150 °C (lit.¹⁵, 148-149 °C); IR (ATR) 1580, 1485, 1448, 1092, 1031, 1008, 802, 741, 725 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3): $\delta = 7.01$ (s, 1H), 7.21-7.32 (m, 2H), 7.42 (d, 2H, $J = 7.2$ Hz), 7.51 (d, 1H, $J = 8.1$ Hz), 7.58 (d, 1H, $J = 7.4$ Hz), 7.79 (d, 2H, $J = 8.3$ Hz) ppm; ^{13}C -NMR (100 MHz, CDCl_3): $\delta = 101.71, 111.17, 120.98, 123.07, 124.53, 125.93, 126.09, 128.93, 129.00, 134.27, 154.73, 154.85$ ppm.

2-(4'-Bromophenyl)benzofuran (2nA)^{5a}: Yield: 124.3 mg (91%); white solid; Mp 160-161 °C (lit.^{5a}, 159-160 °C); IR (ATR) 1577, 1485, 1447, 1399, 1256, 1168, 1069, 1030, 1005, 801, 740 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3): $\delta = 7.03$ (s, 1H), 7.21-7.33 (m, 2H), 7.51 (d, 1H, $J = 7.7$ Hz), 7.55-7.60 (m, 3H), 7.73 (d, 2H, $J = 8.3$ Hz) ppm; ^{13}C -NMR (100 MHz, CDCl_3): $\delta = 101.84, 111.20, 121.01, 122.49, 123.10, 124.60, 126.35, 129.01, 129.39, 131.96, 154.76, 154.89$ ppm.

2-(3'-Bromophenyl)benzofuran (2oA)^{5a}: Yield: 103.8 mg (76%); white solid; Mp 82-83 °C (lit.^{5a}, 84-85 °C); IR (ATR) 1598, 1551, 1450, 1037, 809, 783, 742, 716 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3): $\delta = 7.00$ (s, 1H), 7.20-7.31 (m, 3H), 7.44 (d, 1H, $J = 7.9$ Hz), 7.50 (d, 1H, $J = 8.2$ Hz), 7.57 (d, 1H, $J = 7.9$ Hz), 7.74 (d, 1H, $J = 7.9$ Hz), 7.99 (s, 1H) ppm; ^{13}C -NMR (100 MHz, CDCl_3): $\delta = 102.37, 111.23, 121.11, 122.93, 123.10, 123.34, 124.75, 127.75, 128.86, 130.27, 131.28, 132.38, 154.12, 154.92$ ppm.

2-(4'-Iodophenyl)benzofuran (2pA): Yield: 128.1 mg (80%); white solid; Mp 182 °C; IR (ATR) 1574, 1481, 1449, 1257, 1169, 1002, 803, 744 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3): $\delta = 7.04$ (s, 1H), 7.21-7.33 (m, 2H), 7.51 (d, 1H, $J = 7.8$ Hz), 7.57-7.61 (m, 3H), 7.78 (d, 2H, $J = 8.4$ Hz) ppm; ^{13}C -NMR (100 MHz, CDCl_3): $\delta = 94.07, 101.95, 111.21, 121.03, 123.10, 124.64, 126.47, 127.39, 129.00, 129.94, 154.84, 154.90$ ppm; HRMS (APCI) Calcd for $\text{C}_{14}\text{H}_9\text{OI}$ $[\text{M}]^+ = 319.9693$, Found = 319.9689.

2-(4'-Nitrophenyl)benzofuran (2qA)^{5a}: Yield: 102.9 mg (86%); yellow solid; Mp 183-184 °C (lit.^{5a}, 184.5-185); IR (ATR) 1598, 1514, 1334, 1108, 850, 808, 749 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3): $\delta = 7.24$, (s, 1H), 7.28 (t, 1H, $J = 8.2$ Hz), 7.37 (t, 1H, $J = 7.7$ Hz), 7.56 (d, 1H, $J = 8.2$ Hz), 7.65 (d, 1H, $J =$

7.7 Hz), 8.00 (d, 2H, $J = 9.1$ Hz), 8.31 (d, 2H, $J = 9.1$ Hz) ppm; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 105.08$, 111.47, 121.61, 123.51, 124.28, 125.18, 125.80, 128.61, 136.24, 147.20, 153.21, 155.41 ppm; HRMS (APPI) Calcd for $\text{C}_{14}\text{H}_8\text{O}_3\text{N}$ $[\text{M-H}]^+ = 238.0510$, Found = 238.0514.

Methyl 4-(benzofuran-2'-yl)benzoate (2rA): Yield: 100.9 mg (80%); white solid; Mp 172-174 °C; IR (ATR) 1713, 1606, 1438, 1272, 1104, 770, 749, 698 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 3.95$ (s, 3H), 7.16 (s, 1H), 7.25 (t, 1H, $J = 6.5$ Hz), 7.33 (t, 1H, $J = 7.0$ Hz), 7.54 (d, 1H, $J = 8.4$ Hz), 7.62 (d, 1H, $J = 7.2$ Hz), 7.93 (d, 2H, $J = 8.5$ Hz), 8.12 (d, 2H, $J = 8.5$ Hz) ppm; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 52.20$, 103.43, 111.33, 121.27, 123.20, 124.60, 125.05, 128.88, 129.67, 130.11, 134.47, 154.63, 155.14, 166.67 ppm; HRMS (APCI) Calcd for $\text{C}_{16}\text{H}_{12}\text{O}_3$ $[\text{M}]^+ = 252.0781$, Found = 252.0776.

2-(4'-Phenylphenyl)benzofuran (2sA): Yield: 128.4 mg (95%); white solid; Mp 225 °C; IR (ATR) 1484, 1445, 1408, 1257, 1169, 1038, 803, 746 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.07$ (s, 1H), 7.21-7.33 (m, 2H), 7.37 (t, 1H, $J = 7.2$ Hz), 7.47 (t, 2H, $J = 7.6$ Hz), 7.54 (d, 1H, $J = 8.1$ Hz), 7.60 (d, 1H, $J = 7.2$ Hz), 7.65 (d, 2H, $J = 8.3$ Hz), 7.69 (d, 2H, $J = 8.1$ Hz), 7.94 (d, 2H, $J = 8.1$ Hz) ppm; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 101.52$, 111.27, 121.00, 123.06, 124.40, 125.43, 127.09, 127.55, 127.67, 128.97, 129.36, 129.48, 140.52, 141.33, 155.03, 155.78 ppm; HRMS (APCI) Calcd for $\text{C}_{20}\text{H}_{14}\text{O}$ $[\text{M}]^+ = 270.1039$, Found = 270.1037.

2-(Naphthalen-1'-yl)benzofuran (2tA): Yield: 63.5 mg (52%); colorless oil; IR (ATR) 1509, 1451, 1256, 979, 794, 771, 738 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.07$ (s, 1H), 7.25-7.36 (m, 2H), 7.50-7.61 (m, 4H), 7.65 (d, 1H, $J = 7.5$ Hz), 7.85-7.92 (m, 3H), 8.47 (d, 1H, $J = 8.1$ Hz) ppm; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 105.90$, 111.27, 120.97, 122.92, 124.31, 125.25, 125.49, 126.09, 126.86, 127.28, 128.24, 128.59, 129.02, 129.50, 130.68, 133.90, 154.95, 155.58 ppm; HRMS (APCI) Calcd for $\text{C}_{18}\text{H}_{13}\text{O}$ $[\text{M+H}]^+ = 245.0961$, Found = 245.0956.

2-(Naphthalen-2'-yl)benzofuran (2uA)^{5a}: Yield 100.2 mg (82%); white solid; Mp 163 °C (lit. ^{5a}, 161-162 °C); IR (ATR) 1449, 1255, 952, 801, 738 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.14$ (s, 1H), 7.25 (t, 1H, $J = 7.4$ Hz), 7.31 (t, 1H, $J = 7.4$ Hz), 7.47-7.55 (m, 2H), 7.57 (d, 1H, $J = 8.0$ Hz), 7.61 (d, 1H, $J = 7.6$ Hz), 7.84 (d, 1H, $J = 7.9$ Hz), 7.88-7.94 (m, 3H), 8.38 (s, 1H) ppm; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 101.87$, 101.92, 11.16, 120.94, 122.80, 123.00, 123.83, 124.41, 126.46, 126.63, 127.72, 127.79, 128.40, 128.49, 129.28, 133.27, 133.43, 155.02 ppm.

2-(Thiophen-2'-yl)benzofuran (2vA)^{5a}: Yield: 65.1 mg (65%); white solid; Mp 95 °C (lit. ^{5a}, 95-96.5 °C); IR (ATR) 1587, 1449, 1200, 995, 801, 747, 697 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 6.87$ (s, 1H), 7.11 (t, 1H, $J = 4.4$ Hz), 7.20-7.30 (m, 2H), 7.34 (d, 1H, $J = 4.9$ Hz), 7.47-7.51 (m, 2H), 7.54 (d, 1H, $J = 7.6$ Hz) ppm; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 101.09$, 111.05, 120.73, 123.09, 124.28, 124.58, 125.77, 127.87, 129.09, 133.30, 151.28, 154.53 ppm.

2-(Furan-2'-yl)benzofuran (2wA)¹⁶: Yield: 75.5 mg (82%); white solid; Mp 57-58 °C (lit. ¹⁶, 57-58.5 °C);

IR (ATR) 1644, 1532, 1462, 1438, 1254, 1171, 1006, 795, 735, 591 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 6.53 (m, 1H), 6.80 (d, 1H, J = 3.4 Hz), 6.91 (s, 1H), 7.20-7.31 (m, 2H), 7.48-7.54 (m, 2H), 7.57 (d, 1H, J = 7.2 Hz) ppm; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ = 101.07, 107.62, 111.09, 111.67, 120.99, 123.12, 124.37, 128.70, 143.00, 146.18, 148.07, 154.54 ppm.

6*H*-Benzofuro[3,2-*c*][1]benzopyran (2xA)¹⁷: Yield: 76.7 mg (69%); white solid; Mp 76-77 °C (lit.¹⁷, 76-78 °C); IR (ATR) 1645, 1493, 1456, 1302, 1190, 984, 830, 812, 739 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 5.64 (s, 2H), 6.92 (d, 1H, J = 8.2 Hz), 6.99 (d, 1H, J = 8.2 Hz), 7.20 (d, 1H, J = 7.8 Hz), 7.24-7.33 (m, 2H), 7.40 (d, 1H, J = 6.8 Hz), 7.51-7.56 (m, 2H) ppm; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ = 65.25, 108.18, 111.58, 116.23, 116.30, 118.80, 120.71, 121.53, 123.27, 124.38, 125.60, 129.75, 147.77, 154.07, 155.47 ppm.

5-Chloro-2-(4'-methylphenyl)benzofuran (2gB): Yield: 78.9 mg (65%); white solid; Mp 181 °C; IR (ATR) 1607, 1578, 1504, 1442, 1263, 1161, 822, 794 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 2.40 (s, 3H), 6.90 (s, 1H), 7.21 (dd, 1H, J = 2.1, 8.8 Hz), 7.24-7.28 (m, 3H), 7.41 (d, 1H, J = 8.8 Hz), 7.52 (d, 1H, J = 2.1 Hz), 7.74 (d, 2H, J = 8.2 Hz) ppm; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ = 21.41, 100.04, 112.00, 120.24, 124.09, 125.00, 127.22, 128.38, 129.55, 130.71, 139.13, 153.13, 157.67 ppm; HRMS (APCI) Calcd for $\text{C}_{15}\text{H}_{12}\text{OCl}$ [$\text{M}+\text{H}$]⁺ = 243.0571, Found = 243.0567.

5-Bromo-2-(4'-methylphenyl)benzofuran (2gC): Yield: 84.7 mg (59%); white solid; Mp 186 °C; IR (ATR) 1576, 1504, 1442, 1262, 1160, 822, 795 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 2.40 (s, 3H), 6.90 (s, 1H), 7.24-7.28 (m, 2H), 7.33-7.39 (m, 2H), 7.68 (d, 1H, J = 1.8 Hz), 7.74 (d, 2H, J = 8.4 Hz) ppm; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ = 21.41, 99.88, 112.50, 115.89, 123.28, 125.02, 126.78, 127.16, 129.55, 131.35, 139.16, 153.50, 157.51 ppm; HRMS (APCI) Calcd for $\text{C}_{15}\text{H}_{11}\text{OBr}$ [M]⁺ = 285.9988, Found = 285.9984.

5-Methyl-2-(4'-methylphenyl)benzofuran (2gD): Yield: 77.8 mg (70%); white solid; Mp 149-150 °C; IR (ATR) 1505, 1459, 1264, 1035, 823, 797 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 2.39 (s, 3H), 2.44 (s, 3H), 6.89 (s, 1H), 7.07 (d, 1H, J = 8.2 Hz), 7.25 (d, 2H, J = 8.4 Hz), 7.35 (s, 1H), 7.38 (d, 1H, J = 8.2 Hz), 7.74 (d, 2H, J = 8.4 Hz) ppm; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ = 21.34, 21.37, 100.32, 110.54, 120.56, 124.31, 124.79, 125.23, 127.87, 129.43, 132.22, 138.42, 153.18, 153.24 ppm; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{15}\text{O}$ [$\text{M}+\text{H}$]⁺ = 223.1117, Found = 223.1122.

Preparation of 2,3-Dihydro-4*H*-1-benzopyran-4-one Oxime (1x)¹⁸: To a solution of 4-chromanone (5 mmol, 771.8 mg) in dry MeOH (10 mL) were added AcONa (6.0 mmol, 492.2 mg) and $\text{NH}_2\text{OH} \cdot \text{HCl}$ (6.0 mmol, 429.8 mg). The mixture was stirred for 4 h at 60 °C. Saturated NaHCO_3 aqueous solution (20 mL) was added to the reaction mixture, and the product was extracted with CHCl_3 (20 mL \times 3). The organic layer was dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was

purified by silica-gel column chromatography (eluent: *n*-hexane : AcOEt = 5 : 1) to give 2,3-dihydro-4*H*-1-benzopyran-4-one oxime (**1x**) (807.9 mg, 99% yield). Colorless Crystals; Mp 138-139 °C (lit.¹⁸, 139-141 °C); IR (ATR) 3255, 2920, 1650, 1603, 1576, 1484, 1453, 1311, 1216, 969, 759 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ = 3.00 (t, 2H, *J* = 6.3 Hz), 4.25 (t, 2H, *J* = 6.3 Hz), 6.88-6.97 (m, 2H), 7.24-7.28 (m, 1H), 7.40 (brs, 1H), 7.84 (d, 1H, *J* = 7.9 Hz) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ = 23.53, 64.93, 117.81, 118.13, 121.48, 123.93, 131.13, 149.95, 156.67 ppm.

Preparation of 6*H*-Benzofuro[3,2-*c*][1]benzopyran (2xA**):** 2,3-Dihydro-4*H*-1-benzopyran-4-one oxime (**1x**) (81.6 mg, 0.5 mmol), NaH (24.0 mg, 0.55 mmol), and diphenyliodonium trifluoromethanesulfonate (236.6 mg, 0.55 mmol) were dried by vacuum pump for 30 min at room temperature. Under an argon atmosphere, MeCN (3.0 mL) was added to the flask at 0 °C. The obtained mixture was stirred for 2 h at 60 °C. Then, HCl (4 M in dioxane, 0.75 mL, 3.0 mmol) was added at 80 °C and the mixture was stirred for 4 h at refluxing temperature. Saturated NaHCO₃ aqueous solution (10 mL) was added to the reaction mixture, and the product was extracted with CHCl₃ (15 mL × 3). The organic layer was dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: hexane : CHCl₃ = 30 : 1) to give 6*H*-benzofuro[3,2-*c*][1]benzopyran (**2xA**) (76.7 mg, 69% yield).

Preparation of 6*H*-Benzofuro[3,2-*c*][1]benzopyran-6-one (Coumestan) (3**)^{5a}. Method A:** To a solution of 6*H*-benzofuro[3,2-*c*][1]benzopyran (**2xA**) (0.32 mmol, 70.6 mg) in dry CH₂Cl₂ (20 mL) were added silica gel (70.6 mg) and PCC (0.32 mmol, 70.4 mg). The mixture was stirred for 2 h under refluxing conditions. Then, PCC (0.64 mmol, 140.8 mg) was added to the mixture, and the mixture was stirred for 4 h under refluxing conditions. The cooled mixture was filtered through celite, and then the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane : AcOEt = 5 : 1) to afford 6*H*-benzofuro[3,2-*c*][1]benzopyran-6-one (**3**) (62.7 mg, 83% yield).

Method B: 6*H*-Benzofuro[3,2-*c*][1]benzopyran (**2xA**) (0.2 mmol, 44.4 mg), KI (0.04 mmol, 6.6 mg), MeCN (2 mL), and *tert*-butyl hydroperoxide (70%, 1.2 mmol, 0.16 mL) were added to a 20 mL screw-capped glass flask, then the mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction mixture was quenched by the addition of saturated aq. Na₂SO₃ (10 mL) and extracted with EtOAc (10 mL × 3). The organic layer was dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: *n*-hexane : AcOEt = 5 : 1) to afford 6*H*-benzofuro[3,2-*c*][1]benzopyran-6-one (**3**) (29.3 mg, 62% yield).

6*H*-Benzofuro[3,2-*c*][1]benzopyran-6-one (Coumestan): Colorless crystals; Mp 183 °C (lit.^{5a}, 186.5-187.5 °C); IR (ATR) 2987, 1729, 1625, 1497, 1080, 888, 748 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ = 7.41 (t, 1H, *J* = 7.4 Hz), 7.45-7.53 (m, 3H), 7.61 (t, 1H, *J* = 7.0 Hz), 7.66 (d, 1H, *J* = 7.2 Hz), 8.02 (d,

1H, $J = 7.9$ Hz), 8.14 (d, 1H, $J = 8.0$ Hz) ppm; ^{13}C -NMR (100 MHz, CDCl_3): $\delta = 105.84, 111.73, 1125.60, 117.47, 121.84, 123.40, 124.60, 124.63, 125.19, 126.74, 131.91, 153.63, 155.48, 158.05, 159.96$ ppm.

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