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Domino One-Pot Process for the Synthesis of Isobenzofuran-1(3*H*)-ones via [Cu]-Catalysis Using Water as the Green Solvent

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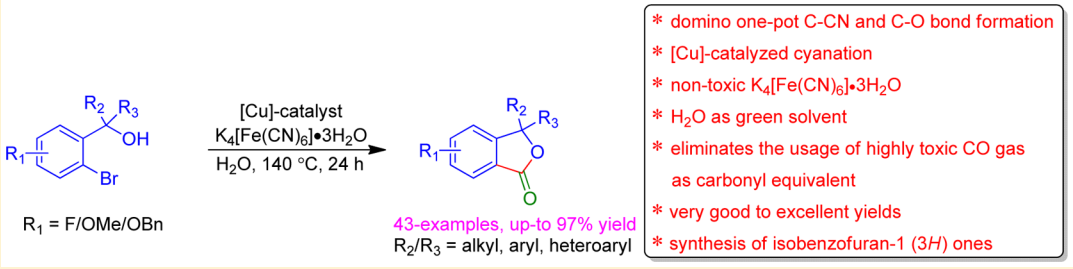
Supporting Information



ABSTRACT: An efficient domino one-pot strategy via [Cu]-catalyzed intermolecular "cyanation" of *o*-bromobenzyl alcohols → in situ intramolecular "nucleophilic attack" → "hydrolysis" is presented, for the synthesis of isobenzofuran-1(3*H*)-ones. Significantly, the reaction is successfully carried out under environmentally benign conditions, using water as sole green solvent.

INTRODUCTION

Domino one-pot processes are ideal for the synthesis of complex molecules by permitting the construction of more than one chemical bond, as they encompass eliminating tedious isolations and purification techniques of the intermediate product(s).[1] Hence, such domino processes enable synthetic chemists to save time, energy and unwanted waste generation. In this context, transition-metal catalysis plays an important role for the development of new synthetic methods through the efficient construction of C−C and C−heteroatom bonds with increasing molecular complexity.[2] In continuation of our ongoing research interest, for the development of one-pot domino processes under transition-metal catalysis,[3,4] we developed an efficient one-pot domino [Cu]-catalyzed intermolecular Sonogashira coupling and intramolecular 5-exo-dig oxacyclization for the synthesis of isobenzofurans.[5] Herein, we present an efficient domino one-pot method for the synthesis of isobenzofuran-1(3*H*)-ones. Notably, unlike established methods for the simple cyanation, particularly, using transition-metal catalyzed cyanation with nontoxic cyanating agents, we aimed at one-pot cyanation → intramolecular nucleophilic oxa-cyclization → hydrolysis sequence for the formation of isobenzofuran-1(3*H*)-ones. Isobenzofuran-1(3*H*)-ones are an important bicyclic lactone present in many natural products that exhibit broad spectrum of biological activity[6] and are versatile building blocks for the synthesis of natural as well as pharmaceutically important products (Figure 1).[7] In this context, there were some interesting reports on the synthesis of isobenzofuran-1(3*H*)-ones (Scheme 1).[8] Significantly, the present method has some notable advantages such as (1) [Cu]-catalyzed intermolecular cyanation using a nontoxic hexacyanoferrate(II) cyanide source;[9] (2) the newly formed nitrile group is ultimately transformed into a carbonyl group with the aid of the pre-existing internal nucleophile (hydroxyl) and hydrolysis sequence; (3) the nontoxic cyanide source assists as a chemical equivalent of highly toxic carbon monoxide (CO) gas[10] (Scheme 1); (4) most importantly, the reaction operates under environmentally benign conditions using water as the sole green solvent.

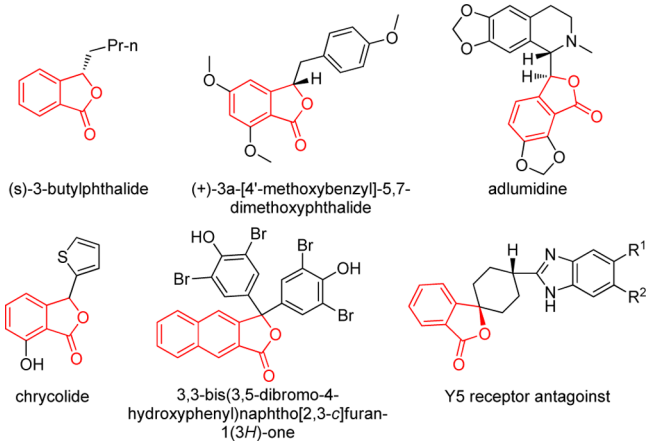


Figure 1. Representative examples of isobenzofuran-1(3*H*)-ones based drugs and natural products.

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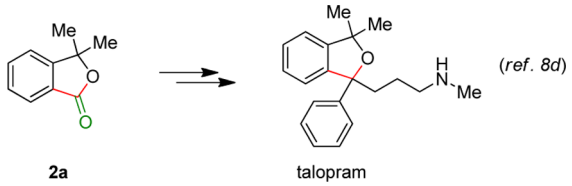
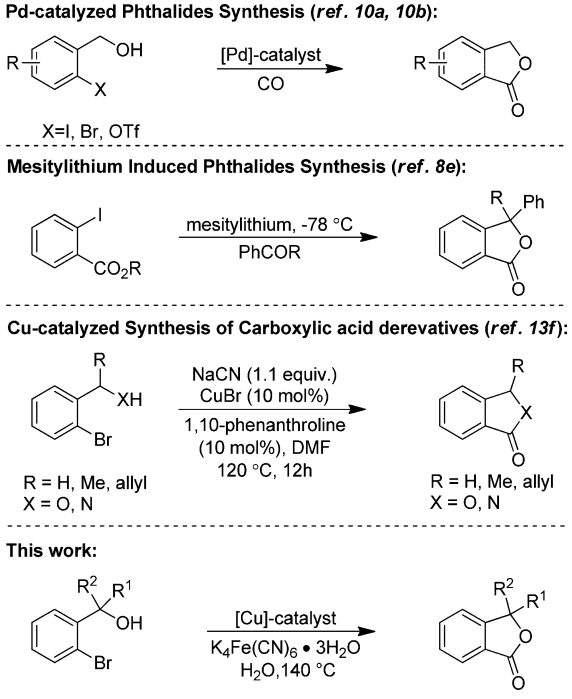
Scheme 1. Reported Approach to Norepinephrine Transporter Inhibitor Talopram from 2a



Notably, the synthesis of talopram (a norepinephrine transporter inhibitor) was accomplished using isobenzofuran-1(3*H*)-one **2a** as the synthetic precursor (Scheme 1).[8d]

Certainly, the preparation of aryl nitriles is indispensable in synthetic chemistry, as the cyano group is a ubiquitous functionality in many natural/unnatural organic compounds.[11] Among the most common classical methods for the preparation of aryl nitriles are the Rosenmund−von Braun reaction of aryl halides and the Sandmeyer reaction of aryl diazonium salts.[12] While stoichiometric amounts of various metal cyanides [AgCN, KCN, NaCN, TMSCN and $Zn(CN)_2$] were also employed as cyanide sources.[13] Very recently, Sudalaia[13f] reported copper mediated one-pot cyanation followed by cyclization to give lactones/amides (Scheme 2). However, the

Scheme 2. Present Study vs Representative Previous Approaches for the Synthesis of Isobenzofuranones

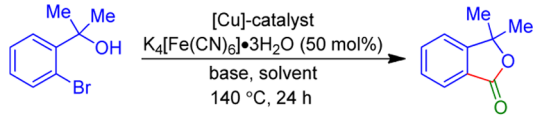


main drawback is the use of a highly toxic metal salt (NaCN) as the source of cyano group. Similarly, Wang et al. reported the synthesis of only one such example using toxic CuCN as cyanating agent, during their synthesis of designed PAR-1 antagonist.[13g] However, recent developments based on transitionmetal mediated cyanation have demonstrated widespread application, particularly, those with the use of less/nontoxic cyanide sources.[14,15] Notably, Buchwald et al. disclosed the [Cu]-catalyzed cyanation of aryl bromides.[16] Quite significantly, Beller and co-workers described the formation of aryl nitriles from aryl bromides using nontoxic cyanide source $K_4[Fe(CN)_6]$ under [Cu]-catalysis.[17]

RESULTS AND DISCUSSION

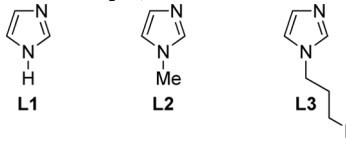
We assumed that the suitably positioned pre-existing nucleophile (hydroxyl group) of the aryl halide would promote an internal nucleophilic addition onto the newly formed cyano group under [Cu]-catalysis in one-pot. The required *α*,*α*-disubstituted (2-bromophenyl)methanols **1a**, were synthesized using the established protocol.[3,5] To identify the optimized reaction conditions, *α*,*α*-dimethyl-(2-bromophenyl)methanol **1a** was screened under different reaction conditions. Beller et al.[9] showed that imidazoles are ideal ligands to improve the stability and selectivity of the [Cu]-catalyst. Therefore, the reaction was explored with the imidazole-based ligands. Gratifyingly, the reaction of **1a** with 50 mol % potassium hexacyanonferrate(II) in the presence of CuI (10 mol %)/imidazole (L1, 200 mol %), in toluene furnished the lactone product **2a** in good yield (71%, Table 1, entry 1). To

Table 1. Optimization One-Pot Cyanation → Internal Nucleophilic Attack → Hydrolysis Protocol



1a **2a**

entry[a]	[Cu] (10 mol %)	ligand (200 mol %)	solvent	base (2 equiv)	**2a** (%)[b]
1	CuI	**L1**	toluene	–	71
2	CuI	**L1**	DMF	–	64
3	CuI	**L2**	toluene	–	58[c]
4	CuBr	**L1**	toluene	–	52[c]
5	$CuSO_4·5H_2O$	**L1**	toluene	–	63
6	CuI	–	toluene	Na_2CO_3	41[c]
7	CuI	–	toluene	K_2CO_3	43[c]
8	CuI	**L1**	1,4-dioxane	–	27[c]
9	CuI	**L3**	toluene	–	68
10	None	**L1**	toluene	–	SM[d]
11	**CuI**	**L1**	**H_2O**	–	**96**
12	CuI	**L1** (**TBAI 2 equiv**)	H_2O	–	93



L1 **L2** **L3**

[a]All reactions were carried out on a 0.5 mmol scale of **1a** in 0.5 mL solvent. [b]Isolated yields of chromatographically pure products. [c]Starting material was also recovered along with the product isolation. [d]Starting material was recovered.

check the scope and limitations of the method, these conditions were applied to 13 analogues as well. Notably, the reaction scope was quite broad and gave the products **2**, in comparable yields (Table 2). Similarly, the reaction in DMF gave the product **2a** in modest yield (64%, Table 1, entry 2). There was not much difference in the yield of **2a** with 1-methylimidazole (**L2**, 200%) (58%, Table 1, entry 3). However, the reaction with other catalysts such as CuBr and $CuSO_4·5H_2O$, gave the product **2a** in 52% and 63% yields, respectively (Table 1, entries 4 and 5). The reaction was inferior in the presence of

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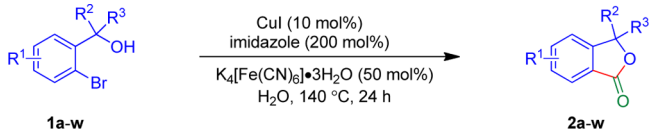
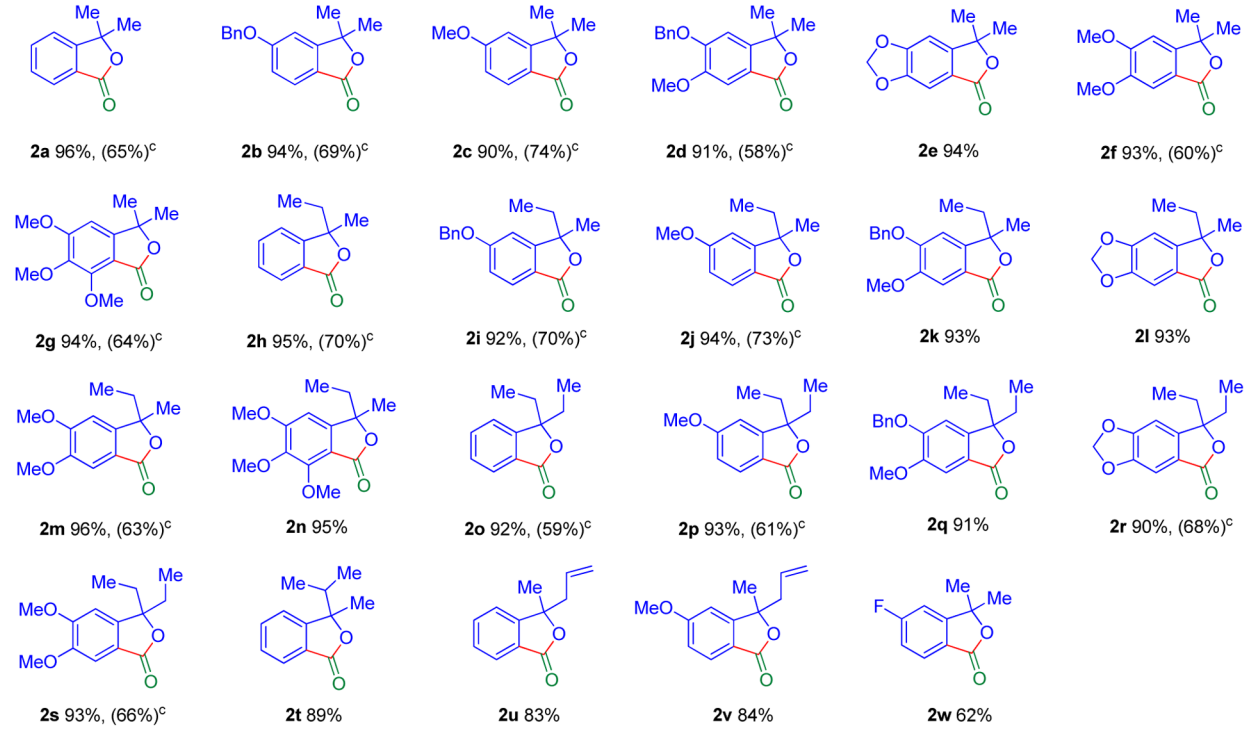
Table 2. Scope of One-Pot Cyanation → Internal Nucleophilic Attack → Hydrolysis to Give 2[a,b]



1a-w 2a-w



[a]Reaction conditions: **1a−w** (0.50 mmol), $K_4Fe(CN)_6{\cdot}3H_2O$ (50 mol %), Imidazole (200 mol %), CuI (10 mol %), in 0.5 mL of H_2O, at 140 °C for 24 h. [b]Isolated yields of chromatographically pure products. [c]Reaction conditions: **1** (0.50 mmol), $K_4Fe(CN)_6{\cdot}3H_2O$ (50 mol %), Imidazole (200 mol %), CuI (10 mol %), 0.5 mL of toluene, at 140 °C for 24 h; yields in the parentheses are isolated yields of chromatographically pure products.

the base (Na_2CO_3 and K_2CO_3) and without ligand(s) (Table 1, entries 6 and 7). On the other hand, 1,4-dioxane as reaction medium, gave poor yield of the product **2a** (Table 1, entry 8). The ligand 1-butylimidazole (L3, 200%) also proved to be as good as imidazole (**L1**), and gave the product **2a** in modest yield (68%, Table 1, entry 9). No progress of the reaction in the absence of catalyst revealed the essence of [Cu]-catalyst to drive the reaction (Table 1, entry 10). Gratifyingly, the use of H_2O as the sole green solvent proved to be the best and furnished the product **2a** in excellent yield (96%, Table 1, entry 11). The use of phase transfer catalyst as an additive, offered no advantage (93%, Table 1, entry 12). It is worth mentioning that low catalytic loading (5 mol % of CuI) or with 20 mol % of $K_4[Fe(CN)_6]$ as cyanating agent or catalytic amount of imidazole ligands (20 mol %), always lead to recovery of starting material **1a** along with product **2a** formation, for the standard duration of time (24 h).

Among all reaction conditions screened, the conditions in entry 11 of Table 1 were found best. Therefore, to check the scope and generality of the method these optimized conditions were applied to other 2-bromobenzyl tertiary alcohols **1a−w**. Delightfully, the reaction showed broad substrate scope and furnished the corresponding cyclic lactones **2a−w** in very good to excellent yields (Table 2). Interestingly, this method was amenable to 2-bromobenzyl tertiary alcohols 1 with simple to dense electron-rich 2-bromoaryl ring and variety of alkyl substituents connected to the benzylic carbon of alcohols **1a−w** (i.e., gem-dialkyl groups). The reaction was also amenable with allyl group on the benzylic carbon and gave the corresponding products **2u** and **2v** (Table 2). The structures of **2** were confirmed by single-crystal X-ray diffraction analysis of **2d** and **2f** (see the Supporting Information). Interestingly, the reaction was also successful to deliver the system **2w** with electron deactivating fluoro substituent on the aromatic ring as well (Table 2).

We also presumed that interesting spiro-tricyclic systems could be obtained by using this protocol. Thus, the tertiary alcohol **1x** was prepared using sonochemically accelerated Barbier conditions by treating the methyl benzoate **8** with excess amount of allyl bromide. Unfortunately, the ring closing metathesis (RCM) reaction did not proceed with Gurbb's first-generation catalyst under different conditions. However, RCM reaction was smooth in the presence of Gurbb's second-generation in refluxing benzene and gave the cyclic tertiary alcohol **1y** in excellent yield 93%. Finally, as expected, the spiro-tricyclic lactone **2x** was accomplished in excellent yield 94%, under standard conditions (Scheme 3).

The scope of the reaction was extended to include aryl substitution at the benzylic position. To our delight, the reaction provided consistent yields with those established systems (Table 2) and led to the formation of analogous lactone products **4a−s** (Table 3). It is noteworthy that this protocol was quite successful in delivering diversified lactone products **4a−s** containing a quaternary carbon atom bearing

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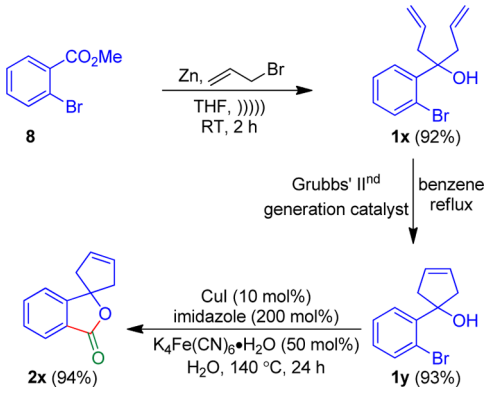
Scheme 3. Approach for the Synthesis of Spiro Cyclic Isobenzofuranone



methyl-phenyl, methyl-(3-methoxylphenyl), methyl-(2-thiophene), allyl-phenyl and diphenyl substituents apart from the simple to electron rich 2-bromoaryl moiety (Table 3). However, the reactions of primary and secondary 2-bromobenzyl alcohols were not successful under the established conditions. Whereas the presence of *N*,*N*′-dimethylethylenediamine (DMEDA), promoted the simple oxidation of alcohol moiety. It may be a favorable gem-dialkyl effect (Thorpe–Ingold effect) to assisting this cyclization.

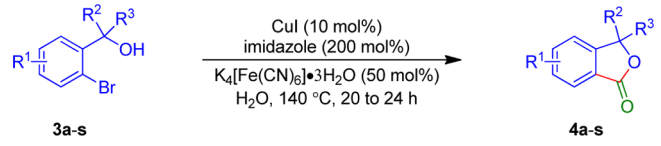
CONCLUSIONS

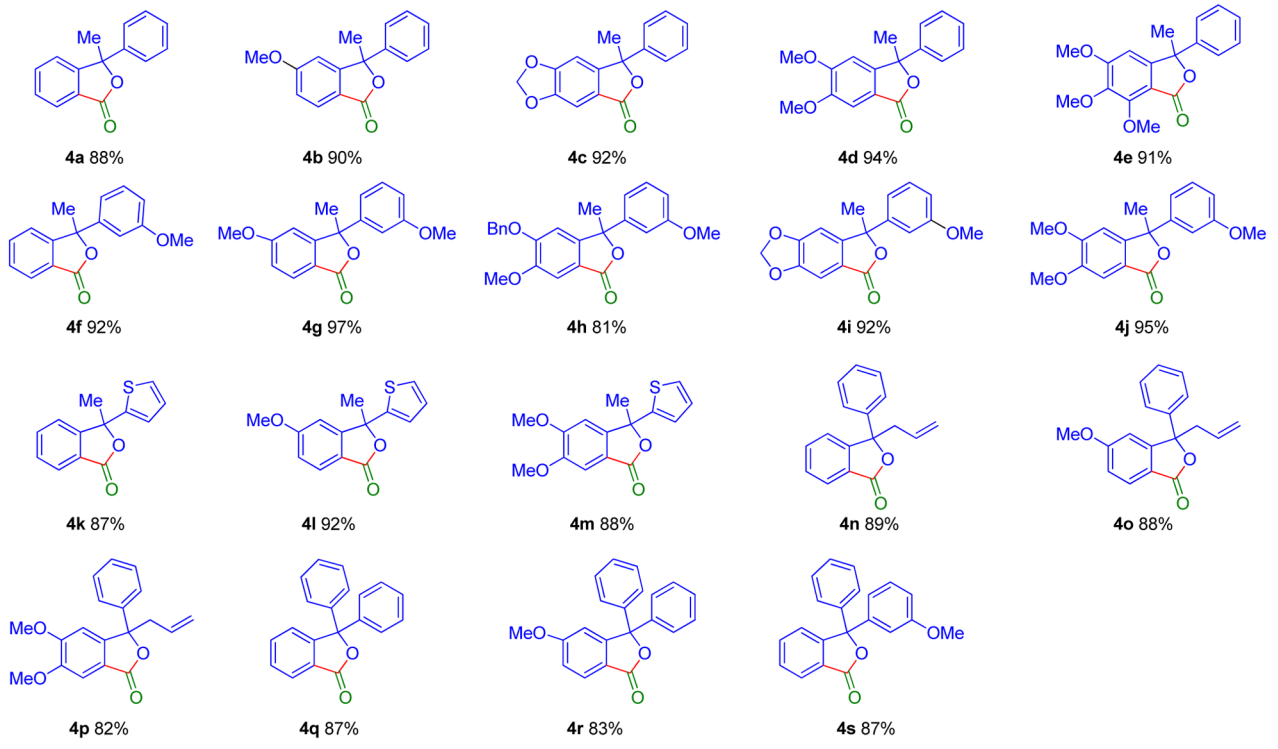
In conclusion, we have developed an efficient one-pot domino [Cu]-catalyzed intermolecular cyanation → oxa-cyclization → hydrolysis strategy for the synthesis of isobenzofuran-1(3*H*) ones. The present method uses environmentally benign water as the sole green solvent. Notably, the [Cu]-catalyzed cyanation was accomplished using cheap and nontoxic cyanide source, potassium hexacyanoferrate(II) ($K_4[Fe(CN)_6]$) and eliminates the use of highly toxic carbon-monoxide gas to synthesis products. The reaction was quite successful on wide variety of 2-bromobenzyl tertiary alcohols.

EXPERIMENTAL SECTION

General Considerations. IR spectra were recorded on a FTIR spectrophotometer. ^{1}H NMR spectra were recorded on 400 MHz spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H = 0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C NMR spectra were recorded on 100 MHz spectrometer at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CHCl_3$ [δ_C = 77.00 ppm (central line of triplet)]. In the ^{13}C NMR, the nature of carbons (C, CH, CH_2, and CH_3) was determined by recording the DEPT-135 spectra and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2) and q = quartet (for CH_3). In the ^{1}H NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet and br s. = broad

Table 3. Scope of One-Pot Cyanation → Internal Nucleophilic Attack → Hydrolysis to Give 4[a,b]





[a]Reaction conditions: **3a–s** (0.50 mmol), $K_4Fe(CN)_6{\cdot}3H_2O$ (50 mol %), Imidazole (200 mol %), CuI (10 mol %), in 0.5 mL of H_2O, at 140 °C for 24 h. [b]Isolated yields of chromatographically pure products.

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singlet. The assignment of signals was confirmed by ^{1}H, ^{13}C CPD (carbon proton decoupled), and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded using Q-TOF multimode source. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. Benzaldehydes, immidazole, aryl halides, methyl iodide, bromoethane, Mg metal and Na_2SO_4 were commercially available (local made) used without further purification, CuI, $K_4[Fe(CN)_6]\cdot 3H_2O$, Cs_2CO_3 purchased from Sigma-Aldrich. All dry solvents were used; diethyl ether, toluene and THF were dried over sodium metal, and DCM and DMF were dried over calcium hydride.

All the solvents (diethyl ether, THF, DCM, DMF) are commercially available (LR grade). All small scale dry reactions were carried out using standard syringe-septum technique. Reactions were monitored by TLC on silica gel using a combination of petroleum ether and ethyl acetate as eluents. Solvents were distilled prior to use; petroleum ether with a boiling range of 40 to 60 °C was used. Acme's silica gel (60−120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

*2-(2-Bromophenyl)-3-methylbutan-2-ol (**1t**).* To a cold (0 °C), magnetically stirred solution of a ketone **3a** (500 mg, 2.20 mmol) in dry ether (30 mL) was added methylmagnesium iodide (8.81 mmol) [prepared from magnesium (211 mg, 8.81 mmol) and methyl iodide (1.250 g, 8.81 mmol) in 10 mL of dry ether]. The reaction mixture was stirred at −10 to 0 °C for 3 h. It was then poured into saturated aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 15). The ethyl acetate extract was dried with Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using petroleum ether/ethyl acetate as eluent furnished the tertiary alcohol **1at** as colorless oil 97% yield (502 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f (**3a**) = 0.50, R_f (**1at**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.63 (dd, 1H, J = 7.8 and 2.0 Hz), 7.53 (dd, 1H, J = 7.8 and 2.0 Hz), 7.25 (ddd, 1H, J = 8.8, 7.3, and 1.5 Hz), 7.04 (ddd, 1H, J = 8.8, 7.3, and 1.5 Hz), 2.90−2.74 (m, 1H), 2.36 (br. s, 1H), 1.63 (s, 3H), 0.88 (d, 3H, J = 6.8 Hz), 0.75 (d, 3H, J = 6.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 145.8 (C_q), 135.1 (CH), 128.6 (CH), 128.2 (CH), 127.1 (CH), 119.8 (C_q), 78.0 (C_q), 33.8 (CH_3), 24.2 (CH), 17.1 (CH_3), 17.0 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 3432, 2979, 2930, 1336, 1286, 1132, 1041, 905, 764, 695 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{11}H_{15}{}^{79}BrOK]^+ = [M + K]^+$ 282.9918, found 282.9915.

*1-(2-Bromo-4,5-dimethoxyphenyl)-1-phenylbut-3-en-1-ol (**3p**).* Allyl bromide (0.60 mL, 6.52 mmol) in THF (1 mL) was added dropwise to a sonicated suspension of zinc dust (423 mg, 6.52 mmol) in THF (2 mL) at room temperature, and the mixture was further sonicated for 30 min, and then *ortho*-bromobenzophenone **5c** (500 mg, 1.62 mmol) in THF (3 mL) was added and continued sonication at room temperature for 2 h. Progress of the reaction was monitored by TLC. The reaction mixture was quenched by addition of aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 15 mL). The collected organic layers were dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue on a silica gel column chromatography (petroleum ether/ethyl acetate) as eluent furnished homoallylic alcohol **3p** as colorless solid 96% yield (546 mg): mp 82−84 °C; [TLC (petroleum ether/ethyl acetate 9:1, R_f (**5c**) = 0.50, R_f (**3p**) = 0.50, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.38 (s, 1H), 7.30−7.15 (m, 5H), 6.94 (s, 1H), 5.78−5.60 (m, 1H), 5.12 (dd, 1H, J = 17.2 and 1.4 Hz), 5.05 (d, 1H, J = 10.2 Hz), 3.87 (s, 3H), 3.81 (s, 3H), 3.42 (dd, 1H, J = 14.2 and 6.6 Hz), 3.06 (br. s, 1H), 2.98 (dd, 1H, J = 14.2 and 7.3 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 148.3 (C_q), 147.6 (C_q), 145.7 (C_q), 136.3 (C_q), 133.9 (CH), 128.0 (2 × CH), 127.1 (CH), 126.5 (2 × CH), 118.6 (CH_2), 117.7 (CH), 112.6 (CH), 111.9 (C_q), 78.0 (C_q), 56.1 (CH_3), 44.7 (CH_2) ppm; IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 3516, 2933, 1598, 1499, 1321, 1208, 1149, 1030, 770, 698 cm^{-1}; HR-MS (ESI+) m/z calculated for $[C_{18}H_{18}{}^{79}BrO_2]^+ = [(M + H) - H_2O]^+$ 345.0485, found 345.0497.

*4-(2-Bromophenyl)hepta-1,6-dien-4-ol (**1x**).* This compound was prepared according to the **3p** and isolated as colorless liquid 92% yield (571 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f (**8**) = 0.50, R_f (**1x**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.68 (dd, 1H, J = 7.8 and 2.0 Hz), 7.57 (dd, 1H, J = 7.8 and 2.0 Hz), 7.28 (dd, 1H, J = 7.8 and 1.5 Hz), 7.08 (ddd, 1H, J = 7.8, 7.3, and 1.5 Hz), 5.65−5.45 (m, 2H), 5.20−4.95 (m, 4H), 3.40−3.25 (m, 2H), 2.68−2.55 (m, 2H), 2.50 (br. s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 143.5 (C_q), 134.9 (CH), 133.4 (2C, 2 × CH), 129.4 (CH), 128.6 (CH), 127.2 (CH), 119.6 (C_q), 118.9 (2C, 2 × CH_2), 76.1 (C_q), 43.5 (2C, 2 × CH_2) ppm; IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 3545, 2977, 1638, 1432, 1340, 1284, 1149, 1018, 915, 739, 693 cm^{-1}; HR-MS (ESI+) m/z calculated for $[C_{13}H_{14}{}^{79}Br]^+ = [(M + H) - H_2O]^+$ 249.0273, found 249.0268.

*1-(2-Bromophenyl)cyclopent-3-enol (**1y**).* To a magnetically stirred solution of the diene **1x** (200 mg, 0.74 mmol) in anhydrous benzene (15 mL), a solution of second-generation Grubbs's catalyst (19 mg, 3 mol %) in anhydrous benzene (15 mL) was added, and the reaction mixture was refluxed for 30 min. Evaporation of the solvent under reduced pressure and purification of the residue on a silica-gel column using ethyl acetate−hexane (1:9) as eluent furnished the tertiary alcohol **1y** (166 mg, 93%) as colorless oil. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.86 (dd, 1H, J = 7.8 and 1.5 Hz), 7.58 (dd, 1H, J = 7.8 and 1.5 Hz), 7.32 (ddd, 1H, J = 8.8, 7.3, and 1.0 Hz), 7.11 (ddd, 1H, J = 7.8, 7.3, and 1.5 Hz), 5.82 (s, 2H), 3.39 (d, 2H, J = 16.6 Hz), 2.59 (d, 2H, J = 16.6 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 144.3 (C_q), 134.6 (CH), 128.5 (CH), 128.2 (2C, 2 × CH), 127.6 (CH), 127.2 (CH), 121.0 (C_q), 81.9 (C_q), 48.8 (2C, 2 × CH_2) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 3450, 2930, 1613, 1457, 1332, 1282, 1142, 1031, 908, 767, 694 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{11}H_{10}{}^{79}Br]^+ = [(M + H) - H_2O]^+$ 220.996, found 220.9954.

*(2-Bromophenyl)(3-methoxyphenyl)phenylmethanol (**3s**).* To a cold (0 °C), magnetically stirred solution of a *o*-bromobenzophenone **5b** (1.72 mmol) in dry THF (2 mL) was added phenylmagnesium bromide (6.88 mmol) [prepared from magnesium (6.88 mmol) and bromobenzene (6.88 mmol) and a catalytic amount of iodine in 10 mL of dry THF or dry ether]. The reaction mixture was stirred at 0 °C to room temperature for 3 h. It was then poured into saturated aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The crude tertiary alcohol **3s** was purified by column chromatography on silica using petroleum ether/ethyl acetate as eluent furnished the tertiary alcohol **3s** as colorless viscous liquid 77% yield (492 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f (**5b**) = 0.50, R_f (**3s**) = 0.45, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.65−7.59 (m, 1H), 7.38−7.26 (m, 3H), 7.27−7.19 (m, 3H), 7.16−7.10 (m, 2H), 6.90 (dd, 1H, J = 2.4 and 1.5 Hz), 6.84 (dd, 1H, J = 2.4 and 2.4 Hz), 6.76 (d, 1H, J = 6.8 Hz), 6.74−6.67 (m, 1H), 4.57 (s, 1H), 3.75 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 159.4 (C_q), 147.2 (C_q), 145.4 (C_q), 144.9 (C_q), 134.8 (CH), 131.9 (CH), 129.2 (CH), 128.8 (CH), 128.0 (2 × CH), 127.8 (2 × CH), 127.4 (CH), 126.9 (CH), 122.9 (C_q), 120.5 (CH), 113.7 (CH), 112.7 (CH), 83.1 (C_q), 55.1 (CH_3) ppm; IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 3541, 3043, 1553, 1442, 1358, 1265, 1153, 1024, 890, 756, 698 cm^{-1}; HR-MS (ESI+) m/z calculated for $[C_{20}H_{16}{}^{79}BrO]^+ = [(M + H) - H_2O]^+$ 351.0379, found 351.0376.

General Procedure (For the Synthesis of Benzofuranones) (2 and 4). In an oven-dried Schlenk tube 2-bromobenzyl tertiary alcohol **1** (0.5 mmol), finely ground $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.25 mmol), copper iodide (0.05 mmol), imidazole (1 mmol) and solvent (toluene or distilled water) (0.5 mL) were added. The resulting reaction mixture was stirred at 140 °C for 24 h. The progress of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was allowed to cool to room temperature, then diluted with (10 mL) ethyl acetate, and water was added followed by extraction with ethyl acetate. The organic layers were dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent furnished the benzofuranone **2**.

*3,3-Dimethyl-2-benzofuran-1(3H)-one (**2a**).* This compound was prepared according to the GP and isolated as colorless liquid 96% yield (101 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f (**1a**) = 0.50, R_f (**2a**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.85 (d, 1H, J = 7.8 Hz), 7.65 (dd, 1H, J = 8.8 and 7.3 Hz), 7.49 (dd, 1H, J =

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8.8 and 7.3 Hz), 7.39 (d, 1H, J = 7.3 Hz), 1.65 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.8 (C_q), 155.0 (C_q), 134.1 (CH), 128.9 (CH), 125.7 (CH), 125.3 (C_q), 120.6 (CH), 85.4 (C_q), 27.3 (2C, 2 × CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2979, 2930, 1750, 1614, 1467, 1336, 1286, 1132, 1041, 905, 764, 695 cm^{-1}. HR-MS (ESI +) m/z calculated for $[C_{10}H_{10}O_2Na]^+$ = [M + Na]$^+$ 185.0573, found 185.0572.

*5-(Benzyloxy)-3,3-dimethyl-2-benzofuran-1(3H)-one (**2b**).* This compound was prepared according to the GP and isolated as colorless crystalline solid 94% yield (127 mg): mp 148−150 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f (**1b**) = 0.60, R_f (**2b**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.77 (d, 1H, J = 8.3 Hz), 7.50−7.30 (m, 5H), 7.07 (dd, 1H, J = 8.3 and 2.4 Hz), 6.89 (d, 1H, J = 2.4 Hz), 5.14 (s, 2H), 1.62 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.5 (C_q), 163.8 (C_q), 157.6 (C_q), 135.7 (C_q), 128.7 (2C, 2 × CH), 128.4 (CH), 127.6 (2C, 2 × CH), 127.4 (CH), 117.8 (C_q), 116.4 (CH), 106.1 (CH), 84.5 (C_q), 70.6 (CH_2), 27.3 (2C, 2 × CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2977, 1742, 1606, 1487, 1306, 1227, 1160, 1039, 908, 743, 694 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{17}H_{16}O_3K]^+$ = [M + K]$^+$ 307.0731, found 307.0732.

*5-Methoxy-3,3-dimethyl-2-benzofuran-1(3H)-one (**2c**).* This compound was prepared according to the GP and isolated as colorless solid 90% yield (94 mg): mp 56−58 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f (**1c**) = 0.50, R_f (**2c**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.76 (d, 1H, J = 8.3 Hz), 6.99 (dd, 1H, J = 8.3 and 2.4 Hz), 6.79 (d, 1H, J = 2.4 Hz), 3.89 (s, 3H), 1.62 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.5 (C_q), 164.7 (C_q), 157.7 (C_q), 127.4 (CH), 117.6 (C_q), 115.9 (CH), 104.9 (CH), 84.5 (C_q), 55.8 (CH_3), 27.3 (2C, 2 × CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2977, 1743, 1603, 1489, 1309, 1232, 1161, 1040, 913, 787, 696 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{11}H_{13}O_3]^+$ = [M + H]$^+$ 193.0859, found 193.0858.

*5-(Benzyloxy)-6-methoxy-3,3-dimethyl-2-benzofuran-1(3H)-one (**2d**).* This compound was prepared according to the GP and isolated as yellow colored solid 91% yield (136 mg): mp 124−126 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f (**1d**) = 0.40, R_f (**2d**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.44 (d, 2H, J = 6.8 Hz), 7.39 (dd, 2H, J = 7.3 and 6.8 Hz), 7.34 (d, 1H, J = 6.8 Hz), 7.26 (s, 1H), 6.79 (s, 1H), 5.21 (s, 2H), 3.91 (s, 3H), 1.57 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.0 (C_q), 153.9 (C_q), 150.8 (C_q), 149.3 (C_q), 135.7 (C_q), 128.7 (2C, 2 × CH), 128.3 (CH), 127.4 (2C, 2 × CH), 117.4 (C_q), 106.5 (CH), 104.2 (CH), 84.6 (C_q), 71.2 (CH_2), 56.3 (CH_3), 27.3 (2C, 2 × CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2926, 1741, 1600, 1497, 1310, 1200, 1175, 1034, 909, 803, 697 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{18}H_{18}O_4Na]^+$ = [M + Na]$^+$ 321.1097, found 321.1083.

*7,7-Dimethylfuro[3,4-f][1,3]benzodioxol-5(7H)-one (**2e**).* This compound was prepared according to the GP and isolated as colorless solid 94% yield (98 mg): mp 182−184 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f (**1e**) = 0.60, R_f (**2e**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.14 (s, 1H), 6.73 (s, 1H), 6.09 (s, 2H), 1.59 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.3 (C_q), 153.6 (C_q), 151.8 (C_q), 149.0 (C_q), 118.8 (C_q), 104.3 (CH), 102.5 (CH), 100.6 (CH_2), 84.4 (C_q), 27.3 (2C, 2 × CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2932, 1746, 1598, 1489, 1274, 1131, 1028, 909, 729, 693 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{11}H_{11}O_4]^+$ = [M + H]$^+$ 207.0652, found 207.0650.

*5,6-Dimethoxy-3,3-dimethyl-2-benzofuran-1(3H)-one (**2f**).* This compound was prepared according to the GP and isolated as brown colored solid 93% yield (104 mg): mp 142−144 °C; [TLC (petroleum ether/ethyl acetate 7:3, R_f (**1f**) = 0.50, R_f (**2f**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.24 (s, 1H), 6.75 (s, 1H), 3.97 (s, 3H), 3.91 (s, 3H), 1.62 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.0 (C_q), 154.8 (C_q), 150.2 (C_q), 149.6 (C_q), 117.1 (C_q), 106.2 (CH), 102.1 (CH), 84.6 (C_q), 56.4 (CH_3), 56.3 (CH_3), 27.4 (2C, 2 × CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2927, 1741, 1600, 1497, 1310, 1200, 1175, 1024, 909, 730, 697 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{12}H_{14}O_4K]^+$ = [M + K]$^+$ 261.0524, found 261.0523.

*5,6,7-Trimethoxy-3,3-dimethyl-2-benzofuran-1(3H)-one (**2g**).* This compound was prepared according to the GP and isolated as pale yellow colored solid 94% yield (119 mg): mp 58−60 °C; [TLC (petroleum ether/ethyl acetate 6:4, R_f (**1g**) = 0.50, R_f (**2g**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 6.52 (s, 1H), 4.11 (s, 3H), 3.94 (s, 3H), 3.84 (s, 3H), 1.59 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.2 (C_q), 159.5 (C_q), 152.9 (C_q), 152.2 (C_q), 141.5 (C_q), 109.7 (C_q), 98.2 (CH), 83.5 (C_q), 62.2 (CH_3), 61.3 (CH_3), 56.4 (CH_3), 27.5 (2C, 2 × CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2930, 1745, 1598, 1474, 1346, 1253, 1133, 1083, 930, 668 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{13}H_{16}O_5Na]^+$ = [M + Na]$^+$ 275.0890, found 275.0889.

*3-Ethyl-3-methyl-2-benzofuran-1(3H)-one (**2h**).* This compound was prepared according to the GP and isolated as pale yellow colored oil 95% yield (85 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f (**1h**) = 0.50, R_f (**2h**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.83 (d, 1H, J = 7.3 Hz), 7.64 (dd, 1H, J = 8.8 and 7.3 Hz), 7.48 (dd, 1H, J = 8.8 and 7.3 Hz), 7.34 (d, 1H, J = 7.3 Hz), 2.13−1.97 (m, 1H), 1.95−1.83 (m, 1H), 1.61 (s, 3H),0.72 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.1 (C_q), 153.6 (C_q), 134.0 (CH), 128.8 (CH), 126.1 (C_q), 125.6 (CH), 120.8 (CH), 88.0 (C_q), 32.8 (CH_2), 25.6 (CH_3), 7.8 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2974, 1749, 1614, 1465, 1345, 1286, 1129, 1060, 920, 761, 695 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{11}H_{13}O_2]^+$ = [M + H]$^+$ 177.0910, found 177.0907.

*5-(Benzyloxy)-3-ethyl-3-methyl-2-benzofuran-1(3H)-one (**2i**).* This compound was prepared according to the GP and isolated as colorless solid 92% yield (131 mg): mp 88−90 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f (**1i**) = 0.60, R_f (**2i**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.77 (d, 1H, J = 8.3 Hz), 7.50−7.30 (m, 5H), 7.07 (dd, 1H, J = 8.3 and 2.0 Hz), 6.84 (d, 1H, J = 2.0 Hz), 5.14 (s, 2H), 2.10−1.95 (m, 1H), 1.92−1.78 (m, 1H), 1.59 (s, 3H), 0.74 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.8 (C_q), 163.8 (C_q), 156.3 (C_q), 135.7 (C_q), 128.7 (2C, 2 × CH), 128.4 (CH), 127.6 (2C, 2 × CH), 127.3 (CH), 118.8 (C_q), 116.3 (CH), 106.3 (CH), 87.1 (C_q), 70.6 (CH_2), 32.8 (CH2), 25.7 (CH_3), 7.8 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2990, 1753, 1590, 1462, 1365, 1245, 1102, 1023, 907, 754, 690 cm^{-1}. HR-MS (ESI +) m/z calculated for $[C_{18}H_{18}O_3Na]^+$ = [M + Na]$^+$ 305.1148, found 305.1152.

*3-Ethyl-5-methoxy-3-methyl-2-benzofuran-1(3H)-one (**2j**).* This compound was prepared according to the GP and isolated as pale yellow colored viscus oil 94% yield (97 mg): [TLC (petroleum ether/ethyl acetate 8:2, R_f (**1j**) = 0.50, R_f (**2j**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.74 (d, 1H, J = 8.8 Hz), 6.98 (dd, 1H, J = 8.8 and 2.0 Hz), 6.74 (d, 1H, J = 2.0 Hz), 3.88 (s, 3H), 2.10−1.95 (m, 1H), 1.93−1.78 (m, 1H), 1.59 (s, 3H), 0.73 (t, 3H, J = 7.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.9 (C_q), 164.7 (C_q), 156.3 (C_q), 127.2 (CH), 118.5 (C_q), 115.8 (CH), 105.1 (CH), 87.1 (C_q), 55.8 (CH_3), 32.8 (CH_2), 25.7 (CH_3), 7.7 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2974, 1744, 1604, 1490, 1320, 1225, 1147, 1031, 923, 784, 696 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{12}H_{15}O_3]^+$ = [M + H]$^+$ 207.1016, found 207.1018.

*5-(Benzyloxy)-3-ethyl-6-methoxy-3-methyl-2-benzofuran-1(3H)-one (**2k**).* This compound was prepared according to the GP and isolated as brown colored solid 93% yield (146 mg): mp 76−78 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f (**1k**) = 0.60, R_f (**2k**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.43 (d, 2H, J = 6.8 Hz), 7.38 (dd, 2H, J = 7.3 and 6.8 Hz), 7.33 (d, 1H, J = 6.8 Hz), 7.26 (s, 1H), 6.73 (s, 1H), 5.21 (s, 2H), 3.92 (s, 3H), 2.04−1.92 (m, 1H), 1.85−1.73 (m, 1H), 0.54 (s, 3H), 0.68 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.3 (C_q), 153.7 (C_q), 150.7 (C_q), 147.8 (C_q), 135.7 (C_q), 128.7 (2C, 2 × CH), 128.3 (CH), 127.4 (2C, 2 × CH), 118.3 (C_q), 106.5 (CH), 104.6 (CH), 87.2 (C_q), 71.2 (CH_2), 56.3 (CH_3), 32.8 (CH_2), 25.7 (CH_3), 7.8 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2922, 1745, 1601, 1463, 1355, 1285, 1170, 1043, 941, 722, 665 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{19}H_{20}O_4Na]^+$ = [M + Na]$^+$ 335.1254, found 335.1256.

*7-Ethyl-7-methylfuro[3,4-f][1,3]benzodioxol-5(7H)-one (**2l**).* This compound was prepared according to the GP and isolated as colorless solid 93% yield (104 mg): mp 116−118 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f (**1l**) = 0.50, R_f (**2l**) = 0.30, UV detection]. 1H

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NMR ($CDCl_3$ 400 MHz) δ = 7.15 (s, 1H), 6.69 (s, 1H), 6.09 (s, 2H), 2.10−1.97 (m, 1H), 1.90−1.75 (m, 1H), 1.57 (s, 3H), 0.74 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.6 (C_q), 153.6 (C_q), 150.4 (C_q), 148.9 (C_q), 119.7 (C_q), 104.3 (CH), 102.5 (CH), 100.8 (CH_2), 87.0 (C_q), 32.8 (CH_2), 25.8 (CH_3), 7.8 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2977, 1732, 1611, 1476, 1308, 1230, 1095, 943, 787, 625 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{12}H_{13}O_4]^+$ = $[M + H]^+$ 221.0808, found 221.0809.

3-Ethyl-5,6-dimethoxy-3-methyl-2-benzofuran-1(3H)-one (**2m**). This compound was prepared according to the GP and isolated as colorless solid 96% yield (113 mg): mp 128−130 °C; [TLC (petroleum ether/ethyl acetate 7:3, R_f (**1m**) = 0.50, R_f (**2m**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.23 (s, 1H), 6.70 (s, 1H), 3.96 (s, 3H), 3.91 (s, 3H), 2.10−1.97 (m, 1H), 1.90−1.78 (m, 1H), 1.59 (s, 3H), 0.72 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.3 (C_q), 154.8 (C_q), 150.2 (C_q), 148.1 (C_q), 118.0 (C_q), 106.1 (CH), 102.2 (CH), 87.2 (C_q), 56.3 (CH_3), 56.2 (CH_3), 32.8 (CH_2), 25.8 (CH_3), 7.8 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2927, 1738, 1600, 1498, 1324, 1229, 1105, 1029, 922, 804, 667 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{13}H_{16}O_4Na]^+$ = $[M + Na]^+$ 259.0941, found 259.0939.

3-Ethyl-5,6,7-trimethoxy-3-methyl-2-benzofuran-1(3H)-one (**2n**). This compound was prepared according to the GP and isolated as yellow colored viscous liquid 95% yield (125 mg): [TLC (petroleum ether/ethyl acetate 6:4, R_f (**1n**) = 0.50, R_f (**2n**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 6.47 (s, 1H), 4.12 (s, 3H), 3.93 (s, 3H), 3.85 (s, 3H), 2.10−1.97 (m, 1H), 1.88−1.75 (m, 1H), 1.57 (s, 3H), 0.76 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.6 (C_q), 159.5 (C_q), 152.2 (C_q), 151.6 (C_q), 141.5 (C_q), 110.7 (C_q), 98.2 (CH), 86.1 (C_q), 62.3 (CH_3), 61.4 (CH_3), 56.4 (CH_3), 33.0 (CH_2), 25.9 (CH_3), 7.8 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2977, 1732, 1611, 1477, 1308, 1230, 1095, 943, 881, 628 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{14}H_{18}O_5Na]^+$ = $[M + Na]^+$ 289.1046, found 289.1047.

3,3-Diethyl-2-benzofuran-1(3H)-one (**2o**). This compound was prepared according to the GP and isolated as pale yellow colored solid 92% yield (88 mg): mp 56−58 °C; [TLC (petroleum ether/ethyl acetate 9:1, R_f (**1o**) = 0.50, R_f (**2o**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.80 (d, 1H, J = 7.8 Hz), 7.52 (dd, 1H, J = 8.8 and 7.3 Hz), 7.42 (dd, 1H, J = 8.8 and 7.3 Hz), 7.19 (d, 1H, J = 7.8 Hz), 2.10−1.92 (m, 2H), 1.91−1.76 (m, 2H), 0.68 (t, 6H J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 168.3 (C_q), 149.1 (C_q), 131.9 (CH), 130.3 (C_q), 128.4 (CH), 123.6 (CH), 120.9 (CH), 92.3 (C_q), 31.9 (2C, 2 × CH_2), 7.8 (2C, 2 × CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2969, 1735, 1599, 1497, 1363, 1249, 1156, 1030, 914, 738, 697 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{12}H_{16}ON]^+$ = $[(M + NH_4)+(-H_2O)]^+$ 190.1226, found 190.1224.

3,3-Diethyl-5-methoxy-2-benzofuran-1(3H)-one (**2p**). This compound was prepared according to the GP and isolated as pale yellow colored oil 93% yield (102 mg): [TLC (petroleum ether/ethyl acetate 8:2, R_f (**1p**) = 0.50, R_f (**2p**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.75 (d, 1H, J = 8.3 Hz), 6.98 (dd, 1H, J = 8.3 and 2.0 Hz), 6.71 (d, 1H, J = 2.0 Hz), 3.88 (s, 3H), 2.13−1.98 (m, 2H), 1.93−1.75 (m, 2H), 0.69 (t, 6H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.2 (C_q), 164.6 (C_q), 154.6 (C_q), 127.1 (CH), 119.6 (C_q), 115.6 (CH), 105.4 (CH), 90.0 (C_q), 55.8 (CH_3), 31.4 (CH_2), 7.4 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2990, 1750, 1598, 1463, 1365, 1255, 1132, 1024, 917, 750, 690 cm^{-1}. HR-MS (ESI +) m/z calculated for $[C_{13}H_{17}O_3]^+$ = $[M + H]^+$ 221.1172, found 221.1174.

5-(Benzyloxy)-3,3-diethyl-6-methoxy-2-benzofuran-1(3H)-one (**2q**). This compound was prepared according to the GP and isolated as pale yellow colored oil 91% yield (149 mg): [TLC (petroleum ether/ethyl acetate 8:2, R_f (**1q**) = 0.50, R_f (**2q**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.42 (d, 2H, J = 7.3 Hz), 7.37 (dd, 2H, J = 7.3 and 6.8 Hz), 7.33 (d, 1H, J = 7.3 Hz), 7.27 (s, 1H), 6.68 (s, 1H), 5.22 (s, 2H), 3.92 (s, 3H), 2.07−1.92 (m, 2H), 1.85−1.70 (m, 2H), 0.63 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.6 (C_q), 153.6 (C_q), 150.7 (C_q), 145.9 (C_q), 135.7 (C_q), 128.7 (2C, 2 × CH), 128.3 (CH), 127.4 (2C, 2 × CH), 119.4 (C_q), 106.4 (CH), 105.0 (CH), 90.0 (C_q), 71.2 (CH_2), 56.2 (CH_3), 31.3 (2C, 2 × CH_2), 7.4 (2C, 2 × CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2922, 1746, 1600, 1499, 1357, 1282, 1171, 1040, 941, 737, 697 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{20}H_{23}O_4]^+$ = $[M + H]^+$ 327.1591, found 327.1594.

7,7-Diethylfuro[3,4-f][1,3]benzodioxol-5(7H)-one (**2r**). This compound was prepared according to the GP and isolated as brown colored solid 90% yield (106 mg): mp 96−98 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f (**1r**) = 0.50, R_f (**2r**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.15 (s, 1H), 6.56 (s, 1H), 6.05 (s, 2H), 2.05−1.88 (m, 2H), 1.85−1.66 (m, 2H), 0.68 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.9 (C_q), 151.9 (C_q), 148.6 (C_q), 144.7 (C_q), 124.0 (C_q), 103.0 (CH), 102.1 (CH), 100.8 (CH_2), 91.6 (C_q), 32.0 (CH_2), 7.5 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2987, 1750, 1590, 1475, 1374, 1275, 1120, 1025, 908, 750, 690 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{13}H_{15}O_4]^+$ = $[M + H]^+$ 235.0965, found 235.0966.

3,3-Diethyl-5,6-dimethoxy-2-benzofuran-1(3H)-one (**2s**). This compound was prepared according to the GP and isolated as yellow colored viscous liquid 93% yield (116 mg): [TLC (petroleum ether/ethyl acetate 7:3, R_f (**1s**) = 0.60, R_f (**2s**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.25 (s, 1H), 6.66 (s, 1H), 3.96 (s, 3H), 3.92 (s, 3H), 2.15−1.97 (m, 2H), 1.94−1.76 (m, 2H), 0.69 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.7 (C_q), 154.8 (C_q), 150.2 (C_q), 146.3 (C_q), 119.2 (C_q), 106.0 (CH), 102.4 (CH), 90.1 (C_q), 56.4 (CH_3), 56.2 (CH_3), 31.4 (2C, 2 × CH_2), 7.5 (2C, 2 × CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2924, 1741, 1601, 1499, 1354, 1284, 1170, 1042, 940, 804, 665 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{14}H_{18}O_4Na]^+$ = $[M + Na]^+$ 273.1097, found 273.1098.

3-Isopropyl-3-methyl-2-benzofuran-1(3H)-one (**2t**). This compound was prepared according to the GP and isolated as colorless oil 89% yield (79 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f (**1t**) = 0.50, R_f (**2t**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.85 (d, 1H, J = 7.3 Hz), 7.63 (dd, 1H, J = 8.8 and 7.3 Hz), 7.48 (dd, 1H, J = 8.8 and 7.3 Hz), 7.36 (d, 1H, J = 7.3 Hz), 2.23−2.08 (m, 1H), 1.62 (s, 3H), 0.98 (d, 3H, J = 6.8 Hz), 0.80 (d, 3H, J = 6.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.3 (C_q), 153.5 (C_q), 133.8 (CH), 128.8 (CH), 126.3 (C_q), 125.6 (CH), 121.3 (CH), 90.1 (C_q), 36.5 (CH), 23.9 (CH_3), 17.1 (CH_3), 16.9 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2977, 1738, 1595, 1472, 1343, 1251, 1131, 1078, 929, 831, 669 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{12}H_{15}O_2]^+$ = $[M + H]^+$ 191.1067, found 191.1065.

3-Allyl-3-methyl-2-benzofuran-1(3H)-one (**2u**). This compound was prepared according to the GP and isolated as colorless viscous liquid 83% yield (79 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f (**1u**) = 0.50, R_f (**2u**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.85 (d, 1H, J = 7.8 Hz), 7.64 (ddd, 1H, J = 7.3, 7.3, and 1.0 Hz), 7.49 (dd, 1H, J = 7.3 and 6.8 Hz), 7.37 (d, 1H, J = 7.8 Hz), 5.65−5.49 (m, 1H), 5.04 (d, 2H, J = 11.7 Hz), 2.75−2.55 (m, 2H), 1.63 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.8 (C_q), 153.4 (C_q), 133.9 (CH), 131.0 (CH), 128.9 (CH), 126.0 (C_q), 125.7 (CH), 121.1 (CH), 120.1 (CH_2), 86.7 (C_q), 44.3 (CH_2), 25.4 (CH_3) ppm; IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2982, 1743, 1612, 1453, 1354, 1281, 1106, 1032, 730, 694 cm^{-1}; HR-MS (ESI+) m/z calculated for $[C_{12}H_{13}O_2]^+$ = $[M + H]^+$ 189.091, found 189.0912.

3-Allyl-5-methoxy-3-methyl-2-benzofuran-1(3H)-one (**2v**). This compound was prepared according to the GP and isolated as colorless viscous liquid 84% yield (92 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f (**1v**) = 0.50, R_f (**2v**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.74 (d, 1H, J = 8.8 Hz), 6.98 (dd, 1H, J = 8.3 and 2.0 Hz), 6.67 (d, 1H, J = 2.0 Hz), 5.66−5.50 (m, 1H), 5.06 (d, 1H, J = 4.9 Hz), 5.03 (s, 1H), 3.88 (s, 3H), 2.74−2.55 (m, 2H), 1.60 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.5 (C_q), 164.6 (C_q), 156.1 (C_q), 131.0 (CH), 127.2 (CH), 120.0 (CH_2), 118.3 (C_q), 115.9 (CH), 105.4 (CH), 85.9 (C_q), 55.8 (CH_3), 44.3 (CH_2), 25.4 (CH_3) ppm; IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2984, 1746, 1617, 1463, 1344, 1282, 1106, 1032, 731, 690 cm^{-1}; HR-MS (ESI+) m/z calculated for $[C_{13}H_{15}O_3]^+$ = $[M + H]^+$ 219.1016, found 219.1025.

5-Fluoro-3,3-dimethylisobenzofuran-1(3H)-one (**2w**). This compound was prepared according to the GP and isolated as colorless solid

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62% yield (56 mg): mp 150−152 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f (**1w**) = 0.50, R_f (**2w**) = 0.45, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.85 (dd, 1H, J = 8.3 and 3.4 Hz), 7.18 (ddd, 1H, J = 8.8, 8.3, and 2.0 Hz), 7.05 (dd, 1H, J = 7.8 and 2.0 Hz), 1.65 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 168.6 (C_q), 166.6 (C_q, d, J = 254 Hz), 157.7 (d, J = 9.5 Hz), 128.2 (d, J = 10.3 Hz), 121.4 (C_q, J = 2.2 Hz), 117.1 (d, J = 23.5 Hz), 108.1 (d, J = 23.5 Hz), 84.7 (C_q, J = 2.9 Hz), 27.2 (q, 2C, 2 × CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 3060, 1742, 1602, 1482, 1307, 1208, 1086, 960, 890, 785, 692 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{10}H_{10}FO_2]^+$ = $[M + H]^+$ 181.0659, found 181.0652.

*3H-Spiro[2-benzofuran-1,1′-cyclopent[3]en]-3-one (**2x**).* This compound was prepared according to the GP and isolated as colorless solid 94% yield (88 mg): mp 110−112 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f (**1y**) = 0.50, R_f (**2x**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.85 (d, 1H, J = 7.3 Hz), 7.66 (ddd, 1H, J = 7.8, 7.3, and 1.0 Hz), 7.50 (dd, 1H, J = 7.8 and 7.3 Hz), 7.46 (d, 1H, J = 7.3 Hz), 5.85 (s, 2H), 2.92 (s, 4H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.9 (C_q), 153.3 (C_q), 134.3 (CH), 129.0 (CH), 128.2 (2C, 2 × CH), 125.4 (CH), 120.9 (CH), 92.8 (C_q), 45.8 (2C, 2 × CH_2) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2930, 1754, 1612, 1465, 1318, 1271, 1080, 905, 753, 691 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{12}H_{11}O_2]^+$ = $[M + H]^+$ 187.0754, found 187.0752.

*3-Methyl-3-phenyl-2-benzofuran-1(3H)-one (**4a**).* This compound was prepared according to the GP and isolated as pale yellow colored viscous liquid 88% yield (99 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f (**3a**) = 0.60, R_f (**4a**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.90 (d, 1H, J = 7.8 Hz), 7.65 (ddd, 1H, J = 8.8, 7.3, and 1.0 Hz), 7.55−7.40 (m, 4H), 7.38−7.27 (m, 3H), 2.03 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.9 (C_q), 154.1 (C_q), 140.6 (C_q), 134.3 (CH), 129.1 (CH), 128.7 (2C, 2 × CH), 128.3 (CH), 125.8 (CH), 125.0 (2C, 2 × CH), 122.0 (CH), 87.6 (C_q), 27.2 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2980, 1748, 1597, 1451, 1346, 1285, 1103, 1038, 921, 737, 693 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{15}H_{13}O_2]^+$ = $[M + H]^+$ 225.091, found 225.0914.

*5-Methoxy-3-methyl-3-phenyl-2-benzofuran-1(3H)-one (**4b**).* This compound was prepared according to the GP and isolated as yellow colored solid 90% yield (115 mg): mp 62−64 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f (**3b**) = 0.60, R_f (**4b**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.80 (d, 1H, J = 8.3 Hz), 7.43 (dd, 2H, J = 8.3 and 1.5 Hz), 7.38−7.28 (m, 3H), 6.99 (dd, 1H, J = 8.3 and 2.4 Hz), 6.83 (d, 1H, J = 2.4 Hz), 3.85 (s, 3H), 2.01 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.7 (C_q), 164.8 (C_q), 156.9 (C_q), 140.7 (C_q), 128.7 (2C, 2 × CH), 128.3 (CH), 127.4 (CH), 125.1 (2C, 2 × CH), 117.3 (C_q), 116.1 (CH), 106.3 (CH), 86.7 (C_q), 55.8 (CH_3), 26.9 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2971, 1738, 1600, 1498, 1324, 1229, 1173, 1028, 922, 730, 666 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{16}H_{14}O_3Na]^+$ = $[M + Na]^+$ 277.0835, found 277.0835.

*7-Methyl-7-phenylfuro[3,4-f][1,3]benzodioxol-5(7H)-one (**4c**).* This compound was prepared according to the GP and isolated as colorless crystalline solid 92% yield (125 mg): mp 130−132 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f (**3c**) = 0.50, R_f (**4c**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.40 (dd, 2H, J = 8.3 and 1.5 Hz), 7.38−7.27 (m, 3H), 7.18 (s, 1H), 6.76 (s, 1H), 6.09 (s, 2H, J = 12.2 and 1.5 Hz), 1.99 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.5 (C_q), 153.8 (C_q), 151.1 (C_q), 149.2 (C_q), 140.6 (C_q), 128.7 (2C, 2 × CH), 128.3 (CH), 125.0 (2C, 2 × CH), 118.6 (C_q), 104.3 (CH), 102.6 (CH), 101.9 (CH_2), 86.6 (C_q), 26.9 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2977, 1732, 1611, 1477, 1308, 1230, 1095, 943, 787, 659 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{16}H_{12}O_4Na]^+$ = $[M + Na]^+$ 291.0628, found 291.0622.

*5,6-Dimethoxy-3-methyl-3-phenyl-2-benzofuran-1(3H)-one (**4d**).* This compound was prepared according to the GP and isolated as colorless viscous liquid 94% yield (134 mg): [TLC (petroleum ether/ethyl acetate 7:3, R_f (**3d**) = 0.60, R_f (**4d**) = 0.50, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.45−7.38 (m, 2H), 7.38−7.29 (m, 3H), 7.28 (s, 1H), 6.76 (s, 1H), 3.92 (s, 6H), 2.01 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.2 (C_q), 154.9 (C_q), 150.4 (C_q), 148.9 (C_q), 140.7 (C_q), 128.7 (2C, 2 × CH), 128.3 (CH), 125.2 (2C, 2 × CH), 117.0 (C_q), 106.1 (CH), 103.3 (CH), 86.8 (C_q), 56.4 (CH_3), 56.3 (CH_3), 26.8 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2977, 1738, 1595, 1472, 1343, 1251, 1131, 1078, 929, 831, 669 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{17}H_{17}O_4]^+$ = $[M + H]^+$ 285.1121, found 285.1121.

*5,6,7-Trimethoxy-3-methyl-3-phenyl-2-benzofuran-1(3H)-one (**4e**).* This compound was prepared according to the GP and isolated as colorless solid 91% yield (156 mg): [TLC (petroleum ether/ethyl acetate 6:4, R_f (**3e**) = 0.50, R_f (**4e**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.42 (dd, 2H, J = 7.8 and 2.0 Hz), 7.38−7.27 (m, 3H), 6.53 (s, 1H), 4.15 (s, 3H), 3.89 (s, 3H), 3.85 (s, 3H), 1.99 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.4 (C_q), 159.7 (C_q), 152.1 (C_q), 141.7 (C_q), 140.9 (C_q), 128.7 (2C, 2 × CH), 128.3 (CH), 125.1 (2C, 2 × CH), 109.5 (C_q), 99.5 (CH), 85.8 (C_q), 62.3 (CH_3), 61.4 (CH_3), 56.4 (CH_3), 27.0 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2935, 1747, 1595, 1473, 1339, 1259, 1121, 1013, 922, 772, 698 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{18}H_{18}O_5Na]^+$ = $[M + Na]^+$ 337.1046, found 337.1044.

*3-(3-Methoxyphenyl)-3-methyl-2-benzofuran-1(3H)-one (**4f**).* This compound was prepared according to the GP and isolated as pale green colored solid 92% yield (118 mg): mp 98−100 °C; [TLC (petroleum ether/ethyl acetate 9:1, R_f (**3f**) = 0.50, R_f (**4f**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.88 (d, 1H, J = 7.8 Hz), 7.64 (dd, 1H, J = 8.8 and 7.3 Hz), 7.54−7.43 (m, 2H), 7.26 (dd, 1H, J = 8.3 and 7.8 Hz), 7.07−6.94 (m, 2H), 6.87−6.78 (m, 1H), 3.77 (s, 3H), 2.01 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.9 (C_q), 159.7 (C_q), 154.0 (C_q), 142.3 (C_q), 134.3 (CH), 129.7 (CH), 129.1 (CH), 125.8 (CH), 124.9 (C_q), 122.0 (CH), 117.3 (CH), 113.2 (CH), 111.3 (CH), 87.4 (C_q), 55.2 (CH_3), 27.3 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2981, 1754, 1599, 1465, 1261, 1125, 1028, 916, 754, 700 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{16}H_{15}O_3]^+$ = $[M + H]^+$ 255.1016, found 255.1017.

*5-Methoxy-3-(3-methoxyphenyl)-3-methyl-2-benzofuran-1(3H)-one (**4g**).* This compound was prepared according to the GP and isolated as brown colored solid 97% yield (140 mg): mp 68−70 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f (**3g**) = 0.50, R_f (**4g**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.79 (d, 1H, J = 8.3 Hz), 7.26 (dd, 1H, J = 8.3 and 7.8 Hz), 7.05−6.91 (m, 3H), 6.88−6.78 (m, 2H), 3.85 (s, 3H), 3.77 (s, 3H), 1.99 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.6 (C_q), 164.8 (C_q), 159.7 (C_q), 156.8 (C_q), 142.3 (C_q), 129.7 (CH), 127.4 (CH), 117.3 (CH), 116.1 (C_q), 113.2 (CH), 111.3 (2C, 2 × CH), 106.3 (CH), 86.5 (C_q), 55.8 (CH_3), 55.3 (CH_3), 27.0 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2935, 1753, 1599, 1465, 1284, 1124, 1028, 916, 754, 700 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{17}H_{15}O_3]^+$ = $[(M + H)(-H_2O)]^+$ 267.1016, found 267.1017.

*5-(Benzyloxy)-6-methoxy-3-(3-methoxyphenyl)-3-methyl-2-benzofuran-1(3H)-one (**4h**).* This compound was prepared according to the GP and isolated as colorless viscous liquid 81% yield (159 mg): [TLC (petroleum ether/ethyl acetate 8:2, R_f (**3h**) = 0.50, R_f (**4h**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.43 (d, 2H, J = 6.8 Hz), 7.41−7.23 (m, 5H), 6.99 (d, 1H, J = 7.8 Hz), 6.95 (dd, 1H, J = 2.4 and 1.9 Hz), 6.83 (dd, 1H, J = 8.3 and 1.9 Hz), 6.79 (s, 1H), 5.17 (s, 2H), 3.93 (s, 3H), 3.77 (s, 3H), 1.98 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.1 (C_q), 159.7 (C_q), 149.5 (C_q), 149.0 (C_q), 142.4 (C_q), 135.9 (C_q), 129.7 (CH), 128.7 (2C, 2 × CH), 128.2 (CH), 127.3 (2C, 2 × CH), 117.4 (CH), 116.7 (C_q), 113.1 (CH), 111.5 (CH), 108.0 (CH), 103.6 (CH), 86.6 (C_q), 71.0 (C_q), 56.4 (CH_3), 55.3 (CH_3), 27.0 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2980, 1748, 1618, 1466, 1346, 1285, 1038, 921, 737, 693 cm^{-1}. HR-MS (ESI+) m/z calculated for $[C_{24}H_{23}O_5]^+$ = $[M + H]^+$ 391.154, found 391.1543.

*7-(3-Methoxyphenyl)-7-methylfuro[3,4-f][1,3]benzodioxol-5(7H)-one (**4i**).* This compound was prepared according to the GP and isolated as pale green colored solid 92% yield (138 mg): mp 86−88 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f (**3i**) = 0.40, R_f (**4i**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.27 (dd, 1H, J = 8.3 and 7.3 Hz), 7.17 (s, 1H), 7.00 (d, 1H, J = 8.8 Hz), 6.95 (dd, 1H, J = 2.4 and 2.0 Hz), 6.83 (dd, 1H, J = 8.3 and 2.4 Hz), 6.79 (s, 1H),

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6.09 (s, 1H), 6.06 (s, 1H), 3.78 (s, 3H), 1.97 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.4 (C_q), 159.7 (C_q), 153.7 (C_q), 150.9 (C_q), 149.1 (C_q), 142.2 (C_q), 129.7 (CH), 118.3 (C_q), 117.2 (CH), 113.1 (CH), 111.2 (CH), 104.1 (CH), 102.6 (CH_2), 101.8 (CH), 88.4 (C_q), 55.2 (CH_3), 26.9 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2980, 1745, 1611, 1475, 1302, 1240, 1095, 943, 747, 627 cm^{-1}. HR-MS (ESI+) *m/z* calculated for $[C_{17}H_{14}O_5K]^+$ = $[M + K]^+$ 337.0473, found 337.0476.

*5,6-Dimethoxy-3-(3-methoxyphenyl)-3-methyl-2-benzofuran-1(3H)-one (**4j**).* This compound was prepared according to the GP and isolated as brown colored semi solid 95% yield (163 mg): [TLC (petroleum ether/ethyl acetate 7:3, R_f (**3j**) = 0.40, R_f (**4j**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.30−7.20 (m, 2H), 7.00−6.90 (m, 2H), 6.84−6.78 (m, 1H), 6.75 (s, 1H), 3.90 (s, 6H), 3.75 (s, 3H), 1.97 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.2 (C_q), 159.7 (C_q), 154.9 (C_q), 150.4 (C_q), 148.8 (C_q), 142.4 (C_q), 129.8 (CH), 117.4 (CH), 116.8 (C_q), 113.1 (CH), 111.5 (CH), 106.0 (CH), 103.3 (CH), 86.6 (C_q), 56.4 (CH_3), 56.3 (CH_3), 55.3 (CH_3), 26.9 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2977, 1732, 1611, 1477, 1308, 1230, 1095, 943, 747, 628 cm^{-1}. HR-MS (ESI+) *m/z* calculated for $[C_{18}H_{18}O_5Na]^+$ = $[M + Na]^+$ 337.1046, found 337.1045.

*3-Methyl-3-thien-2-yl-2-benzofuran-1(3H)-one (**4k**).* This compound was prepared according to the GP and isolated as brown colored oil 87% yield (101 mg): [TLC (petroleum ether/ethyl acetate 8:2, R_f (**3k**) = 0.50, R_f (**4k**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.90 (d, 1H, *J* = 7.3 Hz), 7.69 (dd, 1H, *J* = 8.8 and 7.3 Hz), 7.55 (dd, 1H, *J* = 8.8 and 7.3 Hz), 7.49 (d, 1H, *J* = 7.8 Hz), 7.27 (dd, 1H, *J* = 4.9 and 1.5 Hz), 6.99 (dd, 1H, *J* = 4.9 and 1.5 Hz), 6.94 (dd, 1H, *J* = 4.9 and 1.5 Hz), 2.08 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.2 (C_q), 153.3 (C_q), 144.4 (C_q), 134.4 (CH), 129.5 (CH), 126.9 (CH), 126.2 (CH), 125.9 (CH), 125.3 (CH), 125.1 (C_q), 122.1 (CH), 85.3 (C_q), 28.1 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2982, 1756, 1591, 1465, 1375, 1275, 1122, 1024, 907, 755, 691 cm^{-1}. HR-MS (ESI+) *m/z* calculated for $[C_{13}H_{11}O_2S]^+$ = $[M + H]^+$ 231.0474, found 231.0477.

*5-Methoxy-3-methyl-3-thien-2-yl-2-benzofuran-1(3H)-one (**4l**).* This compound was prepared according to the GP and isolated as black colored viscous liquid 92% yield (121 mg): [TLC (petroleum ether/ethyl acetate 8:2, R_f (**3l**) = 0.50, R_f (**4l**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.80 (d, 1H, *J* = 8.3 Hz), 7.27 (dd, 1H, *J* = 6.4 and 1.5 Hz), 7.04 (dd, 1H, *J* = 8.3 and 2.0 Hz), 7.00 (dd, 1H, *J* = 3.9 and 1.5 Hz), 6.95 (dd, 1H, *J* = 3.9 and 1.5 Hz), 6.87 (d, 1H, *J* = 2.0 Hz), 3.88 (s, 3H), 2.06 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 168.9 (C_q), 164.9 (C_q), 156.1 (C_q), 144.5 (C_q), 127.4 (CH), 126.9 (CH), 126.2 (CH), 125.2 (CH), 117.4 (C_q), 116.7 (CH), 106.2 (CH), 84.4 (C_q), 55.9 (CH_3), 28.1 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2933, 1754, 1604, 1490, 1293, 1124, 1029, 918, 837, 692 cm^{-1}. HR-MS (ESI+) *m/z* calculated for $[C_{14}H_{13}O_3S]^+$ = $[M + H]^+$ 261.0580, found 261.0579.

*5,6-Dimethoxy-3-methyl-3-thien-2-yl-2-benzofuran-1(3H)-one (**4m**).* This compound was prepared according to the GP and isolated as amber colored viscous liquid 88% yield (109 mg): [TLC (petroleum ether/ethyl acetate 8:2, R_f (**3m**) = 0.50, R_f (**4m**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.30−7.23 (m, 2H), 6.98 (dd, 1H, *J* = 3.9 and 1.5 Hz), 6.93 (dd, 1H, *J* = 3.9 and 1.5 Hz), 6.82 (s, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 2.05 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.4 (C_q), 154.9 (C_q), 150.7 (C_q), 147.9 (C_q), 144.6 (C_q), 126.9 (CH), 126.2 (CH), 125.3 (CH), 117.1 (C_q), 105.9 (CH), 103.4 (CH), 84.4 (C_q), 56.4 (CH_3), 56.3 (CH_3), 27.9 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2982, 1746, 1617, 1466, 1285, 1154, 1027, 923, 845, 698 cm^{-1}. HR-MS (ESI+) *m/z* calculated for $[C_{15}H_{15}O_4S]^+$ = $[M + H]^+$ 291.0686, found 291.0686.

*3-Allyl-3-phenyl-2-benzofuran-1(3H)-one (**4n**).* This compound was prepared according to the GP and isolated as colorless oil 89% yield (112 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f (**3n**) = 0.40, R_f (**4n**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.88 (d, 1H, *J* = 7.8 Hz), 7.66 (dd, 1H, *J* = 8.8 and 7.3 Hz), 7.57−7.46 (m, 4H), 7.36 (dd, 2H, *J* = 7.3 and 7.3 Hz), 7.33−7.27 (m, 1H), 5.55−5.38 (m, 1H), 5.12−4.95 (m, 2H), 3.24−3.12 (m, 1H), 3.08−2.98 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.8 (C_q), 152.0 (C_q), 139.9 (C_q), 134.1 (CH), 130.5 (CH), 129.1 (CH), 128.7 (2C, 2 × CH), 128.3 (CH), 125.8 (C_q), 125.7 (CH), 125.2 (2C, 2 × CH), 122.4 (CH), 120.5 (CH_2), 89.1 (C_q), 44.3 (CH_2) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2919, 1754, 1598, 1465, 1285, 1132, 1077, 982, 753, 698 cm^{-1}. HR-MS (ESI+) *m/z* calculated for $[C_{17}H_{14}O_2K]^+$ = $[M + K]^+$ 289.0625, found 289.0637.

*3-Allyl-5-methoxy-3-phenyl-2-benzofuran-1(3H)-one (**4o**).* This compound was prepared according to the GP and isolated as pale yellow colored viscous liquid 88% yield (118 mg): [TLC (petroleum ether/ethyl acetate 8:2, R_f (**3o**) = 0.50, R_f (**4o**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.78 (d, 1H, *J* = 8.3 Hz), 7.49 (d, 2H, *J* = 6.8 Hz), 7.35 (dd, 2H, *J* = 7.3 and 7.3 Hz), 7.30 (d, 1H, *J* = 7.3 Hz), 6.99 (dd, 1H, *J* = 8.8 and 2.4 Hz), 6.92 (d, 1H, *J* = 2.0 Hz), 5.56−5.40 (m, 1H), 5.08 (dd, 1H, *J* = 17.1 and 2.0 Hz), 5.02 (dd, 1H, *J* = 10.8 and 2.0 Hz), 3.87 (s, 3H), 3.23−3.08 (m, 1H), 3.06−2.95 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.5 (C_q), 164.7 (C_q), 154.8 (C_q), 139.9 (C_q), 130.6 (CH), 128.7 (2C, 2 × CH), 128.2 (CH), 127.3 (CH), 125.1 (2C, 2 × CH), 120.3 (CH_2), 118.1 (C_q), 115.8 (CH), 106.9 (CH), 88.2 (C_q), 55.8 (CH_3), 44.0 (CH_2) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2967, 1744, 1597, 1455, 1265, 1112, 1067, 982, 753, 696 cm^{-1}. HR-MS (ESI+) *m/z* calculated for $[C_{18}H_{15}O_2]^+$ = $[(M + H) - H_2O]^+$ 263.1067, found 263.1073.

*3-Allyl-5,6-dimethoxy-3-phenyl-2-benzofuran-1(3H)-one (**4p**).* This compound was prepared according to the GP and isolated as pale yellow colored viscous liquid 82% yield (122 mg): [TLC (petroleum ether/ethyl acetate 8:2, R_f (**3p**) = 0.40, R_f (**4p**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.46 (d, 1H, *J* = 6.8 Hz), 7.36 (dd, 1H, *J* = 7.3 and 6.8 Hz), 7.31 (d, 1H, *J* = 6.8 Hz), 7.26 (s, 1H), 6.84 (s, 1H), 5.55−5.38 (m, 1H), 5.15−4.95 (m, 2H), 3.94 (s, 3H), 3.91 (s, 3H), 3.15 (dd, 1H, *J* = 14.7 and 7.3 Hz), 3.01 (dd, 1H, *J* = 14.7 and 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.1 (C_q), 154.8 (C_q), 150.4 (C_q), 146.6 (C_q), 139.9 (C_q), 130.7 (CH), 128.7 (2C, 2 × CH), 128.3 (CH), 125.2 (2C, 2 × CH), 120.3 (CH_2), 117.8 (C_q), 106.0 (CH), 103.7 (CH), 88.4 (C_q), 56.4 (CH_3), 56.2 (CH_3), 43.8 (CH_2) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2912, 1753, 1598, 1461, 1275, 1142, 1077, 980, 753, 696 cm^{-1}. HR-MS (ESI+) *m/z* calculated for $[C_{19}H_{19}O_4]^+$ = $[M + H]^+$ 311.1278, found 311.1271.

*3,3-Diphenyl-2-benzofuran-1(3H)-one (**4q**).* This compound was prepared according to the GP and isolated as pale yellow colored solid 87% yield (125 mg): mp 96−98 °C; [TLC (petroleum ether/ethyl acetate 9:1, R_f (**3q**) = 0.50, R_f (**4q**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.94 (d, 1H, *J* = 7.3 Hz), 7.69 (dd, 1H, *J* = 8.8 and 7.3 Hz), 7.63−7.50 (m, 2H), 7.43−7.26 (m, 10H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.7 (C_q), 151.9 (C_q), 140.8 (2C, 2 × C_q), 134.1 (CH), 129.3 (CH), 128.5 (2C, 2 × CH), 128.4 (4C, 4 × CH), 127.1 (4C, 4 × CH), 126.0 (CH), 125.5 (C_q), 124.1 (CH), 91.6 (C_q) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 3060, 1754, 1597, 1446, 1250, 1106, 1073, 967, 750, 691 cm^{-1}. HR-MS (ESI+) *m/z* calculated for $[C_{20}H_{15}O_2]^+$ = $[M + H]^+$ 287.1067, found 287.1066.

*5-Methoxy-3,3-diphenyl-2-benzofuran-1(3H)-one (**4r**).* This compound was prepared according to the GP and isolated as colorless solid 83% yield (131 mg): mp 136−138 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f (**3r**) = 0.50, R_f (**4r**) = 0.30, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.85 (d, 1H, *J* = 8.3 Hz), 7.40−7.27 (m, 10H), 7.05 (dd, 1H, *J* = 8.3 and 2.0 Hz), 6.96 (d, 1H, *J* = 2.0 Hz), 3.86 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.4 (C_q), 164.6 (C_q), 154.6 (C_q), 140.9 (C_q), 131.5 (CH), 130.0 (CH), 128.5 (2C, 2 × CH), 128.4 (3C, 3 × CH), 127.6 (CH), 127.1 (3C, 3 × CH), 126.9 (C_q), 117.9 (C_q), 116.1 (CH), 108.8 (CH), 90.9 (C_q), 55.9 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2943, 1755, 1597, 1490, 1341, 1269, 1109, 1023, 968, 725, 697 cm^{-1}. HR-MS (ESI+) *m/z* calculated for $[C_{21}H_{16}O_3Na]^+$ = $[M + Na]^+$ 339.0992, found 339.0991.

*3-(3-Methoxyphenyl)-3-phenyl-2-benzofuran-1(3H)-one (**4s**).* This compound was prepared according to the GP and isolated as colorless viscous liquid 87% yield (138 mg): [TLC (petroleum ether/ethyl acetate 8:2, R_f (**3s**) = 0.50, R_f (**4s**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$ 400 MHz) δ = 7.94 (d, 1H, *J* = 7.3 Hz), 7.69 (dd, 1H, *J* = 7.3 and 7.3 Hz), 7.59 (d, 1H, *J* = 7.8 Hz), 7.55 (d, 1H, *J* = 7.8 and

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7.3 Hz), 7.40−7.20 (m, 6H), 7.00−6.80 (m, 3H), 3.74 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.7 (C_q), 159.5 (C_q), 151.8 (C_q), 142.3 (C_q), 140.7 (C_q), 134.1 (CH), 129.5 (CH), 129.3 (CH), 128.5 (CH), 128.4 (2C, 2 × CH), 127.0 (2C, 2 × CH), 126.0 (CH), 125.4 (C_q), 124.2 (CH), 119.4 (CH), 113.5 (CH), 113.2 (CH), 91.5 (C_q), 55.2 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} = 2987, 1745, 1592, 1480, 1349, 1259, 1103, 1043, 967, 726, 693 cm^{-1}. HR-MS (ESI +) m/z calculated for $[C_{21}H_{16}O_3]^+ = [M]^+$ 316.1094, found 316.1124.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization for all new compounds, copies of NMR spectra, and CIF files (for **2d** and **2f**) provided. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00888.

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Notes

The authors declare no competing financial interest.

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The toc/abstract graphic and Table 3 footnote *a* were corrected on July 7, 2015.

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