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Cu-Catalyzed Consecutive Hydroxylation and Aerobic Oxidative Cycloetherification under Microwave Conditions: Entry to 2-Arylbenzofuran-3-carboxylic Acids

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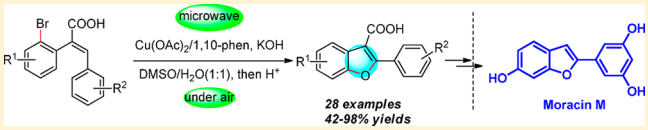
Supporting Information

ABSTRACT: A convenient one-pot synthesis of 2-arylbenzofuran-3-carboxylic acids from (*E*)-2-(2-bromophenyl)-3-phenylacrylic acids via Cu-catalyzed consecutive hydroxylation and aerobic oxidative cycloetherification under microwave conditions has been developed. This protocol employed the reagent combination of $Cu(OAc)_2$, 1,10-phen, and KOH in $DMSO/H_2O$ (1:1), all of which are cost-effective, readily available, and easily removable from the reaction mixture. Utilizing this synthetic protocol, various 2-arylbenzofuran-3-carboxylic acids as well as the natural product moracin M have been synthesized in satisfactory yields under mild conditions.



INTRODUCTION

3-Substituted 2-arylbenzofurans, especially the 3-carbonyl-derived 2-arylbenzofurans, represent an important class of privileged structures prevalent in natural products and active pharmaceutical ingredients.[1] Compounds featuring this scaffold showed great therapeutic potential for the treatment of various diseases such as cancers,[2] infections,[3] inflammations,[4] immunosuppressions,[5] and convulsant symptoms.[6] For instance, the antitumor agents coumestrol[7] and sphenostylisin A,[8] the antioxidative natural product iteafuranal B,[9] the anticomplement compound oryzafuran,[10] the melanin synthesis inhibitor lespeflorin F2,[11] and the transmembrane protein 16A (TMEM16A) inhibitor B13[12] are all characterized by the 3-carbonyl-derived 2-arylbenzofuran motif (Figure 1).

Although the synthesis of specific 3-substituted 2-arylbenzofuran derivatives can be achieved individually, a general and compatible method has not yet been established. From synthetic chemistry perspective, the 3-substituted 2-arylbenzofurans, especially the 3-carbonyl-derived 2-arylbenzofurans, have a common intermediate, namely, the 2-arylbenzofuran-3-carboxylic acids (**2**). Therefore, the efficient synthesis of **2** can pave the way for the assembly of 3-substituted 2-arylbenzofurans as well as the decarboxylated products 2-arylbenzofurans, which were also found to be an intriguing class of natural compounds.[13] Generally, methods to access **2** mainly involved the transition-metal-mediated C−C and C−O bond formation,[14] and the oxidative reaction of 2-hydroxychalcones,[15] and the rearrangement reactions of ethyl 2-(2-methoxyphenyl)-3-oxo-3-phenylpropanoate, 5-benzoyl-5*H*-dibenzo[*b*,*f*]azepin-10-(11*H*)-one, and 2-benzyloxy aromatic cyanohydrin ester.[16] The Zn-catalyzed condensation between benzyolacetates and *p*-benzoquinone reported by Kumar was also workable in the assembly of 5-hydroxy-2-arylbenzofuran-3-carboxylic acids.[12] Despite the advances in the synthesis of **2** and their derivatives, these reported methods still suffered from the use of expensive transition-metal catalysts, the need for harsh reaction conditions, the necessity for preformed substrates, limited structural diversity and functional group tolerability, and relatively low yields. Therefore, a facile, versatile, and practical approach for access to 2-arylbenzofuran-3-carboxylic acids (**2**) is greatly demanded.

Over the past decade, Cu-catalyzed reactions have emerged as powerful tools in organic synthesis.[17] Various Cu-containing catalysts enable direct generation of structurally diversified compounds through the cleavage of C−X (X = H, C, Cl, Br, I) bonds and the construction of a range of new carbon−

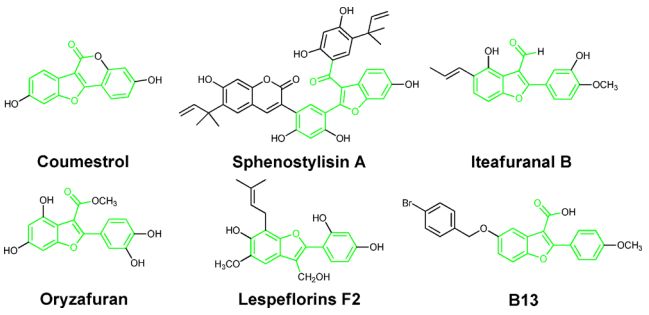


Figure 1. Bioactive compounds containing the 3-carbonyl-derived 2-arylbenzofuran scaffold.

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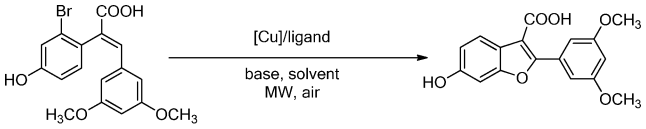
heteroatom (C−N, C−O, C−S, C−P, C−Br, C−F, etc.) and carbon−carbon (C−C) bonds.[18] Our group has also recently disclosed a Cu-catalyzed decarboxylation of (*E*)-2,3-diphenylacrylic acids, leading to the facile formation of a wide range of natural stilbenes and derivatives.[19] As part of our ongoing efforts for the development of new protocols in stilbenoid synthesis and biomass conversion,[20] we herein report a practical method for the assembly of 2-arylbenzofuran-3-carboxylic acids (**2**) from (*E*)-2-(2-bromophenyl)-3-arylacrylic acids (**1**) and its application to the total synthesis of the natural product moracin M.

RESULTS AND DISCUSSION

Optimization of Reaction Conditions. At the outset, (*E*)-2-(2-bromo-4-hydroxyphenyl)-3-(3,5-dimethoxyphenyl)acrylic acid (**1aa**) was selected as a model substrate to screen the optimal reaction conditions (Table 1). To our delight, the corresponding product **2aa** was obtained in 38% yield when the reaction was performed in the presence of catalyst $CuSO_4$ (20 mol %), ligand glycine (20 mol %), and base NaOH (10 equiv) in H_2O at reflux for 1 h under aerobic and microwave conditions (Table 1, entry 1). The structure of **2aa** was confirmed by ^1H NMR spectra, in which the signal of the vinylic proton disappeared, while both the carboxylic and phenolic active hydrogen still existed. HRMS (ESI-TOF) spectra of **2aa** also confirmed the correctness of the molecular formula $C_{17}H_{14}O_6$ (*m*/*z* 337.0678 $[M + Na]^+$, calcd for $C_{17}H_{14}NaO_6$: 337.0683).

Table 1. Optimization of Reaction Conditions[a]



1aa **2aa**

entry	catalyst	ligand	base	solvent	yield[b]
1	$CuSO_4$	glycine	NaOH	H_2O	38
2	CuO	glycine	NaOH	H_2O	54
3	CuI	glycine	NaOH	H_2O	22
4	$Cu(OH)_2$	glycine	NaOH	H_2O	55
5	$Cu_2(OH)_2CO_3$	glycine	NaOH	H_2O	68
6	$Cu(OAc)_2$	glycine	NaOH	H_2O	70
7	$Cu(OAc)_2$	-	NaOH	H_2O	trace
8	$Cu(OAc)_2$	DMAP	NaOH	H_2O	62
9	$Cu(OAc)_2$	TMEDA	NaOH	H_2O	53
10	$Cu(OAc)_2$	oxine	NaOH	H_2O	42
11	$Cu(OAc)_2$	1,10-phen	NaOH	H_2O	73
12	$Cu(OAc)_2$	1,10-phen	Cs_2CO_3	H_2O	46
13	$Cu(OAc)_2$	1,10-phen	K_3PO_4	H_2O	44
14	$Cu(OAc)_2$	1,10-phen	KOH	H_2O	77
15	$Cu(OAc)_2$	1,10-phen	KOH	DMSO	80
16	$Cu(OAc)_2$	1,10-phen	KOH	DMF	78
17	$Cu(OAc)_2$	1,10-phen	KOH	PEG-400	82
18	$Cu(OAc)_2$	1,10-phen	KOH	DMSO−H_2O (1:1)	90
19	$Cu(OAc)_2$	1,10-phen	KOH	DMSO−H_2O (1:1)	88[c]
20	$Cu(OAc)_2$	1,10-phen	KOH	DMSO−H_2O (1:1)	60[d]
21	$Cu(OAc)_2$	1,10-phen	KOH	DMSO−H_2O (1:1)	76[e]
22	$Cu(OAc)_2$	1,10-phen	KOH	DMSO−H_2O (1:1)	trace[f]
23	$Cu(OAc)_2$	1,10-phen	KOH	DMSO−H_2O (1:1)	65[g]

[a]Reaction conditions: **1aa** (1.0 mmol), Cu salt (0.2 mmol, 20 mol %), ligand (0.2 mmol, 20 mol %), base (10.0 mmol), and solvent (5 mL) in an open flask, at 110 °C for 1 h under air and microwave irradiation. [b]Isolated yield. [c]50 mol % Cu salt. [d]10 mol % Cu salt. [e]Reaction performed at 100 °C. [f]Under N_2 atmosphere. [g]6.0 equiv of KOH was used.

To obtain a more satisfactory result, different copper catalysts, ligands, bases, and solvents were used to optimize the reaction conditions (Table 1). Investigation of various copper catalysts showed that $Cu(OAc)_2$ (20 mol %) gave the best result, while other copper species such as CuO, CuI, $CuSO_4$, $Cu(OH)_2$, and $Cu_2(OH)_2CO_3$ were found to be inferior in this reaction (Table 1, entries 1−6). Moreover, a control experiment showed that only a trace amount of **2aa** could be detected (monitored by TLC) in the absence of glycine (Table 1, entry 7), indicating that the addition of a ligand is indispensable in this reaction. Subsequently, various other ligands such as DMAP, TMEDA, 1,10-phen (1,10-phenanthroline), and oxine were screened, among which 1,10-phen proved to be the most optimal (Table 1, entries 6−11). Investigation of bases (NaOH, KOH, Cs_2CO_3, and K_3PO_4) showed that KOH was most effective, while others were found to be less favorable (Table 1, entries 11−14). Solvent screening showed that reactions performed in H_2O, DMF and DMSO slightly increased the product yields (Table 1, entries 14−16). Changing the solvent to the versatile and eco-friendly PEG-400 gave rise to a better yield (82%, Table 1, entry 17). We were pleased to find that an excellent yield (90%) of **2aa** could be obtained when DMSO−H_2O (1/1, v/v) was used as the solvent (Table 1, entry 18). Further inspection of the reaction conditions revealed that there was no significant improvement in the yield when the catalyst loading increased to 50 mol % (Table 1, entry 19), whereas reducing the amount of $Cu(OAc)_2$ to 10 mol % decreased the yield to 60% (entry 20). In addition, experiment showed that when the temperature dropped from 110 to 100 °C, a lower yield was obtained, with the detection (monitored by TLC) of an appreciable amount of unreacted substrate **1aa** (Table 1, entry 21). It is worth noting that carrying out the reaction under nitrogen atmosphere dramatically decreased the yield of **2aa**, suggesting that molecular oxygen might play an important role in this transformation (Table 1, entry 22). Results showed that the yield of **2aa** decreased to 65% when reducing the amount of KOH to 6.0 equiv (Table 1, entry 23). Therefore, the optimal reaction conditions for the synthesis of 2-arylbenzofuran-3-carboxylic acids are established as $Cu(OAc)_2$ (20 mol %), 1,10-phen (20 mol %), and KOH (10.0 equiv) in DMSO−H_2O (1:1) at 110 °C under air and microwave irradiation.

Scope and Generality of the Substrates. To test the scope and generality of the reaction conditions, a variety of substituted (*E*)-2-(2-bromophenyl)-3-phenylacrylic acids (**1**) were prepared and subjected to our optimized conditions (Table 2). It is worth mentioning that the substrates **1** were readily obtained in high yields via Perkin condensation between commercially available *o*-bromophenylacetic acids and benzaldehydes (Scheme 1). Consistent with our previous studies,[20h] compounds **1** which possessed an *E*-configuration (but had a *cis*-phenyl relationship) were obtained as the major products through Perkin condensation.

As we expected, these (*E*)-2-(2-bromophenyl)-3-phenylacrylic acids (**1**) bearing various substituents were successfully

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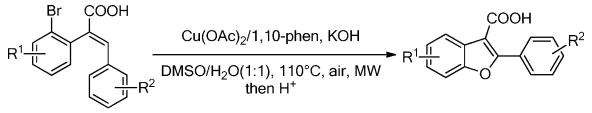
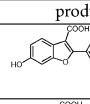
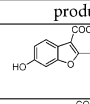
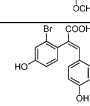
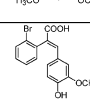
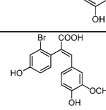
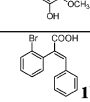
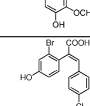
Table 2. Scope of the Copper-Catalyzed 2-Arylbenzofuran-3-carboxylic Acids[a]



1 2

entry	substrate	product	yield(%)[b]	entry	substrate	product	yield(%)[b]
1	 1aa	 2aa	90	16	 1ap	 2ap	ND[c]
2	 1ab	 2ab	88	17	 1aq	 2aq	80
3	 1ac	 2ac	85	18	 1ar	 2ar	75
4	 1ad	 2ad	84	19	 1as	 2as	67
5	 1ae	 2ae	83	20	 1at	 2at	64
6	 1af	 2af	76	21	 1ba	 2ba	70
7	 1ag	 2ag	98	22	 1bb	 2bb	79
8	 1ah	 2ah	95	23	 1bc	 2bc	72
9	 1ai	 2ai	87	24	 1bd	 2bd	84
10	 1aj	 2aj	88	25	 1be	2be	74
11	1ak	2ak	78	26	1bf	2bf	81
12	1al	2al	46	27	1bg	2bg	83
13	1am	2am	42	28	1ca	2ca	66
14	1an	2an	45	29	1cb	2cb	64
15	1ao	2ao	ND[c]	30	1cc	2cc	68

[a]Reaction conditions: **1** (1.0 mmol), $Cu(OAc)_2$ (0.2 mmol, 20 mol %), 1,10-phen (0.2 mmol, 20 mol %), KOH (10.0 mmol), and DMSO−H_2O (1:1) (5 mL), under air in an open flask, at 110 °C for 1 h under microwave irradiation. [b]Isolated yield. [c]ND, no desired product.

Scheme 1. Preparation of (*E*)-2-(2-Bromophenyl)-3-phenylacrylic Acids (1)

1

transformed into the desired 2-arylbenzofuran-3-carboxylic acids (**2**) in moderate to excellent yields under our typical conditions (Table 2). Unlike previously reported methods,[14a,c] we have found that substrates containing a hydroxyl group were compatible with these conditions and afforded higher yields compared to those with a methoxyl or ethoxyl group (Table 2, entries 1, 8 vs 21, 27). Moreover, substrate bearing two hydroxyl groups gave higher yield than substrate with only one hydroxyl group. For example, the tandem reaction of (*E*)-2-(2-bromo-4-hydroxyphenyl)-3-(4-hydroxy-3,5-dimethoxyphenyl)-

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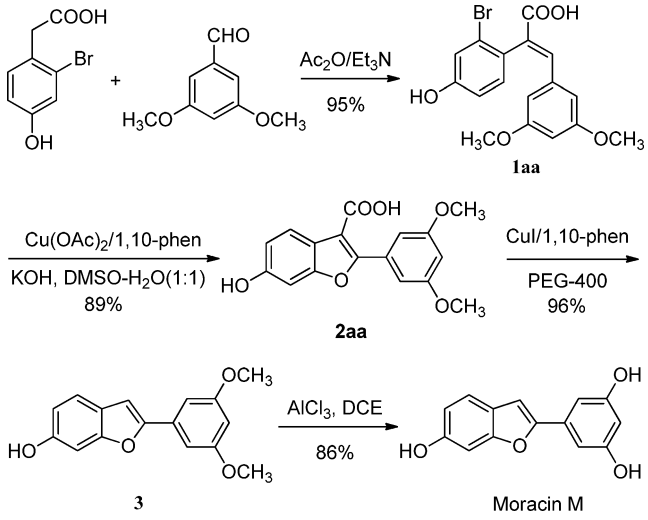
acrylic acid (**1ac**) with $Cu(OAc)_2$, 1,10-phen, and KOH in DMSO−H_2O (1:1) provided the corresponding product **2ac** in 85% isolated yield (Table 2, entry 3), whereas a lower yield (74%) of product **2be** was obtained when (*E*)-2-(2-bromophenyl)-3-(4-hydroxy-3,5-dimethoxyphenyl)acrylic acid (**1be**) was used as the reactant (Table 2, entry 25). Similarly and remarkably, substrate **1ag** which also contained two hydroxyl groups gave 6-hydroxy-2-(4-hydroxyphenyl)-benzofuran-3-carboxylic acid (**2ag**) quantitatively under typical conditions, which might be at least due in part to the unexceptionable solubility in aqueous DMSO (Table 2, entry 7). In addition, the reactivity of **1ah** having an ethoxyl group was higher than **1ae** bearing a methoxyl group (Table 2, compare entry 5 with 8). This correlation was also reinforced by substrates **1bb** and **1bg** (Table 2, entries 22 and 27). It could be concluded from the above results that the ethoxyl group was advantageous over the methoxyl group to give the corresponding products in this consecutive process. Halogen-substituted reactants were also subjected to our optimal reaction conditions and were smoothly transformed into the desired 2-arylbenzofuran-3-carboxylic acids (Table 2, entries 9−11). Results showed that the chlorine-substituted compound afforded a comparable yield (87%) in comparison with fluoro-substituted ones (88%) (Table 2, entries 9 and 10). On the other hand, (*E*)-2-(2-bromo-4-hydroxyphenyl)-3-(2,4-dichlorophenyl)acrylic acid (**1ak**) which contained two chlorine atoms gave rise to 2-(2,4-dichlorophenyl)-6-hydroxybenzofuran-3-carboxylic acid (**2ak**) in a satisfactory yield (78%, Table 2, entry 11). To our delight, substrates bearing electron-withdrawing substituents such as CF_3, CN, and COOH were also compatible with this methodology, giving the desired products (**2al**−**2an**) in moderate yields (46%, 42%, and 45%, respectively, entries 12−14). However, substrate **1ao** which contained a nitro group failed to give the corresponding product **2ao** under typical reaction conditions (Table 2, entry 15). It is notable that substrates containing a heterocyclic aromatic moiety such as furan (**1aq**) and thiophene (**1ar**) were found to be smoothly transformed into the corresponding products in moderate to good yields (80% and 75%, respectively), whereas no desired product was detected when substrate with a pyridine ring (**1ap**) was used (Table 2, entries 16−18). Interestingly, substrate bearing a naphthalene ring (**1as**) could also afford 2-arylbenzofuran-3-carboxylic acid (**2as**) in 67% yield (Table 2, entry 19). We were pleased to find that substrate (2*E*,4*E*)-2-(2-bromo-4-hydroxyphenyl)-5-phenylpenta-2,4-dienoic acid (**1at**) was also amenable to this transformation, generating the corresponding (*E*)-6-hydroxy-2-styrylbenzofuran-3-carboxylic acid (**2at**) in moderate yield (64%, Table 2, entry 20). Moreover, (*E*)-2-(2-bromophenyl)-3-phenylacrylic acid (**1bc**) which contained neither electron-donating nor electron-withdrawing group also gave rise to the corresponding product **2bc** in moderate yield (72%, Table 2, entry 23). It is worth noting that substrates having a methoxyl group adjacent to a bromine such as **1ca**−**1cc** afforded the desired products **2ca**−**2cc** in slightly lower yields (66%, 64%, and 68%, respectively), which might be due to the steric hindrance of the *o*-methoxyl group (Table 2, entries 28−30).

Total Synthesis of Natural Product Moracin M. Next, we applied this protocol to the total synthesis of the natural product moracin M, which was isolated from the stem bark of *Milicia excelsa* and was reported to have antimicrobial and anti-inflammatory activity (Scheme 2).[21] To our delight, the desired reactions were successfully carried out in gram scale. The

Scheme 2. Total Synthesis of the Natural Product Moracin M



Perkin condensation of 2-bromo-4-hydroxyphenylacetic acid and 3,5-dimethoxybenzaldehyde provided (*E*)-2-(2-bromo-4-hydroxyphenyl)-3-(3,5-dimethoxyphenyl)acrylic acid (**1aa**). Subsequently, a consecutive hydroxylation and oxidative C−O coupling of **1aa** (1.89 g, 5 mmol) catalyzed by $Cu(OAc)_2$, 1,10-phen, and KOH in DMSO−H_2O (1:1) gave **2aa** (1.40 g) in 89% yield. Then decarboxylation of **2aa** promoted by CuI/1,10-phen/PEG-400[19] afforded 6-hydroxy-2-(3,5-dimethoxyphenyl)benzofuran (**3**). Finally, demethylation of **3** using $AlCl_3$/DCE afforded moracin M in 69% overall yield, whose spectral data were in good agreement with those reported in the literature.[21b]

Mechanism Investigations. To shed light on the possible mechanism of the cyclization reaction, control experiments were carried out (Scheme 3). It was observed that no desired product 2-phenylbenzofuran-3-carboxylic acid (**2bc**) was obtained in the absence of KOH, revealing the necessity for base in this transformation (Scheme 3, eq 1). However, intermediate (*E*)-2-(2-hydroxyphenyl)-3-phenylacrylic acid (**4bc**) was isolated in 75% yield, and only a trace amount of desired product **2bc** was detected (monitored by TLC) when this reaction was performed under N_2 atmosphere (Scheme 3, eq 2). When 2.0 equiv of TBHP was added into the reaction system under N_2 atmosphere, the acid **2bc** was achieved in 56% yield (Scheme 3, eq 3), indicating that an oxidative process might exist in this protocol. Moreover, the desired product **2bc** was obtained in 48% yield in the presence of 3.0 equiv of $Cu(OAc)_2$ under N_2 atmosphere (Scheme 3, eq 4). We reasoned that the excess amount of $Cu(OAc)_2$ might act as the oxidant in place of air or TBHP and take part in the oxidative C−O coupling process. Further investigation showed that the isolated intermediate **4bc** could be efficiently transformed into **2bc** in 95% yield under $Cu(OAc)_2$/1,10-phen/air without the use of KOH (Scheme 3, eq 5).

Based on the above-mentioned control experiments and the relevant literatures,[17e,18a,d] two plausible pathways for this consecutive process were proposed (Scheme 4). In path A, the hydroxylated intermediate **A** was initially formed in the presence of Cu(II) salt and KOH. The coordination of Cu(II) catalyst with **A** formed complex **B**, which is nonplanar between the phenyl rings.[22] Complex **B** would then undergo a ligand-assisted concerted metalation−deprotonation (CMD)[23] to give

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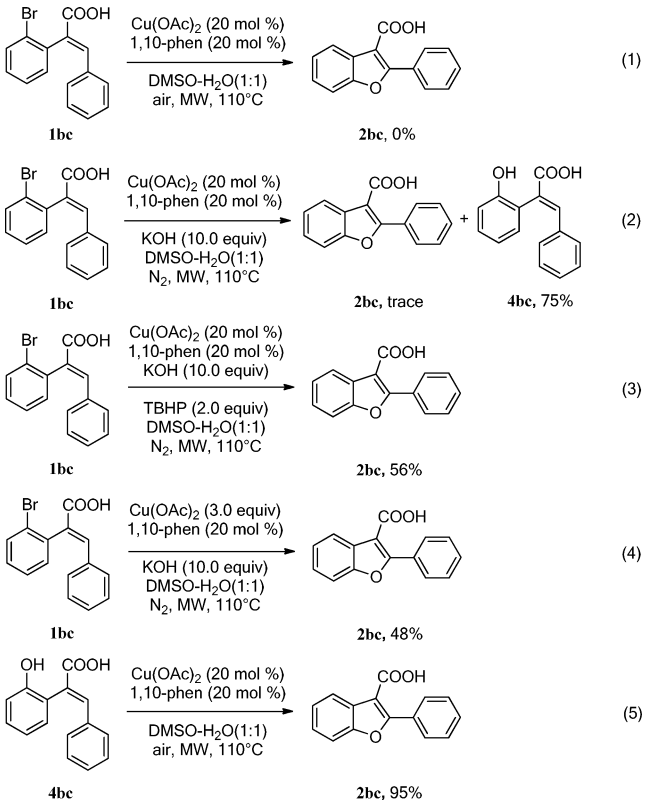
Scheme 3. Control Experiments



the complex **C** in reversed configuration. The decomplexation of complex **C** produced complex **D**, followed by reductive elimination to afford the desired product **2** with concomitant formation of Cu(0). The Cu(0) could then be regenerated to give Cu(II) species under air. Alternatively, coordination of Cu(II) species with **A** could give the η^2 π complex **E**,[24] thus activating the C=C bond and resulting in the nucleophilic attack by the adjacent phenolic group to afford the complex **F** in reversed configuration. Subsequent β-hydride elimination accompanied by reductive elimination would give **2** and Cu(0), which can be reoxidized by air to complete the catalytic circle (path B).

CONCLUSIONS

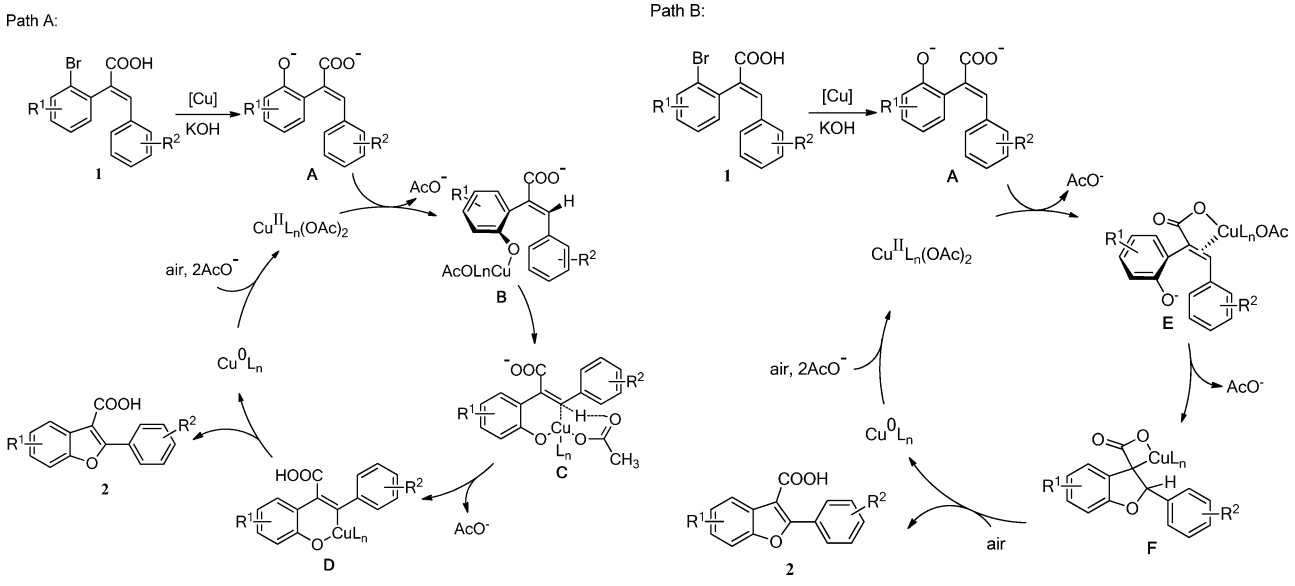
In summary, we have developed a practical and efficient method for the synthesis of 2-arylbenzofuran-3-carboxylic acids from readily available (*E*)-2-(2-bromophenyl)-3-arylacrylic acids. This tandem approach involved the copper-catalyzed hydroxylation and aerobic oxidative cycloetherification process under microwave irradiation. The consecutive C−Br bond cleavage, C−H functionalization, and C−O bond formation were characteristics of this process. The thus obtained 2-arylbenzofuran-3-carboxylic acids can serve as versatile building blocks for further synthesis of various heterocyclic molecules. Moreover, the total synthesis of the natural product moracin M has also been achieved efficiently under this strategy.

EXPERIMENTAL SECTION

General Information. All of the reactions were generally run under air conditions. Unless otherwise noted, materials were obtained commercially and used without further purification. Reactions were monitored by TLC and column chromatography was performed on silica gel (300−400 mesh) using ethyl acetate/petroleum ether (60−90 °C) as the eluent. Microwave reactions were carried out with a scientific WBFY microwave reactor in a flask connected with a condenser. The reaction temperatures were detected in real time using an infrared thermometer, and the ramp time (approximate 0.5 min) is included as part of the reaction time. All melting points were determined on a Thiele apparatus without correction. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) at 295 K using DMSO-d_6 as the solvent. Chemical shift values (δ) were given in parts per million (ppm) using tetramethylsilane (TMS) as the internal standard. HRMS spectra analyses were performed on a LC-Q-TOF (ESI) apparatus.

Typical Procedure for the Synthesis of (*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(3,5-dimethoxyphenyl)acrylic Acid (1aa). 2-Bromo-4-hydroxyphenylacetic acid (2.31 g, 10 mmol), 3,5-dimethoxylbenzaldehyde (1.66 g, 10 mmol), triethylamine (4.16 mL, 30 mmol), and acetic anhydride (2.84 mL, 30 mmol) were added to a 25 mL round-bottom flask. The flask was then placed into an oil bath, and the temperature was raised to 110 °C with stirring for 6 h. After completion of the reaction (monitored by TLC), the mixture was

Scheme 4. Plausible Mechanism



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poured into ice-cold water and acidified with concentrated hydrochloric acid with stirring. A white solid was obtained and collected by filtration. It was dissolved in 10% aq NaOH, and the aqueous solution was decolored by extracting with EtOAc. The organic layers were separated, and the aqueous layer was acidified with concd HCl to pH 3−4. The precipitated crude product was collected by filtration and recrystallized from EtOH to afford **1aa** as a white solid. Yield: 3.60 g (95%); mp 188−190 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.64 (s, 1H), 9.99 (s, 1H), 7.69 (s, 1H), 7.11 (d, J = 2.0 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H), 6.80 (dd, J = 8.4, 2.4 Hz, 1H), 6.42 (s, 1H), 6.27 (d, J = 2.0 Hz, 2H), 3.56 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.7, 160.1, 157.9, 139.8, 136.1, 132.9, 131.8, 127.9, 123.7, 119.0, 115.4, 108.0, 101.6, 55.0; IR (KBr, cm^{-1}): 3625, 3476, 1692, 1660, 1592, 1500, 1464, 1285, 1157, 829, 681; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{17}H_{15}{}^{79}BrNaO_5$: 400.9995; found: 400.9999.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(3-hydroxy-4-methoxyphenyl)acrylic Acid (1ab). White solid; yield: 3.50 g (96%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.39 (s, 1H), 9.95 (s, 1H), 8.98 (s, 1H), 7.60 (s, 1H), 7.09 (d, J = 2.4 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 6.78−6.82 (m, 2H), 6.56 (dd, J = 8.8, 1.6 Hz, 1H), 6.47 (d, J = 1.6 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.0, 157.7, 149.0, 146.0, 140.0, 131.7, 129.5, 128.1, 127.1, 123.8, 122.7, 119.1, 117.0, 115.5, 111.6, 55.5; IR (KBr, cm^{-1}): 3596, 3502, 1673, 1605, 1526, 1494, 1438, 1267, 1133, 880, 763; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{16}H_{13}{}^{79}BrNaO_5$: 386.9839; found: 386.9845.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(4-hydroxy-3,5-dimethoxyphenyl)acrylic Acid (1ac). White solid; yield: 3.79 g (96%); mp 146−148 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.40 (s, 1H), 9.96 (s, 1H), 8.93 (s, 1H), 7.68 (s, 1H), 7.12 (d, J = 2.4 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.85 (dd, J = 8.4, 2.4 Hz, 1H), 6.39 (s, 2H), 3.50 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.0, 157.9, 147.5, 140.6, 137.4, 132.1, 129.1, 128.4, 124.4, 124.1, 119.0, 115.5, 108.1, 55.5; IR (KBr, cm^{-1}):3619, 3501,1690, 1655, 1615, 1513, 1453, 1268, 1115, 878, 837; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{17}H_{15}{}^{79}BrNaO_6$: 416.9944; found: 416.9952.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-phenylacrylic Acid (1ad). White solid; yield: 2.99 g (94%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.62 (s, 1H), 9.99 (s, 1H), 7.76 (s, 1H), 7.22−7.27 (m, 3H), 7.07−7.11 (m, 3H), 6.95 (d, J = 8.4 Hz, 1H), 6.79 (dd, J = 8.4, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.7, 157.8, 139.7, 134.3, 132.5, 131.7, 129.9, 129.3, 128.5, 127.8, 123.7, 119.0, 115.4; IR (KBr, cm^{-1}): 3304, 3073, 1681, 1600, 1576, 1493, 1447, 1178, 1041, 877, 783; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{15}H_{11}{}^{79}BrNaO_3$: 340.9784; found: 340.9786.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(4-hydroxy-3-methoxyphenyl)acrylic Acid (1ae). White solid; yield: 3.58 g (98%); mp 186−188 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.36 (s, 1H), 10.29 (s, 1H), 9.56 (s, 1H), 7.66 (s, 1H), 7.12 (d, J = 2.4 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 6.83 (dd, J = 8.4, 2.4 Hz, 1H), 6.65−6.69 (m, 2H), 6.50 (s, 1H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.1, 157.8, 148.4, 147.1, 140.3, 132.1, 128.8, 128.4, 125.7, 125.1, 124.1, 119.1, 115.5, 115.4, 112.9, 54.9; IR (KBr, cm^{-1}): 3383, 3329, 1640, 1597, 1492, 1455, 1261, 1119, 857, 772; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{16}H_{13}{}^{79}BrNaO_5$: 386.9839; found: 386.9846.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(4-methoxyphenyl)-acrylic Acid (1af). White solid; yield: 3.35 g (96%); mp 170−172 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.45 (s, 1H), 9.98 (s, 1H), 7.71 (s, 1H), 7.11 (d, J = 2.4 Hz, 1H), 7.02 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.4 Hz, 1H), 6.79−6.83 (m, 3H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.0, 160.2, 157.8, 139.6, 131.8, 131.8, 129.7, 128.1, 126.8, 123.8, 119.1, 115.5, 114.1, 55.2; IR (KBr, cm^{-1}): 3624, 3351, 1651, 1601, 1572, 1510, 1460, 1255, 1173, 882, 830; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{16}H_{13}{}^{79}BrNaO_4$: 370.9889; found: 370.9892.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(4-hydroxyphenyl)-acrylic Acid (1ag). White solid; yield: 3.18 g (95%); mp 126−128 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.36 (s, 1H), 9.96 (s, 1H), 9.92 (s, 1H), 7.66 (s, 1H), 7.10 (s, 1H), 6.89−6.97 (m, 3H), 6.80 (d, J = 8.0 Hz, 1H), 6.61 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.1, 158.8, 157.7, 140.0, 132.0, 131.8, 128.6, 128.3, 125.3, 123.9, 119.1, 115.5, 115.4; IR (KBr, cm^{-1}): 3586, 3437, 1668, 1604, 1495, 1415, 1254, 1174, 879, 742; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{15}H_{11}{}^{79}BrNaO_4$: 356.9733; found: 356.9738.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(3-ethoxy-4-hydroxyphenyl)acrylic Acid (1ah). White solid; yield: 3.71 g (98%); mp 180−181 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.36 (s, 1H), 9.96 (s, 1H), 9.47 (s, 1H), 7.64 (s, 1H), 7.11 (d, J = 2.0 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 6.82 (dd, J = 8.4, 2.4 Hz, 1H), 6.66−6.71 (m, 2H), 6.43 (s, 1H), 3.63 (q, J = 8.0 Hz, 2H), 1.15 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.0, 157.8, 148.6, 146.1, 140.3, 131.9, 128.5, 128.4, 125.6, 125.3, 124.0, 119.0, 115.5, 115.4, 113.7, 63.1, 14.5; IR (KBr, cm^{-1}): 3634, 3444, 1653, 1596, 1494, 1434, 1284, 1122, 880, 821; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{17}H_{15}{}^{79}BrNaO_5$: 400.9995; found: 401.0002.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(4-chlorophenyl)acrylic Acid (1ai). White solid; yield: 3.42 g (97%); mp 174−176 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.74 (s, 1H), 10.03 (s, 1H), 7.76 (s, 1H), 7.34 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 8.8 Hz, 3H), 6.95 (d, J = 8.4 Hz, 1H), 6.79 (dd, J = 8.4, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.6, 158.0, 138.4, 133.9, 133.3, 133.2, 131.7, 131.5, 128.6, 127.4, 123.5, 119.1, 115.5; IR (KBr, cm^{-1}): 3626, 3492, 1683, 1600, 1491, 1433, 1409, 1212, 877, 731; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{15}H_{10}{}^{79}Br^{35}ClNaO_3$: 374.9394; found: 374.9399.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(4-fluorophenyl)acrylic Acid (1aj). White solid; yield: 3.23 g (96%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.65 (s, 1H), 10.02 (s, 1H), 7.77 (s, 1H), 7.10−7.14 (m, 5H), 6.96 (d, J = 8.4 Hz, 1H), 6.80 (dd, J = 8.4, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.8, 162.4 (d, $^1J_{F-C}$ = 247.2 Hz), 158.0, 138.6, 132.2, 132.1 (d, $^3J_{F-C}$ = 8.7 Hz), 131.7, 131.0 (d, $^4J_{F-C}$ = 2.3 Hz), 127.6, 123.7, 119.2, 115.6, 115.6 (d, $^2J_{F-C}$ = 21.4 Hz); IR (KBr, cm^{-1}): 3635, 3302, 1691, 1597, 1511, 1425, 1322, 1157, 880, 798; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{15}H_{10}{}^{79}BrFNaO_3$: 358.9690; found: 358.9692.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(2,4-dichlorophenyl)-acrylic Acid (1ak). White solid; yield: 3.72 g (96%); mp 180−182 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.96 (s, 1H), 10.04 (s, 1H), 7.86 (s, 1H), 7.68 (d, J = 2.0 Hz, 1H), 7.25 (dd, J = 8.4, 1.6 Hz, 1H), 7.05 (d, J = 2.0 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.71−6.77 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.1, 158.0, 135.9, 134.7, 134.7, 134.1, 132.0, 131.9, 130.9, 129.1, 127.2, 126.4, 123.6, 119.0, 115.2; IR (KBr, cm^{-1}): 3651, 3420, 1666, 1604, 1497, 1463, 1423, 1281, 1104, 861, 777; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{15}H_9{}^{79}Br^{35}Cl_2NaO_3$: 408.9004; found: 408.9007.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(4-(trifluoromethyl)-phenyl)acrylic Acid (1al). White solid; yield: 3.40 g (88%); mp 86−88 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.88 (s, 1H), 10.06 (s, 1H), 7.84 (s, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 7.6 Hz, 2H), 7.11 (s, 1H), 6.96 (d, J = 8.0 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.5, 158.1, 138.6, 138.1, 135.2, 131.7, 130.3, 129.0 ($^2J_{F-C}$ = 31.5 Hz), 127.2, 125.3 ($^3J_{F-C}$ = 2.3 Hz), 124.0 ($^1J_{F-C}$ = 270 Hz), 123.5, 119.2, 115.5; IR (KBr, cm^{-1}): 3629, 3378, 1687, 1610, 1494, 1421, 1278, 1170, 927, 873; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{16}H_{10}{}^{79}BrF_3NaO_3$: 408.9663; found: 408.9665.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(4-cyanophenyl)acrylic Acid (1am). Yellow solid; yield: 2.89 g (84%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ =12.56 (s, 1H), 9.49 (s, 1H), 7.81 (s, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 2.0 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.79 (dd, J = 8.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.4, 158.1, 139.3, 137.6, 136.0, 132.3, 131.7, 130.3, 127.1, 123.4, 119.2, 118.5, 115.5, 111.2; IR (KBr, cm^{-1}): 3534, 3448, 1679, 1600, 1492, 1421, 1265, 1037, 831, 761; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{16}H_{10}{}^{79}BrNaNO_3$: 365.9742; found: 365.9742.

(*E*)-4-(2-(2-Bromo-4-hydroxyphenyl)-2-carboxyvinyl)benzoic Acid (1an). White solid; yield: 2.72 g (75%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.91 (s, 2H), 10.03 (s, 1H), 7.81 (s, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 2.4 Hz,

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1H), 6.94 (d, J = 8.4 Hz, 1H), 6.77 (dd, J = 8.4, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.6, 166.8, 158.1, 138.8, 138.7, 134.7, 131.8, 131.0, 129.9, 129.3, 127.4, 123.6, 119.2, 115.5; IR (KBr, cm^{-1}): 3478, 3074, 1689, 1608, 1492, 1415, 1270, 1120, 865, 783; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{16}H_{11}{}^{79}BrNaO_5$: 384.9688; found: 384.9685.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(4-nitrophenyl)acrylic Acid (1ao). Gray solid; yield: 2.62 g (72%); mp 114−116 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.34 (s, 1H), 10.08 (s, 1H), 8.10 (d, J = 8.8 Hz, 2H), 7.85 (s, 1H), 7.33 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 2.4 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.78 (dd, J = 8.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.5, 158.3, 146.9, 141.4, 137.1, 136.8, 131.7, 130.6, 130.5, 127.1, 123.5, 123.3, 119.2, 115.5; IR (KBr, cm^{-1}): 3648, 3187, 1687, 1625, 1594, 1490, 1419, 1272, 1039, 860, 734; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{15}H_{10}{}^{79}BrNaNO_5$: 385.9640; found: 385.9641.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(pyridin-4-yl)acrylic Acid (1ap). Yellow solid; yield: 2.62 g (82%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.95 (s, 1H), 10.11 (s, 1H), 8.45 (d, J = 6.4 Hz, 2H), 7.73 (s, 1H), 7.11 (d, J = 2.0 Hz, 1H), 6.95−7.00 (m, 3H), 6.79 (dd, J = 8.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.2, 158.2, 149.9, 141.8, 137.1, 137.0, 131.6, 126.9, 123.6, 123.3, 119.2, 115.5; IR (KBr, cm^{-1}): 3237, 3091, 1668, 1604, 1492, 1421, 1278, 1049, 879, 819; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{14}H_{10}{}^{79}BrNaNO_3$: 341.9742; found: 341.9742.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(furan-2-yl)acrylic Acid (1aq). White solid; yield: 2.41 g (78%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.73 (s, 1H), 10.02 (s, 1H), 7.72 (s, 1H), 7.57 (s, 1H), 7.10 (d, J = 2.0 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.84 (dd, J = 8.4, 2.0 Hz, 1H), 6.48 (s, 1H), 5.91 (d, J = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.4, 157.9, 150.4, 145.3, 131.5, 129.6, 127.7, 127.3, 123.1, 119.0, 115.3, 114.5, 112.6; IR (KBr, cm^{-1}): 3270, 3077, 1677, 1612, 1484, 1467, 1421, 1251, 1193, 871, 750; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{13}H_9{}^{79}BrNaO_4$: 330.9582; found: 330.9583.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(thiophen-2-yl)acrylic Acid (1ar). Yellow solid; yield: 2.43 g (75%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.53 (s, 1H), 10.06 (s, 1H), 8.03 (s, 1H), 7.58 (d, J = 5.2 Hz, 1H), 7.45 (d, J = 2.8 Hz, 1H), 7.12 (d, J = 2.4 Hz, 1H), 7.03−7.06 (m, 2H), 6.86 (dd, J = 8.4, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.5, 158.6, 138.1, 134.2, 133.9, 132.4, 132.0, 128.9, 126.9, 126.7, 124.3, 119.4, 115.8; IR (KBr, cm^{-1}): 3598, 3380, 1662, 1606, 1492, 1419, 1276, 1214, 867, 711; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{13}H_9{}^{79}BrNaO_3S$: 346.9353; found: 346.9353.

(*E*)-2-(2-Bromo-4-hydroxyphenyl)-3-(naphthalen-1-yl)acrylic Acid (1as). White solid; yield: 3.06 g (83%); mp 197−199 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.82 (s, 1H), 9.90 (s, 1H), 8.38 (s, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.55−7.63 (m, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.01−7.03 (m, 2H), 6.80 (d, J = 8.4 Hz, 1H), 6.58 (dd, J = 8.0, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.6, 157.6, 137.8, 135.6, 133.0, 132.2, 131.9, 131.3, 128.9, 128.6, 127.7, 126.8, 126.7, 126.3, 125.2, 124.3, 123.9, 118.8, 114.9; IR (KBr, cm^{-1}): 3655, 3423, 1666, 1604, 1490, 1415, 1268, 1187, 879, 771; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{19}H_{13}{}^{79}BrNaO_3$: 390.9946; found: 390.9947.

(2*E*,4*E*)-2-(2-Bromo-4-hydroxyphenyl)-5-phenylpenta-2,4-dienoic Acid (1at). Yellow solid; yield: 2.93 g (85%); mp 134−136 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.50 (s, 1H), 10.00 (s, 1H), 7.53 (d, J = 11.2 Hz, 1H), 7.28−7.41 (m, 5H), 7.17 (d, J = 15.2 Hz, 1H), 7.09 (d, J = 2.4 Hz, 1H), 7.06 (d, J = 8.4 Hz, 1H), 6.84 (dd, J = 8.4, 2.4 Hz, 1H), 6.48 (dd, J = 15.6, 11.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.4, 157.8, 140.2, 136.0, 133.0, 132.7, 129.1, 129.0, 129.0, 127.1, 126.9, 124.2, 123.9, 118.9, 114.8; IR (KBr, cm^{-1}): 3620, 3489, 1655, 1608, 1500, 1425, 1278, 1160, 883, 750; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{17}H_{13}{}^{79}BrNaO_3$: 366.9940; found: 366.9940.

(*E*)-2-(2-Bromophenyl)-3-(3,5-dimethoxyphenyl)acrylic Acid (1ba). White solid; yield: 3.52 g (97%); mp 148−150 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.78 (s, 1H), 7.73−7.75 (m, 2H), 7.42 (td, J = 7.6, 0.8 Hz, 1H), 7.33 (td, J = 7.6, 1.6 Hz, 1H), 7.21 (dd, J = 7.6, 1.6 Hz, 1H), 6.41 (t, J = 2.0 Hz, 1H), 6.23 (d, J = 2.4 Hz, 2H), 3.52 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.3, 160.2, 139.9, 137.9, 135.8, 132.9, 132.5, 131.3, 129.8, 128.2, 123.7, 108.0, 101.8, 55.0; IR (KBr, cm^{-1}): 3470, 3068, 1667, 1596, 1460, 1428, 1281, 1161, 841, 740; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{17}H_{15}{}^{79}BrNaO_4$: 385.0046; found: 385.0048.

(*E*)-2-(2-Bromophenyl)-3-(4-hydroxy-3-methoxyphenyl)-acrylic Acid (1bb). White solid; yield: 3.42 g (98%); mp 74−76 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.53 (s, 1H), 9.61 (s, 1H), 7.75 (dd, J = 8.0, 0.8 Hz, 1H), 7.71 (s, 1H), 7.44 (td, J = 7.6, 1.2 Hz, 1H), 7.33 (td, J = 7.6, 1.6 Hz, 1H), 7.23 (dd, J = 7.6, 1.6 Hz, 1H), 6.64−6.69 (m, 2H), 6.41 (s, 1H), 3.33(s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.6, 148.5, 147.2, 140.1, 138.4, 132.6, 131.6, 129.6, 128.9, 128.3, 125.4, 125.3, 124.1, 115.4, 112.7, 54.8; IR (KBr, cm^{-1}): 3565, 3470, 1681, 1594, 1526, 1423, 1249, 1129, 815, 732; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{16}H_{13}{}^{79}BrNaO_4$: 370.9889; found: 370.9887.

(*E*)-2-(2-Bromophenyl)-3-phenylacrylic Acid (1bc). White solid; yield: 2.91 g (96%); mp 120−122 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.77 (s, 1H), 7.82 (s, 1H), 7.73 (dd, J = 7.6, 1.2 Hz, 1H), 7.40 (td, J = 7.6, 1.2 Hz, 1H), 7.34 (td, J = 7.6, 1.6 Hz, 1H), 7.18−7.30 (m, 4H), 7.04 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.3, 139.9, 137.7, 134.1, 132.6, 131.2, 129.9, 129.9, 129.5, 128.6, 128.6, 128.2, 123.7; IR (KBr, cm^{-1}): 3486, 3057, 1685, 1620, 1471, 1420, 1290, 1211, 739, 688; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{15}H_{11}{}^{79}BrNaO_2$: 324.9835; found: 324.9833.

(*E*)-2-(2-Bromophenyl)-3-(4-hydroxyphenyl)acrylic Acid (1bd). White solid; yield: 3.12 g (98%); mp 182−184 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.51 (s, 1H), 9.95 (s, 1H), 7.72−7.74 (m, 2H), 7.41 (td, J = 7.6, 1.2 Hz, 1H), 7.33 (td, J = 7.6, 1.6 Hz, 1H), 7.20 (dd, J = 7.6, 1.6 Hz, 1H), 6.86 (d, J = 8.8 Hz, 2H), 6.60 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.7, 159.1, 140.1, 138.3, 132.6, 132.1, 131.4, 129.7, 128.8, 128.3, 125.1, 124.0, 115.6; IR (KBr, cm^{-1}): 3585, 3358, 1672, 1602, 1508, 1468, 1423, 1285, 1170, 835, 736; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{15}H_{11}{}^{79}BrNaO_3$: 340.9784; found: 340.9787.

(*E*)-2-(2-Bromophenyl)-3-(4-hydroxy-3,5-dimethoxyphenyl)-acrylic Acid (1be). White solid; yield: 3.64 g (96%); mp 188−190 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.52 (s, 1H), 8.96 (s, 1H), 7.75−7.77 (m, 1H), 7.73 (s, 1H), 7.46 (td, J = 7.6, 0.8 Hz, 1H), 7.33 (td, J = 7.6, 1.6 Hz, 1H), 7.25 (dd, J = 7.6, 1.6 Hz, 1H), 6.35 (s, 2H), 3.45 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.5, 147.5, 140.5, 138.4, 137.5, 132.6, 131.6, 129.6, 129.2, 128.3, 124.1, 124.1, 108.1, 55.5; IR (KBr, cm^{-1}): 3539, 3510, 1672, 1615, 1589, 1518, 1467, 1269, 1154, 824, 740; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{17}H_{15}{}^{79}BrNaO_5$: 400.9995; found: 400.9999.

(*E*)-2-(2-Bromophenyl)-3-(3-hydroxy-4-methoxyphenyl)-acrylic Acid (1bf). White solid; yield: 3.31 g (95%); mp 176−178 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.50 (s, 1H), 8.97 (s, 1H), 7.72 (dd, J = 7.6, 0.8 Hz, 1H), 7.65 (s, 1H), 7.41 (td, J = 7.6, 0.8 Hz, 1H), 7.33 (td, J = 7.6, 1.6 Hz, 1H), 7.18 (dd, J = 7.6, 1.6 Hz, 1H), 6.79 (d, J = 8.4 Hz, 1H), 6.51 (dd, J = 8.4, 2.0 Hz, 1H), 6.41 (d, J = 2.0 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.6, 149.2, 146.1, 140.0, 138.1, 132.6, 131.3, 129.8, 129.7, 128.2, 126.8, 123.9, 122.7, 117.0, 111.7, 55.5; IR (KBr, cm^{-1}): 3492, 3078, 1677, 1610, 1510, 1439, 1266, 1133, 873, 733; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{16}H_{13}{}^{79}BrNaO_4$: 370.9889; found: 370.9892.

(*E*)-2-(2-Bromophenyl)-3-(3-ethoxy-4-hydroxyphenyl)acrylic Acid (1bg). White solid; yield: 3.52 g (97%); mp 160−162 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.51 (s, 1H), 9.52 (s, 1H), 7.75 (dd, J = 8.0, 0.8 Hz, 1H), 7.70 (s, 1H), 7.44 (td, J = 7.6, 1.2 Hz, 1H), 7.33 (td, J = 7.6, 2.0 Hz, 1H), 7.23 (dd, J = 7.6, 2.0 Hz, 1H), 6.66−6.71 (m, 2H), 6.36 (d, J = 1.6 Hz, 1H), 3.51 (q, J = 8.0 Hz, 2H), 1.12 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.5, 148.8, 146.1, 140.2, 138.3, 132.6, 131.5, 129.6, 128.6, 128.2, 125.4, 125.2, 124.0, 115.4, 113.6, 63.0, 14.4; IR (KBr, cm^{-1}): 3494, 3071, 1672, 1585, 1519, 1473, 1264, 1196, 832, 734; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{17}H_{15}{}^{79}BrNaO_4$: 385.0046; found: 385.0048.

(*E*)-2-(2-Bromo-3,5-dimethoxyphenyl)-3-(4-hydroxy-3-methoxyphenyl)acrylic Acid (1ca). White solid; yield: 3.80 g

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(93%); mp 188−190 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.67 (s, 1H), 7.76 (s, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.80 (d, J = 8.0 Hz, 2H), 6.71 (d, J = 2.4 Hz, 1H), 6.43 (d, J = 2.4 Hz, 1H), 3.84 (s, 3H), 3.73 (s, 3H), 3.45 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.1, 160.1, 156.9, 150.4, 140.1, 139.4, 138.4, 132.8, 132.6, 123.2, 123.0, 113.6, 107.3, 103.4, 99.2, 56.4, 55.7, 55.1; IR (KBr, cm^{-1}): 3627, 3513, 1700, 1620, 1584, 1511, 1464, 1421, 1264, 1162, 852, 734; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{18}H_{17}{}^{79}BrNaO_6$: 431.0101; found: 431.0101.

(*E*)-2-(2-Bromo-3,5-dimethoxyphenyl)-3-(3,4-dimethoxyphenyl)acrylic Acid (1cb). White solid; yield: 3.64 g (86%); mp 158−160 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.49 (s, 1H), 7.70 (s, 1H), 6.87 (d, J = 8.4 Hz, 1H), 6.80 (dd, J = 8.4, 2.0 Hz, 1H), 6.70 (d, J = 2.8 Hz, 1H), 6.60 (d, J = 2.0 Hz, 1H), 6.41 (d, J = 2.8 Hz, 1H), 3.87 (s, 3H), 3.72 (s, 6H), 3.38 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.3, 160.1, 156.9, 150.1, 148.1, 139.9, 139.3, 129.9, 126.6, 124.5, 112.5, 111.4, 107.4, 103.7, 99.1, 56.5, 55.7, 55.5, 54.7; IR (KBr, cm^{-1}): 3468, 3068, 1674, 1589, 1513, 1456, 1262, 1148, 805, 742; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{19}H_{19}{}^{79}BrNaO_6$: 445.0257; found: 445.0253.

(*E*)-2-(2-Bromo-3,5-dimethoxyphenyl)-3-(3-hydroxy-4-methoxyphenyl)acrylic Acid (1cc). White solid; yield: 3.27 g (80%); mp 160−162 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.47 (s, 1H), 9.01 (s, 1H), 7.60 (s, 1H), 6.82 (d, J = 8.4 Hz, 1H), 6.69 (d, J = 2.8 Hz, 1H), 6.60 (dd, J = 8.4, 2.0 Hz, 1H), 6.49 (d, J = 2.0 Hz, 1H), 6.35 (d, J = 2.4 Hz, 1H), 3.87 (s, 3H), 3.74 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.4, 159.9, 156.7, 149.2, 146.0, 139.7, 139.5, 129.6, 126.8, 122.9, 116.9, 111.7, 107.3, 103.6, 99.0, 56.3, 55.6, 55.5; IR (KBr, cm^{-1}): 3627, 3445, 1667, 1584, 1511, 1447, 1264, 1158, 835, 799; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{18}H_{17}{}^{79}BrNaO_6$: 431.0101; found: 431.0098.

Typical Procedure for the Synthesis of 2-(3,5-Dimethoxyphenyl)-6-hydroxybenzofuran-3-carboxylic Acid (2aa). A mixture of (*E*)-2-(2-bromo-4-hydroxyphenyl)-3-(3,5-dimethoxyphenyl)acrylic acid **1aa** (0.379 g, 1 mmol), Cu(OAc)$_2$ (36 mg, 0.2 mmol, 20 mol %), 1,10-phen (36 mg, 0.2 mmol, 20 mol %), KOH (0.56 g, 10.0 mmol, 10.0 equiv), and DMSO−H_2O (1:1) (5 mL) was added into a flask equipped with a condenser. The flask was then placed into the microwave reactor, the mixture was irradiated (240 W) under air with stirring, and the reaction temperature was raised to 110 °C for 1 h. After the reaction was completed (monitored by TLC), the resulting mixture was filtered off and washed with 10 mL EtOAc three times. The aqueous layer was separated from the filtrate and acidified to pH 3−4 with 1 M HCl. The precipitated crude product was collected by filtration and recrystallized from ethyl acetate or purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1:2) as an eluent to afford **2aa** as pale white crystals. Yield 0.28 g, 90%; mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.02 (s, 1H), 9.81 (s, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.16 (d, J = 2.0 Hz, 2H), 6.99 (d, J = 2.0 Hz, 1H), 6.84 (dd, J = 8.8, 2.0 Hz, 1H), 6.62 (t, J = 2.0 Hz, 1H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.7, 160.0, 156.9, 156.4, 154.1, 130.9, 122.6, 118.9, 113.6, 109.8, 106.8, 101.9, 97.3, 55.4; IR (KBr, cm^{-1}): 3469, 3054, 1667, 1603, 1557, 1494, 1443, 1292, 1093, 773, 688; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{17}H_{14}NaO_6$: 337.0683; found: 337.0678; Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.97; H, 4.49. Found: C, 65.26; H, 4.507.

6-Hydroxy-2-(3-hydroxy-4-methoxyphenyl)benzofuran-3-carboxylic Acid (2ab). White acicular crystal; yield: 0.26 g (88%); mp 199−200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.86 (s, 1H), 9.74 (s, 1H), 9.28 (s, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.48 (dd, J = 8.4, 2.0 Hz, 1H), 7.45 (d, J = 2.0 Hz, 1H), 7.04 (d, J = 8.8 Hz, 1H), 6.96 (d, J = 2.0 Hz, 1H), 6.83 (dd, J = 8.4, 2.0 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.8, 158.0, 155.9, 153.8, 149.1, 145.8, 122.3, 121.8, 120.6, 119.1, 115.7, 113.1, 111.4, 107.8, 97.1, 55.5; IR (KBr, cm^{-1}): 3400, 3086, 1679, 1629, 1557, 1510, 1438, 1264, 1148, 797, 727; HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{16}H_{13}O_6$: 301.0707; found: 301.0709; Anal. Calcd for $C_{16}H_{12}O_6$: C, 64.00; H, 4.03. Found: C, 64.28; H, 3.889.

6-Hydroxy-2-(4-hydroxy-3,5-dimethoxyphenyl)benzofuran-3-carboxylic Acid (2ac). White solid; yield: 0.28 g (85%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.92 (s, 1H), 9.74 (s, 1H), 9.03 (s, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.40 (s, 2H), 6.98 (d, J = 2.0 Hz, 1H), 6.82 (dd, J = 8.4, 2.0 Hz, 1H), 3.82 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.1, 158.2, 156.0, 153.8, 147.4, 137.7, 122.4, 119.3, 119.1, 113.2, 107.8, 106.8, 97.2, 56.1; IR (KBr, cm^{-1}): 3633, 3443, 1690, 1620, 1572, 1500, 1433, 1290, 1151, 808, 790; HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{17}H_{15}O_7$: 331.0812; found: 331.0813; Anal. Calcd for $C_{17}H_{14}O_7$: C, 61.82; H, 4.27. Found: C, 62.14; H, 4.401.

6-Hydroxy-2-phenylbenzofuran-3-carboxylic Acid (2ad). White solid; yield: 0.21 g (84%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.04 (s, 1H), 9.84 (s, 1H), 7.97−7.99 (m, 2H), 7.81 (d, J = 8.4 Hz, 1H), 7.51−7.52 (m, 3H), 7.03 (d, J = 1.6 Hz, 1H), 6.90 (dd, J = 8.4, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.7, 157.7, 156.3, 154.4, 129.8, 129.5, 128.9, 128.1, 122.6, 118.9, 113.5, 109.3, 97.3; IR (KBr, cm^{-1}): 3189, 3079, 1688, 1605, 1563, 1492, 1460, 1286, 1071, 820, 760; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{15}H_{10}NaO_4$: 277.0471; found: 277.0467; Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.86; H, 3.96. Found: C, 71.25; H, 3.915.

6-Hydroxy-2-(4-hydroxy-3-methoxyphenyl)benzofuran-3-carboxylic Acid (2ae). White solid; yield: 0.25 g (83%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.81 (s, 1H), 9.72 (s, 1H), 9.63 (s, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 2.0 Hz, 1H), 7.48 (dd, J = 8.4, 2.0 Hz, 1H), 6.97 (d, J = 2.0 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.83 (dd, J = 8.8, 2.0 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.1, 158.4, 155.9, 153.8, 148.5, 146.9, 122.4, 120.4, 119.2, 115.4, 115.1, 113.2, 113.1, 107.5, 97.2, 55.6; IR (KBr, cm^{-1}): 3432, 3090, 1621, 1611, 1572, 1507, 1451, 1307, 1155, 856, 813; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{16}H_{12}NaO_6$: 323.0526; found: 323.0529; Anal. Calcd for $C_{16}H_{12}O_6$: C, 64.00; H, 4.03. Found: C, 63.64; H, 3.680.

6-Hydroxy-2-(4-methoxyphenyl)benzofuran-3-carboxylic Acid (2af). White solid; yield: 0.22 g (76%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.90 (s, 1H), 9.75 (s, 1H), 7.96 (d, J = 8.8 Hz, 2H), 7.76 (d, J = 8.4 Hz, 1H), 7.07 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 2.0 Hz, 1H), 6.84 (dd, J = 8.4, 2.0 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.9, 160.4, 158.1, 156.0, 154.0, 130.5, 122.5, 121.8, 119.1, 113.6, 113.3, 108.0, 97.3, 55.3; IR (KBr, cm^{-1}): 3541, 1677, 1615, 1585, 1507, 1438, 1254, 1121, 840, 753; HRMS (ESI-TOF): m/z [M + H]$^+$ calcd. for $C_{16}H_{13}O_5$: 285.0757; found: 285.0761; Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.25. Found: C, 67.82; H, 3.878.

6-Hydroxy-2-(4-hydroxyphenyl)benzofuran-3-carboxylic Acid (2ag). White solid; yield: 0.26 g (98%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.83 (s, 1H), 10.02 (s, 1H), 9.72 (s, 1H), 7.86 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 8.4 Hz, 1H), 6.96 (d, J = 2.0 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 6.83 (dd, J = 8.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.0, 159.0, 158.6, 155.9, 153.9, 130.6, 122.4, 120.2, 119.2, 115.0, 113.1, 107.4, 97.2; IR (KBr, cm^{-1}): 3371, 3244, 1694, 1601, 1557, 1514, 1441, 1284, 1127, 830, 695; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd. for $C_{15}H_{10}NaO_5$: 293.0420; found: 293.0425; Anal. Calcd for $C_{15}H_{10}O_5$: C, 66.67; H, 3.73. Found: C, 66.93; H, 4.119.

2-(3-Ethoxy-4-hydroxyphenyl)-6-hydroxybenzofuran-3-carboxylic Acid (2ah). White solid; yield: 0.30 g (95%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.89 (s, 1H), 9.72 (s, 1H), 9.55 (s, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 2.0 Hz, 1H), 7.46 (dd, J = 8.4, 1.6 Hz, 1H), 6.96 (d, J = 2.0 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.82 (dd, J = 8.4, 2.0 Hz, 1H), 4.08 (q, J = 8.0 Hz, 2H), 1.37 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.1, 158.4, 155.9, 153.8, 148.8, 146.0, 122.4, 122.3, 120.4, 119.2, 115.2, 114.5, 113.2, 107.5, 97.2, 64.0, 14.7; IR (KBr, cm^{-1}): 3411, 3268, 1688, 1604, 1561, 1501, 1440, 1276, 1094, 860, 754; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{17}H_{14}NaO_6$: 337.0683; found: 337.0685; Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.97; H, 4.49. Found: C, 65.13; H, 4.725.

2-(4-Chlorophenyl)-6-hydroxybenzofuran-3-carboxylic Acid (2ai). White solid; yield: 0.25 g (87%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.11 (s, 1H), 9.85 (s, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 2.0 Hz, 1H), 6.87 (dd, J = 8.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-

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d_6): δ = 164.6, 156.5, 156.3, 154.4, 134.5, 130.6, 128.3, 128.3, 122.7, 118.8, 113.7, 109.9, 97.3; IR (KBr, cm^{-1}): 3447, 3244, 1703, 1629, 1489, 1404, 1279, 1219, 824, 720; HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{15}H_9{}^{35}ClNaO_4$: 311.0082; found: 311.0083; Anal. Calcd for $C_{15}H_9ClO_4$: C, 62.41; H, 3.14. Found: C, 62.53; H, 3.408.

2-(4-Fluorophenyl)-6-hydroxybenzofuran-3-carboxylic Acid (2aj). White solid; yield: 0.24 g (88%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.06 (s, 1H), 9.83 (s, 1H), 8.03−8.06 (m, 2H), 7.79 (d, J = 8.4 Hz, 1H), 7.36 (t, J = 8.8 Hz, 2H), 7.01 (d, J = 2.0 Hz, 1H), 6.88 (dd, J = 8.8, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.7, 162.8 (d, $^1J_{F-C}$ = 246.6 Hz), 156.8, 156.3, 154.3, 131.4 (d, $^3J_{F-C}$ = 8.7 Hz), 126.0 (d, $^4J_{F-C}$ = 3.0 Hz), 122.7, 118.8, 115.2 (d, $^2J_{F-C}$ = 21.8 Hz), 113.6, 109.3, 97.3; IR (KBr, cm^{-1}): 3443, 3219, 1705, 1629, 1608, 1494, 1411, 1285, 1121, 811, 731; HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{15}H_9FNaO_4$: 295.0377; found: 295.0377; Anal. Calcd for $C_{15}H_9FO_4$: C, 66.18; H, 3.33. Found: C, 66.25; H, 3.482.

2-(2,4-Dichlorophenyl)-6-hydroxybenzofuran-3-carboxylic Acid (2ak). White solid; yield: 0.25 g (78%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.90 (s, 1H), 9.85 (s, 1H), 7.79−7.82 (m, 2H), 7.70 (d, J = 8.4 Hz, 1H), 7.57 (dd, J = 8.4, 2.0 Hz, 1H), 7.01 (d, J = 1.6 Hz, 1H), 6.91 (dd, J = 8.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.9, 156.6, 155.1, 154.5, 135.5, 134.4, 133.8, 129.1, 128.5, 127.2, 122.3, 117.6, 113.8, 112.4, 97.6; IR (KBr, cm^{-1}): 3568, 3329, 1688, 1628, 1571, 1494, 1438, 1261, 1148, 869, 806; HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{15}H_8{}^{35}Cl_2NaO_4$: 344.9692; found: 344.9695; Anal. Calcd for $C_{15}H_8Cl_2O_4$: C, 55.76; H, 2.50. Found: C, 55.88; H, 2.642.

6-Hydroxy-2-(4-(trifluoromethyl)phenyl)benzofuran-3-carboxylic Acid (2al). White solid; yield: 0.13 g (46%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.27 (s, 1H), 9.95 (s, 1H), 8.20 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.4 Hz, 1H), 7.05 (d, J = 2.0 Hz, 1H), 6.92 (dd, J = 8.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.5, 156.9, 155.6, 154.7, 133.3, 129.5 (q, $^2J_{F-C}$ = 31.4 Hz), 129.6, 125.1 (d, $^3J_{F-C}$ = 3.1 Hz), 124.1 (q, $^1J_{F-C}$ = 270.6 Hz), 123.0, 118.7, 114.0, 111.0, 97.4; IR (KBr, cm^{-1}): 3285, 3216, 1693, 1623, 1571, 1502, 1444, 1288, 1168, 837, 730; HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{16}H_9NaF_3O_4$: 345.0351; found: 345.0351; Anal. Calcd for $C_{16}H_9F_3O_4$: C, 59.64; H, 2.82. Found: C, 59.83; H, 2.996.

2-(4-Cyanophenyl)-6-hydroxybenzofuran-3-carboxylic Acid (2am). White solid; yield: 0.11 g (42%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.24 (s, 1H), 10.20 (s, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 2.4 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 6.78 (dd, J = 8.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.9, 158.0, 138.6, 138.4, 134.8, 131.7, 131.3, 129.9, 129.7, 129.2, 127.4, 123.5, 119.1, 115.4; IR (KBr, cm^{-1}): 3407, 3197, 1693, 1612, 1500, 1417, 1288, 1147, 799, 729; HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{16}H_9NNaO_4$: 302.0429; found: 302.0430; Anal. Calcd for $C_{16}H_9NO_4$: C, 68.82; H, 3.25; N, 5.02. Found: C, 68.97; H, 3.413; N, 5.14.

2-(4-Carboxyphenyl)-6-hydroxybenzofuran-3-carboxylic Acid (2an). Yellow solid; yield: 0.13 g (45%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.03 (s, 2H), 10.05 (s, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 2.0 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.78 (dd, J = 8.4, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.7, 164.8, 158.1, 156.8, 154.8, 138.8, 134.8, 133.4, 129.9, 129.0, 123.6, 119.2, 115.5, 97.5; IR (KBr, cm^{-1}): 3413, 3077, 1685, 1612, 1498, 1421, 1280, 1039, 862, 786; HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{16}H_{10}NaO_6$: 321.0375; found: 321.0377; Anal. Calcd for $C_{16}H_{10}O_6$: C, 64.43; H, 3.38. Found: C, 64.72; H, 3.299.

2-(Furan-2-yl)-6-hydroxybenzofuran-3-carboxylic Acid (2aq). White solid; yield: 0.19 g (80%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.12 (s, 1H), 9.88 (s, 1H), 7.97 (s, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.68 (d, J = 3.6 Hz, 1H), 7.02 (d, J = 2.0 Hz, 1H), 6.87 (dd, J = 8.8, 2.0 Hz, 1H), 6.76 (dd, J = 3.2, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.1, 156.4, 154.0, 148.7, 144.8, 143.4, 122.5, 118.0, 114.9, 113.6, 112.3, 107.7, 97.2; IR (KBr, cm^{-1}): 3639, 3334, 1683, 1623, 1596, 1542, 1494, 1448, 1295, 921, 817; HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{13}H_8NaO_5$: 267.0269; found: 267.0271; Anal. Calcd for $C_{13}H_8O_5$: C, 63.94; H, 3.30. Found: C, 64.18; H, 3.416.

6-Hydroxy-2-(thiophen-2-yl)benzofuran-3-carboxylic Acid (2ar). Yellow solid; yield: 0.20 g (75%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.22 (s, 1H), 9.86 (s, 1H), 8.19 (dd, J = 3.6, 1.2 Hz, 1H), 7.84 (dd, J = 5.2, 1.2 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.25 (dd, J = 5.2, 3.6 Hz, 1H), 6.98 (d, J = 2.0 Hz, 1H), 6.85 (dd, J = 8.8, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.8, 156.5, 153.8, 153.1, 130.7, 130.2, 130.1, 127.8, 122.7, 118.6, 113.6, 107.5, 97.2; IR (KBr, cm^{-1}): 3284, 3079, 1672, 1625, 1558, 1498, 1442, 1268, 1054, 821, 711; HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{13}H_8NaSO_4$: 283.0041; found: 283.0041; Anal. Calcd for $C_{13}H_8SO_4$: C, 59.99; H, 3.10. Found: C, 60.23; H, 3.261.

6-Hydroxy-2-(naphthalen-1-yl)benzofuran-3-carboxylic Acid (2as). White solid; yield: 0.20 g (67%); mp 178−180 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.69 (s, 1H), 9.84 (s, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.78 (dd, J = 7.2, 1.2 Hz, 1H), 7.62−7.70 (m, 2H), 7.53−7.61 (m, 2H), 7.05 (d, J = 1.6 Hz, 1H), 6.95 (dd, J = 8.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.3, 157.9, 156.3, 155.1, 132.9, 131.3, 130.2, 129.6, 128.4, 127.6, 127.0, 126.2, 125.1, 125.0, 122.3, 118.2, 113.6, 111.9, 97.6; IR (KBr, cm^{-1}): 3438, 3174, 1687, 1602, 1562, 1502, 1436, 1286, 1216, 875, 767; HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{19}H_{12}NaO_4$: 327.0633; found: 327.0634; Anal. Calcd for $C_{19}H_{12}O_4$: C,74.99; H, 3.97. Found: C, 75.11; H, 4.206.

(*E*)-6-Hydroxy-2-styrylbenzofuran-3-carboxylic Acid (2at). White solid; 0.18 g (64%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.04 (s, 1H), 9.89 (s, 1H), 7.81 (d, J = 16.4 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.66 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 16.8 Hz, 1H), 7.43−7.47(m, 2H), 7.38 (d, J = 7.2 Hz, 1H), 6.99 (d, J = 2.0 Hz, 1H), 6.85 (dd, J = 8.8, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.8, 157.1, 156.9, 154.7, 135.8, 133.0, 129.0, 128.9, 127.1, 122.3, 118.4, 115.2, 113.5, 109.7, 97.3; IR (KBr, cm^{-1}): 3524, 3330, 1870, 1610, 1578, 1508, 1438, 1294, 1144, 964, 818; HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{17}H_{12}NaO_4$: 303.0628; found: 303.0629; Anal. Calcd for $C_{17}H_{12}O_4$: C, 72.85; H, 4.32. Found: C, 72.96; H, 4.335.

2-(3,5-Dimethoxyphenyl)benzofuran-3-carboxylic Acid (2ba). White acicular crystals; yield: 0.21 g (70%); mp 198−200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.24 (s, 1H), 9.57 (d, J = 8.4 Hz, 1H), 8.73 (dd, J = 8.4, 1.2 Hz, 1H), 8.37 (s, 1H), 7.58−7.67 (m, 2H), 7.31 (d, J = 2.4 Hz, 1H), 7.01 (d, J = 2.4 Hz, 1H), 4.10 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.9, 159.0, 158.4, 133.3, 131.0, 130.4, 128.3, 127.9, 127.3, 126.7, 125.7, 125.5, 115.8, 103.0, 101.5, 56.1, 55.5; IR (KBr, cm^{-1}): 3468, 3073, 1679, 1615, 1602, 1580, 1455, 1251, 1147, 914, 749; HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{17}H_{15}O_5$: 299.0914; found: 299.0906; Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.47; H, 4.738.

2-(4-Hydroxy-3-methoxyphenyl)benzofuran-3-carboxylic Acid (2bb). White solid; yield: 0.22 g (79%); mp 160−161 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.01 (s, 1H), 9.74 (s, 1H), 7.99−8.01 (m, 1H), 7.74 (d, J = 2.0 Hz, 1H), 7.65−7.67 (m, 1H), 7.54 (dd, J = 8.0, 2.0 Hz, 1H), 7.33−7.40 (m, 2H), 6.92 (d, J = 8.0 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.8, 159.9, 152.6, 148.9, 146.9, 127.3, 124.8, 123.9, 122.8, 122.1, 119.9, 115.1, 113.3, 110.9, 107.4, 55.6; IR (KBr, cm^{-1}): 3466, 3060, 1660, 1600, 1507, 1448, 1271, 1181, 752, 691; HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{16}H_{12}NaO_5$: 307.0577; found: 307.0581; Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.25. Found: C, 67.32; H, 4.582.

2-Phenylbenzofuran-3-carboxylic Acid (2bc). Gray solid; yield: 0.17 g (72%); mp 178−179 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.15 (s, 1H), 7.99−8.05 (m, 3H), 7.70−7.72 (m, 1H), 7.54−7.56 (m, 3H), 7.38−7.45 (m. 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.6, 159.5, 153.2, 130.3, 129.3, 129.2, 128.2, 127.0, 125.5, 124.2, 122.4, 111.3, 109.3; IR (KBr, cm^{-1}): 3447, 3084, 1692, 1601, 1571, 1496, 1463, 1279, 1155, 946, 806; HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{15}H_{10}NaO_3$: 261.0522; found: 261.0523; Anal. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 75.94; H, 3.938.

2-(4-Hydroxyphenyl)benzofuran-3-carboxylic Acid (2bd). Yellow solid; yield: 0.21 g (84%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.98 (s, 1H), 10.12 (s, 1H), 7.98−8.01 (m,

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1H), 7.91 (d, J = 8.8 Hz, 2H), 7.64−7.66 (m, 1H), 7.33−7.39 (m, 2H), 6.90 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.7, 160.2, 159.4, 152.6, 131.0, 127.2, 124.8, 123.9, 122.0, 119.7, 115.0, 110.9, 107.3; IR (KBr, cm^{-1}): 3450, 3076, 1688, 1608, 1573, 1505, 1443, 1383, 1174, 831, 795; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{15}H_{10}NaO_4$: 277.0471; found: 277.0477; Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.86; H, 3.96. Found: C, 71.18; H, 4.325.

2-(4-Hydroxy-3,5-dimethoxyphenyl)benzofuran-3-carboxylic Acid (2be). White solid; yield: 0.23 g (74%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.07 (s, 1H), 9.15 (s, 1H), 7.98−8.01 (m, 1H), 7.67 (dd, J = 6.8, 2.0 Hz, 1H), 7.45 (s, 2H), 7.33−7.40 (m, 2H), 3.83 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.0, 159.8, 152.6, 147.5, 138.2, 127.5, 125.1, 124.0, 122.3, 118.7, 111.1, 107.9, 107.2, 56.1; IR (KBr, cm^{-1}):3482, 3000, 1685, 1604, 1513, 1491, 1451, 1284, 1110, 889, 730; HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{17}H_{15}O_6$: 315.0863; found: 315.0859; Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.97; H, 4.49. Found: C, 65.21; H, 4.199.

2-(3-Hydroxy-4-methoxyphenyl)benzofuran-3-carboxylic Acid (2bf). White solid; yield: 0.23 g (81%); mp 189−190 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.02 (s, 1H), 9.35 (s, 1H), 7.98−8.00 (m, 1H), 7.65−7.67 (m, 1H), 7.55 (dd, J = 8.4, 2.0 Hz, 1H), 7.50 (d, J = 2.0 Hz, 1H), 7.35−7.39 (m, 2H), 7.07 (d, J = 8.4 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.7, 159.5, 152.6, 149.5, 145.9, 127.2, 124.9, 123.9, 122.1, 121.4, 121.1, 116.0, 111.5, 110.9, 107.8, 55.5; IR (KBr, cm^{-1}): 3531, 3426, 1675, 1622, 1564, 1509, 1443, 1258, 1132, 888, 757; HRMS: (ESI-TOF) m/z [M + Na]$^+$ calcd. for $C_{16}H_{12}NaO_5$: 307.0577; found: 307.0582; Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.25. Found: C, 67.95; H, 4.566.

2-(3-Ethoxy-4-hydroxyphenyl)benzofuran-3-carboxylic Acid (2bg). Yellow solid; 0.25 g (83%); mp 184−186 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.97 (s, 1H), 9.66 (s, 1H), 7.96−8.00 (m, 1H), 7.72 (d, J = 2.0 Hz, 1H), 7.62−7.67 (m, 1H), 7.52 (dd, J = 8.4, 2.0 Hz, 1H), 7.32−7.39 (m, 2H), 6.92 (d, J = 8.4 Hz, 1H), 4.09 (q, J = 8.0 Hz, 2H), 1.37 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.9, 160.0, 152.6, 149.3, 146.1, 127.4, 124.9, 123.9, 122.7, 122.1, 119.9, 115.3, 114.7, 111.0, 107.5, 64.0, 14.7; IR (KBr, cm^{-1}): 3537, 3457, 1689, 1602, 1569, 1508, 1455, 1262, 1196, 863, 800; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{17}H_{14}NaO_5$: 321.0733; found: 321.0736; Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.81; H, 4.383.

2-(4-Hydroxy-3-methoxyphenyl)-5,7-dimethoxybenzofuran-3-carboxylic Acid (2ca). White acicular crystals; yield: 0.23 g (66%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.00 (s, 1H), 9.72 (s, 1H), 7.65 (d, J = 2.0 Hz,1H), 7.43 (dd, J = 8.0, 2.0 Hz, 1H), 7.03 (d, J = 2.0 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.60 (d, J = 2.0 Hz, 1H), 3.93 (s, 3H), 3.82 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.9, 160.4, 157.1, 148.8, 146.9, 144.9, 137.2, 128.8, 122.7, 120.1, 115.2, 113.3, 108.1, 97.5, 95.5, 55.9, 55.7, 55.6; IR (KBr, cm^{-1}): 3638, 3511, 1688, 1612, 1569, 1513, 1443, 1287, 1131, 842, 792; HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{18}H_{17}O_7$: 345.0969; found: 345.0965; Anal. Calcd for $C_{18}H_{16}O_7$: C, 62.79; H, 4.68. Found: C, 63.18; H, 4.953.

2-(3,4-Dimethoxyphenyl)-5,7-dimethoxybenzofuran-3-carboxylic Acid (2cb). Gray solid; yield: 0.23 g (64%); mp 168−170 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.88 (s, 1H), 7.66 (s, 1H), 7.56 (dd, J = 8.8, 1.6 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 7.04 (d, J = 2.0 Hz, 1H), 6.61 (d, J = 1.6 Hz, 1H), 3.94 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.9, 160.0, 157.2, 150.5, 148.0, 144.9, 137.3, 128.7, 122.5, 121.5, 112.6, 111.2, 108.6, 97.6, 95.5, 56.0, 55.6, 55.6, 55.5; IR (KBr, cm^{-1}): 3553, 3436, 1686, 1600, 1514, 1491, 1464, 1272, 1106, 815, 731; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{19}H_{18}NaO_7$: 381.0945; found: 381.0946; Anal. Calcd for $C_{19}H_{18}O_7$: C, 63.68; H, 5.06. Found: C, 64.02; H, 5.415.

2-(3-Hydroxy-4-methoxyphenyl)-5,7-dimethoxybenzofuran-3-carboxylic Acid (2cc). White solid; yield: 0.23 g (68%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.95 (s, 1H), 9.71(s, 1H), 7.66 (d, J = 1.6 Hz, 1H), 7.44 (dd, J = 8.4, 1.6 Hz, 1H), 7.03 (d, J = 2.0 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.60 (d, J = 2.0 Hz, 1H), 3.94 (s, 3H), 3.83 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.0, 160.4, 157.2, 148.8, 146.9, 144.9, 137.2, 128.9, 122.7, 120.1, 115.2, 113.3, 108.1, 97.5, 95.5, 55.9, 55.7, 55.6; IR (KBr, cm^{-1}): 3485, 3055, 1689, 1604, 1569, 1490, 1456, 1282, 1110, 890, 769; HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{18}H_{17}O_7$: 345.0969; found: 345.0976; Anal. Calcd for $C_{18}H_{16}O_7$: C, 62.79; H, 4.68. Found: C, 63.14; H, 5.034.

(*E*)-2-(2-Hydroxyphenyl)-3-phenylacrylic Acid (4bc). This reaction was run under N_2 atmosphere. White solid; 0.18 g (75%); mp 148−149 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.39 (s, 1H), 9.40 (s, 1H), 7.68 (s, 1H), 7.11−7.23 (m, 6H), 6.86−6.88 (m, 2H), 6.76 (t, J = 7.2 Hz, 1H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.5, 155.2, 138.8, 134.9, 131.0, 130.4, 129.8, 129.0, 128.8, 128.2, 123.7, 119.0, 115.5; IR (KBr, cm^{-1}): 3431, 3060, 1689, 1600, 1578, 1513, 1443, 1277, 1167, 849, 735; HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{15}H_{13}O_3$: 241.0859; found: 241.0859.

Procedure for the Synthesis of 6-Hydroxy-2-(3,5-dimethoxyphenyl)benzofuran (3). A stirred solution of 2-(3,5-dimethoxyphenyl)-6-hydroxybenzofuran-3-carboxylic acid (**2aa**, 0.628 g, 2 mmol), CuI (38 mg, 0.2 mmol, 10 mol %), 1,10-phen (36 mg, 0.2 mmol, 10 mol %), and PEG-400 (20 mL) was heated to 180 °C for 10 min under microwave irradiation (2 min irradiation each time with a 5 min interval between). After completion of the reaction, the mixture was cooled to room temperature. The resulting reaction solution was added into ethyl acetate (20 mL) and water (20 mL) and filtered. The filtrate was extracted with ethyl acetate. The combined organic layers were washed with water, dried over anhydrous $MgSO_4$, and then concentrated under vacuum to afford the crude product, which was further recrystallized from ethyl acetate/petroleum ether to give yellow pale crystals. Yield 0.52 g (96%); mp 110−112 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.66 (s, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.35 (s, 1H), 6.99 (d, J = 2.4 Hz, 2H), 6.97 (s, 1H), 6.76 (dd, J = 8.4, 2.0 Hz, 1H), 6.49 (t, J = 2.4 Hz, 1H), 3.82 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 160.8, 155.9, 155.4, 153.4, 132.0, 121.3, 120.7, 112.6, 102.7, 102.0, 100.3, 97.5, 55.4; IR (KBr, cm^{-1}): 3436, 3234, 1685, 1600, 1574, 1509, 1442, 1271, 1199, 753, 691; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{16}H_{14}NaO_4$: 293.0784, found: 293.0784.

Procedure for the Synthesis of Moracin M. A mixture of 6-hydroxy-2-(3,5-dimethoxyphenyl)benzofuran (**3**, 0.27 g, 1 mmol) and aluminum chloride (0.40 g, 3 mmol) in 1,2-dichloroethane (20 mL) was stirred at 80 °C until the reaction was complete (monitored by TLC). After cooling, the mixture was subjected to vacuum distillation to recover the 1,2-dichloroethane and poured into hot water (80 °C, 50 mL) with stirring for 20 min. The mother liquor was obtained after the filtration, extracted with 10 mL ethyl acetate three times, dried over anhydrous $MgSO_4$, concentrated to afford crude product, and then further purified by crystallization from ethyl acetate to give white pale crystals. Yield 0.21 g (86%); mp >200 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.59 (s, 1H), 9.44 (s, 2H), 7.38 (d, J = 8.4 Hz, 1H), 7.08 (s, 1H), 6.92 (d, J = 1.6 Hz, 1H), 6.74 (dd, J = 8.4, 2.0 Hz, 1H), 6.67 (d, J = 2.0 Hz, 2H), 6.21 (t, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 158.8, 155.7, 155.2, 153.9, 131.6, 121.1, 120.7, 112.4, 102.6, 102.3, 101.5, 97.4; IR (KBr, cm^{-1}): 3584, 3468, 1684, 1627, 1554, 1494, 1449, 1260, 1095, 865, 800; HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{14}H_{11}O_4$: 243.0652, found: 243.0653.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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