

Oxygen Heterocycles

Syntheses of 2-Benzylbenzofuran Derivatives and 2-Aryl-nitrochroman Derivatives from Nitroalkene Precursors

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Abstract: Simple and straightforward methods for the synthesis of 2-benzylbenzofuran, 3-substituted 2-benzylbenzofuran, and 2-aryl-nitrochroman derivatives are described. Benzofurans were generated from nitroalkenes by reduction with NaBH₄ followed by a Nef reaction and acid-mediated cyclization, whereas 3-substituted 2-benzylbenzofurans were prepared from nitro-

alkenes by reactions with Grignard reagents followed by a Nef reaction and an acid-mediated cyclization in a one-pot process. The synthesis of chromans involved a Knoevenagel condensation and the 1,4-diazabicyclo[2.2.2]octane (DABCO) assisted cyclization of β -(2-hydroxyphenyl)-nitroethanes and benzaldehydes, also in a one-pot process.

Introduction

Benzofuran structures are ubiquitous in a wide variety of natural products and bioactive substances.^[1] In particular, 2-benzylbenzofuran derivatives, possess a variety of biological activities.^[2] For example pteroside (Figure 1, **A**), a natural product extracted from the tree *Pterocarpus marsupium*, has antihyperglycemic activity and is important in the semisynthesis of biomedical compounds.^[3] Further, 2-benzyl-3-biphenylbenzofuran derivatives (Figure 1, **B**) exhibit potent protein tyrosine phosphatase inhibitor activity and also have antihyperglycemic activity,^[4] S24014 (**C**) is an agonist of the melatonin receptors

MT₁ and MT₂,^[5] and 656224 (**D**) is an inhibitor of bronchoconstriction and antigen-induced dyspnea. It also inhibits the production of leukotriene B₄ in polymorphonuclear leukocytes, which are involved in inflammation.^[6]

On the other hand, chroman (3,4-dihydro-2H-1-benzopyran) is a common skeletal structure in natural products. For example, catechin, which is found in cacao beans, vascular bundles, and tea leaves, is a natural antioxidant used in antibacterial and tooth decay preventing drugs, and a large amount of functionalized catechin derivatives can be found in nature.^[7] BW683C, which is a 2-arylchroman derivative, is a potential drug for the reduction of the production of subviral particles of rhino-

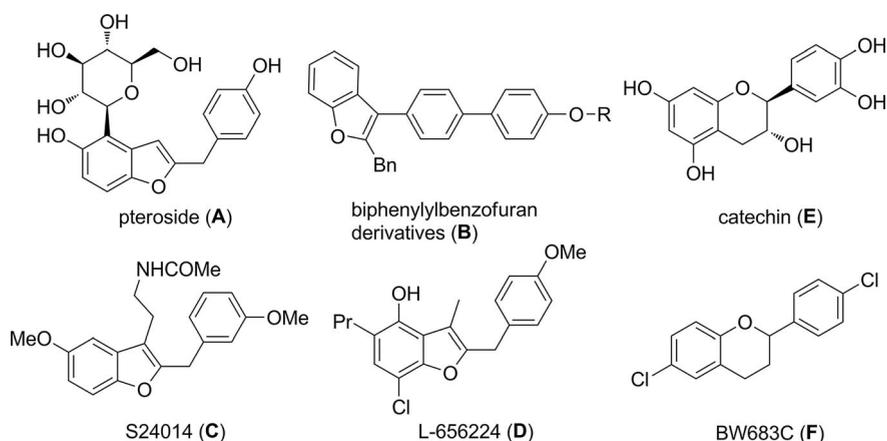


Figure 1. 2-Benzylbenzofuran derivatives.

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virus 1B (Figure 1).^[8] Although several protocols are available for the synthesis of various benzofuran derivatives,^[9] the number of protocols for the synthesis of 2-benzylbenzofuran derivatives remains limited.^[10] Recently, a few more synthetic methods for accessing 2-benzylbenzofuran derivatives from propargyl alcohols such as 2-(3-aryl-1-hydroxyprop-2-yn-1-yl)phenol

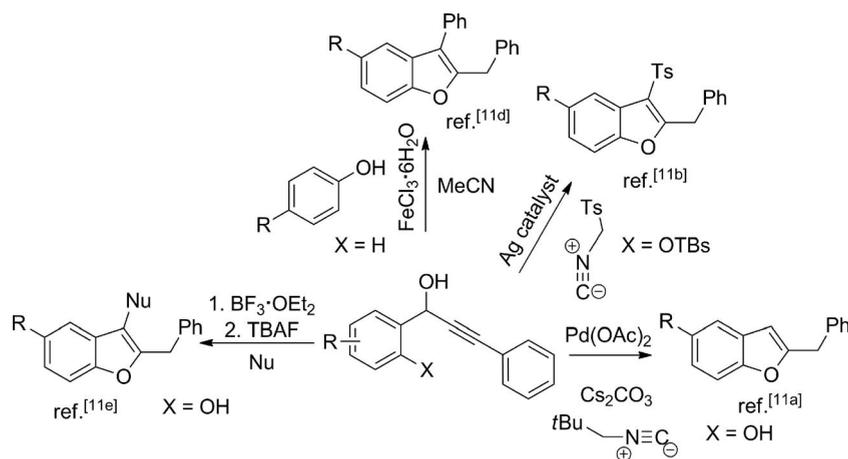
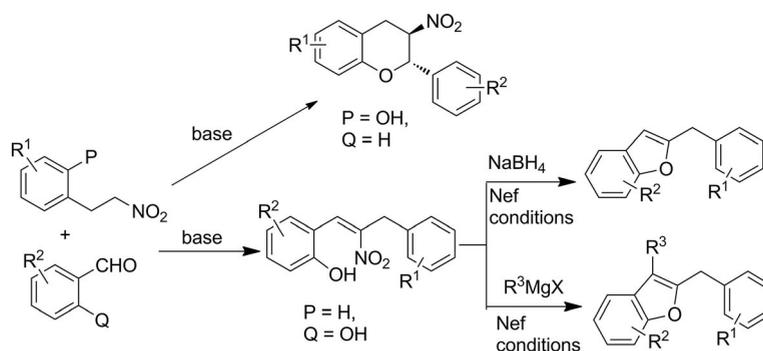


Figure 2. Synthetic methods for the preparation of 2-benzylbenzofuran derivatives.



Scheme 1. Synthetic strategies for the synthesis of 2-benzylbenzofuran derivatives.

and 1,3-diarylprop-2-yn-1-ol as starting materials (Figure 2) have been reported.^[11] There are several reports on the synthesis of 2-arylchroman derivatives.^[12] However, to the best of our knowledge, the only one report of the preparation of 2-aryl-nitrochroman derivatives is that of Kabalka et al.^[12a] Their approach involved the reduction of nitrochromene derivatives with sodium borohydride.

Most of the methods reported for the synthesis of benzylbenzofuran and benzopyran derivatives require special starting materials or expensive catalysts. Hence, a simple, straightforward method for the synthesis of 2-benzylbenzofuran and 2-arylbenzopyran derivatives from readily available starting materials would be highly desirable. We have been investigating functionalized nitroalkenes and derivatives thereof for the past few years.^[13] On the basis of our experience in this area, we considered the possibility of developing a synthetic route for the synthesis of 2-benzylbenzofuran derivatives from nitroalkene derivatives. Our synthetic route involved the Knoevenagel condensation of a β -phenyl-nitroethane and benzaldehyde to produce a nitroalkene followed by NaBH_4 reduction, a Nef reaction, and cyclization to obtain 2-benzylbenzofurans. Moreover, the nitroalkene, on treatment with a Grignard reagent followed by a Nef reaction and cyclization would be predicted to lead to the formation of 3-substituted-2-benzylfuran derivatives (Scheme 1). In addition, 2-aryl-nitrochromans could be obtained from the Knoevenagel condensation of β -(2-hydroxyphenyl)-

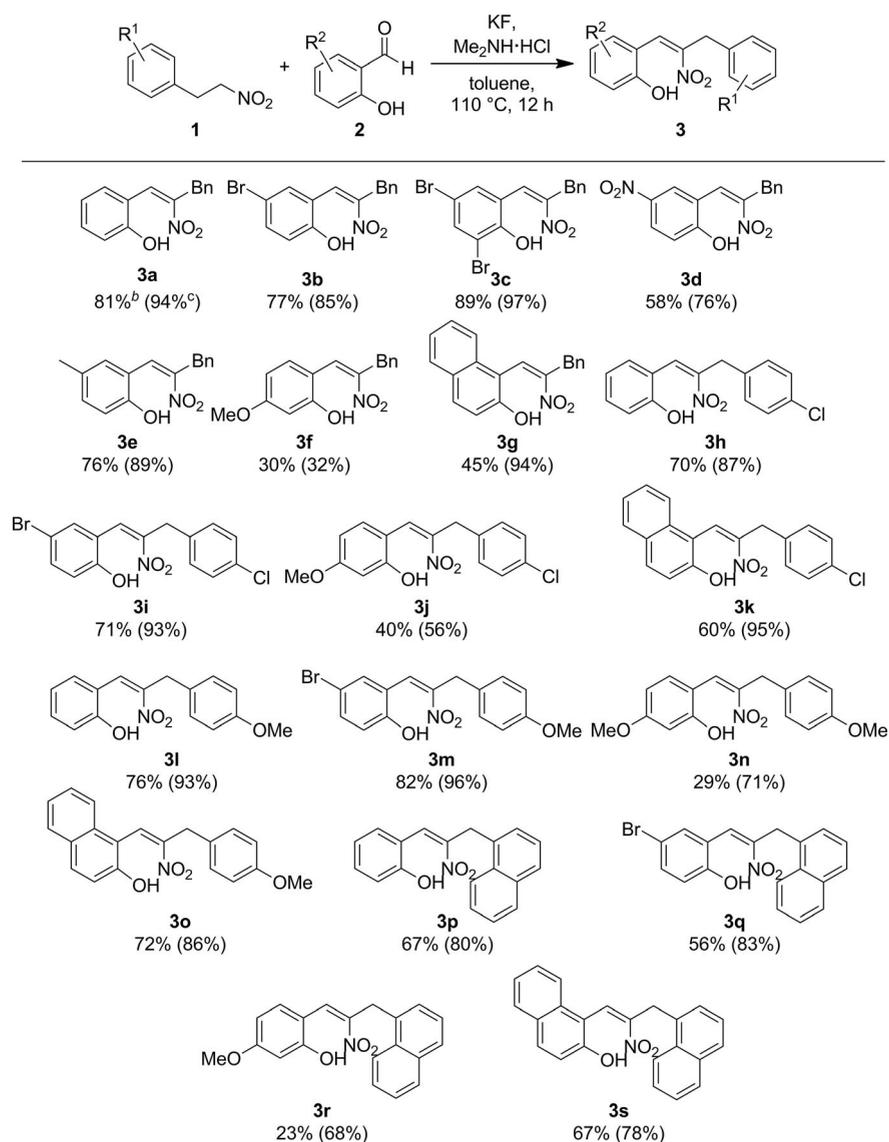
nitroethanes and benzaldehydes followed by a Michael addition reaction (Scheme 1).

Results and Discussion

To implement our plan for the synthesis of benzylbenzofuran derivatives, we initially synthesized various β -phenyl-nitroethane derivatives **1** from the corresponding β -nitrostyrenes by reduction with either NaBH_4 ^[14a] or Hantzsch dihydropyridine.^[14b] The β -phenyl-nitroethanes **1** were then treated with different substituted salicylaldehydes **2** to furnish the corresponding nitroalkenes **3** in the presence of KF and $\text{Me}_2\text{NH}\cdot\text{HCl}$ (Table 1).^[14c]

This method afforded nitroalkenes in good yields, if the salicylaldehyde was unsubstituted or had an electron-withdrawing substituent. However, if the salicylaldehyde had an electron-donating substituent, the corresponding nitroalkenes were produced in low yields.

After the successful preparation of various hydroxy-substituted nitroalkenes **3**, we used the nitroalkene **3a** as a model substrate and attempted the synthesis of 2-benzylbenzofuran by literature cyclization procedures. Unfortunately, methods with acids such as formic acid^[15a] and H_2SO_4 ,^[15b] bases such as triethylamine (TEA) and 1,8-diazabicycloundec-7-ene (DBU), or other reagents such as copper bromide^[15c] and iodine/potas-

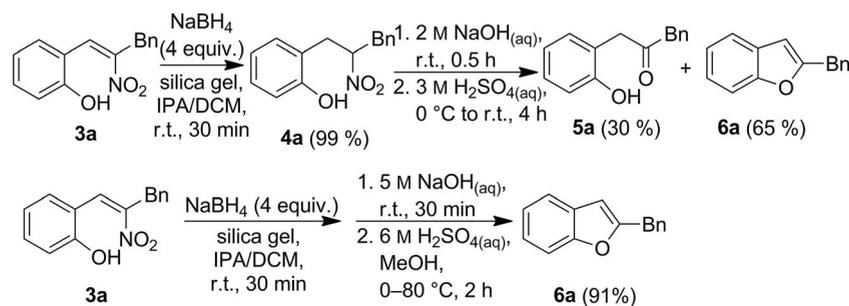
Table 1. Syntheses of nitroalkene derivatives **3a–3s**.

[a] Reaction conditions: **1** (2.5 mmol), **2** (2.6 mmol), KF (0.25 mmol), $\text{Me}_2\text{NH}\cdot\text{HCl}$ (5 mmol), toluene (5 mL), $110\text{ }^\circ\text{C}$, 12 h. [b] Isolated yields. [c] Recovered yields.

sium carbonate^[15d] failed to convert the nitroalkene into the desired product. As a result, we proposed an alternative route for the production of the benzofuran **6a** from **3a**. This route was based on work of Yue;^[9c] the nitroalkene **3a** was reduced by NaBH_4 to give the corresponding nitroalkane (**4a**), which was subjected to Nef reaction conditions to furnish the ketone, followed by cyclization in the presence of an acid to give the corresponding 2-benzylbenzofuran. When the reaction was performed at room temperature in the presence of NaOH and H_2SO_4 , the 2-benzylbenzofuran was produced in moderate yield along with the intermediate ketone (**5a**; Scheme 2). To improve the yield of the desired product, the temperature was increased to $80\text{ }^\circ\text{C}$ to affect the cyclization. Unfortunately, the temperature increase did not improve the yield of the desired product. However, the yield of **6a** was increased drastically when methanol was added to the reaction mixture (methanol may homogenize

the reaction mixture) at $80\text{ }^\circ\text{C}$. Furthermore, we executed all of the transformations in one pot. To our delight, the desired product was obtained in 91% yield in a one-pot process.

After determination of the optimized reaction conditions, we applied them to the preparation of nitroalkenes **3b–3s** to give the corresponding 2-benzylbenzofuran derivatives **6b–6s**, and the results are depicted in Table 2. A substrate with both aryl rings unsubstituted gave the corresponding product in excellent yield, whereas substrates containing an electron-withdrawing group, such as a bromo or a nitro group, or a mild electron-donating group, such as a methyl group, on aryl ring A afforded the desired 2-benzylbenzofuran derivatives in good yields (**6b–6e**). Moreover, substrates containing strong electron-donating groups, such as a methoxy group, on aryl ring A produced the desired products in moderate yields (**6f, 6j, 6n, and 6r**). In contrast, substrates derived from 1-hydroxy-2-naphthaldehyde fur-

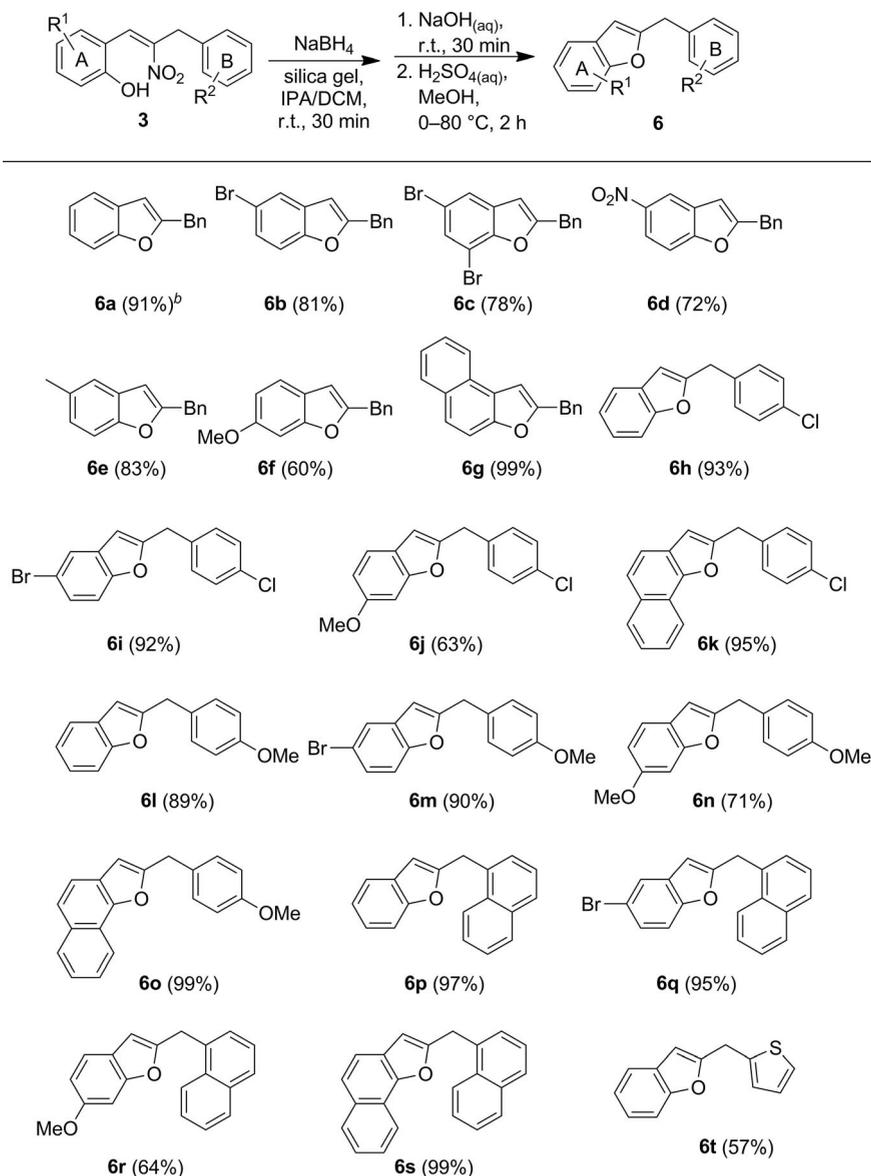


Scheme 2. Synthesis of 2-benzylbenzofuran derivatives.

nished the corresponding benzylbenzofuran derivatives in excellent yields (**6g**, **6k**, **6o**, and **6s**). The substituents on aryl ring B did not significantly affect the yields of the desired prod-

ucts. Furthermore, a substrate containing a thiophene moiety also participated in this reaction to afford the corresponding benzofurane derivative (**6t**) in 57 % yield.

Table 2. Syntheses of 2-benzylbenzofuran derivatives **6a–6s**.



[a] Reaction conditions: (i) **3** (1 mmol), NaBH₄ (4 mmol), silica gel (0.3 g), IPA (2 mL), DCM (10 mL), 0 °C to r.t., 30 min; (ii) **4**, 5 M NaOH (3 mL), r.t., 30 min, then 6 M H₂SO₄ (8 mL), MeOH (30 mL), 0–80 °C, 2 h. [b] Isolated yields.

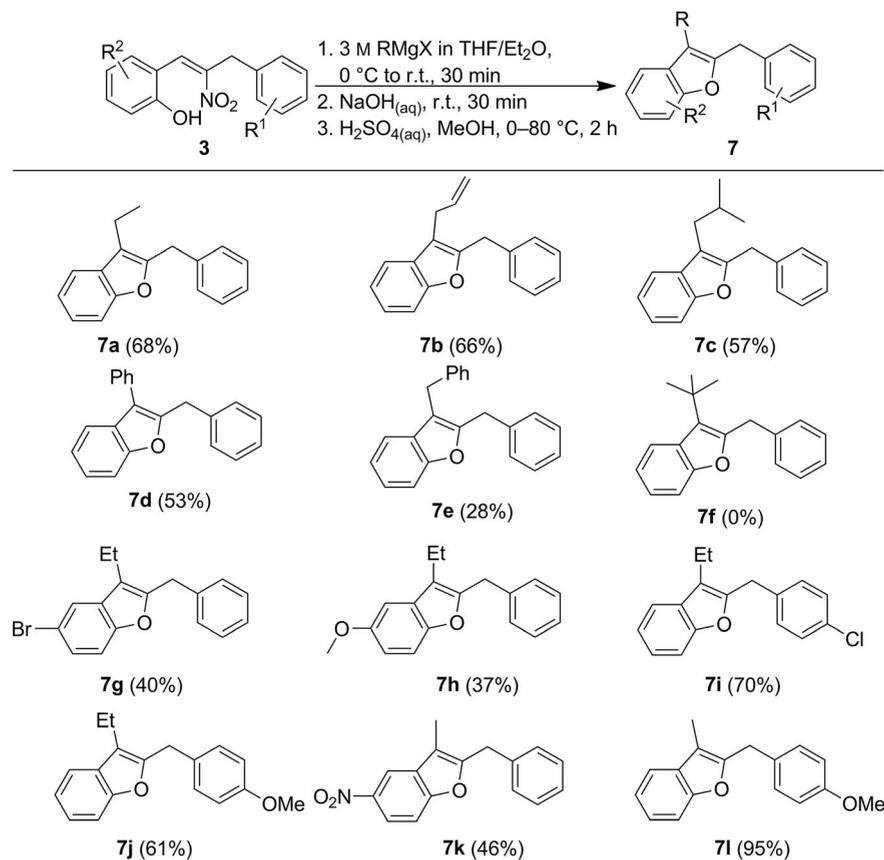
It was observed by us and others that the reactions of nitroalkenes and Grignard reagents afforded high yields of nitroalkanes, *aci*-nitro compounds, or carbonyl compounds.^[16] Hence, by taking advantage of this reaction, we treated the nitroalkenes **3** with various Grignard reagents to obtain the corresponding C-alkylated nitroalkanes, which, when further subjected to Nef reaction conditions, directly gave the corresponding 3-substituted 2-benzylfuran derivatives. Under the present conditions, the reactions of ethylmagnesium bromide or allylmagnesium bromide with the nitroalkene **3a** afforded the corresponding 2-benzyl-3-ethylbenzofuran (**7a**) and 3-allyl-2-benzylbenzofuran (**7b**) derivatives in good yields. The reactions of isobutylmagnesium bromide and phenylmagnesium bromide with nitroalkene **3a** furnished the corresponding 2-benzyl-3-isobutylbenzofuran derivative (**7c**) and 2-benzyl-3-phenylbenzofuran (**7d**) in moderate to good yields. On the other hand, the reaction of *t*BuMgBr failed to produce the desired 2-benzyl-3-*tert*-butylbenzofuran (**7f**) under these conditions. We further treated different substituted nitroalkenes with ethylmagnesium bromide under the same reaction conditions. Substrates possessing an electron-withdrawing or electron-donating group in the salicylaldehyde part of the nitroalkene produced the corresponding 2-substituted 3-ethylbenzofuran derivatives (**7g** and **7h**) in moderate yields. Furthermore, substrates possessing an

electron-withdrawing or an electron-donating group in the nitroalkane part of the nitroalkene also provided the corresponding 2-substituted 3-ethylbenzofuran derivatives (**7i** and **7j**; Table 3).

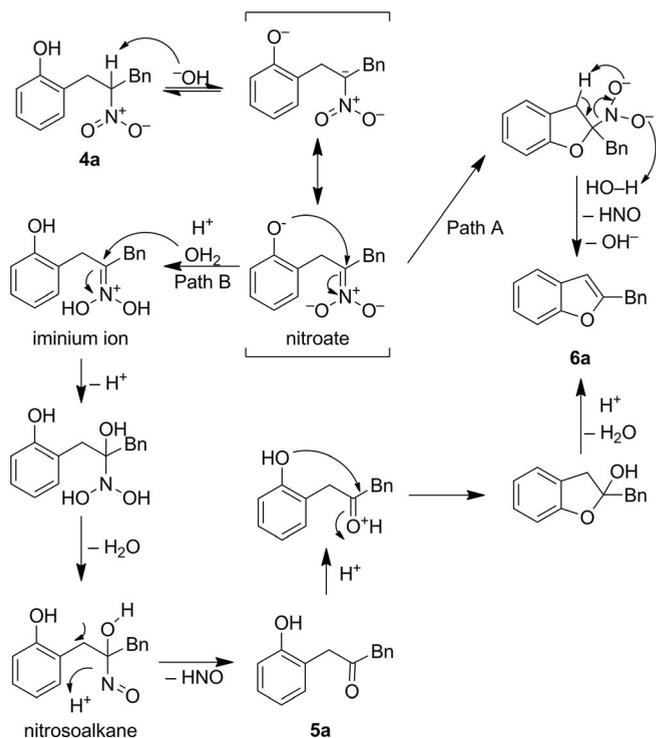
A proposed mechanism for the formation of 2-benzylbenzofuran is shown in Scheme 3. After the deprotonation of the nitroalkane **4a**, there are two plausible pathways to afford the benzofuran **6a**. In Path A, under a basic environment, the intramolecular attack of the phenoxide oxygen atom occurs to form a dihydrobenzofuran intermediate, followed by the elimination of nitric oxide and water. In contrast, Path B involves a conventional Nef reaction: in the presence of an acid, the nitroate forms ketone **5a**, after which the phenol attacks the carbonyl group to complete the cyclization,^[10e] and the subsequent dehydration of the dihydrobenzofuran furnishes the benzofuran **6a**. To investigate the possibility of Path A, we examined the reaction with nitroalkane **4a** in an aqueous NaOH solution, followed by treatment with an aqueous NH₄Cl solution. However, only the starting material was recovered without the formation of cyclized compounds; thus, Path B was confirmed as the only reaction pathway.

The 2-benzylbenzofuran derivatives shown in Table 2 are key precursors in the synthesis of various bioactive compounds. Herein, we synthesized *N*-[2-(2-benzylbenzofuran-3-yl)ethyl]-

Table 3. Syntheses of 2-benzylbenzofuran derivatives **7a–7l**.



[a] Reaction conditions: (i) **3** (0.5 mmol), 3 M RMgX in THF/diethyl ether (1.5 mmol), diethyl ether (2 mL), –20 °C to r.t., 30 min; (ii) **4**, 5 M NaOH (3 mL), r.t., 30 min, then 6 M H₂SO₄ (8 mL), MeOH (30 mL), 0–80 °C, 2 h. [b] Isolated yields.



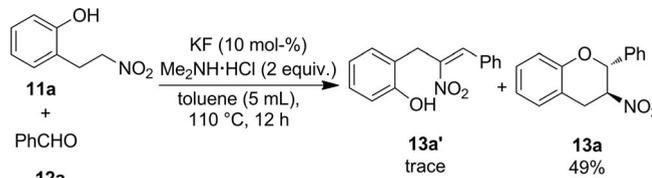
Scheme 3. Proposed mechanism for the conversion of the nitroalkane **4a** into the benzofuran **6a**.

acetamide (**10a**), which is an analogue of S24014.^[17a] As depicted in Scheme 3, the 2-benzylbenzofuran **6a** was treated with 1,3,5-trioxane in concentrated HCl to add the chloromethyl group to the 2-benzylbenzofuran under mild conditions.^[17b] The chloromethyl compound **8a** then underwent cyanation with NaCN in dimethyl sulfoxide (DMSO) to furnish the cyano compound **9a**,^[17c] which was further reduced with LiAlH₄ (LAH) followed by Ac₂O amidation to give the desired benzofuran derivative **10a** in good yield (Scheme 4).

2-Aryl-nitrochromans

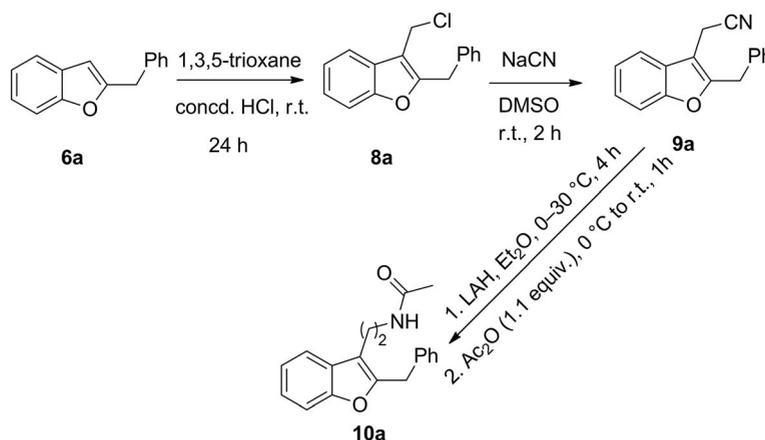
The synthesis of 2-aryl-nitrochroman involves the Knoevenagel condensation of (2-hydroxyphenyl)-nitroethanes **11** and various

benzaldehydes **12** followed by a Michael addition. To determine suitable conditions for the preparation of the desired chroman derivatives, we examined the reaction of (2-hydroxyphenyl)-nitroethane (**11a**) and benzaldehyde (**12a**) as model substrates. The initial reaction was conducted with KF and Me₂NH·HCl in toluene at 110 °C. Under these conditions, we obtained a 49 % yield of *trans*-2-aryl-nitrochroman **13a**,^[12a] as the major product, along with trace amounts of the nitroalkene **13a'** (Scheme 5).

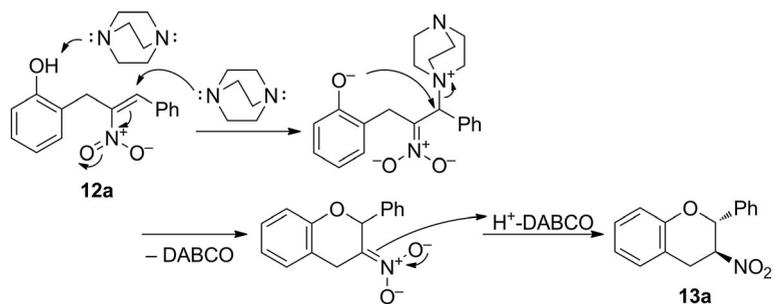


Scheme 5. One-pot conditions for the synthesis **3a**.

Encouraged by the initial results, we then concentrated on optimizing this reaction (Table S1, Supporting Information). First, we screened the solvents including DMSO and *N,N*-dimethylformamide (DMF) and also performed the reaction under solvent-free conditions. The reaction resulted in the production of 39 % of the chroman and 25 % of the nitroalkene in DMF and 22 and 21 % of the chroman and nitroalkene in DMSO, respectively. Moreover, 52 % of the chroman was obtained under solvent-free conditions, and the intermediate nitroalkene was not detected in the reaction mixture. On the basis of these results, we decided to optimize other parameters for this reaction under neat conditions. We next varied the amount of benzaldehyde. Notably, the yield of the chroman was improved by increasing the amount of benzaldehyde used in the reaction. The optimum amount of benzaldehyde needed for the reaction was 5 equiv. relative to the nitroalkane. We then optimized the quantity of KF used in the reaction. The reaction produced the best yield of chroman when 10 mol-% of KF was used as the catalyst. On the other hand, in the absence of KF, a low yield of the desired product along with detectable levels of the intermediate were observed. Further, we examined different additives such as tetrabutylammonium fluoride (TBAF), KHF₂, tetrabutylammonium bromide (TBAB), and cetyltrimethylammo-

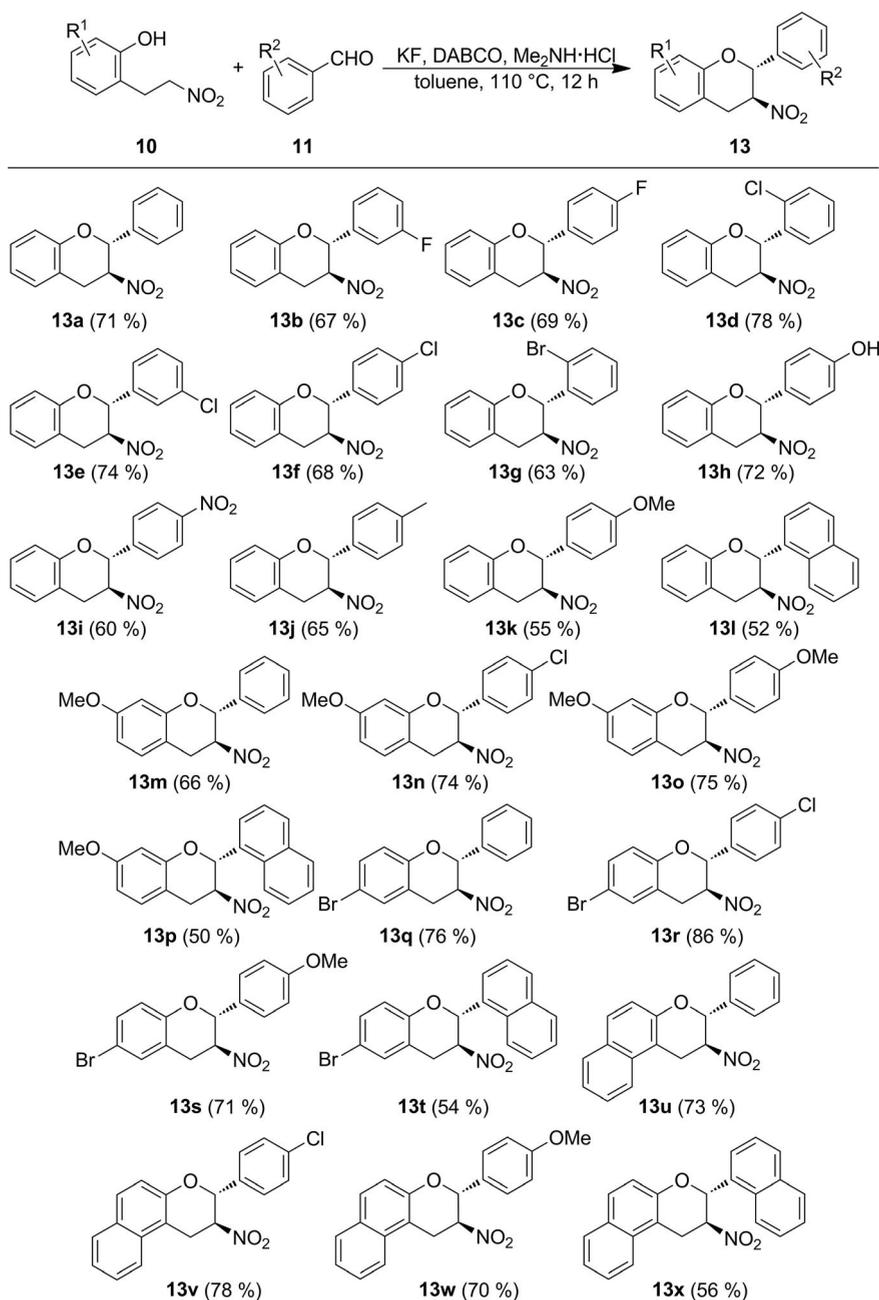


Scheme 4. Synthesis of *N*-[2-(2-benzylbenzofuran-3-yl)ethyl]acetamide.



Scheme 6. Proposed mechanism for the DABCO-catalyzed cyclization of **13a'** to **13a**.

Table 4. Synthesis of 2-aryl-nitrochromans **13a–13x**.



[a] Reaction conditions: **10** (0.5 mmol), **11** (0.75 mmol), KF (0.05 mmol), DABCO (0.25 mmol), Me₂NH·HCl (0.5 mmol), toluene (1 mL), 110 °C, 12 h. [b] Isolated yields.

nium bromide (CTAB). TBAF produced the chroman in lower yield, whereas the others provided the intermediate as the major product.

After screening various parameters such as the solvent, amounts of reagents, and various additives, a maximum yield of 73 % was obtained after 12 h of reaction. Although we obtained the desired product in a satisfactory yield, a large amount of benzaldehyde was required to achieve this. Hence, to solve this problem, we tuned the reaction conditions further. In this regard, we utilized different base additives including TEA, DBU, and 1,4-diazabicyclo[2.2.2]octane (DABCO) along with KF. The use of TEA and DBU did not improve the reaction. However, the reaction in the presence of DABCO produced the product in good yield, even when only 1 equiv. of β -(2-hydroxyphenyl)-nitroethane and 2 equiv. of benzaldehyde were used. On the basis of this finding, we attempted to optimize the amount of $\text{Me}_2\text{NH}\cdot\text{HCl}$ and DABCO required for the reaction (Table S2). The reaction produced the chroman in equally good yield when nitroalkane **10a** was treated with 1.5 equiv. of **11a** in the presence of 1 equiv. of $\text{Me}_2\text{NH}\cdot\text{HCl}$, 50 mol-% of DABCO, and 10 mol-% of KF in toluene at 110 °C.

Further, the role of DABCO in this reaction can be explained through the mechanism depicted in the Scheme 6.

These optimized conditions were applied to the synthesis of various substituted 2-aryl-nitrochroman derivatives **13a–13x** from the corresponding functionalized β -(2-hydroxyphenyl)-nitroethane **10** and benzaldehyde **11** (Table 4). Most of the reactions of β -(2-hydroxyphenyl)-nitroethanes and benzaldehydes furnished moderate to good yields of the corresponding 2-aryl-nitrochromans. Moreover, the reaction of 2-naphthaldehyde and β -(2-hydroxyphenyl)-nitroethane produced the corresponding nitrochromans (**13l**, **13p**, **13t**, and **13x**) in slightly lower yields than those of the other substrates. This may be due to steric effects. On the other hand, β -(2-hydroxy-1-naphthyl)-nitroethane as a substrate resulted in good yields (**13u–13w**). Interestingly, in all of the reactions, we obtained a single diastereomer (*trans*).

Conclusions

We have successfully synthesized 2-benzylbenzofuran and 3-substituted 2-benzylbenzofuran derivatives from nitroalkene precursors. 2-Benzylbenzofurans were generated from nitroalkenes (β -phenyl-nitroethanes and salicylaldehydes) by reduction with NaBH_4 followed by a Nef reaction and acid-mediated cyclization in a two-step reaction. 3-Substituted 2-benzylbenzofuran derivatives were produced from nitroalkenes, β -phenyl-nitroethanes, and salicylaldehydes by treating them with Grignard reagents followed by a Nef reaction and acid-mediated cyclization in a one-pot process. The methods are simple and can be used in conjunction with most types of functionalized precursors. Further, a simple and easy method for accessing nitrochromans was achieved in a diastereoselective manner. No expensive chemicals were used in these reactions, which also represent potential methods for large-scale syntheses.

Experimental Section

General Information: Reagents and solvents were purchased from various commercial sources and used directly without any further purification, unless otherwise stated. Column chromatography was performed with 63–200 mesh silica gel. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts (δ) are reported in ppm with tetramethylsilane (TMS) and chloroform as internal standards, and coupling constants are expressed in Hz. Melting points were recorded with an electrothermal capillary melting-point apparatus. HR mass spectra were recorded in the ESI-TOF or EI+ mode. The starting β -phenyl-nitroethane derivatives were synthesized from β -nitrostyrene by previously reported methods with NaBH_4 ^[16] or Hantzsch dihydropyridine^[17] as the reducing reagents.

General Procedure for Nitroalkenes 3a–3s: The nitroalkane derivative **1** (2.5 mmol), substituted benzaldehyde **2** (2.6 mmol, 1.04 equiv.), KF (0.25 mmol, 10 mol-%), and $\text{Me}_2\text{NH}\cdot\text{HCl}$ (5 mmol, 2 equiv.) were added to toluene (5 mL), and the resulting solution was heated to 110 °C and stirred for 12 h. The reaction mixture was then extracted with dichloromethane (DCM) and water, and the DCM layer was separated, dried with anhydrous MgSO_4 , and concentrated under vacuum to give the crude product, which was further purified by column chromatography with ethyl acetate/hexane [ethyl acetate (EA)/hexane] as the eluent to yield the desired product **3**.

General Procedure for the Preparation of the 2-Benzylbenzofurans 6a–6s: The nitroalkene derivative **3** (1 mmol) was dissolved in 2-propanol (IPA; 2 mL) and DCM (10 mL) with silica gel (0.3 g). NaBH_4 (0.15 g, 4 equiv.) was added slowly, and the resulting solution was stirred for 30 min. The reaction was then quenched with aqueous 6 M HCl (1 mL) and the mixture extracted with DCM and water. The DCM layer was separated, dried with anhydrous MgSO_4 , and concentrated under vacuum to give the crude product **4**. The crude product **4** was added to aqueous 5 M NaOH (6 mL), and the resulting solution was stirred at room temperature for 30 min and then slowly added to a vigorously stirred aqueous 6 M H_2SO_4 solution (15 mL) at 0 °C. The reaction vessel was removed from the ice bath, and MeOH (30 mL) was added. The reaction mixture was further heated to 80 °C for 2 h and then extracted with EA and water. The EA layer was separated, dried with anhydrous MgSO_4 , and concentrated under vacuum to give the crude product, which was further purified by column chromatography with EA/hexane as the eluent to yield the desired product **6**.

General Procedure for the Synthesis of the 2-Benzylbenzofurans 6t–6w: The nitroalkene derivative **3** (0.5 mmol) was dissolved in anhydrous THF (2 mL) under N_2 , and the solution was then cooled to –20 °C. The alkyl/arylmagnesium bromide/chloride (3 M diethyl ether/THF solution, 0.5 mL, 3 equiv.) was then added slowly to the solution. After the addition, the reaction mixture was warmed to room temperature and stirred for 30 min. The solvent was removed under vacuum to give the crude product **4**. The crude product **4** was added to aqueous 5 M NaOH (3 mL), and the solution was stirred at room temperature for 30 min and then slowly added to vigorously stirred aqueous 6 M H_2SO_4 (7 mL) at 0 °C. The reaction mixture was removed from the ice bath, MeOH (10 mL) was added, and the mixture was further heated to 80 °C for 2 h. The reaction mixture was then extracted with EA and water, and the EA layer was separated, dried with anhydrous MgSO_4 , and concentrated under vacuum to give the crude product, which was further purified by column chromatography with EA/hexane as the eluent to yield the desired product **6**.

2-(2-Benzylbenzofuran-3-yl)acetonitrile (9a): 1,3,5-Trioxane (10 mmol, 5 equiv.) was dissolved in concd. HCl (3 mL), and 2-benzylbenzofuran (**6a**, 2 mmol) was added dropwise to the solution. The reaction mixture was stirred at room temperature for 24 h and then extracted with diethyl ether and water. The diethyl ether layer was washed several times with water, dried with anhydrous $MgSO_4$, and concentrated under vacuum to give the crude product **8a**. The crude product **8a** was added to NaCN (2.2 mmol, 1.1 equiv.) in DMSO (2 mL) at room temperature and allowed to react for 2 h. The reaction mixture was extracted with EA and water, and the EA layer was separated, dried with anhydrous $MgSO_4$, and concentrated under vacuum to give the pure product **9a** as a yellow oil.

N-[2-(2-Benzylbenzofuran-3-yl)ethyl]acetamide (10a): 2-(2-Benzylbenzofuran-3-yl)acetonitrile (**9a**; 1 mmol) was dissolved in diethyl ether (2 mL), and the solution was added to a slurry of LAH (4 mmol, 4 equiv.) in diethyl ether (8 mL) at 0 °C. The reaction mixture was then heated slowly to 30 °C and allowed to react for 4 h. After completion of the reaction, the mixture was cooled to 0 °C, and the reaction was quenched carefully with water (1 mL). The solid that formed was removed by filtration, and the filtrate was dried with anhydrous $MgSO_4$ and concentrated under vacuum to afford a yellow oil, which was diluted with DCM (1 mL); Ac_2O (1.1 mmol, 1.1 equiv.) was added dropwise at 0 °C, and the reaction mixture was then warmed to room temperature and stirred for 1 h. The reaction mixture was extracted with DCM and water, and the DCM layer was separated, dried with anhydrous $MgSO_4$, and concentrated under vacuum to give the crude product, which was further purified by column chromatography with DCM/MeOH as eluent to yield the desired product **10a**.

General Procedure for the Synthesis of 2-Aryl-nitrochromans 13a–13x: Nitroalkane derivative **10** (0.5 mmol), substituted salicylaldehyde **11** (0.75 mmol, 1.5 equiv.), KF (0.05 mmol, 10 mol-%), DABCO (0.25 mmol, 50 mol-%), and $Me_2NH \cdot HCl$ (0.5 mmol, 1 equiv.) were added to toluene (1 mL), and the mixture was heated to 110 °C and stirred for 12 h. The reaction mixture was then extracted with DCM and water, and the DCM layer was separated, dried with anhydrous $MgSO_4$, and concentrated under vacuum to give the crude product, which was dissolved in MeOH (1 mL); NH_2OH (0.25 mmol, 0.5 equiv.) was added, and the mixture was stirred for 30 min; the reaction was monitored by TLC. After the disappearance of the benzaldehyde, the reaction mixture was extracted with DCM and water, and the DCM layer was separated, dried with anhydrous $MgSO_4$, and concentrated under vacuum to give the crude product, which was further purified by column chromatography with EA/hexane as the eluent to yield the desired product **13**.

2-[(Z)-2-Nitro-3-phenylprop-1-en-1-yl]phenol (3a): Yield: 517 mg, 81 %. Yellow solid. M.p. 122–123 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 8.54 (s, 1 H), 7.37–7.27 (m, 5 H), 7.24 (d, J = 7.2 Hz, 2 H), 6.96–6.88 (m, 2 H), 5.70 (s, 1 H), 4.26 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 150.0, 136.6, 132.2, 131.4, 129.5, 129.1, 127.9, 127.1, 121.3, 119.6, 116.3, 33.3 ppm. HRMS (EI): calcd. for $C_{15}H_{13}NO_3$ [M] $^+$ 255.0895; found 255.0899.

4-Bromo-2-[(Z)-2-nitro-3-phenylprop-1-en-1-yl]phenol (3b): Yield: 641 mg, 77 %. Yellow solid. M.p. 176–177 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (s, 1 H), 7.40–7.37 (m, 2 H), 7.33–7.30 (m, 2 H), 7.26–7.23 (m, 1 H), 7.17 (d, J = 7.0 Hz, 2 H), 6.77 (d, J = 8.3 Hz, 1 H), 5.30 (s, 1 H), 4.17 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.5, 151.7, 136.3, 134.5, 132.2, 129.2, 129.2, 128.0, 127.3, 121.7, 117.9, 113.4, 33.3 ppm. HRMS (EI): calcd. for $C_{15}H_{12}BrNO_3$ [M] $^+$ 333.0001; found 332.9992.

2,4-Dibromo-6-[(Z)-2-nitro-3-phenylprop-1-en-1-yl]phenol (3c): Yield: 914 mg, 89 %. Yellow solid. M.p. 118–119 °C. 1H NMR

(400 MHz, $CDCl_3$): δ = 8.27 (s, 1 H), 7.66 (d, J = 2.2 Hz, 1 H), 7.34–7.30 (m, 3 H), 7.27–7.25 (m, 1 H), 7.17 (d, J = 7.2 Hz, 2 H), 5.90 (s, 1 H), 4.16 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.0, 150.3, 136.0, 135.8, 131.7, 129.2, 128.9, 128.0, 127.4, 122.2, 113.0, 111.9, 33.3 ppm. HRMS (EI): calcd. for $C_{15}H_{11}Br_2NO_3$ [M] $^+$ 410.9106; found 410.9112.

4-Nitro-2-[(Z)-2-nitro-3-phenylprop-1-en-1-yl]phenol (3d): Yield: 435 mg, 58 %. Yellow solid. M.p. 93–94 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1 H), 8.21–8.17 (m, 2 H), 7.34–7.30 (m, 2 H), 7.27–7.23 (m, 2 H), 7.19 (d, J = 7.3 Hz, 2 H), 6.98 (d, J = 8.7 Hz, 1 H), 4.21 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 152.5, 141.7, 135.7, 129.3, 128.3, 128.0, 127.5, 127.4, 126.0, 120.3, 116.4, 33.3 ppm. HRMS (EI): calcd. for $C_{15}H_{12}N_2O_5$ [M] $^+$ 300.0746; found 300.0747.

4-Methyl-2-[(Z)-2-nitro-3-phenylprop-1-en-1-yl]phenol (3e): Yield: 511 mg, 76 %. Yellow solid. M.p. 110–112 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 8.43 (s, 1 H), 7.33–7.19 (m, 5 H), 7.10–7.06 (m, 2 H), 6.76 (d, J = 8.2 Hz, 1 H), 5.34 (s, 1 H), 4.21 (s, 2 H), 2.20 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.6, 150.3, 136.9, 132.6, 131.1, 130.7, 129.9, 129.0, 128.0, 127.0, 119.5, 116.1, 33.4, 20.7 ppm. HRMS (EI): calcd. for $C_{16}H_{15}NO_3$ [M] $^+$ 269.1052; found 269.1058.

5-Methoxy-2-[(Z)-2-nitro-3-phenylprop-1-en-1-yl]phenol (3f): Yield: 214 mg, 30 %. Yellow solid. M.p. 129–131 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 8.54 (s, 1 H), 7.34–7.20 (m, 6 H), 6.56 (dd, J = 8.7, 2.3 Hz, 1 H), 6.42 (d, J = 2.3 Hz, 1 H), 5.51 (s, 1 H), 4.25 (s, 2 H), 3.79 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2, 156.7, 148.0, 136.9, 130.9, 130.8, 129.1, 127.8, 127.0, 112.5, 107.5, 102.2, 55.7, 33.5 ppm. HRMS (EI): calcd. for $C_{16}H_{15}NO_4$ [M] $^+$ 285.1001; found 285.1000.

1-[(Z)-2-Nitro-3-phenylprop-1-en-1-yl]naphthalen-2-ol (3g): Yield: 343 mg, 45 %. Yellow solid. M.p. 150–151 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1 H), 7.84 (d, J = 8.7 Hz, 2 H), 7.72 (d, J = 8.4 Hz, 1 H), 7.57–7.53 (m, 1 H), 7.46–7.42 (m, 1 H), 7.18–7.13 (m, 4 H), 7.04–7.02 (m, 2 H), 5.23 (s, 1 H), 3.93 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4, 150.6, 136.0, 132.3, 131.8, 129.1, 128.9, 128.8, 128.7, 128.6, 128.0, 127.0, 124.6, 123.7, 117.9, 111.9, 34.1 ppm. HRMS (EI): calcd. for $C_{19}H_{15}NO_3$ [M] $^+$ 305.1052; found 305.1057.

2-[(Z)-3-(4-Chlorophenyl)-2-nitroprop-1-en-1-yl]phenol (3h): Yield: 506 mg, 70 %. Yellow solid. M.p. 174–175 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 8.47 (s, 1 H), 7.34–7.22 (m, 5 H), 7.13 (d, J = 8.4 Hz, 1 H), 6.96–6.92 (m, 1 H), 6.87 (d, J = 8.0 Hz, 1 H), 5.20 (s, 1 H), 4.17 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6, 149.9, 135.2, 133.0, 132.2, 131.3, 129.6, 129.3, 129.2, 121.6, 119.6, 116.3, 32.8 ppm. HRMS (EI): calcd. for $C_{15}H_{12}ClNO_3$ [M] $^+$ 289.0506; found 289.0511.

4-Bromo-2-[(Z)-3-(4-chlorophenyl)-2-nitroprop-1-en-1-yl]phenol (3i): Yield: 651 mg, 71 %. Yellow solid. M.p. 189–190 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 1 H), 7.40 (dd, J = 8.6, 2.3 Hz, 1 H), 7.33 (d, J = 2.3 Hz, 1 H), 7.28 (d, J = 8.4 Hz, 2 H), 7.11 (d, J = 8.3 Hz, 2 H), 6.77 (d, J = 8.6 Hz, 1 H), 5.29 (s, 1 H), 4.13 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.5, 151.2, 134.8, 134.6, 133.2, 132.2, 129.6, 129.5, 129.3, 121.6, 118.0, 113.4, 32.8 ppm. HRMS (EI): calcd. for $C_{15}H_{11}BrClNO_3$ [M] $^+$ 366.9611; found 366.9617.

2-[(Z)-3-(4-Chlorophenyl)-2-nitroprop-1-en-1-yl]-5-methoxyphenol (3j): Yield: 319 mg, 40 %. Yellow solid. M.p. 182–183 °C. 1H NMR (400 MHz, $[D_6]DMSO$): δ = 8.56 (s, 1 H), 8.62 (s, 1 H), 7.39 (d, J = 8.4 Hz, 2 H), 7.22 (d, J = 8.5 Hz, 3 H), 6.54 (d, J = 2.4 Hz, 1 H), 6.47 (dd, J = 8.8, 2.4 Hz, 1 H), 4.22 (s, 2 H), 3.74 (s, 3 H) ppm. ^{13}C NMR [100 MHz, $(CD_3)_2SO$]: δ = 163.2, 159.3, 145.1, 136.0, 131.3, 131.2, 130.1, 129.2, 128.7, 111.1, 106.5, 101.1, 55.3, 32.2 ppm. HRMS (EI): calcd. for $C_{16}H_{14}ClNO_4$ [M] $^+$ 319.0611; found 319.0618.

1-[(Z)-3-(4-Chlorophenyl)-2-nitroprop-1-en-1-yl]naphthalen-2-ol (3k): Yield: 509 mg, 60 %. Yellow solid. M.p. 117–118 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.32 (s, 1 H), 7.84 (d, *J* = 8.6 Hz, 2 H), 7.69 (d, *J* = 8.3 Hz, 1 H), 7.57–7.54 (m, 1 H), 7.46–7.43 (m, 1 H), 7.14–7.10 (m, 3 H), 6.95 (d, *J* = 8.3 Hz, 2 H), 5.18 (s, 1 H), 3.89 (s, 2 H), 3.74 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 153.9, 150.5, 134.6, 132.9, 132.3, 132.0, 130.0, 129.3, 129.2, 129.0, 128.8, 128.1, 124.7, 123.6, 117.9, 111.8, 33.6 ppm. HRMS (EI): calcd. for C₁₉H₁₄ClNO₃ [M]⁺ 339.0662; found 339.0656.

2-[(Z)-3-(4-Methoxyphenyl)-2-nitroprop-1-en-1-yl]phenol (3l): Yield: 542 mg, 76 %. Yellow solid. M.p. 104–105 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.43 (s, 1 H), 7.31–7.28 (m, 2 H), 7.11 (d, *J* = 8.6 Hz, 2 H), 6.94–6.90 (m, 1 H), 6.88–6.83 (m, 3 H), 5.61 (s, 1 H), 4.15 (s, 2 H), 3.19 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 158.7, 154.8, 150.7, 132.0, 130.6, 129.7, 129.0, 128.6, 121.4, 119.8, 116.2, 114.5, 55.5, 32.5 ppm. HRMS (EI): calcd. for C₁₆H₁₅NO₄ [M]⁺ 285.1001; found 285.0999.

4-Bromo-2-[(Z)-3-(4-methoxyphenyl)-2-nitroprop-1-en-1-yl]phenol (3m): Yield: 744 mg, 82 %. Yellow solid. M.p. 167–169 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.29 (s, 1 H), 7.41 (s, 1 H), 7.36–7.33 (m, 2 H), 7.10 (d, *J* = 8.6 Hz, 2 H), 6.85–6.80 (m, 3 H), 4.11 (s, 2 H), 3.78 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 158.8, 154.7, 151.5, 134.4, 132.0, 129.5, 129.2, 128.4, 121.8, 118.0, 114.5, 112.5, 55.5, 32.5 ppm. HRMS (EI): calcd. for C₁₆H₁₄BrNO₄ [M]⁺ 363.0106; found 363.0109.

5-Methoxy-2-[(Z)-3-(4-methoxyphenyl)-2-nitroprop-1-en-1-yl]phenol (3n): Yield: 228 mg, 29 %. Yellow solid. M.p. 133–135 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.49 (s, 1 H), 7.24 (d, *J* = 8.8 Hz, 1 H), 7.12 (d, *J* = 8.7 Hz, 2 H), 6.86–6.84 (m, 2 H), 6.47 (dd, *J* = 8.7, 2.4 Hz, 1 H), 6.41 (d, *J* = 2.4 Hz, 1 H), 5.33 (s, 1 H), 4.18 (s, 2 H), 3.80 (s, 3 H), 3.79 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 163.2, 158.7, 156.5, 148.6, 130.8, 130.4, 128.9, 128.8, 114.5, 112.5, 107.6, 102.1, 55.7, 55.5, 32.6 ppm. HRMS (EI): calcd. for C₁₇H₁₇NNaO₅ [M + Na]⁺ 338.1004; found 338.1002.

1-[(Z)-3-(4-Methoxyphenyl)-2-nitroprop-1-en-1-yl]naphthalen-2-ol (3o): Yield: 603 mg, 72 %. Yellow solid. M.p. 131–132 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.24 (s, 1 H), 7.83 (d, *J* = 8.7 Hz, 2 H), 7.70 (d, *J* = 8.3 Hz, 1 H), 7.57–7.53 (m, 1 H), 7.45–7.41 (m, 1 H), 7.14 (d, *J* = 8.9 Hz, 1 H), 6.93 (d, *J* = 8.7 Hz, 2 H), 6.70–6.68 (m, 2 H), 5.26 (s, 1 H), 3.86 (s, 2 H), 3.71 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 163.2, 158.7, 156.5, 148.6, 130.8, 130.4, 128.9, 128.8, 114.5, 112.5, 107.6, 102.1, 55.7, 55.5, 32.6 ppm. HRMS (EI): calcd. for C₂₀H₁₇NO₄ [M]⁺ 335.1158; found 335.1151.

2-[(Z)-3-(Naphthalen-1-yl)-2-nitroprop-1-en-1-yl]phenol (3p): Yield: 511 mg, 67 %. Yellow solid. M.p. 163–165 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.68 (s, 1 H), 7.99–7.97 (m, 1 H), 7.92–7.90 (m, 1 H), 7.80 (d, *J* = 8.3 Hz, 1 H), 7.56–7.54 (m, 2 H), 7.43–7.39 (m, 1 H), 7.28–7.24 (m, 2 H), 7.14 (d, *J* = 7.8 Hz, 1 H), 6.85 (d, *J* = 8.2 Hz, 1 H), 6.79–6.75 (m, 1 H), 5.34 (s, 1 H), 4.66 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 154.9, 149.5, 134.2, 132.3, 132.3, 131.8, 131.7, 129.6, 129.2, 128.0, 126.6, 126.2, 125.9, 124.0, 123.2, 121.7, 119.8, 116.1, 30.9 ppm. HRMS (EI): calcd. for C₁₉H₁₅NO₃ [M]⁺ 305.1052; found 305.1047.

4-Bromo-2-[(Z)-3-(naphthalen-1-yl)-2-nitroprop-1-en-1-yl]phenol (3q): Yield: 536 mg, 56 %. Yellow solid. M.p. 167–169 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.44 (s, 1 H), 7.99–7.97 (m, 1 H), 7.95–7.88 (m, 2 H), 7.78 (d, *J* = 8.3 Hz, 1 H), 7.57–7.51 (m, 2 H), 7.42–7.33 (m, 2 H), 7.24–7.22 (m, 1 H), 6.74 (d, *J* = 8.6 Hz, 1 H), 5.14 (s, 1 H), 4.62 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 154.6, 150.5, 134.6, 134.2, 132.0, 131.7, 130.5, 129.2, 128.1, 126.6, 126.1, 125.7, 124.3, 123.1,

121.6, 117.9, 112.7, 30.6 ppm. HRMS (EI): calcd. for C₁₉H₁₄BrNO₃ [M]⁺ 383.0157; found 383.0167.

5-Methoxy-2-[(Z)-3-(naphthalen-1-yl)-2-nitroprop-1-en-1-yl]phenol (3r): Yield: 193 mg, 23 %. Yellow solid. M.p. 176–178 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.73 (s, 1 H), 8.04–8.01 (m, 1 H), 7.93–7.91 (m, 1 H), 7.80 (d, *J* = 8.2 Hz, 1 H), 7.59–7.54 (m, 2 H), 7.42–7.38 (m, 1 H), 7.22 (dd, *J* = 7.1, 1.0 Hz, 1 H), 7.05 (d, *J* = 8.7 Hz, 1 H), 6.40 (d, *J* = 2.3 Hz, 1 H), 6.30 (dd, *J* = 8.8, 2.4 Hz, 1 H), 5.28 (s, 1 H), 4.67 (s, 2 H), 3.74 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 163.3, 156.8, 147.2, 134.2, 132.4, 131.9, 131.6, 130.9, 129.2, 127.9, 126.6, 126.2, 125.9, 123.8, 123.2, 112.5, 107.6, 102.2, 55.7, 31.2 ppm. HRMS (EI): calcd. for C₂₀H₁₇NO₄ [M]⁺ 335.1158; found 335.1164.

1-[(Z)-3-(Naphthalen-1-yl)-2-nitroprop-1-en-1-yl]naphthalen-2-ol (3s): Yield: 595 mg, 67 %. Yellow solid. M.p. 186–188 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.41 (s, 1 H), 7.83–7.80 (m, 2 H), 7.76 (d, *J* = 8.4 Hz, 2 H), 7.66–7.64 (m, 2 H), 7.57–7.53 (m, 1 H), 7.45–7.36 (m, 2 H), 7.28 (d, *J* = 5.2 Hz, 2 H), 7.22–7.18 (m, 1 H), 7.09 (d, *J* = 8.9 Hz, 1 H), 5.24 (s, 1 H), 4.42 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 163.3, 156.8, 147.2, 134.2, 132.4, 131.9, 131.6, 130.9, 129.2, 127.9, 126.6, 126.2, 125.9, 123.8, 123.2, 112.5, 107.6, 102.2, 55.7, 31.2 ppm. HRMS (EI): calcd. for C₂₃H₁₇NO₃ [M]⁺ 355.1208; found 355.1204.

2-(2-Nitro-3-phenylpropyl)phenol (4a): Yield: 636 mg, 99 %. Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.32–7.23 (m, 3 H), 7.18–7.06 (m, 4 H), 6.88–6.84 (m, 1 H), 6.70 (d, *J* = 8.0 Hz, 1 H), 5.30 (s, 1 H), 5.21–5.16 (m, 1 H), 3.35–3.23 (m, 3 H), 3.13 (dd, *J* = 14.4, 5.0 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 153.8, 135.7, 131.3, 129.1, 128.9, 128.9, 127.5, 122.1, 121.1, 115.6, 89.6, 40.0, 35.2 ppm. HRMS (EI): calcd. for C₁₅H₁₅NO₃ [M]⁺ 257.1052; found 257.1053.

1-(2-Hydroxyphenyl)-3-phenylpropan-2-one (5a): Colorless solid. M.p. 115–116 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.35–7.29 (m, 3 H), 7.19–7.18 (m, 3 H), 7.05 (s, 1 H), 6.91 (d, *J* = 8.1 Hz, 2 H), 6.86–6.82 (m, 1 H), 3.86 (s, 2 H), 3.76 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 155.2, 133.1, 130.9, 130.7, 129.6, 129.1, 128.9, 128.5, 127.4, 120.9, 117.5, 50.0, 44.7 ppm. HRMS (EI): calcd. for C₁₅H₁₄O₂ [M]⁺ 226.0994; found 226.0996.

2-Benzylbenzofuran (6a): Yield: 189 mg, 91 %. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.57 (d, *J* = 7.5 Hz, 1 H), 7.51 (d, *J* = 7.6 Hz, 1 H), 7.44–7.25 (m, 7 H), 6.46 (s, 1 H), 4.20 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 158.0, 155.2, 137.4, 129.1, 129.0, 128.8, 127.0, 123.6, 122.7, 120.6, 111.1, 103.6, 35.2 ppm. HRMS (EI): calcd. for C₁₅H₁₂O [M]⁺ 208.0888; found 208.0889.

2-Benzyl-5-bromobenzofuran (6b): Yield: 232 mg, 81 %. Colorless solid. M.p. 43–44 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.62 (d, *J* = 1.8 Hz, 1 H), 7.40–7.28 (m, 7 H), 6.35 (d, *J* = 0.8 Hz, 1 H), 4.13 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 159.5, 153.9, 137.0, 131.0, 129.1, 128.9, 127.1, 126.5, 123.3, 115.8, 112.6, 103.1, 35.2 ppm. HRMS (EI): calcd. for C₁₅H₁₁BrO [M]⁺ 285.9993; found 285.9993.

2-Benzyl-5,7-dibromobenzofuran (6c): Yield: 284 mg, 78 %. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.51 (s, 1 H), 7.38–7.29 (m, 5 H), 6.31 (s, 2 H), 4.14 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.7, 151.3, 136.5, 131.6, 129.2, 129.0, 128.9, 127.3, 122.5, 115.9, 104.5, 103.9, 35.1 ppm. HRMS (EI): calcd. for C₁₅H₁₀Br₂O [M]⁺ 363.9098; found 363.9097.

2-Benzyl-5-nitrobenzofuran (6d): Yield: 182 mg, 72 %. Colorless solid. M.p. 100–101 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.40 (d, *J* = 2.2 Hz, 1 H), 8.16 (d, *J* = 9.0, 2.4 Hz, 1 H), 7.47 (d, *J* = 9.0 Hz, 1 H), 7.38–7.28 (m, 5 H), 6.51 (s, 1 H), 4.15 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 161.8, 158.1, 144.3, 136.4, 129.4, 129.2, 129.1, 127.4, 119.8, 117.1, 111.4, 104.3, 35.3 ppm. HRMS (EI): calcd. for C₁₅H₁₁NO₃ [M]⁺ 253.0739; found 253.0733.

2-Benzyl-5-methylbenzofuran (6e): Yield: 184 mg, 83 %. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.39–7.28 (m, 7 H), 7.06 (d, J = 8.4 Hz, 1 H), 6.34 (s, 1 H), 4.13 (s, 2 H), 2.46 (s, 3 H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 158.1, 153.6, 137.6, 132.1, 129.1, 128.8, 126.9, 124.8, 120.5, 110.6, 103.3, 35.2, 21.5 ppm. HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{14}\text{O}$ $[\text{M}]^+$ 222.1045; found 222.1047.

2-Benzyl-6-methoxybenzofuran (6f): Yield: 143 mg, 60 %. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.36–7.25 (m, 6 H), 6.99 (d, J = 2.1 Hz, 1 H), 6.84 (dd, J = 8.4, 2.2 Hz, 1 H), 6.32 (s, 1 H), 4.09 (s, 2 H), 3.83 (s, 3 H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 157.6, 157.0, 156.1, 137.7, 129.1, 128.8, 126.9, 122.3, 120.6, 111.5, 103.2, 96.1, 55.9, 35.2 ppm. HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{14}\text{O}_2$ $[\text{M}]^+$ 238.0994; found 238.0995.

2-Benzyl-naphtho[2,1-*b*]furan (6g): Yield: 256 mg, 99 %. Colorless solid. M.p. 85–86 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 8.04 (d, J = 8.2 Hz, 1 H), 7.91 (d, J = 8.1 Hz, 1 H), 7.65 (d, J = 8.9 Hz, 1 H), 7.59 (d, J = 8.9 Hz, 1 H), 7.55–7.51 (m, 1 H), 7.46–7.42 (m, 1 H), 7.31–7.26 (m, 5 H), 6.87 (s, 1 H), 4.21 (s, 2 H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 157.3, 152.5, 137.7, 136.7, 130.5, 129.2, 128.9, 127.7, 127.0, 126.2, 124.5, 124.4, 124.1, 123.6, 112.4, 102.7, 35.4 ppm. HRMS (EI): calcd. for $\text{C}_{19}\text{H}_{14}\text{O}$ $[\text{M}]^+$ 258.1045; found 258.1039.

2-(4-Chlorobenzyl)benzofuran (6h): Yield: 225 mg, 93 %. Colorless solid. M.p. 70–71 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.49 (d, J = 7.1 Hz, 1 H), 7.41 (d, J = 7.9 Hz, 1 H), 7.31–7.29 (m, 2 H), 7.25–7.17 (m, 4 H), 6.39 (s, 1 H), 4.08 (s, 2 H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 157.3, 155.2, 135.9, 132.9, 130.5, 129.0, 128.9, 123.8, 122.8, 120.7, 111.1, 103.8, 34.6 ppm. HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{11}\text{ClO}$ $[\text{M}]^+$ 242.0498; found 242.0494.

5-Bromo-2-(4-chlorobenzyl)benzofuran (6i): Yield: 294 mg, 92 %. Yellow solid. M.p. 53–55 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.60 (d, J = 1.9 Hz, 1 H), 7.33–7.29 (m, 3 H), 7.28–7.27 (m, 1 H), 7.22 (d, J = 8.5 Hz, 2 H), 6.33 (s, 1 H), 4.07 (s, 2 H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 158.8, 154.0, 135.4, 133.1, 130.9, 130.4, 129.1, 126.7, 123.4, 115.9, 112.6, 103.3, 34.6 ppm. HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{10}\text{BrClO}$ $[\text{M}]^+$ 319.9604; found 319.9610.

2-(4-Chlorobenzyl)-6-methoxybenzofuran (6j): Yield: 171 mg, 63 %. Colorless solid. M.p. 81–82 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.34 (dd, J = 8.5 Hz, 1 H), 7.29 (d, J = 8.5 Hz, 2 H), 7.22 (d, J = 8.6 Hz, 2 H), 6.96 (d, J = 2.0 Hz, 1 H), 6.83 (dd, J = 8.6, 2.3 Hz, 1 H), 6.31 (s, 1 H), 4.04 (s, 2 H), 3.83 (s, 3 H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 157.7, 156.2, 156.1, 136.2, 132.8, 130.4, 128.9, 122.1, 120.7, 111.6, 103.5, 96.1, 55.9, 34.5 ppm. HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{13}\text{ClO}_2$ $[\text{M}]^+$ 272.0604; found 272.0605.

2-(4-Chlorobenzyl)naphtho[1,2-*b*]furan (6k): Yield: 277 mg, 95 %. Colorless solid. M.p. 100–101 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 8.05 (d, J = 8.2 Hz, 1 H), 7.92 (d, J = 8.2 Hz, 1 H), 7.67 (d, J = 8.8 Hz, 1 H), 7.59 (d, J = 8.8 Hz, 1 H), 7.57–7.52 (m, 1 H), 7.48–7.44 (m, 1 H), 7.33–7.26 (m, 4 H), 6.87 (s, 1 H), 4.18 (s, 2 H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 157.7, 156.2, 156.1, 136.2, 132.8, 130.4, 128.9, 122.1, 120.7, 111.6, 103.5, 96.1, 55.9, 34.5 ppm. HRMS (EI): calcd. for $\text{C}_{19}\text{H}_{13}\text{ClO}$ $[\text{M}]^+$ 292.0655; found 292.0664.

2-(4-Methoxybenzyl)benzofuran (6l): Yield: 252 mg, 89 %. Colorless solid. M.p. 62–63 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.51–7.49 (m, 1 H), 7.45–7.43 (m, 1 H), 7.28–7.19 (m, 4 H), 6.91 (d, J = 8.6 Hz, 2 H), 6.39 (s, 1 H), 4.09 (s, 2 H), 3.83 (s, 3 H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 158.7, 158.5, 130.1, 129.5, 129.0, 123.5, 122.7, 120.6, 114.2, 111.1, 103.3, 55.5, 34.3 ppm. HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{14}\text{O}_2$ $[\text{M}]^+$ 283.0994; found 283.0997.

5-Bromo-2-(4-methoxybenzyl)benzofuran (6m): Yield: 284 mg, 90 %. Colorless solid. M.p. 62–63 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ =

7.59 (d, J = 1.7 Hz, 1 H), 7.32 (d, J = 1.7 Hz, 1 H), 7.31 (dd, J = 8.6, 1.9 Hz, 1 H), 7.22 (d, J = 8.6 Hz, 2 H), 6.89 (d, J = 8.6 Hz, 2 H), 6.30 (s, 1 H), 4.04 (s, 2 H), 3.81 (s, 3 H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 160.1, 158.8, 153.9, 131.0, 130.1, 128.9, 126.4, 123.2, 115.7, 114.3, 112.5, 102.9, 55.5, 34.3 ppm. HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{13}\text{BrO}_2$ $[\text{M}]^+$ 316.0099; found 316.0097.

6-Methoxy-2-(4-methoxybenzyl)benzofuran (6n): Yield: 190 mg, 71 %. Colorless solid. M.p. 92–94 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.32 (d, J = 8.4 Hz, 1 H), 7.21 (d, J = 8.6 Hz, 2 H), 6.96 (d, J = 2.0 Hz, 1 H), 6.86 (d, J = 8.6 Hz, 2 H), 6.81 (dd, J = 8.44, 2.4 Hz, 1 H), 6.27 (s, 1 H), 4.01 (s, 2 H), 3.82 (s, 3 H), 3.80 (s, 3 H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 160.1, 158.8, 153.9, 131.0, 130.1, 128.9, 126.4, 123.2, 115.7, 114.3, 112.5, 102.9, 55.5, 34.3 ppm. HRMS (EI): calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_3$ $[\text{M}]^+$ 268.1099; found 268.1096.

2-(4-Methoxybenzyl)naphtho[1,2-*b*]furan (6o): Yield: 285 mg, 99 %. Colorless solid. M.p. 101–102 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 8.07 (d, J = 7.6 Hz, 1 H), 7.94 (d, J = 8.1 Hz, 1 H), 7.68 (d, J = 9.0 Hz, 1 H), 7.62 (d, J = 9.0 Hz, 1 H), 7.58–7.54 (m, 1 H), 7.49–7.45 (m, 1 H), 7.30 (d, J = 8.6 Hz, 2 H), 6.92 (d, J = 8.6 Hz, 2 H), 6.87 (s, 1 H), 4.18 (s, 2 H), 3.84 (s, 3 H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 158.7, 157.8, 152.5, 130.5, 130.2, 129.7, 128.9, 127.7, 126.2, 124.4, 124.3, 124.1, 123.6, 114.3, 112.4, 102.5, 55.5, 34.5 ppm. HRMS (EI): calcd. for $\text{C}_{20}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$ 288.1150; found 288.1152.

2-(Naphthalen-1-ylmethyl)benzofuran (6p): Yield: 277 mg, 97 %. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 8.09–8.07 (m, 1 H), 7.92–7.89 (m, 1 H), 7.83 (dd, J = 7.1, 2.3 Hz, 1 H), 7.53–7.49 (m, 2 H), 7.47–7.41 (m, 4 H), 7.25–7.15 (m, 2 H), 6.26 (s, 1 H), 4.58 (s, 2 H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 157.8, 155.0, 134.1, 133.3, 132.2, 129.1, 128.9, 128.0, 127.6, 126.4, 125.9, 125.8, 124.1, 123.6, 122.7, 120.6, 111.1, 103.9, 32.7 ppm. HRMS (EI): calcd. for $\text{C}_{19}\text{H}_{14}\text{O}$ $[\text{M}]^+$ 258.1045; found 258.1037.

5-Bromo-2-(naphthalen-1-ylmethyl)benzofuran (6q): Yield: 319 mg, 95 %. Colorless solid. M.p. 85–86 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 8.04 (dd, J = 6.2, 3.5 Hz, 1 H), 7.91 (dd, J = 6.2, 3.5 Hz, 1 H), 7.84 (d, J = 7.9 Hz, 1 H), 7.54–7.42 (m, 5 H), 7.33–7.28 (m, 2 H), 6.19 (s, 1 H), 4.56 (s, 2 H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 159.3, 153.7, 134.1, 132.8, 132.1, 131.0, 129.0, 128.2, 127.6, 126.5, 126.4, 126.0, 125.8, 124.0, 123.2, 115.8, 112.5, 103.5, 32.6 ppm. HRMS (EI): calcd. for $\text{C}_{19}\text{H}_{13}\text{BrO}$ $[\text{M}]^+$ 336.0150; found 336.0146.

6-Methoxy-2-(naphthalen-1-ylmethyl)benzofuran (6r): Yield: 184 mg, 64 %. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 8.09–8.06 (m, 1 H), 7.90–7.88 (m, 1 H), 7.82–7.80 (m, 1 H), 7.52–7.42 (m, 4 H), 7.27 (d, J = 8.5 Hz, 1 H), 6.99 (d, J = 2.3 Hz, 1 H), 6.81 (dd, J = 8.6, 2.3 Hz, 1 H), 6.18 (s, 1 H), 4.54 (s, 2 H), 3.83 (s, 3 H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 157.6, 156.7, 155.9, 134.1, 133.5, 132.2, 128.9, 127.9, 127.5, 126.4, 125.9, 125.8, 124.1, 122.3, 120.6, 111.5, 103.6, 96.1, 55.9, 32.6 ppm. HRMS (EI): calcd. for $\text{C}_{20}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$ 288.1150; found 288.1146.

2-(Naphthalen-1-ylmethyl)naphtho[1,2-*b*]furan (6s): Yield: 305 mg, 99 %. Colorless solid. M.p. 164.165 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 8.13–8.11 (m, 1 H), 7.97–7.91 (m, 3 H), 7.86–7.84 (m, 1 H), 7.67 (d, J = 8.9 Hz, 1 H), 7.63 (d, J = 8.9 Hz, 1 H), 7.54–7.42 (m, 6 H), 6.75 (s, 1 H), 4.68 (s, 2 H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 157.0, 152.3, 134.2, 133.5, 132.2, 130.4, 129.0, 128.8, 128.0, 127.6, 127.6, 126.5, 126.1, 126.0, 125.8, 124.4, 124.4, 124.2, 123.6, 112.4, 103.0, 32.8 ppm. HRMS (EI): calcd. for $\text{C}_{23}\text{H}_{16}\text{O}$ $[\text{M}]^+$ 308.1201; found 308.1196.

2-(Thiophen-2-ylmethyl)benzofuran (6t): Yield: 112 mg, 52 %. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.52 (d, J = 7.4 Hz, 1 H), 7.46 (d, J = 7.9 Hz, 1 H), 7.28–7.20 (m, 3 H), 6.99 (s, 2 H), 6.50 (s, 1 H), 4.34 (s, 2 H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 156.9, 155.1,

139.4, 128.9, 127.1, 126.3, 124.6, 123.8, 122.8, 120.8, 111.2, 103.5, 29.4 ppm. HRMS (EI): calcd. for $C_{13}H_{10}OS$ [M]⁺ 214.0452; found 214.0454.

2-Benzyl-3-ethylbenzofuran (7a): Yield: 80 mg, 68 %. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.55–7.52 (m, 1 H), 7.41–7.39 (m, 1 H), 7.33–7.20 (m, 7 H), 4.12 (s, 2 H), 2.74 (q, J = 7.6 Hz, 2 H), 1.28 (t, J = 7.6 Hz, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 154.4, 151.8, 138.3, 129.5, 128.8, 128.7, 126.7, 123.5, 122.2, 119.3, 117.3, 111.1, 32.8, 17.2, 14.9 ppm. HRMS (EI): calcd. for $C_{17}H_{16}O$ [M]⁺ 236.1201; found 236.1201.

2-Benzyl-3-allylbenzofuran (7b): Yield: 82 mg, 66 %. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.53 (d, J = 6.9 Hz, 1 H), 7.42 (d, J = 7.1 Hz, 1 H), 7.35–7.22 (m, 7 H), 6.06–5.96 (m, 1 H), 5.17 (dd, J = 17.0, 1.6 Hz, 1 H), 5.12 (dd, J = 10.0, 1.4 Hz, 1 H), 4.14 (s, 2 H), 3.49 (d, J = 6.1 Hz, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 154.4, 152.9, 138.0, 135.8, 129.6, 128.8, 126.8, 123.7, 122.3, 119.6, 116.1, 113.1, 111.1, 32.9, 28.2 ppm. HRMS (EI): calcd. for $C_{18}H_{16}O$ [M]⁺ 248.1201; found 248.1202.

2-Benzyl-3-isobutylbenzofuran (7c): Yield: 75 mg, 57 %. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.60–7.57 (m, 1 H), 7.47–7.44 (m, 1 H), 7.39–7.27 (m, 7 H), 4.17 (s, 2 H), 2.79 (q, J = 7.6 Hz, 2 H), 1.33 (t, J = 7.6 Hz, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 154.4, 151.8, 138.3, 129.5, 128.6, 128.8, 126.7, 123.5, 122.2, 119.3, 117.3, 111.1, 32.8, 17.2, 14.9 ppm. HRMS (EI): calcd. for $C_{19}H_{20}O$ [M]⁺ 264.1514; found 264.1514.

2-Benzyl-3-phenylbenzofuran (7d): Yield: 75 mg, 53 %. Colorless solid. M.p. 79–81 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.60 (d, J = 7.6 Hz, 1 H), 7.54–7.45 (m, 5 H), 7.41–7.37 (m, 1 H), 7.33–7.22 (m, 7 H), 4.22 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 154.6, 152.8, 138.1, 132.7, 129.3, 129.1, 128.8, 128.7, 127.5, 126.8, 124.2, 122.9, 120.0, 118.5, 114.6, 111.4, 33.1 ppm. HRMS (EI): calcd. for $C_{21}H_{16}O$ [M]⁺ 284.1201; found 284.1201.

2-Benzyl-5-bromo-3-ethylbenzofuran (7g): Yield: 63 mg, 40 %. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.46–7.44 (m, 1 H), 7.61 (d, J = 1.7 Hz, 1 H), 7.31–7.22 (m, 7 H), 4.07 (s, 2 H), 2.66 (q, J = 7.6 Hz, 2 H), 1.23 (t, J = 7.6 Hz, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 153.4, 153.2, 137.8, 131.6, 128.9, 128.7, 126.9, 126.4, 122.1, 117.1, 115.4, 112.6, 32.8, 17.1, 14.8 ppm. HRMS (EI): calcd. for $C_{17}H_{15}BrO$ [M]⁺ 314.0306; found 314.0303.

2,3-Dibenzylbenzofuran (7e): Yield: 41 mg, 28 %. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.41 (d, J = 8.2 Hz, 1 H), 7.32–7.20 (m, 12 H), 7.16–7.11 (m, 1 H), 4.16 (s, 2 H), 4.09 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 154.5, 153.4, 139.8, 137.9, 129.7, 128.8, 128.7, 128.6, 126.8, 126.4, 123.7, 122.4, 119.8, 114.3, 111.1, 33.0, 29.9 ppm. HRMS (EI): calcd. for $C_{22}H_{18}O$ [M]⁺ 298.1358; found 298.1357.

2-Benzyl-3-ethyl-5-methoxybenzofuran (7h): Yield: 49 mg, 37 %. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.35–7.23 (m, 6 H), 7.00 (d, J = 2.4 Hz, 1 H), 6.85 (dd, J = 8.8, 2.5 Hz, 1 H), 4.10 (s, 2 H), 3.89 (s, 3 H), 2.72 (q, J = 7.6 Hz, 2 H), 1.28 (t, J = 7.6 Hz, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 155.8, 152.8, 149.4, 138.3, 130.1, 128.8, 128.7, 126.7, 117.5, 111.7, 111.5, 102.5, 56.2, 32.9, 17.2, 14.8 ppm. HRMS (EI): calcd. for $C_{18}H_{18}O_2$ [M]⁺ 266.1307; found 266.1307.

2-(4-Chlorobenzyl)-3-ethylbenzofuran (7i): Yield: 94 mg, 70 %. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.56 (d, J = 7.1 Hz, 1 H), 7.43 (d, J = 7.2 Hz, 1 H), 7.32–7.21 (m, 6 H), 4.10 (s, 2 H), 2.75 (q, J = 7.4 Hz, 2 H), 1.31 (t, J = 7.6 Hz, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 154.4, 151.2, 136.7, 132.5, 130.0, 129.4, 128.9, 123.7, 122.3, 119.4, 117.6, 111.2, 32.1, 17.2, 14.9 ppm. HRMS (EI): calcd. for $C_{17}H_{15}ClO$ [M]⁺ 270.0811; found 270.0812.

3-Ethyl-2-(4-methoxybenzyl)benzofuran (7j): Yield: 81 mg, 61 %. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.54–7.51 (m, 1 H), 7.41–

7.39 (m, 1 H), 7.25–7.18 (m, 4 H), 6.86 (d, J = 8.7 Hz, 2 H), 4.06 (s, 2 H), 3.79 (s, 3 H), 2.73 (q, J = 7.6 Hz, 2 H), 1.28 (t, J = 7.6 Hz) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 158.5, 154.3, 152.2, 130.3, 129.6, 123.5, 122.2, 119.3, 117.1, 114.2, 111.1, 55.5, 31.9, 17.2, 14.9 ppm. HRMS (EI): calcd. for $C_{18}H_{18}O_2$ [M]⁺ 266.1307; found 266.1305.

2-Benzyl-3-methyl-5-nitrobenzofuran (7k): Yield: 61 mg, 46 %. Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 8.38 (d, J = 2.3 Hz, 1 H), 8.15 (dd, J = 9.0, 2.3 Hz, 1 H), 7.42 (dd, J = 9.0 Hz, 1 H), 7.34–7.31 (m, 2 H), 7.27–7.25 (m, 3 H), 4.12 (s, 2 H), 2.28 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 157.3, 156.0, 144.0, 137.1, 131.0, 129.5, 129.0, 128.7, 127.1, 119.8, 115.8, 112.1, 111.3, 32.9, 8.1 ppm. HRMS (EI): calcd. for $C_{16}H_{13}NO_3$ [M]⁺ 267.0895; found 267.0895.

2-(4-Methoxybenzyl)-3-methylbenzofuran (7l): Yield: 120 mg, 95 %. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.46–7.44 (m, 1 H), 7.38–7.36 (m, 1 H), 7.23–7.16 (m, 4 H), 6.84 (d, J = 8.7 Hz, 2 H), 4.04 (s, 2 H), 3.78 (s, 3 H), 2.22 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 158.5, 154.3, 152.7, 130.5, 130.3, 129.7, 123.6, 122.2, 119.1, 114.2, 111.0, 110.7, 55.5, 32.0, 8.2 ppm. HRMS (EI): calcd. for $C_{17}H_{16}O_2$ [M]⁺ 252.1150; found 252.1150.

2-(2-Benzylbenzofuran-3-yl)acetonitrile (9a): Yield: 411 mg, 83 %. ¹H NMR (400 MHz, CDCl₃): δ = 7.59–7.57 (m, 1 H), 7.45–7.43 (m, 1 H), 7.36–7.26 (m, 7 H), 4.18 (s, 2 H), 3.65 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 154.3, 154.2, 136.5, 129.1, 128.8, 127.8, 127.3, 124.8, 123.3, 118.7, 116.9, 111.5, 105.0, 33.1, 12.8 ppm. HRMS (EI): calcd. for $C_{17}H_{13}NO$ [M]⁺ 247.0997; found 247.0996.

N-[2-(2-Benzylbenzofuran-3-yl)ethyl]acetamide (10a): Yield: 235 mg, 80 %. Colorless solid. M.p. 99–101 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.51 (d, J = 6.4 Hz, 1 H), 7.42 (d, J = 7.6 Hz, 1 H), 7.32–7.20 (m, 7 H), 5.40 (s, 1 H), 4.11 (s, 2 H), 3.50 (q, J = 6.4 Hz, 2 H), 2.91 (d, J = 6.4 Hz, 2 H), 1.74 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 170.3, 154.5, 153.7, 138.1, 129.3, 129.0, 128.6, 126.9, 124.0, 122.7, 119.2, 112.6, 111.3, 39.4, 32.7, 24.0, 23.3 ppm. HRMS (EI): calcd. for $C_{19}H_{19}NO_2$ [M + H]⁺ 294.1494; found 294.1494.

(Z)-2-(2-Nitro-3-phenylallyl)phenol (13a^z): Yellow solid. M.p. 103–104 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.30 (s, 1 H), 7.43–7.42 (m, 5 H), 7.16–7.12 (m, 1 H), 7.19 (d, J = 7.5 Hz, 1 H), 6.88–6.85 (m, 1 H), 7.80 (d, J = 8.0 Hz, 1 H), 5.06 (s, 1 H), 4.23 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 153.6, 149.8, 135.8, 132.3, 130.5, 130.0, 129.3, 128.7, 128.5, 123.0, 121.6, 116.0, 27.7 ppm. HRMS (EI): calcd. for $C_{15}H_{13}NO_3$ [M]⁺ 255.0895; found 255.0902.

3-Nitro-2-phenylchroman (13a): Yield: 91 mg, 71 %. Colorless solid. M.p. 176–177 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.40 (s, 5 H), 7.21 (t, J = 7.7 Hz, 1 H), 7.16 (d, J = 7.4 Hz, 1 H), 7.01–6.96 (m, 2 H), 5.42 (d, J = 7.9 Hz, 1 H), 5.05 (ddd, J = 9.2, 8.0, 5.4 Hz, 1 H), 3.67 (dd, J = 16.2, 5.4 Hz, 1 H), 3.33 (dd, J = 16.2, 5.4 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 153.5, 136.0, 129.7, 129.5, 129.2, 128.7, 127.0, 122.1, 117.9, 117.2, 84.2, 78.2, 30.0 ppm. HRMS (EI): calcd. for $C_{15}H_{13}NO_3$ [M]⁺ 255.0895; found 255.0901.

2-(3-Fluorophenyl)-3-nitrochroman (13b): Yield: 91 mg, 67 %. Colorless solid. M.p. 135–136 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.40–7.35 (m, 1 H), 7.24–7.20 (m, 1 H), 7.18–7.06 (m, 4 H), 7.02–6.96 (m, 2 H), 5.42 (d, J = 7.9 Hz, 1 H), 5.03–4.98 (m, 1 H), 3.66 (dd, J = 16.2, 9.2 Hz, 1 H), 3.33 (dd, J = 16.2, 5.5 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 163.1 (J_{C,F} = 247.6 Hz), 153.1, 138.4 (J_{C,F} = 7.2 Hz), 130.8 (J_{C,F} = 8.1 Hz), 129.5, 128.8, 122.7 (J_{C,F} = 2.8 Hz), 122.3, 117.7, 116.7 (J_{C,F} = 21.1 Hz), 114.1 (J_{C,F} = 22.8 Hz), 84.1, 77.4, 29.8 ppm. HRMS (EI): calcd. for $C_{15}H_{12}NO_3F$ [M]⁺ 273.0801; found 273.0802.

2-(4-Fluorophenyl)-3-nitrochroman (13c): Yield: 94 mg, 69 %. Colorless solid. M.p. 144–145 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.41–

7.38 (m, 2 H), 7.23–7.08 (m, 4 H), 7.02–6.94 (m, 2 H), 5.34 (d, $J = 8.4$ Hz, 1 H), 5.00 (ddd, $J = 9.8, 8.4, 5.5$ Hz, 1 H), 3.68 (dd, $J = 16.1, 9.8$ Hz, 1 H), 3.36 (d, $J = 16.1, 5.5$ Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 164.7, 162.3, 153.4, 131.7$ (d, $J_{\text{C,F}} = 3.1$ Hz), 129.2 (d, $J_{\text{C,F}} = 79.0$ Hz), 129.1, (d, $J_{\text{C,F}} = 8.5$ Hz), 122.3, 117.8, 117.2, 116.2 (d, $J_{\text{C,F}} = 21.8$ Hz), 84.4, 77.7, 30.4 ppm. HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{12}\text{FNO}_3$ $[\text{M}]^+$ 273.0801; found 273.0805.

2-(2-Chlorophenyl)-3-nitrochroman (13d): Yield: 113 mg, 78 %. Colorless solid. M.p. 104–106 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.44$ –7.42 (m, 1 H), 7.40–7.38 (m, 1 H), 7.34–7.27 (m, 2 H), 7.25–7.21 (m, 1 H), 7.14–7.13 (m, 1 H), 7.01–6.96 (m, 2 H), 6.16 (d, $J = 5.4$ Hz, 1 H), 5.26–5.22 (m, 1 H), 3.62 (dd, $J = 16.7, 6.5$ Hz, 1 H), 3.16 (dd, $J = 16.7, 5.1$ Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 152.9, 134.2, 132.5, 130.4, 130.3, 129.4, 128.7, 128.0, 127.5, 121.9, 117.1, 116.7, 80.7, 74.4, 27.5$ ppm. HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{12}\text{ClNO}_3$ $[\text{M}]^+$ 289.0506; found 289.0504.

2-(3-Chlorophenyl)-3-nitrochroman (13e): Yield: 107 mg, 74 %. Colorless solid. M.p. 140–141 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.42$ (s, 1 H), 7.38–7.31 (m, 2 H), 7.27–7.20 (m, 2 H), 7.16–7.14 (m, 1 H), 7.02–6.96 (m, 2 H), 5.38 (d, $J = 8.0$ Hz, 1 H), 5.03–4.98 (m, 1 H), 3.66 (dd, $J = 16.2, 9.4$ Hz, 1 H), 3.34 (dd, $J = 16.2, 5.4$ Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 152.9, 137.8, 135.0, 130.2, 129.7, 129.3, 128.6, 127.0, 125.1, 122.1, 117.5, 117.0, 83.9, 29.8$ ppm. HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{12}\text{ClNO}_3$ $[\text{M}]^+$ 289.0506; found 289.0505.

2-(4-Chlorophenyl)-3-nitrochroman (13f): Yield: 98 mg, 68 %. Colorless solid. M.p. 153–154 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.39$ –7.33 (m, 4 H), 7.23–7.19 (m, 1 H), 7.15 (d, $J = 7.5$ Hz, 1 H), 7.01–6.94 (m, 2 H), 5.36 (d, $J = 8.1$ Hz, 1 H), 5.02–4.96 (m, 1 H), 3.66 (dd, $J = 16.2, 9.7$ Hz, 1 H), 3.34 (dd, $J = 16.2, 5.3$ Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.3, 135.7, 134.4, 129.6, 129.4, 128.8, 128.5, 122.3, 117.8, 117.2, 84.2, 77.6, 30.1$ ppm. HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{12}\text{ClNO}_3$ $[\text{M}]^+$ 289.0506; found 285.0505.

2-(2-Bromophenyl)-3-nitrochroman (13g): Yield: 105 mg, 63 %. Colorless solid. M.p. 113–115 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.62$ (d, $J = 8.0$ Hz, 1 H), 7.39–7.30 (m, 2 H), 7.25–7.21 (m, 2 H), 7.15–7.13 (m, 1 H), 7.01–6.96 (m, 1 H), 6.15 (d, $J = 5.16$ Hz, 1 H), 5.26–5.22 (m, 1 H), 3.62 (dd, $J = 16.7, 6.2$ Hz, 1 H), 3.15 (dd, $J = 16.7, 5.1$ Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.0, 135.8, 133.6, 130.6, 129.4, 128.8, 128.2, 128.1, 122.2, 121.9, 117.0, 116.7, 80.7, 76.4, 27.3$ ppm. HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{11}\text{BrNO}_3$ $[\text{M}]^+$ 333.0001; found 333.0005.

4-(3-Nitrochroman-2-yl)phenol (13h): Yield: 98 mg, 72 %. Colorless solid. M.p. 191–192 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.29$ (d, $J = 8.6$ Hz, 2 H), 7.22–7.14 (m, 2 H), 7.00–6.94 (m, 2 H), 6.85 (d, $J = 8.6$ Hz, 2 H), 5.29 (d, $J = 8.4$ Hz, 1 H), 5.01 (ddd, $J = 9.8, 8.4, 5.5$ Hz, 1 H), 4.85 (s, 1 H), 3.67 (dd, $J = 16.1, 9.7$ Hz, 1 H), 3.36 (dd, $J = 16.1, 5.6$ Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 156.7, 153.6, 129.5, 128.8, 128.7, 128.1, 122.1, 117.9, 117.2, 116.0, 84.4, 78.1, 30.6$ ppm. HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_4$ $[\text{M}]^+$ 271.0845; found 271.0846.

3-Nitro-2-(4-nitrophenyl)chroman (13i): Yield: 90 mg, 60 %. Colorless solid. M.p. 165–166 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 8.27$ (d, $J = 8.7$ Hz, 2 H), 7.61 (d, $J = 8.7$ Hz, 2 H), 7.24–7.16 (m, 2 H), 7.05–6.97 (m, 2 H), 5.51 (d, $J = 8.1$ Hz, 1 H), 5.01 (ddd, $J = 9.2, 8.1, 5.6$ Hz, 1 H), 3.70 (dd, $J = 16.3, 9.2$ Hz, 1 H), 3.35 (dd, $J = 16.3, 5.3$ Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 152.9, 148.8, 142.9, 129.6, 129.0, 128.2, 124.4, 122.7, 117.5, 117.2, 84.1, 29.9$ ppm. HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_5$ $[\text{M}]^+$ 300.0746; found 300.0743.

3-Nitro-2-(*p*-tolyl)chroman (13j): Yield: 87 mg, 65 %. Colorless solid. M.p. 144–145 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.29$ (d, $J = 8.0$ Hz, 2 H), 7.22–7.19 (m, 3 H), 7.15 (d, $J = 7.5$ Hz, 1 H), 7.00–6.95 (m, 2 H), 5.36 (d, $J = 8.0$ Hz, 1 H), 5.07–5.01 (m, 1 H), 3.66 (dd, $J =$

16.2, 9.4 Hz, 1 H), 3.33 (dd, $J = 16.2, 5.4$ Hz, 1 H), 2.36 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.6, 139.6, 132.9, 129.8, 129.5, 128.7, 127.0, 122.0, 117.9, 117.2, 84.3, 78.2, 30.2, 21.5$ ppm. HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{15}\text{NO}_3$ $[\text{M}]^+$ 269.1052; found 269.1047.

2-(4-Methoxyphenyl)-3-nitrochroman (13k): Yield: 78 mg, 55 %. Colorless solid. M.p. 144–145 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.33$ (d, $J = 8.6$ Hz, 2 H), 7.22–7.14 (m, 2 H), 7.00–6.91 (m, 4 H), 5.30 (d, $J = 8.4$ Hz, 1 H), 5.06–5.00 (m, 1 H), 3.81 (s, 3 H), 3.67 (dd, $J = 16.0, 9.9$ Hz, 1 H), 3.36 (dd, $J = 16.0, 5.5$ Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 160.7, 153.7, 129.5, 128.6, 128.5, 127.8, 122.1, 118.0, 117.2, 114.6, 84.4, 78.1, 55.5, 30.5$ ppm. HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{15}\text{NO}_4$ $[\text{M}]^+$ 285.1001; found 285.1002.

2-(Naphthalen-1-yl)-3-nitrochroman (13l): Yield: 72 mg, 47 %. Colorless solid. M.p. 193–194 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 8.14$ (d, $J =$ Hz, 1 H), 7.92 (d, $J = 8.2$ Hz, 2 H), 7.88 (d, $J = 8.2$ Hz, 3 H), 7.62–7.53 (m, 1 H), 7.46–7.42 (m, 1 H), 7.18 (d, $J = 7.3$ Hz, 1 H), 7.04–7.00 (m, 2 H), 6.42 (d, $J = 6.0$ Hz, 1 H), 5.41–5.37 (m, 1 H), 3.65 (dd, $J = 16.6, 7.3$ Hz, 1 H), 3.23 (dd, $J = 16.6, 5.2$ Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.4, 134.3, 131.9, 130.3, 130.2, 129.6, 129.6, 128.9, 127.4, 126.3, 125.5, 125.2, 122.7, 122.1, 117.5, 117.1, 82.3, 75.7, 28.5$ ppm. HRMS (EI): calcd. for $\text{C}_{19}\text{H}_{15}\text{NO}_3$ $[\text{M}]^+$ 305.1052; found 305.1054.

7-Methoxy-3-nitro-2-phenylchroman (13m): Yield: 94 mg, 66 %. Colorless solid. M.p. 150–151 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.39$ (s, 5 H), 7.03 (d, $J = 8.4$ Hz, 1 H), 6.58 (dd, $J = 8.4, 2.5$ Hz, 1 H), 6.51 (d, $J = 2.5$ Hz, 1 H), 5.41 (d, $J = 7.9$ Hz, 1 H), 5.02 (ddd, $J = 9.0, 7.9, 5.4$ Hz, 1 H), 3.77 (s, 3 H), 3.58 (dd, $J = 15.9, 9.0$ Hz, 1 H), 3.26 (dd, $J = 15.9, 5.4$ Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 159.9, 154.0, 135.8, 129.8, 129.4, 128.9, 126.8, 109.5, 109.2, 101.6, 84.1, 78.0, 55.4, 29.2$ ppm. HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{15}\text{NO}_4$ $[\text{M}]^+$ 285.1001; found 285.1000.

2-(4-Chlorophenyl)-7-methoxy-3-nitrochroman (13n): Yield: 118 mg, 74 %. Colorless solid. M.p. 132–133 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.39$ –7.32 (m, 4 H), 7.03 (d, $J = 8.5$ Hz, 1 H), 6.59 (dd, $J = 8.5, 2.5$ Hz, 1 H), 6.50 (d, $J = 2.5$ Hz, 1 H), 5.36 (d, $J = 8.1$ Hz, 1 H), 4.97 (ddd, $J = 9.4, 8.1, 5.5$ Hz, 1 H), 3.77 (s, 3 H), 3.58 (dd, $J = 15.9, 9.4$ Hz, 1 H), 3.27 (dd, $J = 15.9, 5.5$ Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 159.9, 153.8, 153.6, 135.5, 134.2, 129.8, 129.2, 128.3, 109.3, 101.6, 84.1, 55.4, 29.4$ ppm. HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{14}\text{ClNO}_4$ $[\text{M}]^+$ 319.0611; found 319.0620.

7-Methoxy-2-(4-methoxyphenyl)-3-nitrochroman (13o): Yield: 118 mg, 75 %. Colorless solid. M.p. 123–124 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.34$ –7.31 (m, 2 H), 7.03 (d, $J = 8.3$ Hz, 1 H), 6.94–6.89 (m, 2 H), 6.58 (dd, $J = 8.4, 2.5$ Hz, 1 H), 6.50 (d, $J = 2.5$ Hz, 1 H), 5.30 (d, $J = 8.4$ Hz, 1 H), 5.00 (ddd, $J = 9.7, 8.4, 5.4$ Hz, 1 H), 3.81 (s, 3 H), 3.77 (s, 3 H), 3.59 (dd, $J = 15.7, 9.7$ Hz, 1 H), 3.29 (dd, $J = 15.7, 5.4$ Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 160.4, 159.9, 154.2, 129.8, 128.3, 127.5, 114.4, 109.6, 109.1, 101.6, 84.3, 77.9, 55.4, 55.3, 29.8$ ppm. HRMS (EI): calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_5$ $[\text{M}]^+$ 315.1107; found 315.1111.

7-Methoxy-2-(naphthalen-1-yl)-3-nitrochroman (13p): Yield: 94 mg, 56 %. Colorless solid. M.p. 157–158 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 8.13$ (d, $J = 8.4$ Hz, 1 H), 7.93–7.87 (m, 2 H), 7.63–7.52 (m, 3 H), 7.46–7.42 (m, 1 H), 7.06 (d, $J = 8.4$ Hz, 1 H), 6.61 (dd, $J = 8.4, 2.5$ Hz, 1 H), 6.56 (d, $J = 2.5$ Hz, 1 H), 6.42 (d, $J = 5.9$ Hz, 1 H), 5.39–5.34 (m, 1 H), 3.80 (s, 3 H), 3.57 (dd, $J = 16.3, 6.9$ Hz, 1 H), 3.15 (dd, $J = 16.3, 5.2$ Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 160.0, 153.9, 134.0, 131.6, 130.1, 129.9, 129.3, 127.1, 126.1, 125.3, 124.9, 122.4, 109.1, 109.0, 101.5, 82.1, 75.5, 55.4, 27.6$ ppm. HRMS (EI): calcd. for $\text{C}_{20}\text{H}_{17}\text{NO}_4$ $[\text{M}]^+$ 335.1158; found 335.1155.

6-Bromo-3-nitro-2-phenylchroman (13q): Yield: 127 mg, 76 %. Colorless solid. M.p. 146–147 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.40–7.38 (m, 3 H), 7.37–7.35 (m, 2 H), 7.32–7.28 (m, 2 H), 6.86 (d, *J* = 8.6 Hz, 1 H), 5.49 (d, *J* = 7.2 Hz, 1 H), 5.05–5.01 (m, 1 H), 3.61 (dd, *J* = 16.6, 8.4 Hz, 1 H), 3.25 (dd, *J* = 16.6, 5.4 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 152.3, 135.5, 131.8, 131.5, 129.5, 129.0, 126.5, 119.8, 118.8, 114.0, 83.2, 77.9, 28.7 ppm. HRMS (EI): calcd. for C₁₅H₁₂BrNO₃ [M]⁺ 333.0001; found 333.0003.

6-Bromo-2-(4-chlorophenyl)-3-nitrochroman (13r): Yield: 159 mg, 86 %. Colorless solid. M.p. 167–168 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.39–7.36 (m, 2 H), 7.32–7.28 (m, 4 H), 6.85 (d, *J* = 8.6 Hz, 1 H), 5.42 (d, *J* = 7.6 Hz, 1 H), 4.97 (ddd, *J* = 8.8, 7.6, 5.4 Hz, 1 H), 3.62 (dd, *J* = 16.6, 8.8 Hz, 1 H), 3.27 (dd, *J* = 16.6, 5.4 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 152.1, 135.6, 133.9, 131.8, 131.6, 129.3, 128.0, 119.6, 118.8, 114.3, 83.2, 29.0 ppm. HRMS (EI): calcd. for C₁₅H₁₁BrClNO₃ [M]⁺ 368.9611; found 368.9612.

6-Bromo-2-(4-methoxyphenyl)-3-nitrochroman (13s): Yield: 129 mg, 71 %. Colorless solid. M.p. 158–159 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.30–7.28 (m, 4 H), 6.93–6.90 (m, 2 H), 6.84 (d, *J* = 8.4 Hz, 1 H), 5.35 (d, *J* = 7.8 Hz, 1 H), 5.01 (ddd, *J* = 9.0, 7.8, 5.4 Hz, 1 H), 3.81 (s, 3 H), 3.62 (dd, *J* = 16.4, 9.0 Hz, 1 H), 3.28 (dd, *J* = 16.4, 5.4 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.5, 152.5, 131.8, 131.4, 128.1, 127.2, 119.9, 118.8, 114.4, 113.9, 83.4, 77.9, 55.3, 29.4 ppm. HRMS (EI): calcd. for C₁₇H₁₈BrNO₄ [M]⁺ 363.0106; found 363.0103.

6-Bromo-2-(naphthalen-1-yl)-3-nitrochroman (13t): Yield: 132 mg, 69 %. Colorless solid. M.p. 182–183 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.10 (d, *J* = 84 Hz, 1 H), 7.94–7.87 (m, 2 H), 7.64–7.54 (m, 2 H), 7.47–7.41 (m, 2 H), 7.35 (dd, *J* = 8.7, 2.4 Hz, 1 H), 7.30 (d, *J* = 2.4 Hz, 1 H), 6.91 (d, *J* = 8.7 Hz, 1 H), 6.52 (d, *J* = 5.2 Hz, 1 H), 5.37–5.32 (m, 1 H), 3.56 (dd, *J* = 17.0, 6.1 Hz, 1 H), 3.11 (dd, *J* = 17.0, 5.1 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 152.2, 134.0, 131.9, 131.7, 131.4, 130.1, 129.7, 129.4, 127.3, 126.2, 125.3, 124.5, 122.1, 119.3, 118.5, 113.9, 81.2, 75.5, 27.0 ppm. HRMS (EI): calcd. for C₁₉H₁₄BrNO₃ [M]⁺ 383.0157; found 383.0149.

2-Nitro-3-phenyl-2,3-dihydro-1H-benzo[f]chromene (13u): Yield: 111 mg, 73 %. Colorless solid. M.p. 188–189 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.83 (d, *J* = 8.0 Hz, 1 H), 7.77–7.72 (m, 2 H), 7.58–7.54 (m, 1 H), 7.46–7.41 (m, 6 H), 7.18 (d, *J* = 9.0 Hz, 1 H), 5.49 (d, *J* = 8.1 Hz, 1 H), 5.24–5.18 (m, 1 H), 3.89 (dd, *J* = 16.3, 9.0 Hz, 1 H), 3.67 (dd, *J* = 16.3, 5.8 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 151.1, 135.5, 132.2, 129.5, 129.1, 129.0, 128.7, 127.2, 126.9, 124.3, 121.7, 118.3, 109.9, 84.4, 77.9, 27.0 ppm. HRMS (EI): calcd. for C₁₉H₁₅NO₃ [M]⁺ 305.1052; found 305.1046.

3-(4-Chlorophenyl)-2-nitro-2,3-dihydro-1H-benzo[f]chromene (13v): Yield: 132 mg, 78 %. Colorless solid. M.p. 181–182 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.84 (d, *J* = 7.8 Hz, 1 H), 7.77–7.72 (m, 2 H), 7.59–7.55 (m, 1 H), 7.47–7.43 (m, 1 H), 7.4 (s, 4 H), 7.16 (d, *J* = 9.0 Hz, 1 H), 5.43 (d, *J* = 8.3 Hz, 1 H), 5.18–5.12 (m, 1 H), 3.88 (dd, *J* = 16.3, 9.2 Hz, 1 H), 3.69 (dd, *J* = 16.3, 5.9 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 150.9, 135.6, 134.0, 132.1, 129.5, 129.3, 129.2, 128.8, 128.4, 127.3, 124.4, 121.7, 118.2, 109.9, 84.4, 27.7 ppm. HRMS (EI): calcd. for C₁₉H₁₄ClNO₃ [M]⁺ 339.0662; found 339.0663.

3-(4-Methoxyphenyl)-2-nitro-2,3-dihydro-1H-benzof]chromene (13w): Yield: 117 mg, 70 %. Colorless solid. M.p. 186–187 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.83 (d, *J* = 8.0 Hz, 1 H), 7.77–7.71 (m, 2 H), 7.58–7.54 (m, 1 H), 7.45–7.41 (m, 1 H), 7.40–7.36 (m, 2 H), 7.15 (d, *J* = 9.0 Hz, 1 H), 6.96–6.92 (m, 2 H), 5.38 (d, *J* = 8.5 Hz, 1 H), 5.21–5.15 (m, 1 H), 3.87 (dd, *J* = 16.2, 9.4 Hz, 1 H), 3.82 (s, 3 H), 3.71 (dd, *J* = 16.2, 5.9 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.5, 151.3, 132.2, 129.5, 129.0, 128.7, 128.4, 127.3, 127.2, 124.3,

121.7, 118.3, 114.4, 110.0, 84.6, 77.8, 55.3, 27.6 ppm. HRMS (EI): calcd. for C₂₀H₁₇NO₄ [M]⁺ 335.1158; found 335.1160.

3-(Naphthalen-1-yl)-2-nitro-2,3-dihydro-1H-benzo[f]chromene (13x): Yield: 135 mg, 76 %. Colorless solid. M.p. 204–205 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.20 (d, *J* = 8.4 Hz, 1 H), 7.94–7.85 (m, 3 H), 7.80–7.76 (m, 2 H), 7.62–7.54 (m, 4 H), 7.47–7.40 (m, 2 H), 7.22 (d, *J* = 9.0 Hz, 1 H), 6.48 (d, *J* = 6.3 Hz, 1 H), 5.60–5.55 (m, 1 H), 3.97 (dd, *J* = 16.7, 6.9 Hz, 1 H), 3.50 (dd, *J* = 16.7, 5.6 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 151.0, 134.0, 132.2, 131.2, 130.3, 130.1, 129.6, 129.3, 129.2, 128.8, 127.2, 127.1, 126.1, 125.3, 125.0, 124.2, 122.5, 121.6, 118.2, 109.4, 82.3, 77.2, 75.3, 25.4 ppm. HRMS (EI): calcd. for C₂₃H₁₇NO₃ [M]⁺ 355.1208; found 355.1213.

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