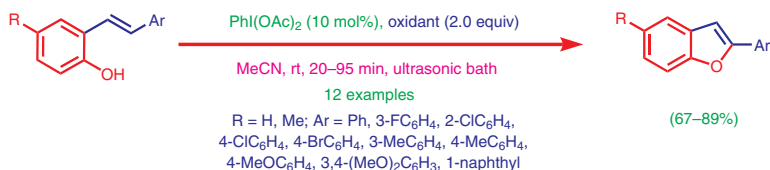


Hypervalent Iodine(III)-Catalyzed Synthesis of 2-Arylbenzofurans

Fateh V. Singh*

Saeesh R. Mangaonkar

Chemistry Division, School of Advanced Science, VIT Institute,
Chennai Campus, Chennai-60017, Tamil Nadu, India
Fatehveer.singh@vit.ac.in



Received: 20.06.2018

Accepted after revision: 07.07.2018

Published online: 16.08.2018

DOI: 10.1055/s-0037-1610650; Art ID: ss-2018-t0424-op

Abstract An alternative route for the synthesis of 2-arylbenzofurans is described by iodine(III)-catalyzed oxidative cyclization of 2-hydroxystilbenes using 10 mol% (diacetoxyiodo)benzene [PhI(OAc)₂] as catalyst in the presence of *m*-chloroperbenzoic acid. The 2-arylbenzofurans were isolated in good to excellent yields.

Key words cyclization reactions, *o*-hydroxystilbenes, 2-arylbenzofurans, hypervalent iodine reagents, hypervalent iodine catalyst

Benzofuran-cored compounds are an important architecture in medicinal and natural product chemistry.^{1–3} These scaffolds are a common structural motif found in various biologically active compounds **1–4** (Figure 1). Ailanthoidol (**1**) was isolated from the Chinese herbal medicine *Zanthoxylum ailanthoides* and is known for its anti-inflammatory properties.⁴

Egonol (**2**) and homoegonol (**3**) were isolated from the seeds of *Styrax japonicum* and *Styrax officinalis* respectively, which are known for their antimicrobial properties.^{5,6} Machicendiol (**4**) was isolated from the leaf extracts of *Breynia fruticosa*, which can be used for the treatment of asthma, rheumatism, and ulcers.⁷ In addition, various synthetic benzofurans have been reported with diverse biological activities⁸ including anticancer,⁹ antifungal,¹⁰ antivasoconstriction,¹¹ 5-lipoxygenase inhibitory,¹² angiotensin II inhibitory,¹³ anti-inflammatory,¹⁴ antimicrobial,¹⁵ and antioxidant activity.¹⁶

Numerous synthetic approaches are available for the synthesis of 2-arylbenzofurans, but most of them are associated with Heck- or Sonogashira-type annulation reactions of *ortho*-halogenated phenol and terminal alkenes or alkynes catalyzed by transition metals such as palladium,¹⁷

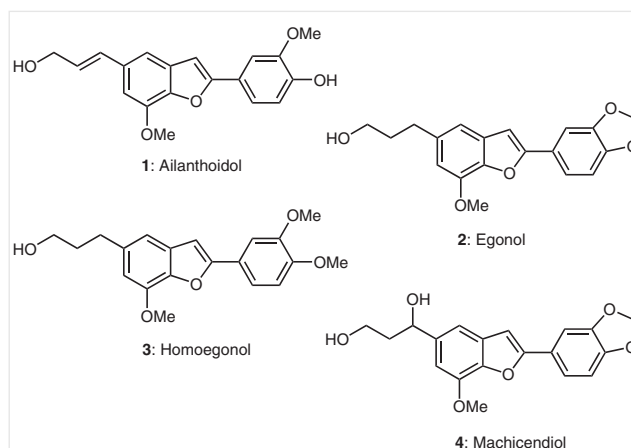


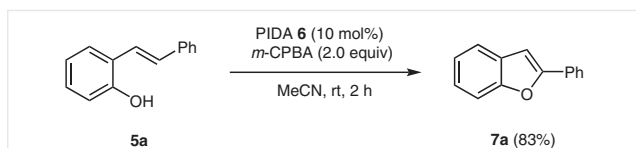
Figure 1 The structures of benzofuran-cored naturally occurring compounds

copper,¹⁸ gold,¹⁹ and zinc.²⁰ In addition, a few non-classical approaches have been used for the construction of substituted benzofurans including [3,3]-sigmatropic rearrangement of *N*-trifluoroacetylene-hydroxylamines²¹ and the intramolecular Wittig reaction.^{22a,b} Stevenson and co-workers developed a synthesis of benzofurans in two steps that involve the epoxidation of 2-hydroxystilbenes using *m*-CPBA followed by acid-catalyzed annulation in the presence of *p*-toluenesulfonic acid.^{22c} In 2014, the synthesis of benzofurans was achieved by base-catalyzed cyclization of 2-(phenylethynyl)phenol derivatives under heterogeneous reaction condition.²³

Hypervalent iodine compounds have received particular attention in the area of synthetic chemistry and have found wide applications in organic synthesis due to their environmentally friendly nature, low toxicity, favorable safety profile, and easy handling.²⁴ Various iodine(III) reagents have

been successfully used to achieve number of organic transformations including cyclization reactions.²⁵ Singh and Wirth have reported an efficient metal-free approach for the cyclization of *o*-hydroxystilbenes to benzofuran using an iodine(III) reagent.²⁶ Recently, hypervalent iodine reagents have been used as catalysts to achieve several useful organic transformations.²⁷

Herein, we report a catalytic approach for the cyclization of a series of *o*-hydroxystilbenes **5** into the corresponding 2-arylbenzofurans **7** using (diacetoxyiodo)benzene (**6**) as a catalyst and *m*-CPBA as the terminal oxidant. The parent precursors **5** were prepared by palladium-catalyzed Heck reaction of 2-iodophenol with functionalized styrenes.²⁶ Initially, our efforts were directed to get the best reaction condition for the cyclization of *o*-hydroxystilbenes **5** and (*E*)-2-styrylphenol (**5a**) was selected as a model substrate. The cyclization of (*E*)-2-styrylphenol (**5a**) was performed in MeCN using 10 mol% of (diacetoxyiodo)benzene (PIDA, **6**) in the presence of 2.0 equiv of *m*-CPBA at room temperature. The cyclized product was characterized as 2-phenylbenzofuran (**7a**) and isolated in 83% yield (Scheme 1).

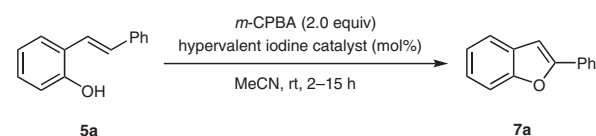


Scheme 1 Cyclization of (*E*)-2-styrylphenol to 2-phenylbenzofuran using PIDA as catalyst

Initially, the course of cyclization reaction was studied with various hypervalent iodine based catalysts (Table 1). Both cyclic and acyclic hypervalent iodine reagents were used as the catalyst and acyclic hypervalent iodine species showed better results than cyclic ones (Table 1, entries 1–5). In the beginning, cyclization reaction was performed with (diacetoxyiodo)benzene (**6**) and cyclic product **7a** was obtained in 83% yield (Table 1, entry 1). The cyclic product **7a** was isolated in 80% yield with more reactive catalyst [bis(trifluoroacetoxy)iodo]benzene (Table 1, entry 2). The same reaction was carried out using Koser's reagent [PhI(OH)OTs], but the yield of cyclic product **7a** was reduced up to 63% (Table 1, entry 3). Furthermore, similar reaction was employed with cyclic hypervalent iodine(III) reagent 1-hydroxy-3-oxobenziodoxole (IBA) as catalyst and desired product **7a** was observed in 45% yield (Table 1, entry 4). Finally, the reaction was also performed with cyclic hypervalent iodine(V) reagent 1-hydroxy-1,2-benziodoxol-3-(1*H*)-one 1-oxide (IBX), but cyclic product **7a** was not observed and only starting material was recovered (Table 1, entry 5). Additionally, the cyclization reaction was per-

formed using 10 mol% of PhI as precatalyst in the presence of same oxidant *m*-CPBA, but no reaction was observed (Table 1, entry 9).

Table 1 Optimization of Hypervalent Iodine Based Catalysts for the Cyclization of (*E*)-2-Styrylphenol (**5a**)

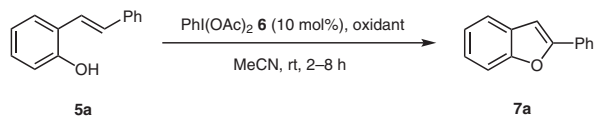


Entry	Hypervalent iodine catalyst (mol%)	Time (h)	Yield (%)
1	PhI(OAc) ₂ (10)	2	83
2	PhI(OCOCF ₃) ₂ (10)	2	80
3	PhI(OH)OTs (10)	2	63
4	IBA (10)	15	45
5	IBX (10)	15	–
6	PhI(OAc) ₂ (5.0)	15	45
7	PhI(OAc) ₂ (7.5)	15	56
8	PhI(OAc) ₂ (15)	2	84
9	PhI (10)	15	–
10 ^a	PhI (10)	15	42

^a AcOH was used as an additive.

After identifying an iodine(III) reagent as the best catalyst, our efforts were directed towards the optimization of the amount of the catalyst (diacetoxyiodo)benzene (**6**; Table 1, entries 6–8). The cyclization of compound **5a** was performed with 5.0 and 7.5 mol% of catalyst **6** and **7a** was obtained in 45% and 56% yields, respectively (Table 1, entries 6 and 7). In addition, the same reaction was attempted with 15 mol% of catalyst **6** and **7a** was obtained in 84% yield (Table 1, entry 8). Finally, 10 mol% of catalyst **6** was preferred for further cyclization reactions as the yield of cyclic product **7a** was quite similar to that with 15 mol% of catalyst **6** (Table 1, entry 1 vs 8).

Furthermore, we next identified find the most appropriate oxidant to regenerate the active catalytic iodine(III) species. In order to find the best oxidant, the cyclization reaction of (*E*)-2-styrylphenol (**5a**) was studied with different organic and inorganic oxidants (Table 2, entries 1–5). Initially, organic oxidants *m*-CPBA and peracetic acid were used for iodine(III)-catalyzed cyclization of (*E*)-2-styrylphenol (**5a**) and cyclic product **7a** was obtained in 83% and 39% yields, respectively (Table 2, entries 1 and 2). The desired product **7a** was isolated in 70% and 75% yields with inorganic oxidants sodium perborate tetrahydrate and Oxone, respectively (Table 2, entries 3 and 4). Finally, H₂O₂ was also used as an oxidant, but catalytic reaction did not work and cyclic product **7a** was observed in only trace amounts (Table 2, entry 5).

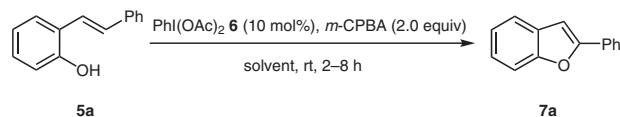
Table 2 Optimization of Oxidant for Iodine(III)-Catalyzed Oxidative Cyclization of (*E*)-2-Styrylphenol (**5a**)

Entry	Oxidant	Time (h)	Yield (%)
1	<i>m</i> -CPBA (2.0 equiv)	2	83
2	AcOOH (2.0 equiv)	8	39
3	$\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ (2.0 equiv)	8	70
4	Oxone (2.0 equiv)	8	75
5	H_2O_2 (2.0 equiv)	8	traces
6	<i>m</i> -CPBA (3.0 equiv)	2	83
7	<i>m</i> -CPBA (1.0 equiv)	8	44
8	<i>m</i> -CPBA (1.5 equiv)	8	68

In addition, the stoichiometry of *m*-CPBA required for the efficient conversion of (*E*)-2-styrylphenol (**5a**) to 2-phenylbenzofuran (**7a**) was also screened. An initial oxidant study demonstrated that using 2.0 and 3.0 equivalents of *m*-CPBA resulted in complete conversion, but **7a** was isolated in 83% yield in both cases (Table 2, entries 1 and 6). Furthermore, the cyclization reaction was performed with 1.0 and 1.5 equivalents of *m*-CPBA and cyclized product **7a** was isolated in 44% and 68% yields respectively (Table 2, entries 7 and 8) along with unreacted starting material.

In addition, different polar and non-polar solvents were investigated during the cyclization of (*E*)-2-styrylphenol (**5a**) to 2-phenylbenzofuran (**7a**) (Table 3, entries 1–6). Initially, the cyclization reaction was performed in acetonitrile and **7a** was isolated in 83% yield (Table 3, entry 1). The cyclization reaction was also proceeded in tetrahydrofuran and dichloromethane, but cyclization product **7a** was observed in 70% and 50% yields, respectively (Table 3, entries 2 and 3). Unlike previously discussed polar and aprotic solvents, the reaction did not proceed in DMSO (Table 3, entry 4). The course of cyclization reaction was also examined in polar and protic solvents such as methanol and 2,2,2-trifluoroethanol (TFE) and **7a** was obtained in 56% and 70% yields, respectively (Table 3, entries 5 and 6).

Next, our efforts were directed to monitor the effect of temperature on rate of the reaction. Initially, cyclization reaction was performed at 60 °C in acetonitrile solvent. The reaction proceeded well and cyclized product **7a** was obtained in 81% yield, but reaction took 1.5 hours for complete conversion of starting material **5a** (Table 3, entry 7). Furthermore, the reaction was carried out at reflux temperature (80 °C) and all the starting material was consumed in 1 hour. Notably, the cyclization suffered with some side reac-

Table 3 Optimization of Solvent for the Cyclization of (*E*)-2-Styrylphenol (**5a**)

Entry	Solvent	Time (h)	Yield (%)
1	MeCN	2	83
2	THF	8	70
3	CH_2Cl_2	8	50
4	DMSO	8	–
5	MeOH	8	56
6	TFE	8	70
7 ^a	MeCN	1.5	81
8 ^b	MeCN	1.0	79
9 ^c	MeCN	30 min	85

^a Reaction was carried out at 60 °C.

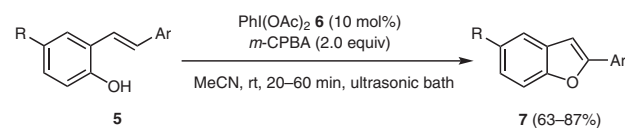
^b Reaction was carried out at 80 °C.

^c Reaction was carried out in ultrasonic bath at 25 °C.

tions at reflux temperature and desired product **7a** was obtained in 79% yield (Table 3, entry 8). Further, there are several reports in which reaction time has been reduced significantly using ultrasonic waves as a source of energy.^{28a–c} After that the cyclization reaction of compound **5a** was performed with 10 mol% of PIDA in presence of 2.0 equivalents of *m*-CPBA in acetonitrile at room temperature in an ultrasonic bath. The reaction was completed only in 30 minutes and cyclized product **7a** was isolated in 85% yield (Table 3, entry 9). During the reaction in the ultrasonic bath, the reaction temperature was controlled by a thermostat (at 25 °C), but it was increased by 6.0 °C after the completion of reaction (30 min).

After getting the optimal reaction conditions, a series of 2-hydroxystilbenes **5a–I** were successfully cyclized to yield the benzofuran products **7a–I** in 67–89% yields (Table 4, entries 1–22). Various electron-donating and -withdrawing groups at the aromatic ring in substrates **5** were successfully tolerated during this cyclization reaction. It was observed that the cyclic products were isolated in slightly lower yields when electron-withdrawing groups at aromatic ring were used in substrates **5** (Table 4, entries 2–5). In addition, cyclization reactions with bulky styrene **5c** were successful, but the corresponding cyclic product **7c** was obtained in 67% yield (Table 4, entry 3). Furthermore, inorganic oxidants such as Oxone and sodium perborate were employed in similar cyclization reactions and 2-arylbenzofurans **7** were isolated in good yields (Table 4, entries 13–22).

Table 4 The Scope of Cyclization Reaction with Different *o*-Hydroxystilbenes **5a–l** to 2-Arylbenzofurans **7a–l** Using $\text{PhI}(\text{OAc})_2$ (**6**) as Catalyst



Entry	Ar	R	Time (min)	7	Yields (%)
1	Ph	H	30	7a	85
2	3-FC ₆ H ₄	H	50	7b	68
3	2-ClC ₆ H ₄	H	60	7c	67
4	4-ClC ₆ H ₄	H	60	7d	76
5	4-BrC ₆ H ₄	H	55	7e	82
6	3-MeC ₆ H ₄	H	30	7f	83
7	4-MeC ₆ H ₄	H	30	7g	86
8	4-MeOC ₆ H ₄	H	20	7h	89
9	3,4-(MeO) ₂ C ₆ H ₃	H	20	7i	79
10	1-naphthyl	H	45	7j	86
11	Ph	Me	30	7k	83
12	4-ClC ₆ H ₄	Me	60	7l	77
13 ^a	Ph	H	70	7a	78
14 ^a	4-ClC ₆ H ₄	H	90	7d	71
15 ^a	4-BrC ₆ H ₄	H	80	7e	75
16 ^a	4-MeC ₆ H ₄	H	70	7g	82
17 ^a	4-MeOC ₆ H ₄	H	65	7h	84
18 ^b	Ph	H	80	7a	75
19 ^b	4-ClC ₆ H ₄	H	95	7d	69
20 ^b	4-BrC ₆ H ₄	H	90	7e	72
21 ^b	4-MeC ₆ H ₄	H	80	7g	80
22 ^b	4-MeOC ₆ H ₄	H	75	7h	81

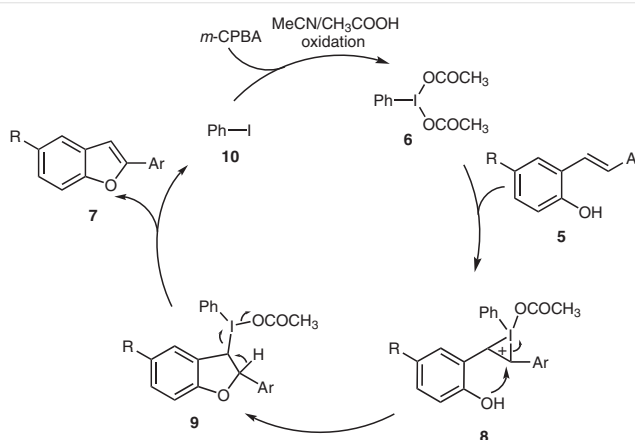
^a Oxone (2.0 equiv) was used as oxidant.

^b Sodium perborate (2.0 equiv) was used as oxidant.

A proposed catalytic cycle for the cyclization of (*E*)-2-styrylphenols **5** to 2-arylbenzofuran **7** using PIDA **6** as catalyst is depicted in Scheme 2. Initially the PIDA **6** activates the double bond of stilbene **5** and forms a three-membered iodonium intermediate **8**. The intermediate **8** then cyclizes intramolecularly with the phenolic oxygen atom to form intermediate **9**. On reductive elimination, intermediate **9** forms the desired product **7** along with formation of iodo-benzene (**10**). Probably, iodobenzene (**10**) reoxidizes to active iodine(III) species in the presence of *m*-CPBA and acetic acid generated in situ during the reduction of PIDA to continue the catalytic cycle.^{28d}

In conclusion, we have developed an iodine(III)-catalyzed synthesis of 2-arylbenzofurans **7** in good to excellent yields by oxidative cyclization of *o*-hydroxystilbenes using (diacetoxyiodo)benzene as catalyst and *m*-CPBA as an oxidant. Our method for the synthesis of 2-arylbenzofurans is very simple, economical and metal-free. Further investigations about this catalytic approach are currently in progress.

Melting points were measured with a REMI DDMS 2545 melting point apparatus. IR spectra were recorded on a Thermo Scientific Nicolet Nexus 470FT-IR spectrometer as a pellet with KBr. CHN data were recorded on a Elementar VarioMICRO Select 15162036 Analyzer. ¹H and ¹³C NMR spectra were recorded on a AV-400 Bruker using the solvents indicated at 400 and 100 MHz, respectively. Mass spectra were recorded under the conditions of electron ionization (EI). The reaction were carried out in a 2.5-L ultrasonic bath (Model: CUB 2.5L, Citizon, India) with power dissipation as 50 W and frequency of 40 kHz was used for the synthesis. All reactions were monitored by TLC chromatography (pre-coated sheets of silica gel 60) and column chromatography was performed with silica gel 60 (Avra synthesis Pvt. Ltd., 100–200 mesh). Hexane and EtOAc were used as eluting solvents and bought from Avra Synthesis Pvt. Ltd. The reaction solvents THF, CH₂-Cl₂, DMSO, MeOH, Et₂O, and 2,2,2-trifluoroethanol were bought from Avra Synthesis Pvt. Ltd. MeCN of HPLC grade was used directly in the reactions. All other purchased chemicals were used without further purification.



Scheme 2 Catalytic cycle for iodine(III)-catalyzed cyclization of (*E*)-2-styrylphenol to 2-phenylbenzofuran

2-Iodo-4-methylphenol^{28e}

To a 50-mL round-bottom flask containing H₂O (10 mL) and 12 M HCl (2 mL) was added 2-amino-4-methylphenol (615 mg, 5.0 mmol) and the mixture was stirred and cooled to 5 °C using an external ice bath. NaNO₂ (355 mg, 5.15 mmol) in H₂O (2 mL) was added dropwise to this mixture with vigorous stirring and stirring was continued for 30 min after the addition was complete. The solution turned brown in color indicating the formation of diazonium salt which was then treated with a solution of KI (885 mg, 5.35 mmol) in H₂O (2 mL), leading to the formation of dark brown emulsion that was allowed to stir for 45 min. The mixture was then warmed to 40 °C, at this time an evolution of gas was observed; the mixture was reflux for 1 h and then was placed in an ice bath at 0 °C. Excess of iodine was quenched by addition of sodium bisulfite and the mixture was extracted with Et₂O (3 × 10 mL). The combined organic layers were dried (anhyd Na₂SO₄) and filtered and solvent was removed under vacuum. The crude product was purified by column chromatography (hexane) to give the product^{28f} a red oil; yield: 947 mg (81%); bp 76–78 °C.

IR (KBr): 800, 880, 920, 1040, 1099, 1159, 1180, 1270, 1388, 1450, 1505, 1800, 2699, 2790, 3030 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.09 (s, 3 H, CH₃), 5.26 (s, 1 H, OH), 7.74 (d, *J* = 8.4 Hz, 1 H, ArH), 6.86 (dd, *J*₁ = 1.6 Hz, *J*₂ = 6.8 Hz, 1 H, ArH), 7.32 (s, 1 H, ArH).

¹³C NMR (100 MHz, CDCl₃): δ = 20.1, 85.5, 114.9, 130.9, 132.1, 138.5, 152.7.

GC-MS: *m/z* (%) = 234 (100), 127 (10), 107 (70), 78 (25), 77 (70), 53 (17), 51 (30), 50 (17).

(E)-2-Styrylphenols 5a–i; General Procedure

A mixture of 2-iodophenol or 2-iodo-4-methylphenol (1.0 mmol), the styrene derivative (1.3 mmol), Et₃N (0.32 mL, 2.3 mmol), Pd(OAc)₂ (6 mg, 10 mol%), and Ph₃P (19 mg, 0.04 mmol) was refluxed for 7 h. The progress of reaction was monitored by TLC. After completion of the reaction, ice-cold H₂O (10 mL) was added and the mixture was acidified using 1 M aq HCl with continuous stirring to dissolve the solid. The mixture was then extracted with EtOAc (3 × 10 mL) and the organic layer was dried (anhyd Na₂SO₄), filtered, and evaporated in vacuo. Finally, the crude products were purified by column chromatography (silica gel, EtOAc/hexane, 1:8). The isolated products were characterized as (E)-2-styrylphenols **5** by their spectroscopic analysis.

(E)-2-Styrylphenol (5a)²⁶

White solid; yield: 141 mg (72%); mp 141–143 °C (Lit.²⁰ 142–144 °C). IR (KBr): 691, 727, 753, 846, 976, 1080, 1190, 1250, 1340, 1455, 1500, 1590, 3018, 3030, 3573 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 5.09 (br s, 1 H, OH), 6.80 (d, *J* = 8.0 Hz, 1 H, ArH), 6.95 (t, *J* = 7.2 Hz, 1 H, ArH), 7.11 (d, *J* = 16.4 Hz, 1 H, CH), 7.14 (dt, *J*₁ = 1.6 Hz, *J*₂ = 8.4 Hz, 1 H, ArH), 7.25 (t, *J* = 7.6 Hz, 1 H, ArH), 7.35 (d, *J* = 15.2 Hz, 1 H, CH), 7.38 (t, *J* = 6.8 Hz, 2 H, ArH), 7.53 (d, *J* = 8.0 Hz, 3 H, ArH).

¹³C NMR (100 MHz, CDCl₃): δ = 115.9, 121.1, 123.0, 124.7, 126.6, 127.3, 127.6, 127.7, 128.7, 130.2, 137.7, 153.1.

(E)-2-(3-Fluorostyryl)phenol (5b)²⁶

Yellow solid; yield: 132 mg (62%); mp 92–94 °C (Lit.²⁶ 94–96 °C).

IR (KBr): 752, 811, 962, 1093, 1173, 1458, 1501, 1599, 1630, 2228, 3036, 3386 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 4.98 (br s, 1 H, OH), 6.78 (dd, *J*₁ = 1.2 Hz, *J*₂ = 8.0 Hz, 1 H, ArH), 6.93–6.99 (m, 2 H, ArH), 7.10 (d, *J* = 16.4 Hz, 1 H, CH), 7.17 (dt, *J*₁ = 1.6 Hz, *J*₂ = 7.6 Hz, 1 H, ArH), 7.22–7.34 (m, 3 H, ArH), 7.39 (d, *J* = 16.4 Hz, 1 H, CH), 7.53 (dd, *J*₁ = 1.4 Hz, *J*₂ = 7.8 Hz, 1 H, ArH).

¹³C NMR (100 MHz, CDCl₃): δ = 113.3 (d, *J* = 21.4 Hz), 114.8 (d, *J* = 21.3 Hz), 116.4, 121.7, 122.9 (d, *J* = 2.6 Hz), 124.6, 124.8, 127.4, 129.1 (d, *J* = 2.7 Hz), 129.5, 130.5 (d, *J* = 8.4 Hz), 140.5 (d, *J* = 7.8 Hz), 153.5, 163.6 (d, *J* = 243.6 Hz).

(E)-2-(2-Chlorostyryl)phenol (5c)²⁶

Yellow solid; yield: 165 mg (72%); mp 138–140 °C (Lit.²⁶ 138–140 °C). IR (KBr): 533, 694, 727, 761, 846, 978, 1088, 1196, 1251, 1333, 1456, 1499, 1584, 3018, 3047 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 5.01 (br s, 1 H, OH), 6.84 (dd, *J*₁ = 1.0 Hz, *J*₂ = 8.0 Hz, 1 H, ArH), 7.01 (t, *J* = 7.5 Hz, 1 H, ArH), 7.17–7.24 (m, 2 H, ArH), 7.29 (t, *J* = 7.5 Hz, 1 H, ArH), 7.39 (dd, *J*₁ = 1.5 Hz, *J*₂ = 8.0 Hz, 1 H, CH), 7.56 (d, *J* = 16.5 Hz, 1 H, CH), 7.61 (dd, *J*₁ = 1.5 Hz, *J*₂ = 8.0 Hz, 1 H, ArH), 7.75 (dd, *J*₁ = 1.5 Hz, *J*₂ = 8.0 Hz, 1 H, ArH).

¹³C NMR (100 MHz, CDCl₃): δ = 116.0, 121.3, 124.5, 125.7, 126.1, 126.6, 126.9, 127.6, 128.5, 129.1, 129.8, 133.4, 135.8, 153.1.

(E)-2-(4-Chlorostyryl)phenol (5d)²⁶

White solid; yield: 156 mg (68%); mp 123–125 °C (Lit.²⁶ 124–126 °C).

IR (KBr): 750, 979, 1081, 1196, 1256, 1338, 1497, 1586, 1738, 3020, 3521 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 6.69 (dd, *J*₁ = 0.8 Hz, *J*₂ = 8.8 Hz, 1 H, ArH), 6.85 (dt, *J*₁ = 0.8 Hz, *J*₂ = 8.0 Hz, 1 H, ArH), 6.96 (d, *J* = 16.4 Hz, 1 H, CH), 7.04 (dt, *J*₁ = 1.2 Hz, *J*₂ = 8.0 Hz, 1 H, ArH), 7.2 (d, *J* = 8.8 Hz, 2 H, ArH), 7.25 (d, *J* = 16.4 Hz, 1 H, CH), 7.33 (d, *J* = 8.4 Hz, 2 H, ArH), 7.41 (dd, *J*₁ = 1.6 Hz, *J*₂ = 9.2 Hz, 1 H, ArH).

¹³C NMR (100 MHz, CDCl₃): δ = 116.0, 121.7, 123.7, 124.4, 127.2, 127.7, 128.6, 128.8, 128.9, 133.1, 136.2, 153.0.

(E)-2-(4-Bromostyryl)phenol (5e)²⁹

White solid; yield: 197 mg (72%); mp 124–125 °C (Lit.³² 123–124 °C).

IR (KBr): 752, 813, 966, 1087, 1454, 1484, 1498, 1583, 1599, 3060, 3532 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 6.70 (d, *J* = 8.0 Hz, 1 H, ArH), 6.86 (t, *J* = 7.6 Hz, 1 H, ArH), 6.96 (d, *J* = 16.4 Hz, 1 H, CH), 7.08 (dt, *J*₁ = 1.2 Hz, *J*₂ = 8.0 Hz, 1 H, ArH), 7.26 (d, *J* = 6.4 Hz, 2 H, ArH), 7.27 (d, *J* = 14.8 Hz, 1 H, CH), 7.37 (d, *J* = 8.4 Hz, 2 H, ArH), 7.43 (d, *J* = 7.2 Hz, 1 H, ArH).

¹³C NMR (100 MHz, CDCl₃): δ = 116.0, 121.3, 123.8, 124.4, 127.2, 128.1, 128.7, 128.9, 131.8, 136.6, 153.0.

(E)-2-(3-Methylstyryl)phenol (5f)²⁶

Colorless solid; yield: 162 mg (78%); mp 118–120 °C (Lit.²⁶ 118–120 °C).

IR (KBr): 688, 801, 860, 966, 1099, 1263, 1313, 1409, 1486, 1595, 2917, 3022, 3509 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.41 (s, 3 H, CH₃), 5.00 (br s, 1 H, OH), 6.84 (d, *J* = 8.0 Hz, 1 H, ArH), 6.99 (t, *J* = 7.4 Hz, 1 H, ArH), 7.11 (d, *J* = 8.0 Hz, 1 H, ArH), 7.13 (d, *J* = 16.4 Hz, 1 H, CH), 7.18 (dt, *J*₁ = 1.6 Hz, *J*₂ = 8.0 Hz, 1 H, ArH), 7.29 (d, *J* = 16.0 Hz, 1 H, CH), 7.36–7.41 (m, 3 H, ArH), 7.55 (d, *J* = 7.6 Hz, 1 H, ArH).

¹³C NMR (100 MHz, CDCl₃): δ = 21.9, 116.4, 121.6, 123.1, 124.2, 125.2, 127.6, 127.7, 128.9, 129.0, 129.1, 130.7, 137.9, 138.7, 153.3.

(E)-2-(4-Methylstyryl)phenol (5g)²⁶

Light-yellow solid; yield: 164 mg (78%); mp 128–130 °C (Lit.²⁶ 128–130 °C).

IR (KBr): 751, 808, 977, 1089, 1196, 1253, 1334, 1454, 1557, 1617, 1654, 2920, 3530 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.27 (s, 3 H, CH₃), 6.70 (d, *J* = 8.0 Hz, 1 H, ArH), 6.86 (t, *J* = 7.6 Hz, 1 H, ArH), 7.00 (d, *J* = 16.4 Hz, 1 H, CH), 7.07 (t, *J* = 8.4 Hz, 1 H, ArH), 7.08 (d, *J* = 8.4 Hz, 2 H, ArH), 7.23 (d, *J* = 16.4 Hz, 1 H, CH), 7.34 (d, *J* = 8.0 Hz, 2 H, ArH), 7.43 (d, *J* = 7.6 Hz, 1 H, ArH).

¹³C NMR (100 MHz, CDCl₃): δ = 21.3, 115.9, 121.2, 122.0, 124.9, 126.5, 127.2, 128.5, 129.4, 130.2, 134.8, 137.6, 152.9.

(E)-2-(4-Methoxystyryl)phenol (5h)²⁶

Light-yellow solid; yield: 180 mg (80%); mp 144–146 °C (Lit.²⁶ 144–146 °C).

IR (KBr): 755, 818, 856, 951, 1009, 1091, 1161, 1224, 1351, 1452, 1503, 1605, 1744, 3007, 3363 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 3.75 (s, 3 H, OCH₃), 6.72 (d, *J* = 8.0 Hz, 1 H, ArH), 6.82 (d, *J* = 8.8 Hz, 2 H, ArH), 6.86 (t, *J* = 8.0 Hz, 1 H, ArH), 6.99 (d, *J* = 16.4 Hz, 1 H, CH), 7.04 (dt, *J*₁ = 1.6 Hz, *J*₂ = 7.6 Hz, 1 H, ArH), 7.15 (d, *J* = 17.2 Hz, 1 H, CH), 7.39 (d, *J* = 8.4 Hz, 2 H, ArH), 7.42 (dd, *J*₁ = 1.2 Hz, *J*₂ = 7.6 Hz, 1 H, ArH).

¹³C NMR (100 MHz, CDCl₃): δ = 55.4, 114.1, 115.9, 120.9, 121.1, 124.9, 127.0, 127.8, 128.3, 129.8, 130.5, 152.9, 159.9.

(E)-2-(3,4-Dimethoxystyryl)phenol (5i)³⁰

Light-yellow solid; yield: 184 mg (72%); mp 135–137 °C (Lit.³⁰ Yellow oil).

IR (KBr): 760, 840, 954, 1020, 1085, 1161, 1230, 1370, 1510, 1611, 1750, 3369 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 3.87 (s, 3 H, OCH₃), 3.89 (s, 3 H, OCH₃), 6.82–6.88 (m, 2 H, ArH), 6.93 (t, *J* = 7.6 Hz, 1 H, ArH), 7.09 (d, *J* = 16.0 Hz, 1 H, CH), 7.10–7.15 (m, 3 H, ArH), 7.35 (d, *J* = 16.4 Hz, 1 H, CH), 7.55 (dd, *J*₁ = 1.2 Hz, *J*₂ = 7.6 Hz, 1 H, ArH).

¹³C NMR (100 MHz, CDCl₃): δ = 55.8, 60.7, 108.9, 111.3, 115.9, 120.0, 120.6, 121.5, 124.9, 126.6, 128.3, 129.1, 131.1, 148.7, 148.9, 153.6.

(E)-2-[2-(1-Naphthyl)vinyl]phenol (5j)^{20b}

White solid; yield: 184 mg (75%); mp 114–115 °C (Lit.^{20b} 114–115.7 °C).

IR (KBr): 690, 750, 844, 980, 1085, 1200, 1240, 1365, 1475, 1570, 1588, 3020, 3033, 3580 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 5.12 (br s, 1 H, OH), 6.74 (d, *J* = 8.0 Hz, 1 H, ArH), 6.91 (t, *J* = 7.2 Hz, 1 H, ArH), 7.09 (d, *J* = 16.4 Hz, 1 H, CH), 7.28–7.42 (m, 4 H, ArH), 7.54 (d, *J* = 7.6 Hz, 1 H, ArH), 7.69 (t, *J* = 8.2 Hz, 2 H, ArH), 7.78 (d, *J* = 7.2 Hz, 1 H, ArH), 7.83 (d, *J* = 16.4 Hz, 1 H, CH), 8.17 (d, *J* = 7.6 Hz, 1 H, ArH).

¹³C NMR (100 MHz, CDCl₃): δ = 116.1, 121.2, 123.7, 123.8, 125.0, 125.7, 125.8, 126.1, 126.2, 127.4, 127.6, 128.0, 128.6, 128.8, 131.4, 133.7, 135.3, 153.2.

(E)-4-Methyl-2-styrylphenol (5k)^{20b}

White solid; yield: 147 mg (70%); mp 105–107 °C (Lit.^{20b} 106–106.6 °C).

IR (KBr): 690, 750, 850, 971, 1091, 1180, 1253, 1337, 1443, 1591, 1609, 3031, 3580 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.21 (s, 3 H, CH₃), 5.01 (br s, 1 H, OH), 6.61 (d, *J* = 8.0 Hz, 1 H, ArH), 6.84 (dd, *J*₁ = 1.6 Hz, *J*₂ = 6.4 Hz, 1 H, ArH), 7.01 (d, *J* = 16.4 Hz, 1 H, CH), 7.15 (dt, *J*₁ = 1.6 Hz, *J*₂ = 8.4 Hz, 1 H, ArH), 7.23–7.28 (m, 1 H, ArH), 7.31–7.36 (m, 2 H, ArH), 7.43 (d, *J* = 16.2 Hz, 1 H, CH), 7.60–7.67 (m, 2 H, ArH).

¹³C NMR (100 MHz, CDCl₃): δ = 20.6, 115.9, 123.2, 126.5, 127.4, 128.5, 128.6, 129.2, 129.7, 130.1, 131.6, 132.3, 151.0.

GC-MS: *m/z* (%) = 210 (100), 209 (40), 195 (27), 167 (20), 165 (35), 152 (17), 115 (12), 90 (17), 77 (19), 63 (10).

(E)-2-(4-Chlorostyryl)-4-methylphenol (5l)

Anal. Calcd for C₁₅H₁₃O: C, 73.62; H, 5.35. Found: C, 73.70; H, 5.29.

White solid; yield: 168 mg (69%); mp 110–112 °C.

IR (KBr): 756, 980, 1082, 1191, 1260, 1340, 1489, 1590, 1741, 3030, 3525 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.22 (s, 3 H, CH₃), 6.62 (d, *J* = 8.0 Hz, 1 H, ArH), 6.85 (dd, *J*₁ = 1.6 Hz, *J*₂ = 6.4 Hz, 1 H, ArH), 6.97 (d, *J* = 16.4 Hz, 1 H, CH), 7.19 (d, *J* = 14.8 Hz, 1 H, CH), 7.22–7.26 (m, 2 H, ArH), 7.34–7.38 (m, 1 H, ArH), 7.61–7.66 (m, 2 H, ArH).

¹³C NMR (100 MHz, CDCl₃): δ = 20.6, 116.0, 123.9, 127.4, 127.7, 128.5, 128.8, 129.5, 130.2, 131.6, 132.3, 132.9, 151.1.

GC-MS: *m/z* (%) = 246 (35), 244 (100), 209 (20), 194 (15), 181 (21), 166 (25), 166 (29), 165 (50), 89 (27), 76 (22), 75 (14).

Iodine(III)-Catalytic Cyclization of (E)-2-Styrylphenols 5a–l; General Procedure

The mixture of *o*-hydroxystilbene **5** (0.5 mmol, 1.0 equiv), PIDA **6** (16.1 mg, 10 mol%), and *m*-CPBA (–69% pure, 226 mg for 1.0 mmol, 2.0 equiv) in MeCN (5 mL) was irradiated in an ultrasonic bath at r.t. for 20–95 min. The progress of the reaction was monitored by TLC. When the reaction was complete, MeCN was removed under vacuum and water (5.0 mL) was added. The mixture was extracted with EtOAc (3 × 10 mL), and the combined organic layers were dried (anhyd. Na₂SO₄) and filtered and solvent was removed under vacuum. The crude products were purified by column chromatography (hexane) and characterized as 2-arylbenzofurans **7** by spectroscopic analysis.

2-Phenylbenzofuran (7a)²⁶

Colourless solid; yield: 83 mg (85%); mp 233–235 °C (Lit.²⁶ 118–120 °C).

IR (KBr): 685, 742, 800, 920, 1028, 1167, 1205, 1256, 1357, 1452, 1497, 1561, 1567, 1732, 2912, 3051 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.03 (s, 1 H, CH), 7.23 (t, *J* = 7.6 Hz, 1 H, ArH), 7.29 (t, *J* = 7.2 Hz, 1 H, ArH), 7.35 (t, *J* = 7.2 Hz, 1 H, ArH), 7.45 (t, *J* = 8.0 Hz, 2 H, ArH), 7.52 (d, *J* = 8.0 Hz, 1 H, ArH), 7.58 (d, *J* = 6.8 Hz, 1 H, ArH), 7.87 (d, *J* = 7.2 Hz, 2 H, ArH).

¹³C NMR (100 MHz, CDCl₃): δ = 101.3, 111.2, 120.9, 122.9, 124.3, 124.9, 128.6, 128.8, 129.2, 130.5, 154.9, 155.9.

GC-MS: *m/z* (%) = 194 (100), 166 (15), 165 (65), 139 (10), 97 (19), 82 (30), 81 (20), 51 (10).

Anal. Calcd for C₁₄H₁₀O: C, 86.57; H, 5.19. Found: C, 86.78; H, 5.03.

2-(3-Fluorophenyl)benzofuran (7b)²⁶

Colourless solid; yield: 72 mg (68%); mp 78–80 °C (Lit.²⁶ 78–80 °C).

IR (KBr): 800, 870, 930, 1021, 1111, 1230, 1260, 1264, 1280, 1331, 1479, 1562, 1580, 1730, 2980, 3000, 3060 cm⁻¹.

IR (KBr): 675, 740, 810, 931, 1028, 1200, 1255, 1360, 1464, 1567, 1701, 2910, 3060 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 6.99 (s, 1 H, CH), 7.10–7.29 (m, 2 H, ArH), 7.40–7.50 (m, 4 H, ArH), 7.58 (dd, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 1 H, ArH), 7.75–7.86 (m, 3 H, ArH), 8.35–8.42 (m, 1 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 104.8, 110.2, 119.9, 121.9, 123.2, 124.2, 124.4, 125.1, 125.9, 126.3, 127.2, 127.6, 128.0, 128.5, 129.7, 132.9, 153.9, 154.6.

GC-MS: m/z (%) = 244 (100), 180 (50), 110 (37), 93 (50), 72 (35), 53 (60).

Anal. Calcd for $\text{C}_{18}\text{H}_{12}\text{O}$: C, 88.50; H, 4.95. Found: C, 88.37; H, 4.67.

5-Methyl-2-phenylbenzofuran (7k)^{20b}

Colourless solid; yield: 86 mg (83%); mp 128–130 °C (Lit.^{20b} 128–129.6 °C).

IR (KBr): 690, 738, 810, 921, 1030, 1165, 1201, 1266, 1352, 1460, 1496, 1570, 1563, 2910, 3042 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 2.36 (s, 3 H, CH_3), 6.87 (s, 1 H, CH), 7.01 (dd, J_1 = 1.2 Hz, J_2 = 7.2 Hz, 1 H, ArH), 7.21–7.28 (m, 2 H, ArH), 7.30–7.38 (m, 3 H, ArH), 7.74–7.79 (m, 2 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 21.4, 101.1, 110.7, 120.8, 124.9, 125.6, 128.4, 128.8, 129.3, 130.7, 132.4, 153.4, 156.0.

GC-MS: m/z (%) = 208 (100), 207 (45), 179 (15), 178 (25), 165 (30), 104 (17), 89 (14), 76 (18).

2-(4-Chlorophenyl)-5-methylbenzofuran (7l)³²

Colourless solid; yield: 93 mg (77%); mp 189–191 °C (Lit.³² 185–187 °C).

IR (KBr): 728, 807, 840, 920, 1010, 1072, 1217, 1260, 1254, 1309, 1358, 1391, 1445, 1575, 1741, 2859, 2923, 3060 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 2.37 (s, 3 H, CH_3), 6.86 (s, 1 H, CH), 7.02 (dd, J_1 = 1.6 Hz, J_2 = 6.8 Hz, 1 H, ArH), 7.26–7.38 (m, 4 H, ArH), 7.64–7.72 (m, 2 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 21.4, 101.5, 110.7, 120.8, 125.9, 126.1, 128.7, 129.0, 129.1, 132.5, 134.2, 153.4, 154.9.

GC-MS: m/z (%) = 244 (35), 242 (100), 241 (32), 179 (25), 178 (40), 121 (22), 89 (18), 76 (20).

Funding Information

Financial support by the DST New Delhi (Grant No.: SB/FT/CS-068/2014) is gratefully acknowledged.

Acknowledgment

We thank the SAIF department, VIT Vellore for spectrometric data.

Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0037-1610650>.

References

- (1) (a) Sill, M. C.; Das, A. K.; Itou, T.; Karmakar, S.; Mukherjee, P. K.; Mizuguchi, H.; Kashiwada, Y.; Fukui, H.; Nemoto, H. *Bioorg. Med. Chem.* **2015**, *23*, 6869. (b) Simonetti, S. O.; Larghi, E. L.; Bracca, A. B. J.; Kaufman, T. S. *Nat. Prod. Rep.* **2013**, *30*, 941. (c) Dawood, K. M. *Expert Opin. Ther. Pat.* **2013**, *23*, 1133. (d) Clair, J. J. L.; Rheingold, A. L.; Burkart, M. D. *J. Nat. Prod.* **2011**, *74*, 2045. (e) Jakupovic, J.; Schuster, A.; Ganzer, U.; Bohlmann, F.; Boldt, P. E. *Phytochemistry* **1990**, *29*, 2217. (f) Gommers, F. J. *Phytochemistry* **1971**, *10*, 1945. (g) Stark, J. B.; Walter, E. D.; Owens, H. S. *J. Am. Chem. Soc.* **1950**, *72*, 1819.
- (2) (a) Li, M.-Y.; Xiao, Q.; Pan, J.-Y.; Wu, J. *Nat. Prod. Rep.* **2009**, *26*, 281. (b) Miles, D. H.; Lho, D. S.; De la Cruz, A. A.; Gomez, E. D.; Weeks, J. A.; Atwood, J. L. *J. Org. Chem.* **1987**, *52*, 2930.
- (3) Bohlmann, F.; Zdero, C. *Chem. Ber.* **1977**, *110*, 487.
- (4) Wine-show, S.; Ian-Lih, T.; Che-Ming, T.; Ih-Sheng, C. *Phytochemistry* **1994**, *36*, 213.
- (5) (a) Timmers, M. A.; Guerrero-Medina, J. L.; Esposito, D.; Grace, M. H.; Paredes-Lopez, O.; Garcia-Saucedo, P. A.; Lila, M. A. *J. Agric. Food Chem.* **2015**, *63*, 10459. (b) Yurdanur, Y.; Huseyin, A. *Phytochemistry* **2003**, *63*, 939.
- (6) Abdel-Wahab, B. F.; Abdel-Aziz, H. A.; Ahmed, E. M. *Eur. J. Med. Chem.* **2009**, *44*, 2632.
- (7) Li, Y.-P.; Dong, L.-B.; Chen, D.-Z.; Li, H.-M.; Zhong, J.-D.; Liu, X.; Wang, B.; Li, R.-T. *Phytochem. Lett.* **2013**, *6*, 281.
- (8) (a) Naik, R.; Harmalkar, D. S.; Xu, X.; Jang, K.; Lee, K. *Eur. J. Med. Chem.* **2015**, *90*, 379. (b) Khanam, H.; Shamsuzzaman *Eur. J. Med. Chem.* **2015**, *97*, 483. (c) Nevagi, R. J.; Dighe, S. N. *Eur. J. Med. Chem.* **2015**, *97*, 561.
- (9) (a) Kucuksayan, E.; Ozben, T. *Curr. Top. Med. Chem.* **2017**, *17*, 907. (b) Giordano, C.; Rovito, D.; Barone, I.; Mancuso, R.; Bonfiglio, D.; Giordano, F.; Catalano, S.; Gabriele, B.; Ando, S. *DNA Repair* **2017**, *51*, 20. (c) Zaher, A. F.; Abuel-Maaty, S. M.; El-Nassan, H. B.; Amer, S. A. S.; Abdelghany, T. M. *J. Enzyme Inhib. Med. Chem.* **2016**, *31*, 145. (d) Ghorab, M. M.; Ragab, F. A.; Heiba, H. I.; Soliman, A. M. *Eur. J. Med. Chem.* **2016**, *117*, 8. (e) Khodarahmi, G.; Asadi, P.; Hassanzadeh, F.; Khodarahmi, E. *J. Res. Med. Sci.* **2015**, *20*, 1094. (f) Shioya, H. R.; Agatruna, T.; Furukawa, H.; Naruto, S.; Sugano, Y. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 455.
- (10) (a) Ryu, C. K.; Song, A. L.; Lee, J. Y.; Hong, J. A.; Yoon, J. H.; Kim, A. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 6777. (b) Aslam, S. N.; Stevenson, P. C.; Phythian, S. J.; Vietch, N. C.; Hall, D. R. *Tetrahedron* **2006**, *62*, 4214.
- (11) Kaltenbronn, J. S.; Quin, I.; Reisdorph, B. R.; Kiutchko, S.; Reynolds, E. E.; Welch, K. M.; Flynn, M. A.; Doherty, A. M. *Eur. J. Med. Chem.* **1997**, *32*, 425.
- (12) Ohemeng, K. A.; Apollina, M. A.; Nguyen, V. N.; Schwender, C. F.; Singer, M.; Steber, M.; Ansell, J.; Argentieri, D.; Hageman, W. *J. Med. Chem.* **1994**, *37*, 3663.
- (13) Kiyama, R.; Homna, T.; Hayashi, K.; Ogawa, M.; Hara, M.; Fujimoto, M.; Fujishita, T. *J. Med. Chem.* **1995**, *38*, 2728.
- (14) (a) Shankar, B.; Jalapathi, P.; Vianala, S.; Kundle, K. R. *Pharma Chem.* **2016**, *8*, 192. (b) Zelova, H.; Hanakova, Z.; Cermakova, Z.; Smejkal, K.; Acqua, S. D.; Babula, P.; Cvacka, J.; Hosek, J. *J. Nat. Prod.* **2014**, *77*, 1297.
- (15) (a) He, W.; Xu, B.; Bao, J.; Deng, X.; Liu, W.; Zhang, Y.; Jiang, F.; Fu, L. *Med. Chem. Res.* **2016**, *25*, 2485. (b) Hiremathad, A.; Patil, M. R.; Chethana, K. R.; Chand, K.; Santos, M. A.; Keri, R. S. *RSC Adv.* **2015**, *5*, 96809. (c) Kone, W. M.; Atindehou, K. K.; Terreaux, C.; Hostettmann, K.; Traore, D.; Dosso, M. *J. Ethnopharmacol.* **2004**, *93*, 43.

- (16) (a) Tang, H.-J.; Zhang, X.-W.; Yang, L.; Li, W.; Li, J.-H.; Wang, J.-X.; Chen, J. *Eur. J. Med. Chem.* **2016**, *124*, 637. (b) Khan, M. W.; Alam, M. J.; Rashid, M. A.; Chowdhury, R. *Bioorg. Med. Chem.* **2005**, *13*, 4796.
- (17) (a) Melvin, P. R.; Hazari, N.; Beromi, M. M.; Shah, H. P.; Williams, M. J. *Org. Lett.* **2016**, *18*, 5784. (b) Wang, X.-Y.; Song, H.-X.; Wang, S.-M.; Yang, J.; Qin, H.-L.; Jiang, X.; Zhang, C.-P. *Tetrahedron* **2016**, *72*, 7606. (c) Rajesh, M.; Puri, S.; Kant, R.; Reddy, M. S. *Org. Lett.* **2016**, *18*, 4332. (d) Watanabe, K.; Mino, T.; Ikematsu, T.; Hatta, C.; Yoshida, Y.; Sakamoto, M. *Org. Chem. Front.* **2016**, *3*, 979. (e) Yang, D.; Zhu, Y.; Yang, N.; Jiang, Q.; Liu, R. *Adv. Synth. Catal.* **2016**, *358*, 1731. (f) Bosiak, M. J. *ACS Catal.* **2016**, *6*, 2429. (g) Kumar, A.; Gangwar, M. K.; Prakasham, A. P.; Mhatre, D.; Kalita, A. C.; Ghosh, P. *Inorg. Chem.* **2016**, *55*, 2882. (h) Mandali, P. K.; Chand, D. K. *Synthesis* **2015**, *47*, 1661. (i) Zhou, R.; Wang, W.; Jiang, Z.-J.; Wang, K.; Zheng, X.-L.; Fu, H.-Y.; Chen, H.; Li, R.-X. *Chem. Commun.* **2014**, *50*, 6023. (j) Chen, W.; Li, P.; Miao, T.; Meng, L.-G.; Wang, L. *Org. Biomol. Chem.* **2013**, *11*, 420. (k) Arcadi, A.; Blesi, F.; Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Marinelli, F. *Tetrahedron* **2013**, *69*, 1857. (l) Thevenin, M.; Thoret, S.; Grellier, P.; Dubois, J. *Bioorg. Med. Chem.* **2013**, *21*, 4885. (m) Wang, S.; Li, P.; Yu, L.; Wang, L. *Org. Lett.* **2011**, *13*, 5968.
- (18) (a) Qin, D.-D.; Chen, W.; Tang, X.; Yu, W.; Wu, A.-A.; Liao, Y.; Chen, H.-B. *Asian J. Org. Chem.* **2016**, *5*, 1345. (b) Woo, H.; Kim, D.; Park, J. C.; Kim, J. W.; Park, S.; Lee, J. M.; Park, K. H. *J. Mater. Chem. A* **2015**, *3*, 20992. (c) Wang, Y.; Zhou, C.; Wang, R. *Green Chem.* **2015**, *17*, 2910. (d) Arcadi, A.; Blesi, F.; Cacchi, S.; Fabrizi, G.; Goggiamani, A. *Tetrahedron Lett.* **2011**, *52*, 5149.
- (19) (a) Alcaide, B.; Almendros, P.; Busto, E.; Lazaro-Milla, C. J. *Org. Chem.* **2017**, *82*, 2177. (b) Xia, Z.; Khaled, O.; Mouries-Mansuy, V.; Ollivier, C.; Fensterbank, L. J. *Org. Chem.* **2016**, *81*, 7182.
- (20) (a) Thankachan, A. P.; Sindhu, K. S.; Ujwaldev, S. M.; Anilkumar, G. *Tetrahedron Lett.* **2017**, *58*, 536. (b) Duan, X.-F.; Zeng, J.; Zhang, Z.-B.; Zi, G.-F. *J. Org. Chem.* **2007**, *72*, 10283.
- (21) Takeda, N.; Miyata, O.; Naito, T. *Eur. J. Org. Chem.* **2007**, 1491.
- (22) (a) Ghosh, S.; Das, J. *Tetrahedron Lett.* **2011**, *52*, 1112. (b) Yuan, Y.; Men, H.-B.; Lee, C. J. *Am. Chem. Soc.* **2004**, *126*, 14720. (c) Aslam, S. N.; Stevenson, P. C.; Phythian, S. J.; Veitch, N. C.; Hall, D. R. *Tetrahedron* **2006**, *62*, 4214.
- (23) Sun, S.-X.; Wang, J.-J.; Xu, Z.-J.; Cao, L.-Y.; Shi, Z.-F.; Zhang, H.-L. *Tetrahedron* **2014**, *70*, 3798.
- (24) (a) Singh, F. V.; Mangaonkar, S. R.; Kole, P. B. *Synlett* **2018**, 29, 199. (b) Yoshimura, A.; Zhdankin, V. V. *Chem. Rev.* **2016**, *116*, 3328. (c) Singh, F. V.; Wirth, T. *Comprehensive Organic Chemistry*, 2nd ed.; Knochel, P., Ed.; Elsevier: Amsterdam, **2014**, 881. (d) Zhdankin, V. V. *J. Org. Chem.* **2011**, *76*, 1185. (e) Merritt, E. A.; Olofsson, B. *Angew. Chem. Int. Ed.* **2009**, *48*, 9052. (f) Zhdankin, V. V. *ARKIVOC* **2009**, (i), 1; <http://www.arkat-usa.org/home>. (g) Farooq, U.; Shah, A. A.; Wirth, T. *Angew. Chem. Int. Ed.* **2009**, *48*, 1018. (h) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2008**, *108*, 5299. (i) Ladziata, U.; Zhdankin, V. V. *Synlett* **2007**, 527. (j) Wirth, T. *Angew. Chem. Int. Ed.* **2005**, *44*, 3656. (k) Moriarty, R. M. J. *Org. Chem.* **2005**, *70*, 2893. (l) Wirth, T. *Inorganic Synthesis Highlights V*; Schmalz, H.-G.; Wirth, T., Eds.; Wiley-VCH: Weinheim, **2003**, 144. (m) Wirth, T. *Top. Curr. Chem.* **2003**, *224*. (n) Zhdankin, V. V. *Chem. Rev.* **2002**, *102*, 2523. (o) Wirth, T. *Angew. Chem. Int. Ed.* **2001**, *40*, 2812.
- (25) (a) Qian, G.; Liu, B.; Tan, Q.; Zhang, S.; Xu, B. *Eur. J. Org. Chem.* **2014**, 4837. (b) Mizar, P.; Wirth, T. *Angew. Chem. Int. Ed.* **2014**, *53*, 5993. (c) Singh, F. V.; Wirth, T. *Synthesis* **2013**, *45*, 2499; and references cited therein. (d) Singh, F. V.; Rehbein, J.; Wirth, T. *ChemistryOpen* **2012**, *1*, 245. (e) Kajiyama, D.; Saitoh, T.; Yamaguchi, S.; Nishiyama, S. *Synthesis* **2012**, *44*, 1667. (f) Paz, N. R.; Santana, A. G.; Suarez, C. G.; Francisco, E.; Gonzalez, C. C. *Org. Lett.* **2012**, *14*, 3388. (g) Wardrop, D. J.; Yermolina, M. V.; Bowen, E. G. *Synthesis* **2012**, *44*, 1199. (h) Singh, F. V.; Wirth, T. *Org. Lett.* **2011**, *13*, 6504. (i) Du, X.; Chen, H.; Chen, Y.; Chen, J.; Liu, Y. *Synlett* **2011**, 1010. (j) Wang, H.; Fan, R. J. *Org. Chem.* **2010**, *75*, 6994. (k) Moriarty, R. M.; Tyagi, S.; Kinch, M. *Tetrahedron* **2010**, *66*, 5801. (l) Bose, S. S.; Idrees, M. *Synthesis* **2010**, 393. (m) Pardo, L. M.; Tellitu, I.; Domínguez, E. *Synthesis* **2010**, 971.
- (26) Singh, F. V.; Wirth, T. *Synthesis* **2012**, *44*, 1171.
- (27) Singh, F. V.; Wirth, T. *Chem. Asian J.* **2014**, *9*, 950; and references cited therein.
- (28) (a) Mason, T. J. *Chem. Soc. Rev.* **1997**, *26*, 443. (b) Ramazani, A.; Rouhani, M.; Joo, S. W. *Ultrason. Sonochem.* **2016**, *28*, 393. (c) Cappelletti, L.; Vaghi, L.; Rinaldi, L.; Rotolo, L.; Palmisano, G.; Cravotto, G.; Penoni, A. *Ultrason. Sonochem.* **2015**, *27*, 30. (d) Dohi, T.; Maruyama, A.; Yoshimura, M.; Morimoto, K.; Tohma, H.; Kita, Y. *Angew. Chem. Int. Ed.* **2005**, *44*, 6193. (e) Reddy, R. K.; Venkateshwar, M.; Maheswari, U. C.; Kumar, S. P. *Tetrahedron Lett.* **2010**, *51*, 2170. (f) Keipour, H.; Khalilzadeh, M. A.; Mohtat, B.; Hosseini, A.; Zareyee, D. *Chin. Chem. Lett.* **2011**, *22*, 1427.
- (29) Zhang, Y.; Shen, M.; Cui, S.; Hou, T. *Bioorg. Med. Chem. Lett.* **2014**, *24*, 5470.
- (30) Chong, K.-W.; Hong, F.-J.; Thomas, N. F.; Low, Y.-Y.; Kam, T.-S. *J. Org. Chem.* **2017**, *82*, 6172.
- (31) Liao, L.-Y.; Shen, G.; Zhang, X.; Duan, X.-F. *Green Chem.* **2012**, *14*, 695.
- (32) Wang, X.; Liu, M.; Xu, L.; Wang, Q.; Chen, J.; Ding, J.; Wu, H. *J. Org. Chem.* **2013**, *78*, 5273.